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Exploring Inorganic and Organometallic Chemistry

W. Christopher Boyd, Ph.D.

Cleveland State University

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In nova fert animus mutatas dicere formas
corpora; di, coeptis (nam vos mutastis et illas)
adspirate meis primaque ab origine mundi
ad mea perpetuum deducite tempora carmen!

- Publius Ovidius Naso, *Metamorphoses* 1.1-4

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Introduction

This textbook arose from over a decade of experience teaching inorganic chemistry at Cleveland State University. The inorganic curriculum at CSU consists of one semester of lecture and one semester of lab at the undergraduate level, and two graduate courses, one focusing on inorganic reaction chemistry and mechanisms (including organometallic catalysis and bioinorganic chemistry) and the other focusing on the application of quantum mechanics and group theory to the structure, bonding, magnetism, and spectroscopy of transition metal complexes.

It has been my experience that no commercially available textbook covers the relevant material at the appropriate level for these classes. At the undergraduate level, some texts are very theory-heavy, with little space devoted for discussing trends in actual chemical reactions, while others are almost purely descriptive, focusing on listing the behavior of each column in the Periodic Table with little theoretical underpinning. At the graduate level, there are many fine texts dealing with inorganic topics at an advanced level, but many are too advanced for a one-semester course that may be taken by first-year M.S. or Ph.D. students. For example, many texts on the use of transition metals in the catalysis of organic reactions assume a knowledge of synthetic organic chemistry greater than those possessed by first-year graduate students, while many bioinorganic chemistry texts assume a greater knowledge of biology than many students have whose primary interests are in chemistry. Similarly, many texts on electronic structure and bonding in transition metal complexes assume greater mathematical sophistication than most students possess even after a year of undergraduate physical chemistry.

To remedy these issues, I developed a series of detailed lecture notes for my undergraduate and graduate inorganic classes, and eventually expanded those notes into the present text. This text, therefore, contains a mixture of material appropriate for junior or senior undergraduates, and more advanced material more suited for graduate students. It is my intent that this will serve as a modular text, from which instructors can pick and choose sections according to the interests and preparations of their students. For instance, undergraduates will benefit from the symmetry material discussed in chapter 2 and its application in chapter 3 to basic MO theory, but the discussion of the overall symmetries of electronic states in section 8.3 might better be deferred to graduate school. To aid such a modular usage, I have endeavored to make later chapters dependent on only the more basic sections of earlier ones.

I wish to thank many people for their support and assistance in the production of this text. First and foremost, I would like to acknowledge CSU's Michael Schwartz Library and its Textbook Affordability Grant program for supporting the production of open-access teaching material. In particular, Heather Caprette, Amanda Goodsett, Barbara Loomis, and Theresa Nawalaniec have been tremendously helpful in assisting me with the design and formatting of this work. I would also like to thank my department chair, Michael Kalafatis, for his support of teaching excellence in the Chemistry Department, and to Melanie Chiu (Michigan State University) and Yiming Wang (University of Pittsburgh) for helpful comments on draft

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Finally, I would like to thank my wife, Stephanie Johnson, for her loving and tireless support of my academic endeavors. Her love and companionship have kept me grounded during many a busy end-of-semester period, and my gratitude for her cannot be overstated. *Te amo quam plurimum, mea carissima.*

W. Christopher Boyd
Cleveland, OH
November 2025

Chapter 1: Atomic Structure and Periodic Trends

1.1. Introduction to Inorganic Chemistry

Inorganic chemistry is the study of compounds and materials that are not primarily carbon-based, as well as compounds which contain carbon along with other elements not commonly encountered by organic chemists. As such, it can be understood to encompass the entire Periodic Table. Inorganic chemistry has applications in materials science (*e.g.* the design and preparation of alloys with novel properties), organic synthesis (*e.g.* the preparation of transition metal complexes that catalyze useful organic reactions), medicinal chemistry (*e.g.* platinum-containing anticancer drugs), and many other areas of research.

The goal of this textbook is to provide you with a strong foundation in both the underlying theory of inorganic chemistry and the descriptive chemistry of the elements and their compounds. We will begin with a symmetry-based discussion of molecular structure, continue with some descriptive chemistry of the main-group elements, and then spend a great deal of time discussing the chemistry of the transition metals. Before discussing *molecular* structure, however, it is worthwhile to review some key elements of *atomic* structure, as described by quantum mechanics.

1.2. The Schrödinger Equation

The fundamental equation of quantum mechanics is the famous Schrödinger equation, devised by Erwin Schrödinger (1887-1961, Nobel Prize in Physics 1933). It is expressed in its most general form as follows:

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Here Ψ is the wavefunction of the system under consideration. It is a function of the spatial coordinates of each particle in the system, as well as of the time t . For a single particle, $\Psi = \Psi(x, y, z, t) = \Psi(r, \theta, \phi, t)$, depending on whether Cartesian or spherical polar coordinates are used. The quantity $\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ J} \cdot \text{s}$ is the reduced Planck constant, and i is the imaginary unit: $i = \sqrt{-1}$.

The operator $\hat{H}$ is known as the Hamiltonian operator (or just the Hamiltonian, for short), and it is the quantum-mechanical counterpart to the total energy function in classical mechanics. The carat or “hat” is used to denote the fact that it is an operator (a function on functions). In this text, we will use carats to denote operators, but you should be aware that this convention is not universally followed, and some sources write the Hamiltonian simply as H . For a system of N particles, the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{j=1}^N \frac{1}{m_j} \nabla_j^2 + U$$

where m_j is the mass of the j th particle, ∇^2 is the Laplacian operator, given for a single particle by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

or

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

in Cartesian and spherical polar coordinates respectively, and U is the potential energy of the system, which can be a function of the spatial coordinates of each particle and of time.

For many systems, the potential energy U is a function of spatial coordinates, but *not* of time. This means that there is no time dependence of either the Hamiltonian or the total energy for these systems. In such cases, the total wavefunction Ψ is separable: it can be factored into the product of a time-independent wavefunction ψ and a time-dependent function f , according to $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})f(t)$, where the vector $\mathbf{r}$ is a shorthand representing the spatial coordinates of all particles in the system. Under these circumstances, the time-dependent Schrödinger equation applies:

$$\hat{H}\psi = E\psi$$

where E is the total energy (kinetic and potential) of the system. It can be shown that, when Ψ is separable, the time-dependent portion is given by

$$f(t) = e^{-iEt/\hbar}$$

This time-independent Schrödinger equation is useful for a wide variety of chemical problems involving structure and bonding, when one is interested in the configuration of atoms leading to the lowest possible energy (or, at least, a local minimum of energy). However, one must consider time-dependence when studying chemical reactions or spectroscopic transitions, which by their nature *do* involve a change in the system's energy over time.

The wavefunction Ψ or ψ has no physical meaning in and of itself. However, according to the interpretation put forward by Max Born (1882-1970, Nobel Prize in Physics 1954), the square of its absolute value,¹ $|\psi|^2 = \psi^*\psi$ or $|\Psi|^2 = \Psi^*\Psi$, is the probability density function of a particle, that is, the likelihood of finding the particle in some differential volume element $d\tau$. Alternatively, since quantum mechanics teaches us that particles are delocalized in space, $\psi^*\psi$ can be thought of as the fraction of the total particle that is present in $d\tau$. As a probability distribution function, $\psi^*\psi$ must be normalized, since the probability of finding the particle *somewhere* in the entire universe is exactly 1. Mathematically, this is expressed by

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi(x, y, z)^* \psi(x, y, z) dx dy dz = 1$$

in Cartesian coordinates or

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \psi(r, \theta, \phi)^* \psi(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi = 1$$

in spherical polar coordinates. We can express this rather cumbersome triple integral over all space with the shorthand notation $\int \psi^*\psi d\tau$. An even more concise shorthand for integrals over all space, the so-called “bra-ket notation,” was devised by Paul Dirac (1902-1984, Nobel Prize in Physics 1933): for any two wavefunctions ψ_1 and ψ_2 , and any operator $\hat{A}$, the following notation applies:

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^* \psi_2 d\tau$$

¹ The wavefunction may be complex, with both a real and an imaginary portion. Thus, one must multiply it by its complex conjugate, or (equivalently) square its absolute value. Some wavefunctions are all real; it depends on the system.

$$\langle \psi_1 | \hat{A} | \psi_2 \rangle = \int \psi_1^* \hat{A} \psi_2 d\tau$$

If you have studied vector spaces in a linear algebra course, the Dirac bra-ket notation may remind you of the notation used for inner products of abstract vectors. In fact, the integration over all space of a wavefunction times the complex conjugate of another wavefunction is indeed the inner product of those two wavefunctions considered as vectors.

1.3. The Variational Method

It is usually the case that we cannot solve the time-independent Schrödinger equation precisely, that is, we cannot write, in analytical form, a wavefunction ψ that exactly satisfies the eigenvalue equation $\hat{H}\psi = E\psi$. However, suppose that we have a “trial function” ϕ that we believe might serve as a reasonable approximation to ψ . We can use the following technique to calculate the approximate energy E_ϕ corresponding to our trial function as follows. First, we write the Schrödinger equation *as if* ϕ were an eigenfunction of the Hamiltonian, even though this is not exactly correct:

$$\hat{H}\phi = E_\phi\phi$$

Next, we left-multiply by the complex conjugate of the trial function:

$$\phi^* \hat{H} \phi = \phi^* E_\phi \phi$$

We now integrate over all space, noting that, since E_ϕ is a number, not an operator, it can be pulled outside the integral:

$$\begin{aligned} \langle \phi | \hat{H} | \phi \rangle &= E_\phi \langle \phi | \phi \rangle \\ \Rightarrow E_\phi &= \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \end{aligned}$$

If our trial function ϕ was already normalized, then the denominator of this expression equals 1, so $E_\phi = \langle \phi | \hat{H} | \phi \rangle$.

The usefulness of the above energy expression lies in the variational theorem, which states that, for any approximate wavefunction (trial function) ϕ , the energy calculated as above must be greater than or equal to the true energy corresponding to the (unknown) true ground-state wavefunction ψ , or

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \geq E$$

where E is the true energy. (The equality holds only in the unlikely event that our trial function has the same form as the true wavefunction.) This means that any energy calculation involving an approximate trial wavefunction will (at least slightly) *overestimate* the energy of the system, but it will never *underestimate* it. The calculation of approximate energy values using trial wavefunctions is called the variational method. It should be emphasized that the inequality represented by the variational theorem only applies to approximations to the ground-state wavefunction of the system in question. A variational calculation with a wavefunction approximating an excited state of the system may underestimate the excited-state energy, though it will still give an energy value greater than the ground state energy.

The variational theorem is very useful when one has a trial wavefunction with a given algebraic form, but with several parameters $c_1, c_2, c_3 \dots c_n$ with a range of possible values. Thus, while the trial wavefunction ϕ is a function of the spatial coordinates of the system, the approximate energy E_ϕ is a function of each parameter c_j . Setting $\frac{\partial E_\phi}{\partial c_j} = 0$ for each j allows for the calculation of the values of each c_j that will lead to the lowest approximate energy E_ϕ , which, according to the variational theorem, is the closest approximation to the true energy obtainable with a trial wavefunction of that algebraic form. It is often the case that the trial wavefunction has a linear dependence on the variational parameters. Consider the case where ϕ is a linear combination of basis functions f_j , or

$$\phi = \sum_{j=1}^n c_j f_j$$

Setting $\frac{\partial E_\phi}{\partial c_j} = 0$ for each j yields the following set of linear equations:

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) + \dots + c_n(H_{1n} - ES_{1n}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) + \dots + c_n(H_{2n} - ES_{2n}) &= 0 \\ \vdots & \\ c_1(H_{1n} - ES_{1n}) + c_2(H_{2n} - ES_{2n}) + \dots + c_n(H_{nn} - ES_{nn}) &= 0 \end{aligned}$$

where the overlap integrals S_{ab} and the resonance integrals H_{ab} (together known as matrix elements) are defined by

$$S_{ab} = \langle f_a | f_b \rangle = S_{ba} = \langle f_b | f_a \rangle$$

$$H_{ab} = \langle f_a | \hat{H} | f_b \rangle = H_{ba} = \langle f_b | \hat{H} | f_a \rangle$$

and E is the approximate energy corresponding to the approximate wavefunction ϕ . If, as is often (but not always) the case, the basis functions f_j are normalized, then $S_{jj} = 1$ for any j .

For the above set of linear equations to have a unique, nontrivial solution, the following determinant, known as the secular determinant, must equal zero:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{1n} - ES_{1n} & H_{2n} - ES_{2n} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

Determining the energies corresponding to an $n \times n$ secular determinant requires solving an n th-order polynomial equation. If n is large, this is difficult to do by hand, but an easy problem for a computer. An $n \times n$ secular determinant potentially yields n different roots, or energies (fewer if two or more states of the system are degenerate, *i.e.* have the same energy). The lowest such value obtained is an estimate of the ground-state energy, and it is guaranteed to be greater than or equal to the actual ground-state energy, according to the variational theorem. We will see later in this course that group theory often allows us to determine that some S_{ab} and H_{ab} values are exactly zero, thus simplifying the secular determinants that we (or a computer) must solve. It should be noted that, while the variational method in general gives an upper bound only to the ground-state energy, if a variational function is *linearly* dependent on the variational parameters, its n energy solutions are upper bounds to the n lowest energy levels of the system. Thus, the lowest energy is an upper bound to the ground state, the next lowest energy is an upper bound to the first excited state, and so on.

1.4. Perturbation Theory

In addition to the variational method, another key technique for performing approximate calculations in quantum mechanics is perturbation theory.² The logic of perturbation theory is as follows: suppose we wish to solve the (time-independent) Schrödinger equation $\hat{H}\psi_n = E_n\psi_n$ for different states n , but the nature of the Hamiltonian is such that this differential equation has no analytical solution for ψ_n . However, suppose that we can write our actual Hamiltonian $\hat{H}$ as the sum of two operators: $\hat{H} = \hat{H}^{(0)} + \hat{H}'$, and that if $\hat{H} = \hat{H}^{(0)}$, we could solve the Schrödinger equation *exactly*: $\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. Now suppose further that $\hat{H}'$ is expected to have a significantly smaller effect on a function than $\hat{H}^{(0)}$. We thus say that $\hat{H}'$ is a *perturbation* to $\hat{H}^{(0)}$. Under such circumstances, we can write the true wavefunction ψ_n and true energy E_n in terms of $\psi_n^{(0)}$ (the zeroth-order wavefunction) and $E_n^{(0)}$ (the zeroth-order energy) corrected by successively smaller perturbation terms:

$$\begin{aligned}\psi_n &= \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \dots \\ E_n &= E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots\end{aligned}$$

Note that the superscript numbers in parentheses are *not* powers to which a wavefunction or energy is being raised, but simply indices. A superscript 1 in parentheses is called the first-order correction, a superscript 2 in parentheses is the second-order correction, and so on. Since perturbations of increasing order are generally each smaller than the last, we can often accurately approximate the true value of the energy by using first-order perturbation theory:

$$E_n \approx E_n^{(0)} + E_n^{(1)}$$

It can be shown that³ the first-order energy correction is given in terms of the unperturbed wavefunction and the perturbation to the Hamiltonian as follows:

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \left| \hat{H}' \right| \psi_n^{(0)} \right\rangle$$

Thus, the value of the energy, correct to first order, is

² The type of perturbation theory shown here is sometimes known as Rayleigh-Schrödinger perturbation theory. It was devised by Schrödinger based on earlier work by John William Strutt, 3rd Baron Rayleigh (1842-1919).

³ Derivations of the perturbation theory formulae in this section can be found in chapter 9 of *Quantum Chemistry*, 7th edition, by Ira N. Levine, Pearson Education: Upper Saddle River, NJ, 2014.

$$E_n \approx E_n^{(0)} + \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

The use of the index n above for different quantum states indicates that, unlike the variational method in general, perturbation theory can be used to estimate the energies of excited states, in addition to that of the ground state.

The first-order correction to the wavefunction, $\psi_n^{(1)}$, is not as straightforward to calculate as the first-order correction to the energy. It is given by the following, more complicated, formula:

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

This formula expresses a correction to the zeroth-order wavefunction $\psi_n^{(0)}$ in terms of all the other zeroth-order wavefunctions (for different states) $\psi_m^{(0)}$. One cannot, in general, solve for $\psi_n^{(1)}$ exactly, as there are usually an infinite number of possible states $m \neq n$. However, note the $\frac{1}{E_n^{(0)} - E_m^{(0)}}$ dependence of each term in the sum. If a zeroth-order wavefunction $\psi_m^{(0)}$ corresponds to a highly excited state, with a zeroth-order energy $E_m^{(0)}$ much greater than the zeroth-order energy $E_n^{(0)}$, then its contribution to the correction $\psi_n^{(1)}$ will be small in magnitude. Thus, one can obtain an approximate value of $\psi_n^{(1)}$ (an approximation to an approximation!) by only including the zeroth-order wavefunctions that are relatively close in energy to the wavefunction to be modified. Perturbation theory can be viewed as correcting a zeroth-order wavefunction by mixing in wavefunctions corresponding to excited states (as well as those corresponding to lower states, if the zeroth-order wavefunction to be corrected represents an excited state itself). The second-order correction to the energy is given by a similarly cumbersome formula:

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

The perturbation theory that we have discussed so far assumes that the zeroth-order wavefunctions $\psi_n^{(0)}$ are nondegenerate. If two zeroth-order wavefunctions $\psi_n^{(0)}$ and $\psi_m^{(0)}$ have equal zeroth-order energies $E_n^{(0)}$ and $E_m^{(0)}$, then some of the terms in the expression previously given for $\psi_n^{(1)}$ would have a zero denominator. However, we frequently encounter systems with a set of degenerate zeroth-order wavefunctions whose degeneracy is reduced, or removed entirely, by a perturbation that lowers the symmetry of the system. For example, in a free transition metal atom or ion, all five d orbitals in a given subshell ($3d$, $4d$, or $5d$) have the same energy. Once a set of molecules or ions (ligands) binds to the transition metal, however, its $3d$ orbitals (for example) will no longer be a fivefold degenerate set.

There exists an important theorem, which results from the fact that the Hamiltonian is a linear operator. The theorem is as follows: if multiple wavefunctions ψ_j are degenerate solutions to the Schrödinger equation, that is, $\hat{H}\psi_j = E\psi_j$ with the same energy E for different j , then if we take a linear combination of those functions

$$\psi_{\text{LC}} = \sum_{j=1}^N c_j \psi_j$$

this linear combination is also a solution of the Schrödinger equation with the same energy eigenvalue: $\hat{H}\psi_{\text{LC}} = E\psi_{\text{LC}}$. This theorem might seem to suggest that we can use any one of an infinite number of sets of degenerate zeroth-order wavefunctions as the starting point for a perturbation theory treatment. However, this is not in fact the case. Only a particular set of degenerate, zeroth-order wavefunctions is correct for the perturbation theory, since the perturbing part of the Hamiltonian $\hat{H}'$ breaks the degeneracy.

Let us say that we have a set of n zeroth-order, degenerate wavefunctions $\psi_m^{(0)}$, which are also orthonormal, meaning that $\langle \psi_p^{(0)} | \psi_q^{(0)} \rangle = \delta_{pq}$. (The Kronecker delta δ_{pq} is equal to 1 if $p = q$, but equal to zero if $p \neq q$.) We can *always* choose a set of linear combinations that are orthogonal by using an algorithm such as the Gram-Schmidt orthogonalization procedure (see chapter 3), and normalization simply amounts to multiplying a function by a constant.

Now let the correct set of n zeroth-order wavefunctions, suitable for perturbation theory, be denoted by

$$\phi_j^{(0)} = \sum_{m=1}^n c_m \psi_m^{(0)}$$

where the set of coefficients c_m are different for every j . This leads to a set of n linear equations

$$\begin{aligned} c_1(H'_{11} - E_j^{(1)}) + c_2 H'_{12} + \cdots + c_n H'_{1n} &= 0 \\ c_1 H'_{21} + c_2(H'_{22} - E_j^{(1)}) + \cdots + c_n H'_{2n} &= 0 \\ \vdots & \\ c_1 H'_{n1} + c_2 H'_{n2} + \cdots + c_n(H'_{nn} - E_j^{(1)}) &= 0 \end{aligned}$$

where

$$H'_{pq} = \langle \psi_p^{(0)} | \hat{H}' | \psi_q^{(0)} \rangle$$

For this set of linear equations to have a unique, nontrivial solution, we must again have a secular determinant equal to zero:

$$\begin{vmatrix} H'_{11} - E_j^{(1)} & H'_{12} & \cdots & H'_{1n} \\ H'_{21} & H'_{22} - E_j^{(1)} & \cdots & H'_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{n1} & H'_{n2} & \cdots & H'_{nn} - E_j^{(1)} \end{vmatrix} = 0$$

The roots of this secular determinant are the values of $E_j^{(1)}$, which are the first-order energy corrections to the energies of each correct zeroth-order wavefunction $\phi_j^{(0)}$. If two or more $E_j^{(1)}$ values are equal, this means that the degeneracy has only partially been removed. For example, when six of the same kind of ligand are arranged around a metal atom or ion with an octahedral geometry, the initially fivefold degenerate d orbitals are split into one triply degenerate set and one doubly degenerate pair. As with the secular determinants that we encounter when using the variational method, if we can show by symmetry considerations

that some of the matrix elements H'_{pq} must be exactly equal to zero, we can simplify our calculations considerably.

1.5. One-Electron Atoms

For the vast majority of systems, we cannot obtain an analytical solution to the Schrödinger equation. However, we *can* obtain an exact solution for the case of a hydrogen atom, with only one electron, if we neglect relativistic effects. Similarly, we can obtain an exact solution (again, neglecting relativity) for any one-electron ion, such as He^+ , Li^{2+} , Be^{3+} , *etc.* One-electron atoms or ions are often called “hydrogenlike atoms.” For a nucleus with Z protons ($Z = 1$ for H, $Z = 2$ for He, *etc.*), the potential energy function for the electron in terms of its distance r from the nucleus is given by Coulomb’s law:

$$U(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

where e is the elementary charge (1.602×10^{-19} C) and ϵ_0 is the permittivity of vacuum ($4\pi\epsilon_0 = 1.113 \times 10^{-10}$ C²·J⁻¹·m⁻¹). We can neglect the gravitational attraction between the electron and the nucleus, as it is miniscule compared to the Coulombic attraction. Since U is not a function of time, the time-independent Schrödinger equation can be used, and thus the full form of the Schrödinger equation for a one-electron atom or ion (neglecting nuclear motion as per the Born-Oppenheimer approximation) is

$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi$$

This is a complicated partial differential equation, but it does have a series of analytical solutions⁴ categorized by three quantum numbers: the principal quantum number n , which may have any positive integer value, the azimuthal quantum number l , which can have any non-negative integer value such that $l < n$, and the magnetic quantum number m (sometimes denoted m_l), which can have any integer value (positive, negative, or zero) such that $-l \leq m \leq l$. Each one of the set of wavefunctions $\psi_{n,l,m}$ can be factored into the product of a

⁴ The detailed solution can be found in Section 20.3 of *Mathematical Methods for Physical and Analytical Chemistry*, by David Z. Goodson, John Wiley & Sons, Inc.: Hoboken, NJ, 2011.

radial function R , dependent only on r , and an angular function Y , dependent only on the angular coordinates:

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r)Y_l^m(\theta, \phi)$$

The angular functions Y are commonly known as the spherical harmonics. The general formulae for R and Y , for different values of n , l , and m , are as follows (note that here e is the base of the natural logarithm, not the elementary charge, except in the expression for a_0).

$$R_{n,l}(r) = \left\{ \frac{(n-l-1)!}{2n[(n+1)!]^3} \right\}^{1/2} \left(\frac{2Z}{na_0} \right)^{l+3/2} r^l e^{-Zr/na_0} L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right)$$

$$Y_l^m(\theta, \phi) = \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) e^{-im\phi}$$

$$L_k^j(x) = \frac{d^j}{dx^j} \left[e^x \frac{d^k}{dx^k} (x^k e^{-x}) \right]$$

$$P_k^j(x) = (1-x^2)^{j/2} \frac{d^{k+j}}{dx^{k+j}} \left[\frac{(x^2-1)^k}{2^k k!} \right]$$

$$a_0 = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2} = 5.292 \times 10^{-11} \text{ m}$$

Here $L_k^j(x)$ and $P_k^j(x)$ are the associated Laguerre polynomial and associated Legendre polynomial, respectively. The quantity a_0 is called the Bohr radius, and is commonly used as a measure of distance in atomic units. The radial functions for the first few n and l values are shown in Table 1.1 below, and the spherical harmonics for the first few l values (with their associated m values) are shown in Table 1.2 below.

For one-electron atoms, the energy of the system depends only on the value of n , not on that of the other quantum numbers, according to

$$E_n = -\frac{Z^2}{2n^2} E_h$$

where the hartree E_h , a useful atomic unit of energy, is given (with e here being the elemental charge) by

$$E_h = \frac{m_e e^4}{(4\pi\epsilon_0 \hbar)^2} = 4.360 \times 10^{-12} \text{ J}$$

Note that energy is an increasing function of n : while it is always negative, it becomes less negative as n increases, and $E \rightarrow 0$ as $n \rightarrow \infty$. One can think of an n value of ∞ as indicating a fully ionized hydrogen atom, *i.e.* an H^+ ion and an electron separated by an infinite distance. Thus, the zero point for the energy is ionized hydrogen, with all quantum states of a hydrogen atom more stable than that. Since the ground-state energy of a hydrogen atom ($Z = 1$, $n = 1$) is $-\frac{E_h}{2}$, the ionization energy of a ground-state hydrogen atom is $\frac{E_h}{2}$.

Table 1.1. Radial wavefunctions through $n = 4$.

n	l	$R_{n,l}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	$\frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$
2	1	$\frac{1}{\sqrt{24}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
3	0	$\frac{2}{\sqrt{27}}\left(\frac{Z}{a_0}\right)^{3/2} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2r^2}{27a_0^2}\right) e^{-Zr/3a_0}$
3	1	$\frac{4\sqrt{2}}{27\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) \left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$
3	2	$\frac{2\sqrt{2}}{81\sqrt{15}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$
4	0	$\frac{1}{4}\left(\frac{Z}{a_0}\right)^{3/2} \left(1 - \frac{3Zr}{4a_0} + \frac{Z^2r^2}{8a_0^2} - \frac{Z^3r^3}{192a_0^3}\right) e^{-Zr/4a_0}$
4	1	$\frac{\sqrt{5}}{16\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) \left(1 - \frac{Zr}{4a_0} + \frac{Z^2r^2}{80a_0^2}\right) e^{-Zr/4a_0}$
4	2	$\frac{1}{64\sqrt{5}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 \left(1 - \frac{Zr}{12a_0}\right) e^{-Zr/4a_0}$
4	3	$\frac{1}{768\sqrt{35}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^3 e^{-Zr/4a_0}$

Table 1.2. Spherical harmonics through $l = 3$.

l	m	$Y_l^m(\theta, \phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}} \cos \theta$
1	± 1	$\sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$
2	0	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
2	± 1	$\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
2	± 2	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$\sqrt{\frac{7}{16\pi}} \cos \theta (5 \cos^2 \theta - 3)$
3	± 1	$\sqrt{\frac{21}{64\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
3	± 2	$\sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
3	± 3	$\sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{\pm 3i\phi}$

The wavefunctions $\psi_{n,l,m}$ for a hydrogenlike atom are commonly called atomic orbitals (the name is a holdover from the old Bohr theory of the hydrogen atom, in which the electron moved about the nucleus in well-defined orbits). In the atomic orbital nomenclature that is

standard for chemists ($1s$, $2s$, $2p$, *etc.*), the initial number specifies n and the letter specifies l as follows: s means $l = 0$, p means $l = 1$, d means $l = 2$, and f means $l = 3$.

Different orbitals can be distinguished by their nodes, which are surfaces where $\psi = 0$. Whenever one crosses a node, the sign of ψ changes from positive to negative or *vice versa*. Each orbital has $n - l - 1$ radial nodes and l angular nodes. Since $l = 0$ for all s orbitals, each s orbital is spherically symmetrical, with $n - 1$ radial nodes, so a $1s$ orbital has no nodes, a $2s$ orbital has 1 node, and so on. In contrast, the presence of angular nodes in p , d , and f orbitals makes these orbitals no longer spherically symmetrical. The angular nodes consist of planes or conical surfaces. The total number of nodes (radial and angular combined) for a given atomic orbital is $n - 1$.

The spherically symmetrical s orbitals are easy to visualize: the wavefunctions are all real, and consist of concentric spheres separated by radial nodes. In contrast, the p , d , and f orbitals are not so easily visualized, since some of them have imaginary components. Let us first consider the set of three $2p$ orbitals ($n = 2$ is the lowest principal quantum number for which p orbitals, with $l = 1$, are possible). There are three possible values of m for a p orbital: -1 , 0 , and 1 . If $m = 0$, the orbital is readily visualized as having the “dumbbell” shape familiar from introductory chemistry courses:

$$\psi_{2,1,0} = R_{2,1} \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$$

$$R_{2,1} = \frac{1}{\sqrt{24}} \left(\frac{Z}{a_0} \right)^{5/2} r e^{-Zr/2a_0}$$

This orbital is the familiar $2p_z$ orbital. The z in this name comes from the fact that it can also be written as

$$\psi_{2,1,0} = R_{2,1} \left(\frac{3}{4\pi} \right)^{1/2} \frac{z}{r}$$

since $\cos \theta = \frac{z}{r}$. Thus, the $2p_z$ orbital has the same symmetry as a vector lying along the z -axis. The $2p$ orbitals with $m = \pm 1$ are more difficult to visualize, since they are not pure real. Their formulae are

$$\psi_{2,1,1} = R_{2,1} \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{i\phi}$$

$$\psi_{2,1,-1} = R_{2,1} \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{-i\phi}$$

We can recast these $2p$ orbitals as purely real functions by making use of the previously mentioned theorem according to which, if multiple functions are degenerate solutions to the Schrödinger equation, any linear combination of those functions is also a solution with the same energy eigenvalue. We thus construct (normalized) linear combinations of these $2p$ orbitals to remove the imaginary components:

$$2p_x = \frac{1}{\sqrt{2}} (\psi_{2,1,1} + \psi_{2,1,-1}) = R_{2,1} \left(\frac{3}{4\pi} \right)^{1/2} \sin \theta \cos \phi = R_{2,1} \left(\frac{3}{4\pi} \right)^{1/2} \frac{x}{r}$$

$$2p_y = \frac{1}{\sqrt{2}i} (\psi_{2,1,1} - \psi_{2,1,-1}) = R_{2,1} \left(\frac{3}{4\pi} \right)^{1/2} \sin \theta \sin \phi = R_{2,1} \left(\frac{3}{4\pi} \right)^{1/2} \frac{y}{r}$$

The resulting $2p_x$ and $2p_y$ wavefunctions, each all real, have the symmetries of vectors lying along the x - and y -axes, respectively. The conversion of exponential functions of $i\phi$ to trigonometric functions was made using Euler's formula, $e^{i\phi} = \cos \phi + i \sin \phi$.

Similar manipulations are made to transform d orbitals ($l = 2$) into all-real forms. The d_{xz} and d_{yz} orbitals are formed from linear combinations of the complex d orbitals with $m = \pm 1$, and they have the symmetries of the products xz and yz , respectively (the familiar “four-leaf clover” shape). Similarly, the d_{xy} and $d_{x^2-y^2}$ orbitals are formed from linear combinations of the d orbitals with $m = \pm 2$, and they have the symmetries of xy and $x^2 - y^2$, respectively. The d_{z^2} orbital is the d orbital with $m = 0$, which is already all real (*cf.* the all-real p orbital with $m = 0$). Instead of a clover-leaf shape, it has the shape of two lobes with a torus (a “donut” shape), with two conical nodes rather than two nodal planes. It has the symmetry *not* simply of z^2 , but of $2z^2 - x^2 - y^2$. It would be more correct to label it as the $d_{2z^2-x^2-y^2}$ orbital, but d_{z^2} is used as a convenient shorthand. The $1s$, $2p$, and $3d$ orbitals (each with no radial nodes) are shown in Figure 1.1 below, and representative examples of orbitals with radial nodes are shown in Figure 1.2. There exist sets of all-real linear combinations of the f orbitals ($l = 3$), though in the case of these orbitals, different linear combinations are conventionally used under different circumstances.

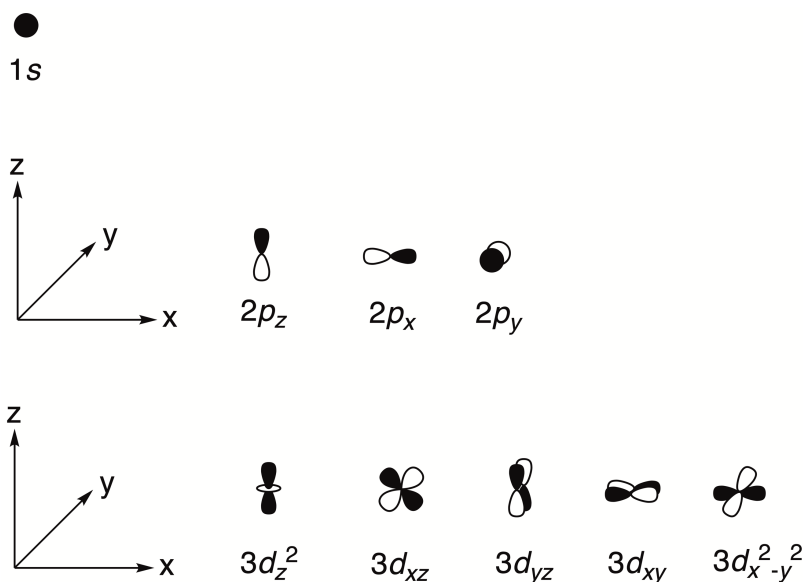


Figure 1.1. The 1s, 2p, and 3d orbitals.

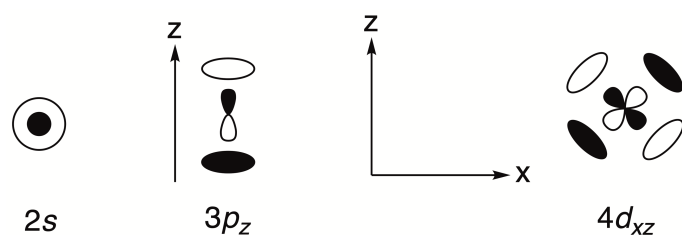


Figure 1.2. The 2s, 3p_z, and 4d_{xz} orbitals, as examples of orbitals with radial nodes.

In addition to the quantum numbers n , l , and m , an electron in a hydrogenlike atom has a fourth quantum number, denoted m_s . This is called the spin quantum number, and reflects the fact that part of the electron's angular momentum is due to a quantity known as spin. The term "spin" comes from the fact that each electron is associated with a magnetic moment similar to that generated, in classical electrodynamics, by a spinning electrical charge. This does *not* mean that electrons are actually spinning, but it is a serviceable classical analogy. Electron spin is not predicted by the Schrödinger equation, but it is predicted from the relativistic quantum mechanics developed by Dirac. While Dirac's quantum mechanics is more correct than the quantum mechanics of Schrödinger in that it accounts for relativity, it is mathematically much more complicated, so most chemists content themselves to use nonrelativistic quantum mechanics and then add spin as a correction.

The spin quantum number m_s reflects the projection of the spin angular momentum vector S on the z-axis. This projection S_z is given simply by

$$S_z = m_s \hbar$$

There are only two possible values of m_s , $\frac{1}{2}$ and $-\frac{1}{2}$, and they are degenerate in the absence of an external magnetic field. We can formally write the total time-independent wavefunction for a hydrogenlike atom as

$$\psi_{n,l,m,m_s} = \psi_{n,l,m}(r, \theta, \phi) \alpha$$

or

$$\psi_{n,l,m,m_s} = \psi_{n,l,m}(r, \theta, \phi) \beta$$

where α denotes $m_s = \frac{1}{2}$ (sometimes referred to as “spin-up”) and β denotes $m_s = -\frac{1}{2}$ (sometimes referred to as “spin-down”). As we will see shortly, spin is very important to the properties of many-electron atoms.

1.6. Many-Electron Atoms and Slater Determinants

The time-independent Schrödinger equation for a two-electron atom or ion, neglecting nuclear motion and relativistic effects, has the following as its Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0 r_{1,2}}$$

In the above expression, r_1 is the distance between electron 1 and the nucleus, r_2 is the distance between electron 2 and the nucleus, and $r_{1,2}$ is the distance between electrons 1 and 2. For the neutral two-electron atom, helium, $Z = 2$, of course. This Hamiltonian is *almost* the sum of the Hamiltonians for two one-electron atoms, differing only by the potential energy term that reflects electron-electron repulsion, $U_{e-e} = \frac{e^2}{4\pi\epsilon_0 r_{1,2}}$. If the interelectron repulsion

term were *not* there, then we could write the wavefunction ψ as the product of two one-electron wavefunctions. The ground-state wavefunction would then be simply given by

$$\psi = 1s(1)1s(2)$$

where the numbers in parentheses indicate the coordinates of electrons 1 and 2.

One might think that a good approximate wavefunction would be this product of one-electron wavefunctions, which, including the spin functions α and β , could be written as

$$\psi = 1s\alpha(1)1s\beta(2) = u_1(1)u_2(2)$$

where the “spin orbitals” u_1 and u_2 are equal to $1s\alpha$ and $1s\beta$, respectively. However, there is a problem with this approximate wavefunction beyond its neglect of interelectronic repulsion, namely, that it is not antisymmetric upon the exchange of electrons. Wolfgang Pauli (1900-1958, Nobel Prize in Physics 1945) used relativistic quantum mechanics to show that any acceptable multielectron wavefunction must change sign (*i.e.* must be multiplied by -1) when the coordinates of any two electrons are exchanged, a result known as the Pauli antisymmetry principle. For a two-electron system, this result can be written in shorthand as

$$\psi(2,1) = -\psi(1,2)$$

We can see immediately that our simple product of spin orbitals does not satisfy this criterion:

$$\begin{aligned}\psi(1,2) &= 1s\alpha(1)1s\beta(2) \\ \psi(2,1) &= 1s\alpha(2)1s\beta(1) \neq -\psi(1,2)\end{aligned}$$

John Slater (1900-1975) showed that one can write an approximate helium atom wavefunction that displays this property of antisymmetry as a determinant:

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

The factor of $1/\sqrt{2}$ is a normalization constant. Switching the coordinates of electrons 1 and 2 in this determinantal wavefunction gives

$$\psi(2,1) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(2) & 1s\beta(2) \\ 1s\alpha(1) & 1s\beta(1) \end{vmatrix} = -\psi(1,2)$$

This switching of electronic coordinates *must* yield the negative of the first wavefunction because it consists of exchanging two rows in a determinant, and every time two rows (or two columns) of a determinant are exchanged, the determinant’s value is multiplied by -1 .

In general, a system with n electrons in n spin orbitals can be represented by a so-called Slater determinant with the form⁵

$$\psi(1,2,\dots,n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_n(1) \\ u_1(2) & u_2(2) & \cdots & u_n(2) \\ \vdots & \vdots & & \vdots \\ u_1(n) & u_2(n) & \cdots & u_n(n) \end{vmatrix}$$

(Slater determinants are sometimes written with the rows and columns interchanged from the form above. This is also perfectly correct, since the interchange of all rows of a determinant with its columns does not change the determinant's value.)

The ground state wavefunction of a lithium atom, with three electrons, could be approximated by the following Slater determinant:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

It should be emphasized that Slater determinants are not “exact” wavefunctions, since for systems with more than one electron, the *true* solution to the nonrelativistic Schrödinger equation cannot be written in closed form. What Slater determinants do is ensure that approximate wavefunctions accurately reflect a *particular* physical reality, namely, the antisymmetry of real wavefunctions upon the exchange of two electrons.

The use of Slater determinants also yields the familiar Pauli exclusion principle, according to which no more than two electrons (with different spin) can occupy a single spatial atomic orbital (a particular set of quantum numbers n , l , and m). The Slater determinant we previously wrote for Li reflects the (actual) ground-state electron configuration $(1s)^2(2s)^1$. Now, suppose that we naïvely thought that Li had the (impossible) electron configuration $(1s)^3$. This would mean that the third electron, with only two choices for spin, α or β , would

⁵ Closed-subshell systems, systems with only one unpaired electron, and systems in which all unpaired electrons have the same spin (either α or β) can be represented by a single Slater determinant. Systems containing more than one unpaired electron with different spin sometimes require a linear combination of a few Slater determinants to approximately describe the wavefunction. For further details and some examples, see pages 40-43 of *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, 2nd edition, by Isaac B. Bersuker, John Wiley & Sons: Hoboken, NJ, 2010.

occupy the spin orbital $1s\alpha$ or $1s\beta$. This would yield either of the two following Slater determinants:

$$\psi[(1s)^3] = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 1s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 1s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 1s\alpha(3) \end{vmatrix}$$

or

$$\psi[(1s)^3] = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) & 1s\beta(2) \\ 1s\alpha(3) & 1s\beta(3) & 1s\beta(3) \end{vmatrix}$$

Each of the above determinants has two columns that are the same as each other. But a well-known theorem about determinants states that any determinant with two columns the same (or two rows the same) has a value of zero.⁶ So the determinantal “wavefunctions” that could be written for the electron configuration $(1s)^3$ have $\psi = 0$ everywhere, *i.e.* they represent systems that do not exist.

1.7. Electron Configurations, Terms, and States

Keeping in mind that each (spatial) orbital can hold up to two electrons (with different spin), we can predict the ground-state electron configurations of neutral atoms by supposing that electrons will fill orbitals in order of increasing energy, with lower-energy orbitals being filled first. The construction of electron configurations in this fashion is known as the Aufbau principle, from the German *Aufbau*, “construction.” Thus, the ground-state electron configurations of the first 18 elements are shown in Table 1.3 below. As the atomic number (and thus the number of electrons in a neutral atom) grows, the full electron configuration becomes long and unwieldy to write, so we often use a shorthand in which we write the symbol for the previous noble gas in parentheses, followed by the electrons added following this last noble gas “core.”

⁶ This follows from the fact that interchanging two columns or two rows of a determinant gives you the negative of that determinant. Suppose a determinant with value D has two columns (or rows) the same. Interchanging those two columns (or rows) to give a new determinant with the same value D , since the columns (or rows) interchanged were identical. But since interchanging two columns (or rows) takes the value of the determinant to its negative, so the new determinant has the value $-D$. We thus have the equation $D = -D$, which can only be true if $D = 0$.

To use the Aufbau principle correctly, we must know the relative ordering of orbital energies in multielectron atoms. For orbitals with a given value of l , energy increases with n , and for orbitals with a given value of n , energy increases with l . In the absence of an external magnetic field, energy is independent of m for a given pair of n and l . This gets us the ordering $1s < 2s < 2p < 3s < 3p$, which is reflected in the electron configurations shown in Table 1.3. However, once we reach the fourth row of the Periodic Table (K through Kr), we see that some orbitals with higher n but lower l are lower in energy than others with lower n and higher l . In particular, the $4s$ orbitals are filled before the $3d$, so the ground-state electron configurations of K and Ca are $[\text{Ar}](4s)^1$ and $[\text{Ar}](4s)^2$, respectively, with the d orbitals beginning to be filled as we move into the transition metals: the first two transition metals, Sc and Ti, have ground-state electron configurations $[\text{Ar}](4s)^2(3d)^1$ and $[\text{Ar}](4s)^2(3d)^2$, respectively.

How may we predict the energy ordering of orbitals with various different n and l values? One way would be simply to memorize a list in order: $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$. But such a list is not the easiest thing to memorize, especially if the patterns are not clear. Fortunately, you need not memorize such a list as long as you have access to a Periodic Table. The trick to easily constructing electron configurations is to recognize “blocks” of two elements (to the left of the transition metals) as corresponding to the filling of an s orbital,⁷ blocks of six elements (to the right of the transition metals) as corresponding to the filling of a p subshell, blocks of ten elements (the transition metals) as corresponding to the filling of a d subshell, and blocks of fourteen elements (the lanthanides and actinides, usually appended below the rest of the elements in a Periodic Table) as corresponding to the filling of an f subshell. If you have not committed to memory the fact that the $4s$ orbital is filled before the $3d$ orbitals, you could still recognize that the block of two elements (K and Ca) preceding a block of ten (Sc through Zn) reflects the filling of $4s$ before $3d$.

⁷ The first such block, corresponding to the filling of the $1s$ orbital, consists of H and He. How this block works would be clearer if He were above Be in the Periodic Table, since He has the electron configuration $(1s)^2$ and Be has the configuration $[\text{He}](2s)^2$. He is instead placed in the rightmost column, with the other noble gases, due to its similar (lack of) reactivity.

Table 1.3. Ground-state electron configurations of the first 18 elements.

Element	Electron configuration (full)	Electron configuration (shorthand)
H	$(1s)^1$	$(1s)^1$
He	$(1s)^2$	$(1s)^2$
Li	$(1s)^2(2s)^1$	$[\text{He}](2s)^1$
Be	$(1s)^2(2s)^2$	$[\text{He}](2s)^2$
B	$(1s)^2(2s)^2(2p)^1$	$[\text{He}](2s)^2(2p)^1$
C	$(1s)^2(2s)^2(2p)^2$	$[\text{He}](2s)^2(2p)^2$
N	$(1s)^2(2s)^2(2p)^3$	$[\text{He}](2s)^2(2p)^3$
O	$(1s)^2(2s)^2(2p)^4$	$[\text{He}](2s)^2(2p)^4$
F	$(1s)^2(2s)^2(2p)^5$	$[\text{He}](2s)^2(2p)^5$
Ne	$(1s)^2(2s)^2(2p)^6$	$[\text{He}](2s)^2(2p)^6$
Na	$(1s)^2(2s)^2(2p)^6(3s)^1$	$[\text{Ne}](3s)^1$
Mg	$(1s)^2(2s)^2(2p)^6(3s)^2$	$[\text{Ne}](3s)^2$
Al	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1$	$[\text{Ne}](3s)^2(3p)^1$
Si	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$	$[\text{Ne}](3s)^2(3p)^2$
P	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3$	$[\text{Ne}](3s)^2(3p)^3$
S	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^4$	$[\text{Ne}](3s)^2(3p)^4$
Cl	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^5$	$[\text{Ne}](3s)^2(3p)^5$
Ar	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$	$[\text{Ne}](3s)^2(3p)^6$

This Periodic Table-based technique for predicting ground-state electron configurations works very well for those elements which do not have anomalous ground-state configurations. Examples of such anomalous elements include Cr, whose ground-state configuration is $[\text{Ar}](4s)^1(3d)^5$ rather than $[\text{Ar}](4s)^2(3d)^4$, and Cu, whose ground-state configuration is $[\text{Ar}](4s)^1(3d)^{10}$ rather than $[\text{Ar}](4s)^2(3d)^9$. I do not recommend attempting to commit these anomalous configurations to memory (especially since the electron configurations of ions, as opposed to neutral atoms, are quite regular), but you should be aware that they exist.

When considering the ground-state electronic structure of an atom, the electron configuration, which shows only the number of electrons in each subshell defined by n and l , is not the whole story. We must also consider the values of m and m_s of electrons within a given subshell. In general, two electrons in the same subshell have an energetic preference for occupying different orbitals in that subshell, if possible, to minimize the Coulombic potential energy required to pair two negative charges in the same region of space. Let us denote this Coulombic energy as Π_c . Now consider a carbon atom, with ground-state electron configuration $[\text{He}](2s)^2(2p)^2$. Of its four valence electrons, the two in the $2s$ subshell must occupy the same orbital, since there is only one orbital in each ns subshell. However, since there are three orbitals in the $2p$ subshell, it is energetically more favorable to place the two electrons in the $2p$ subshell in different orbitals. This means that, for instance, the configurations $[\text{He}](2s)^2(2p_x)^1(2p_z)^1$, $[\text{He}](2s)^2(2p_y)^1(2p_z)^1$, and $[\text{He}](2s)^2(2p_x)^1(2p_y)^1$ are equal in energy to each other, but each is lower in energy (by Π_c) than $[\text{He}](2s)^2(2p_x)^2$, $[\text{He}](2s)^2(2p_y)^2$, or $[\text{He}](2s)^2(2p_z)^2$.

Additionally, when multiple electrons occupy orbitals with different values of m , the configuration with the highest net spin S (where S is the sum of m_s values) is lowest in energy; this fact is known as Hund's rule of maximum multiplicity (after Friedrich Hund, 1896-1997). Qualitatively, Hund's rule works because of a quantity called exchange energy, symbolized by Π_e ; this quantity has no classical analog. Whenever two electrons in a set of degenerate orbitals have the same spin, they are indistinguishable, and each way that two such electrons could be swapped with each other adds Π_e to the energy of the configuration. Since Π_e is a negative quantity, exchange energy terms are stabilizing, so they lower the system's total energy. For example, consider a free nitrogen atom, with electron configuration $[\text{He}](2s)^2(2p)^3$. Two possible states of the $2p$ electrons in an N atom are shown below, labeled A and B in Figure 1.3 below.

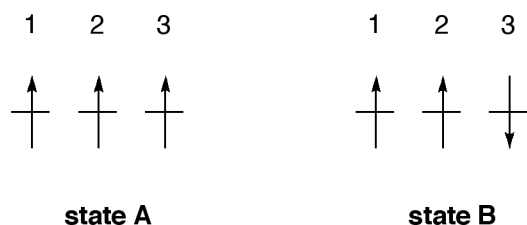


Figure 1.3. Two possible states of the 2p electrons in a nitrogen atom.

We first may note that neither state A nor state B has any Coulomb energy terms, since neither has two electrons occupying the same 2p orbital. The two states are not, however, equal in energy. For state A, the pairs of electrons that we can swap to yield indistinguishable configurations are (1, 2), (2, 3), and (1, 3), so the total exchange energy of state A is $3\Pi_e$. For state B, we can make the swap (1, 2), but since electron 3 has the opposite spin from electrons 1 and 2, we cannot swap the pairs (1, 3) or (2, 3). Thus, state B has a total exchange energy of only Π_e , and since Π_e is a negative quantity, state A is lower in energy, and it in fact represents the ground state of a free N atom.

The above discussion of the Coulomb energy Π_c and exchange energy Π_e (collectively often referred to as the pairing energy) is semiquantitative. To more formally consider the possible electronic states of atoms, we must consider an extension of the quantum numbers n , l , m , and m_s , defined for single electrons (or one-electron atoms) to multielectron atoms. We can describe a multielectron atom by four quantum numbers, L , S , M , and M_s . Importantly, a given electron *configuration* for a multielectron atom can give rise to more than one *term*, where an atomic term (and its corresponding *term symbol*) indicates the values of L and S . Different terms have different energies, even for the same electron configuration of the same element.

As an example, we can return to the example of a neutral carbon atom, with electron configuration $[\text{He}](2s)^2(2p)^2$. A closed subshell, in which all orbitals with a given set of n and l values are doubly occupied, has no effect on the overall atomic term, so we do not need to consider the 1s electrons (from the He “core”) or the 2s electrons. This means that the analysis that we are about to perform is valid for any atom or ion with an p^2 electron

configuration in the ground state, so it would work just as well for an Si, Ge, Sn, or Pb atom. To understand why a $(2p)^2$ electron configuration would give rise to multiple terms, remember that there are three degenerate $2p$ orbitals with different values of m ($2p_1$, $2p_0$, and $2p_{-1}$).⁸ The two electrons might be in the same $2p$ orbital, or they might be in different $2p$ orbitals. If they are in different orbitals, they might have the same spin or the opposite spin.

The multielectron atom quantum numbers M and M_S are defined, summing over each electron i , by

$$M = \sum_i m_i$$

$$M_S = \sum_i m_{s,i}$$

To calculate M , we simply add the m values of all the electrons, and to calculate M_S , we add all their m_s values. Each set of m and m_s values for all the electrons in partially filled subshells is called a *microstate*. The first step in determining the term symbols for an electron configuration is to prepare a table of all the possible microstates, organized by the values of M and M_S that they give rise to. The notation we will use is a simple numeral to indicate the value of m , and a superscript $+$ or $-$ to indicate an m_s value of $+\frac{1}{2}$ or $-\frac{1}{2}$, respectively. For example, if one electron is in the $2p_0$ orbital with $m_s = +\frac{1}{2}$ and another is in the $2p_{-1}$ orbital with $m_s = -\frac{1}{2}$, we denote that microstate by $0^+, -1^-$. We are not concerned about the order in which the electrons' quantum numbers are written, so the microstate denoted $0^+, -1^-$ is the same as that denoted by $-1^-, 0^+$.

The largest value of M we can obtain for $(2p)^2$ is $+2$, where both electrons are in the $2p_1$ orbital, and the smallest is -2 , where both are in $2p_{-1}$. Similarly, the largest M_S is $+1$, where both electrons have $m_s = +\frac{1}{2}$, and the smallest M_S is -1 , where both have $m_s = -\frac{1}{2}$. When

⁸ It is more numerically convenient here to deal with potentially complex orbitals, with well-defined values of m , than with the all-real linear combinations such as $2p_x$ and $2p_y$.

preparing a microstate table, we must be careful to ensure that we obey the Pauli exclusion principle: for any microstate with $M = 2$, we must have $M_S = 0$, since if the two electrons are both in the $2p_1$ orbital, they must have opposite spins that cancel each other out. The microstate table for $(2p)^2$, or any p^2 , is shown below (Table 1.4).

Table 1.4. Microstates of a p^2 atom.

		M_S		
		-1	0	+1
M	+2		$1^+, 1^-$	
	+1	$1^-, 0^+$	$1^+, 0^-$ $1^-, 0^+$	$1^+, 0^+$
	0	$-1^-, 1^-$	$-1^+, 1^-$ $0^+, 0^-$ $-1^-, 1^+$	$-1^+, 1^+$
	-1	$-1^-, 0^-$	$-1^+, 0^-$ $-1^-, 0^+$	$-1^+, 0^+$
	-2		$-1^+, -1^-$	

To extract the terms, which specify the quantum numbers L and S , from this microstate table, we need to define the possible values of L and S in terms of M and M_S . Each term consists of a number of degenerate microstates. A term with quantum number L has $2L + 1$ possible values of M , integers with values of $M = -L, -L + 1, -L + 2 \dots L - 2, L - 1, L$. A term with quantum number S has $2S + 1$ possible values of M_S , integers *or half-integers* with values of $M_S = -S, -S + 1, -S + 2 \dots S - 2, S - 1, S$. The notation for term symbols is ^{2S+1}L , where the quantity $2S + 1$ is called the multiplicity, and the value of L is denoted by a letter: L values of 0, 1, 2, 3, 4, 5, and 6 are given the letters S, P, D, F, G, H , and I , respectively.⁹ The terms “singlet,”

⁹ The first four of these letters, S, P, D , and F , are analogous to the s, p, d , and f labels for orbitals. Note that, while no currently known elements have g, h , or i orbitals occupied in their ground states, G, H , and I terms for multielectron atoms *are* spectroscopically important. Be careful not to confuse the quantum number S with the use of S to denote a term where the quantum number $L = 0$.

“doublet,” “triplet,” *etc.* are often used to denote the multiplicity, so the term ^1S is read as “singlet S ,” ^3P as “triplet P ,” and so on. The degeneracy (number of microstates) corresponding to each term is given by the product $(2S + 1)(2L + 1)$.

To extract the terms from the microstate table, we draw the table again without actually denoting all the microstates. Instead, we just denote each separate microstate with a letter x . So a pair of M and M_S values corresponding to three microstates will have xxx noted in the table. Doing this with our p^2 table yields

		M_S		
		-1	0	+1
M	+2		x	
	+1	x	xx	x
	0	x	xxx	x
	-1	x	xx	x
	-2		x	

The maximum S value possible here is $S = 1$, since that is the maximum value of M_S . Thus, $S = 1$ corresponds to $M_S = -1, 0$, or $+1$. This means that we need a row with three columns (three values of M_S), which excludes $M = -2$ or $+2$. If $L = 1$, then $M = -1, 0$, or $+1$. Thus, a 3×3 grid corresponds to $S = 1$ and $L = 1$, or a ^3P term:

		M_S		
		-1	0	+1
M	+2			
	+1	x	x	x
	0	x	x	x
	-1	x	x	x
	-2			

If we subtract the x markings corresponding to this table from the initial table, we obtain

		M_S		
		-1	0	+1
M	+2		x	
	+1		x	
	0		xx	
	-1		x	
	-2		x	

Now if $L = 2$, corresponding to $M = -2, -1, 0, +1$, or $+2$, we need a column with five rows. We see that, for this term, $M_S = 0$ only, so $S = 0$. (This is what we deduced earlier from the Pauli exclusion principle.) So our chart corresponding to the ^1D term is as follows:

		M_S		
		-1	0	+1
M	+2		x	
	+1		x	
	0		x	
	-1		x	
	-2		x	

Subtracting this chart leaves only one chart left, with only one microstate:

		M_S		
		-1	0	+1
M	+2			
	+1			
	0		x	
	-1			
	-2			

This is a microstate with $M = 0$ and $M_S = 0$, corresponding to $L = 0$ and $S = 0$, a ^1S term.

We thus see that a p^2 electron configuration gives rise to the terms ^1S , ^3P , and ^1D . To determine which of these terms corresponds to the lowest energy (the ground state), we use Hund's first rule, introduced before as Hund's rule of maximum multiplicity, states that the lowest energy term is that with the greatest value of S . This means that, for p^2 , the ground-state term is ^3P . Hund's second rule states that, if there are multiple terms with the greatest value of S , that with the greatest value of L is the ground state. For instance, if an electron configuration had the possible ground states ^4P and ^4F , Hund's second rule would state that ^4F is the ground-state term. Note that Hund's rules do not allow the ranking of non-ground-state terms by energy. So while Hund's rules will allow you to determine the ground-state term, there is no simple way to determine which term corresponds to the first excited state, which to the second excited state, *etc.* For the p^2 configuration, Hund's rules tell us that ^3P is the ground state, but they do not tell us whether ^1S is lower in energy than ^1D or *vice versa*.

So far, this treatment of quantum mechanics for multielectron atoms has only been relativistic in that it acknowledges the phenomena of spin and the Pauli exclusion principle. However, for heavier atoms, spin-orbit coupling becomes important. The multielectron quantum numbers L and S reflect orbital and spin angular momentum, respectively, but when these two forms of angular momentum couple, we must define a *total* angular momentum quantum number J , which is always a non-negative integer or half-integer, and whose possible values are $J = L + S, L + S - 1, L + S - 2, \dots |L - S|$. Term symbols which include

spin-orbit coupling are denoted by $^{2S+1}L_J$. A single *term* (defined by its L and S values) can thus be split into more than one *state* (defined by the value of J), where different states of a given term have different energies, thus (at least partially) lifting the degeneracy of a term.

For our p^2 example, the ^1S term can only have $J = 0$, so its only state is $^1S_0$. Similarly, the ^1D term can only have $J = 2$, so its only state is $^1D_2$. For the ^3P term, however, there are three different states, with $J = 2, 1$, or 0 . Thus ^3P is split into three states: $^3P_2$, $^3P_1$, and $^3P_0$. To decide which state is lowest in energy, we use Hund's third rule: for a subshell that is less than half-filled, the state with the lowest value of J is lowest in energy, while for a subshell that is more than half-filled, the state with the highest value of J is lowest in energy. (When a subshell is exactly half-filled, *e.g.* s^1 , p^3 , d^5 , only one value of J is possible.) For this example, we have a p^2 configuration, so the p subshell is less than half-filled. Thus, the lowest-energy state is $^3P_0$.

As spin-orbit coupling is a relativistic effect, it is much more pronounced in heavier atoms. For C, the $^3P_2$ state lies only 43.5 cm^{-1} above the $^3P_0$ ground state, while the first excited term, $^1D_2$, lies 10193.7 cm^{-1} above $^3P_0$. Thus, the energy difference between states of the ^3P term is minuscule compared to the energy differences between terms. This is not the case, however, for the heavy element Pb. For Pb, $^3P_2$ lies 10650.5 cm^{-1} above $^3P_0$, while $^1D_2$ lies 21457.9 cm^{-1} above $^3P_0$. For this heavy element, energy differences between states are comparable to energy differences between terms.

A considerable, and tedious, amount of labor was required to derive the possible term symbols for a p^2 atom. For atoms with some other valence electron configurations, it is even worse. The microstate table for a d^2 atom contains 45 entries,¹⁰ and for systems with valence f electrons, the task is more laborious still. Fortunately, the possible terms for various d electron configurations have been tabulated.¹¹ I do not ask my inorganic chemistry students to derive all the terms for a given electron configuration as a problem on either homework

¹⁰ See Table 2.8 on page 41 of *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, 2nd edition, by Isaac B. Bersuker, John Wiley & Sons: Hoboken, NJ, 2010.

¹¹ *Ibidem*, page 37.

or an exam. However, it *is* possible, without too much tedium, to derive the term *for the ground state* of a given electron configuration, and you should know how to do this.

We may consider a d^6 system as an example. To find the ground state, we sketch the configuration with as many electrons unpaired as possible, with all unpaired electrons spin-up, to maximize M_S . We then preferentially put electrons into orbitals with the highest m values, in order to maximize M . This is shown below in Figure 1.4.

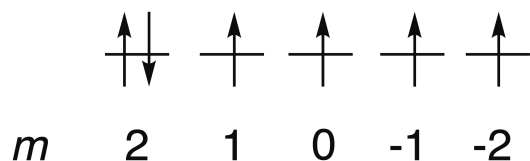


Figure 1.4. A pictorial representation of the ground state of a d^6 system.

Here $M = 2 + 2 + 1 + 0 + (-1) + (-2) = 2$. We assign the value of L where this is the highest possible M value, so $L = 2$ and we have a D term. $M_S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2$. We assign the value of S where this is the highest possible M_S value, so $S = 2$ and $2S + 1 = 5$. We thus have a quintet term: ^5D . To determine the ground-state J value using spin-orbit coupling, we first note that the possible J values are 4, 3, 2, 1, and 0. Now we use Hund's third rule: since d^6 is a more than half-filled subshell, the highest J value corresponds to the lowest energy, so the ground state is $^5D_4$.

Three other tips for the rapid evaluation of ground-state term symbols are as follows:

(1) All atoms with only completely full and completely empty subshells have the $^1S_0$ ground state.

(2) All singlet terms ($S = 0$) have no splitting from spin-orbit coupling, so $J = L$.

(3) For atoms and ions whose only unfilled subshell is a d subshell, a d^n configuration gives rise to the same terms as a d^{10-n} configuration, so d^1 and d^9 have the same terms, d^2 and d^8

have the same terms, *etc.* Note that the ground-state J value will differ between d^n and d^{10-n} , because the use of Hund's third rule depends on whether a subshell is more or less than half-filled. This result is sometimes called the "hole formalism," since adding n electrons to an empty d subshell gives the same terms as removing n electrons (adding n "holes") to a full d subshell.

We can go beyond the simple pairing energy approach discussed earlier to see how quantum mechanics is used, with more mathematical rigor, to calculate the energies of terms. If there were no interactions between electrons, then all terms corresponding to a given electron configuration would be degenerate. Thus, we can use perturbation theory to calculate the lifting of this degeneracy. We write the perturbation Hamiltonian for a multielectron atom to reflect the electron-electron repulsion:

$$\hat{H}' = \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

where r_{ij} is the distance between electrons i and j . The zeroth-order wavefunctions are the multielectron wavefunctions $\Psi(L, M, S, M_S)$ corresponding to the multielectron quantum numbers L , M , S , and M_S . Each of these wavefunctions can be represented, as mentioned above, as either a Slater determinant or as a linear combination of Slater determinants. It turns out that, for a given pair of L and S values, the secular equation of degenerate perturbation theory gives rise to an exceptionally simple secular equation, whose only nonzero matrix elements are the diagonal ones. Thus, one can simply read off the diagonal matrix elements as the energy corrections due to interelectron interactions. These first-order energy corrections all have the form

$$E^{(1)}(L, S) = \left\langle \Psi(L, M, S, M_S) \left| \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right| \Psi(L, M, S, M_S) \right\rangle$$

where all wavefunctions $\Psi(L, M, S, M_S)$ that give rise to the same value of $E^{(1)}$ belong to the same term. Since each wavefunction $\Psi(L, M, S, M_S)$ is a linear combination of Slater determinants $\Phi(m_1, m_{s1}, m_2, m_{s2} \dots)$, where the order of the determinant depends on the number of electrons, the energy correction integrals are themselves linear combinations of integrals of the form

$$\left\langle \Phi(m_1, m_{s1}, m_2, m_{s2} \dots) \left| \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right| \Phi(m_1, m_{s1}, m_2, m_{s2} \dots) \right\rangle$$

It turns out that, for these integrals to be nonzero, the Slater determinants Φ must differ by no more than two one-electron states, that is, at most two of the electrons represented by those Slater determinants can have different pairs of m and m_s values. This means that all the nonzero integrals that make up $E^{(1)}$ are two-electron integrals with the form

$$\left\langle \phi_a(1)\phi_b(2) \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \phi_c(1)\phi_d(2) \right\rangle$$

where the functions ϕ_a , *etc.* are one-electron functions, perhaps hydrogenlike orbitals. Two types of such two-electron integrals are often given particular names and notations, the Coulomb integral I_{ab} (sometimes denoted J_{ab}) and the exchange integral K_{ab} . These integrals are defined as follows:

$$I_{ab} = \left\langle \phi_a(1)\phi_b(2) \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \phi_a(1)\phi_b(2) \right\rangle$$

$$K_{ab} = \left\langle \phi_a(1)\phi_b(2) \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \phi_b(1)\phi_a(2) \right\rangle$$

These integrals have dimensions of energy, and so they are sometimes referred to as the Coulomb energy and exchange energy, respectively. They are the more rigorous versions of the Π_c and Π_e terms we saw earlier. The name of the Coulomb integral comes from the fact that it represents the Coulombic like charge/like charge repulsion between electron 1, in orbital ϕ_a , and electron 2, in orbital ϕ_b . It is always positive, so I_{ab} terms are destabilizing. The exchange integral has no obvious classical analogy. Its name comes from the fact that it represents the possibility of exchanging electrons 1 and 2 between orbitals ϕ_a and ϕ_b . It is always negative, so K_{ab} terms are stabilizing.

It is sometimes claimed that the exchange integral is the energetic result of a purely quantum-mechanical “exchange force.” This is, in fact, incorrect. Neglecting gravitational attractions between electrons and nuclei, the only one of the four fundamental forces¹² that

¹² The other two fundamental forces are the strong and weak nuclear forces, which are important in understanding the structure of nuclei and nuclear reactions such as radioactive

we consider in atomic and molecular calculations is the electromagnetic force, represented by the Coulomb's law potential energy terms in the Hamiltonian. The approximate solutions to the Schrödinger equation that we employ leads to the appearance of exchange integrals when calculating their approximate energies, but these energy terms do not reflect any separate force.

The various integrals have been calculated and tabulated in the forms of parameters. One set of these parameters is known as the Slater-Condon parameters, after Slater and Edward Condon (1902-1974), and the other is known as the Racah parameters, after Giulio Racah (1909-1965). The Slater-Condon and Racah parameters are just linear combinations of each other, cast in ways that are more or less convenient for different problems. The energies of the various d^n configurations have been tabulated¹³ in terms of the Racah parameters A , B , and C . While the values of the Racah parameters can be calculated by a computer program from definite integrals involving approximate wavefunctions, they are often instead treated as empirical parameters, whose values are determined experimentally from the energies of spectroscopic transitions between different electronic states.

The above discussion has sketched out (though not formally derived) how the relative energies of different terms are calculated. This methodology does not, however, consider how spin-orbit coupling affects the energies. Such calculations require a consideration of relativistic effects, and they are mathematically more challenging.

1.8. Effective Nuclear Charge

It is very useful to use one-electron orbitals as an approximation of orbitals in multielectron atoms, as these orbitals are easy to visualize and convenient to draw in pictorial

decay and fission. They are not, however, necessary to consider when studying chemical, as opposed to nuclear, reactions.

¹³ See Table 2.6 on page 37 of *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, 2nd edition, by Isaac B. Bersuker, John Wiley & Sons: Hoboken, NJ, 2010.

representations of chemical bonding. However, as we have seen, the energy of such orbitals in multielectron atoms now depends on l as well as n , making the simple orbital energy formula $E_n = -\frac{Z^2}{2n^2}E_h$ no longer correct. Slater devised an approximate parametrization scheme for this phenomenon, known as effective nuclear charge. The qualitative idea behind effective nuclear charge is that, since the simple formula for energy as a function of n only no longer holds for multielectron atoms because of electron-electron repulsion, we can think of each electron as no longer “feeling” the full attraction of the nucleus with its positive nuclear charge Z (equal to the atomic number, the number of protons in the nucleus). Instead, each electron is said to be “shielded” by the negative charges of its fellow electrons, and it experiences a decreased *effective* nuclear charge Z_{eff} . Because a multielectron Schrödinger equation has no closed-form solution, there is no set of Z_{eff} values corresponding to an exact algebraic expression for an electron’s energy as a function of Z_{eff} . However, Slater devised a series of simple rules for approximating Z_{eff} in a way that is useful for rationalizing trends in atomic behavior and chemical bonding.

Slater’s rules begin with writing $Z_{\text{eff}} = Z - \sigma$, where σ is known as the shielding constant, reflecting how an electron is partially shielded from the nuclear charge. To calculate σ , we first write the electron configuration of the atom or ion in the following form with the following order: $(1s)(2s, 2p)(3s, 3p)(3d)(4s, 4p)(4d)(4f)(5s, 5p)(5d)(5f) \dots$ etc. Note that this ordering is not the same as the order in which electrons fill atomic orbitals according to the Aufbau principle. Once the numbers of electrons in each such category has been noted, we apply the following rules:

- (1) Electrons in each category are not shielded at all by electrons in categories to their right.
- (2) For an ns or np electron, each electron in the same category contributes 0.35 to σ (with the exception that a $1s$ electron only contributes 0.30 to σ for another $1s$ electron). Each electron with principal quantum number $n - 1$ contributes 0.85, and each electron with principal quantum number $n - 2$ or less contributes 1.00.

(3) For an nd or nf electron, each electron in the same category contributes 0.35 to σ , while each electron in *any* category to the left (even one with the same value of n) contributes 1.00.

We can use Slater's rules to rationalize a feature of the electron configurations of ions that you may have found puzzling when you encountered it in general chemistry. Recall that, while the $4s$ orbitals are (with exceptions) filled before the $3d$ orbitals when writing ground-state electron configurations for neutral atoms, the $4s$ electrons are removed *before* the $3d$ electrons when positive ions of transition metals are formed. For instance, neutral Co has the ground-state electron configuration $[\text{Ar}](4s)^2(3d)^7$, but a Co^{2+} cation has the ground-state configuration $[\text{Ar}](4s)^0(3d)^7$, rather than $[\text{Ar}](4s)^2(3d)^5$. This pattern is sometimes called the "first-in, first-out rule," since the $4s$ orbitals are filled before the $3d$, but their electrons are also ionized first. (The same pattern holds for $5s$ and $4d$, and for $6s$ and $5d$.)

This rule may have struck you as odd when you first learned it: after all, if the $3d$ orbitals are higher in energy when filling an electron configuration, you might expect electrons in them to be easier to ionize. To see how Slater's rules address this question, we can calculate Z_{eff} for both a $4s$ and a $3d$ electron in Co. A neutral Co atom has the following ground-state electron configuration in a Slater's rules order: $(1s)^2(2s, 2p)^8(3s, 3p)^8(3d)^7(4s, 4p)^2$. For all electrons, the actual nuclear charge $Z = 27$, but the effective nuclear charge $Z_{\text{eff}} = Z - \sigma$ differs for the $4s$ and $3d$ electrons. For a $4s$ electron in Co, $\sigma = 0.35 + (15)(0.85) + (10)(1.00) = 23.10$, and so $Z_{\text{eff}} = 3.90$. For a $3d$ electron in Co, $\sigma = (6)(0.35) + (18)(1.00) = 20.10$, and $Z_{\text{eff}} = 6.90$. Thus, a $3d$ electron in Co experiences a greater effective nuclear charge than a $4s$ electron, and it is thus more difficult to ionize.

One can gain further insight into shielding by considering the radial distribution function $P(r)$, which is the probability distribution function for an electron in a given orbital as a function of radius. It is related to the radial function¹⁴ $R_{n,l}(r)$ by

$$P(r) = 4\pi r^2 [R_{n,l}(r)]^2$$

¹⁴ The factor of 4π comes from the fact that one integrates over all values of the angular coordinates θ and ϕ .

and the probability that a given electron is located between two distances r_1 and r_2 is given by

$$P(r_1 \leq r \leq r_2) = \int_{r_1}^{r_2} P(r) dr = 4\pi \int_{r_1}^{r_2} r^2 [R_{n,l}(r)]^2 dr$$

Atomic orbitals which have nodes containing the nucleus (p , d , and f orbitals) have larger most probable radii r_{mp} , *i.e.* values of r at which $P(r)$ is a maximum, than orbitals which do not (s orbitals). Since a d orbital has two nodes that pass through the nucleus, as compared to only one for a p orbital, the value of r_{mp} for a d orbital will be larger than that for a p orbital. Since a smaller fraction of the probability density of a d electron is close to the nucleus than that of a p electron, than that of an s electron, the shielding ability of electrons decreases as a function of l in the order $s > p > d$, for any given n .

1.9. Ionization Energy, Electron Affinity, and Electronegativity

The properties of orbitals and the concept of shielding can help explain periodic trends in ionization energy, electron affinity, and electronegativity. The ionization energy E_{ion} is the energy required to remove an electron from an atom in the gas phase, *i.e.* ΔE for the reaction $A(g) \rightarrow A^+(g) + e^-$, for an atom of some element A . It is always a positive quantity. One can similarly define second, third, *etc.* ionization energies; for instance, the second ionization energy $E_{\text{ion},2}$ is ΔE for $A^+(g) \rightarrow A^{2+}(g) + e^-$. A larger ionization energy means that the valence electrons in an atom or ion are held more tightly. The second ionization energy is always greater than the first, and in general, the $(n + 1)$ st ionization energy is always greater than the n th. Once one electron has been removed, the remaining electrons are less strongly shielded, and thus the effective nuclear charge they experience increases. Related to ionization energy is the electron affinity E_{ea} , defined as ΔE for the removal of an electron from the monoanion in the gas phase: $A^-(g) \rightarrow A(g) + e^-$. You may find it easier to remember the reaction equation corresponding to electron affinity if you think of the electron affinity for an atom as being that atom's "zeroth ionization energy." Unlike ionization energies, electron affinities can be either positive or negative, depending on the element.

In general, ionization energies increase across a period (a row of the Periodic Table). This makes sense from the standpoint of effective nuclear charge: as the actual nuclear charge Z increases, the additional electrons provide incomplete shielding, so the effective nuclear charge Z_{eff} also increases, albeit more slowly than Z . Ionization energies generally decrease down a column, however, despite the increase in Z , because the principal quantum number n of the valence electrons increases. The valence electrons are thus farther from the nucleus on average, and so they experience a significantly smaller Z_{eff} . In general, a useful mnemonic is that ionization energies are greatest at the upper right corner of the Periodic Table, and smallest at the lower left corner. For example, F has a very high E_{ion} ($1681.0 \text{ kJ}\cdot\text{mol}^{-1}$), as does Ne ($2080.6 \text{ kJ}\cdot\text{mol}^{-1}$), while E_{ion} for Cs is very low ($375.7 \text{ kJ}\cdot\text{mol}^{-1}$). Electron affinity displays a similar periodic trend, but shifted horizontally by one element. In each period, the halogens have the highest electron affinities, and these electron affinities are positive, since halide monoanions are isoelectronic to noble gases. In contrast, electron affinities are lowest for the noble gases, since a noble gas monoanion has one electron with a higher principal quantum number. For instance, while Ar has the electron configuration $[\text{Ne}](3s)^2(3p)^6$, Ar would have electron configuration $[\text{Ne}](3s)^2(3p)^6(4s)^1$. The single $4s$ electron is considerably higher in energy than any of the others, and is thus most easily removed.

Like many good mnemonics in chemistry, the general trends for ionization energies have some notable, and interesting, exceptions. One such exception is that ionization energy tends to decrease whenever a new value of the azimuthal quantum number l is first populated. For instance, boron, with electron configuration $[\text{He}](2s)^2(2p)^1$ has a *lower* ionization energy ($800.6 \text{ kJ}\cdot\text{mol}^{-1}$) than beryllium ($899.4 \text{ kJ}\cdot\text{mol}^{-1}$), with configuration $[\text{He}](2s)^2$. This is due to the fact that $2p$ orbitals are higher in energy than $2s$ orbitals, so it is easier to remove a $2p$ electron from boron than to remove a $2s$ electron from beryllium. Similarly, the ionization energy of aluminium ($577.6 \text{ kJ}\cdot\text{mol}^{-1}$) is lower than that of magnesium ($737.8 \text{ kJ}\cdot\text{mol}^{-1}$). Atoms with a half-filled subshell also tend to have especially high ionization energies. For instance, the ionization energy of nitrogen ($1402.3 \text{ kJ}\cdot\text{mol}^{-1}$) is higher than that of oxygen ($1314.0 \text{ kJ}\cdot\text{mol}^{-1}$). This is because each $2p$ orbital in a ground-state N atom contains only one electron per Hund's rule, whereas one of the $2p$ orbitals of an O atom is doubly occupied.

Each electron in this doubly occupied orbital is higher in energy due to Coulombic repulsion, and is thus more easily removed.

Another chemical property with notable periodic trends is electronegativity (often symbolized χ). Linus Pauling (1901-1994, Nobel Prize in Chemistry 1954, Nobel Peace Prize 1962) was the first to attempt to quantify the chemically intuitive notion that some elements are more likely to bear a partial negative charge than others in polar covalent bonds, that is, the electrons in the bond are not equally shared between the two atoms, and on average lie closer to the more electronegative element.¹⁵ Different mathematical definitions of electronegativity have been proposed by (among others) Pauling, Leland Allen (1926-2012), and Robert Mulliken (1896-1986, Nobel Prize in Chemistry 1966). Of these definitions, Mulliken's is the simplest: he proposed that an element's electronegativity is simply the mean of its first ionization energy and first electron affinity, or

$$\chi = \frac{E_{\text{ion}} + E_{\text{ea}}}{2}$$

Mulliken electronegativities naturally have dimensions of energy (usually $\text{kJ}\cdot\text{mol}^{-1}$ or eV per atom), though they are sometimes scaled to match the ranges of other electronegativity scales, such as Pauling's or Allen's. Mulliken's definition makes intuitive sense, in that it should require substantial energy to remove an electron from a highly electronegative element (high E_{ion}) and that the addition of an electron to a highly electronegative element should either release energy (negative E_{ea}) or at least not require much addition of energy (small positive E_{ea}). In general, electronegativity increases across a row and decreases down a column. The least electronegative element is Cs (the heaviest alkali metal with any stable isotopes), and the most electronegative element is F (the lightest halogen).¹⁶

¹⁵ The term "electronegativity" was coined by Jöns Jacob Berzelius (1779-1848), but Berzelius did not propose a quantitative metric for it.

¹⁶ He and Ne are arguably more electronegative than F by some numerical definitions, but since no compounds are known in which He or Ne participates in a covalent bond, the electronegativity of these elements is not a relevant quantity.

1.10. Atomic and Ionic Size

Atomic size is another quantity that follows important periodic trends, but it can be a surprisingly difficult measure to pin down. Quantum mechanics tells us that atoms and ions do not really have well-defined “radii,” since they are delocalized. However, one can define a radius within which some high percentage (often taken to be 90% or 95%) of the electron density is present. The covalent radius of an element is defined as the radius of an atom of that element participating in a covalent bond, so the sum of the atoms’ covalent radii should equal the bond length. If a bond length can be measured in a molecule with two equivalent fragments, the covalent radius is half of the bond length. For example, ethane, $\text{H}_3\text{C}-\text{CH}_3$, is constructed from two methyl (CH_3) fragments. One reasonable estimate of the covalent radius of carbon would be half of the carbon–carbon bond length in ethane. Another measure of atomic size is the van der Waals radius, which applies to atoms that are *not* covalently bound to one another. The only attractive forces between such atoms will be noncovalent interactions, otherwise known as van der Waals forces, after Johannes Diderik van der Waals (1837-1923, Nobel Prize in Physics 1910). Like covalent radii, the sum of the van der Waals radii should equal the interatomic distance, but because van der Waals forces are considerably weaker than the forces involved in covalent bonds, van der Waals radii are generally much larger than covalent radii.

Periodic trends in atomic size can be explained in a similar fashion as the trends in ionization energy. Across a row, as both nuclear charge and effective nuclear charge increase, atomic radii decrease, as the electron cloud around an atom is held more tightly. Down a column, as valence electrons occupy orbitals of larger principal quantum number n , atomic radii increase, as the most probable electron-nucleus distance r increases with n . One interesting observation is that, while elements in the $4d$ block (the second transition series, Y-Cd) are significantly larger than those in the $3d$ block (the first transition series, Sc-Zn), elements in the $5d$ block (the third transition series, Lu-Hg) are often the same size, or just barely larger, than those in the $4d$ block. For instance, if we consider the transition metals of Group 8, we see that the covalent radius of Fe is 117 pm, while that of Ru is 125 pm, a significant (6.8%) increase. The covalent radius of Os, however, is only 126 pm, only 0.8% greater than that of Ru, despite the fact that the valence electrons of Os are in $5d$ orbitals, which should be further

from the nucleus than the electrons in the $4d$ orbitals of Ru. The explanation for this and other similar observations is that the $4f$ orbitals, which hold the valence electrons of the lanthanides (La-Yb), are filled before the $5d$ orbitals of Os, with a corresponding increase in nuclear charge. Since $4f$ orbitals are fairly diffuse (they have low electron density near the nucleus, due to having multiple nodal planes containing the nucleus), they poorly shield the increase in nuclear charge caused by the addition of 14 protons going from La to Yb. Thus, the *effective* nuclear charge experienced by a $5d$ electron is significantly greater than that which would be expected based only on the number, but not the probability density functions, of the additional electrons. This phenomenon is commonly known as the lanthanide contraction. The term “lanthanide contraction” is, however, somewhat of a misnomer, since atomic radii do not *decrease* between the $4d$ and $5d$ blocks; rather, they stay the same or increase only slightly. The “lanthanide contraction” is really more of a “lanthanide smaller-than-expected expansion.”

Ionic radii can be estimated by the measurement of distances between ions in crystalline salts *via* X-ray diffraction. Of course, the central assumption when discussing ionic radii is that the bonding in salts is entirely ionic, with no covalent character. This is often, but not always, a good approximation. The periodic trends for ionic radii generally follow those for covalent or van der Waals radii, but cationic radii are invariably smaller than the corresponding nonpolar covalent radii, since after one or more electrons is removed, the effective nuclear charge acting on the remaining electrons increases, and those electrons are held closer to the nucleus. Conversely, anionic radii are invariably large than the corresponding nonpolar covalent radii, since the addition of one or more electrons to an atom increases the shielding and decreases the effective nuclear charge acting on those atoms. Another way to think of it is that, when an atom develops an overall negative charge as an anion, the electrons repel each other, and the ion's size increases.

Chapter 2: Symmetry and Group Theory

2.1. The Importance of Symmetry

The concept of symmetry is critically important in chemistry, and it is used widely in our understanding of bonding, spectroscopy, and many other applications. One can see intuitively that a molecule such as the linear CO_2 or the regular tetrahedron CCl_4 is “more symmetrical” than many other structures, such as most large organic molecules produced by living things. The recognition of symmetry is an important part of what might be called chemical intuition, and you have already used some symmetry arguments, at least implicitly, in your previous study of chemistry. For instance, despite the fact that each bond in CO_2 or CCl_4 is strongly polar, you can see that each of these molecules has a net zero dipole moment due to symmetry; considering each bond dipole moment as a separate vector, the vector sum of all the bond dipole moments in each of these molecules is zero. Similarly, the concept of chirality (critically important in organic chemistry, biochemistry, and pharmacology) is based on symmetry: if the shape of a molecule lacks certain features (symmetry elements), it will not be superimposable upon its mirror image.

We will now spend some time considering symmetry more precisely, and in a more quantitative manner than you may have previously encountered. By considering symmetry in the context of a mathematical field called group theory, we will be able to use symmetry arguments to simplify many chemical calculations quite considerably, and to determine some molecular properties without performing any calculations at all.

2.2. Symmetry Elements and Symmetry Operations

When discussing molecular symmetry, it is crucial to distinguish between two intimately related, but different, concepts: symmetry operations and symmetry elements. A symmetry *operation* is an operation that we can perform on a structure (such as the structure of a molecule) that results in a new structure which is indistinguishable from the initial structure before the symmetry operation was performed. Let us pretend that we could photograph molecules: if we took a picture of the molecule before and after we performed the symmetry

operation, we would be able to see no difference. A symmetry *element*, on the other hand, is a feature of the molecule's structure that allows a symmetry operation or operations to be performed. (One symmetry element may give rise to several symmetry operations.) Often, a symmetry element and a symmetry operation are given the same symbol, so symmetry element A might correspond to symmetry operation A . In such cases, the use must be determined from context. Alternatively, one may use a carat to denote a symmetry operation, so that symmetry element A corresponds to symmetry operation $\hat{A}$. This latter convention is the one we will employ in this text, but you should be aware that not all authors use it.

There are five main types of symmetry element and symmetry operation, and we will define and give examples of each one in turn.

(1) The simplest symmetry operation is the identity operation, symbolized by $\hat{E}$. The identity operation consists of doing *nothing* to the molecule, so it is barely an operation at all. (The notation is short for the German word *Einheit*, which means “unity” or “oneness.” The identity operation acting on a structure is akin to multiplying a number or a function by 1, that is, no change.) You might wonder why we even define something so trivial as an identity operation; we will see later that it is required for any set of symmetry operations to possess the characteristics of a mathematical group. The corresponding symmetry element E is just the molecule itself, rather than any particular geometric feature of it. Thus, *every* molecule has the symmetry element E and symmetry operation $\hat{E}$.

(2) Perhaps the simplest non-trivial symmetry operation is rotation about an axis, sometimes called proper rotation. If we rotate a molecule by $\frac{360^\circ}{n}$ (or $\frac{2\pi}{n}$, if you prefer to work in radians) counterclockwise¹⁷ about some axis, we denote the rotation as the symmetry operation $\hat{C}_n$. Any axis possessed by a molecule that allows such a rotation to lead to an

¹⁷ Taking the direction of rotation as counterclockwise is conventional, and it corresponds to a counterclockwise rotation being positive in plane polar coordinates. It is mathematically just as valid to take the rotation as being clockwise, but once you choose which convention to use when approaching a problem, it is essential to maintain the same convention throughout your analysis.

indistinguishable state is a symmetry element denoted C_n and known as an n -fold rotation axis or an n -fold proper rotation axis. For instance, consider any molecule with the symmetry of a regular tetrahedron, such as CH_4 : each C–H bond lies along a C_3 axis, as rotation by $\frac{360^\circ}{n} = 120^\circ$ about one of these bonds will interchange the other H atoms with each other, resulting in a new arrangement with exactly the same appearance. Note that, for a carbon atom to be truly “tetrahedral” in the symmetry sense, it must be a *regular* tetrahedron, with all of its substituents the same. While a molecule like CHCl_3 is commonly said to be “tetrahedral at carbon,” it only has one C_3 axis, along which the C–H bond lies. Rotation by 120° about this axis will interchange the Cl atoms, so this is a legitimate symmetry operation. Rotation by 120° about one of the C–Cl bonds, however, will interchange the H atom with one of the other Cl atoms, leading to a new orientation distinguishable from the first, so this is *not* a symmetry operation, and the C–Cl bonds in CHCl_3 do *not* lie along C_3 axes.

Many molecules have multiple C_n axes, with different values of n . For example, consider benzene (C_6H_6), with its planar, regular hexagonal structure. Benzene possesses a C_6 axis perpendicular to the plane of the molecule, which passes through the center of the ring. Thus, rotation of benzene by $\frac{360^\circ}{6} = 60^\circ$ about this axis (the $\hat{C}_6$ operation) will lead to a configuration indistinguishable from the starting one. If a molecule has multiple C_n axes, the one with the largest value of n is known as the highest-order axis or principal axis. Many molecules have C_2 axes perpendicular to the principal axis. For instance, benzene has two sets of three C_2 axes each. Each C_2 axis in one set goes through each C–H bond and the C–H bond opposite to it on the ring (*para*), and each C_2 axis in the other set bisects each C–C bond and the one opposite to it. In general, when a molecule has C_2 axes in addition to a principal C_n axis, the C_2 axes that pass through atoms are denoted C_2' , and those that pass through bonds, between atoms, are denoted C_2'' .

A symmetry axis C_n with $n > 2$ always gives rise to more than one symmetry operation. To understand how this occurs, note that one can write a sequence of operations as a single operation, with an exponent used to indicate how many times each operation was applied. For instance, if one subjects a molecule to five $\hat{C}_6$ operations in a row, we denote this

combined operation as $\hat{C}_6^5$, and it corresponds to a rotation of 300° about the C_6 axis. In general, when one executes a C_n operation m times in a row, the net operation is denoted $\hat{C}_n^m$, and it corresponds to a rotation by $m\left(\frac{360^\circ}{n}\right)$ about the C_n axis. If n is an integer multiple of m , then we write $\hat{C}_n^m$ in lowest terms as $\hat{C}_{n/m}$. For instance, two $\hat{C}_6$ operations in a row (two rotations by 60° in a row) are equivalent to a single rotation by 120° (a $\hat{C}_3$ operation). Thus, $\hat{C}_6^2 = \hat{C}_{6/2} = \hat{C}_3$. If we rotate a molecule n times about a C_n axis, we get back to where we started, so $\hat{C}_n^n = \hat{C}_{n/n} = \hat{C}_1 = \hat{E}$. (Remember, the identity operation $\hat{E}$ consists of doing nothing to the molecule. In the case of our example, benzene, iteration of the $\hat{C}_6$ operation gives us the following symmetry operations:

$$\begin{aligned}\hat{C}_6 \\ \hat{C}_6^2 &= \hat{C}_3 \\ \hat{C}_6^3 &= \hat{C}_2 \\ \hat{C}_6^4 &= \hat{C}_3^2 \\ \hat{C}_6^5 \\ \hat{C}_6^6 &= \hat{E}\end{aligned}$$

Iterating further, a $\hat{C}_6^7$ operation is just $\hat{C}_6$, a $\hat{C}_6^8$ operation is just $\hat{C}_6^2 = \hat{C}_3$, and so on. We see that not only did the $\hat{C}_6$ operation give rise to $\hat{C}_3$ and $\hat{C}_2$ operations as well, but that a C_6 axis is also a C_3 axis and a C_2 axis. The proper rotations of the benzene molecule due to the C_6 axis are shown in Figure 2.1 on the following page, with carbon atoms labeled 1 through 6.

Note also that rotating a molecule by some angle ϕ clockwise is the same as rotating it by $360^\circ - \phi$ counterclockwise, so $\hat{C}_n^{-1} = \hat{C}_n^{n-1}$. For example, rotation about a C_6 axis by 60° clockwise is the same as rotation about the same axis by 300° counterclockwise, so $\hat{C}_6^{-1} = \hat{C}_6^5$. Finally, we note that, for a linear molecule such as HCl or CO_2 , rotation about the internuclear axis by *any* angle, no matter how small, leads to an indistinguishable configuration. We thus say that the internuclear axis of a linear molecule is an infinite-fold rotation axis. Such an axis is denoted by the special symbol C_∞^ϕ , and its corresponding rotation is denoted by $\hat{C}_\infty^\phi$.

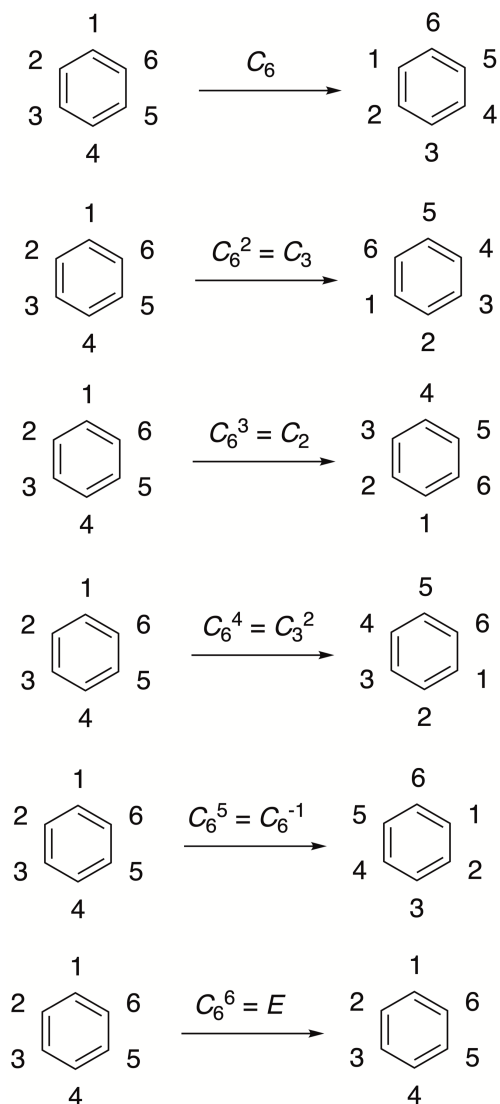


Figure 2.1. Proper rotation operations of the benzene molecule arising from the C_6 axis.

(3) Another symmetry operation is reflection across a mirror plane, which is a plane that divides a molecule into two symmetrical halves. A mirror plane is denoted by σ , and the corresponding reflection operation by $\hat{\sigma}$. Unlike rotation, reflection is not an operation that one can perform on an actual object like a plastic model of a molecule. Mathematically, one way to envision this operation is to imagine that a molecule is symmetrical across the yz plane. If a point in the molecule has Cartesian coordinates (x, y, z) , then reflection across the yz plane takes that point to the new coordinates $(-x, y, z)$. The fact that the yz plane is a

symmetry element means that this point will end up on another, indistinguishable part of a molecule. Any molecule containing a σ plane must be achiral.¹⁸ If a σ plane is perpendicular to the principal axis of rotation, it is denoted σ_h (the h stands for “horizontal”) and the corresponding reflection operation by $\hat{\sigma}_h$. If the σ plane contains the principal axis, it is denoted σ_v or σ_d (and the corresponding reflection operation by $\hat{\sigma}_v$ or $\hat{\sigma}_d$), depending on the symmetry of the rest of the molecule. Benzene has a set of three σ_v and three σ_d planes: σ_v denotes the planes passing through two carbon and two hydrogen atoms each (the v stands for “vertical”), and σ_d denotes the planes that bisect two C–C bonds each (the d stands for “dihedral”). Every reflection operation (regardless if it is labeled with an h , a v , or a d subscript, or with no subscript) is its own inverse, so $\hat{\sigma}^2 = \hat{E}$. Examples of the reflection operations on a benzene molecule are shown in Figure 2.2 below, with carbon atoms labeled 1 through 6.

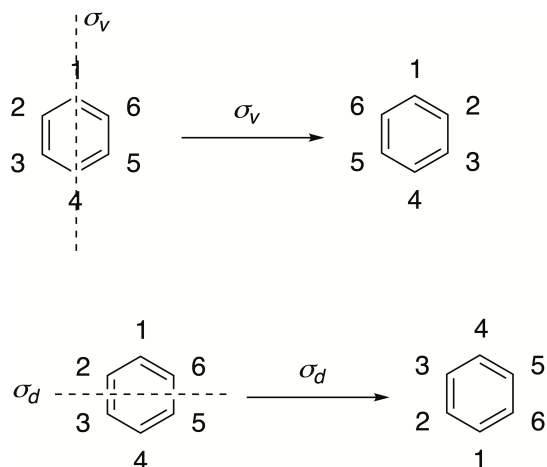


Figure 2.2. Examples of reflection operations on the benzene molecule.

(4) Another operation that cannot actually be performed on a molecular model is inversion, denoted by $\hat{i}$. If the center of the molecule is defined as the origin of a Cartesian coordinate system, inversion consists of taking each point in the molecule with coordinates (x, y, z) and moving them to new coordinates $(-x, -y, -z)$. If this operation yields an indistinguishable

¹⁸ The presence of a σ plane is a sufficient, but not a necessary, condition for achirality. Some molecules are achiral even though they have no σ plane. See Section 2.5.

arrangement of atoms, then we say that the molecule is symmetric to inversion, and we refer to its center as a center of inversion or inversion center, a symmetry element denoted by i . (Be careful not to confuse this i with the imaginary number, or with a unit vector along the x -axis.) Benzene has an inversion center in the middle of its ring, as does CO_2 at the center of its carbon atom, but HCl , H_2O , and cyclopropane lack inversion centers. One instance of a molecule with an inversion center that is perhaps more difficult to see at first is the staggered conformation of ethane, $\text{H}_3\text{C}-\text{CH}_3$, as its inversion center lies at the midpoint of the $\text{C}-\text{C}$ bond. Examples of inversion for benzene and the staggered conformation of ethane are shown in Figure 2.3 below.

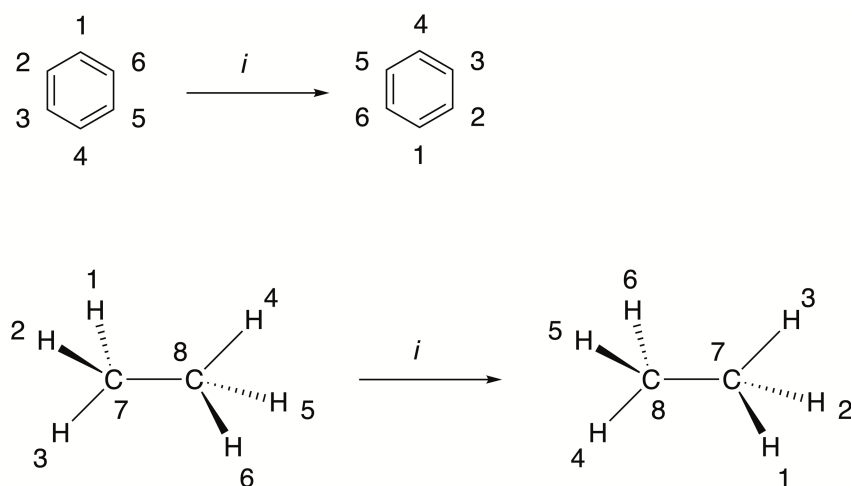


Figure 2.3. Results of the inversion operation on benzene and staggered ethane.

It should be noted that some molecules have an obvious center, but no *inversion* center. It is clear that any regular tetrahedral molecule, such as CH_4 , has its center of mass at the center of the tetrahedron, but such a molecule is not symmetric with respect to inversion. Molecules with inversion centers are often said to be “centrosymmetric,” but it is important not to confuse this term with meaning that the molecule has any obvious center at all. The inversion operation is its own inverse, so $i^2 = \hat{E}$.

(5) The final, and most complicated, type of symmetry operation is improper rotation (also known as rotation-reflection), denoted by $\hat{S}_n$. The $\hat{S}_n$ operation consists first of a $\hat{C}_n$ rotation,

followed by reflection across a plane perpendicular to the axis of rotation. An axis allowing this operation is the symmetry element S_n , called an improper rotation axis. Any molecule with a C_n axis perpendicular to a mirror plane σ has an S_n axis coincident with the C_n axis: for instance, the C_6 axis in benzene is also an S_6 axis. However, it is very important to note that an S_n axis can be a symmetry element *without* also being a C_n axis, and that the plane perpendicular to the S_n axis need not itself be a mirror plane. For example, CH_4 has no C_4 axes, but it does have three S_4 axes. Consider the three C_2 axes of CH_4 , each of which bisects a pair of H–C–H bond angles. Each of these C_2 axes is also an S_4 axis: rotation by 90° about one of these axes is not a symmetry operation by itself, but such a rotation followed by a reflection across a plane perpendicular to that axis *is* a symmetry operation, $\hat{S}_4$. Note that the reflection involved in this $\hat{S}_4$ operation is not a symmetry operation by itself, either. This is why rotation-reflection is its own category of symmetry operation, not just a combination of the separate symmetry operations of proper rotation and reflection. An example of the $\hat{S}_4$ operation on methane is shown in Figure 2.4 below, along with how it can be considered to result from a “ $\hat{C}_4$ ” rotation followed by a “ $\hat{\sigma}_h$ ” reflection, even though neither $\hat{C}_4$ nor $\hat{\sigma}_h$ is by itself a symmetry operation for methane.

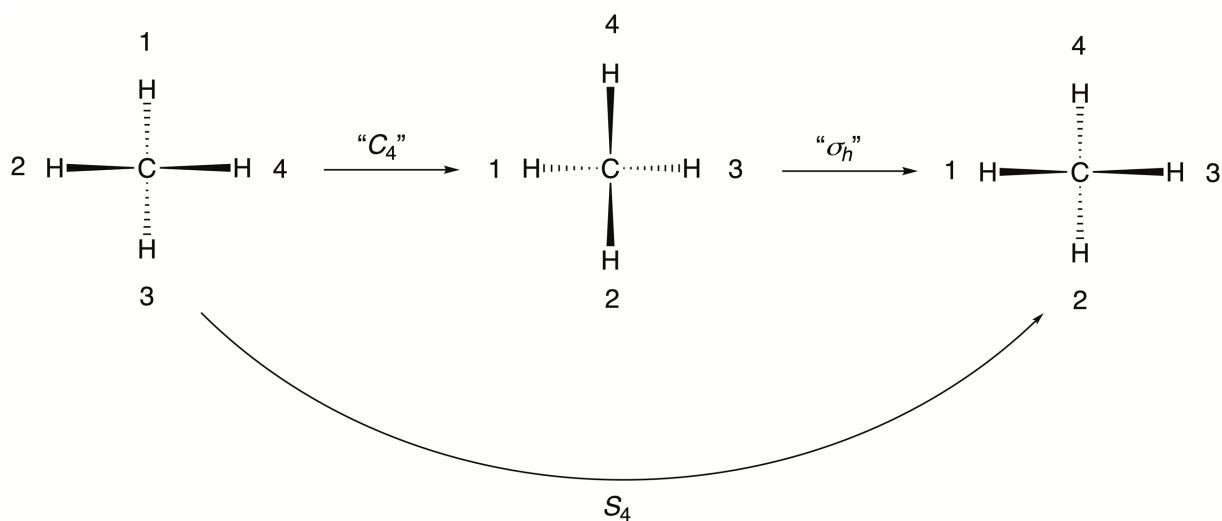


Figure 2.4. Results of the $\hat{S}_4$ operation on methane.

Reflection without rotation is just the same thing as an $\hat{S}_1$ operation, so $\hat{\sigma} = \hat{S}_1$. Similarly, rotation by 180° followed by reflection is the same as inversion, so $\hat{i} = \hat{S}_2$. However, one

almost always writes $\hat{\sigma}$ and $\hat{\iota}$, rather than $\hat{S}_1$ and $\hat{S}_2$. Other useful relations are that $\hat{S}_n^n = \hat{E}$ if n is even, $\hat{S}_n^n = \hat{\sigma}$ and $\hat{S}_n^{2n} = \hat{E}$ if n is odd, $\hat{S}_n^m = \hat{C}_n^m$ if m is even and $m < n$, and $\hat{S}_n^m = \hat{C}_n^{m-n}$ if m is even and $m > n$.

2.3. Point Groups

In mathematics, the word “group” has a more precise meaning than its nontechnical usage, in which it is more or less synonymous with “assortment” or “set.” For a set of elements to comprise a mathematical group, there must be some “multiplication” operation that defines the “product” AB of any two elements in the group A and B . This multiplication need not be the same as the multiplication used in arithmetic and algebra. Once a multiplication operation is defined, a set of elements forms a group if (and *only* if) they have the following four properties:

(1) Closure to multiplication: A group of elements must be closed to multiplication, meaning that the product of any two elements in the group is also an element in that group. That is, if A and B are elements in a group, and $AB = C$, then C must be an element in that group as well. Similarly, the square of any element A^2 must also be an element in the group.

(2) Associativity: The multiplication operation in a group must be associative, meaning that, if A , B , and C are elements in the group, $(AB)C = A(BC)$. Of course, by the closure requirement, such a product must also be an element in the group.

(3) Existence of identity: Every group must have, as one of its elements, an identity element E , such that $AE = EA = A$ for every element A of the group.

(4) Existence of inverses: For each element A in the group, there must also exist in the group an element A^{-1} such that $AA^{-1} = A^{-1}A = E$.

It should be noted that the multiplication operation for a group is not necessarily commutative. This means that, unlike multiplication in arithmetic and algebra, the order of

multiplication can matter: for two arbitrary elements A and B in a group, the product AB may not be equal to the product BA . For some groups multiplication *is* commutative, so $AB = BA$ for any elements A and B . Such groups are known as Abelian groups, after the mathematician Niels Henrik Abel (1802-1829). Some symmetry groups in chemistry are Abelian, but most are not.

It turns out that, for any type of structure (such as that of a molecule), all the symmetry operations of that structure are also the elements of a group. Note that the symmetry *operations*, not the symmetry *elements*, are the elements of the group. This can be confusing, but it is the result of two different common uses of the word “element” (a third common use, of course, is to refer to chemical elements). We will not rigorously prove that every set of symmetry operations for a structure define a group, but we can at least see that this statement is plausible.

Requirement 1 (closure) is easy to understand: operating on a molecule with a symmetry operation leaves it indistinguishable from the initial orientation, and operating on the molecule again gives us another indistinguishable orientation. This means that the product of two symmetry operations leaves the molecule indistinguishable, and thus that product is itself a symmetry operation.

Requirement 2 (associativity of multiplication) is not easy to prove in general, but by drawing a perspective diagram of a molecule and trying different arrangements of symmetry operations, you can at least verify this fact for any given group.

Requirement 3 (existence of identity) is satisfied by the identity operation $\hat{E}$, which consists of doing nothing to the molecule.

Requirement 4 (existence of an inverse) is easy to see for the operations $\hat{E}$, $\hat{\sigma}$, and $\hat{i}$, since each of these operations is its own inverse. For any $\hat{C}_n$ or $\hat{S}_n$ operation, the operation

involving rotation by the same angle in the opposite direction is the inverse of the initial proper or improper rotation.

Groups whose elements are defined by a set of symmetry operations are often called point groups. This name comes from the fact that all the symmetry elements corresponding to these symmetry operations intersect in at least one point, and in some groups they all intersect in a line. The molecule's center of mass always lies at this point of intersection (or somewhere along the line of intersection), and no symmetry operation involves translation of a molecule, so no symmetry operation changes the location of the molecule's center of mass. When considering quasi-infinite arrays of molecules or ions in crystals (crystal lattices), one can define space groups, as opposed to point groups, in which translation of an element of the crystal lattice to an equivalent point in the lattice *does* qualify as a symmetry operation. Space groups are essential to the theory and practice of X-ray crystallography. In this course, however, we will primarily be concerned with the symmetries of individual molecules, not extended lattices.

The fact that all the symmetry operations for a molecule comprise a group allows us to use various results of a mathematical discipline called group theory to simplify many molecular calculations. Before we discuss how to do this, however, we will first see how to assign a given molecule to its appropriate point group.

2.4. Classification of Molecules by Point Group

The “brute force” way to determine a molecule's point group is to identify all of the symmetry operations that can be performed on its structure, and then to compare such a list to the lists of symmetry operations tabulated for each point group. This method can become very tedious very quickly, since some point groups have 48 or more symmetry operations, and for highly symmetric molecules, it is easy to miss a symmetry operation here or there by mistake. Instead, we will consider the hallmarks of some common point groups, and then present a flowchart that can be used to systematically assign a molecule to its appropriate point group.

First, we consider those point groups with very few symmetry operations. A molecule belonging to one of these groups can often be recognized by inspection. The least symmetric point group is C_1 , whose only symmetry operation is the trivial identity operation $\hat{E}$. We would say that such a molecule is lacking in any practical symmetry. Bromochlorofluoromethane, CHFCIBr , is a member of this group, as are many complicated “natural products,” organic molecules produced endogenously by living things. The point group C_s contains only $\hat{E}$ (as all groups must) and a single $\hat{\sigma}$ reflection operation. Examples of C_s molecules include 1-bromo-1-chloroethene, $\text{H}_2\text{C}=\text{CClBr}$, and the useful hydrocarbon norbornene. Finally, the rare group C_i has only $\hat{E}$ and $\hat{i}$ as its operations. While this is a rare point group, it is exemplified by the staggered conformation of *meso*-1,2-dibromo-1,2-dichloroethane.

At the other extreme, some groups have a very large number of symmetry operations, and are commonly referred to as “high-symmetry” groups. Molecules in high-symmetry groups are often easily recognized by inspection. One of the most familiar such groups is the tetrahedral point group T_d , to which CH_4 , CCl_4 , and many homoleptic¹⁹ metal complexes ML_4 belong. The phosphorus allotrope P_4 , commonly known as “white phosphorus,” is also in the T_d point group; it consists of a tetrahedron with a phosphorus atom at each vertex, but no central atom. Note that only *regular* tetrahedra are members of T_d : while a molecule like dichloromethane is commonly said to be “tetrahedral at carbon,” the fact that not all of its substituents are identical makes it not a regular tetrahedron, according to symmetry considerations. Related to T_d are the groups T and T_h , which are much less common in chemistry.

The octahedral group O_h has the symmetry of a regular octahedron, and it is commonly encountered in coordination chemistry: there are many homoleptic, hexacoordinate compounds of general formula ML_6 , such as $\text{Cr}(\text{CO})_6$ and CoCl_6^{3-} . Note that six ligands (of the same type) around a metal serve as the vertices of a regular octahedron: an octahedron has eight faces, but only six vertices. Main-group members of this group include SF_6 and PF_6^- . The

¹⁹ A homoleptic metal complex is one that contains only one type of ligand.

borane cluster anion $\text{B}_6\text{H}_6^{2-}$ is also of O_h symmetry (with no central atom, but with a BH group at each vertex), as is a simple cube. The related group O is only rarely encountered in chemistry.

Another common high-symmetry group is the icosahedral group I_h . A regular icosahedron (the Platonic solid with 20 faces) lies in this group. Boron forms many species with icosahedral or approximately icosahedral symmetry, such as the borane cluster anion $\text{B}_{12}\text{H}_{12}^{2-}$. Buckminsterfullerene, a molecular allotrope with formula C_{60} , also has I_h symmetry; it is shaped like a soccer ball. A non-chemical example of I_h symmetry is a 20-faced die used in *Dungeons & Dragons* and similar tabletop rôle-playing games, if one ignores the numbers written on each face. The related group I is very rarely encountered in chemistry.

Every linear molecule belongs to one of two high-symmetry point groups: linear molecules containing an inversion center, such as N_2 and CO_2 , belong to the $D_{\infty h}$ group, while linear molecules without an inversion center, such as CO and N_2O , belong to the $C_{\infty v}$ group. A non-chemical way to think about this distinction is that a cylinder has $D_{\infty h}$ symmetry, while a cone has $C_{\infty v}$ symmetry.

A final example of a high-symmetry point group corresponds to a perfect sphere, and has the symbol K_h (the K is from the German *Kugelgruppe*, literally “sphere-group”). No molecule or polyatomic ion is a perfect sphere, so the only chemically important species belonging to K_h are free atoms and free monatomic ions. (Note that a *solvated* ion will no longer have the symmetry of a perfect sphere.)

Many molecules that belong to neither high-symmetry nor low-symmetry point groups belong to groups of type C_n (C_n , C_{nv} , and C_{nh}) or D_n (D_n , D_{nh} , and D_{nd}). Here n designates the order of the highest-order $\hat{C}_n$ rotation operation. The difference between C_n -type groups and D_n -type groups is that the latter have n C_2 axes (known as dihedral axes) perpendicular to the principal C_n axis, while the former do not.

C_n groups have as their symmetry operations *only* $\hat{E}$, $\hat{C}_n$, and those operations arising from $\hat{C}_n$ (for instance, any molecule with the $\hat{C}_4$ operation must also have the $\hat{C}_2$ operation). Examples include the gauche conformation of hydrazine, $\text{H}_2\text{N}-\text{NH}_2$ (C_2) and triphenylphosphine with its phenyl rings twisted (C_3).

C_{nv} groups have n σ planes, each containing the C_n axis; such planes are denoted σ_v or σ_d . These planes may all be of the same type (the same class), or they may be different. Examples include water (C_{2v}), ammonia (C_{3v}), and square pyramidal molecules like BrF_5 (C_{4v}).

C_{nh} groups all contain a horizontal mirror plane σ_h (a mirror plane perpendicular to the C_n axis). Examples include *trans*- N_2F_2 and the planar conformation of H_2O_2 (both C_{2h}) and the planar conformation of boric acid (C_{3h}).

D_n groups have the symmetry of a boat propeller. Common examples include octahedral (*not* regular octahedral) metal complexes with three of the same, symmetrical, bidentate ligand, such as $\text{Co}(\text{en})_3^{3+}$, which is D_3 . (The bidentate ligand en is short for ethane-1,2-diamine a.k.a. ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.) The propeller analogy is helpful for realizing that all molecules in D_n point groups are chiral: rotating a propeller one way will make the boat move forward, while rotating it in the other direction will make it move backward.

D_{nh} groups have, in addition to the n dihedral axes, a horizontal mirror plane σ_h . Examples include cyclopropane, BF_3 , PF_5 , and $\text{Fe}(\text{CO})_5$ (all D_{3h}), PtCl_4^{2-} (D_{4h}), C_5H_5^- and the eclipsed conformation of ferrocene (D_{5h}), and benzene (D_{6h}). Note that molecules in D_{nh} groups also contain vertical mirror planes, but it is usually most helpful to look for the horizontal mirror plane when classifying such molecules.

D_{nd} groups have, in addition to the n dihedral axes, n vertical mirror planes (denoted σ_d), but no horizontal ones. Examples include allene (D_{2d}), the staggered conformation of ethane (D_{3d}), and the staggered conformation of ferrocene (D_{5d}).

In addition, there also exist S_{2n} groups, whose principal axis is not a proper rotation axis, but an improper rotation axis S_{2n} , collinear with a proper rotation axis C_n . These groups are not common in chemistry, but molecules belonging to them do exist, such as 1,3,5,7-tetrafluorocyclooctatetraene (S_4).

Examples of molecules in some common point groups are shown in Figure 2.5 below, and a flowchart for assigning molecules to point groups is shown in Figure 2.6 on the following page.

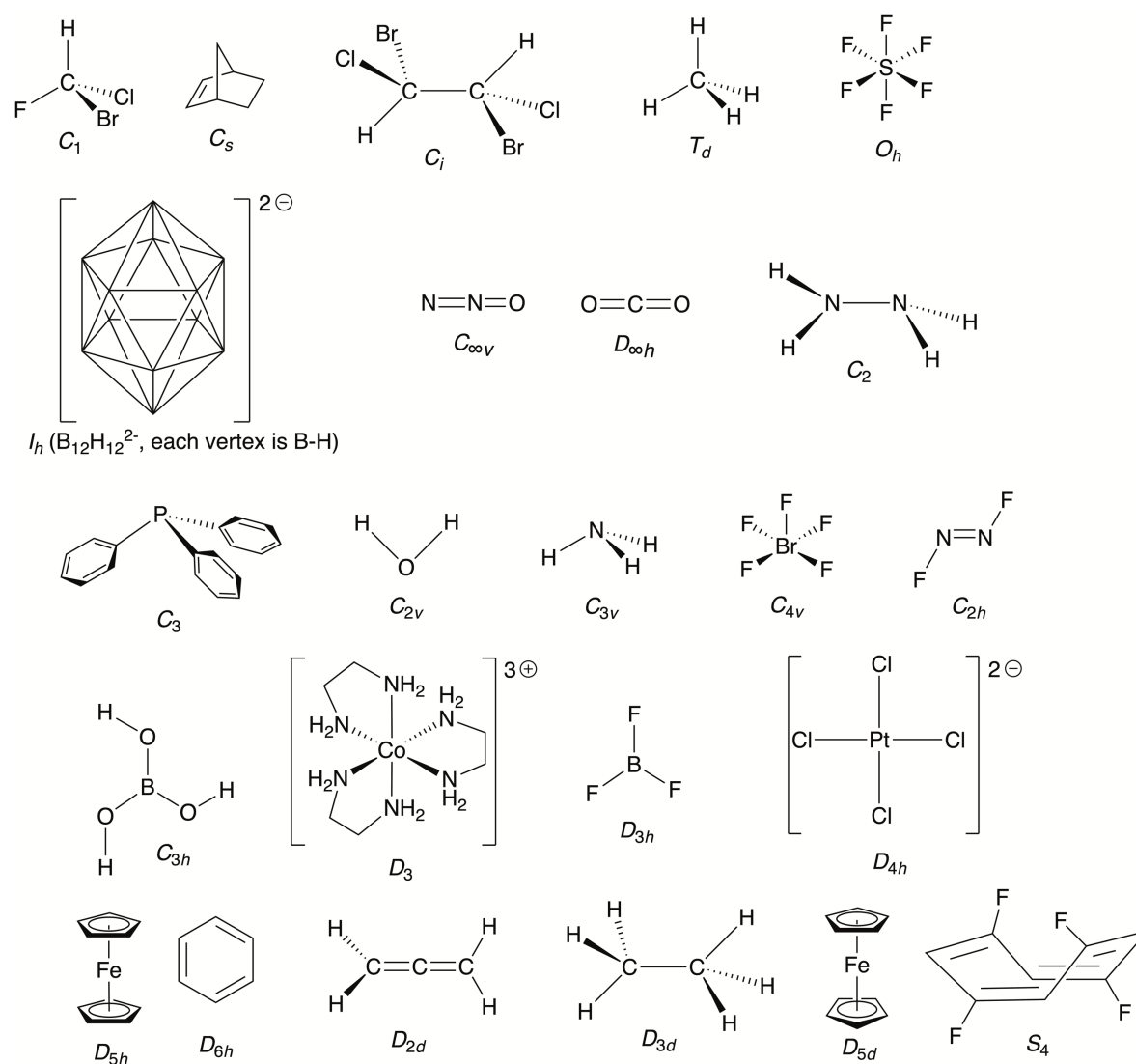


Figure 2.5. Representative examples of molecules in some common point groups.

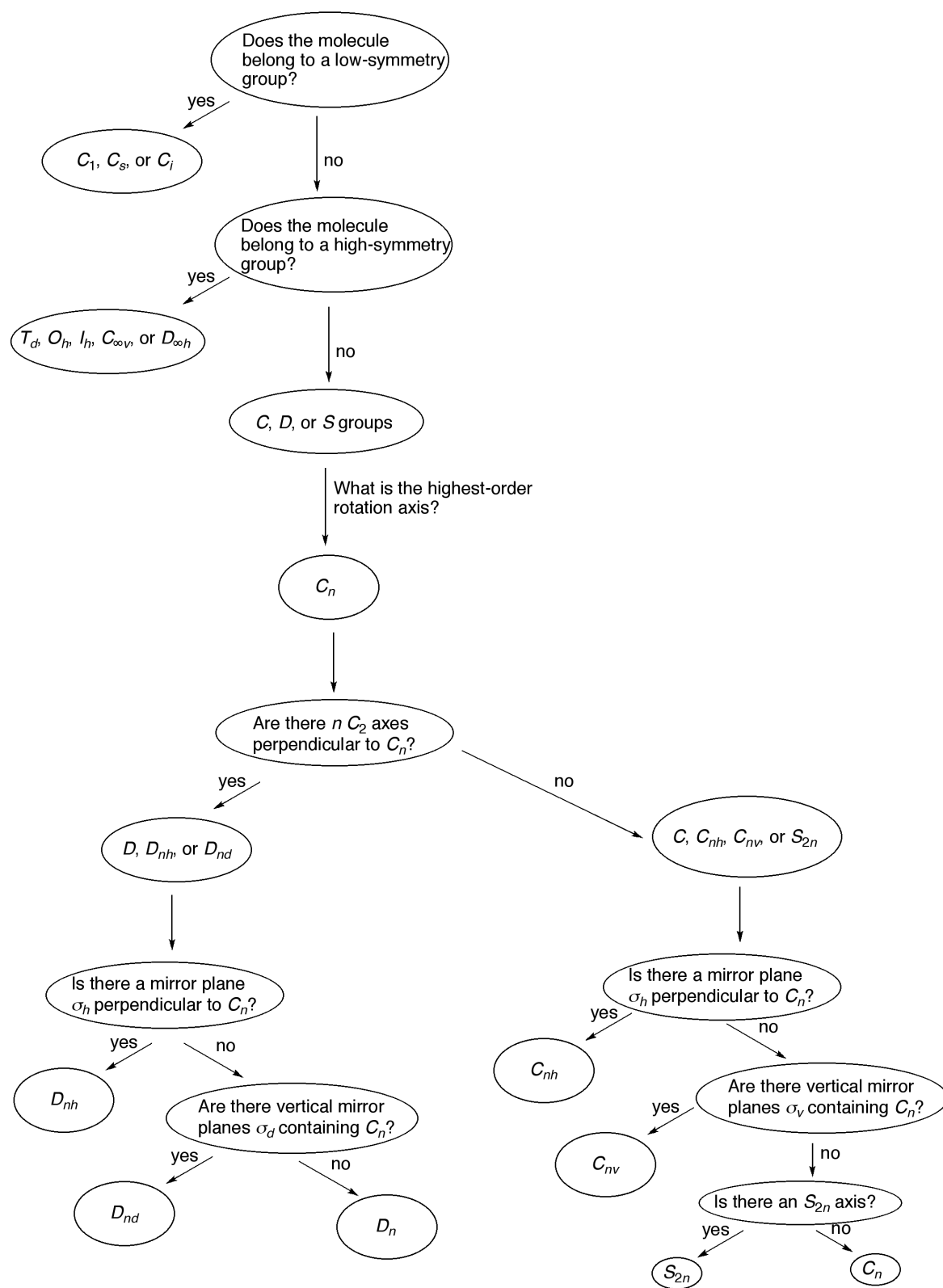


Figure 2.6. Flowchart for assigning molecules to point groups.

When assigning molecules to point groups, it is common to assume rapid rotation about single bonds, unless a particular conformation is specified (*e.g.* staggered ethane). Thus, one assigns the molecule's time-averaged shape to a point group. For instance, using this convention, both hexachlorobenzene and hexamethylbenzene belong to the D_{6h} point group, despite the fact that a methyl group is less symmetric than a chlorine atom. At any given moment, a molecule of hexamethylbenzene is less symmetric than hexachlorobenzene, but over a long enough period of time, the two molecules have the same average symmetry.

2.5. Chirality and Polarity

One immediate application of point groups is in determining chirality. A molecule is chiral if it is not superimposable on its mirror image; that is, if it and its mirror image are molecules of different compounds.²⁰ A pair of molecules that are nonsuperimposable mirror images are known as enantiomers.²¹ Molecules that are superimposable on their mirror images are achiral; the “enantiomer” of an achiral molecule is the same molecule.

Chirality is crucially important in chemistry. Each of the two enantiomers of a chiral molecule have the same energy and the same physical properties²² in an achiral environment, and each enantiomer will react identically with an achiral reactant. Consider, however, the reaction of two chiral reactants, **1** and **2**. The reaction of (*R*)-**1** with (*R*)-**2** will have the same thermodynamics and kinetics as the reaction of (*S*)-**1** with (*S*)-**2**. However, the reaction of (*R*)-**1** with (*S*)-**2**, or of (*S*)-**1** with (*R*)-**2**, will have a different free energy change, equilibrium constant, and rate constant. In biological systems, many important molecules (such as proteins and DNA) are chiral, and only one enantiomer is found. This means that if a drug is chiral, its enantiomers will react with chiral biological target molecules differently. In some cases, one enantiomer might be an effective medication, while the other enantiomer might be ineffective or even toxic.

²⁰ The term “chiral” comes from the Greek χείρ, “hand.” One’s left and right hands are (approximately) mirror images of one another, but they are not superimposable.

²¹ From Greek ἐναντίος, “opposite” + μέρος, “part.”

²² Except for the direction in which a sample of each enantiomer will rotate plane-polarized light.

Introductory organic chemistry classes often state that a molecule is achiral if it contains a mirror plane σ . It turns out that the presence of a mirror plane is a sufficient, but not a necessary, condition for a molecule to be achiral. The rigorous rule based on symmetry elements is as follows: a molecule is chiral *if and only if* it lacks any improper rotation axis S_n . Mirror planes and inversion centers count as improper rotation axes for this rule, since $S_1 = \sigma$ and $S_2 = i$. Thus, C_1 , all C_n , all D_n , T , O , and I molecules are all chiral, while C_s , C_i , all C_{nv} , all C_{nh} , all D_{nd} , all D_{nh} , all S_{2n} , T_d , T_h , O_h , and I_h molecules are all achiral. Note that while it is common to (informally) refer to chiral molecules as “asymmetric,” many of the point groups to which chiral molecules belong actually contain several symmetry elements each.

Symmetry considerations can also be used to determine whether a molecule is polar or nonpolar. Recall that while each of the C–O bonds in CO_2 and the C–Cl bonds in CCl_4 is polar, the molecular dipole moments of CO_2 and CCl_4 are each zero. The presence of some symmetry operations can make polar bonds equivalent, and this is why a molecule containing polar covalent bonds may have no net molecular dipole moment. The only point groups to which polar molecules belong are C_1 , C_s , all C_n , and all C_{nv} . In C_n and C_{nv} molecules, the molecular dipole moment vector lies along the C_n axis.

2.6. Symmetry Operations as Transformation Matrices

To move from cataloging point groups to performing molecular calculations using group theory, it is necessary to discuss the representation of groups. One way to represent symmetry point groups is to represent each symmetry operation as a transformation matrix (*vide infra*). Recall that the product $\mathbf{AB}$ of two matrices $\mathbf{A}$ and $\mathbf{B}$ is defined only if the first matrix $\mathbf{A}$ has p rows and r columns, and the second matrix $\mathbf{B}$ has r rows and q columns. Only under these circumstances does there exist a product matrix $\mathbf{C}$, with p rows and q columns, such that $\mathbf{C} = \mathbf{AB}$. Note that this means that matrix multiplication is *not* commutative, so in general $\mathbf{AB} \neq \mathbf{BA}$, and indeed $\mathbf{BA}$ may not even be defined, though $\mathbf{AB}$ is. The elements of the product matrix $\mathbf{C}$ are denoted C_{ij} , referring to the i th row and j th column, and they are given by

$$C_{ij} = \sum_{k=1}^r A_{ik} B_{kj}$$

where A_{ik} and B_{kj} are the elements in row i and column k of $\mathbf{A}$ and row k and column j of $\mathbf{B}$, respectively.

We will most frequently be concerned with square, N by N matrices (*i.e.* matrices with N rows and N columns) that operate on (multiply from the left) matrices with N rows and only 1 column. We say that we have a square transformation matrix $\mathbf{T}$ operating on a column matrix (also called a column vector) $\mathbf{r}$. The product of this matrix multiplication is a new column matrix $\mathbf{r}'$. Let us consider 3-row column matrices representing Cartesian coordinate vectors in 3D space, where a set of coordinates (x, y, z) is transformed to a new set of coordinates (x', y', z') . In this case, we write $\mathbf{r}$, $\mathbf{T}$, and $\mathbf{r}'$ as

$$\mathbf{r} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$\mathbf{T} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix}$$

$$\mathbf{r}' = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

and the matrix multiplication is

$$\mathbf{r}' = \mathbf{T}\mathbf{r}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} T_{11}x + T_{12}y + T_{13}z \\ T_{21}x + T_{22}y + T_{23}z \\ T_{31}x + T_{32}y + T_{33}z \end{bmatrix}$$

Now let us consider the fairly simple point group C_{2v} . A standard textbook example of a molecule belonging to C_{2v} is H_2O (see Figure 2.5). We will set the O atom at the origin of the Cartesian coordinate system. Additionally, we will have the xz plane be the plane of the molecule, and the z -axis will be collinear with the C_2 axis.

There are 4 symmetry operations in the C_{2v} point group: $\hat{E}$, $\hat{C}_2$, $\hat{\sigma}_v(xz)$, and $\hat{\sigma}_v'(yz)$. Note that there are two mirror planes, corresponding to the xz and yz planes, but they are clearly different: they do not belong to the same *class* of symmetry element, and their corresponding operations do not belong to the same class of symmetry operation. We will shortly develop a way of defining whether more than one mirror plane, C_n axis, *etc.* and their corresponding operations belong to the same class. Now, we see what each symmetry operation in turn does to a set of coordinates (x, y, z) .

First, the identity operation $\hat{E}$ changes nothing: it “transforms” (x, y, z) to (x, y, z) . The matrix representation is thus

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Consider the elements of the $\mathbf{E}$ matrix that lie along the principal diagonal (upper-left to lower-right), which is often just called the “diagonal” for short. Every diagonal element is equal to 1, meaning that x , y , and z are each only multiplied by 1, thus leaving them unchanged. All off-diagonal matrix elements are zero, meaning that x , y , and z are not transformed into each other, or into linear combinations of each other.

Next, the $\hat{C}_2$ operation (rotation by 180° about the z -axis) transforms (x, y, z) to $(-x, -y, z)$, so its matrix representation is

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$$\mathbf{C}_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The $\hat{\sigma}_v(xz)$ operation transforms (x, y, z) to $(x, -y, z)$, so its matrix representation is

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

$$\sigma_v(\mathbf{xz}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Finally, the $\hat{\sigma}_v'(yz)$ operation transforms (x, y, z) to $(-x, y, z)$, so its matrix representation is

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

$$\sigma_v'(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

All square matrices (with the same number of rows as columns), including transformation matrices corresponding to symmetry operations, are associated with an important number called the character (also known as the trace), symbolized by χ (from the Greek χαρακτήρ, “character”). The character of a square matrix is the sum of all the matrix elements along the upper-left to lower-right diagonal, which is known as the “principal diagonal.” Thus, for a matrix $\mathbf{A}$ with N rows and N columns and matrix elements A_{ij} , the character is given by

$$\chi(\mathbf{A}) = \sum_{i=1}^N A_{ii}$$

Based on the above formula, the transformation matrices corresponding to the symmetry operations of C_{2v} have the following characters:

Transformation matrix	χ
E	3
C₂	-1
$\sigma_v(\mathbf{xz})$	1
$\sigma_v'(\mathbf{yz})$	1

This set of characters, just like the set of transformation matrices themselves, is a *representation* of the group C_{2v} , but it is a *reducible* representation, meaning that it can be

described as a sum of more fundamental, *irreducible* representations. To see how this is so, we note that each of the transformation matrices worked out above can be *block diagonalized*, meaning that they can be broken down into smaller matrices that lie along the principal diagonal, with all other elements being zero.

$$\mathbf{E} = \begin{bmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$$

$$\mathbf{C}_2 = \begin{bmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$$

$$\sigma_v(\mathbf{xz}) = \begin{bmatrix} [1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$$

$$\sigma_v'(\mathbf{yz}) = \begin{bmatrix} [-1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$$

The characters of the smaller matrices corresponding to the transformation matrices' effect on x are (1, -1, 1, -1); this is one irreducible representation of the group. The characters of the smaller matrices corresponding to the transformation of y are (1, -1, -1, 1); this is another irreducible representation, as is the corresponding set of character for the transformation of z : (1, 1, 1, 1). In this case, since each of the smaller matrices has only one row and one column, they are simply numbers, and the single element of each matrix is thus equal to its character. However, we will shortly see that some transformation matrices, once block-diagonalized, have some blocks with non-zero off-diagonal elements, so they have more than one row and one column apiece.

The character table of the C_{2v} point group is shown below (Table 2.1), and it shows all of the irreducible representations (often called "irreps" for short) that make up this point group, consisting of each of their characters under each of the symmetry operations:

Table 2.1. The character table for the C_{2v} point group.

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{xyz}	3	-1	1	1		

The second-to-rightmost column of the character table indicates that the z -axis, and any functions with the same symmetry as a vector along the z -axis (such as a p_z orbital) transforms as the irrep A_1 , the x -axis (or a p_x orbital) transforms as B_1 , and the y -axis (or a p_y orbital) transforms as B_2 . Also in this column are the terms R_x , R_y , and R_z ; these are vectors corresponding to rotations about the x , y , and z -axes, respectively. The rightmost column indicates the irreps corresponding to products of Cartesian functions and the d orbitals corresponding to them. For instance, since the product xy transforms as A_2 , a d_{xy} orbital does as well. Any linear combinations of two functions that transform as the same irrep also transforms as that irrep, so A_1 is the irrep corresponding not only to d_{z^2} , but also to $d_{x^2-y^2}$. (Remember that a so-called d_{z^2} orbital is more accurately written as $d_{z^2-x^2-y^2}$.)

The reducible representation Γ_{xyz} , which represents the characters of the transformation matrices corresponding to x , y , and z together, is seen here to be equal to $A_1 + B_1 + B_2$. With simple character tables, one can sometimes see by inspection which irreps sum to a reducible representation, but we will shortly see a systematic formula for determining this for any given reducible representation.

Some other features of transformation matrices can be exemplified by considering the C_{3v} point group, whose character table is shown on the following page (Table 2.2). A standard textbook example of a molecule belonging to C_{3v} is NH_3 (see Figure 2.5). We define our coordinate system such that the C_3 axis is coincident with the z -axis.

Table 2.2. The character table for the C_{3v} point group.

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

In general, the matrix representation for how a counterclockwise rotation by some angle θ about the z -axis affects a set of coordinates (x, y, z) is as follows:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \cos \theta - y \sin \theta \\ x \sin \theta + y \cos \theta \\ z \end{bmatrix}$$

Thus, the transformation matrix (here called the rotation matrix $\mathbf{R}_\theta$) is given by

$$\mathbf{R}_\theta = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

For the $\hat{C}_3$ operation (counterclockwise rotation by $120^\circ = \frac{2\pi}{3}$ about the z -axis), the transformation matrix is

$$\mathbf{C}_3 = \begin{bmatrix} \cos\left(\frac{2\pi}{3}\right) & -\sin\left(\frac{2\pi}{3}\right) & 0 \\ \sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Examining the principal diagonal of this matrix, we can see that its character is zero. Also,

we can only block-diagonalize this matrix so far, into a 2×2 matrix $\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$, representing

the effect of the transformation on x and y together, with a character of -1 , and a 1×1 matrix $[1]$, representing the effect of the transformation on z , with a character of 1 .

Now consider the symmetry operation $\hat{C}_3^2 = \hat{C}_3^{-1}$, which consists of a counterclockwise rotation by $240^\circ = \frac{4\pi}{3}$ (or, equivalently, a clockwise rotation by $120^\circ = \frac{2\pi}{3}$) about the z -axis: its corresponding transformation matrix is

$$\mathbf{C}_3^2 = \begin{bmatrix} \cos\left(\frac{4\pi}{3}\right) & -\sin\left(\frac{4\pi}{3}\right) & 0 \\ \sin\left(\frac{4\pi}{3}\right) & \cos\left(\frac{4\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

While the off-diagonal elements of $\mathbf{C}_3^2$ are different from those of $\mathbf{C}_3$, their principal diagonal elements are identical, so these two transformation matrices have the same character. Thus, their corresponding symmetry operations $\hat{C}_3$ and $\hat{C}_3^2$ are said to be in the same *class*, and they are listed together in the character table as $2\hat{C}_3$. Similarly, the transformation matrices corresponding to reflection through each of the three σ_v mirror planes have the same character, so these three reflection operations are in the same class, and they are listed together as $3\hat{\sigma}_v$ in the character table. Every point group has the same number of irreps as it does classes. It may, however, have *more* symmetry operations than irreps, if it contains any class which consists of more than one symmetry operation.

When we considered the characters of the transformation matrices for (x, y, z) in C_{2v} , we noted that the characters of these matrices, taken together, formed a reducible representation of the group, which was a sum of irreducible representations. Any linear combinations of irreps in a group, as long as all the coefficients are nonnegative integers, forms a reducible representation of that group. As an example, let us again consider the C_{3v} character table, with a reducible representation Γ (this representation is not that corresponding to the transformation of x, y , and z).

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy),$ (xz, yz)
Γ	5	-1	1		

How do we determine the coefficients for each of the irreps A_1 , A_2 , and E for this linear combination, that is, how many times each of these irreps appears in the reducible representation Γ ? First, we define some notation: h is the order of the group (the total

number of symmetry operations, *not* the number of classes), each class of symmetry operations is denoted R_c , and the number of operations in each class is g_c . The number of times irrep i appears in the reducible representation Γ is n_i , the character of irrep i under a class of symmetry operations R_c is $\chi_i(R_c)$, and the character of the reducible representation Γ under R_c is $\chi_\Gamma(R_c)$. Using this notation, we calculate n_i for each irrep according to the following formula:

$$n_i = \frac{1}{h} \sum_{R_c} g_c \chi_i(R_c) \chi_\Gamma(R_c)$$

This formula, often called the reduction formula or decomposition formula, is one of the most important and widely used equations in the application of group theory to chemistry and physics.

In C_{3v} , $h = 6$, and $g_c = 1$ for $\hat{E}$, 2 for $\hat{C}_3$, and 3 for $\hat{\sigma}_v$. Thus, we calculate all the n_i values for our example representation Γ as follows:

$$\begin{aligned} n_{A_1} &= \frac{1}{6} [(1)(1)(5) + (2)(1)(-1) + (3)(1)(1)] = \frac{1}{6} (5 - 2 + 3) = \frac{1}{6} (6) = 1 \\ n_{A_2} &= \frac{1}{6} [(1)(1)(5) + (2)(1)(-1) + (3)(-1)(1)] = \frac{1}{6} (5 - 2 - 3) = \frac{1}{6} (0) = 0 \\ n_E &= \frac{1}{6} [(1)(2)(5) + (2)(-1)(-1) + (3)(0)(1)] = \frac{1}{6} (10 + 2 + 0) = \frac{1}{6} (12) = 2 \end{aligned}$$

We have thus reduced (or decomposed) the reducible representation Γ to its component irreps, and we can write $\Gamma = A_1 + 2E$. When using the reduction formula, remember that every n_i must equal either a positive integer or zero. If you obtain a noninteger or negative value for any n_i , this result indicates that you have made an arithmetic error. Also note that the reduction formula cannot be used for reducible representations in the point groups $C_{\infty v}$, $D_{\infty h}$, or K_h , since each of these groups has infinitely many symmetry operations, *i.e.* an order of $h = \infty$.

2.7. Mulliken Symbols for Irreducible Representations

You may wonder about where the symbols for irreps, such as A_1 , B_2 , E , *etc.* come from. You do not need to know what these symbols indicated in order to solve problems using a

character table, and I do not expect students in my classes to know their meanings on exams. Nevertheless, you may find that an understanding of these symbols helps you understand the logic of the properties of different orbitals, vibrational modes, *etc.* which correspond to a given irrep. These symbols are sometimes called Mulliken symbols, after Robert S. Mulliken, who did seminal work on molecular orbital theory. Note that the notation for point groups, such as C_{2v} , D_{6h} , *etc.* is not due to Mulliken; it is known as the Schönflies notation, after the mathematician Arthur Moritz Schönflies (1853-1928), who applied group theory to problems in crystallography.

The first, and most important, part of a Mulliken symbol is the letter. The letters A and B both indicate that an irrep is *nondegenerate*: its dimension, defined by its character under the symmetry operation $\hat{E}$, is 1. A doubly degenerate irrep (dimension of 2, character of 2 under $\hat{E}$) is denoted by E (not to be confused with the symmetry element E or the symmetry operation $\hat{E}$). A triply degenerate irrep is denoted by T , a quadruply degenerate irrep by G , and a quintuply degenerate irrep by H . The practical meaning of degeneracy in this context is that, if we find that some property of a molecule (such as a molecular orbital or a vibrational mode) has an irrep with N -fold degeneracy, then that irrep corresponds to N MOs (or vibrational modes, or whatever) with the same energy as each other. Thus, if we find that a molecule has an MO denoted T , this means that we really have three MOs, all with the same energy. Nondegenerate irreps are labeled A if they have the character of 1 under the principal rotation operation (the $\hat{C}_n$ with the largest value of n), *i.e.* they are symmetric with respect to this rotation. They are labeled B if they have the character of -1 under the principal rotation, *i.e.* they are antisymmetric with respect to this rotation.

The subscript number 1 or 2 of a Mulliken symbol (such as 1 in A_1 or 2 in B_2) denotes symmetry or antisymmetry with respect to rotation about a C_2 axis perpendicular to the principal axis. Symmetry (a character of 1) leads to a subscript 1, and antisymmetry (a character of -1) leads to a subscript 2. Some molecules have no C_2 axes perpendicular to the principal axis: in such cases, the 1 and 2 subscripts denote symmetry or antisymmetry, respectively, with respect to reflection through a vertical mirror plane.

The subscripts g and u are very important. For instance, we will see later in this course that, in a regular octahedral complex of a transition metal (point group O_h), the central metal atom's d AOs split into two groups, belonging to the irreps E_g and T_{2g} . The g subscript (from the German *gerade*, “even”) means that an irrep is symmetric (character of 1) with respect to the inversion operation $\hat{i}$, while the u subscript (from the German *ungerade*, “uneven” or “odd”) means that the irrep is antisymmetric (character of -1) with respect to inversion. Irreps of groups with no inversion operation do not have g or u labels.

In molecules with a mirror plane perpendicular to the principal rotation axis (σ_h), a single prime ($'$) denotes symmetry (character of 1) with respect to reflection through this plane (the $\hat{\sigma}_h$ operation), while a double prime ($''$) denotes antisymmetry (character of -1) with respect to reflection through this plane.

The columns of a character table to the right of the characters for the irreps denote which irreps Cartesian vectors (*e.g.* z) and products of Cartesian vectors (*e.g.* xy) belong to. It should be noted that the s orbitals of any unique atom in a molecule (such as the central metal atom in a complex) *always* belong to the most symmetric irrep in the molecule's point group, the first listed in the character table, which has a character of 1 for every symmetry operation. This is not usually indicated in the character tables themselves, but it is important to know when applying group theory to problems in chemical bonding.

2.8. Direct Products of Irreducible Representations

There is an additional operation we can perform with irreps, which will prove important in many chemical applications. We can, in a sense, “multiply” two irreps by taking the *direct product* of the two of them, which will generate a new representation (either reducible or irreducible) of the point group to which the irreps belong. The character of a direct product of two irreps under each class of symmetry operation is the simple arithmetic product of the characters of each irrep under that class of symmetry operation. In equation form, if P and Q are irreps, then, for each class of symmetry operation R_c , the characters of the direct product $P \times Q$ are given by

$$\chi_{P \times Q}(R_c) = \chi_P(R_c)\chi_Q(R_c)$$

Because direct products involve the simple arithmetic multiplication of characters, direct product formation is commutative, *i.e.* $P \times Q = Q \times P$ for any two irreps P and Q in a point group. This notion can be extended to the direct product of three or more irreps: for instance, if we take the direct product of any three irreps P , Q , and R in a point group, the characters of the representation $P \times Q \times R$ are given by

$$\chi_{P \times Q \times R}(R_c) = \chi_P(R_c)\chi_Q(R_c)\chi_R(R_c)$$

with similar formulae holding for the direct products of four, five, *etc.* irreps.

The direct product of two nondegenerate (Mulliken symbol A or B) irreps is also a nondegenerate irrep. For instance, consider the direct product $A_1 \times B_2$ in point group C_{2v} :

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
$A_1 \times B_2$	1	-1	-1	1		

In this case, we can simply compare the characters of $A_1 \times B_2$ under each class of operations with the standard set of irreps and see that $A_1 \times B_2 = B_2$.

The direct product of a nondegenerate (A or B) irrep with a degenerate irrep is also a degenerate irrep with the same dimension as the starting degenerate irrep. For instance, consider the direct products $A_1 \times E$ and $A_2 \times E$ in the group C_{3v} :

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy),$ (xz, yz)
$A_1 \times E$	2	-1	0		
$A_2 \times E$	2	-1	0		

In this case, we see that $A_1 \times E$ and $A_1 \times E$ are both equal to E . Since there is only one degenerate irrep in C_{3v} (namely, E), the direct product of E with either nondegenerate irrep must return E itself. However, in the point group O_h , there are two doubly degenerate irreps, E_g and E_u . In that point group, the direct product of E_g with a nondegenerate irrep may give back E_g , or it may give E_u , depending on the nondegenerate irrep.

As mentioned previously, every group has a totally symmetric irrep with dimension 1, with a character of 1 under every class of symmetry operation. Its Mulliken symbol will vary depending on the point group: in different point groups, it may be denoted A , A_1 , A' , A_1' , or A_{1g} . For simplicity and generality, let us denote the totally symmetric irrep in a given group by S . The direct product of S with *any* other irrep P is just P : $S \times P = P \times S = P$. This can be seen from the fact that S has a character of 1 under every class of symmetry operation, so each character of P will simply be multiplied by 1 and thus unchanged.

The direct product of two degenerate irreps (that is, two irreps of dimension > 1) will be a *reducible* representation, that is, a sum of irreps. As an example, let us consider the point group T_d , to which molecules with the symmetry of a regular tetrahedron (*e.g.* CH_4 , FeCl_4^-) belong, and take the direct product of the doubly degenerate irrep E and the triply degenerate irrep T_2 , as shown in Table 2.3 below.

Table 2.3. The character table for the T_d point group.

T_d	$\hat{E}$	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
$E \times T_2$	6	0	-2	0	0		

Even without inspecting the irreps in detail, we can immediately see that the direct product $E \times T_2$ is *not* equal to any of the irreps, because its dimension is 6, and the maximum dimension of any irrep in T_d is 3. If we use the decomposition formula, we can find that $E \times T_2 = T_1 + T_2$.

The direct product of any *nondegenerate* irrep with itself is equal to the totally symmetric irrep. This can easily be seen to be true by noting that every nondegenerate irrep has a character of either 1 or -1 under every class of symmetry elements, so their direct product with themselves will have characters of $(1)(1) = 1$ or $(-1)(-1) = 1$ under all classes, corresponding to the totally symmetric irrep. The direct product of a *degenerate* irrep with itself will be a reducible representation, but this reducible representation will always contain the totally symmetric irrep. For example, in T_d , $T_1 \times T_1 = A_1 + E + T_1 + T_2$.

Finally, it should be noted that the *only* way that a direct product of two irreps will either equal the totally symmetric irrep or be a reducible representation containing the totally symmetric irrep is if the two irreps are the same.

2.9. Group Theory and Quantum Mechanics

We have just discussed a considerable amount of what might appear to be very abstract mathematics. Now, let us see why group theory is of importance to atomic and molecular calculations. First of all, it turns out that all wavefunctions pertaining to a molecular system, whether they are one-electron orbital wavefunctions, many-electron term wavefunctions, or vibrational or rotational wavefunctions relevant to spectroscopy, must be eigenfunctions of each of the symmetry operations in the point group in the molecule. The eigenvalues of the wavefunctions under each symmetry operation are the characters under each class of operations for one of the irreps in the group. That is, any valid wavefunction²³ *transforms as* (has the symmetry of) one of the irreps of the molecule's point group. Similarly, any relevant operator $\hat{A}$ that corresponds to a physical property of the system must also have the symmetry of one of the irreps in the molecule's point group. This is true not only of scalar operators (*e.g.* the Hamiltonian), but also of vector operators (*e.g.* linear momentum, angular momentum) and tensor operators (*e.g.* polarizability).

²³ Here "valid" means properly constructed according to symmetry principles. It does *not* mean "exact," so an approximate wavefunction (such as one constructed using a computational technique such as the Hartree-Fock self-consistent field method) will have these useful symmetry properties, even though it is not exactly equal to the exact wavefunction of the molecule in question (which will have no analytic form).

The classification of wavefunctions and operators according to which irreps they transform as is very important when it comes to simplifying calculations. We often encounter integrals (inner products, matrix elements) of the form $S_{ij} = \langle \psi_i | \psi_j \rangle$. For instance, if ψ_i and ψ_j are atomic orbitals on different atoms, then S_{ij} is the overlap integral, reflecting formation of a molecular orbital from two atomic orbitals. It turns out that inner products of the form $\langle \psi_i | \psi_j \rangle$ are *exactly* equal to zero unless the direct product of the irrep corresponding to ψ_i and the irrep corresponding to ψ_j is either equal to or contains the totally symmetric irrep of the molecule's point group. But, as we saw in Section 2.8, the only way for this direct product to contain the totally symmetric irrep is if ψ_i and ψ_j transform as the same irrep. Thus, only wavefunctions transforming as the same irrep (sometimes referred to as “belonging to the same symmetry species” or simply “having the same symmetry”) can have nonzero overlap.

Similarly, when an operator $\hat{A}$ acts on a wavefunction ψ_j , it produces a new function $\hat{A}\psi_j$. (We need not assume that ψ_j is an eigenfunction of $\hat{A}$ in this case; it may or may not be.) The irrep (symmetry species) or irreps corresponding to $\hat{A}\psi_j$ can be described by the direct product of the irrep corresponding to $\hat{A}$ and the irrep corresponding to ψ_j . Now consider matrix elements of the form $A_{ij} = \langle \psi_i | \hat{A} | \psi_j \rangle$. Any such A_{ij} will be exactly zero unless the direct product of the irrep corresponding to ψ_i , the irrep corresponding to $\hat{A}$, and the irrep corresponding to ψ_j is either equal to, or contains, the totally symmetric irrep. Since direct products of irreps are commutative, another way to say this is that A_{ij} will only be nonzero if the direct product of the irreps corresponding to ψ_i and ψ_j is either equal to or contains the irrep corresponding to $\hat{A}$.

This result has direct implications in spectroscopy. When we conduct a spectroscopic experiment, we subject a system (such as a molecule or an extended structure) to some kind of electromagnetic radiation that induces a transition between one state, described by the wavefunction ψ_i , and another state, described by the wavefunction ψ_j . The interaction of radiation with the molecule can be described by an operator $\hat{M}$, whose symmetry we know from the theory of electromagnetism. The probability of a transition between state ψ_i and state ψ_j (and thus the intensity of the signal measured by our spectrometer) is proportional

to M_{ij}^2 , the square of the transition moment integral, which is defined as $M_{ij} = \langle \psi_i | \hat{M} | \psi_j \rangle$. While the calculation of the numerical value of a nonzero M_{ij} might well be complicated, we can use symmetry arguments to determine whether or not M_{ij} is nonzero without evaluating any integrals. If the direct product of the irreps corresponding to ψ_i and ψ_j is either equal to or contains the irrep corresponding to $\hat{M}$, then M_{ij} is nonzero. Otherwise, $M_{ij} = 0$ and we say that, in this form of spectroscopy, the transition between state ψ_i and state ψ_j is “forbidden.” By knowing the symmetry species (irreps) of the initial and final wavefunctions and that of the electromagnetic radiation operator, we can thus derive “selection rules” for which transitions are allowed and which are forbidden. It should be noted, however, that the nature of the approximations sometimes used to describe the spectroscopic states can lead to transitions being classified as “forbidden” that nevertheless still occur, albeit usually with low intensity. We will return to this complication when we discuss selection rules later.

The most important operator in quantum mechanics is, of course, the Hamiltonian $\hat{H}$, and when we calculate approximate energies of orbitals and terms, we are often confronted with matrix elements of the form $H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle$, which have dimensions of energy. It turns out that the Hamiltonian for a molecule *always* transforms as the totally symmetric irrep of that molecule’s point group, so matrix elements H_{ij} are only nonzero if ψ_i and ψ_j transform as the same irrep.

Chapter 3: Molecular Orbital Theory

3.1. The LCAO-MO Method for Molecular Orbitals

Computational chemistry techniques such as the Hartree-Fock (HF) self-consistent field method usually approximate the total wavefunction Φ of a multielectron atom or ion as a Slater determinant (or a linear combination of Slater determinants) of one-electron wavefunctions ϕ_i (atomic orbitals or AOs). The energetically optimal forms of the AOs are determined by repeated application of the variational method, with the calculations being iterated until successive calculations give the same answer (*i.e.* they are “self-consistent”). Similarly, such methods can be used for calculations on molecules or polyatomic ions, by approximating the total wavefunction Ψ of the molecule as a Slater determinant (or linear combination of Slater determinants) of one electron *molecular* wavefunctions ψ_i (molecular orbitals or MOs), in what is known as molecular orbital theory (MOT).

This description of MOT necessarily raises the question of what form the trial functions representing the MOs should take. Clemens Roothaan (1918-2019) and George Hall (1925-2018) proposed that each MO ψ_i be approximated as a linear combination of AOs ϕ_j from the atoms that make up the molecule. For a set of MOs constructed from a set of n AOs (the basis set), we construct n MOs, each of which has the following general form:

$$\psi_i = \sum_{j=1}^n c_{ji} \phi_j$$

Here each weighting coefficient c_{ji} indicates the contribution of the AO ϕ_j to the MO ψ_i . This method is known as the linear combination of atomic orbitals – molecular orbitals method, or the LCAO-MO method for short.

We now have a set of MO trial functions, each of which is linearly dependent in the variational parameters c_{ji} . To use the variational theorem to find the best values of c_{ji} (corresponding to the lowest-energy MOs), we set an $n \times n$ secular determinant equal to zero and solve for the energies:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{1n} - ES_{1n} & H_{2n} - ES_{2n} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

Here E is the one-electron orbital energy for each MO, and the other matrix elements are given by

$$S_{ab} = \langle \phi_a | \phi_b \rangle = S_{ba} = \langle \phi_b | \phi_a \rangle$$

$$H_{ab} = \langle \phi_a | \hat{H} | \phi_b \rangle = H_{ba} = \langle \phi_b | \hat{H} | \phi_a \rangle$$

Note that, in these equations, $\hat{H}$ does not represent the full Hamiltonian operator, but is instead a sort of “one-electron Hamiltonian” known as the Fock operator, which gives the energy of an electron in a given orbital as a result of the average electric field from all the other electrons. The detailed form of the Fock operator need not concern us in this course,²⁴ but what is important for our purposes is that it has the same symmetry as the full Hamiltonian.

The physical interpretations of the matrix elements are as follows: if the basis set of AOs is normalized (as is usually the case), then all $S_{aa} = 1$. S_{ab} is called the *overlap integral* of ϕ_a and ϕ_b . If ϕ_a and ϕ_b are AOs on the *same* atom, and the basis set of AOs on each atom is orthogonal (as is usually the case), then $S_{ab} = 0$, while if ϕ_a and ϕ_b are AOs on *different* atoms, S_{ab} is a measure of how much the two AOs can overlap in space to form MOs (hence the term “overlap integral”). H_{aa} is the one-electron energy of the AO ϕ_a , and H_{ab} may be thought of (somewhat crudely) as the “energy of interaction” between the AOs ϕ_a and ϕ_b . The value of H_{ab} is most important if ϕ_a and ϕ_b are AOs on different atoms, and thus interact to form a lower-energy (bonding) MO and a higher-energy (antibonding) MO. At most, our solutions to this secular determinant will give us n different values of the MO energy E , but they will yield fewer different E values if some of the MOs are degenerate.

²⁴ Details of the Hartree-Fock technique can be found in chapter 3 of *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, by Attila Szabo and Neil S. Ostlund, Dover Publications, Inc.: Mineola, NY, 1996.

The *conceptually* simplest way to approach this problem is to solve it by “brute force,” that is, to set up a secular determinant involving all the AOs to be considered (often all the valence AOs of all the atoms in the molecule) and then to solve that $n \times n$ secular determinant, by hook or by crook. Unfortunately, this strategy is computationally very inefficient: even a reasonably large molecule will have a great many valence AOs in its basis set, so we must ask our computer to calculate a large number of definite integrals and then to solve some very large determinants, tasks that can take a great deal of time. If, however, we can set some of the matrix elements S_{ab} and H_{ab} equal to zero without having to evaluate the integrals, we can save computational time on integration, as well as being able to rewrite each secular determinant as a set of smaller determinants lying along its principal diagonal. To do this, we will use symmetry techniques, and we will see that this symmetry-based method is useful not only for computational chemistry, but also for the qualitative construction of MO diagrams, which we may do with pencil and paper without evaluating any integrals.

3.2. Symmetries of Atomic Orbitals and Symmetry-Adapted Linear Combinations (SALCs)

It is a fact (which we state here without proof) that both the total molecular wavefunction Ψ and each of the MOs ψ_i will transform as one of the irreps of the point group to which the molecule belongs. (Two or more MOs will transform together in the case of degeneracy.) The LCAO-MO calculations become simpler, allowing us to immediately set some matrix elements equal to zero by symmetry, if we ensure that each of the basis set orbitals also transforms as one of the irreps. When we have a unique atom in a molecule, the irreps that its AOs transform as are readily identified simply by examining the two rightmost columns of the character table for the molecule's point group: a p_x AO transforms the same way as x , a d_{yz} AO transforms the same way as yz , *etc.* (Remember that an s AO on a unique atom always transforms as the totally symmetric irrep in the molecule's point group, even though most character tables, as printed, do not indicate this fact.) Now suppose that we have a molecule ML_n , with several equivalent terminal atoms L bound to a unique central atom M : while we can identify the irreps corresponding to the AOs of M easily enough, what about the AOs of the terminal L atoms? It turns out that an individual AO of one of the L atoms will not

transform as any of the irreps, but that an appropriately constructed symmetry-adapted linear combination (SALC) of the terminal atom AOs *will* have the symmetry of one of the irreps in the molecule's point group.

Our task is now to identify the appropriate irreps of the SALCs formed from the terminal atom AOs. The first step is to create a reducible representation of the terminal atom AOs of each type. For instance, in CH_4 we would consider the $1s$ AO on each H, while in CCl_4 , we would construct three reducible representations: one corresponding to the $3s$ AOs on each Cl, one corresponding to the $3p_z$ AOs (taking these AOs to be oriented along the C–Cl bond axes), and one corresponding to the $3p_x$ and $3p_y$ AOs together. We could, of course, derive these representations by constructing a transformation matrix for each of the symmetry operations of the molecule applied to the set of AOs as a column matrix, followed by computing the character of each matrix. This procedure would get very tedious very quickly, and there is fortunately a *much* simpler way to obtain the characters of the reducible representations. This shortcut method is as follows:

(1) If an operation leaves an AO unchanged, that AO contributes 1 to the character under that operation.

(2) If an operation takes an AO into the negative of itself (*e.g.* reflecting a p_x AO through the yz plane), that AO contributes -1 to the character under that operation.

(3) If an operation interchanges an AO with another AO (*e.g.* swapping a pair of s AOs on different atoms, or swapping the p_x and p_y AOs on a single atom), that AO contributes zero to the character under that representation, since such interchanges are represented by off-diagonal elements of transformation matrix, and they thus contribute nothing to the character. Any time an atom moves in space as the result of a symmetry operation, each of its AOs contributes zero to the character.

(4) Only if an operation takes an AO to a *mixture of that AO and another AO* do we need to write out a transformation matrix to compute the character. An example of such a mixing of

orbitals can be seen by considering the $\hat{C}_3$ rotation on (x, y, z) , assuming the z axis is the C_3 axis, which transforms x and y into linear combinations of each other (see the C_{3v} example in Section 2.6). For many examples, this step is not required. However, for a T_d species ML_4 , we would need to write a rotation matrix for the mixing of p_x and p_y AOs on the L atoms by rotation about one of the molecule's C_3 axes.

Like many things, the method of deriving SALCs is best illustrated by example. In the following three sections, we will consider (in order of least to most complicated) the group theory-based MO treatment of the main-group hydrides H_2O , NH_3 , and CH_4 .

3.3. MO Theory for H_2O and Projection Operators

For H_2O , in the C_{2v} point group, a reasonable basis set would be the valence AOs of all the atoms: a $1s$ AO for each H atom, and a $2s$ and three $2p$ AOs for O. Without the use of symmetry, the LCAO-MO method would give us a 6×6 secular determinant to solve, with many off-diagonal matrix elements to evaluate by definite integration. Let us now see how to simplify this by making the H $1s$ AOs a basis for H atom SALCs. The first step is to construct a reducible representation corresponding to the H $1s$ AOs. These AOs are shown, along with a coordinate system, in Figure 3.1 below, and the C_{2v} character table and the SALC reducible representation are shown in Table 3.1 on the following page.

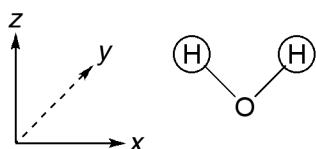


Figure 3.1. The hydrogen $1s$ AOs in H_2O .

The characters for Γ_{SALC} are obtained as follows: $\hat{E}$ leaves both AOs unchanged for a character of 2. $\hat{C}_2$ switches the AOs with each other for a character of 0. $\hat{\sigma}_v(xz)$ leaves both AOs

unchanged (since the AOs lie in the xz plane²⁵) for a character of 1, and $\hat{\sigma}_v'(yz)$ switches them with each other for another character of 0. This representation reduces to $\Gamma_{\text{SALC}} = A_1 + B_1$, which means that we have one SALC that transforms as A_1 and one that transforms as B_1 . Note that whenever we construct a set of SALCs from a basis set of n AOs, we will end up with n SALCs. The forms of the SALCs are shown in Figure 3.2 below.

Table 3.1. The character table for the C_{2v} point group.

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_{SALC}	2	0	2	0		

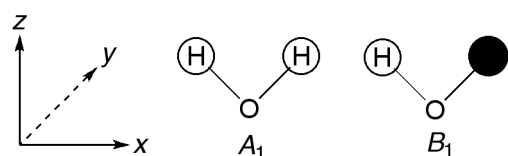


Figure 3.2. SALCs for the H 1s AOs in H_2O .

In this case, the forms of the SALCs are readily predicted: the only real options are a sum or a difference of the AOs (*i.e.* whether the two AOs have the same phase, or different phases). In general, SALCs are linear combinations of the AOs used as their basis. There is a systematic method for determining the coefficients in this linear combinations, using an algorithm called the projection operator. The way the projection operator works is that we apply the projection operator for a given irrep to any one of a set of equivalent AOs, and it “projects out” a SALC belonging to the appropriate irrep.

There are two forms of the projection operator. One form, the “complete projection operator,” gives us unambiguous expressions for a set of SALCs in *any* point group.

²⁵ Strictly speaking, the $\hat{\sigma}_v(xz)$ operation takes a hemisphere of each 1s AO to the other hemisphere. This is not considered to be any net motion from the standpoint of symmetry, because the sign does not change (s AOs are spherically symmetrical).

Unfortunately, it requires that we know the transformation matrices corresponding to all the symmetry operations for basis functions of each irrep. These matrices are not widely tabulated, and working out all of them *de novo* would be extremely tedious. Instead, we will use a simpler type of operator, the “incomplete projection operator,” which only requires that we know the characters corresponding to each symmetry operation for basis functions belonging to each irrep. Fortunately, these characters are precisely the numbers provided for us in the standard character tables. For a set of SALCs that are all nondegenerate (all the irreps are of the *A* or *B* type, with no *E*, *T*, *G*, or *H* irreps), the incomplete projection operators are enough to give us the full forms of the SALCs – the incomplete projection operators are not, in fact incomplete for degenerate SALCs. However, to get forms of SALCs belonging to degenerate sets (in this course, we will only encounter doubly degenerate *E* and triply degenerate *T* irreps), we must use a combination of projection operators and a certain amount of pictorial intuition.

The form of the incomplete projection operator (which will henceforth simply be referred to as the projection operator) is as follows:

$$\hat{P}_j = \sum_{\hat{R}} \chi_j(\hat{R}) \hat{R}$$

Here *j* is any given irrep in the group, $\chi_j(\hat{R})$ is the character of irrep *j* under each symmetry operation $\hat{R}$, and $\hat{R}$ means that we apply the symmetry operation $\hat{R}$ to a given member of the basis set, perhaps turning it into another member of the basis set, or to the negative of itself. Note that, while the characters for multiple operations $\hat{R}$ in the same class are equal, the effect of each $\hat{R}$ in a class on a given basis AO will be different for different $\hat{R}$ in that class. This is why the summation in the projection operator is over symmetry operations, not classes of symmetry operations. The effect of the projection operator is to turn any one of a set of equivalent AOs ϕ_i into a SALC belonging to the irrep *j* represented by the projection operator, or

$$\hat{P}_j \phi_i = \phi_j^{\text{SALC}}$$

The first step is to determine the effect of each symmetry operation on one of the equivalent AOs. It is convenient to construct a table of the effects of these operations on one of the AOs before explicitly applying the projection operator. For H₂O, let us label the 1s AO on the left H atom of Figure 3.1 as σ_1 and that on the right H atom as σ_2 . $\hat{E}$ leaves σ_1 as σ_1 , $\hat{C}_2$ transforms it to σ_2 , $\hat{\sigma}_v(xz)$ leaves it as σ_1 , and $\hat{\sigma}_v'(yz)$ transforms it into σ_2 . Table 3.2 below shows these results.

Table 3.2. Effect of each symmetry operation in C_{2v} on the 1s AO σ_1 .

Operation $\hat{R}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v'(yz)$
$\hat{R}\sigma_1$	σ_1	σ_2	σ_1	σ_2

Using the characters of the A_1 irrep with the results of Table 3.2 yields

$$\phi_{A_1}^{\text{SALC}} = \sigma_1 + \sigma_2 + \sigma_1 + \sigma_2 = 2\sigma_1 + 2\sigma_2$$

While this is indeed a symmetry-adapted orbital, SALCs should also be normalized. If we assume that the basis orbitals of the SALC are sufficiently far apart from one another that there is zero overlap between them (usually a very good approximation), then the normalization constant is easy to work out without actually evaluating any integrals. If an (unnormalized) SALC is a linear combination of n basis orbitals

$$\phi_j^{\text{SALC}} = \sum_{i=1}^n c_i \phi_i$$

then the appropriate normalization constant N by which it must be multiplied is given by

$$N = \frac{1}{\sqrt{\sum_{i=1}^n c_i^2}}$$

Applying this normalization to the A_1 SALC which we derived for the H 1s AOs of H₂O, we see that

$$\phi_{A_1}^{\text{SALC}} = \frac{1}{\sqrt{2^2 + 2^2}} (2\sigma_1 + 2\sigma_2) = \frac{1}{\sqrt{2}} (\sigma_1 + \sigma_2)$$

We can similarly construct the SALC of B_1 symmetry as follows:

$$\phi_{B_1}^{\text{SALC}} = \sigma_1 - \sigma_2 + \sigma_1 - \sigma_2 = 2\sigma_1 - 2\sigma_2$$

Normalizing gives

$$\phi_{B_1}^{\text{SALC}} = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2)$$

With the addition of normalization, these SALCs correspond to the simple sum and difference of 1s AOs that we envisioned earlier.

At this point, we can simplify the consideration of the MOs considerably. Oxygen AOs and hydrogen SALCs can only interact with each other if they transform as the same irreducible representation. The oxygen 2s and 2p_z AOs transform as A₁, its 2p_x AO transforms as B₁, its 2p_y AO transforms as B₂, and the hydrogen 1s SALCs transform as A₁ and B₁, as we just derived. Thus, to form MOs, we have 3 basis orbitals of A₁ symmetry, 2 basis orbitals of B₁ symmetry, and 1 basis orbital of B₂ symmetry. Thus, if we were to run an HF calculation, instead of dealing with a 6 × 6 secular determinant, we would only have to deal with a 3 × 3 determinant, a 2 × 2 determinant, and a 1 × 1 determinant (*i.e.* just a number).

The “1 × 1 determinant” corresponds to the oxygen 2p_y AO of B₂ symmetry; since it has no symmetry match among the SALCs or the other oxygen AOs, it can neither form bonding/antibonding interactions with the SALCs or mix (hybridize) with other oxygen AOs. Thus, it is a rigorously nonbonding MO in this basis set, denoted 1b₂. (Mulliken symbols with lower-case letters are conventionally used to denote MOs of a given irrep, while those with capital letters are used to denote SALCs and vibrational modes.) The matrix element H_{aa} for the MO 1b₂ roughly corresponds to the one-electron energy of an oxygen 2p_y AO.

The oxygen 2p_x (B₁) AO and the B₁ SALC will interact to form a bonding MO (1b₁), lower in energy than either basis orbital, as well as a higher-energy, antibonding MO (2b₁). The oxygen 2s and 2p_z (A₁) AOs and the A₁ SALC will mix to form three MOs, labeled 1a₁, 2a₁, and 3a₁. (Remember that, whenever *n* AOs, whether AOs or SALCs, interact with each other, they will form *n* MOs.) In general, these three-orbital mixings result in a strongly bonding MO, a strongly antibonding MO, and a third MO which is *roughly* nonbonding energy-wise, but not *rigorously* nonbonding due to symmetry (contrast with 1b₁ in this example).

An approximate MO energy-level diagram, showing the correlations between the MOs of H₂O and the AOs of O and the SALCs of H, as well as sketches of the MOs, is shown in Figure 3.3 below.

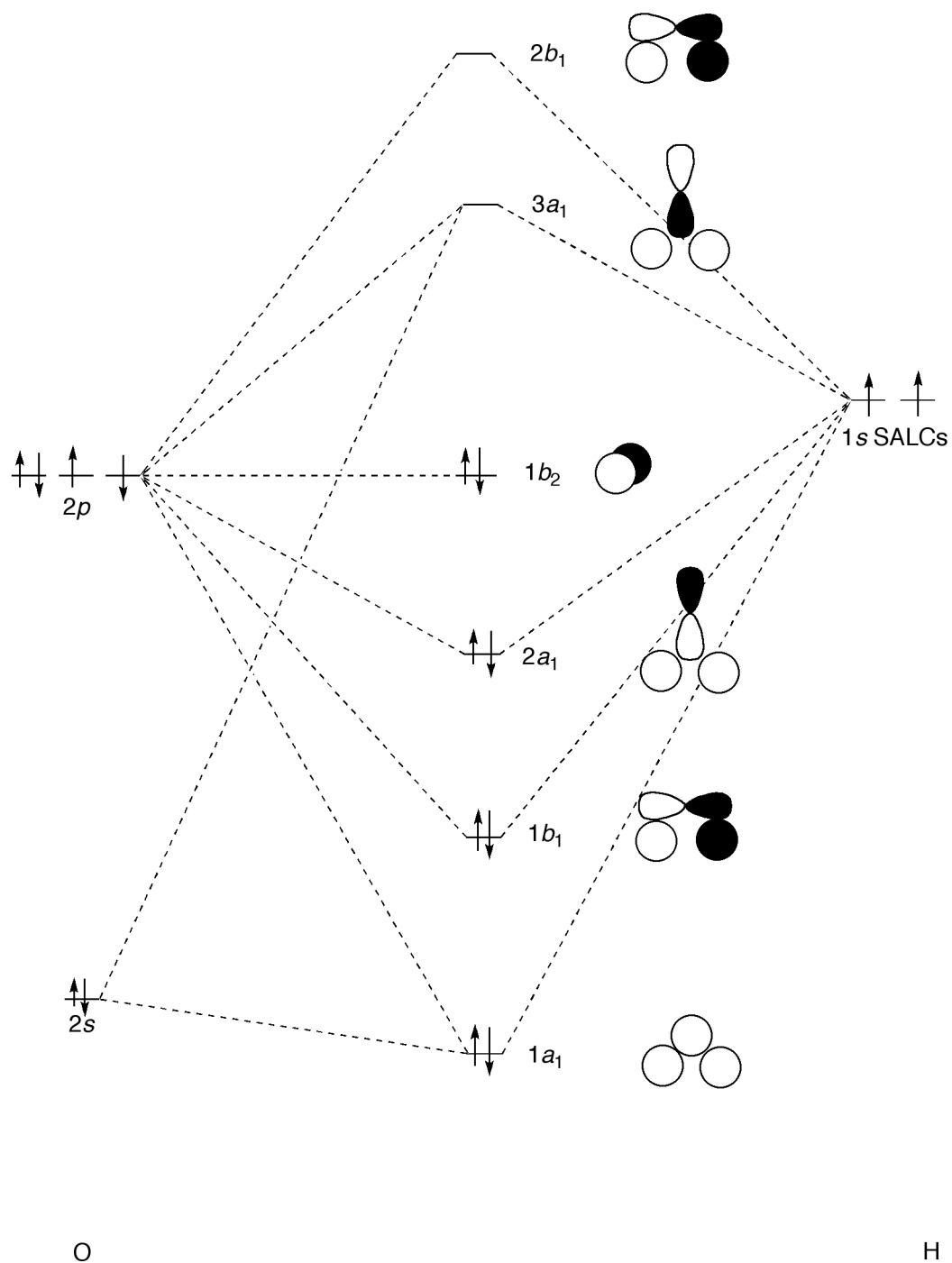


Figure 3.3. Qualitative MO diagram for H₂O.

Here the O $2p_z$ AO interacts more strongly with the H A_1 SALC, because it is closer in energy to the H $1s$ than O $2s$ is. Thus, $2a_1$ and $3a_1$ are significantly bonding and antibonding, respectively, while $1a_1$ is mostly an O $2s$ AO, stabilized slightly by bonding interactions with the H A_1 SALC. It can be considered roughly nonbonding, but not rigorously nonbonding in the way that $1b_2$ is. You may wonder why we consider the $1a_1$ MO to be roughly nonbonding, even though it is the lowest-energy MO in the diagram. This is because it is not significantly lowered in energy *relative* to the O $2s$ AO, which is already quite low in energy due to the electronegativity of O.

Note how different the diagram in Figure 3.3 is from the standard Lewis structure/valence bond theory (hybrid orbitals) picture of H_2O : instead of two equivalent O–H bond orbitals, each localized between O and a single H, we have two different bonding orbitals of different energies, $1b_1$ and $2a_1$, each of which is involved in both O–H interactions. Additionally, instead of two equivalent, nonbonding lone pairs on O, we have two (at least approximately) nonbonding MOs, $1a_1$ and $1b_2$. Furthermore, one of these “lone pairs,” $1a_1$, is actually the valence MO of lowest energy, since it is of chiefly low-energy O $2s$ character.

3.4. MO Theory for NH_3 and Projection Operators for Degenerate Irreps

Moving on from H_2O , we next consider NH_3 . As before, we use the $1s$ AOs on the H atoms (labeled σ_1 through σ_3 in Figure 3.4 below) to construct a reducible representation Γ_{SALC} in C_{3v} (Table 3.3 on the following page), taking the C_3 axis to be the z axis.

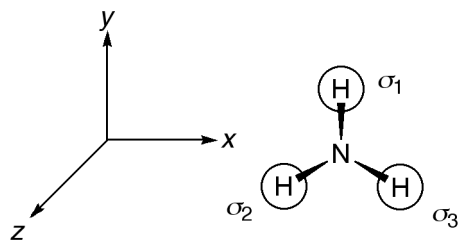


Figure 3.4. Coordinate system for the hydrogen $1s$ AOs in NH_3 .

Table 3.3. The character table for the C_{3v} point group.

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$
Γ_{SALC}	3	0	1		

The characters are obtained as follows: $\hat{E}$ leaves all H 1s AOs alone for a character of 1 each (3 total). Either $\hat{C}_3$ operation interchanges the AOs, for a character of 0. Each σ_v plane contains one AO, so each $\hat{\sigma}_v$ operation leaves that AO alone while interchanging the other two, for a character of 1. The representation can be reduced to $\Gamma_{\text{SALC}} = A_1 + E$. It is important to understand that we still obtained three SALCs from three basis AOs (as we must), since the doubly degenerate E representation indicates two degenerate SALCs. The forms of the SALCs are shown below in Figure 3.5 (we will shortly derive them), but this form is common to three AOs forming a pair of degenerate SALCs: one SALC has one AO, with a larger coefficient, out of phase with the other two, while the other SALC has no contribution from the AO with the larger coefficient in the first SALC, but has the other two out of phase with each other. This pattern appears frequently in molecules with a unique C_3 axis: the SALCs constructed from the fluorine 2s AOs in BF_3 (a trigonal planar molecule, with D_{3h} symmetry) have the same form.

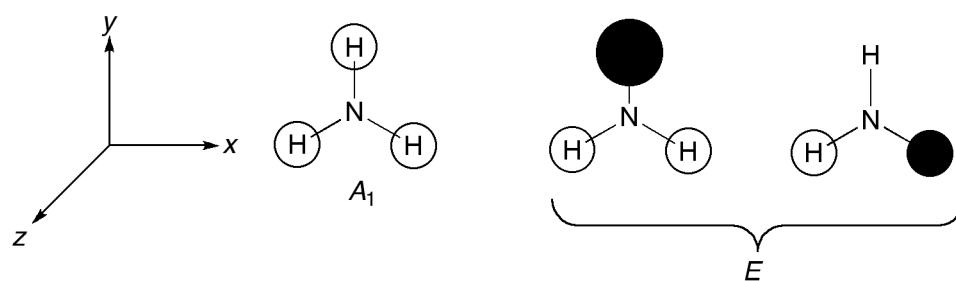


Figure 3.5. SALCs for the H 1s AOs in NH_3 .

We will now derive the forms of the SALCs. First, we tabulate the effect of each symmetry operation on the H 1s AO σ_1 (Table 3.4). We denote the three $\hat{\sigma}_v$ operations based on which

H 1s AO the corresponding σ_v mirror plane contains: $\hat{\sigma}_{v1}$ denotes reflection across mirror plane σ_{v1} , which contains 1s AO σ_1 , and so on.

Table 3.4. Effect of each symmetry operation in C_{3v} on the 1s AO σ_1 .

Operation $\hat{R}$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_{v1}$	$\hat{\sigma}_{v2}$	$\hat{\sigma}_{v3}$
$\hat{R}\sigma_1$	σ_1	σ_2	σ_3	σ_1	σ_3	σ_2

The A_1 SALC is derived using the A_1 projection operator:

$$\phi_{A_1}^{\text{SALC}} = \hat{P}_{A_1}\sigma_1 = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_1 + \sigma_3 + \sigma_2 = 2\sigma_1 + 2\sigma_2 + 2\sigma_3$$

Normalizing this SALC gives

$$\phi_{A_1}^{\text{SALC}} = \frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3)$$

Deriving the E SALCs is not as simple, since E is a doubly degenerate representation. We first apply the E projection operator to σ_1 , to get one of the E symmetry SALCs.

$$\phi_{E,1}^{\text{SALC}} = \hat{P}_E\sigma_1 = 2\sigma_1 - \sigma_2 - \sigma_3 + 0\sigma_1 + 0\sigma_3 + 0\sigma_2 = 2\sigma_1 - \sigma_2 - \sigma_3$$

Normalization gives

$$\phi_{E,1}^{\text{SALC}} = \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3)$$

We now have one E symmetry SALC. To get the other, we might try using the E projection operator on σ_2 , instead. First, we tabulate the effects of each operation on σ_2 in Table 3.5 below:

Table 3.5. Effect of each symmetry operation in C_{3v} on the 1s AO σ_2 .

Operation $\hat{R}$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_{v1}$	$\hat{\sigma}_{v2}$	$\hat{\sigma}_{v3}$
$\hat{R}\sigma_2$	σ_2	σ_3	σ_1	σ_3	σ_2	σ_1

$$\phi_{E,2}^{\text{SALC}} = \hat{P}_E\sigma_2 = 2\sigma_2 - \sigma_3 - \sigma_1 + 0\sigma_3 + 0\sigma_2 + 0\sigma_1 = 2\sigma_2 - \sigma_3 - \sigma_1$$

Normalization gives

$$\phi_{E,2}^{\text{SALC}} = \frac{1}{\sqrt{6}}(2\sigma_2 - \sigma_3 - \sigma_1)$$

There is a problem with these two SALCs, namely, that they are not orthogonal to each other, as is shown here. (The overlap integrals between the 1s AOs are all taken as zero, and we assume that each 1s AO is normalized.)

$$\begin{aligned}
 \langle \phi_{E,1}^{\text{SALC}} | \phi_{E,2}^{\text{SALC}} \rangle &= \left\langle \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \left| \frac{1}{\sqrt{6}}(2\sigma_2 - \sigma_3 - \sigma_1) \right. \right\rangle \\
 &= \frac{1}{6} \langle 2\sigma_1 - \sigma_2 - \sigma_3 | 2\sigma_2 - \sigma_3 - \sigma_1 \rangle \\
 &= \frac{1}{6} (4\langle \sigma_1 | \sigma_2 \rangle - 2\langle \sigma_1 | \sigma_3 \rangle - 2\langle \sigma_1 | \sigma_1 \rangle - 2\langle \sigma_2 | \sigma_2 \rangle + \langle \sigma_2 | \sigma_3 \rangle + \langle \sigma_2 | \sigma_1 \rangle - 2\langle \sigma_3 | \sigma_2 \rangle \\
 &\quad + \langle \sigma_3 | \sigma_3 \rangle + \langle \sigma_3 | \sigma_1 \rangle) = \frac{1}{6} (0 + 0 - 2 - 2 + 0 + 0 + 0 + 1 + 0) = -\frac{1}{2} \neq 0
 \end{aligned}$$

When we have two functions f_1 and f_2 which are not orthogonal to each other, we can transform them into a pair of functions that *are* orthogonal using an algorithm called Gram-Schmidt orthogonalization, after the mathematicians Jørgen Pedersen Gram (1850-1916) and Erhard Schmidt (1876-1959). First, we select an initial function f_1 , which must be normalized. Here, we will take f_1 to be the first SALC with E symmetry:

$$f_1 = \phi_{E,1}^{\text{SALC}} = \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3)$$

Similarly, we will take the second function f_2 to be the second SALC with E symmetry:

$$f_2 = \phi_{E,2}^{\text{SALC}} = \frac{1}{\sqrt{6}}(2\sigma_2 - \sigma_3 - \sigma_1)$$

Our task now is to modify f_2 to become a new function f_2' which is orthogonal to f_1 . We do this by making f_2' a linear combination of f_2 and f_1 , and we determine the coefficient in the linear combination by requiring orthogonality:

$$\begin{aligned}
 f_2' &= f_2 + cf_1 \\
 \langle f_1 | f_2' \rangle &= 0
 \end{aligned}$$

The orthogonality condition allow us to calculate the value of the coefficient c as follows:

$$\begin{aligned}
 \langle f_1 | f_2' \rangle &= \langle f_1 | f_2 + cf_1 \rangle = \langle f_1 | f_2 \rangle + c\langle f_1 | f_1 \rangle = 0 \\
 c\langle f_1 | f_1 \rangle &= -\langle f_1 | f_2 \rangle \\
 c &= -\frac{\langle f_1 | f_2 \rangle}{\langle f_1 | f_1 \rangle}
 \end{aligned}$$

For the NH_3 SALC problem, $f_1 = \phi_{E,1}^{\text{SALC}}$ and $f_2 = \phi_{E,2}^{\text{SALC}}$, so

$$c = -\frac{\langle \phi_{E,1}^{\text{SALC}} | \phi_{E,2}^{\text{SALC}} \rangle}{\langle \phi_{E,1}^{\text{SALC}} | \phi_{E,1}^{\text{SALC}} \rangle} = -\frac{-\frac{1}{2}}{1} = \frac{1}{2}$$

so

$$\begin{aligned} f_2' = \phi_{E,2'}^{\text{SALC}} &= \phi_{E,2}^{\text{SALC}} + \frac{1}{2} \phi_{E,1}^{\text{SALC}} = \frac{1}{\sqrt{6}}(2\sigma_2 - \sigma_3 - \sigma_1) + \frac{1}{2\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \\ &= \frac{3}{2\sqrt{6}}(\sigma_2 - \sigma_3) \end{aligned}$$

Normalizing this new SALC, we have our two E symmetry SALCs for the purpose of this problem, which are pictorially represented in Figure 3.5 above:

$$\begin{aligned} \phi_{E,1}^{\text{SALC}} &= \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \\ \phi_{E,2'}^{\text{SALC}} &= \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3) \end{aligned}$$

Gram-Schmidt orthogonalization is very reliable, and the technique can readily be extended to construct sets of 3, 4, or more orthogonal functions. (In practice, no chemically important point groups have irreps with a dimension larger than 5.) However, while the algorithm remains conceptually straightforward, it quickly becomes tedious when orthogonalizing larger numbers of functions. (Constructing N orthogonal functions using the Gram-Schmidt technique requires solving $N - 1$ simultaneous linear equations, in addition to all the computations of inner products.) When constructing SALCs belonging to degenerate irreps, we can often forego the Gram-Schmidt process for a less rigorous, but still reliable, pictorial technique.

We see from the C_{3v} character table (Table 3.3) that the $2p_x$ and $2p_y$ AOs of N must transform together as E . Now, suppose that we used the projection operator for E just once, to obtain $\phi_{E,1}^{\text{SALC}} = \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3)$. We can see that this SALC is well set up to interact with the N $2p_y$ AO (see Figure 3.5 for the coordinate system), since one lobe of that p_y AO interacts with the larger $2\sigma_1$, and the other lobe interacts with σ_2 and σ_3 , which have the opposite phase as σ_1 .

If $\phi_{E,1}^{\text{SALC}}$ interacts with $2p_y$, then $\phi_{E,2}^{\text{SALC}}$ should interact with $2p_x$. But there should be no contribution from σ_1 to $\phi_{E,2}^{\text{SALC}}$, since if there were, the constructive interaction of σ_1 with one lobe of the $2p_x$ AO would be exactly canceled out by its destructive interaction with the other lobe, for zero net overlap. Instead, σ_2 and σ_3 have different phases, and interact with the two lobes of $2p_x$. This reasoning gives us (after normalization) the same form of $\phi_{E,2}^{\text{SALC}}$ as that derived by the Gram-Schmidt procedure.

Comparing H SALCs with N AOs, we see that N $2s$ and $2p_z$ both transform as A_1 , and can interact with the A_1 SALC, and that N $2p_x$ and $2p_y$ transform together as E , and can interact with the E SALCs. The E interactions result in two pairs of doubly degenerate MOs: one bonding pair ($1e$) and one antibonding pair ($2e$), while the A_1 interactions present us with another three-orbital problem. In this case, the N $2p_z$ AO is closer in energy to H $1s$ than N $2s$ is, so we might be tempted to describe the $1a_1$ MO, with heavy N $2s$ character, as roughly nonbonding, and the $2a_1$ MO, with heavy N $2p_z$ character, as strongly bonding. However, the $2s$ and $2p$ AOs are closer in energy for N than for O, so these orbitals mix (or hybridize) strongly, lowering the energy of $1a_1$ (making it strongly bonding) while raising the energy of $2a_1$ (making it only slightly bonding, and roughly nonbonding). Thus, the intermediate-energy, approximately nonbonding $2a_1$ MO corresponds to the lone pair of the Lewis structure of NH_3 , and the $3a_1$ MO is strongly antibonding.

An MO diagram for NH_3 , including pictures of the MOs, is shown in Figure 3.6 on the following page.

3.5. MO Theory for CH_4

We now consider the bonding in CH_4 , which belongs to the T_d point group and which will provide us with our first example of a triply degenerate set of MOs. The easiest way to consider the coordinate system for CH_4 is to inscribe the tetrahedral shape of the molecule in a cube, with C at the center, the x -, y -, and z -axes perpendicular to opposite faces of the cube and passing through the center of each face, and the H atoms (and their $1s$ AOs, denoted σ_1 , σ_2 , σ_3 , and σ_4) at alternating vertices of the cube. This coordinate system is shown in

Figure 3.7 on the following page, and the character table for the T_d point group, with the characters for Γ_{SALC} , is shown in Table 3.6 on the following page.

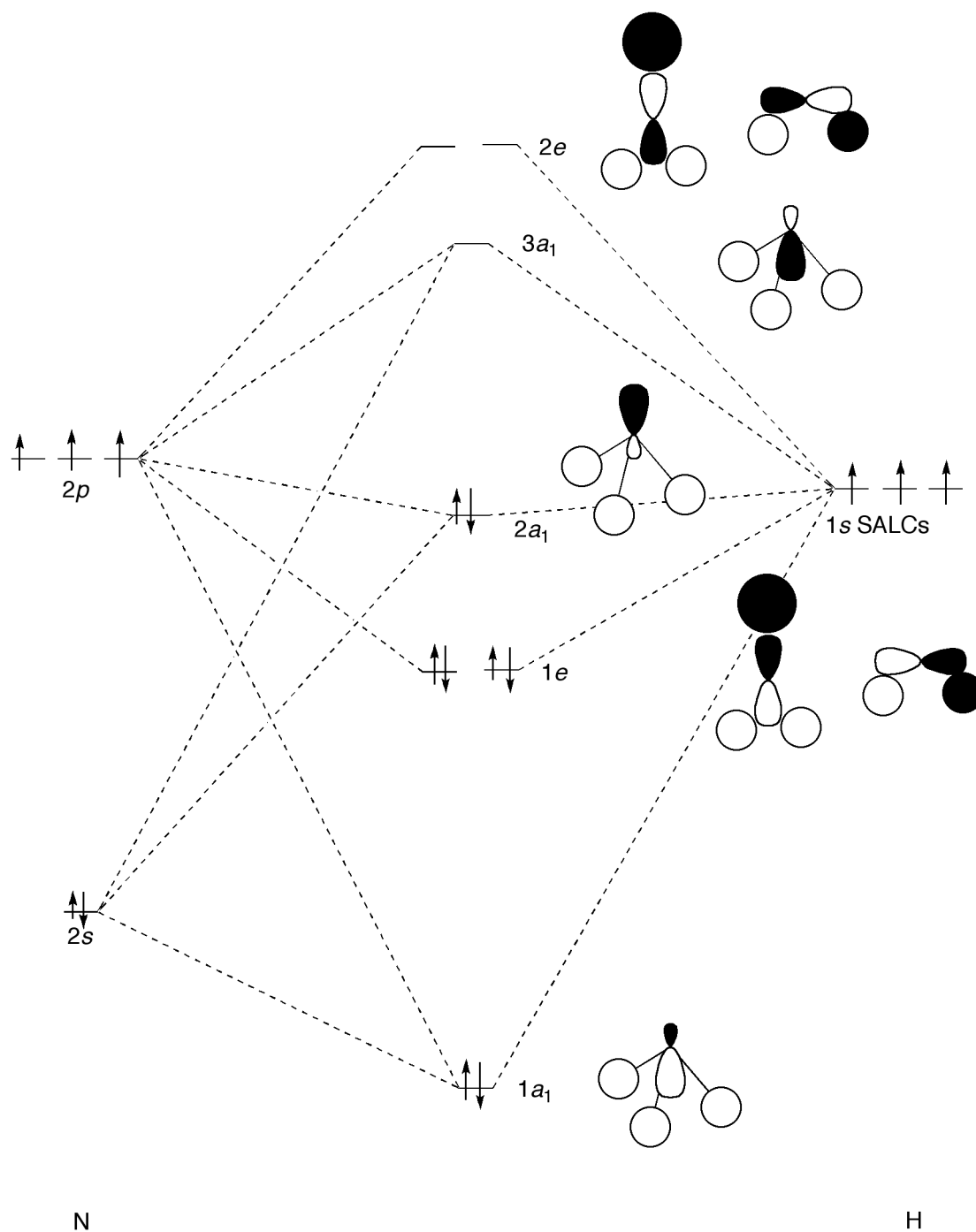


Figure 3.6. Qualitative MO diagram for NH_3 .

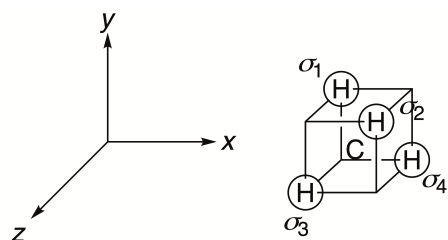


Figure 3.7. Coordinate system for the hydrogen 1s AOs in CH₄.

Table 3.6. The character table for the T_d point group.

T_d	$\hat{E}$	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
Γ_{SALC}	4	1	0	0	2		

The characters of Γ_{SALC} are determined as follows: as always, $\hat{E}$ takes each AO into itself, for a character of 4. Each C_3 axis contains the central C atom and one H atom; this H atom is unchanged by $\hat{C}_3$, while the others are interchanged with each other, for a character of 1. Both each of the $\hat{C}_2$ operations and each of the $\hat{S}_4$ operations involve interchanging all of the AOs, so the character for each of these operations is zero. Finally, each σ_d plane contains two H atoms and the central C. Thus, each $\hat{\sigma}_d$ operation leaves two of the AOs unchanged, while interchanging the other two, for a character of 2. Use of the reduction formula yields $\Gamma_{\text{SALC}} = A_1 + T_2$.

Examination of the T_d character table shows us that the carbon 2s AO transforms as A_1 , allowing it to form a bonding MO ($1a_1$) and an antibonding MO ($2a_1$) with the A_1 SALC, while $2p_x$, $2p_y$, and $2p_z$ transform together as T_2 , allowing them to form a triply degenerate set of bonding MOs ($1t_2$) and a triply degenerate set of antibonding MOs ($2t_2$) with the T_2 SALC. In a sense, the MO energy-level diagram for CH₄ is actually simpler than that of H₂O or NH₃, as there are no “three-orbital problems” leading to bonding, antibonding, and roughly nonbonding MOs. Instead, we simply have one clearly bonding and one clearly antibonding MO each of A_1 symmetry, and one clearly bonding set and one clearly antibonding set, of

three MOs each, of T_2 symmetry. If we were to carry through an approximate numerical calculation for the orbital energies, we would need to solve only two 2×2 secular determinants, one for the two energies of the MOs of A_1 symmetry, and the other for the two energies of the MOs of T_2 symmetry.

We can draw an MO energy-level diagram without knowing the shape (or algebraic form) of the MOs. However, we can determine the appearances of the H 1s SALCs as follows. First, we can recognize that the A_1 SALC must simply consist of all the 1s AOs present with the same sign and the same coefficient, since this is how they can interact most strongly with the spherically symmetrical C 2s AO. Thus, the normalized A_1 SALC is given by

$$\phi_{A_1}^{\text{SALC}} = \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

To obtain equations for the T_2 SALCs, we could use projection operators and Gram-Schmidt orthogonalization. However, we can derive the forms of these SALCs more efficiently using a pictorial argument. We reason that, since the central C atom's 2p AOs transform together as T_2 , one of the T_2 SALCs must be able to interact with C 2p_x, one with C 2p_y, and one with C 2p_z. Thus, we construct T_2 SALCs in which each of which has two 1s AOs of one phase (to interact with one lobe of the relevant C 2p AO, and two of the other phase (to interact with the other lobe of C 2p). The forms are given by the following equations, and displayed in Figure 3.8 on the following page (using the same coordinate system and labels for the H 1s AOs as Figure 3.7):

$$\phi_{T_2,x}^{\text{SALC}} = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

$$\phi_{T_2,y}^{\text{SALC}} = \frac{1}{2}(-\sigma_1 - \sigma_2 + \sigma_3 + \sigma_4)$$

$$\phi_{T_2,z}^{\text{SALC}} = \frac{1}{2}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)$$

The MO diagram for CH₄ is shown in Figure 3.9 on the following page. Note that, while the Lewis structure/valence bond picture for CH₄ shows four equivalent, localized C–H bond orbitals, the MO treatment predicts two energy levels of C–H bonding: $1a_1$ and $1t_2$.

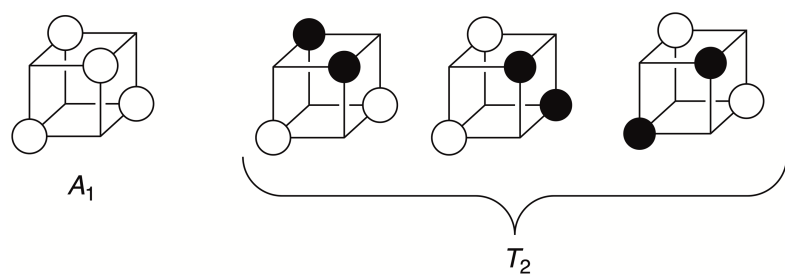


Figure 3.8. SALCs for the H 1s AOs in CH_4 .

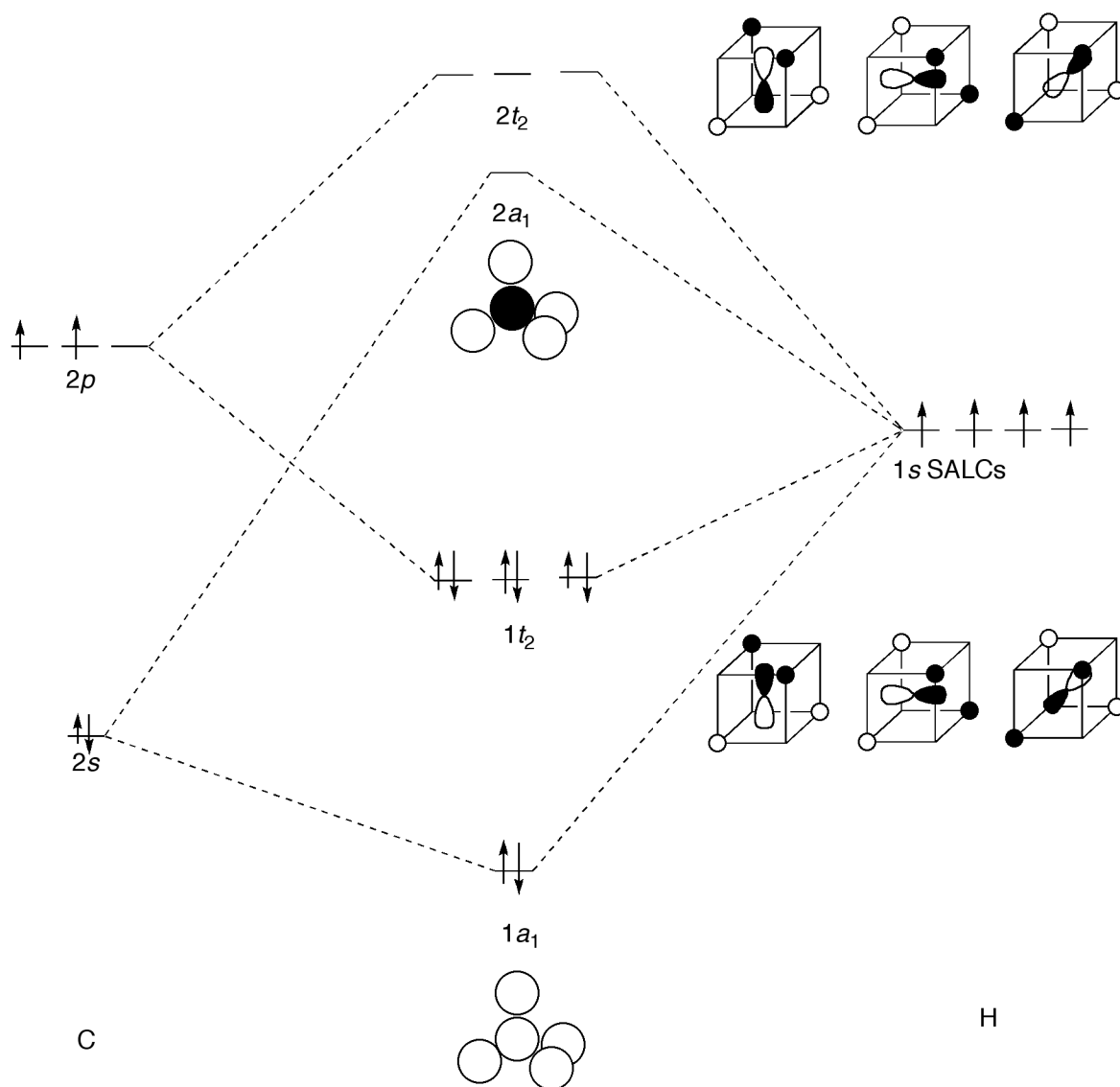


Figure 3.9. Qualitative MO diagram for CH_4 .

Photoelectron spectroscopy (PES) is a way of measuring the energies of electrons in MOs, by determining the energy required to remove an electron from each MO energy level. PES of CH₄ shows, in the energy region expected for valence MOs, two peaks, not one: the lower-energy peak, corresponding to $1t_1$ (it takes less energy to remove an electron from a higher-energy MO) has about three times the intensity of the higher-energy peak, corresponding to $1a_1$. This result is consistent with the $1t_1$ MOs constituting a triply degenerate energy level populated by three times the number of electrons as populate the nondegenerate $1a_1$ energy level.

You might wonder why the four C–H bond lengths in CH₄ are equal, if there are two types of C–H bonding MOs with different energies. The reason is that each C–H *connection* in a CH₄ molecule is due to a combination of the bonding due to the $1a_1$ MO and that due to the $1t_2$ MOs. The total electron *density*, from the $1a_1$ and $1t_2$ MOs combined, is equal along each C–H connection. Another way of looking at this is that there *are* four equivalent C–H bonds, if a “bond” is taken merely to mean a connection between C and an H atom, but there are *not* four equivalent C–H *bonding MOs*.

3.6. MO Theory for SF₆ and Main-Group Hypervalency

A delocalized MO treatment is very useful in describing the bonding in so-called “hypervalent” molecules, in which a main-group atom from the third period or lower appears to exceed the octet rule by having more than 8 valence electrons in its coordination sphere. Common examples of hypervalent molecules include PF₅ (10 valence electrons around P) and SF₆ (12 valence electrons around S). Traditionally, hypervalency has been explained by the use of *d* orbitals in bonding: according to this model, the P atom in PF₅ is taken to be dsp^3 hybridized, with its $3d_{z^2}$ AO used in addition to $3s$ and $3p$, and the S atom in SF₆ is taken to be d^2sp^3 hybridized, with its $3d_{z^2}$ and $3d_{x^2-y^2}$ AOs used in addition to $3s$ and $3p$. Treating these $3d$ AOs as valence orbitals allows the P or S atoms to accept more electron density. This model has been criticized, however, based on more recent numerical calculations, which indicate that the $3d$ AOs, while they have the right *symmetry* to participate in the bonding, are sufficiently higher in energy than the $3s$ or $3p$ AOs that their total contribution to bonding

is very low (*e.g.* their coefficients in an LCAO-MO expression would be very small in magnitude). We will now see that delocalized MO theory allows us to construct a model of bonding in SF₆ (or PF₅) *without* having to invoke participation by 3*d* AOs.

We begin by considering the regular octahedral (*O_h*) SF₆ molecule. We will make the approximation that only the 2*p* AOs of the F atoms are used in bonding; this approximation is reasonable because the 2*s* AOs of F are very low in energy, much lower than F 2*p* or S 3*s* or 3*p*. Additionally, we will consider only one 2*p* AO per F atom, pointing directly towards the central S: this approximation amounts to treating the bonding in SF₆ as σ -only, with no π interactions. With this in mind, the F 2*p* AOs can be represented as vectors pointing toward S as depicted in Figure 3.10 below, and a reducible representation Γ_{SALC} is constructed in *O_h*, whose character table is Table 3.7 below.

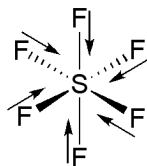


Figure 3.10. Vectors on F atoms of SF₆ with the symmetry of 2*p* AOs.

Table 3.7. The character table for the *O_h* point group.

<i>O_h</i>	$\hat{E}$	$8\hat{C}_3$	$6\hat{C}_2$	$6\hat{C}_4$	$3\hat{C}_2$ ($=\hat{C}_4^2$)	$\hat{i}$	$6\hat{S}_4$	$8\hat{S}_6$	$3\hat{\sigma}_h$	$6\hat{\sigma}_d$		
<i>A_{1g}</i>	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
<i>A_{2g}</i>	1	1	-1	-1	1	1	-1	1	1	-1		
<i>E_g</i>	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
<i>T_{1g}</i>	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
<i>T_{2g}</i>	3	0	1	-1	-1	3	-1	0	-1	1		(xy, xz, yz)
<i>A_{1u}</i>	1	1	1	1	1	-1	-1	-1	-1	-1		
<i>A_{2u}</i>	1	1	-1	-1	1	-1	1	-1	-1	1		
<i>E_u</i>	2	-1	0	0	2	-2	0	1	-2	0		
<i>T_{1u}</i>	3	0	-1	1	-1	-3	-1	0	0	1	(x, y, z)	
<i>T_{2u}</i>	3	0	1	-1	-1	-3	1	0	0	-1		
Γ_{SALC}	6	0	0	2	2	0	0	0	4	2		

This representation can be reduced to $\Gamma_{\text{SALC}} = A_{1g} + E_g + T_{1u}$. The S 3s AO has A_{1g} symmetry, so it can form bonding and antibonding MOs with the A_{1g} SALC. The S 3p AOs together have T_{1u} symmetry, and thus can form a set of bonding MOs and a set of antibonding MOs with the T_{1u} SALC. The E_g SALCs have no symmetry match among the S 3s or 3p AOs. They *do* have a match with the S $3d_{z^2}$ and $3d_{x^2-y^2}$ AOs, but since these 3d AOs are so high in energy, we will not invoke their participation in the bonding scheme. This means that the E_g SALCs must be considered (in this model) as strictly nonbonding MOs, with purely F 2p character and no admixture from any S AOs. The MO diagram for SF₆ is shown in Figure 3.11 below.

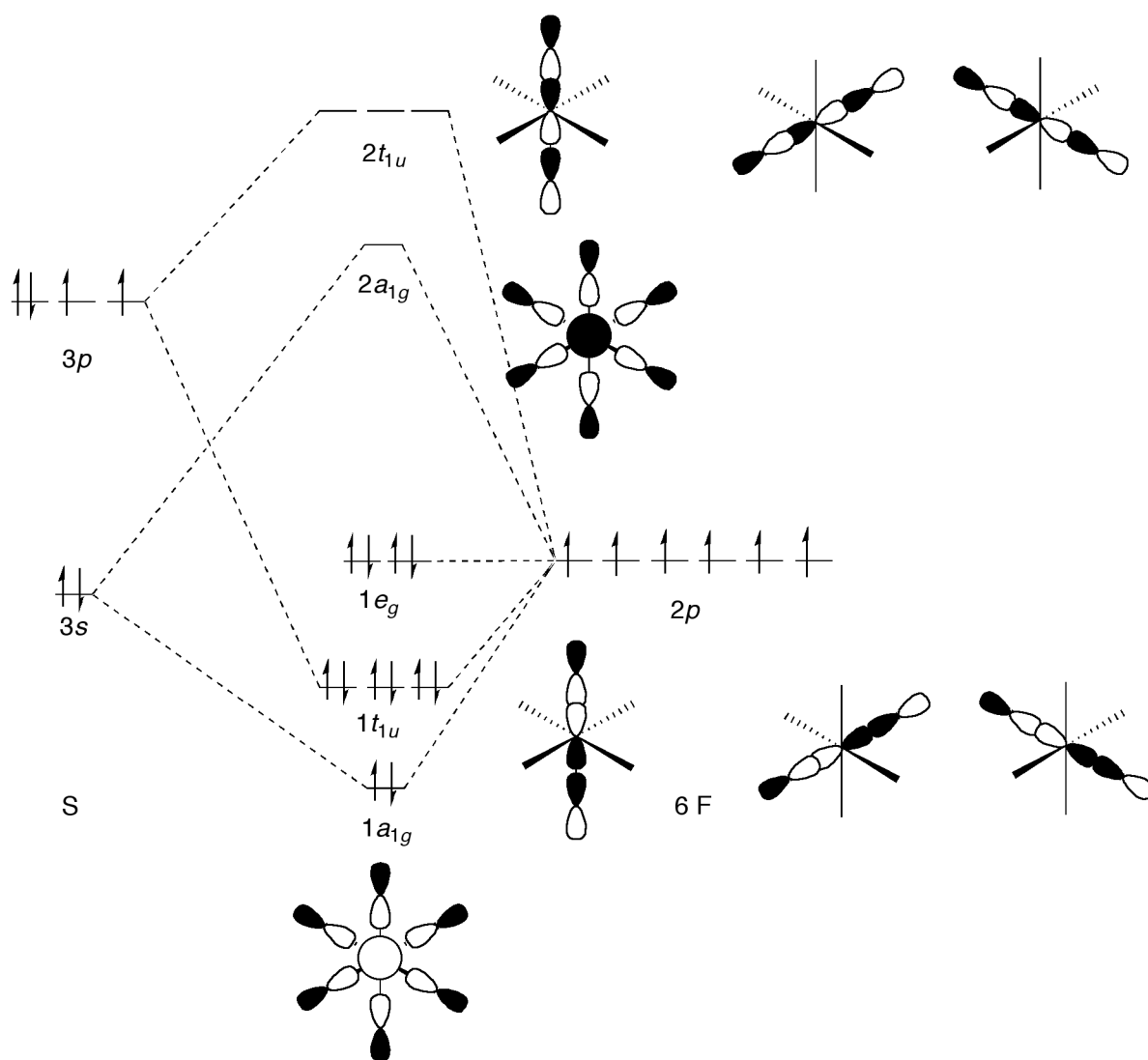


Figure 3.11. Qualitative MO diagram for SF₆.

We have not, at this point, derived the forms of the A_{1g} or T_{1u} SALCs, and Figure 3.11 does not show the forms of the E_g SALCs (which are nonbonding MOs in this example). We will more formally derive these SALCs when we discuss the bonding in O_h complexes of transition metals, in which d AOs on the central metal atom *are* significantly involved in the bonding.

Examining our MO diagram, we see that 4 electrons are in the nonbonding $1e_g$ MOs, while 8 electrons are in bonding MOs ($1a_{1g}$ and $1t_{1u}$). There are no electrons in any of the antibonding MOs. Because the $1e_g$ MOs are nonbonding, the electrons in them do not contribute to the bond order. Therefore, the *total* S–F bond order is $\frac{8}{2} = 4$, but the bond order per S–F connection is only $\frac{4}{6} = \frac{2}{3}$. By this accounting, each of the S–F σ bonds portrayed in the Lewis structure is really $\frac{2}{3}$ of a bond. Now note that the nonbonding $1e_g$ MOs are just SALCs derived from F $2p$ AOs, with no contribution from any S AOs. This means that 4 electrons are located just on the F atoms, not S. Thus, this delocalized σ MO picture of SF₆ is akin to drawing a series of resonance structures, each of which contains an SF₄²⁺ cation and two F[–] anions. This type of bonding is sometimes referred to as “electron-rich” bonding, in which “extra” electrons are present in nonbonding orbitals on the terminal atoms. One can similarly imagine, pictorially, the bonding in PF₅ by writing resonance structures which each contain a PF₄⁺ cation and an F[–] anion.²⁶

While this type of charge separation may seem as if it would lead to a very high-energy structure, bear in mind that F is the single most electronegative element in the Periodic Table, so highly polar covalent bonding, with considerable partial F[–] character, is plausible. In fact, SF₆ is an exceptionally stable molecule, being chemically inert to a wide range of

²⁶ A symmetry-based MO treatment of PF₅ (point group D_{3h}) may be analyzed similarly to that of SF₆, but two sets of F $2p$ SALCs will be constructed, one representing the two axial F atoms, and the other representing the three equatorial F atoms. This is because these two types of F atom in PF₅ are not chemically equivalent, while all six F atoms in SF₆ *are* equivalent. Symmetry operations can interconvert the F atoms in SF₆, but no symmetry operation can interconvert axial and equatorial F atoms in PF₅.

reagents and conditions. (It is completely nontoxic, though it is a notorious greenhouse gas.) Similarly, the anion PF_6^- , which is isoelectronic with SF_6 , is widely used in synthesis as a stable, unreactive counterion for large metal complex cations. On the other hand, the related compound SH_6 has never been isolated. This makes sense from the standpoint of MO theory: imagine the MO diagram of Figure 3.11 adapted to SH_6 , with H 1s AOs in place of F 2p AOs. In this hypothetical molecule, 4 electrons would still be in the nonbonding $1e_g$ MOs, but those MOs would be of H 1s character, rather than F 2p character. Because the H 1s orbital energy is considerably higher than F 2p, those 4 electrons would be in a pair of much higher-energy MOs, a much less stable situation. One can also understand this based on a resonance picture: just as one can imagine SF_6 as consisting of resonance structures involving SF_4^{2+} and 2 F^- , one could imagine the hypothetical SH_6 as consisting of resonance structures involving SH_4^{2+} and 2 H^- . Given the low electronegativity of H, such a bonding scheme with considerable hydride character would not be expected to be stable. If some SH_6 molecules were to be generated transiently, they would be expected to rapidly decompose according to $\text{SH}_6 \rightarrow \text{H}_2\text{S} + 2 \text{H}_2$.

Finally, let us consider the fact that PF_5 and SF_6 are stable molecules, while NF_5 and OF_6 are not. The old invocation of 3d AOs on P or S provided a rationale for this observed difference; after all, there is no such thing as a “2d” AO for N or O to use in bonding. But if the 3d AOs of P or S are *not* strongly involved in bonding, why do NF_5 and OF_6 not exist? One reason has to do with charge separation, since there is considerable F^- character in PF_5 and SF_6 . Since N and O are considerably more electronegative than P and S, respectively, the partial positive character acquired by N and O in NF_5 and OF_6 , respectively, would be expected to be destabilizing. Additionally, N and O atoms are simply smaller than P and S atoms, so they are sterically less able to accommodate 5 or 6 F atoms.

3.7. MO Theory for B_2H_6 and Electron-Deficient Bonding

Borane, BH_3 , is commonly mentioned in introductory chemistry textbooks as an example of an “electron-deficient” molecule, since its central B atom lacks a full octet. BH_3 is trigonal planar, with D_{3h} symmetry, and it has only 6 valence electrons (in 3 B–H bonds) around B, in

contrast to “hypervalent” molecules, whose central atoms have more than 8 valence electrons according to their Lewis structures. However, the behavior of borane is stranger still even than this. It turns out that one cannot concentrate BH_3 in a gas cylinder, since at any significant pressure, it dimerizes to form diborane, B_2H_6 , a molecule with four terminal H atoms and two H atoms that bridge both B atoms. B_2H_6 has D_{2h} symmetry, with the axes of its coordinate system defined in Figure 3.12 below:

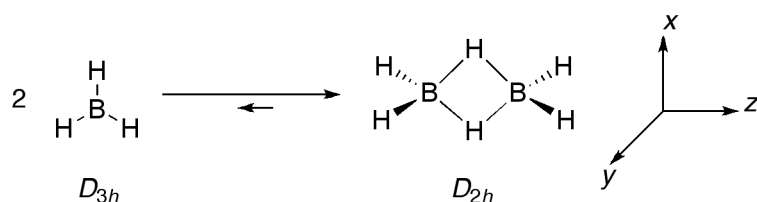


Figure 3.12. The structure of B_2H_6 with its coordinate system indicated.

The structure of B_2H_6 strikes many students of chemistry as bizarre because each of the two bridging H atoms appear to have two bonds (and four valence electrons) each, in violation of the Lewis structure “duet rule” for H, according to which an H atom can have only two electrons around it in a stable molecule. To understand how the bonding in B_2H_6 works, we can use a mixture of the localized, valence-bond picture and the delocalized MO theory. In the model that we will use for B_2H_6 , we will assume that each *terminal* B–H bond is a “normal,” two-electron bond between an H 1s AO and a B sp^3 hybrid orbital. This leaves two sp^3 hybrid orbitals on each B atom (four total, labeled h_1 through h_4 in Figure 3.13 below) to form more delocalized bonds with the bridging H 1s AOs (labeled s_1 and s_2 in Figure 3.13).

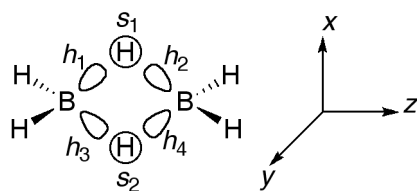


Figure 3.13. Basis orbitals for the delocalized bonding model of B_2H_6 .

There is no unique central atom in B_2H_6 , so we must form a set of four SALCs from the B sp^3 hybrids and a set of two SALCs from the H $1s$ AOs. The D_{2h} character table, with the reducible representations Γ_B and Γ_H , is shown in Table 3.8 below.

Table 3.8. The character table for the D_{2h} point group

D_{2h}	$\hat{E}$	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	$\hat{i}$	$\hat{\sigma}(xy)$	$\hat{\sigma}(xz)$	$\hat{\sigma}(yz)$		
A_g	1	1	1	1	1	1	1	1	R_z	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_y	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_x	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1		yz
A_u	1	1	1	1	-1	-1	-1	-1	z	
B_{1u}	1	1	-1	-1	-1	-1	1	1	y	
B_{2u}	1	-1	1	-1	-1	1	-1	1	x	
B_{3u}	1	-1	-1	1	-1	1	1	-1		
Γ_B	4	0	0	0	0	0	4	0		
Γ_H	2	0	0	2	0	2	2	0		

Decomposition into irreps yields $\Gamma_B = A_g + B_{2g} + B_{1u} + B_{3u}$ and $\Gamma_H = A_g + B_{3u}$. We see that the boron B_{2g} and B_{3u} SALCs must form nonbonding MOs in this model ($1b_{2g}$ and $1b_{3u}$), since they have no H SALCs of like symmetry with which to interact. The bridging H SALCs of A_g and B_{3u} symmetry form bonding ($1a_g$ and $1b_{3u}$) and antibonding ($2a_g$ and $2b_{3u}$) MOs with the B SALCs of A_g and B_{3u} symmetry. There are 12 valence electrons in B_2H_6 , but we assume that 8 of them are used in the four “localized” terminal B–H bonds, which leaves us with only four electrons to put in the system of bridging B–H–B bonds. The MO energy-level scheme for the bridging B–H–B bond system is shown in Figure 3.14 on the following page, along with sketches of the MOs.

We can see that the four electrons available for the B–H–B bond system fill two bonding MOs, $1a_g$ and $1b_{3u}$, with two electrons each, and that no electrons are present in any nonbonding or antibonding MOs. This means that there is a net bond order of two for the whole bridging B–H–B system. But since this system consists of four B–H connections, each such connection has its own bond order of $\frac{2}{4} = \frac{1}{2}$, so each bridging B–H “bond” is really only half a bond, according to the MO scheme. In a way, the Lewis structure rule that each H atom forms only

one bond is preserved, since each of these bridging H atoms forms two half-bonds, or one full bond, apiece. This type of bonding scheme is sometimes referred to as “three-center, two-electron bonding,” or “3c-2e bonding” for short. Each B–H–B bridge involves a net two electrons spread over three nuclei (“centers”). This certainly might seem like electron-deficient bonding compared to that usually observed in organic compounds (hydrocarbons and their derivatives), in which fractional σ -bond order is not at all common. But electron-deficiency is in the eye of the beholder, depending on which field of chemistry is being considered. There are now known a great many boranes (compounds of B and H), some of which consist of quite large clusters: the dianion $\text{B}_{12}\text{H}_{12}^{2-}$ is a good example (and also a good example of a chemical species with regular icosahedral, or I_h , symmetry). The description of boranes larger than B_2H_6 makes use of similar types of delocalized, multicenter σ -bonding. One might call such bonding schemes electron-deficient, but for this important class of molecules, it is the norm!

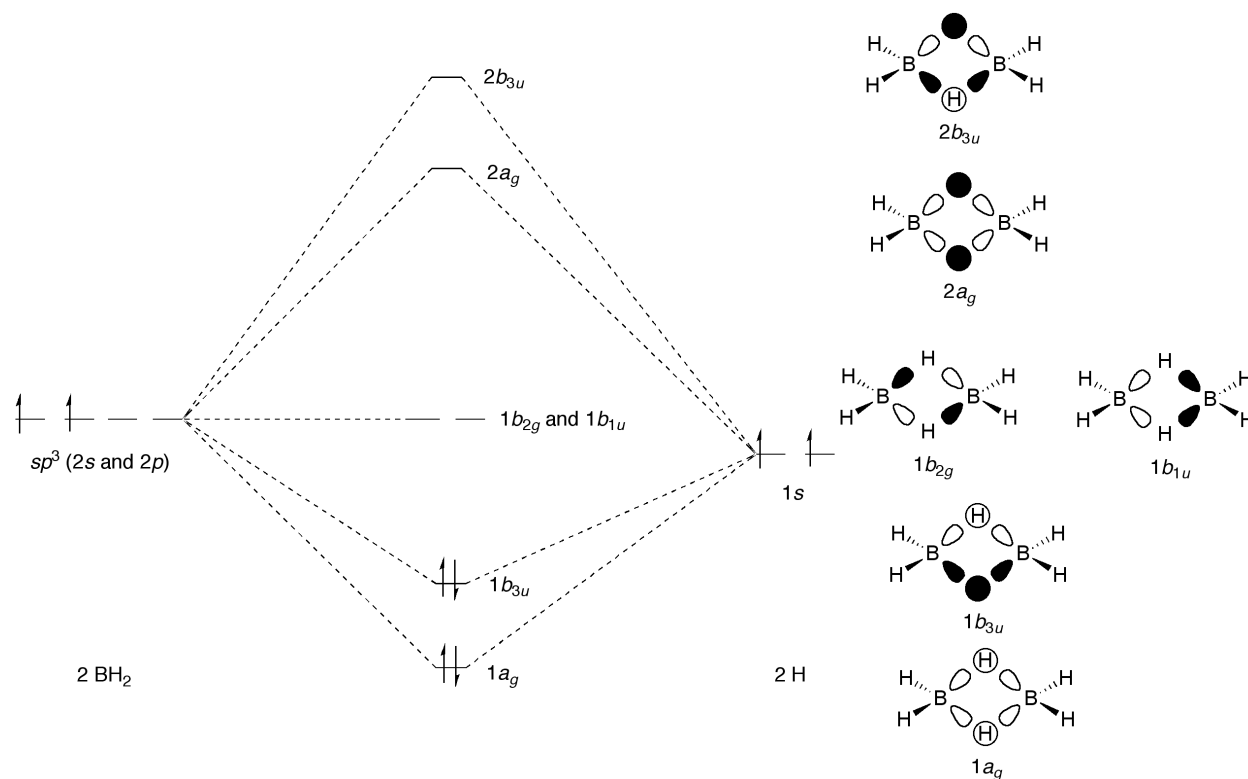


Figure 3.14. Qualitative MO diagram for the B–H–B bridging bond system of B_2H_6 .

Chapter 4: Applications of Symmetry Principles to Vibrational Spectroscopy

4.1. The Born-Oppenheimer Approximation

The full Hamiltonian operator $\hat{H}$ for a system to be analyzed by the Schrödinger equation contains a term for the kinetic energy of every particle in the system. That is, for a system of N particles, the Hamiltonian has the form

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{j=1}^N \frac{1}{m_j} \nabla_j^2 + U$$

where m_j is the mass of the j th particle and $-\frac{\hbar^2}{2m_j} \nabla_j^2$ is the operator corresponding to its kinetic energy. Since the magnitude of this operator is proportional to $\frac{1}{m_j}$, the more massive the particle, the smaller its kinetic energy. The Born-Oppenheimer approximation,²⁷ also called the simple adiabatic approximation, states that, since nuclei are so much more massive than electrons, the kinetic energy corresponding to nuclear motion can often be neglected compared to that corresponding to electronic motion. The least massive nucleus is that of a ^1H atom, which consists of only one proton and no neutrons, so its mass is the same as the mass of a proton m_p . If we compare this to the mass of an electron m_e , we find that $\frac{m_e}{m_p} \approx 5.4 \times 10^{-4}$. Thus, the Born-Oppenheimer approximation appears to be a good one even if the only nuclei are ^1H nuclei, and it should be an even better approximation for all other nuclei, since they are all heavier than that of ^1H .

Another statement of the Born-Oppenheimer approximation is that the electronic and nuclear motion of a molecule are not correlated, meaning that the total wavefunction of the molecule can be written as the simple product of the electronic wavefunction (corresponding to electronic motion) and the vibrational wavefunction (corresponding to nuclear motion). Thus, we can write $\Psi = \psi_{\text{elec}}\psi_{\text{vib}}$. Now, to consider this in more detail, suppose our system contains n electrons, each of which has coordinate vector $\mathbf{r}_i$

²⁷ Proposed by Born and J. Robert Oppenheimer (1904-1967), the latter of whom is better known as the “father of the atomic bomb” for his work on the Manhattan Project during World War II.

($i = 1, 2, 3 \dots n$), and m nuclei, of which has coordinate vector $\mathbf{q}_\alpha$ ($\alpha = 1, 2, 3 \dots m$). We now write the separation of the wavefunction as

$$\Psi(\mathbf{r}_i, \mathbf{q}_\alpha) = \psi_{\text{elec}}(\mathbf{r}_i; \mathbf{q}_\alpha) \psi_{\text{vib}}(\mathbf{q}_\alpha)$$

Note that ψ_{vib} is a function only of the nuclear coordinates $\mathbf{q}_\alpha$, while ψ_{elec} is a *function* only of the electronic coordinates $\mathbf{r}_i$, but it has the nuclear coordinates $\mathbf{q}_\alpha$ as *parameters*. (This is what the semicolon in the parentheses between $\mathbf{r}_i$ and $\mathbf{q}_\alpha$ means.)

To understand the difference between the variables $\mathbf{r}_i$ and the parameters $\mathbf{q}_\alpha$ of ψ_{elec} , consider the full expression for the purely electronic Hamiltonian, which does not consider nuclear motion, but which does include the potential energy terms for the repulsion between electrons and the attraction of nuclei for electrons:

$$\hat{H}_{\text{elec}} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_\alpha \sum_i \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{q}_\alpha|} + \frac{e^2}{4\pi\epsilon_0} \sum_j \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

When we solve (or have a computer solve) the electronic Schrödinger equation $\hat{H}_{\text{elec}}\psi_{\text{elec}} = E_{\text{elec}}\psi_{\text{elec}}$, we are solving a differential equation with respect to only the electronic coordinates $\mathbf{r}_i$, since there are no derivatives with respect to the nuclear coordinates $\mathbf{q}_\alpha$. The eigenvalue in such an equation, the electronic energy E_{elec} , is characteristic of the form of ψ_{elec} , but it is a *function* of the numerical values of the nuclear coordinates $\mathbf{q}_\alpha$. One way to think about this is that physical constants, such as Planck's constant or the mass of an electron, are parameters, not variables: if, for some reason, we decided to use different (and incorrect!) values for those constants, the form of the Schrödinger equation would be the same, but the energy eigenvalues would be numerically different.

In practice, the minimum-energy (ground-state) geometry of a molecule is determined by solving the electronic Schrödinger equation with a wide variety of values of the nuclear coordinates. The electronic energies $E_{\text{elec}}(\mathbf{q}_\alpha)$ are then plotted as a function of the nuclear coordinates. Such a plot is called an *adiabatic potential energy surface* (APES, for short), and the point on the APES at which E_{elec} has its global minimum value corresponds to the nuclear coordinates of the molecule at equilibrium.

In chemistry, the Born-Oppenheimer approximation is not always valid. While it may seem intuitively reasonable that electronic motion will be much faster than any nuclear motion, electronic and nuclear motion cannot *always* be independent, or else chemical reactions could not occur. After all, when two molecules interact in a chemical reaction, both their electronic and their nuclear coordinates will change, often considerably, in the formation of the product or products. It turns out that there can be *vibronic coupling* between two electronic states, in which a transition between electronic states is enabled by vibrational motion (a type of nuclear motion).²⁸ For vibronic coupling *not* to be important, *i.e.* for the Born-Oppenheimer approximation to hold, the energy difference between electronic states must be much larger than the energy difference $\hbar\omega$ between vibrational states in the harmonic-oscillator approximation of vibrational motion (see the next section), or

$$E_{\text{elec}}(\text{state B}) - E_{\text{elec}}(\text{state A}) \gg \hbar\omega$$

4.2. The Harmonic-Oscillator Approximation and Normal Coordinates

The standard quantum-mechanical treatment of molecular vibrations treats the stretching and compression of bonds like the stretching and compression of springs, in the manner of Hooke's law in classical mechanics. For a diatomic molecule, the potential energy of the system is proportional to the square of the difference between the bond length l and the equilibrium bond length l_0 , or

$$U = \frac{1}{2}k(l - l_0)^2 = \frac{1}{2}kx^2, x = l - l_0$$

Here k is the force constant, which corresponds (semi-classically) to the “stiffness” of the molecular “spring.” The Hamiltonian operator for molecular vibration is thus

$$\hat{H}_{\text{vib}} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

where μ , the reduced mass of the two nuclei, is defined for two nuclei A and B with masses m_A and m_B , respectively, as

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

²⁸ The word “vibronic” is a portmanteau of “vibrational” and “electronic.”

When the vibrational Schrödinger equation is solved,²⁹ it is found that the vibrational energies E_v , dependent on the vibrational quantum number v (which can be any nonnegative integer) are given by

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right)$$

where ω is the angular frequency of the vibration,³⁰ and thus the energy difference between any two successive values of v is $E_{v+1} - E_v = \hbar\omega$. The vibrational wavefunctions ψ_v are given by

$$\psi_v(x) = (2^v v!)^{-1/2} \left(\frac{a}{\pi} \right)^{1/4} H_v(a^{1/2}x) e^{-ax^2/2}$$

$$a = \frac{(k\mu)^{1/2}}{\hbar}$$

$$H_v(u) = (-1)^v e^{u^2} \frac{d^v}{du^v} e^{-u^2}$$

The functions $H_v(u)$ are known as the Hermite polynomials, after the mathematician Charles Hermite (1822-1901).

Of course, we will need to consider, at length, the vibrations of molecules that contain many more than two atoms. It turns out that one can construct a set of symmetry-adapted coordinates Q , often called the normal coordinates (or normal modes) of a molecule. Each normal coordinate may consist of a combination of bond stretching, bond compression, and the expansion and compression of bond angles. Importantly for our symmetry-based perspective, each normal coordinate has the symmetry properties of one of the irreps of the molecule's point group. When these normal coordinates are used, the potential energy for a change along each is given by

²⁹ For the derivation of this solution (using different notation for some of the quantities), see pages 308 and 309 of Section 20.3 of *Mathematical Methods for Physical and Analytical Chemistry*, by David Z. Goodson, John Wiley & Sons, Inc.: Hoboken, NJ, 2011.

³⁰ Many sources write this equation with $h\nu$ rather than $\hbar\omega$, where ν (a lower-case Greek letter nu) is the frequency (not the angular frequency) of vibration. But since $\hbar = \frac{h}{2\pi}$ and $\omega = 2\pi\nu$, we have $h\nu = \hbar\omega$, and we can avoid any potential confusion between ν and ν , which are very similar in appearance!

$$U = \frac{1}{2}kQ^2$$

and thus each normal coordinate is associated with a set of vibrational wavefunctions

$$\psi_v(Q) = (2^v v!)^{-1/2} \left(\frac{a}{\pi}\right)^{1/4} H_v(a^{1/2}Q) e^{-aQ^2/2}$$

where the value of the parameter a (which depends on force constant and mass) is different for different normal coordinates. The ground-state ($v = 0$) vibrational wavefunction $\psi_0(Q)$ always transforms as the totally symmetric irrep of the molecule's point group, and the first excited ($v = 1$) vibrational wavefunction $\psi_1(Q)$ always transforms as the same irrep as Q .

4.3. Derivation of Normal Coordinate Symmetry

We will now see how to derive reducible and irreducible representations corresponding to the normal coordinates of molecules. First, we recall that a molecule containing N atoms has $3N$ possible motions that it can undergo ($3N$ "degrees of freedom"), one for each of the three axes along which each atom can move. In a molecule, the atoms no longer move independently, but when we consider the motion of an entire molecule, every form of molecular motion must still consist of a linear combination of motions of the constituent atoms. Out of the degrees of freedom, three (the translational modes) consist of simple translation of the entire molecule, without any rotation or any changes in bond lengths or bond angles. For nonlinear molecules, there are three rotational modes, corresponding to rotations without translation (*i.e.* rotations in which the molecule's center of mass does not move) and without any changes in bond lengths or bond angles. Linear molecules, however, have only two rotational modes each, since rotation along the axis of a linear molecule does not involve the motion of any atoms. Finally, the remaining degrees of freedom are vibrational modes, consisting of bond stretching and compression, and bond angle expansion and contraction, in which the molecule's center of mass remains stationary. By subtraction, we can see that a nonlinear molecule has $3N - 6$ vibrational modes, while a linear molecule has $3N - 5$ vibrational modes. Our focus in this book will be on nonlinear molecules.

The basic methodology for a symmetry analysis of molecular motion is to assign each atom in a molecule a set of vectors representing Cartesian coordinates, and then to use the

characters of these coordinates under the operations of the point group as a reducible representation. As a simple example, let us consider H_2O , with the coordinates for each of its atoms shown in Figure 4.1 below.

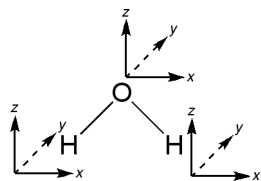


Figure 4.1. Cartesian coordinates for each atom in H_2O .

We *could* calculate the characters for the representation by writing a 9×9 transformation matrix for each symmetry operation in C_{2v} , describing how each operation transforms the vectors. Fortunately, we can save ourselves the tedium of constructing such large matrices by using the following shortcut rules, which are the same as those that we use to obtain reducible representations corresponding to sets of atomic orbitals.

- (1)** If an operation leaves a vector unchanged, that vector contributes 1 to the character under that operation.
- (2)** If an operation takes a vector into the negative of itself (such as transforming x into $-x$), that vector contributes -1 to the character under that operation.
- (3)** If an operation interchanges a vector with another vector (such as transforming x into y), that vector contributes zero to the character under that representation, since such interchanges are represented by off-diagonal elements in the transformation matrix, and so they contribute nothing to the character. *Any* time an atom moves in space, *all* of its vectors contribute zero to the character.
- (4)** Only if an operation transforms a vector into a *mixture of that vector and another vector*, as in the example of a $\hat{C}_3$ rotation in Section 2.6, do we need to write out a transformation matrix to determine the character under that operation. For many examples (including the

current example of H₂O), we do not need to do this. (We will, however, have to do this when considering the $\hat{C}_3$ rotation in a tetrahedral molecule, in the following section.)

The reducible representation Γ for the vectors of all the atoms in an H₂O molecule is shown below under the character table for C_{2v} (Table 4.1).

Table 4.1. The character table for the C_{2v} point group.

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ	9	-1	3	1		

$\hat{E}$ leaves all vectors unchanged, so $\chi = 9$. $\hat{C}_2$ moves all vectors on the H atoms, for zero contributions from each. It also takes the x and y vectors on O to their negatives, while leaving the z vector on O unchanged, so $\chi = -1$. $\hat{\sigma}_v(xz)$ takes the y vectors on each atom into the negatives of themselves, contributing -3 , but it leaves the x and z vectors on each atom unchanged, contributing 6. Combining these contributions, we have $\chi = 3$. Finally, $\hat{\sigma}_v'(yz)$ interchanges all the H atom vectors, takes the x vector on O to its negative, and leaves the y and z vectors on O unchanged, so $\chi = 1$.

If we use the decomposition formula on Γ , we find that $\Gamma = 3A_1 + A_2 + 3B_1 + 2B_2$. This, however, is the sum of irreps for *all* possible forms of motion of H₂O, not just vibrations. To identify which irreps correspond to the translational motions, we look in the second-to-rightmost column in the character table for the irreps to which the Cartesian coordinates belong. In C_{2v} , z , x , and y transform as A_1 , B_1 , and B_2 , respectively, so $\Gamma_{\text{trans}} = A_1 + B_1 + B_2$. Similarly, to find which irreps correspond to rotation, we look for the irreps to which the rotation pseudovectors belong. In C_{2v} , R_z , R_y , and R_x transform as A_2 , B_1 , and B_2 , respectively, which means that $\Gamma_{\text{rot}} = A_2 + B_1 + B_2$. Together, $\Gamma_{\text{trans}} + \Gamma_{\text{rot}} = A_1 + A_2 + 2B_1 + 2B_2$. The rest of the motions are all vibrational modes, so $\Gamma_{\text{vib}} = \Gamma - (\Gamma_{\text{trans}} + \Gamma_{\text{rot}}) = 2A_1 + B_1$.

At this point, you may wonder what these normal modes look like. We know that, for H₂O, two of the three normal modes have A_1 symmetry and the other has B_1 symmetry, but how can we depict them pictorially or write algebraic expressions for them in terms of the Cartesian coordinates for each atom? It turns out that projection operators can be applied to the individual atom vectors to derive symmetry-adapted coordinates, much like the derivation of AO SALCs described in Sections 3.3 and 3.4. However, accounting for the masses of the atoms involved makes the overall calculation considerably more lengthy, and we will not be deriving the forms of the normal modes in this text.³¹ Fortunately, we do not need to derive the normal modes in order to predict the results of vibrational spectroscopy experiments, as will be described in the next section.

4.4. Infrared and Raman Activity of Normal Modes

The vibrational modes of molecules are commonly studied using infrared (IR) and Raman spectroscopy. However, not all normal modes of every molecule are excited by each spectroscopic technique. Recall that, for a spectroscopic technique, the intensity of a transition from state ψ_i to state ψ_j is proportional to the square of the transition moment integral $M_{ji} = \langle \psi_j | \hat{M} | \psi_i \rangle$. We are primarily interested in transitions from the ground vibrational state ψ_0 to the first excited vibrational state ψ_1 , so the relevant transition moment integral is $M_{10} = \langle \psi_1 | \hat{M} | \psi_0 \rangle$. Since ψ_0 always belongs to the totally symmetric irrep, for M_{10} to be nonzero, the direct product of the irreps corresponding to ψ_1 and the operator $\hat{M}$ must be equal to or contain the totally symmetric irrep. If $\hat{M}$ corresponds to a sum of irreps (which it usually does), then ψ_1 must have the symmetry of one of those irreps.

For IR spectroscopy, the terms in $\hat{M}$ have the symmetry of the x , y , and z coordinates, so the only vibrational modes that are IR-active are those which also have the symmetry of x , y , or z . In terms of symmetry, these vibrational modes are those belonging to the same irreps as the x , y , and z coordinates. The vibrational modes of water, $2A_1 + B_1$, are all IR-active, since z transforms as A_1 and x transforms as B_1 in C_{2v} . Thus, the IR spectrum of water should show

³¹ For an explanation of this method, see Section 10.5 of *Chemical Applications of Group Theory*, 3rd edition, by F. Albert Cotton, John Wiley & Sons, Inc.: New York, 1990.

three bands, two with A_1 symmetry and one with B_1 symmetry. It turns out that all IR-active vibrational modes (for any molecule, not just water) involve a change in the dipole moment of the molecule during the vibration. Note that this requirement means that a homonuclear diatomic molecule such as N_2 or O_2 will not absorb IR radiation, as it will have an exactly zero dipole moment no matter how much the bond is stretched or compressed. In contrast, a heteronuclear diatomic molecule such as HF, which has a nonzero dipole moment due to the differing electronegativities of the atoms, will absorb IR radiation, because its dipole moment will increase upon bond stretching and decrease upon bond compression.

Raman spectroscopy is more complicated to understand. In this technique, discovered and named after Chandrasekhara Venkata Raman (1888-1970, Nobel Prize in Physics 1930), a molecule absorbs a photon of angular frequency ω_1 , which temporarily excites it into a short-lived, higher-energy state known (somewhat confusingly) as a “virtual state.” The virtual state then returns to a lower-energy state (*not* necessarily the ground state) by emission of a second photon of angular frequency ω_2 . The net process is not absorption of a photon, as in IR spectroscopy, but rather scattering of a photon. However, if the second photon has a lower energy than the first photon, the molecule will have increased in energy by an amount given by

$$\Delta E = \hbar(\omega_1 - \omega_2)$$

Note that, while IR spectroscopy requires the photons from the spectrometer to be in the IR region, in Raman spectroscopy it is common for the sample to be struck with higher-energy (and higher-frequency) photons from a laser, and then to scatter fairly high-energy photons, as long as the *difference* in the frequencies is in the IR region.

Qualitatively, a vibrational mode is Raman-active if it gives rise to a change in polarizability of the molecule. The polarizability is a measure of the dipole moment μ_{ind} that can be induced in a molecule by an external electric field $\mathbf{E}$. In an isotropic system, without unique axes (such as a free atom or monatomic ion, with spherical symmetry), the polarizability α is simply the scalar proportionality constant such that $\mu_{\text{ind}} = \alpha \mathbf{E}$. Any molecule of interest, however, is an *anisotropic* system, which is easier to polarize in some directions than in others. In such a case, the scalar polarizability α must be replaced by the polarizability tensor $\boldsymbol{\alpha}$, a 3×3 matrix

with nine scalar components, such that the shorthand equation $\boldsymbol{\mu}_{\text{ind}} = \boldsymbol{\alpha}\mathbf{E}$ corresponds to the following matrix equation:

$$\begin{bmatrix} \mu_{\text{ind},x} \\ \mu_{\text{ind},y} \\ \mu_{\text{ind},z} \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

Here, a vibrational mode is Raman-active if it induces a change in any component of $\boldsymbol{\alpha}$.

Whether or not a given vibrational mode induces a *change* in polarizability is difficult to assess from a pictorial representation of a vibrational mode, but it can be easily deduced by symmetry. For Raman spectroscopy, the terms in the operator $\hat{M}$ have the symmetry of the binary products $xy, xz, yz, x^2, y^2, z^2$, and perhaps linear combinations of these products. (These binary products correspond to the subscripts of the components of $\boldsymbol{\alpha}$.) The vibrational modes of water, $2A_1 + B_1$, are all Raman-active as well as IR-active, because x^2, y^2 , and z^2 transform as A_1 and xz transforms as B_1 . This means that the Raman spectrum of water should show three peaks, just as the IR spectrum does, and that these peaks should occur at the same energies. Note that vibrational modes that belong to the same irrep as a term such as $2z^2 - x^2 - y^2$ or $x^2 + y^2 + z^2$ are Raman active, since these terms are linear combinations of the binary products.

For water, and every triatomic molecule with C_{2v} symmetry, the IR and Raman spectra should contain the same number of peaks, at the same energies as each other. However, many molecules with different symmetries will show different numbers of signals in the two spectra, and this result can be a useful way of distinguishing between possible structures. Note that, in larger point groups, some irreps are both IR- and Raman-active, some are IR-active but not Raman-active, some are Raman-active but not IR-active, and some are neither IR-active nor Raman-active. A vibrational mode that is neither IR- nor Raman-active will not appear in either an IR or a Raman spectrum. Such modes are often known as “silent modes.”

As an example of the use of vibrational spectroscopy to distinguish between structures, we may consider the unusual xenon compound XeF_4 . (While noble gases are unreactive with other elements under most circumstances, Xe is able to form some compounds with highly

electronegative elements such as F and O.) Two plausible structures for XeF_4 , shown in Figure 4.2 below, are tetrahedral (point group T_d) and square planar (point group D_{4h}).

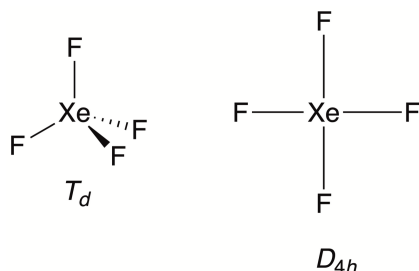


Figure 4.2. Two plausible structures for XeF_4 .

First, we consider the possibility of T_d XeF_4 . The character table for T_d , with the reducible representation of molecular motion Γ , are shown in Table 4.2 below.

Table 4.2. The character table for the T_d point group.

T_d	$\hat{E}$	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
Γ	15	0	-1	-1	3		

The characters for Γ can mostly be obtained without considering matrices, but the character under $\hat{C}_3$ is an exception, and its derivation is as follows. First, consider that that each $\hat{C}_3$ operation consists of rotation about an axis that contains Xe and one F atom (and it interchanges the other three F atoms). If we take this axis to be the z-axis for Xe and the one F atom, we first note that the other three F atoms, which are interchanged with each other, contribute nothing to the character. Next, we note that the z coordinate on both Xe and the one F atom will be unchanged upon rotation, together contributing +2 to the character. However, the x and y coordinates on both Xe and the one F are each intermixed according to a rotation matrix, as shown in the following matrix equation:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\left(\frac{2\pi}{3}\right) & -\sin\left(\frac{2\pi}{3}\right) \\ \sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ \frac{\sqrt{3}}{2}x - \frac{1}{2}y \end{bmatrix}$$

Each rotation matrix for the x and y coordinates has a character of -1 , so the two such matrices, one for X_e and one for F , together contribute -2 to the character under $\hat{C}_3$, so the net character is $\chi(\hat{C}_3) = 2 - 2 = 0$.

Reduction of Γ gives $\Gamma = A_1 + E + T_1 + 3T_2$. Since (x, y, z) transform together as T_2 , $\Gamma_{\text{trans}} = T_2$. Since (R_x, R_y, R_z) transform together as T_1 , $\Gamma_{\text{rot}} = T_1$. Subtracting Γ_{trans} and Γ_{rot} from Γ yields $\Gamma_{\text{vib}} = A_1 + E + 2T_2$. The A_1 and E modes are Raman-active, but not IR-active, while the T_2 modes are both IR- and Raman-active. Thus, if XeF_4 is T_d , we expect to see two signals in the IR spectrum, and four signals in the Raman spectrum. Note that each E term in Γ corresponds to two motions of equal energy, so while an E term contributes two motions to the total $3N - 6$ vibrational modes, it only yields one signal in the spectrum. Similarly, each T_2 term corresponds to three motions of equal energy, so two T_2 terms correspond to two sets of three degenerate motions each, for two signals in the spectrum (not six).

Now suppose that XeF_4 were D_{4h} . The character table and reducible representation of molecular motion Γ are shown in in Table 4.3 below:

Table 4.3. The character table for the D_{4h} point group.

D_{4h}	$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$2\hat{C}_2'$	$2\hat{C}_2''$	$\hat{i}$	$2\hat{S}_4$	$\hat{\sigma}_h$	$2\hat{\sigma}_v$	$2\hat{\sigma}_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	
Γ	15	1	-1	-3	-1	-3	-1	5	3	1		

Reduction of Γ to its component irreps yields $\Gamma = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$. Since (x, y) transform together as E_u and z transforms as A_{2u} , $\Gamma_{\text{trans}} = A_{2u} + E_u$. Since (R_x, R_y) transform together as E_g and R_z transforms as A_{2g} , $\Gamma_{\text{rot}} = A_{2g} + E_g$. Subtracting Γ_{trans} and Γ_{rot} from Γ yields $\Gamma_{\text{vib}} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$. The A_{1g} , B_{1g} , and B_{2g} modes are Raman-active, but not IR-active, while the A_{2u} and E_u modes are IR-active, but not Raman-active. Thus, if XeF_4 is D_{4h} , we expect to see three signals in the IR spectrum and three signals in the Raman spectrum, with the two different sets of signals having different energies (since different vibrational modes are IR-active and Raman-active). The actual vibrational spectra of XeF_4 are consistent with the D_{4h} geometry, which has also been established in the solid state *via* single-crystal X-ray diffraction.

A helpful mnemonic when solving vibrational spectroscopy problems is that, in molecules belonging to centrosymmetric point groups (that is, molecules with an inversion center i in their structure, and the inversion operator $\hat{i}$ in their group), all IR-active vibrations will be Raman-inactive, and all Raman-active vibrations will be IR-inactive. This result, which is sometimes known as the “mutual exclusion rule,” follows from the fact that the inversion operation takes (x, y, z) to $(-x, -y, -z)$. Thus, any simple Cartesian coordinate will be taken to the negative of itself and will transform as one of the *ungerade* (u) irreps, while for a binary product of Cartesian coordinates, the negative signs will cancel out and be unchanged upon inversion, *e.g.* $(-x)(-z) = xz$, so all such binary products will transform as one of the *gerade* (g) irreps.

Although I have not explicitly derived it here, the vibrational modes for a regular octahedral (O_h) metal complex ML_6 with monatomic ligands (*e.g.* CoCl_6^{3-}) are given by $\Gamma_{\text{vib}} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$. Examination of the O_h character table shows that $2T_{1u}$ are IR-active, while $A_{1g} + E_g + T_{2g}$ are Raman-active. The T_{2u} modes are silent, *i.e.* they will not show up in either the IR or the Raman spectrum. Since octahedral coordination geometry is the most common geometry for transition metal complexes, this result will prove useful to us later in our study of transition metal chemistry.

Chapter 5: Acid-Base and Oxidation-Reduction Chemistry

5.1. Organizing Principles of Reactivity

The science of chemistry involves the study of an enormous number of different substances, and an even more enormous number of reactions between them. It is critical, therefore, to be able to organize chemical reactions by broad type. Two of the most important general types of reactions are acid-base reactions and oxidation-reduction (redox) reactions. While many chemists and chemistry textbooks treat acid-base and redox reactions as fundamentally separate categories, we will see in this chapter that there are important connections between the two.

5.2. The Arrhenius Definition of Acids and Bases

The first general definition of acids and bases was proposed by Svante Arrhenius (1859-1927, Nobel Prize in Chemistry 1903). According to Arrhenius, an acid is a proton (hydrogen ion, H^+) donor, while a base is a hydroxide (OH^-) donor. The Arrhenius definition of acids encompasses a very large number of substances; any substance with a hydrogen atom which can be deprotonated (removed as H^+) qualifies. In contrast, the Arrhenius definition of bases encompasses only salts of the OH^- ion, such as NaOH and $\text{Ca}(\text{OH})_2$. This is clearly a limited definition, since other substances, such as NH_3 or salts of carbonate (CO_3^{2-}) can neutralize acidic solutions, and can thus be sensibly considered bases. Yet they do not qualify as bases by Arrhenius' definition. Thus, this definition is rarely used by practicing chemists today. We will shortly see several other definitions of acids and bases that are "nested," in the sense that each successive definition encompasses all the substances defined as acids or bases by the previous one, as well as including more substances.

5.3. The Brønsted-Lowry Definition of Acids and Bases

More widely applicable than the Arrhenius definition is the Brønsted-Lowry definition (often simply called the Brønsted definition for short), which was proposed independently by Johannes Nicolaus Brønsted (1879-1947) and Thomas Martin Lowry (1874-1936), and is still in widespread use today. A Brønsted acid is any proton donor, that is, any substance with

a hydrogen atom that can be deprotonated. Thus, for acids, the Brønsted and Arrhenius definitions are equivalent. A Brønsted base, however, is any substance that can be protonated (a proton acceptor). Every Arrhenius base (OH^- salt) is also a Brønsted base, since OH^- can be protonated to form H_2O . The Brønsted definition, however, also counts as bases substances such as NH_3 or any organic amine R_3N , since they can be protonated to form an ammonium ion (NH_4^+ or R_3NH^+ , respectively). Similarly, CO_3^{2-} can be protonated to form bicarbonate (HCO_3^-) and again to form carbonic acid (H_2CO_3), which decomposes to CO_2 and H_2O . The Brønsted definition shows how bases without OH^- in their formulae can nevertheless neutralize acidic solutions.

A Brønsted acid-base reaction does not require the presence of any solvent at all; for instance, in the reaction $\text{HCl} (g) + \text{NH}_3 (g) \rightarrow \text{NH}_4\text{Cl} (s)$, HCl is a Brønsted acid and NH_3 is a Brønsted base, even though this reaction consists of two gases reacting to form a solid. A great many chemical reactions do, however, occur in liquid solvents, and many popular solvents are capable of acting as both acids and bases by the Brønsted definition. Such solvents are known as amphoteric, from the Greek ἀμφότεροι, “both.” The most common solvent of all, water, is amphoteric: when it acts as an acid, it is deprotonated to form its conjugate base, OH^- , and when it acts as a base, it is protonated to form its conjugate acid, the hydronium ion (H_3O^+). NH_3 is another fairly common amphoteric solvent: while it is not as convenient to work with as water, since it requires cooling to be a liquid at standard pressure (b.p. -33.3°C), it is useful for a wide range of reactions, and has the conjugate acid NH_4 and the conjugate base amide (NH_2^-). Alcohols ROH and primary or secondary amines RNH_2 or R_2NH can also be amphoteric solvents for acid-base chemistry.

The strength of an acid HA in water is measured by the value of K_a , the equilibrium constant for the reaction of the acid with water, $\text{HA} (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{A}^- (aq)$. Its formula, in terms of thermodynamic activities, is

$$K_a = \frac{a_{\text{H}_3\text{O}^+} a_{\text{A}^-}}{a_{\text{HA}} a_{\text{H}_2\text{O}}}$$

where a_x is the activity of species X. The activity of a pure liquid is exactly 1, and for a dilute aqueous solution, the activity of water as solvent will vary little from this value, so $a_{\text{H}_2\text{O}} \approx 1$. For a solute X, the activity is given by

$$a_x = \gamma_x \frac{[X]}{c^\circ}$$

where $[X]$ is the concentration of X, c° is the standard-state concentration (usually 1 M, but sometimes 1 mol·kg⁻¹), and γ_x is the activity coefficient of X, which is close to 1 for dilute solutions. Approximating the activity coefficients as equal to 1, we have

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

where each concentration is implicitly divided by $c^\circ = 1$ M, so that K_a (like any equilibrium constant) is unitless.

Similarly, the strength of a base B in water is measured by the value K_b , the equilibrium constant for the reaction of the base with water, $\text{B} (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{BH}^+ (aq) + \text{OH}^- (aq)$. It is given by

$$K_b = \frac{a_{\text{BH}^+} a_{\text{OH}^-}}{a_{\text{B}} a_{\text{H}_2\text{O}}}$$

or, using the same simplifying approximations that we used with K_a ,

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Stronger acids have larger values of K_a , and stronger bases have larger values of K_b . It should be kept in mind that, while the “generic” acid in the above equations is written as neutral HA, and the “generic” base as B, an acid or base can be either neutral, positively charged, or negatively charged.

Since water is amphoteric, a reaction can occur between two water molecules in which one deprotonates the other: $2 \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq)$. The equilibrium constant for this reaction, called the autoionization constant of water and represented by K_w , is given by

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Near the standard textbook “room temperature” of 25 °C, K_w is equal to approximately 10^{-14} .

There is a reciprocal relationship between the strength of an acid and the strength of its conjugate base. Using the standard rules for manipulating equilibrium constants for sums of reactions, one can show that

$$K_a(\text{HA})K_b(\text{A}^-) = K_w = 10^{-14} \text{ (at } 25^\circ\text{C)}$$

or

$$\text{p}K_a(\text{HA}) + \text{p}K_b(\text{A}^-) = \text{p}K_w = 14 \text{ (at } 25^\circ\text{C)}$$

Equilibrium constants analogous to K_a and K_b can be defined for amphoteric solvents other than water, as can autoionization constants for such solvents. An important principle called the leveling effect can be used to determine the utility of different solvents for different acid-base reactions. The leveling effect states that (1) the strongest acid that can exist in a solvent in appreciable amounts is the conjugate acid of that solvent, and (2) the strongest base that can exist in a solvent in appreciable amounts is the conjugate base of that solvent. This means that any acid stronger than H_3O^+ will, upon addition to water, react essentially completely to form its conjugate base and H_3O^+ , and any base stronger than OH^- will, upon addition to water, react essentially completely to form its conjugate acid and OH^- . For instance, in solvents less basic than water, trifluoromethanesulfonic acid or triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) is an even stronger Brønsted acid than nitric acid (HNO_3). However, both of these acids are stronger than H_3O^+ , so a 1 M solution of $\text{CF}_3\text{SO}_3\text{H}$ in water and a 1 M solution of HNO_3 in water will each have a pH of 0, since each will react essentially completely to form 1 M H_3O^+ . Thus, while these two acids are not equally strong in all solvents, the fact that they are each stronger than H_3O^+ means that they are “leveled” to the same apparent strength in water. Similarly, NH_2^- is a stronger base than OH^- , so a 1 M solution of NaNH_2 in water will have a pH of 14, as the NH_2^- will react essentially completely with the water to form a solution of 1 M OH^- (giving pH = 14) and 1 M NH_3 . However, a base that is stronger than OH^- , but weaker than NH_2^- , *could* exist in significant concentrations in a liquid ammonia solution.

5.4. The Lewis Definition of Acids and Bases

The next level of our “nested” acid-base definitions is the Lewis definition, proposed by Gilbert Newton Lewis (1875-1946), who also devised the system of electron-dot structures

that now bears his name. This definition and the Brønsted-Lowry definition are the acid-base definitions used most often by practicing chemists today. According to the Lewis definition, an acid is an electron-pair acceptor: a species that accepts a pair of electrons from another species to form a new covalent bond. Conversely, a base, according to the Lewis definition, is an electron-pair donor: a species that donates a pair of electrons to another species to form a new covalent bond. The most obvious examples of Lewis acids and bases are those that react with each other to form an adduct, with no displacement of any group. A classic example of Lewis acid-base adduct formation is the reaction of BF_3 , a Lewis acid with an empty $2p_z$ AO on boron,³² with NH_3 , a Lewis base with a nonbonding lone pair on nitrogen.³³ A new B–N σ bond is formed to yield the adduct $\text{F}_3\text{B}-\text{NH}_3$, as shown in Figure 5.1.

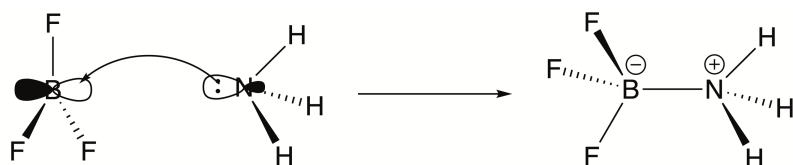


Figure 5.1. Lewis acid-base adduct formation between BF_3 and NH_3 .

Lewis acid-base reactions often involve displacement of chemical groups, not just simple adduct formation. For instance, consider the protonation of water by nitric acid. This reaction, $\text{HNO}_3 (aq) + \text{H}_2\text{O} (l) \rightarrow \text{H}_3\text{O}^+ (aq) + \text{NO}_3^- (aq)$, can be viewed as a competition between two Lewis bases, NO_3^- and H_2O , for the Lewis acid H^+ . The protonated species HNO_3 and H_3O^+ can each be thought of as a Lewis acid-base adduct, between H^+ and either NO_3^- or H_2O , respectively. But since these adducts can transfer the Lewis acid H^+ , it makes sense to consider them Lewis acids themselves. Thus, we see that all Brønsted acids are also Lewis acids, and all Brønsted bases are also Lewis bases, since they have a tendency to react with (by donating an electron pair to form a covalent bond to) the Lewis acid H^+ .

³² Strictly speaking, this empty orbital is really an MO with weak B–F π antibonding character, but treating it as a pure B $2p_z$ MO is a fair approximation.

³³ Strictly speaking, this filled orbital is a slightly bonding, but approximately nonbonding, MO, as shown in Section 3.4.

Students of organic chemistry will be familiar with another type of displacement reaction, which is also a type of Lewis acid-base reaction, namely, the nucleophilic substitution of an alkyl halide or pseudohalide. For instance, suppose an alkyl iodide reacts with Cl^- to form an alkyl chloride and I^- , according to the reaction $\text{R-I} + \text{Cl}^- \rightarrow \text{R-Cl} + \text{I}^-$. Such a reaction amounts to a competition between the Lewis bases I^- and Cl^- for the Lewis acid R^+ . In an $\text{S}_{\text{N}}1$ reaction, whose mechanism consists of two steps with the alkyl cation R^+ as an actual intermediate, the Lewis acid-base nature of the reaction is perhaps more obvious. However, in an $\text{S}_{\text{N}}2$ reaction, in which R-I and Cl^- react in a single elementary step, with no intermediates and only one transition state, both R-I and R-Cl can still be considered Lewis acids, since they are sources of the R^+ moiety. This is very much akin to viewing Brønsted acids as a subset of Lewis acids, since they are sources of the Lewis-acidic unit H^+ , even though a free proton is very unlikely to be an intermediate in any reaction. A proton-transfer reaction can, in fact, be thought of as an $\text{S}_{\text{N}}2$ reaction on hydrogen as opposed to carbon.

The terms “electrophile” and “nucleophile” are often used by organic chemists, and they are essentially equivalent to the terms “Lewis acid” and “Lewis base,” respectively.³⁴ A Lewis acid is an electrophile (“electron-lover”) because it readily accepts a pair of electrons to form a bond, while a Lewis base is a nucleophile (“nucleus-lover”) because it generously donates an electron pair to another nucleus to form a bond.

A very important subset of Lewis acid-base reactions consists of those in which the Lewis acid is a metal atom or metal ion. In such reactions, the Lewis base is called a ligand (from Latin *ligare*, “to bind”) and the resulting Lewis acid-base adduct is known as a coordination complex, or simply a complex. The reactions of metals with ligands comprises the field of coordination chemistry, which will be the focus of most of the second half of this text.

³⁴ Some chemists talk about the strength of a “Lewis acid” or “Lewis base” in the context of the thermodynamics of a reaction, while using the terms “electrophilicity” or “nucleophilicity” to refer to a species’ reactivity in terms of kinetics. By this convention, a more nucleophilic species would react with electrophiles more quickly (with a greater rate constant), but the reaction would not necessarily have a larger equilibrium constant. Conversely, a strong Lewis base might react with a strong Lewis acid essentially completely once equilibrium is reached, but the reaction could still be slow.

5.5. The Usanovich Definition of Acids and Bases

Many textbooks simply define a Lewis acid as an electron-pair acceptor, and a Lewis base as an electron-pair donor. I have used somewhat more cumbersome language, emphasizing that the electron pairs being accepted and donated must form covalent bonds, in order to exclude types of reactivity that most chemists would *not* consider Lewis acid-base reactions. For instance, consider the reaction $\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$, which occurs in an early type of battery known as the Daniell cell, devised by John Fredric Daniell (1790-1845). While two electrons are transferred from Zn to Cu^{2+} , we do not consider this to be a Lewis acid-base reaction, since no Cu–Zn covalent bond is formed: instead, we classify this as a two-electron redox reaction, and we classify Cu^{2+} as an oxidizing agent, rather than a Lewis acid, and Zn as a reducing agent, rather than a Lewis base.

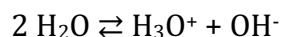
While we may consider redox reactions as separate from Lewis acid-base reactions, it is useful to consider the possibility of a connection between them. After all, many highly charged metal ions are both strong Lewis acids and strong oxidizing agents, and many species with lone pairs are both good Lewis bases (often ligands in coordination complexes) and easily oxidized. For instance, trimethylphosphine (PMe_3) is a common ligand (Lewis base) in transition metal chemistry, but it is also a reducing agent that is readily oxidized by O_2 : in fact, PMe_3 must be handled under a nitrogen or argon atmosphere, since it is pyrophoric (spontaneously flammable in air). The connection between redox and Lewis acid-base chemistry was noted by Mikhail Usanovich (1894-1981), who proposed the most general³⁵ definition of acids and bases that is currently used. By Usanovich's definition, an

³⁵ The generality of the Usanovich acid-base definition has led to its criticism by some educators. For example, on page 170 of *Inorganic Chemistry*, 5th edition, by Gary L. Miessler, Paul J. Fischer, and Donald A. Tarr (Pearson: New York, 2014), the Usanovich definition is described as “all-inclusive” and “too broad.” It is worth noting, however, that while this definition encompasses a great many chemical reactions, it does not encompass all of them. For example, consider an organic cycloaddition reaction such as the Diels-Alder reaction between 1,3-butadiene and ethene: in this reaction, the diene and the dienophile are both transferring electrons *to each other* by forming new C–C bonds, but neither reactant is overall either an electron donor or electron acceptor. Similarly, the formation of an alloy between two metals of very similar electronegativities is a chemical reaction, but does not involve a transfer of electrons in any meaningful sense.

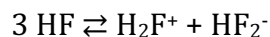
acid is any species that can accept one or more electrons, and a base is any species that can donate one or more electrons. If the electrons are accepted and donated in pairs to form bonds, then we have Lewis acid-base behavior as one type of Usanovich acid-base behavior. Additionally, however, the Usanovich definition encompasses redox reactions as a subset of acid-base reactions, with oxidizing agents being a type of acid and reducing agents being a type of base.

5.6. The Solvent-System Definition of Acids and Bases

A final acid-base definition that is useful to understand is the solvent-system definition. This definition is conceptually somewhat separate, as it does not fall into the “nested” scheme that the Arrhenius, Brønsted-Lowry, Lewis, and Usanovich definitions do. The solvent-system definition only applies to reactions that take place in solvents which are capable of autoionization, that is, the reaction of solvent molecules with each other to form a cation and an anion. All amphoteric solvents are capable of ionization: we have already seen that water and liquid ammonia autoionize as follows:



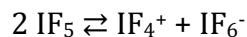
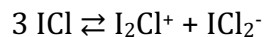
Autoionization reactions do not always involve two solvent molecules on the side of the reactants. For instance, liquid hydrogen fluoride autoionizes according as follows:



The autoionization does not have to proceed to a great extent in order to be an important part of the solvent’s behavior. For example, for water, $K_w = 10^{-14}$ at 25 °C, but water is still the most common textbook example of an autoionizing solvent.

The autoionization reactions shown above are also Brønsted-Lowry acid-base reactions, since they involve the transfer of protons. However, autoionizing solvents need not be protic, and in fact, they need not have any hydrogen atoms in their formulae at all. They simply need to be able to react with themselves to form ions. Examples include N_2O_4 , SbCl_3 , BrF_3 , ICl , IBr , I_2Cl_6 , and IF_5 , whose autoionization reactions are as follows:





According to the solvent-system definition, any reagent that increases the concentration of the cation formed during solvent autoionization is an acid, and any reagent that increases the concentration of the solvent anion is a base. Clearly, this includes salts of the solvent cations and anions themselves, so the salts NOBF_4 (containing NO^+ and BF_4^-) and KNO_3 are an acid and a base, respectively, when dissolved in liquid N_2O_4 . However, a reagent can still be an acid or base by the solvent-system definition if it reacts with the solvent to form the relevant product of solvent autoionization. For instance, KCl (or any other Cl^- salt) would be a base in liquid SbCl_3 , because it would react to increase the concentration of the solvent anion SbCl_4^- according to $\text{SbCl}_3 + \text{Cl}^- \rightleftharpoons \text{SbCl}_4^-$. Similarly, SbF_5 would be an acid in liquid BrF_5 , because it would react to increase the concentration of the solvent cation BrF_4^+ according to $\text{BrF}_5 + \text{SbF}_5 \rightleftharpoons \text{BrF}_2^+ + \text{SbF}_6^-$.

5.7. Trends in Brønsted Acid and Base Strength

Having considered some acid-base definitions, we may now examine trends in the strengths of acids and bases. We consider Brønsted acids first, since the trends in their strengths are usually simplest to understand. This is because steric factors are generally unimportant to Brønsted acidity and basicity, since the group being transferred, H^+ , is so small. An important factor is the electronegativity of the atom being protonated or deprotonated. When considering the neutral binary hydrides of the main-group elements, acidity generally increases across a row of the Periodic Table, just as electronegativity does. For instance, CH_4 has no significant acid-base properties, NH_3 is slightly acidic in some solvents (though not in water), H_2O is more acidic still, and HF is significantly acidic. The stronger the acid, the weaker its conjugate base, so CH_3^- (or any compound with a carbanion-like group, such as

the main-group organometallics CH_3Li or CH_3MgCl) is a very strong base, NH_2^- is less strong but still a stronger base than OH^- , and F^- is only a weak base.

The above electronegativity argument does not hold when comparing hydrides going down a row of the Periodic Table. For instance, with the chalcogen (oxygen group) hydrides, acidity increases as $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$, even though electronegativity decreases as $\text{O} > \text{S} > \text{Se}$. The reason for this trend is that S and Se are larger atoms than O (the average radii of their valence electrons are greater), and thus, when the hydrides are deprotonated, the resulting negative charge occupies a larger volume, decreasing Coulombic repulsion. HF is the strongest hydrohalic acid, and HI the weakest, for this same reason. (Note, however, that in water, HCl, HBr, and HI are approximately equally strong due to the leveling effect.)

Similar arguments can be made to rationalize the relative basicities of main-group hydrides. NH_3 is more basic than H_2O , which is more basic than HF, since the “lone pair” (really, a roughly nonbonding MO) that is ready to form a new bond with H^+ is on a less electronegative element, so it is higher in energy. Going down a column, however, basicity tends to decrease, even though the lone pair is higher in energy, since the electrons in it experience less Coulombic repulsion due to the atom’s larger size. For instance, PH_3 is significantly less basic than NH_3 , even though a P $3p$ AO is higher in energy (-9.65 eV) than an N $2p$ AO (-13.18 eV).

The acidity or basicity of a molecule at a given atom (that is, how readily that atom will donate or accept H^+) is often affected by the identity of atoms near it. Even if the identity of the acidic or basic atom does not change, the presence of more electronegative atoms nearby will usually lead to greater acidity or lower basicity. This phenomenon is known as the inductive effect, and is familiar to most students of organic chemistry. A classic example is the increase in acidity (K_a) of acetic acid derivatives in which one or more of the methyl H atoms is replaced with F: $\text{CH}_3\text{COOH} < \text{CH}_2\text{FCOOH} < \text{CHF}_2\text{COOH} < \text{CF}_3\text{COOH}$. The more strongly electronegative F atoms present, the more electron density is pulled away from the carboxyl group, making its H atom more like H^+ and thus more acidic.

A type of inductive effect especially important to inorganic chemists is the acidity of oxyacids,³⁶ an important class of Brønsted acids whose formulae are of the form $(\text{HO})_m\text{AO}_n$, where A is the identity of the central atom, m is the number of hydroxyl groups attached to A, and n is the number of terminal oxo groups, *i.e.* oxygen atoms attached to A and no other atom. For example, the familiar acid sulfuric acid (H_2SO_4) has, in oxyacid notation, the formula $(\text{HO})_2\text{SO}_2$, so $m = 2$ and $n = 2$ for this compound. Conventionally, terminal oxo groups are drawn in Lewis structures with double bonds between O and the central atom A, as in the left structure for H_2SO_4 in Figure 5.2 below. However, these double bonds often imply that the main-group central atom uses d AOs in bonding, which is not correct according to more recent calculations (see Section 3.6). One can avoid such “hypervalent” resonance structures by invoking nonzero formal charges, as in the right structure in Figure 5.2, which is more correct but less tidy. You should feel free to draw oxyacids the old-fashioned way, as long as you keep in mind that the apparent π bonds likely have very little π bond character.

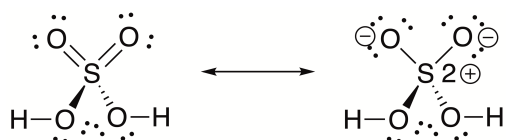


Figure 5.2. Traditional (hypervalent) and formal charge-separated depictions of H_2SO_4 .

The hydroxyl groups of oxyacids tend to be acidic due to the inductive electron-withdrawing effects of the strongly electronegative terminal O atoms. For a given central atom A, the more terminal O atoms there are, the stronger the acid is. (Another way of saying this is that the higher the oxidation state of A is, the stronger the acid is.) For instance, the acidity of the oxyacids of chlorine increase as $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$, and nitric acid (HONO_2) is a strong acid, while nitrous acid (HONO) is weak. A very approximate rule for estimating the acidity of oxyacids from their formulae was formulated by Pauling:

$$\text{p}K_{\text{a}} \approx 8 - 5n$$

³⁶ Also known as oxoacids (the two terms are synonymous).

Note that this approximate equation does not take into account the number of hydroxyl groups (it predicts pK_a for the first ionization only), nor the identity of A. However, while the number of terminal O atoms is the most important factor in determining acidity, for a given n a more electronegative central atom A will lead to a more acidic compound, as A will bear part of the negative charge after deprotonation. This means, for instance, that HOClO_2 is more acidic than HOBrO_2 , since Cl is more electronegative than Br.

Inductive effects are important in Brønsted basicity as well, but not always as directly as one might suppose. It is well known to organic chemists that alkyl groups tend to be σ -donating compared to H atoms, so it is not surprising that NH_2Me is more basic than NH_3 , since its N atom is more electron rich. What may be surprising, however, is that the order of basicity of NH_3 and the methylamines in water is $\text{NH}_3 < \text{NMe}_3 < \text{NH}_2\text{Me} < \text{NHMe}_2$. NMe_3 seems out of order, being less basic than expected given its three electron-donating methyl groups. This is because its conjugate acid NHMe_3^+ is poorly solvated, since it has only one N-bound H atom available to participate in hydrogen bonding with water. In the gas phase, the order of basicity is $\text{NH}_3 < \text{NH}_2\text{Me} < \text{NHMe}_2 < \text{NMe}_3$, which is what one would expect based solely on inductive effects when solvation is not an issue.

5.8. An MO Picture of Lewis Acid-Base Reactivity; Steric and Electronic Effects

Understanding trends in Lewis acid-base reactivity is more complicated than understanding Brønsted acid-base reactivity, since now both the acid and the base can vary. MO theory can be used to discuss electronic factors that influence Lewis acid-base strength. Recall that a Lewis acid accepts a pair of electrons to form a covalent bond, while a Lewis base donates a pair of electrons to form a covalent bond. This definition suggests that we must consider the MOs of both the Lewis acid and the Lewis base. We need not, however, go through the trouble of considering all the different MOs for each species. Instead, we can gain a good qualitative understanding of the bonding by considering only the *frontier* MOs of each species. The frontier MO concept, devised by Kenichi Fukui (1918-1998, Nobel Prize in Chemistry 1981) states that the most important MO for the reactivity of an electron-donating species is the highest-energy occupied MO (HOMO), while the most important MO for the reactivity of an

electron-accepting species is the lowest-energy unoccupied MO (LUMO). Thus, when considering Lewis acid-base reactions, we consider the HOMO of the Lewis base and the LUMO of the Lewis acid; it is primarily these two orbitals which will interact to form a new σ -bonding MO in the Lewis acid-base adduct that is the product of the reaction.³⁷

Let us consider the reaction between the common Lewis acid BF_3 and the common Lewis base NH_3 (see Figure 5.1). The HOMO of NH_3 has primarily N $2p_z$ character (approximate energy -13.18 eV), while the LUMO of BF_3 has primarily B $2p$ character (approximate energy -8.30 eV). This relatively high-energy filled orbital and relatively low-energy empty orbital can interact to form a new σ -bonding and a new σ -antibonding MO, as shown in the simple orbital interaction diagram in Figure 5.3. Since we have two electrons to distribute between these two new MOs, the bonding MO is filled and the antibonding MO is empty, and we thus have formed a new σ bond.

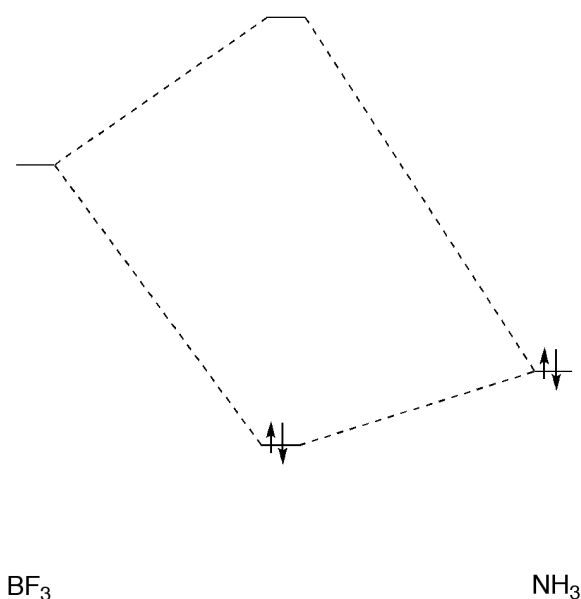


Figure 5.3. A simple HOMO/LUMO interaction diagram for Lewis acid-base adduct formation.

³⁷ When discussing species with unpaired electrons, such as organic radicals and many transition metal ions, we must also consider orbitals containing a single, unpaired electron; such orbitals are known as singly-occupied MOs (SOMOs).

Several factors are involved in the relative strengths of Lewis acids and bases. First and foremost, the Lewis base HOMO and the Lewis acid LUMO must have matching symmetry, so that their interaction in a σ fashion leads to nonzero overlap.³⁸ Steric effects are also, in general, important in Lewis acid-base chemistry, unlike in Brønsted acid-base chemistry, where one of the reacting partners is always the very small H^+ . For instance, one measure of the strength of a Lewis bases is its standard enthalpy of reaction ΔH° with the common Lewis acid BF_3 : the more negative the value of ΔH° (*i.e.* the more exothermic the Lewis acid-base reaction), the stronger the Lewis base. For instance, we might well expect methylamines to be stronger bases than NH_3 , since methyl groups are more electron-donating than H. Yet the order of Lewis base strength with respect to BF_3 is $NH_3 < NMe_3 < NH_2Me < NHMe_2$. The reason NMe_3 is “out of order” is that there are steric clashes in its approach to BF_3 to form a new σ bond: it cannot approach as closely, and thus the orbital overlap (and bond strength) is not as great as it would be with an inductively similar, but smaller, Lewis base.

Inductive effects are, however, still important, as can be seen by the fact that NH_2Me and $NHMe_2$ are stronger Lewis bases with respect to BF_3 than NH_3 is, despite their greater bulk. Similarly, NF_3 is a very weak Lewis base indeed, because of the inductively electron-withdrawing effect of the F atoms, which are more electronegative than N. Inductive effects matter for the Lewis acid, as well: BF_3 , with its electronegative F, is a stronger Lewis acid toward amine bases (more negative ΔH° for adduct formation) than BMe_3 is, since the F atoms make the B atom more electron-deficient. In this case, inductive and steric effects act in the same direction, since F is both smaller *and* more electron-withdrawing than methyl.

In some cases, a Lewis base will be very electron-rich, and a Lewis acid very electron-deficient, but each will be so sterically hindered that the adduct formation reaction cannot proceed to any significant extent. A good example of such a pair is the Lewis acid $B(C_6F_5)_3$

³⁸ “Matching symmetry” here means that the frontier MOs belong to the same irrep in the point group corresponding to the new molecule (the Lewis acid-base adduct). The HOMO of NH_3 and the LUMO of BF_3 belong to different irreps in the free molecules, since the molecules belong to different point groups (NH_3 is C_{3v} , and BF_3 is D_{3h}). However, both the staggered and the eclipsed conformations of the adduct F_3B-NH_3 belong to the point group C_{3v} , and in this point group, both frontier orbitals have A_1 symmetry.

and the Lewis base $\text{P}(\text{tBu})_3$. Such Lewis acid-base pairs have been termed “frustrated Lewis pairs,” or FLPs for short, since their electronic (inductive) inclination to form an adduct is “frustrated” by their steric bulk. FLPs will often react together with a small molecule, which behaves as a Lewis acid to the frustrated Lewis base, and as a Lewis base to the frustrated Lewis acid. Examples of this sort of reactivity include the heterolytic cleavage of the H–H σ bond in H_2 , addition across the C–C π -bond in 1-hexene, and addition across one of the C–O π bonds in CO_2 , as shown in Figure 5.4 below. FLP chemistry is currently a very active research area.

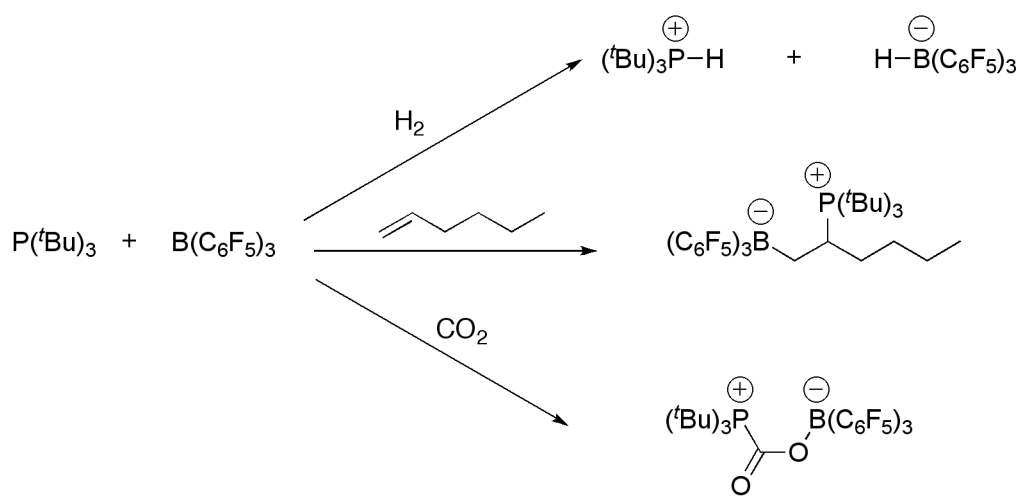


Figure 5.4. Reactivity of the $\text{B}(\text{C}_6\text{F}_5)_3/\text{P}(\text{tBu})_3$ frustrated Lewis pair with small molecules.

When assessing the strengths of Lewis acids and bases, we not only must consider both steric and electronic effects, but we also must consider the fact that a set of Lewis bases might have one order of strength with respect to one Lewis acid, but a different order of strength with respect to another, and *vice versa*. There is thus no single parameter for Lewis acid strength, nor a single parameter for Lewis base strength, comparable to the K_a and K_b values for Brønsted acids and bases, respectively. If favorable adduct formation is to occur (large, negative values of ΔH° , assuming enthalpy is more important than entropy), we must consider whether the members of the Lewis acid-base pair are a good “match” for each other,

rather than an absolute scale of strength. The predominant model for this phenomenon is discussed in the following section.

5.9. Hard-Soft Acid-Base (HSAB) Theory

The predominant way (though not the only way) in which chemists organize species according to their Lewis acid-base reactivity is by using the hard-soft acid-base (HSAB) theory, pioneered by Ralph Pearson (1919-2022). Pearson proposed that Lewis acids and bases could be described as either “hard” or “soft,” and that the formation of hard acid-hard base and soft acid-soft base adducts was highly favorable, while the formation of hard acid-soft base and soft acid-hard base adducts was not. What makes a Lewis acid or base hard or soft? Pearson noted that soft acids and bases tend to be highly polarizable species, whereas hard acids and bases are not very polarizable. Recall that the polarizability α is a measure of the dipole moment μ_{ind} that can be induced in an atom, ion, or molecule by an external electric field $\mathbf{E}$, or $\mu_{\text{ind}} = \alpha\mathbf{E}$. The polarizability tensor is a 3×3 matrix with 9 components, but only a qualitative understanding of polarizability is necessary to understand HSAB theory. For our purposes here, it is important to note that species with a high charge/size ratio³⁹ tend to be less polarizable, since their electrons are more tightly held, and thus respond less to an external electric field.

The HSAB concept can be understood in terms of MO theory. Highly polarizable (soft) bases tend to have relatively high-energy HOMOs, and soft acids tend to have relatively low-energy LUMOs, so the energy difference between the HOMO of the base and the LUMO of the acid is small. In general, when two basis orbitals interact to form a new pair of bonding and antibonding MOs, the magnitude of the orbital interaction (*i.e.* the degree to which the new bonding MO is stabilized, and the new antibonding MO is destabilized) is inversely proportional to the difference in energy between the basis orbitals: basis orbitals with

³⁹ The sign of the charge matters here; it is not merely a question of the magnitude of the charge. For instance, S^{2-} is a more polarizable (softer) Lewis base than HS^- , because a 2-charge is considered lower than a 1- charge. Similarly, for neutral Lewis acids or bases with significant dipole moments, the partial charge on the reactive atom is relevant.

similar energies thus have stronger interactions.⁴⁰ What this means is that soft acid-soft base interactions lead to strong covalent bonds. In contrast, hard bases tend to have low-energy HOMOs (often based on strongly electronegative elements such as O), and hard acids tend to have high-energy LUMOs, so the *covalent* portion of a hard acid-hard base interaction is weak. General orbital interaction diagrams for soft acid-soft base and hard acid-hard base interactions are shown in Figure 5.5 below.

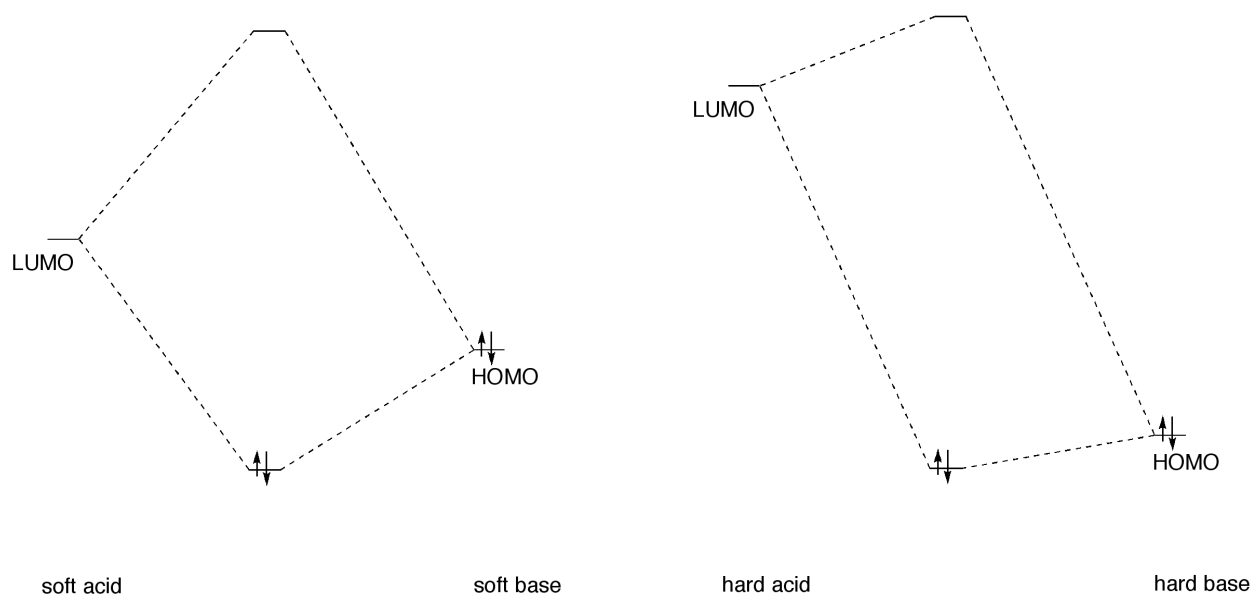


Figure 5.5. Frontier orbital interactions in soft-soft and hard-hard Lewis acid-base interactions.

The above MO discussion should not be understood to mean that hard acid-hard base interactions are energetically unfavorable. Electrostatic, but noncovalent, interactions, such as the Coulombic attractions between an anionic Lewis base and a cationic Lewis acid or between the negative end of a strongly dipolar Lewis base with the positive end of a strongly dipolar Lewis acid, can be very strong indeed, even though they are not covalent. Orbital

⁴⁰ For a mathematical justification of this rule, see pages 15-26 of *Orbital Interactions in Chemistry*, 2nd edition, by Thomas A. Albright, Jeremy K. Burdett, and Myung-Hwan Whangbo, John Wiley & Sons: Hoboken, NJ, 2013.

mixing is an important way in which the energy of a chemical system can be lowered, but it is not the only one.

5.10. Trends in Hardness and Softness of Lewis Acids and Bases

In general, the hardness of a Lewis acid or base decreases as one moves down the column of the Periodic Table to which the atom at the Lewis-acidic or Lewis-basic site belongs. Similarly, an increase in charge, while not significantly increasing molecular or ionic size, increases hardness. When discussing hard-soft trends, it should be kept in mind that chemists will sometimes say that a Lewis acid or base is “borderline,” *i.e.* neither especially hard nor especially soft. Different chemists will draw the lines between “hard” and “borderline” and between “borderline” and “soft” in different places, so when studying these trends, do not worry so much about assigning a given species as being hard or soft, but rather strive to be able to rank a series of acids or bases in terms of *relative* hardness or softness.

Among acids, H^+ , Li^+ , Na^+ , and K^+ are all considered soft, although the hardness of alkali metal cations decreases down the column, as their electrons are located farther from the nucleus. (H^+ , of course, has no electrons at all.) The heavier alkali metal cations Rb^+ and Cs^+ are considered fairly soft. Similarly, Be^{2+} , Mg^{2+} , Ca^{2+} , and Sr^{2+} are all considered hard, while Ba^{2+} and Ra^{2+} are soft. Among the *p*-block, boron-based, neutral Lewis acids can be either hard or soft, depending on how electron-withdrawing their substituents are. BF_3 , BCl_3 , and B(OR)_3 ($\text{R} = \text{alkyl}$) are hard, BH_3 is soft, and BMe_3 is borderline. Despite the fact that Al is below B in the Periodic table, Al-based Lewis acids tend to be hard, such as AlH_3 , AlMe_3 , and Al^{3+} in salts such as AlCl_3 . This is probably because Al is sufficiently less electronegative than B that it is a true metal (while B is usually considered a nonmetal or a semimetal), making the bonds between Al and other elements more polar, and the Al center more like an Al^{3+} ion. The Tl-based Lewis acids, however, such as Tl^+ salts or the Tl(III) species TlMe_3 , are soft acids, as would be expected from the large size of Tl. Among acids derived from the metallic elements of the crystallogens (Group 14), Sn^{2+} and Sn^{4+} are hard, while Pb^{2+} is soft. Pb^{4+} is rarely seen, since compounds of Pb in the +4 oxidation state tend to be strong oxidizing agents, with the exception of the formerly common gasoline additive PbEt_4 , but Pb^{4+} would presumably be

hard, or at least borderline. The heavier pnictogens (Group 15) can form compounds that can be either Lewis acids or Lewis bases; acidic species of these elements, such as AsCl_3 and SbCl_3 , are soft.

Transition metal (TM) atoms and ions are generally Lewis acids, as we will see later in our study of coordination chemistry. Here oxidation state is very important: for a given TM, ions (or complexes) of the $+(n + 1)$ oxidation state are always harder than those of the $+n$ oxidation state. In general, TM species in which the metal has an oxidation state of +4 or higher are considered hard, since even larger species with that charge have a high charge/size ratio. Conversely, we will see metal compounds in which the metal has an oxidation state of zero, such as $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$. These compounds are invariably soft Lewis acids.

Most of the softest TM ions are of elements towards the right of the *d*-block, often known as “late” TMs, and in the second and third transition series, these are generally the more electronegative metals. Compounds of Rh, Pd, Ag, Cd, Ir, Pt, Au, and Hg are very often soft. Note that Rh and Ir are softer than Co, Pd and Pt are softer than Ni (which is borderline), Ag and Au are softer than Cu, and Cd and Hg are softer than Zn (Zn, almost always found as Zn^{2+} , tends to be hard or borderline hard in most of its compounds). Moving left, the group 8 metals (Fe, Ru, Os) can be hard or soft in their compounds, depending on their oxidation state and ligand set. The importance of oxidation state can be illustrated by the fact that Cu^+ , Rh^+ , and Ir^+ are soft acids, while Cu^{2+} , Rh^{3+} , and Ir^{3+} are considered borderline, or by the fact that Fe^{2+} and Co^{2+} are borderline acids, while Fe^{3+} and Co^{3+} are hard. Most ions of TMs to the left of the *d*-block (“early” TMs) are hard, and such elements are also usually present in high oxidation states (*e.g.* Sc^{3+} , Ti^{4+} , Zr^{4+} , V^{5+} , Ta^{5+}). Most TMs that are soft acids have *d* electrons present in their electron configuration, which can be used for π -“backbonding” to ligands, as will be discussed in chapter 8. The lanthanide ions Ln^{3+} (the most common oxidation state, where Ln is any of the lanthanides) are hard acids.

In terms of bases, Lewis-basic species with F or O donor atoms, such as F^- , H_2O , OH^- , and O^{2-} , are generally hard. This list includes the conjugate bases of oxyacids, so NO_3^- , CO_3^{2-} , SO_4^{2-} ,

PO_4^{3-} , and all carboxylates RCOO^- are hard, as are alcohols ROH and alkoxides RO^- . Among the halides, hardness decreases down the Periodic Table, so F^- is hard, Cl^- is borderline hard, Br^- is borderline soft, and I^- is very soft indeed. The hardness of Lewis-basic anions also affects the hardness of Lewis acids with those anions as displaceable groups (leaving groups or nucleofuges): alkyl chlorides RCl are harder acids than alkyl bromides RBr , which are harder acids than alkyl iodides RI . Basic nitrogen species NR_3 ($\text{R} = \text{H}$ or alkyl) are hard or borderline bases, while phosphines PR_3 and arsines AsR_3 are soft: amines are common ligands for hard metal ions like Co^{3+} , while phosphines are common ligands for soft metal ions like Rh^+ or Pt^{2+} . Lewis bases with S or Se donor atoms (H_2S , HS^- , S^{2-} , R_2S , RSH , RS^-) are also all quite soft: in fact, the toxicity of many soft-acid metal ions is primarily due to their ability to bind the thiol groups in cysteine residues in proteins (more on this in Chapter 18). Lewis bases with carbon donor atoms, such as CO and CN^- , are also generally soft.

The hardness and softness of Lewis acids and bases have many practical results. Salts formed between hard acid cations and hard base anions, on the one hand, or soft acid cations and soft base anions on the other, tend to be much less soluble in water than those with a soft acid and a hard base or *vice versa*. For example, AgF is highly soluble in water, but AgCl , AgBr , and AgI are all essentially insoluble, with K_{sp} values decreasing in the order $\text{AgCl} > \text{AgBr} > \text{AgI}$. This trend can be rationalized by considering the soft acid character of Ag^+ , whose halide salts are less soluble the softer the halide is. Conversely, the solubility of halides of the hard acid Li^+ increases in the order $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$.

HSAB theory can also be used to explain the behavior of so-called “ambidentate” ligands, *i.e.* ligands with more than one potentially Lewis-basic donor atom. For instance, thiocyanate (SCN^-) can bind to a metal ion through either N or S. When this ligand binds to Group 12 metal ions in the +2 oxidation state, we see $[\text{Zn}(\text{NCS})_4]^{2-}$ (N-bound) but $[\text{Hg}(\text{SCN})_4]^{2-}$ (S-bound). The harder N donor site binds to the harder acid Zn^{2+} , but the softer S donor site binds to the softer acid Hg^{2+} .

5.11. Drago's Enthalpy Equation and the E and C Parameters

We noted before that, because of the energetic preference for hard-hard and soft-soft Lewis acid-base adduct formation, there is no single scale for Lewis acid strength, nor a single scale for Lewis base strength: a given Lewis acid might be strong with respect to one Lewis base and weak with respect to another, and *vice versa*. Russell Drago (1928-1997) proposed an equation for the standard enthalpy of acid-base adduct formation $A + B \rightleftharpoons AB$ that includes parameters for the strength of the acid and the base in both hard and soft types of interactions. Drago's equation has the following form:

$$\frac{\Delta H^\circ}{\text{kcal} \cdot \text{mol}^{-1}} = -(E_A E_B + C_A C_B)$$

Here E_A and C_A are measures of the acid's strength in electrostatic (hard) and covalent (soft) interactions, respectively. Similarly, E_B and C_B are measures of the base's strength in electrostatic and covalent interactions. The E and C parameters were derived for a wide range of Lewis acids and Lewis bases by choosing those values that would be a best fit to experimentally measured ΔH° values for adduct formations. Reference points were defined so that I_2 has $E_A = 1$ and $C_A = 1$, N,N' -dimethylacetamide, MeC(O)NMe_2 , has $E_B = 1.32$, and diethyl sulfide, Et_2S , has $C_B = 7.40$.

Drago's equation has the limitation that it allows estimation of ΔH° only for adduct formation reactions, and not for Lewis acid-base reactions involving displacement, such as a nucleophilic substitution reaction at carbon or a ligand substitution reaction at a TM. For adduct formation reactions, however, one may generally conclude that the more negative the value of ΔH° is (the more exothermic the reaction is), the more favorable the reaction will be, since adduct formation reactions will generally have $\Delta S^\circ < 0$ (two molecules becoming one results in a net decrease in entropy). In general, ΔH° will be large in magnitude if either of the products $E_A E_B$ or $C_A C_B$ is large, but not if both such products are small. Thus, Drago's equation is a mathematical formulation of the result that hard-hard and soft-soft acid interactions are more favorable than hard-soft or soft-hard ones.

Note that Drago compiled the E and C parameters at a time when cal and kcal were common units of energy used by chemists. More recently, the SI units J and kJ have become more

widespread. Since $1 \text{ cal} = 4.184 \text{ kJ}$ (and thus $1 \text{ kcal} = 4.184 \text{ kJ}$), you can multiply a ΔH° obtained in $\text{kcal}\cdot\text{mol}^{-1}$ using Drago's equation by 4.184 to obtain a value in $\text{kJ}\cdot\text{mol}^{-1}$.

5.12. Oxidation, Reduction, and Cell Potentials

Oxidation-reduction (redox) reactions are defined as those involving a transfer of electrons, or substantial electron density, from one or more elements to other element(s). Sometimes, the transfer of electrons is direct, as in the reaction $\text{Cu}^{2+} (aq) + \text{Zn} (s) \rightarrow \text{Cu} (s) + \text{Zn}^{2+} (aq)$, seen in the Daniell cell, while in other instances involving covalent bonding, there is a transfer of electron density and a change in oxidation state, such as in combustion reactions. For example, when methane is burned according to the reaction $\text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2 \text{H}_2\text{O} (l)$, no ions are involved, but the oxidation state of C increases from -4 to $+4$, while the oxidation state of O decreases from 0 to -2 . Oxidation is the loss of electrons or electron density, while reduction is the gain of electrons or electron density; a helpful mnemonic for this rule is OIL RIG (**O**xidation **I**nvolves **L**oss; **R**eduction **I**nvolves **G**ain).

Redox reactions can often be written as the sum of two half-reactions. A reduction half-reaction has a free electron or electrons (e^-) as a reactant, while an oxidation half-reaction has a free electron or electrons as a product. For example, the Daniell cell reaction can be understood as the sum of the reduction half-reaction $\text{Cu}^{2+} (aq) + 2 e^- \rightarrow \text{Cu} (s)$ and the oxidation half-reaction $\text{Zn} (s) \rightarrow \text{Zn}^{2+} (aq) + 2 e^-$. If the number of electrons involved in a pair of half-reactions is different between the half-reactions, one or more half-reactions must be multiplied by an appropriate coefficient so that the electrons on the reactants and the products side cancel. A balanced redox reaction equation may not have e^- as a species.

In principle, the Gibbs energy change ΔG of a redox reaction can be related to the potential E of an electrochemical cell in which the reaction occurs, according to

$$\Delta G = -nFE$$

where n is the number of electrons transferred in the balanced equation (*e.g.* for the Daniell cell, $n = 2$)⁴¹ and $F = 96485 \text{ C}\cdot\text{mol}^{-1}$ is the magnitude of charge per mole of electrons, known as Faraday's constant after Michael Faraday (1791-1867). For a thermodynamically favorable process ($\Delta G < 0$) we have $E > 0$, and the relevant electrochemical cell will be a battery, in which a spontaneous chemical reaction is used to perform electrical work. For a thermodynamically unfavorable process ($\Delta G > 0$), we have $E < 0$, and the relevant electrochemical cell will be an electrolytic cell, in which an electrical potential is applied to force a nonspontaneous chemical reaction to occur.

Under standard-state conditions (a thermodynamic activity of exactly 1 for all reactants and products), we have

$$\Delta G^\circ = -nFE^\circ$$

From basic thermodynamics, ΔG and ΔG° are related by

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where $R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the ideal gas constant and Q is the reaction quotient. At equilibrium, $Q = K$, so

$$\Delta G^\circ = -RT \ln K$$

Replacing ΔG with $-nFE$ and ΔG° with $-nFE^\circ$ gives the very important equation

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

which is known as the Nernst equation, after Walther Hermann Nernst (1864-1941, Nobel Prize in Chemistry⁴² 1920). At equilibrium, where $Q = K$,

$$E^\circ = \frac{RT}{nF} \ln K$$

so equilibrium constants can be measured by measuring cell potentials under standard-state conditions. Note that $E^\circ > 0$ corresponds to $K > 1$, and $E^\circ < 0$ corresponds to $K < 1$.

⁴¹ Note here that n is a unitless quantity (number of electrons per balanced reaction equation), *not* an amount with units of moles. The per-mole part of the equation comes from Faraday's constant.

⁴² Nernst was awarded the Nobel Prize not for his work in electrochemistry, but for his formulation of the third law of thermodynamics, which states that the entropy of a perfect crystalline substance approaches zero as the temperature approaches absolute zero.

While the cell potential of a net redox reaction is straightforwardly enough defined, it is often useful to consider so-called half-cell potentials, the potentials corresponding to either a reduction or an oxidation half-reaction. Such potentials are known as half-cell potentials because a half-reaction occurs in half of an electrochemical cell. However, we cannot, strictly speaking, define a half-cell potential, because a battery without one of its halves will have no potential at all. To get around this problem, we define a reference potential of exactly 0 V for the reduction of the aqueous hydrogen ion,⁴³ $2 \text{H}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g})$. Since E° for any net reaction is the sum of the half-cell potentials for each half-reaction, all other half-cell potentials can be defined relative to this reference.

Half-cell potentials are conventionally tabulated as reduction potentials, but when using them to calculate a net cell potential, one need only switch the sign on a reduction potential to obtain the corresponding oxidation potential. For instance, if we wished to use tabulated reduction potentials to calculate E° for $\text{Cu}^{2+} (\text{aq}) + \text{Zn} (\text{s}) \rightarrow \text{Cu} (\text{s}) + \text{Zn}^{2+} (\text{aq})$, we would look in a table of reduction potentials to find $E^\circ = 0.340 \text{ V}$ for $\text{Cu}^{2+} (\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu} (\text{s})$ and $E^\circ = -0.762 \text{ V}$ for $\text{Zn}^{2+} (\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn} (\text{s})$. Since in the net reaction Zn is being oxidized, rather than Zn^{2+} being reduced, we switch the sign on the reduction potential for Zn^{2+} to obtain $E^\circ = 0.762 \text{ V}$ for $\text{Zn} (\text{s}) \rightarrow \text{Zn}^{2+} (\text{aq}) + 2 \text{e}^-$. For the net reaction, we sum the half-cell potentials, so $E^\circ = E^\circ (\text{Cu}^{2+} \rightarrow \text{Cu}) + E^\circ (\text{Zn} \rightarrow \text{Zn}^{2+}) = 1.102 \text{ V}$. It is important to note that one can simply sum half-cell potentials even if the values of n for the two half-reactions are different: one does *not* multiply the half-cell potentials the way one would have to multiply the half-reactions to obtain a balanced net reaction.

It is, however, necessary to consider the number of electrons transferred when calculating E° for a sequence of reductions whose individual E° values are known. Suppose that the reduction half-reaction $\text{X} + n_1 \text{e}^- \rightarrow \text{Y}$ has the reduction potential E_1° , and the reduction half-reaction $\text{Y} + n_2 \text{e}^- \rightarrow \text{Z}$ has the reduction potential E_2° . What, then, is the value of the reduction potential E_3° for the sum of these reductions, $\text{X} + (n_1 + n_2) \text{e}^- \rightarrow \text{Z}$? To determine this, we must

⁴³ This is how the half-reaction is usually listed in tables, but of course it is more correct to write it as $2 \text{H}_3\text{O}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2 \text{H}_2\text{O} (\text{l})$.

first convert the individual reductions' E° values to ΔG° values, add them to determine ΔG° for the net reaction, and then convert this net ΔG° back into an E° . This is done as follows:

$$\begin{aligned}\Delta G_1^\circ &= -n_1 F E_1^\circ \\ \Delta G_2^\circ &= -n_2 F E_2^\circ \\ \Delta G_3^\circ &= \Delta G_1^\circ + \Delta G_2^\circ = -n_1 F E_1^\circ - n_2 F E_2^\circ \\ E_3^\circ &= -\frac{\Delta G_3^\circ}{(n_1 + n_2)F} = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_1 + n_2}\end{aligned}$$

5.13. Periodic Trends in Reduction Potentials

While numerical values of reduction potentials for various atoms, molecules, and ions can be looked up in tables, it is worthwhile to develop some chemical intuition for the relative reduction potentials of different chemical species based on periodic trends. The following discussion will be in terms of reduction potentials, because standard half-cell potentials are usually tabulated as reductions, but in all cases the corresponding oxidation potentials are simply the reduction potentials multiplied by -1 .

For electronegative main-group elements such as the halogens, electronegativity plays an important role in reduction potentials. Consider the generic reduction half-reaction $X_2 + 2 e^- \rightarrow 2 X^- (aq)$, where X is any of the stable halogens (Group 17 elements). The E° values are 2.890 V, 1.360 V, 1.078 V, and 0.535 V for $X = F, Cl, Br,$ and I , respectively, and the physical state of the halogen is gaseous for $X = F$ and Cl , liquid for $X = Br$, and solid for $X = I$. As the halogen in question become less electronegative, its reduction becomes less thermodynamically favorable. One can only make such straightforward comparisons based on electronegativity, however, when the formulae of the different species are comparable. For example, O is the second most electronegative element in the Periodic Table by most scales, behind F but ahead of Cl and N . One might wish to compare E° for the half-reaction $O_2 (g) + 4 e^- \rightarrow 2 O^{2-} (aq)$ with the standard reduction potentials of the halogens. The problem is that the potential for this half-reaction cannot be measured, because the oxide ion O^{2-} is too strong of a Brønsted base to exist in aqueous solution. Instead, we may consider the reduction half-reaction of O_2 to water, which requires H^+ as an additional reactant: $O_2 (g) + 4 H^+ (aq) + 4 e^- \rightarrow 2 H_2O (l)$. $E^\circ = 1.229$ V for this half-reaction, but it cannot be directly

compared to the halogen reduction potentials, since we are considering a compound, H_2O , in addition to elemental molecules and monatomic ions.

When considering the reduction potentials of metal ions, electronegativity is an important consideration, but again not the only ones. Consider the stable alkali metals (Group 1 elements), Li, Na, K, Rb, and Cs. The electronegativity of these elements decreases monotonically down Group 1, but now consider the reduction $\text{M}^+ (\text{aq}) + \text{e}^- \rightarrow \text{M} (\text{s})$. The E° values for this half-reaction are -3.040 V , -2.714 V , -2.936 V , -2.923 V , and -3.026 V , for $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$, respectively. This is *not* a monotonic trend, and it is surprising to note that Li, the *most* electronegative of the alkali metals, has the *least* negative standard reduction potential! To understand the main reason for this surprising result, we note that $\text{Li}^+ (\text{aq})$ is a shorthand for the hydrated ion $\text{Li}(\text{H}_2\text{O})_4^+$. Because Li^+ is the hardest Lewis acid among the alkali metal cations due to its small size, it interacts most strongly with water, which is a hard Lewis base. Thus, formation of the aqua ion is enthalpically most favorable for Li^+ , making its reduction to elemental Li and uncoordinated water molecules quite unfavorable.

A common application of tables of standard reduction potentials is the construction of an “activity series” of the metals. An activity series is constructed by listing metals in increasing order of the standard reduction potentials of their aqueous ions, where the metals with the hardest to reduce ions (*e.g.* Li^+) are at the top. This allows rapid prediction of whether an elemental metal will be able to reduce a metal ion to a significant extent ($K > 1$). If the elemental metal is above the metal ion in the activity series, reduction will occur. Thus, for example, Li metal will reduce Fe^{2+} to elemental Fe, but Pt metal will not. Such rankings of reactivity have applications to corrosion and metallurgy, but we must also consider the effects of pH and complexation, as is discussed in the next section.

5.14. Applications to Corrosion and Metallurgy

Corrosion is a perennial problem in engineering. Chemically speaking, corrosion is the unwanted oxidation of any material (usually a metal or alloy) that harms the function of a

structure or piece of machinery. The most common oxidizing agents in most environments are dioxygen (O_2) and water.

It is thermodynamically favorable for many metals to form oxides at room temperature, simply as a result of reaction with O_2 in the atmosphere. The familiar rusting of an iron nail is due to the formation of rust, which is primarily a hydrated form of iron(III) oxide, Fe_2O_3 . However, the vulnerability of metals to corrosion by oxidation depends on kinetic, as well as thermodynamic, parameters. Aluminium⁴⁴ is widely used as a building material (*e.g.* in bicycle frames), since it is mechanically very sturdy, but also very light (low-density). It is also a strongly reducing metal: $E^\circ = -1.676 \text{ V}$ for $\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$, and its reaction with O_2 to form the oxide Al_2O_3 is thermodynamically very favorable. Finely ground Al metal is an example of a pyrophoric substance,⁴⁵ one which spontaneously ignites in air at room temperature, with no spark required. A large piece of Al, however, will not spontaneously burn, since a protective coating of Al_2O_3 will rapidly form on its surface, and O_2 molecules will not be able to diffuse through the Al_2O_3 layer to oxidize the rest of the Al metal inside. When the Al metal is finely ground, however, the surface area/volume ratio is much greater, so more of the material is exposed to O_2 . A layer of Al_2O_3 is only able to protect the Al metal inside because it is not friable (prone to forming flakes). In contrast, the hydrated iron oxides that make up rust are highly friable, and when they flake off, more Fe metal surface is exposed for oxidation. This is why a layer of rust does not protect the bulk of an iron object from oxidation.

HSAB theory is also important for understanding corrosion. Silver metal is not strongly reducing, since $E^\circ = 0.80 \text{ V}$ for $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$. Thus silver jewelry and silver tableware are not vulnerable to corrosion by oxide formation. However, silver tableware will develop a “tarnish,” a layer of the sulfide Ag_2S , when exposed to high-sulfur⁴⁶ foods such as eggs and

⁴⁴ “Aluminium” is the conventional spelling in British English, while “aluminum” predominates in American English. However, the International Union for Pure and Applied Chemistry (IUPAC) prefers the British spelling, and so that spelling will be used in this book.

⁴⁵ From Greek πυροφόρος, literally “fire-bearing.”

⁴⁶ The IUPAC prefers the American spelling “sulfur” to the British spelling “sulphur.”

onions. This can be understood in light of the fact that Ag^+ is a soft Lewis acid, and will more strongly interact with the soft Lewis base S^{2-} than the hard Lewis base O^{2-} .

Water is also an important substance in the chemistry of corrosion. While we tend to think of water as a Lewis-basic solvent, or as a reactant in the hydrolysis of organic compounds such as carboxylic acid amides (*e.g.* in the peptide bonds of proteins), it can also react as either an oxidizing agent or (less commonly) as a reducing agent.

Considering the oxidizing behavior of water first, the relevant reduction half-reaction is $2 \text{H}_2\text{O} (l) + 2 e^- \rightarrow \text{H}_2 (g) + 2 \text{OH}^- (aq)$, with $E^\circ = -0.828 \text{ V}$. While water is not a particularly strong oxidizing agent, it will oxidize the more strongly reducing metals; a notable example of this reactivity is the reaction of the alkali metals with water, according to the equation $2 \text{M} (s) + 2 \text{H}_2\text{O} (l) \rightarrow \text{H}_2 (g) + 2 \text{M}^+ (aq) + 2 \text{OH}^- (aq)$, where $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$. While many common metals will not be oxidized by pure water to any significant extent, some are still vulnerable to corrosion by acidic solutions. Consider the reduction half-reaction of acid, which can be written as $2 \text{H}^+ (aq) + 2 e^- \rightarrow \text{H}_2 (g)$ or $2 \text{H}_3\text{O}^+ (aq) + 2 e^- \rightarrow \text{H}_2 (g) + 2 \text{H}_2\text{O} (l)$. Since $E^\circ = 0$ for this half-reaction (by definition), any metal whose ion has a negative reduction potential will be oxidized by water under standard-state conditions. However, it is worth reminding ourselves that standard-state conditions mean an activity of 1 for all species, and if H_3O^+ has an activity of 1, this corresponds to a pH of 0, quite an acidic solution indeed. Thus, some metals that are apparently vulnerable to acid corrosion may not react significantly with mildly acidic solutions (*e.g.* a metal plate on which is served a dish made with tomatoes). Still, it is relevant that metals used for jewelry, such as Ag, Pt, and Au, all have ions with positive reduction potentials. Au, in particular, cannot be dissolved in any common acid, though it is soluble in “aqua regia,” a solution prepared from 3 parts concentrated HCl to 1 part concentrated HNO_3 by volume.⁴⁷

⁴⁷ *Aqua regia* is Latin for “royal water,” since gold was considered to be a metal fit only for kings and queens. The reason aqua regia can dissolve gold by oxidizing it to ions is that, when it is prepared, the strong oxidizing agents Cl_2 and nitrosyl chloride (ONCl) are generated. Since both Cl_2 and ONCl are gases at ambient temperature and pressure, aqua regia must be prepared freshly and cannot be stored.

The role of H^+ and OH^- in some redox reactions makes those reactions strongly pH-dependent. Any redox reaction with $\text{H}^+/\text{H}_3\text{O}^+$ among its reactants will be favored at lower pH and disfavored at higher pH according to Le Châtelier's principle, and *vice versa* for a reaction with $\text{H}^+/\text{H}_3\text{O}^+$ among its products. Analogously, any reaction (including redox reactions) with OH^- among its reactants will be favored at higher pH and disfavored at lower pH, and *vice versa* for a reaction with OH^- among its products. While corrosion of metals by acids is a more familiar phenomenon, some metals are also corroded effectively by strong bases. For instance, $E^\circ = -2.31 \text{ V}$ for $\text{Al}(\text{OH})_4^- (\text{aq}) + 3 \text{ e}^- \rightarrow \text{Al} (\text{s}) + 4 \text{ OH}^- (\text{aq})$, so Al metal is readily corroded by solutions of OH^- salts. When biochemists consider pH-dependent redox reactions (of which there are many in living systems), the use of conventional E° values is not useful, since a standard state of $\text{pH} = 0$ is not relevant for living systems, most of which have pH values near 7. Thus, in the biochemical literature one often sees $E^{\circ'}$ values, which are like E° values, except the activities of H_3O^+ and OH^- are both equal to 10^{-7} , corresponding to $\text{pH} = 7$.

Coordination chemistry, the binding of Lewis-basic ligands to metal ions or atoms to form metal complexes, will be the focus of much of the second half of this book. At this point, however, it is worth noting that complexation can strongly affect redox reactions. This has interesting implications for the extraction of gold. While most metals are found on earth as mineral salts such as oxides and must be reduced to their elemental states after they are mined, oxidation-resistant metals such as Ag and Au can sometimes be mined as “veins” of the pure metal. However, one also sometimes finds small fragments of Au, so-called “gold dust,” mixed in with other minerals. To separate the Au from other materials, mixtures are treated with NaCN solutions⁴⁸, dissolving the Au as $\text{Au}(\text{CN})_2^-$. The solutions containing $\text{Au}(\text{CN})_2^-$ are then treated with a more strongly reducing metal such as Zn to recover the elemental Au.

⁴⁸ Due to the high toxicity of CN^- and the environmental hazard of spills, other avenues for gold separation are now being explored.

Why does this work? First, we note that $E^\circ = 1.83 \text{ V}$ for $\text{Au}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Au} (\text{s})$, so pure water will not oxidize Au metal to any significant extent. However, coordination by CN^- stabilizes the +1 oxidation state of Au, as the complex ion $\text{Au}(\text{CN})_2^-$, relative to the simple hydrated Au^+ ion: $E^\circ = -0.595 \text{ V}$ for $\text{Au}(\text{CN})_2^- (\text{aq}) + \text{e}^- \rightarrow \text{Au} (\text{s}) + 2 \text{CN}^- (\text{aq})$. Since $E^\circ = -0.828 \text{ V}$ for $2 \text{H}_2\text{O} (\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2 \text{OH}^- (\text{aq})$, we can calculate $E^\circ = -0.233 \text{ V}$ for the net reaction $2 \text{Au} (\text{s}) + 4 \text{CN}^- (\text{aq}) + 2 \text{H}_2\text{O} (\text{l}) \rightleftharpoons 2 \text{Au}(\text{CN})_2^- (\text{aq}) + 2 \text{OH}^- (\text{aq}) + \text{H}_2 (\text{g})$, which corresponds to $K = 1.33 \times 10^{-8}$ at 25°C . This is not a large equilibrium constant, but the use of a large excess of CN^- (which is cheap, albeit toxic) allows the reaction to be driven to the right per Le Châtelier's principle. In general, the ability of ligands to stabilize metal ions in complexes relative to binding by water will make it easier to oxidize the metals in question in aqueous solution. In the case of this gold extraction process, the soft Lewis base CN^- binds to the soft Lewis acid Au^+ much more strongly than does the hard Lewis base H_2O .

As noted above, most metals cannot be mined as their elemental forms, and much of human society has depended on our ability to obtain elemental metals from their ores *via* reduction, a type of chemistry that dates back to antiquity, well before chemistry (or even alchemy) was defined as a science. One of the earliest examples of such a reduction to be discovered was that of copper, which is mined as the sulfide ore chalcocite, Cu_2S . Millennia ago, humans found that Cu metal could be obtained by heating Cu_2S in air, removing the S as the gaseous SO_2 , according to the equation $\text{Cu}_2\text{S} (\text{s}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{Cu} (\text{s}) + \text{SO}_2 (\text{g})$. Pure Cu is too malleable to be useful for the construction of tools and weapons, but it could be hardened by alloying with other metals or semimetals such as Sn, Zn, or As, leading to alloys called bronzes.⁴⁹ The historical period after the widespread use of bronze in metallurgy, but before the widespread use of iron and steel, is now generally known as the "Bronze Age," though it should be kept in mind that this practice, and thus the start of the Bronze Age, occurred at different times in different parts of the world.

⁴⁹ Traditionally, "bronze" has been used to refer to alloys of Cu with Sn, while alloys of Cu with Zn are called "brass." However, since Cu was alloyed with a wide variety of other elements in antiquity, archaeologists now describe alloys whose main component is Cu as "bronzes" in general; they can be specified further as "tin bronze," "zinc bronze," "arsenical bronze," *etc.* For the baleful effect of arsenic on early blacksmiths, see Section 18.6.

Later in antiquity, humans began to construct tools and weapons out of metallic iron and steel (alloys of Fe with a few percent C, which makes them less vulnerable to corrosion), since iron and steel are harder still than the various bronzes. Iron ores such as hematite, Fe_2O_3 , are smelted in a furnace, a process that consists of heating the iron ores with charcoal or coke (elemental carbon), limestone, CaCO_3 , and silica, SiO_2 (the main component of sand) in a furnace. At the high temperatures of the furnace, CaCO_3 decomposes according to $\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g)$, the CO_2 produced reacts with elemental C according to $\text{CO}_2 (g) + \text{C} (s) \rightarrow 2 \text{CO} (g)$, and the CO formed is the active reducing agent, reducing Fe_2O_3 according to $\text{Fe}_2\text{O}_3 (s) + 3 \text{CO} (g) \rightarrow 2 \text{Fe} (l) + 3 \text{CO}_2 (g)$, with the oxides Fe_3O_4 and FeO as intermediates. The CaO formed reacts with the SiO_2 to form a layer of molten calcium silicate, Ca_2SiO_4 , according to $2 \text{CaO} (s) + \text{SiO}_2 (l) \rightarrow \text{Ca}_2\text{SiO}_4 (l)$; this layer of Ca_2SiO_4 , known as “slag,” floats above the molten Fe formed, so the Fe can be drained. The net reaction is (roughly) $4 \text{Fe}_2\text{O}_3 (s) + 6 \text{C} (s) + 6 \text{CaCO}_3 (s) + 3 \text{SiO}_2 (l) \rightarrow 8 \text{Fe} (l) + 3 \text{Ca}_2\text{SiO}_4 (l) + 12 \text{CO}_2 (g)$.

The temperatures necessary to accomplish the smelting of iron are significantly higher than those needed to obtain copper from chalcocite, and thus smelting could not be performed until more advanced furnaces capable of those temperatures were developed. The “Iron Age,” which began when metallurgy with iron and steel was widespread, began at different times in different places (much like the Bronze Age), but in a given area, it always came after the Bronze Age for this reason.

Chapter 6: A Survey of Main-Group Chemistry

6.1. Periodic Trends in Electronegativity and Bond Strength

Main-group chemistry is a major topic indeed. Organic chemistry is, of course a (very large!) subset of main-group chemistry, but inorganic main-group chemistry has been experiencing something of a renaissance in recent years. While much of this text focuses on transition-metal chemistry, this chapter discusses some of the chemical behavior of the main-group elements. First, however, it is useful to discuss some general periodic trends that will inform our understanding of reactivity.

One very important principle in main-group chemistry is, of course, the periodic trend for electronegativity, in which electronegativity decreases down a column of the Periodic Table and increases across a row. For instance, all of the alkali metals readily react with water according to $2 M (s) + 2 H_2O (l) \rightarrow 2 M^+ (aq) + 2 OH^- (aq) + H_2 (g)$, but while this reaction leads to an amusing fizzing with $M = Li$, it will cause an explosion with $M = Rb$ or Cs , since the flammable H_2 is formed very exothermically. Similarly, the high electronegativity of F makes F_2 a terrifyingly powerful oxidizing agent: it is intensely poisonous to all living things, and high F_2 concentrations will ignite organic materials. In contrast, I_2 is only a mild oxidizing agent, and it is sufficiently benign biologically that it is a safe antiseptic for minor cuts and scrapes.

Simply remembering the existence of these periodic trends may, however, lead one to think (mistakenly) that such changes are smooth and gradual when one moves about the Periodic Table. In fact, there is often a dramatic, qualitative difference between the chemistry of the second-period elements (Li through Ne) and that of the third-period elements (Na through Ar), while from the third period on the changes down a column are more gradual. This phenomenon is predominantly due to the differences in atomic size and bond strength between compounds of second-period and third-period elements. The $2s$ and $2p$ electrons are much closer to the nucleus than the $3s$ and $3p$, so third-period elements have “bigger” atoms, which means, in practical terms, that they can accommodate more atoms directly

bound to them (higher coordination numbers). These more diffuse 3s and 3p AOs (and, similarly, 4s and 4p, *etc.*) also influence bond strength. Third-period elements form, on average, somewhat weaker σ bonds than do second-period elements, due to the greater diffuseness of their valence AOs, but the greater difference by far is the strength of their π bonds. Because of the radial node in 3p AOs that is not present in 2p AOs (and, similarly, two radial nodes in 4p AOs, *etc.*), much less orbital overlap is possible for third-period elements participating in π interactions. Thus, most main-group chemistry of elements of the third period and below involves σ bonding, rather than π bonding, and what π bonds do occur tend to be weak.⁵⁰ With this said, the smallest reactivity differences between the second and third periods occur among Groups 1 and 2, *i.e.* Li vs. Na and Be vs. Mg, since the chemistry of elements in these groups is primarily ionic (although a fair number of covalent Be compounds are known).

6.2. Group 1: The Alkali Metals

Group 1 of the Periodic Table consists of hydrogen (H), lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs),⁵¹ and francium (Fr). Of these elements, Fr has little known chemistry, since all of its isotopes are radioactive (its longest-lived isotope, ²²³Fr, has a half-life of only 22 min).

The Group 1 elements other than hydrogen (for which, *vide infra*) are collectively known as the alkali metals, since they all react with water to form basic (alkaline) solutions according to the equation $2 \text{ M (s)} + 2 \text{ H}_2\text{O (l)} \rightarrow 2 \text{ M}^+ \text{ (aq)} + 2 \text{ OH}^- \text{ (aq)} + \text{H}_2 \text{ (g)}$. In general, the similarity of the alkali metals to each other is greater than the similarity of the elements in any other group of the Periodic Table. The vast majority of their chemistry is ionic, since each has an $(ns)^1$ valence electron configuration well suited to the formation of an M^+ cation.

⁵⁰ It should be noted, however, that substantial π bonding *does* occur between transition metals and main-group elements of the third period and below. This will be discussed in chapter 8.

⁵¹ The spelling “cesium” is more common in American English, but the IUPAC prefers the British English spelling “caesium.”

Just as the reaction of alkali metals with water produces hydroxide salts, their reaction with liquid ammonia produces salts of the amide ion (NH_2^-), the conjugate base of ammonia. For $\text{M} = \text{Li}$ or Na , the following equation applies: $2 \text{M} (\text{s}) + 2 \text{NH}_3 (\text{l}) \rightarrow 2 \text{MNH}_2 (\text{s}) + \text{H}_2 (\text{g})$. This reaction is a convenient source of LiNH_2 or NaNH_2 , since both salts are insoluble in liquid ammonia. The above reaction, however, is fairly slow, and the addition of elemental Na to liquid ammonia leads to the formation of a deep blue solution before any precipitation of NaNH_2 occurs. The blue color arises from electrons released from Na atoms and trapped in a cage of ammonia molecules, according to $\text{Na} (\text{s}) \rightarrow \text{Na}^+ (\text{am}) + \text{e}^- (\text{am})$, where (am) denotes a species dissolved in ammonia, just as (aq) denotes a species in aqueous solution. The solvated electron $\text{e}^- (\text{am})$ is more accurately written as $(\text{NH}_3)_n^-$, a cluster of ammonia molecules with an overall -1 charge. The color of these solutions can be approximately explained by considering the solvated electron as being a “particle in a box,” well known to physical chemistry students as a simple system for which the Schrödinger equation has an analytical solution.⁵² Such “sodium electride” solutions, as well as similar solutions prepared from other electropositive metals, are used by synthetic organic chemists as powerful reducing agents in what are commonly known as “dissolving metal reductions.”

The powerful reducing ability of the alkali metals can lead to some surprising chemistry. All of the alkali metals will react readily with O_2 , but only for lithium is the predominant product the oxide, Li_2O . Sodium preferentially forms the peroxide, Na_2O_2 , containing the peroxide anion O_2^{2-} , while the other alkali metals preferentially form the superoxide MO_2 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$), containing the superoxide radical anion O_2^- . While Li is the least electronegative of the alkali metals, it is the only one that reacts with N_2 to form the nitride Li_3N , probably because the size match of the small ions Li^+ and N^{3-} gives the resulting salt a high lattice energy. Because of this, elemental Li cannot be safely stored in a nitrogen glovebox; an argon atmosphere is instead required.

⁵² See pages 90-97 of *Physical Chemistry: Quantum Chemistry and Molecular Interactions*, by Andrew Cooksy, Pearson: New York, 2014.

Alkali metals can be made even more reactive by the use of crown ethers, macrocyclic molecules with general formula $(\text{CH}_2\text{CH}_2\text{O})_n$. These molecules are named according to the template *a*-crown-*b*, where *a* is the total number of atoms in the ring and *b* is the number of O atoms. Because of the general formula of a crown ether, we always have $\frac{a}{b} = 3$. Crown ethers are powerful ligands for alkali metals, with each binding most strongly to an alkali metal ion whose size matches the size of the cavity inside the crown ether. The crown ethers 12-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7 bind most strongly to the Li^+ , Na^+ , K^+ , and Cs^+ , respectively. Similar to the crown ethers are the cryptates or cryptands (from Greek κρύπτειν, “to hide”), which encapsulate metal ions in a three-dimensional cavity with both O and N Lewis basic sites. The crown ethers 12-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7, as well as the commonly used cryptate 2,2,2-crypt, are shown in Figure 6.1 below.

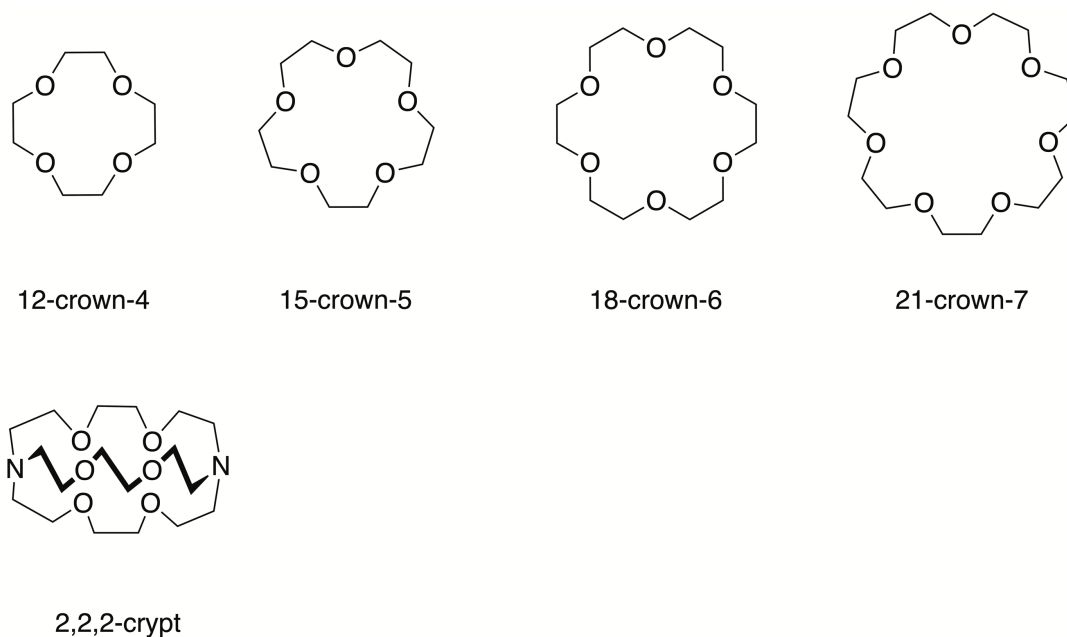


Figure 6.1. Crown ethers and 2,2,2-crypt.

The high affinity of 2,2,2-crypt for alkali metal cations leads to their formation in circumstances where it might well not be expected. Treatment of elemental Na with 2,2,2-crypt in EtNH_2 as solvent, or treatment of elemental K, Rb, or Cs with 2,2,2-crypt in $i\text{PrNH}_2$ as solvent, leads to a disproportionation of the metal into cryptate-complexed M^+ cations and alkalide (M^-) anions, according to $2 \text{ M} + 2,2,2\text{-crypt} \rightarrow \text{M}(2,2,2\text{-crypt})^+ + \text{M}^-$. While these

alkalide salts are extremely oxygen- and moisture-sensitive, and stable only at low temperatures even under strictly dry and anaerobic conditions, their existence has been confirmed by single-crystal X-ray diffraction, and show the extremely surprising presence of anions of extremely electropositive elements.

The difference in reactivity of hydrogen compared to its Group 1 congeners is partly due to its lower electronegativity, favoring covalent bonding in molecules such as H_2 and hydrocarbons, and partly due to the lack of valence p orbitals in first-period elements (*i.e.* there are no such things as $1p$ AOs). Because the only valence AO for H is $1s$, addition of an electron takes H to the $(1s)^2$ configuration, akin to He. This leads to H following a “duet rule” as opposed to the normal octet rule for main-group elements. This duet of electrons can be obtained by the formation of a single covalent bond, but also in the formation of the hydride ion H^- (isoelectronic with neutral He) as an alternative to H^+ . While H^+ (really, protonated solvents such as H_3O^+) is a much more common chemical species than H^- , the latter is present in hydride salts of highly electronegative metals, such as NaH and CaH_2 . Hydride salts are extremely moisture-sensitive, since H^- is the conjugate base of H_2 , which is usually not considered a Brønsted acid at all, and the reaction of NaH or CaH_2 with large quantities of water presents a serious fire hazard due to the highly exothermic generation of flammable H_2 gas. Nonetheless, NaH and CaH_2 are useful for removing traces of water from aprotic organic solvents in moisture-free chemistry.

6.3. Group 2: The Alkaline Earth Metals

Group 2 of the Periodic Table consists of beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).⁵³ While all isotopes of Ra are radioactive, its longest-lived isotope, ^{226}Ra , has a half-life of 1599 years, so its chemistry, unlike that of Fr, is well established. These elements are known as the alkaline earth metals.

⁵³ One could, in principle, place helium (He) in Group 2, since its valence electron configuration is $(1s)^2$, compared with $(2s)^2$ for Be, $(3s)^2$ for Mg, *etc.* However, since He, unlike the alkaline earth metals, has a closed shell as a free atom, it is chemically unreactive and thus usually considered to belong to Group 18 (the noble gases).

The chemistry of alkaline earth metals is almost exclusively the chemistry of their +2 oxidation states. All the alkaline earth metals other than Be react readily with water according to $M(s) + 2 H_2O(l) \rightarrow M^{2+}(aq) + 2 OH^-(aq) + H_2(g)$, while Be forms the insoluble oxide BeO (though the aqueous Be^{2+} ion is formed by the reaction of elemental Be with aqueous solutions of strong acids). In general, the bonding in alkaline earth metal compounds is strongly ionic, though Be, with its smaller size, forms bonds with more covalent character. For example, the bonding in $MgCl_2$ and $CaCl_2$ is almost entirely ionic (both compounds are commonly used as “road salt” in winter to lower the freezing point of ice). In contrast, the halides BeX_2 ($X = F, Cl, Br, I$) exist in the gas phase as linear molecules (molecular BeF_2 is isoelectronic to CO_2 and N_3^-), while in the solid phase they are better thought of as network covalent solids, with tetrahedral Be centers, than as ionic lattices.

Perhaps the most notable, and certainly the most widely used, covalent alkaline earth metal compounds are the organomagnesium halides $RMgX$ or $ArMgX$ ($R = \text{alkyl}$, $Ar = \text{aryl}$, $X = Cl, Br, I$), commonly known as “Grignard reagents” after their discoverer Victor Grignard (1871-1935, Nobel Prize in Chemistry 1912). Similar to organolithium reagents RLi or $ArLi$, Grignard reagents have hydrocarbyl ligands with considerable carbanionic character, and they are widely used by organic chemists to convert aldehydes or ketones into alcohols, as shown in Figure 6.2 below: nucleophilic attack of the carbanion-like hydrocarbyl group on the carbonyl carbon yields an alkoxide, which is protonated upon aqueous or mildly acidic workup to yield the alcohol product.

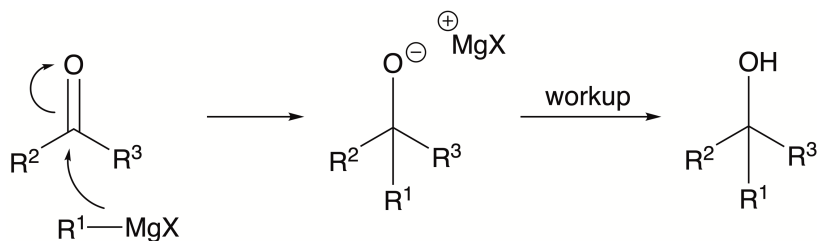


Figure 6.2. Grignard reagents in the synthesis of alcohols from aldehydes or ketones.

Grignard reagents must be handled in dry, deoxygenated solvents, since the carbanionic hydrocarbyl portion is vulnerable both to oxidation by O_2 and to protonation by trace water

to form the corresponding hydrocarbon. They are generally prepared, stored, and sold as solutions in ethers such as diethyl ether or THF, but they are in equilibrium in solution with dialkylmagnesium species R_2Mg (or the diaryl Ar_2Mg) and the halide MgX_2 , according to the reaction $2 RMgX \rightleftharpoons R_2Mg + MgX_2$. This reaction is commonly known as the Schlenk equilibrium, after Wilhelm Schlenk (1879-1943), a chemist well known for his invention of the Schlenk vacuum lines commonly used by researchers handling air-sensitive materials. The addition of 1,4-dioxane drives the Schlenk equilibrium towards products, and can be used in preparations of pure R_2Mg or Ar_2Mg species. Analogous organometallic complexes of Ca, Sr, and Ba are known, and tend to be more reactive than their Mg congeners since they have even greater carbanionic character due to the lower electronegativity of the heavier alkaline earth metals. Similarly, organoberyllium species are known, but relatively little-studied due to the high toxicity of Be.

6.4. Group 13: The Icosagens

Group 13 of the Periodic Table consists of boron (B), aluminium (Al), gallium (Ga), indium (In), thallium (Tl), and nihonium (Nh). Of these elements, Nh has no known experimental chemistry to speak of, since all of its isotopes are radioactive and very short-lived (its longest-lived isotope, ^{286}Nh , has a half-life of only 9.5 s). This group is sometimes known as the icosagens, since some of its members (chiefly B and Al) form icosahedral structures in the elemental form and/or in compounds, or as the triels, because each element has three valence electrons (but see the discussion below of the inert-pair effect in Tl). B is usually considered a semimetal, while Al, Ga, In, Tl, and presumably Nh are metals, though some chemists consider B simply to be a nonmetal, and Ga a semimetal.

A notable feature of covalent icosagen compounds is the presence of so-called multicenter bonding, a highly delocalized form of σ -bonding in which each atom-atom connection (each "bond") does not correspond to two bonding electrons. The simplest example of an icosagen compound with multicenter bonding is diborane (B_2H_6), which contains a pair of bridging H atoms; an MO model for diborane was discussed in Section 3.7. There exist many more complicated boron compounds with multicenter bonding, particularly dianions with general

formula $B_nH_n^{2-}$, including the O_h $B_6H_6^{2-}$ and the I_h $B_{12}H_{12}^{2-}$. We will discuss bonding schemes and electron-counting rules for such “cluster compounds” in chapter 17.

Not all covalent B compounds exhibit multicenter bonding that does not satisfy the octet rule at B. Boron trifluoride, BF_3 , is often presented in the Lewis structures chapter of introductory chemistry textbooks as an electron-deficient molecule, with only 6 valence electrons around B. In fact, BF_3 is not electron-deficient in the Lewis structure sense, as is shown by the series of resonance structures in Figure 6.3 below: while the first resonance structure, with formal charges all zero, has only 6 valence electrons around B, the others, which involve B–F π -bonding, satisfy the octet rule for all of their atoms. These three π -bonding resonance structures are akin to those commonly drawn for NO_3^- and CO_3^{2-} , which are both isoelectronic to BF_3 . An MO treatment of BF_3 will show considerable π -delocalization and an average B–F bond order of $\frac{4}{3}$, while the LUMO of BF_3 (involved in its behavior as a Lewis acid) is, strictly speaking, a weakly antibonding π MO, rather than a truly nonbonding B $2p$ AO.

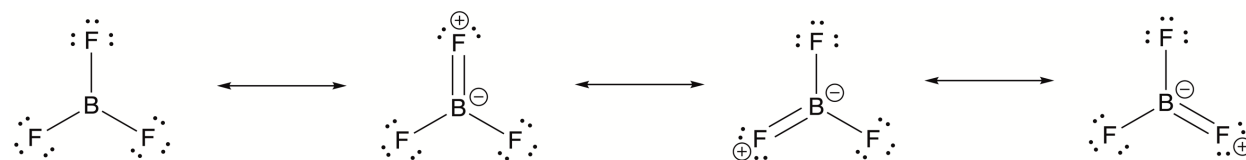


Figure 6.3. Resonance structures for BF_3 .

The π -bonding in BF_3 has important consequences in reactivity. BF_3 is used as a strong Lewis acid in many synthetic contexts (it is usually sold as a weakly-bound adduct with diethyl ether), but it is actually the *weakest* Lewis acid of the boron trihalides: for most Lewis bases, the boron trihalide acidity increases as $BF_3 < BCl_3 < BBr_3 < BI_3$. This trend may seem at first glance to be counterintuitive: one might expect the more electronegative halogens to withdraw more electron density from the B center, increasing the Lewis acidity. Instead, the opposite trend is observed. It is indeed the case that F is the most electron-withdrawing substituent in a σ -bonding sense, but it is also the strongest π -donor, since π -bonding becomes much weaker for main-group elements beyond the second period. The stronger π -

donation outweighs the stronger σ -withdrawing effect, making BF_3 the least electron-deficient boron trihalide, and thus the weakest Lewis acid.

Al is significantly less electronegative than B, and it is, of course, metallic in its elemental state, in contrast to the semimetal nature of B. Nonetheless, Al still forms a variety of covalent compounds, some of which display similar multicenter bonding to many B compounds. Bridging carbon atoms are common in organoaluminium compounds such as $[\text{Me}_2\text{Al}(\mu\text{-Me})]_2$ and $[\text{Ph}_2\text{Al}(\mu\text{-Ph})]_2$, and the phenomenon is qualitatively similar to that of bridging H atoms in B compounds. The bridging C atoms apparently violate the octet rule (just as the bridging H atoms in B_2H_6 apparently violate the “duet rule” for H), but the bonding can be understood in terms of 3c-2e bonds between two Al AOs or sp^3 hybrids and a lone-pair MO or hybrid on each bridging C, for Al–C bonds with a bond order of $\frac{1}{2}$. In contrast, one need not invoke multicenter bonding to describe the aluminium trihalides. AlF_3 is best thought of as a thoroughly ionic compound, and AlCl_3 behaves as a network covalent solid (albeit one with strongly polar bonds). When molten, however, AlCl_3 consists of dimeric molecules Al_2Cl_6 with bridging Cl atoms, while AlBr_3 and AlI_3 exist as molecular dimers Al_2Br_6 and Al_2I_6 even as solids. The dimers Al_2X_6 have an analogous structure to B_2H_6 , with a pair of bridging halogen atoms, but the presence of additional valence electrons on the halogens allows for a valence-bond picture of bonding, with the octet rule followed.

Ga and In are metallic in the elemental state, and prone to forming ionic or very polar covalent bonds. They adopt the +3 oxidation state in the majority of their compounds. Tl, however, is quite different, forming the Tl^+ ion much more readily than Tl^{3+} . The thallium(I) halides TlF , TlCl , TlBr , and TlI are all readily available, while the thallium(III) halides TlF_3 , TlCl_3 , and TlBr_3 are all strong oxidizing agents which are difficult to prepare. The compound with formula TlI_3 exists, but its crystal structure shows that each formula unit consists of a Tl^+ cation and an I_3^- anion, rather than a Tl^{3+} and three I^- anions. The preference of Tl for the +1 oxidation state over the +3, displaying a reluctance to use two of its valence electrons in bonding, has been dubbed the “inert pair effect.” Various explanations for the inert pair effect have been put forward, but it is believed to be due, at least in part, to relativistic effects,

which are commonly ignored in the quantum mechanics of chemistry, but which can become important for heavier elements, *i.e.* those with higher atomic number Z .

The fact that electrons are highly delocalized means that they can be treated as being, in a sense, in motion. The higher the atomic number Z , the more positive the nuclear charge, and the “faster” the electrons are moving. For elements with sufficiently large Z , this effective speed becomes a significant fraction of the speed of light, and the electrons have a greater mass as per the theory of relativity. If m_0 is the rest mass of an electron (9.109×10^{-31} kg), then the relativistic mass m of an electron moving at speed v is given by

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where $c = 3.00 \times 10^8$ m·s⁻¹ is the speed of light *in vacuo*. This greater mass corresponds to a shorter average distance from the nucleus. For a hydrogenlike (one-electron) atom or ion with atomic number Z , the average distance from the nucleus of an electron in an ns AO is given by

$$\langle r \rangle_{ns} = \frac{3\varepsilon_0 h^2 n^2}{2\pi Z m e^2}$$

While the exact form of this equation is invalid for multielectron atoms, the average distance of an ns electron from the nucleus is, in general, a decreasing function of its mass.

In this manner, the 6s electrons of Tl are significantly contracted and, since they are closer to the nucleus, they are less available for use in chemical bonding. These two electrons are the “inert pair.” One might think that the 6s electrons of Tl are simply lower in energy, and thus harder to ionize, than those of Ga or In. This is not quite so. The sum of the second and third ionization energies of Tl (corresponding to the removal of the two 6s electrons, not the one 6p electron) is 4820 kJ·mol⁻¹. This is indeed greater than the corresponding value for In (4501 kJ·mol⁻¹), but it is actually somewhat lower than the value for Ga (4916 kJ·mol⁻¹). The greater relativistic atomic mass is partially compensated for by the greater principal quantum number. However, the covalent bond energies of Tl with other elements (*e.g.* Cl) are significantly lower than those for Ga or In. Perhaps the best way to think about the inert

pair effect is that the energy required to mix the 6s AOs with 6p (in an MO or hybrid orbital bonding scheme) is not compensated for by the subsequent lowering of energy upon bond formation.

The ready formation and stability of the Tl^+ ion is of important practical significance, as Tl(I) compounds are invariably highly toxic. The hydrated ionic radius of Tl^+ (330 pm) is very similar to that of K^+ (331 pm), and this allows Tl^+ ions to disrupt process of nerve transmission involving K^+ ions, leading to neurotoxicity. Soluble Tl^+ salts, however, are useful as Cl^- abstraction agents in synthetic chemistry, as the TlCl formed is only sparingly soluble ($K_{\text{sp}} = 1.8 \times 10^{-4}$ in water at 25 °C). Soluble Ag^+ salts can also be used for this purpose, as AgCl is also sparingly soluble, and this does remove the requirement that the chemist work with toxic Tl . However, Ag^+ is a fairly potent one-electron oxidizing agent, so its use can lead to undesired side reactions when one of the reactants is vulnerable to oxidation (*e.g.* if one is abstracting Cl^- from a TM salt or complex with an accessible oxidation state one unit higher). Tl^+ is not strongly oxidizing, so its use avoids this potential problem.

6.5. Group 14: The Crystallogens

Group 14 of the Periodic Table consists of carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb), and flerovium (Fl). Of these elements, Fl has very little known experimental chemistry, since all of its isotopes are radioactive and very short-lived (its longest-lived isotope, ^{289}Fl , has a half-life of only 1.9 s). This group is sometimes known as the crystallogens, because of the beautiful crystals formed by the diamond allotrope of C; elemental Si and Ge, and the α -allotrope of Sn, have the same crystal structure. Another name sometimes used for the Group 14 elements is the tetrrels, since each element has four valence electrons (though the chemistry of Pb displays a marked inert-pair effect). C is a nonmetal, Si and Ge are semimetals (both widely used as semiconductors in industrial processes and electronic devices), and Sn, Pb, and presumably Fl are metals.

The chemistry of C is usually considered in the domain of organic, rather than inorganic chemistry, though the boundaries between areas of chemistry are often porous (see chapters

12-14 on organometallic chemistry, and chapter 18 on bioinorganic chemistry). Similarly, many ores and minerals commonly considered as “inorganic” contain the carbonate anion (CO_3^{2-}). The chemistry of crystallogens displays a very notable second-period to third-period change. While C forms strong π bonds with itself and with many other elements, making many of the wide variety of organic compounds possible, Si does not. The $3p$ valence AOs of Si all have one radial node apiece, unlike the $2p$ valence AOs of C; this affects the ability of Si to form π bonds much more than its ability to form σ bonds. For example, CO_2 , with its two $\text{C}=\text{O}$ double bonds, is a very stable molecule. On the other hand, silicon dioxide, while it has the *empirical* formula SiO_2 , it does not exist as discrete SiO_2 molecules with $\text{Si}=\text{O}$ double bonds. Rather, SiO_2 is a network covalent solid, existing as a quasi-infinite lattice in which each Si atom is tetrahedrally coordinated to four O atoms, with σ bonding only. There do exist a small number of compounds with $\text{Si}=\text{Si}$ double bonds (the Si analog of alkenes, known as silenes), but they require very large substituents on Si to be kinetically stable. One example of such a compound is $\text{Mes}_2\text{Si}=\text{SiMes}_2$, where the substituent Mes is an abbreviation for the bulky aryl group mesityl, or 2,4,6-trimethylphenyl. Even in this compound, the *ipso* C atoms of the Mes groups and the two Si atoms do not all lie in a plane (Figure 6.4), indicating that the $\text{Si}=\text{Si}$ double bonding character is not strong, due to the weakness of its π component. Since $\text{C}=\text{C}$, $\text{C}=\text{O}$, and $\text{C}=\text{N}$ double bonds are frequently formed in the organic compounds of life, the frequent suggestion by science-fiction writers⁵⁴ that Si-based life could exist, with all the C atoms in familiar biomolecules replaced by Si, is not a plausible one.

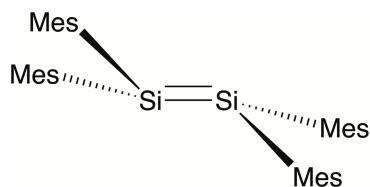


Figure 6.4. Structure of tetramesitylsilene.

⁵⁴ The *X-Files* episode “Firewalker” (season 2, episode 9) is an entertainingly gruesome example of this trope.

The change from C to Si also provides a good example of how the larger atomic sizes of third-row elements influence their reactivity. Consider the hydrolysis of carbon tetrachloride, CCl_4 : $\text{CCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{HCl}$. You may be surprised to learn that this reaction is highly favored thermodynamically, but it is exceedingly slow kinetically. If you mix some CCl_4 and water in a test tube, you will simply form two layers, with the denser CCl_4 at the bottom. At room temperature, no detectable chemical reaction will occur on any reasonable time frame. In contrast, the analogous reaction for Si, $\text{SiCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{HCl}$, is very fast indeed: if a bottle of SiCl_4 is opened in moist air, it will appear to smoke, an effect which is actually due to hydrolysis and the formation of small SiO_2 particles. Addition of liquid SiCl_4 to water will result in a rapid, highly exothermic reaction in which the SiO_2 precipitate is deposited at the bottom of the reaction vessel. The reason CCl_4 is so kinetically unreactive with water is that the C atom is small, so it is covered essentially completely by the Cl atoms. Hydrolysis requires that the O atom of water be able to attack the C atom of CCl_4 for nucleophilic displacement, but this process cannot occur, since its approach is blocked by the Cl atoms. Since Si is larger than C, in SiCl_4 part of the Si atom's surface is exposed between the Cl atoms, allowing nucleophilic attack by water. (GeCl_4 and SnCl_4 also undergo rapid hydrolysis, for the same reason.) The greater size of Si compared to C also allows for the existence of Si compounds with a coordination number above 4 (which is exceedingly rare for C). For instance, while tetrahedral SiF_4 is a stable molecule itself under many circumstances, it can react with 2 equivalents of F^- ions to form SiF_6^{2-} , a stable anion which is isoelectronic to PF_6^- and SF_6 , which are also well known as stable species. (See Section 3.6 for MO theory applied to the bonding in SF_6 .)

Ge is a semimetal with broadly similar chemistry to that of Si, but Sn is generally considered to be a true metal, whose ability to alloy with Cu to form bronze has been known since antiquity. However, the metallic character of Sn is dependent on temperature: above 13.2°C , Sn exists as the allotrope β -Sn or "white tin," which is an electrically conductive, ductile metal with a body-centered tetragonal crystal structure. Below this temperature, however, elemental Sn converts to the allotrope α -Sn or "gray tin," which has the same crystal structure as diamond (and elemental Si and Ge), and which is not only much less electrically conductive, but also brittle. While α -Sn is thermodynamically favored at these lower

temperatures, the $\beta\text{-Sn} \rightarrow \alpha\text{-Sn}$ conversion is kinetically slow for pure samples. However, trace amounts of other elements such as Ge can catalyze this transformation, and once some $\alpha\text{-Sn}$ has been formed, its presence catalyzes the formation of more (an autocatalytic process). This phenomenon poses a problem for the preservation of Sn-containing pipe organs in mediaeval churches, since they can form brittle $\alpha\text{-Sn}$ during cold winters, a phenomenon known as “tin disease” or “tin pest.”

Sn has an extensive organometallic chemistry, and a variety of stannanes $\text{SnR}_x\text{H}_{4-x}$, where R is a hydrocarbyl group, are known. Tributylstannane, Bu_3SnH , is used as a mild source of H atoms by synthetic organic chemists, in processes such as the Barton-McCombie deoxygenation. The related compound tributyltin oxide, a distannyl ether with formula $(\text{Bu}_3\text{Sn})_2\text{O}$, was once widely used in “antifouling” paints applied to the hulls of ships to prevent the growth of organisms such as seaweed, barnacles, and shipworms⁵⁵ on the hulls. In recent decades, however, the use of Sn-based antifouling agents has been restricted due to their overall toxicity to aquatic environments when they leach into the water.

The inert pair effect begins to come into play with the chemistry of Sn. Sn(II) and Ge(II) compounds are rare and unstable. In contrast, while many Sn(IV) compounds, such as SnCl_4 and SnO_2 , exist and are stable, a wide range of Sn(II) compounds are also well known, such as the halides SnX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$); small amounts of SnF_2 are in fact added to many toothpastes as an F^- source. The inert pair effect becomes significantly more prominent with Pb: the vast majority of stable Pb compounds are Pb(II) , with Pb(IV) compounds generally behaving as strong oxidizing agents. Lead(IV) acetate, Pb(OAc)_4 , is a useful reagent for the oxidation of a variety of organic compounds, and PbO_2 is used in the lead-acid batteries commonly found in automobiles. PbCl_4 is stable only below 0°C , and it can decompose explosively to PbCl_2 and Cl_2 at higher temperatures.

⁵⁵ So-called “shipworms” are not actually worms, but rather bivalve molluscs of the family Teredinidae. They can damage wooden structures by boring into them.

An important exception to the trend that Pb(IV) compounds are highly oxidizing consists of the tetraalkylplumbanes PbR_4 . However, while these compounds formally contain Pb in the +4 oxidation state, the low electronegativity of C in the alkyl substituents means that the Pb–C bonds are not terribly polar. However, the Pb–C bonds have low bond dissociation energies, making them weak with respect to homolytic cleavage; this property has been exploited in the use of tetraethyllead, PbEt_4 , as an antiknock agent. Engine knocking occurs when the flame in the engine is cooler than that required for proper ignition, and it can be caused by the buildup of organic radicals that are formed as combustion intermediates. At engine temperatures, PbEt_4 decomposes to elemental Pb by homolytic cleavage of the Pb–C bonds, and the elemental Pb reacts with these radicals, preventing them from causing engine knocking. PbEt_4 was not the only additive in so-called leaded gasoline. If PbEt_4 by itself were added to gasoline, the elemental Pb formed by its decomposition would foul an engine. Instead, leaded gasoline contained a mixture of PbEt_4 and 1,2-dibromoethane. Once elemental Pb was formed, it would react with the 1,2-dibromoethane to yield ethene and PbBr_2 , which, while a solid at room temperature, has a boiling point of 916 °C, causing it to be vaporized at engine temperatures and be emitted in the car exhaust.

The toxicity, to both humans and the environment as a whole, of leaded gasoline, was extreme. Not only is PbEt_4 highly toxic (for details on the toxicity of many soft Lewis acids such as Pb compounds, see chapter 22), but 1,2-dibromoethane, an electrophilic alkylating agent, is strongly carcinogenic, and the PbBr_2 released in exhaust can enter groundwater through the soil and be taken up by plants and fungi. Leaded gasoline has now been legally phased out in most circumstances, with the exception of some types of airplane fuel. The use of leaded gasoline was pioneered by the engineer Thomas Midgley, Jr. (1889-1944), who holds the dubious distinction of being involved with two of the most environmentally damaging technologies in history. In addition to leaded gasoline, he developed some of the chlorofluorocarbon (CFC) refrigerants connected to ozone depletion. In fairness to Midgley, laboratory equipment in his day would not have been conducive to low-pressure experiments now used to model atmospheric chemistry, so he could not reasonably have anticipated the harm done by CFCs, but the same cannot be said of his work on PbEt_4 : Midgley himself had been sickened by this compound during his experiments, but he

nonetheless did not warn chemical plant workers, much less the general public, about its hazards.

6.6. Group 15: The Pnictogens

Group 15 of the Periodic Table consists of nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi), and moscovium (Mc). Of these elements, Mc has very little known experimental chemistry, since all of its isotopes are radioactive and very short-lived (its longest-lived isotope, ^{290}Mc , has a half-life of only 650 ms). For a long time, Bi was thought to be the element with the largest atomic number to have stable isotopes. However, it was later found that its only naturally occurring isotope, ^{209}Bi , was in fact radioactive, undergoing α decay with a half-life of 2.01×10^{19} years. The experimental observation of the decay of ^{209}Bi was important in confirming theoretical predictions from nuclear physics, but it has no practical significance, since its half-life is vastly greater than the estimated age of the universe (1.38×10^{10} years). Chemists studying the reactions of Bi need not take any special precautions associated with the handling of radioactive material. Group 15 elements are often known as the pnictogens, a name that is really only a reference to N, the lightest pnictogen: it is derived from the Greek πνίγειν, “to choke, to stifle,” a reference to the fact that aerobic organisms such as animals cannot respire in an atmosphere of pure N_2 with no O_2 . N and P are nonmetals, As and Sb are semimetals, and Bi and (presumably) Mc are metals.

The chemistry of N differs significantly from C due to the presence of lone pairs (or, alternatively, doubly occupied roughly nonbonding MOs) on the N atom(s) of most compounds. These lone pairs make simple N compounds such as NH_3 and amines $\text{NR}_x\text{H}_{3-x}$ weak Brønsted bases, and many organic compounds exist with multiple basic N atoms in the same molecule (*e.g.* the “alkaloids” of natural products chemistry, pharmacology, and toxicology). Unlike the long chains of C atoms found in organic and biological chemistry, however, single bonds between N atoms tend to be fairly weak because of Coulombic repulsions between the lone pairs on the adjacent atoms. Hydrazine (H_2NNH_2) and its organic derivatives are dangerously flammable for this reason, and in fact they have been employed as rocket fuels in the space program.

In contrast, the triple bond in N_2 is one of the strongest bonds in chemistry, with a bond dissociation energy of $945 \text{ kJ}\cdot\text{mol}^{-1}$. Compounds with single or double bonds between N atoms often undergo exothermic decomposition reactions with N_2 as a product. The formation of N_2 is so thermodynamically favorable that it can even be generated from explosives such as nitroglycerin and 2,4,6-trinitrotoluene (TNT), which do not have N–N bonds in their structures. An example of an explosive with a widespread, life-saving use is sodium azide (NaN_3), whose anion azide, N_3^- , is isoelectronic with CO_2 . Automobile airbags contain NaN_3 , and a sufficient impact (such as a car crash) causes a spark which provides the activation energy for the reaction $2 \text{NaN}_3 (s) \rightarrow 2 \text{Na} (s) + 3 \text{N}_2 (g)$. The rapid release of N_2 gas by this reaction inflates the airbag, cushioning the driver or passenger and reducing the risk of serious injuries from the crash.⁵⁶ It should be noted that, while NaN_3 will explode upon exposure to a spark or sufficient heat, it is not a shock-sensitive explosive. In contrast, N_3^- salts of soft-acid cations, such as AgN_3 and $\text{Pb}(\text{N}_3)_2$, are sufficiently shock-sensitive that scraping with a spatula can cause them to detonate: they must be handled with extreme caution. The N_3^- ion is also acutely toxic, due to its ability to inhibit cytochrome c oxidase, a metalloenzyme in the mitochondrial electron-transport chain, by binding to the Fe atom at its active site. This is the same mechanism by which the infamously poisonous cyanide ion (CN^-) exerts its toxic effects.

The difference in chemistry between N and P is another excellent example of the difference between main-group elements of the second and third periods. N_2 is an exceptionally stable molecule because of its strong π bonding, while the poor π bonding ability of third-period elements makes P_2 unstable. Elemental P has a wide variety of allotropes, but they all display σ , rather than π , bonding. In the liquid and gas phases, elemental P exists as discrete, regular tetrahedral P_4 (“white phosphorus”) molecules, which have high ring strain but no π bonding. This level of ring strain makes P_4 a highly reactive species in both the thermodynamic and kinetic senses: it is both highly toxic⁵⁷ and highly flammable. In fact, P_4

⁵⁶ Most modern airbags also contain KNO_3 and SiO_2 , to convert the (dangerously flammable) elemental Na initially formed by the NaN_3 decomposition to stable sodium silicates.

⁵⁷ In Arthur Conan Doyle’s (1859-1930) mystery novel *The Hound of the Baskervilles*, perhaps the most famous work to feature his detective character Sherlock Holmes, the villain intends

samples appear to glow in the dark under an O₂-containing atmosphere because of gradual oxidation; this behavior is what gave the element its name (from the Greek for “light-bearing”).

P forms two main oxides, P₄O₆ and P₄O₁₀. Like P₄, each consists of molecules with the symmetry of a regular tetrahedron (point group *T_d*), but unlike P₄, there are no P–P bonds; O atoms instead bridge neighboring P atoms. In P₄O₁₀, each P atom is bound to an additional terminal O atom. The structures of P₄O₆ and P₄O₁₀ are shown, alongside that of P₄, in Figure 6.5 below. P₄O₁₀ is widely used as a strong dehydrating agent; it rapidly reacts with water to form the oxyacid phosphoric acid, H₃PO₄, according to the reaction $\text{P}_4\text{O}_{10} + 6 \text{H}_2\text{O} \rightarrow 4 \text{H}_3\text{PO}_4$. The structures of As₄O₆ and As₄O₁₀ are analogous.

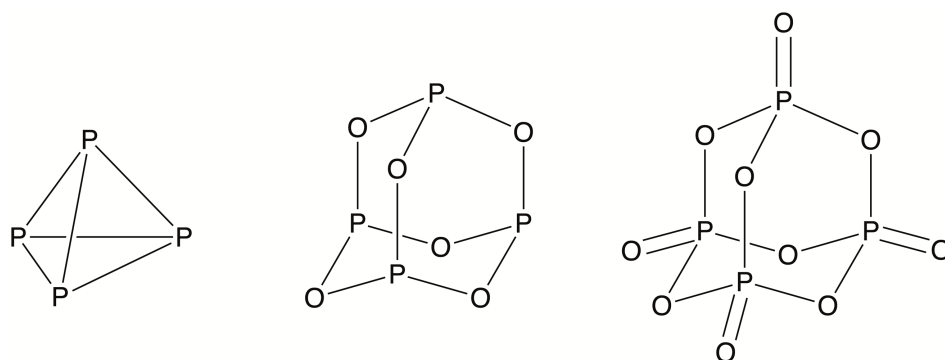


Figure 6.5. Structures of P₄, P₄O₆, and P₄O₁₀ (all in point group *T_d*).

A variety of esters of H₃PO₄ are known; many of these have a sinister reputation because of their use as chemical weapons (“nerve gases”⁵⁸ such as sarin and tabun) or as pesticides (such as parathion and malathion) that attack the nervous systems of insects, but which can

to kill Sir Henry Baskerville and inherit his estate by setting a vicious dog on him. To make the murder appear to be the doing of a hell-hound of Baskerville family legend, he smears P₄ on the dog’s snout to give it a spectral appearance at night. As clever as the story is, the toxicity of P₄ would likely prove fatal to the beast, and certainly leave it in no shape to maul its intended victim. As Conan Doyle was a medical doctor in addition to a mystery writer, one might expect him to have known this, but perhaps he was exercising artistic license.

⁵⁸ The term “nerve gas” is a misnomer, since these compounds are liquids at atmospheric pressure and ambient temperature. However, they are sufficiently volatile that one can be poisoned *via* inhalation, as well as absorption through the skin.

be dangerously toxic to people as well. All of these compounds, commonly known as organophosphates,⁵⁹ are neurotoxic because they irreversibly inhibit the enzyme acetylcholinesterase. However, other H_3PO_4 esters, far from being weapons or pesticides, are essential to life: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) are phosphate esters, with $-\text{O}-\text{P}(\text{O})(\text{O}^-)-\text{O}-$ groups connecting the sugar/nitrogenous base groups (nucleotides).

Phosphine, PH_3 , and its organic derivatives, the phosphines $\text{PR}_x\text{H}_{3-x}$, are the P analogs of ammonia and amines. While phosphines and amines have structural similarities, their chemistries are significantly different, largely resulting from the soft Lewis-base nature of phosphines. Unlike amines, phosphines do not display significant Brønsted basicity; they do, however, coordinate avidly to soft-acid TM ions. Triphenylphosphine, PPh_3 , is a particularly common ligand in TM coordination chemistry; it has the convenient property of being (kinetically) stable with respect to oxidation by atmospheric O_2 . In contrast, trialkylphosphines react rapidly with atmospheric O_2 (some are pyrophoric) to form the phosphine oxides R_3PO .

As and Sb are generally considered semimetals (gallium arsenide, GaAs, is widely used in industry as a semiconductor), though they can display more metallic or nonmetallic character depending on the compounds. In general, metallic character is displayed by As and Sb compounds with highly electronegative elements, such as AsCl_3 , SbCl_3 , SbCl_5 , As_4O_6 , As_4O_{10} , Sb_2O_3 , and Sb_2O_5 , while nonmetallic character is displayed by molecules such as the arsines $\text{AsR}_x\text{H}_{3-x}$ and stibines $\text{SbR}_x\text{H}_{3-x}$, the As and Sb analogs of amines or phosphines. The more metallic compounds of As and Sb generally behave as soft Lewis acids, while their more nonmetallic compounds generally behave as soft Lewis bases. Bi is a metal, predominantly (but not exclusively) forming ionic compounds; it also displays the inert-pair effect: while $\text{P}(\text{V})$, $\text{As}(\text{V})$, and $\text{Sb}(\text{V})$ compounds are all well known, $\text{Bi}(\text{V})$ compounds are uncommon; examples include the organobismuth species BiPh_5 , Ph_3BiCl_2 , and Ph_3BiCO_3 .

⁵⁹ “Organophosphate” is another misnomer, because the compounds do not contain P–C bonds!

6.7. Group 16: The Chalcogens

Group 16 of the Periodic Table consists of oxygen (O), sulfur⁶⁰ (S), selenium (Se), tellurium (Te), polonium (Po), and livermorium (Lv). Of these elements, Lv has no known experimental chemistry to speak of, since all of its isotopes are radioactive and very short-lived (its longest-lived isotope, ²⁹³Lv, has a half-life of only 70 ms). Po is also an element with no stable isotopes, but its experimental chemistry has been studied, since its longest-lived isotope ²⁰⁹Po, has a half-life of 125.2 years. Another isotope, ²¹⁰Po, is more easily synthesized, but shorter-lived, with a half-life of 138.4 days; this is still a long enough half-life to permit studies of reaction chemistry. Special precautions, however, must be taken by researchers working with Po due to its extreme toxicity. Group 16 elements are commonly known as the chalcogens.⁶¹ Of these elements, O and S are nonmetals, Se and Te are semimetals (both important in the semiconductor field), and Po is usually considered a metal, but sometimes considered a semimetal.

The chalcogens display another excellent example of the difference in chemistry between elements of the second and third periods. Elemental O is strongly oxidizing in both of its allotropes: dioxygen, O₂, and ozone, O₃, as O is the second most electronegative element in the Periodic Table, surpassed only by F. O₃ is a particularly strong oxidizing agent, and it is used by synthetic organic chemists as a reagent in a variety of reactions, such as the ozonolysis of alkenes. Its reactivity with many organic molecules also makes tropospheric (ground-level) O₃ an air pollutant that can cause lung irritation. In contrast, its presence in the stratosphere, in the so-called “ozone layer,” is helpful, as it absorbs a significant proportion of harmful ultraviolet radiation from the Sun. O–O single bonds tend to be quite weak, due to the repulsion between lone pairs on adjacent, small O atoms: aqueous solutions

⁶⁰ The IUPAC prefers the American English spelling “sulfur” to the British English spelling “sulphur,” in contrast to their preference for the British spellings of caesium and aluminium.

⁶¹ The etymology of “chalcogen” is rather confusing. The Greek word χαλκός means “copper” or “bronze,” so “chalcogen” would apparently mean “copper-former,” a strange designation for a group of (mostly) nonmetals and semimetals. The term may have arisen from an understanding (or misunderstanding) of χαλκός as referring to a metal ore, rather than a pure metal or alloy. O and S are certainly “ore-formers,” as many common metal ores are oxides or sulfides.

of hydrogen peroxide, H_2O_2 , are commonly used both as a laboratory reagent and a topical antiseptic. The decomposition reaction $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$ is both thermodynamically favorable and faster in more concentrated solutions, especially in the presence of a variety of substances, both organic and inorganic, that can catalyze this decomposition. For this reason, concentrated or “high-test” H_2O_2 solutions present an explosion hazard. The fizzing observed when a wound is disinfected with a dilute H_2O_2 solution is due to the release of gaseous O_2 : the iron-containing enzyme catalase, found in blood, catalyzes H_2O_2 decomposition very effectively. Organic derivatives of H_2O_2 such as peroxides ROOR' and hydroperoxides ROOH can be shock-sensitive explosives. Many ethers commonly used as solvents gradually form peroxides after being opened under air; this can pose a serious hazard when the solvent is removed on a rotary evaporator, as this will concentrate any peroxide present, potentially leading to a detonation.

The chemistry of S is very different from O, due partly to its much lower electronegativity (S is barely more electronegative than C) and partly to the general reluctance of third-period main-group elements to engage in π bonding. Both O_2 and O_3 have $\text{O}=\text{O}$ π bonds, while elemental S (a yellow powder or yellow crystals) exists primarily as cyclic, crown-shaped S_8 molecules, whose S–S bonds are less destabilized by repulsion between lone pairs due to the larger size of the S atoms. Heating of S_8 causes the formation of rubbery polymers with long chains of singly-bound S atoms. Thiols RSH and thioethers RSR' , the S analogs of alcohols and ethers, are common and usually stable (albeit evil-smelling) molecules, and are crucial to biochemistry: the amino acids cysteine and methionine are a thiol and a thioether, respectively. While persulfides RSSH are not common, disulfides RSSR' are common and usually stable (in contrast with the explosive nature of organic peroxides); disulfide formation between cysteine residues is important in stabilizing the secondary and tertiary structure of proteins.

An important part of the environmental chemistry of sulfur comes from its oxides SO_2 and SO_3 , which are perhaps the most important inter-chalcogen compounds. While coal is commonly thought of as a form of elemental C, it also contains a variety of organic compounds, including organosulfur compounds. When coal is burned as a fuel, oxidation of

the organosulfur compounds yields SO_2 and SO_3 , which react with water in the atmosphere to form sulfurous acid, H_2SO_3 , and sulfuric acid, H_2SO_4 , respectively. These two oxyacids are major contributors to acid rain.

Se and Te have chemistries broadly similar to S, but their lower electronegativities make them behave in a more metallic fashion, so both Se and Te are usually considered to be semimetals. Both Se and Te are toxic in large quantities, but small amounts of Se are essential to life: the amino acid selenocysteine (the Se analog of serine and cysteine) is present in some proteins, though it is genetically encoded in a different manner from that of the standard 20 amino acids.⁶² A selenocysteine residue is present at the active site of the important antioxidant enzyme glutathione peroxidase.

6.8. Group 17: The Halogens

Group 17 of the Periodic Table consists of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At), and tennessine (Ts). Very little experimental chemistry of At has been studied, and none at all of Ts, because all isotopes of each of these two elements are radioactive and very short-lived (their most stable isotopes, ^{210}At and ^{294}Ts , have half-lives of 8.1 h and 51 ms, respectively). Group 17 elements are commonly known as the halogens, literally “salt-formers” (from Greek ἅλς, “salt”), as they commonly form ionic compounds with a wide variety of metals. All the halogens are generally considered to be nonmetals, though the luster of solid I_2 can be understood in terms of the periodic trend of metallic character increasing down a group. Based on this periodic trend, it is possible that At and Ts may be considered as semimetals, but since macroscopic quantities of neither element have yet to be prepared, this supposition cannot be confirmed experimentally.

As is often the case, the behavior of the second-period element F is notably different from that of its congeners. It is exceedingly reactive in elemental form: by some estimates, F_2 is the strongest oxidizing agent known. This reactivity is due to the very small size of the

⁶² See page 1361 of *Biochemistry*, 4th edition, by Donald Voet and Judith G. Voet, John Wiley & Sons, Inc.: Hoboken, NJ, 2011.

valence AOs of F, which lead to a short F-F bond in F₂ with strong electron-electron repulsion. The F-F bond is thus quite weak, with a bond dissociation energy of only 158.8 kJ·mol⁻¹; after this anomalously low value, the Cl₂ has the strongest bond of any elemental halogen, with the bond dissociation energies then decreasing down the period (the bond dissociation energies for Cl-Cl, Br-Br, and I-I bonds are 242.6, 192.8, and 151.1 kJ·mol⁻¹, respectively).

While F atoms form very weak bonds with each other, they bond very strongly to atoms of many other elements. Haloalkanes with C-Cl, C-Br, and C-I bonds tend to be Lewis acids (electrophiles) from which a halide anion can be displaced as a nucleofuge (leaving group), making them useful as reagents that transfer an R⁺ moiety (as in the S_N1 and S_N2 reactions of organic chemistry, or the formation of certain TM alkyl complexes, as will be discussed in chapter 14). In contrast, fluorinated organic compounds are not generally electrophilic at C, and do not react to give F⁻ displacement. For example, the polymer poly(tetrafluoroethene) or Teflon, -(CF₂CF₂)_n-, is well known for its inertness under most conditions. Similarly, Si-F bonds are exceedingly strong: in fact, F⁻ is one of the few species that can react with compounds with Si-O bonds to displace a nucleophilic oxygen species. For instance, mixed alkyl/silyl ethers RO-SiR'₃ react with F⁻ sources such as tetrabutylammonium fluoride or TBAF, Bu₄NF, to yield the alkoxide RO⁻ and the silyl fluoride R'₃Si-F. F⁻ also reacts with the Si-O bonds in glass (which is mostly SiO₂); this is why hydrofluoric acid (an aqueous solution of HF) can be used to etch glass.

An aspect of halogen chemistry often given short shrift in introductory courses is the formation of interhalogen compounds. Some of these are simple heteronuclear diatomics, such as chlorine monofluoride, ClF, or iodine monochloride, ICl. ICl, in particular, is notable as a good source of electrophilic I (I⁺), and it reacts with a generalized nucleophile Nu as follows: Nu + ICl → NuI⁺ + Cl⁻. Many interhalogens, however, have more complicated structures, which often contain a central halogen atom with multiple terminal atoms (of another halogen) as substituents. In such compounds, the central atom is usually the least electronegative of the halogens present, as this atom will be in the highest oxidation state. An alternative way of thinking about this phenomenon is that such interhalogens are

hypervalent compounds, with occupied MOs that are largely (or completely) based on the substituents (*cf.* the discussion of SF₆ in Section 3.6), leaving the central atom electron-poor. Such an arrangement will be most favorable for less electronegative central halogens and more electronegative terminal halogens. Important interhalogens include XF₃ and XF₅ (where X = Cl, Br, I) and IF₇. In each of these cases, the F atoms are terminal, and the less electronegative halogen is central. The large size and low electronegativity of I allows it to form the heptafluoride IF₇, while neither ClF₇ nor BrF₇ is known. Many interhalogens can be used as aprotic, but autoionizing, solvents that display solvent-system acid-base behavior, such as $2 \text{ BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$ or $2 \text{ IF}_5 \rightleftharpoons \text{IF}_4^+ + \text{IF}_6^-$.

The less electronegative halogens can have oxidation states between -1 (as in simple halide ions X⁻ and many organohalogen compounds) and 0 (as in the elemental forms X₂). The best known example of a species with this property is the triiodide ion I₃⁻, in which the average oxidation state of I is $-\frac{1}{3}$. I₃⁻ results from the mild oxidation of I⁻: $3 \text{ I}^- \rightarrow \text{I}_3^- + 2 \text{ e}^-$. Alternatively, I₃⁻ can be thought of as the adduct of the Lewis acid I₂ and the Lewis base I⁻. The analogous tribromide ion Br₃⁻ is also known, but it is more strongly oxidizing than I₃⁻. Larger polyiodide ions are known, such as linear I₄²⁻, bent I₅⁻, and doubly bent I₈²⁻.

A fascinating phenomenon is the existence of so-called pseudohalogens, diatomic or polyatomic groups that behave similarly to halogen atoms, at least in certain respects. The cyano moiety CN is the classic example of a pseudohalogen. Like the true halogens, it forms the molecular dimer cyanogen, NC-CN, which is an oxidizing agent, and the monoanion cyanide, CN⁻, whose silver(I) salt AgCN is only sparingly soluble in water. Its hydride, HCN, is a Brønsted acid (albeit only a weak one), and it forms analogs of interhalogen compounds in the cyanogen halides XCN (X = F, Cl, Br, I). A more complicated example of a pseudohalogen is the tetracarbonylcobalt fragment Co(CO)₄, which has the neutral dimer Co₂(CO)₈, the anion Co(CO)₄⁻, the sparingly soluble silver salt Ag[Co(CO)₄], the acidic hydride HCo(CO)₄, and the interhalogen analog ICo(CO)₄. The isolobal analogy of Hoffmann (discussed in chapter 21) can be used to rationalize pseudohalogen behavior, among other surprising similarities in reactivity between apparently dissimilar chemical groups.

6.9. Group 18: The Noble Gases

Group 18 of the Periodic Table consists of helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Rn) and oganesson (Og). Very little experimental chemistry of Rn has been studied, and none at all of Og, because all isotopes of each of these two elements are radioactive and short-lived: the most stable isotope of Rn, ^{222}Rn , has a half-life of 3.8 days, and the only isotope of Og, ^{294}Og , has a half-life of only 0.7 ms. The Group 18 elements are commonly known as the noble gases, due to their lack of chemical reactivity arising from a full valence shell: for example, Ar is commonly used as an inert gas for gloveboxes and Schlenk lines, as it is less reactive even than N_2 .

For quite some time, the noble gases were thought to form *no* stable compounds whatsoever. However, Neil Bartlett (1932-2008), the founder of the field of noble gas chemistry, discovered that this was not so, based on very clever experiments devised in analogy to another type of surprising reactivity. Bartlett found that the reaction of O_2 with the extremely powerful oxidizing agent platinum(VI) fluoride, PtF_6 , yielded the salt dioxygenyl hexafluoroplatinate(V), O_2PtF_6 , which contains the O_2^+ cation and the PtF_6^- anion. Bartlett noted that the ionization energies of O_2 and Xe were very similar (1175 and 1170 $\text{kJ}\cdot\text{mol}^{-1}$, respectively), and reasoned that if PtF_6 could oxidize O_2 , it might be able to oxidize Xe as well. The mixture of Xe and PtF_6 clearly resulted in a chemical reaction, whose product Bartlett initially proposed was XePtF_6 , the PtF_6^- of the Xe^+ cation. Later work suggested that Bartlett's identification was mistaken, and that the predominant product was the salt $\text{XeFPt}_2\text{F}_{11}$, containing the XeF^+ cation and the bimetallic $\text{Pt}_2\text{F}_{11}^-$ anion. Nonetheless, Bartlett's work was absolutely seminal, in that it forever shattered the idea that noble gases were *always* chemically unreactive.

Since Bartlett's initial experiments, a variety of well-defined noble gas compounds have been prepared and characterized, primarily of Xe, but some of Kr. The other elements present are usually O, F, or both, which makes sense given that O and F are the two most electronegative elements in the Periodic Table, and are thus most able to prevail upon a closed-shell Xe atom to use some of its valence electrons in bonding. Major examples of Xe compounds include the neutral fluorides XeF_2 ($D_{\infty h}$), XeF_4 (D_{4h}), and XeF_6 (C_{3v} , a distorted, not a regular octahedron),

the explosive oxides XeO_3 (C_{3v}) and XeO_4 (T_d), and the oxofluorides XeOF_2 , XeOF_4 , XeO_2F_2 , and XeO_3F_2 . Rare examples of compounds containing bonds between Xe and elements other than O or F include $[\text{F}_3\text{SNXeF}^+][\text{AsF}_6^-]$, with an Xe–N bond, and even the compounds $[\text{AuXe}_4^{2+}][\text{Sb}_2\text{F}_{11}^-]_2$ and *trans*- $\text{AuXe}_2(\text{SbF}_6)_2$, in which Xe acts as a ligand to gold in the (itself rare) Au(II) oxidation state. Compounds such as XeF_2 and XeF_4 are useful to synthetic chemists as convenient electrophilic fluorine sources (that is, sources of an F^+ moiety). For instance, XeF_4 reacts with SF_4 to form the very stable SF_6 , and XeF_2 reacts with PhI to form PhIF_2 . These reactions are similar on paper to fluorinations by F_2 itself, but the Xe compounds are much less dangerous to work with than the terrifyingly reactive F_2 .

Chapter 7: Introduction to Coordination Chemistry

7.1. Ligands and the Lewis Acid-Base Concept

We will now begin our study of coordination chemistry. Simply put, coordination chemistry is the study of compounds of metals with ligands. A ligand (from Latin *ligare*, “to bind”) is simply any atom, molecule, or ion that binds to a metal atom or ion. In most cases, a ligand has at least one fairly high-energy pair of electrons (a so-called “lone pair”) that can be donated into an empty orbital of a metal atom or ion.⁶³ Thus, coordination chemistry may be understood as a large and important subset of Lewis acid-base chemistry, with ligands as Lewis bases and metals as Lewis acids. In these cases, the resulting Lewis acid-base adducts are known as “coordination complexes,” or simply “complexes.” The bonding situation in transition metal (TM) complexes is different from that in main-group metal complexes, due to the involvement of *d* AOs in TM complexes. When we discuss the MO picture of bonding in coordination chemistry in chapter 8, we will focus on TM complexes, but the principles of nomenclature and isomerism discussed in this chapter hold just as well for main-group complexes.

7.2. Nomenclature, Ligand Charges, and Oxidation State

The vast majority of ligands are either neutral or anionic as closed-shell species (that is, species with no unpaired electrons that obey the octet rule at all non-H atoms). When naming coordination complexes, it is important to note that many ligands have different names when bound to a metal center than when they are free species. In general, free species whose names end in “-ide” correspond to ligands whose names end in “-ido,” *e.g.* chloride/chlorido, oxide/oxido, and azide/azido.⁶⁴ The suffix “-ate” usually becomes “-ato,” as in carbonate/carbonato, acetate/acetate. In general, multi-word names of free species have the spaces between words removed when named as ligands, so dimethyl sulfoxide as a ligand is dimethylsulfoxide, and methyl isocyanide as a ligand is methylisocyanide. A few ligands have

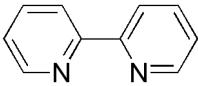
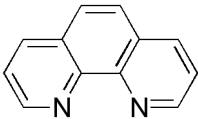
⁶³ Certain organic ligands, such as alkenes and arenes, can bind a metal center through a π -bonding MO, rather than a lone pair. This type of bonding will be discussed in chapter 13.

⁶⁴ In the older literature, “-ido” is sometimes replaced with simply “-o,” as in chloro and oxo for Cl^- and O^{2-} .

names when bound that are very different from their names as free species: water becomes aqua, ammonia becomes ammine (note the double “m,” though organic amines as ligands still have names ending in “-amine”), carbon monoxide becomes carbonyl, carbon monosulfide becomes thiocarbonyl, and nitrosonium, (NO^+ , one of the few examples of a cationic closed-shell ligand) becomes nitrosyl. Some ligands commonly encountered in coordination chemistry are listed in Table 7.1 below.

Table 7.1. Names and formulae of common ligands.

Formula	Name as free species	Name as bound ligand	Abbreviation
H^-	hydride	hydrido	
F^-	fluoride	fluorido (fluoro)	
Cl^-	chloride	chlorido (chloro)	
Br^-	bromide	bromido (bromo)	
I^-	iodide	iodido (iodo)	
N^{3-}	nitride	nitrido	
O^{2-}	oxide	oxido (oxo)	
S^{2-}	sulfide	sulfido	
N_3^-	azide	azido	
O_2^{2-}	peroxide	peroxido (peroxo)	
CN^-	cyanide	cyanido (cyano)	
CO	carbon monoxide	carbonyl	
SCN^-	thiocyanate	thiocyanato- κS (when bound to metal through S), thiocyanato- κN (when bound to metal through N)	
OH^-	hydroxide	hydroxido (hydroxo)	
H_2O	water	Aqua	
NH_3	ammonia	ammine	
NH_2^-	amide	Amido	
NH^{2-}	imide	imido	
CS	carbon monosulfide	Thiocarbonyl	
NO^+	nitrosonium	nitrosyl	
NO_2^-	nitrite	nitrito- κN (when bound to metal through N), nitrito- κO (when bound to metal through O)	
$\text{H}_3\text{C}-\text{CN}$	acetonitrile	acetonitrile	MeCN
$\text{H}_3\text{C}-\text{NC}$	methyl isocyanide	methylnisocyanide	MeNC
CH_3^-	methyl anion	methyl	Me^-
C_6H_5^-	phenyl anion	phenyl	Ph^-
	pyridine	pyridine	py or pyr
PH_3	phosphine	phosphine	
$\text{P}(\text{CH}_3)_3$	trimethylphosphine	trimethylphosphine	PMe_3
$\text{P}(\text{C}_6\text{H}_5)_3$	triphenylphosphine	triphenylphosphine	PPh_3
$(\text{C}_2\text{H}_5)_2\text{O}$	diethyl ether	diethylether	Et_2O

$(\text{CH}_3)_2\text{S}$	dimethyl sulfide	dimethylsulfide	Me_2S
$(\text{C}_2\text{H}_5)_2\text{S}$	diethyl sulfide	diethylsulfide	Et_2S
	tetrahydrofuran	tetrahydrofuran	THF or thf
$(\text{CH}_3)_2\text{SO}$	dimethyl sulfoxide	dimethylsulfoxide	DMSO or dmsO
NO_3^-	nitrate	nitrato	
SO_4^{2-}	sulfate	sulfato	
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	ethane-1,2-diamine (ethylenediamine)	ethane-1,2-diamine (ethylenediamine)	en
$(\text{H}_3\text{C})_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	<i>N,N,N',N'</i> -tetramethylethane- 1,2-diamine (tetramethylethylenediamine)	<i>N,N,N',N'</i> -tetramethylethane- 1,2-diamine (tetramethylethylenediamine)	TMEDA or tmeda
	2,2'-bipyridyl	2,2'-bipyridyl	bpy or bipy
	1,10-phenanthroline	1,10-phenanthroline	phen
$\text{O}_2\text{C}-\text{CO}_2^{2-}$	oxalate	oxalato	ox^{2-}
CO_3^{2-}	carbonate	carbonato	
$(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$	<i>P,P,P',P'</i> -tetraphenylethane- 1,2-diphosphine	<i>P,P,P',P'</i> -tetraphenylethane- 1,2-diphosphine	dppe

For neutral complexes, one simply lists the ligands in alphabetical order before the name of the metal, using the Greek-derived prefixes di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-, to specify number. If the name of the ligand already contains a numerical prefix, one of the alternate numerical prefixes, bis-, tris-, tetrakis-, pentakis-, hexakis-, heptakis-, octakis-, nonakis-, or decakis-. Finally, the oxidation state of the metal is specified in parentheses in Roman numerals. For instance, the drug cisplatin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, has the systematic name diamminedichloridoplatinum(II). To determine the metal's oxidation state, one first considers each ligand with the charge it would have as a closed-shell free species (see Table 7.1), and sums this over all the ligands. Next, one determines the number that one must add to the sum of ligand charges to yield the overall charge of the complex. This number is the metal's oxidation state. For $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, each NH_3 is neutral, but each Cl^- contributes -1 to the charge, for a sum of ligand charges of -2 . To yield an overall zero charge on this neutral complex, we must add $+2$, so Pt is in the $+2$ oxidation state and we say that cisplatin is a platinum(II) complex. When the metal is in the zero oxidation state, the Arabic numeral 0 is used (since there is no Roman numeral zero), so $\text{Ni}(\text{CO})_4$ is tetracarbonylnickel(0). In the (fairly rare) cases in which the metal is in a negative oxidation state, a negative sign is placed

before the Roman numeral: $\text{Cr}(\text{NO})_4$ has four NO^+ ligands, which together contribute a +4 charge, so Cr must be in the -4 oxidation state to compensate. The systematic name of this complex is tetranitrosylchromium(-IV).

Positively charged complexes (complex cations) are named using the same method, keeping in mind that the oxidation state is calculated so that the metal's oxidation state, added to the sum of ligand charges, equals the overall complex charge. For instance, the cation $\text{Cr}(\text{H}_2\text{O})_5\text{Br}^{2+}$ would be named pentaquabromidochromium(III). Each H_2O is neutral, and the Br^- contributes -1 to the charge, so a +3 oxidation state for Cr is needed to yield the overall +2 complex charge. When naming a salt of a complex cation, the anion is named after the cation, just as with simple salts. $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}](\text{NO}_3)_2$ is pentaquabromidochromium(III) nitrate.

With negatively charged complexes (complex anions), the name of the metal is changed to end in the suffix "-ate," and the metal's oxidation state is still given as Roman numerals in parentheses. Thus, PtCl_4^{2-} is tetrachloridoplatinate(II), and $\text{V}(\text{CO})_6^-$ is hexacarbonylvanadate(-I). When naming a salt, the name of the cation is given before that of the anion, even when the anion is complex, so $\text{K}_2[\text{PtCl}_4]$ is potassium tetrachloridoplatinate(II).

Some metals have anion names which are *not* derived from the full *name* of the element, but rather from the Latin word from which the element's *symbol* is derived. They are as follows:

Iron $\rightarrow$ Fe $\rightarrow$ *ferrum* $\rightarrow$ ferrate

Copper $\rightarrow$ Cu $\rightarrow$ *cuprum* $\rightarrow$ cuprate

Silver $\rightarrow$ Ag $\rightarrow$ *argentum* $\rightarrow$ argentate

Tin $\rightarrow$ Sn $\rightarrow$ *stannum* $\rightarrow$ stannate

Antimony $\rightarrow$ Sb $\rightarrow$ *stibium* $\rightarrow$ stibate (or sometimes antimonate)

Gold $\rightarrow$ Au $\rightarrow$ *aurum* $\rightarrow$ aurate

Lead $\rightarrow$ Pb $\rightarrow$ *plumbum* $\rightarrow$ plumbate

Note that, while mercury has the unusual chemical symbol Hg (from the Latinized Greek word *hydrargyrum*, which literally means "wet silver"), complex anions of mercury are

named as mercurates, not as “hydrargyrates.” Tungsten also has an unusual chemical symbol, W, from the German *Wolfram* (the German name for tungsten, after the tungsten ore wolframite). However, complex anions of tungsten are named as tungstates, not as “wolframates.”

There exist salts in which both the cation *and* the anion are coordination complexes. In such cases, the cation is again listed before the anion as usual. Thus, the salt $[\text{Co}(\text{H}_2\text{O})_6]^{2+}_3[\text{Fe}(\text{CN})_6]^{3-}_2$ is properly named as hexaaquacobalt(II) hexacyanidoferrate(III).

Some ligands have names that already contain a numerical prefix such as di-, tri-, *etc.* When naming complexes with more than one of such a ligand, the name of the ligand is put in parentheses, and a different set of numerical prefixes is used: bis-, tris-, tetrakis-, pentakis-, hexakis-, heptakis-, octakis-, and so on. For instance, $\text{Co}(\text{en})_3^{3+}$ is the tris(ethylenediamine)cobalt(III) cation, $\text{Pd}(\text{PPh}_3)_4$ is tetrakis(triphenylphosphine)palladium(0), and $\text{W}(\text{CO})_3(\text{PPh}_3)_3$ is tricarbonyltris(triphenylphosphine)tungsten(0).

7.3. Coordination Numbers and Isomerism

Isomerism is an important phenomenon in many fields of chemistry, including coordination chemistry. One type of isomerism that may not be familiar to you from your other chemistry courses is ionization isomerism, which often occurs in compounds containing a complex cation: in one isomer, one anionic species is coordinated to the metal as a ligand, while the other is associated as a counteranion, but is not directly bound to the metal center. In the other isomer, the anions switch roles. For example, the Co(III) compound $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{NO}_3$ consists of a $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]^+$ cation and an NO_3^- anion. Here SO_4^{2-} is bound to the Co(III) center as a ligand, while NO_3^- is associated with the complex cation only *via* ion-pairing interactions. In contrast, the coordination isomer $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$, still a Co(III) compound, contains a $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{2+}$ cation, in which NO_3^- is a ligand coordinated to Co, while the SO_4^{2-} is a counteranion.

The related phenomenon of coordination isomerism consists of the existence of salts where both the cation and anion are metal complexes, but where the ligands bound to each metal differ. The oxidation states of the metal centers can vary, as well. For example, $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$ contains a $\text{Co}(\text{en})_3^{3+}$ cation and a $\text{Cr}(\text{CN})_6^{3-}$ anion, while the coordination isomer $[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$ contains a $\text{Cr}(\text{en})_3^{3+}$ cation and a $\text{Co}(\text{CN})_6^{3-}$ anion. In this case, while the ligands bound to each metal change, the metals' oxidation states do not: each salt contains Cr(III) and Co(III). In contrast, consider the coordination isomer salts $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$ and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$. The first salt contains a Pt(II) cation, $\text{Pt}(\text{NH}_3)_4^{2+}$, and a Pt(IV) anion, PtCl_6^{2-} , while the second contains a Pt(IV) cation, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}$, and a Pt(II) anion, PtCl_4^{2-} .

Linkage isomerism is a type of isomerism which can occur in complexes of a ligand with more than one Lewis-basic site, *i.e.* one which can coordinate to a metal *via* either of two (or more) different atoms. Such ligands are commonly termed *ambidentate*. A classic example of an ambidentate ligand is nitrite, NO_2^- , which can bind *via* its N atom or by either of its two (equivalent) O atoms. The Co(III) complex cations $\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{2+}$, in which NO_2^- is N-bound, and $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$, in which it is O-bound, are linkage isomers of each other.

The above examples of isomerism in coordination compounds all fall into the category of constitutional isomerism, since the topologies of the element–element bonds (*i.e.* which atoms are bound to which other atoms) differ between isomers. Now, we consider stereoisomers, sets of molecules or ions in which the atoms are arranged differently in space, but in which the topologies of the element–element bonds do not differ. To discuss stereoisomers, we need to know what coordination geometries metal complexes can have. The answer is “almost any,” but for TM complexes, the most common coordination numbers and geometries by far are, in descending order, 6 (octahedral), 4 (tetrahedral), and 4 (square planar). If the complexes are homoleptic (all ligands are the same) and the metal–ligand bond lengths are all the same, then octahedral ML_6 has O_h symmetry, tetrahedral ML_4 has T_d symmetry, and square planar ML_4 has D_{4h} symmetry. These ideal geometries are shown in Figure 7.1 below, and the bonding in such complexes will be discussed in chapter 8. If the complexes are heteroleptic (containing more than one type of ligand), or if the metal–ligand

bond lengths are not all the same, then they will belong to point groups of lower symmetry, but they will still be roughly octahedra, tetrahedral, or square planar, and we will continue to refer to them as such.

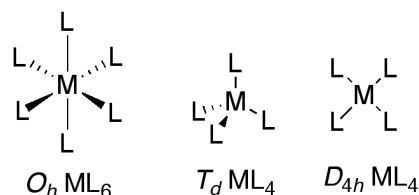


Figure 7.1. General structures of homoleptic octahedral, tetrahedral, and square planar metal complexes.

In tetrahedral complexes, the only type of stereoisomerism possible occurs when a complex contains four ligands of different types (formula MABCD). Such a complex is chiral, and it can exist as either the *R* or the *S* enantiomer, just like an organic compound in which a carbon atom has four different substituents. With octahedral and square planar complexes, on the other hand, if at least two different ligands are of the same type, their stereochemistry can be classified as either *cis* or *trans*, depending on whether the metal–ligand bonds are at (approximately) 90° to each other (*cis*) or approximately 180° to each other (*trans*). This type of *cis/trans* stereoisomerism is best demonstrated by some generic examples, as shown in Figure 7.2 on the following page. There is considerable practical importance to *cis/trans* isomerism. The Pt(II) complex *cis*-Pt(NH₃)₂Cl₂, commonly known as cisplatin, is an effective drug for the treatment of many types of cancer, one of the very few widely used pharmaceuticals with no carbon atoms in its formula. In contrast, its *trans* isomer is both generally toxic and ineffective as a cancer treatment. (See chapter 22 for a discussion of the mechanism of action of cisplatin.)

In octahedral complexes with three of a given ligand, the ligands can define a single face of the octahedron, in which case the stereochemistry is termed facial or *fac*. Alternatively, they can define a meridional plane (one which divides the entire complex in half), in which case the stereochemistry is termed meridional or *mer*. The *fac* and *mer* isomers of Co(NH₃)₃Cl₃ are shown in Figure 7.3 on the following page.

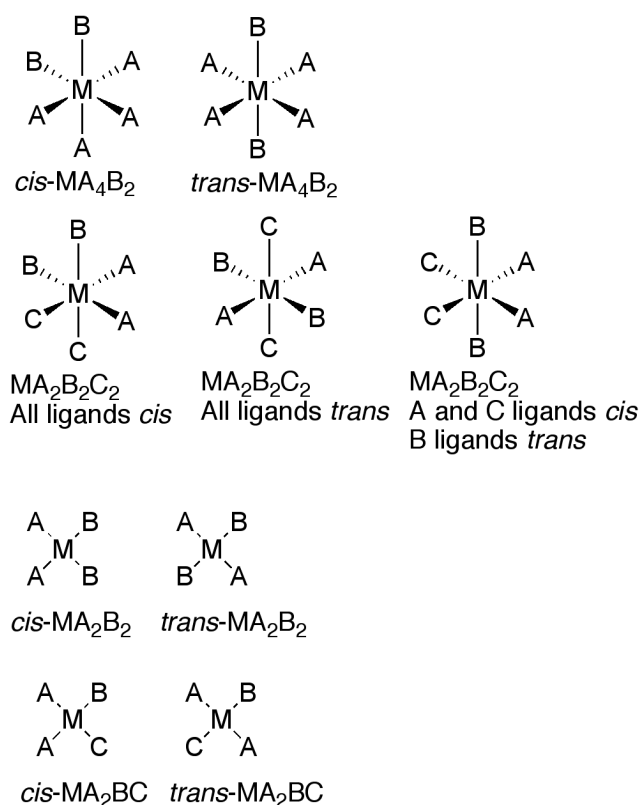


Figure 7.2. The *cis* and *trans* stereoisomers of octahedral and square planar metal complexes.

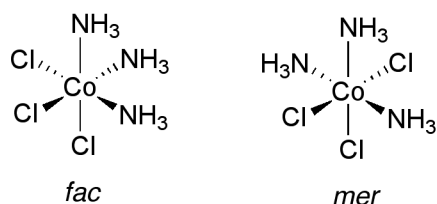


Figure 7.3. The *fac* and *mer* stereoisomers of $Co(NH_3)_3Cl_3$.

7.4. Chelating Ligands and the Chelate Effect

Many common ligands, such as ethylenediamine and 2,2'-bipyridyl, are *bidentate*, meaning that they have two Lewis-basic sites by which they may coordinate a *single* metal center. (This case should be contrasted with an ambidentate ligand such as SCN^- , which has two Lewis-basic sites, but these sites cannot coordinate the same metal center simultaneously, due to the ligand's linear geometry.) Such ligands are commonly known as chelating ligands or chelators, and their complexes as chelates. These terms have a rather picturesque origin,

since they are derived from the Greek word $\chi\eta\lambda\acute{\eta}$, meaning “crab’s claw.” The image suggested is that of the ligand grasping the metal like a pincer.

Ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (commonly abbreviated as “en” in shorthand formulae), can be used to illustrate a general trend, commonly known as the “chelate effect,” according to which chelating ligands tend to bind metals more strongly than similar monodentate ligands. We will see in chapter 8 that different ligands can bind to metal centers with different strengths based on considerations such as the identities of the donor atom and metal center and the level of orbital overlap in covalent bonding. However, the chelate effect applies even when the chelating and monodentate ligands are electronically very similar. Consider the reaction $\text{Ni}(\text{NH}_3)_6^{2+}(\text{aq}) + 3 \text{ en}(\text{aq}) \rightleftharpoons \text{Ni}(\text{en})_3^{2+}(\text{aq}) + 6 \text{ NH}_3(\text{aq})$, in which six monodentate NH_3 ligands are replaced by three en ligands, each of which binds the Ni center through both N atoms. It is reasonable to suppose that the Ni–N bonds in the octahedral complexes $\text{Ni}(\text{NH}_3)_6^{2+}$ and $\text{Ni}(\text{en})_3^{2+}$ should have similar strength, since the lone pair-bearing N atoms in NH_3 and en are electronically similar. Indeed, the above ligand substitution reaction is only weakly exothermic, with $\Delta H^\circ = -12.1 \text{ kJ} \cdot \text{mol}^{-1}$.

Despite the fact that this reaction is only slightly exothermic, it is very favorable indeed at 298 K, with an equilibrium constant of $K = 4.68 \times 10^9$ at that temperature. This is because it has a large, positive standard-state entropy change: $\Delta S^\circ = 145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Since $\Delta G^\circ = -RT \ln K$, we see that the reaction has $\Delta G^\circ = -55.1 \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K, and we can use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to compare the enthalpic and entropic contributions to ΔG° : $\Delta H^\circ = -12.1 \text{ kJ} \cdot \text{mol}^{-1}$ and $-T\Delta S^\circ = -43.0 \text{ kJ} \cdot \text{mol}^{-1}$. Thus, at 298 K, the entropic contribution to ΔG° is almost four times as large as the enthalpic one, making the reaction predominantly entropy-driven.

Why does this reaction have such a favorable entropy change? One can certainly discuss entropy at a mathematically detailed level, in terms of microstates and partition functions, but in many cases, including this one, a straightforward, qualitative argument will suffice: we may simply note that there are four molecules among the reactants (the starting Ni complex and 3 en) and seven molecules among the products (the product Ni complex and 6 NH_3). By

increasing the number of free-floating molecules in solution by 3, this reaction has significantly increased the system's number of degrees of freedom, corresponding to a higher net "disorder" or entropy. In general, chelating ligands will bind metals more strongly than monodentate ligands with electronically similar donor atoms, for entropic reasons. Note here that "binding more strongly" refers to the equilibrium constant for complex formation, not to bond dissociation energy (which is related to changes in internal energy or enthalpy, *not* entropy). This is the thermodynamic reason for the chelate effect.

Some chelating ligands contain more than two Lewis-basic atoms that can bind a single metal center. A common tridentate ligand with three Lewis-basic sites is 1,4,7-triazaheptane (commonly known as diethylenetriamine, or dien for short), $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$. Similarly, 1,4,7,10-tetraazadecane (commonly known as triethylenetetramine, or trien for short), $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, is a common tetradentate ligand. An important class of polydentate chelating ligands are the so-called macrocyclic ligands or macrocycles, in which the Lewis-basic atoms are all part of a ring system in the free ligand, as opposed to merely forming a ring when coordinating to the metal. The coordination of a macrocyclic ligand to a metal is often associated with an even more positive ΔS° than that of an acyclic chelating ligand. An acyclic chelating ligand will have to lose a certain amount of freedom of motion for its "arms" to coordinate to the metal, and there is an entropy cost to this. A macrocycle, however, is already a ring, and the metal can simply fit inside the ring. In a sense, the entropy cost was already paid when the macrocyclic molecule was synthesized from acyclic starting materials, and there is very little additional entropy cost (further organization) when it binds a metal. The crown ethers discussed in Section 6.2, which bind strongly to alkali metal ions, are some of the most famous and frequently encountered macrocycles.

The presence of chelating ligands can lead to new types of isomerism: species of the form $\text{M}(\text{L-L})_3^{n+}$, where L-L is a symmetrical bidentate ligand such as en or bpy, usually display "octahedral coordination," but their actual point group is D_3 . Molecules in this point group are chiral, so each species of this sort can exist as either of two enantiomers. Common real

examples include $\text{Co}(\text{en})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^{2+}$. The basic symmetry of such complexes are shown in Figure 7.4 below.

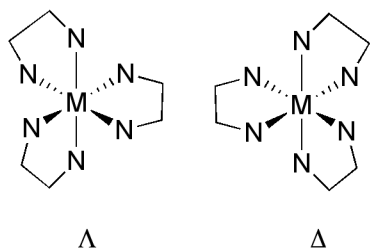


Figure 7.4. The enantiomers of metal complexes of the $\text{M}(\text{L-L})_3^{n+}$ kind.

One way to understand the chirality in such complexes is to compare their structures to the shape of a propeller on a motorboat. The propeller is chiral, and if it turns one way, the boat goes forward, while if it turns the other way, the boat goes in reverse. If one equipped a boat with the enantiomer of the propeller, one would have to turn it in the opposite direction to make the boat go forward. We assign the chirality labels as follows: for each bidentate ligand, pick the donor atom that is closer to you (either coming out of the page, or at least not going into the page). Now go around the structure from closer atom to closer atom, always going in the direction that finds each closer atom's partner atom (the other donor atom on the same ligand molecule) before it finds the closer atom on the next ligand molecule. If you go counterclockwise, the configuration is labeled Λ (lambda); if you go clockwise, the configuration is labeled Δ (delta).

Chapter 8: Ligand Field Theory

8.1. Crystal Field Theory

We will now proceed to a discussion of the electronic structure and bonding in TM complexes. We have seen, in chapter 3, several illustrative examples of how symmetry principles are used to prepare MO diagrams, as well as the algebraic forms of some LCAO-MOs themselves, for main-group molecules. The general behavior of TM AOs in complexes is known as ligand field theory (LFT), whose name comes from the fact that the fivefold degeneracy of a TM atom or ion's d AOs is lifted, at least partially, by the electrostatic "field" of the ligands around it. Modern treatments of LFT are a type of MO theory, in which the bonding in TM complexes is treated similarly to the bonding in main-group species, with the key difference being that the d AOs of the central TM are now considered to be valence orbitals. Historically, however, the electronic structure of TM complexes was first discussed in terms of a simpler model called crystal field theory (CFT). Many of the assumptions of CFT are quite heavy ones, and CFT will not yield quantitatively accurate results in the way that high-level MO calculations will. Nevertheless, much of the terminology of CFT persists in more sophisticated treatments, and we will see that the symmetry arguments used in CFT are precisely the same symmetry arguments used in an MO treatment.

CFT was first proposed in 1929 by Hans Bethe (1906-2005, Nobel Prize in Physics 1967) as a model to help explain the electronic spectra of TM ions in salts, which varied from those of free TM atoms or ions. Bethe's model was extended by John Hasbrouck Van Vleck (1899-1980, Nobel Prize in Physics 1977), who realized that the symmetry ideas of Bethe's CFT were still valid in systems in which some of Bethe's assumptions were no longer quantitatively accurate. Van Vleck also used the results of CFT to rationalize the magnetic properties of TM compounds.

The central assumption of CFT is that the only interactions between a TM atom or ion and its ligands are electrostatic, that is, that there is *no* TM-ligand covalent bonding. This assumption is clearly not a good one for many molecular TM complexes, but it is a reasonable

first approximation for crystals containing anions of strongly electronegative elements, such as FeCl_3 or CoCl_2 : while there is not precisely zero covalent interactions in these crystals, the majority of their energetic stabilization comes from Coulombic attraction between the TM cations and the Cl^- anions. One can then extend this idea to consider molecular TM complexes, which contain ligands that are either anionic (*e.g.* Cl^-) or dipolar (*e.g.* NH_3), with the negative end of the dipole lined up with the TM cation.

CFT treats the electronic structure of the TM ion explicitly, but it considers the ligands as only point charges or line dipoles. If the TM ion has n electrons and atomic number Z , and there are N anionic ligands, each of which has charge q_i , then the CFT Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + W + V$$

Here $\hat{H}_0$ is the “zeroth-order” Hamiltonian for the free TM ion, which takes into account the kinetic energy of the electrons and the nucleus, the attractions between the electrons and the nucleus, and the Coulombic repulsion between the electrons. W is the electrostatic attraction between the central TM nucleus and the anionic ligands (note that, in the absence of covalent bonding, this attraction is the reason the complex is stable), given by

$$W = \sum_{i=1}^N \frac{Ze q_i}{4\pi\epsilon_0 R_i}$$

where R_i is the distance between the TM nucleus and each ligand i . We can see that $W < 0$ (this is a stabilizing interaction), since $q_i < 0$ for the common anionic ligands, and the charge on the TM nucleus is $Ze > 0$. The V term represents the interaction energy between each TM electron j and each ligand i , and it is given by

$$V = - \sum_{i=1}^N \sum_{j=1}^n \frac{e q_i}{4\pi\epsilon_0 |\mathbf{r}_j - \mathbf{R}_i|}$$

where $\mathbf{r}_j$ is the position vector of electron j and $\mathbf{R}_i$ is the position vector of ligand i . This is a repulsive interaction ($V > 0$): while the complex is overall stabilized by the Coulombic attractions between the anionic ligands and the TM nucleus, each electron in the TM ion is made higher in energy by interaction with the ligands.

CFT is a form of perturbation theory that treats the ligand charges as a perturbation to $\hat{H}_0$. The attractive perturbation W is independent of the spatial coordinates for each electron, so it does not lead to a breaking of the fivefold degeneracy of a set of d AOs. The repulsive perturbation V , however, does depend on the electronic coordinates, so it will make some AOs in a given d subshell higher in energy than others. Thus, for a d^1 TM ion, we solve a degenerate perturbation theory problem, with the degenerate zeroth-order wavefunctions ψ_m and $\psi_{m'}$ being d AO wavefunctions with m and m' each being equal to $-2, -1, 0, 1$, or 2 . (Note that these are not the all-real d wavefunctions that chemists commonly use to visualize orbital interactions.) This results in the secular determinantal equation

$$\begin{vmatrix} V_{2,2} - E & V_{2,1} & V_{2,0} & V_{2,-1} & V_{2,-2} \\ V_{1,2} & V_{1,1} - E & V_{1,0} & V_{1,-1} & V_{1,-2} \\ V_{0,2} & V_{0,1} & V_{0,0} - E & V_{0,-1} & V_{0,-2} \\ V_{-1,2} & V_{-1,1} & V_{-1,0} & V_{-1,-1} - E & V_{-1,-2} \\ V_{-2,2} & V_{-2,1} & V_{-2,0} & V_{-2,-1} & V_{-2,-2} - E \end{vmatrix} = 0$$

where E is the energy of an electron in one of the d AOs after the perturbation, and the other matrix elements $V_{m,m'}$ are given by

$$V_{m,m'} = \langle \psi_m | V | \psi_{m'} \rangle = - \sum_{i=1}^N \frac{eq_i}{4\pi\epsilon_0} \left\langle \psi_m \left| \frac{1}{\mathbf{r} - \mathbf{R}_i} \right| \psi_{m'} \right\rangle$$

Note that there is only one summation, over the ligands, in the above equation, since these are matrix elements for a system with only one d electron. From here, the details of the solution depend on the number and coordinates of the ligands, which will be different for different geometries (octahedral, tetrahedral, *etc.*)

Let us now consider a d^1 TM complex with octahedral (O_h) symmetry, with 6 of the same ligand (each with charge q) arranged around the central TM, so that the ligands define the vertices of a regular octahedron. It is convenient to consider the TM as being at the center of a Cartesian coordinate system, with two ligands lying along each axis: the ligands thus have coordinates $(R, 0, 0)$, $(-R, 0, 0)$, $(0, R, 0)$, $(0, -R, 0)$, $(0, 0, R)$, and $(0, 0, -R)$. The calculation of

the matrix elements and solution of the secular determinant are laborious,⁶⁵ but once these calculations are complete, we see that two energy values are obtained. One energy value corresponds to a pair of d AOs with e_g symmetry, and another corresponds to a trio of d AOs with t_{2g} symmetry. The energies are given by

$$E(e_g) = E_0 + \frac{3}{5}\Delta_o$$

$$E(t_{2g}) = E_0 - \frac{2}{5}\Delta_o$$

Here E_0 is *not* the energy of an electron in a d AO of a free TM ion. Instead, it is the energy that a d electron would have if the charge distribution from the ligands were spherically symmetrical, rather than octahedral. Thus, as a set, the d AOs are raised in energy (due to Coulombic repulsion) compared to a free TM ion. The quantity E_0 is sometimes called the “center of gravity” or “barycenter.” However, once the spherical symmetry is changed to octahedral (with the total charge from all the ligands being the same), three d AOs (with symmetry label t_{2g}) are lowered in energy by $\frac{2}{5}\Delta_o$ each, while the other two d AOs (with symmetry label e_g) are raised in energy further by $\frac{3}{5}\Delta_o$ each. Here Δ_o , a positive quantity with dimensions of energy, formed as a linear combination of definite integrals, is called the octahedral ligand field (or crystal field) splitting parameter. (The capital delta indicates a change or difference, and the O subscript is short for “octahedral.”) The raising of d AO energies, followed by their partial loss of degeneracy, can be depicted pictorially in Figure 8.1 on the following page. Note that the *average* energy of the five d AOs following the splitting is still E_0 ; the move to a spherical field of negative charge gives the overall increase in total energy, while the move from a spherical to an octahedral field partially lifts the degeneracy.

⁶⁵ For the details, see Chapter 4 and Appendices 2 and 3 of *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, 2nd edition, by Isaac B. Bersuker, John Wiley & Sons: Hoboken, NJ, 2010.

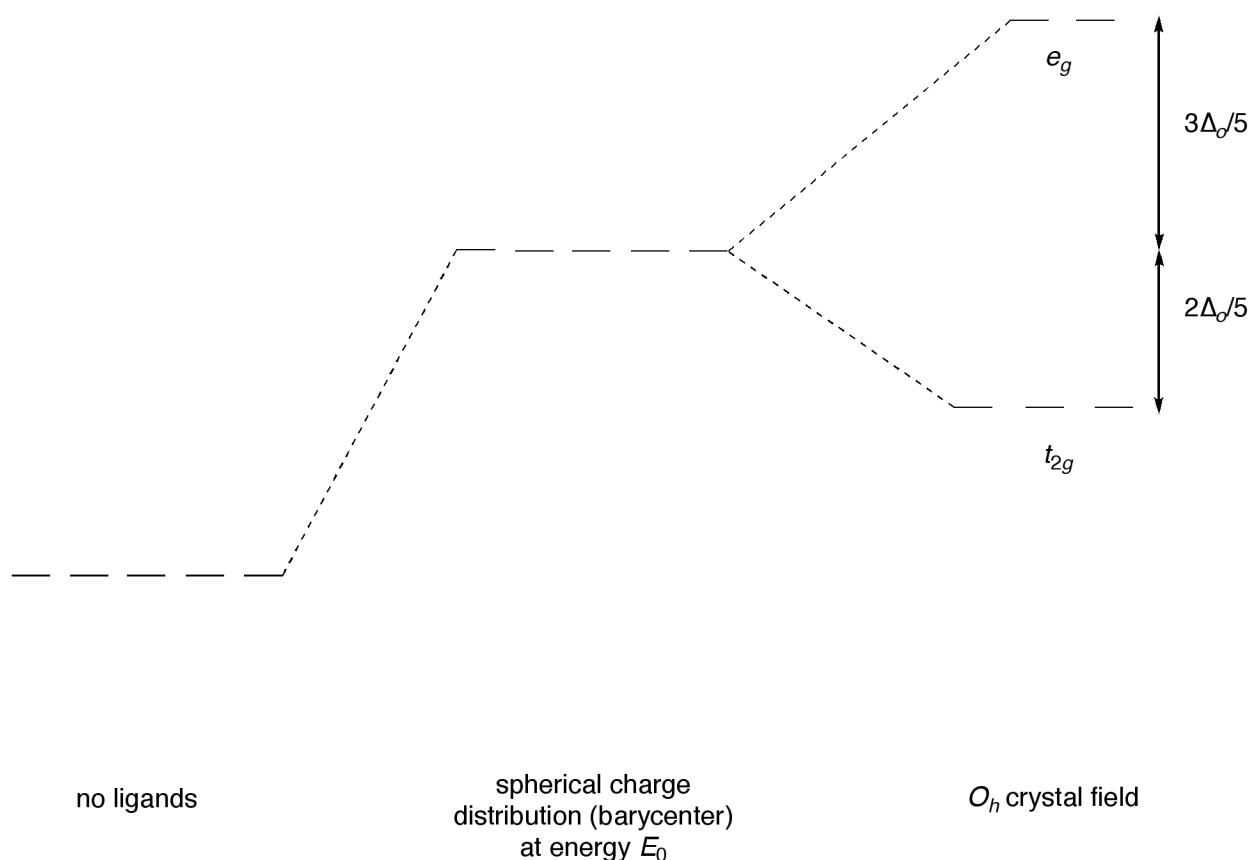


Figure 8.1. Splitting of d AOs in a crystal field of O_h symmetry.

When the correct linear combinations of the canonical d AOs are taken, one finds that the t_{2g} d AOs are the familiar, all-real d_{xy} , d_{yz} , and d_{xz} wavefunctions, while the e_g d AOs are the (also all-real) $d_{2z^2-x^2-y^2}$ (commonly abbreviated as d_{z^2}) and $d_{x^2-y^2}$. This result could be anticipated by examining the rightmost column of the O_h character table (shown as Table 8.1 on the following page) and noting that (xy, yz, xz) transform together as T_{2g} , while $(2z^2 - x^2 - y^2, x^2 - y^2)$ transform together as E_g . When transformation matrices are prepared for symmetry operations acting on a set of d AOs in O_h symmetry, and their characters are calculated to form a reducible representation Γ_d , it is found that $\Gamma_d = E_g + T_{2g}$.

One can appreciate visually how it is plausible that an electron in one of the t_{2g} set of d AOs will be repelled by ligand charges less than one in an e_g AO. The t_{2g} d AOs all have lobes that point between the Cartesian axes along which the ligands lie, so the regions of maximum electron density for each of these orbitals will not be pointing directly at the negatively

charged ligands. In contrast, the e_g d AOs all have lobes lying directly along one or more Cartesian axes: the x and y axes for $d_{x^2-y^2}$, and primarily the z axis for d_{z^2} . The degeneracy of $d_{x^2-y^2}$ and d_{z^2} is not obvious visually, but it is ensured by the O_h symmetry of the system.

Table 8.1. The character table for the O_h point group.

O_h	$\hat{E}$	$8\hat{C}_3$	$6\hat{C}_2$	$6\hat{C}_4$	$3\hat{C}_2$ ($=\hat{C}_4^2$)	$\hat{i}$	$6\hat{S}_4$	$8\hat{S}_6$	$3\hat{\sigma}_h$	$6\hat{\sigma}_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	0	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	0	-1		

The most common coordination geometry for TM complexes is octahedral ML_6 , which, as previously noted, gives molecules or ions with O_h symmetry as long as all ligands L are identical (and lower-symmetry point groups for heteroleptic complexes). The second most common coordination geometry is tetrahedral ML_4 . If all ligands L are identical, this leads to complexes with T_d symmetry, where each ligand is the vertex of a regular tetrahedron. One can imagine the TM center lying at the origin of a Cartesian coordinate system, each of whose axes passes, perpendicularly, through each of two faces of a cube. One then inscribes a tetrahedron in the cube, with the ligands lying on alternating vertices of the cube. This is the same coordinate system that we used in Section 3.5 when we considered the MO treatment of CH_4 .

When $d^1 T_d ML_4$ complexes are thus treated with CFT and the secular equation of degenerate perturbation theory is solved, it is found once again that the previously fivefold degenerate set of d AOs is split into a doubly degenerate set and a triply degenerate set, with energies

$$E(t_2) = E_0 + \frac{2}{5}\Delta_T$$

$$E(e) = E_0 - \frac{3}{5}\Delta_T$$

The correct linear combinations of the canonical d AOs for this perturbation consist of the lower-energy e AOs, d_{z^2} and $d_{x^2-y^2}$, and the higher-energy t_2 AOs, d_{xy} , d_{yz} , and d_{xz} . Note that, in this case, the triply degenerate set of AOs lies higher in energy than the doubly degenerate one, which is the opposite of what is observed for O_h symmetry. Note also the lack of a “ g ” subscript of the orbital labels, since the T_d point group lacks an inversion center. Figure 8.2 below shows the relevant energy levels. As before, E_0 is the energy of the d AOs in a spherical field (the “barycenter”), and Δ_T is the tetrahedral ligand field splitting parameter (T for “tetrahedral”). Once the spherical symmetry is reduced to tetrahedral, the e AOs are lowered in energy by $\frac{3}{5}\Delta_T$ each, and the t_2 AOs are raised in energy by $\frac{2}{5}\Delta_T$ each.

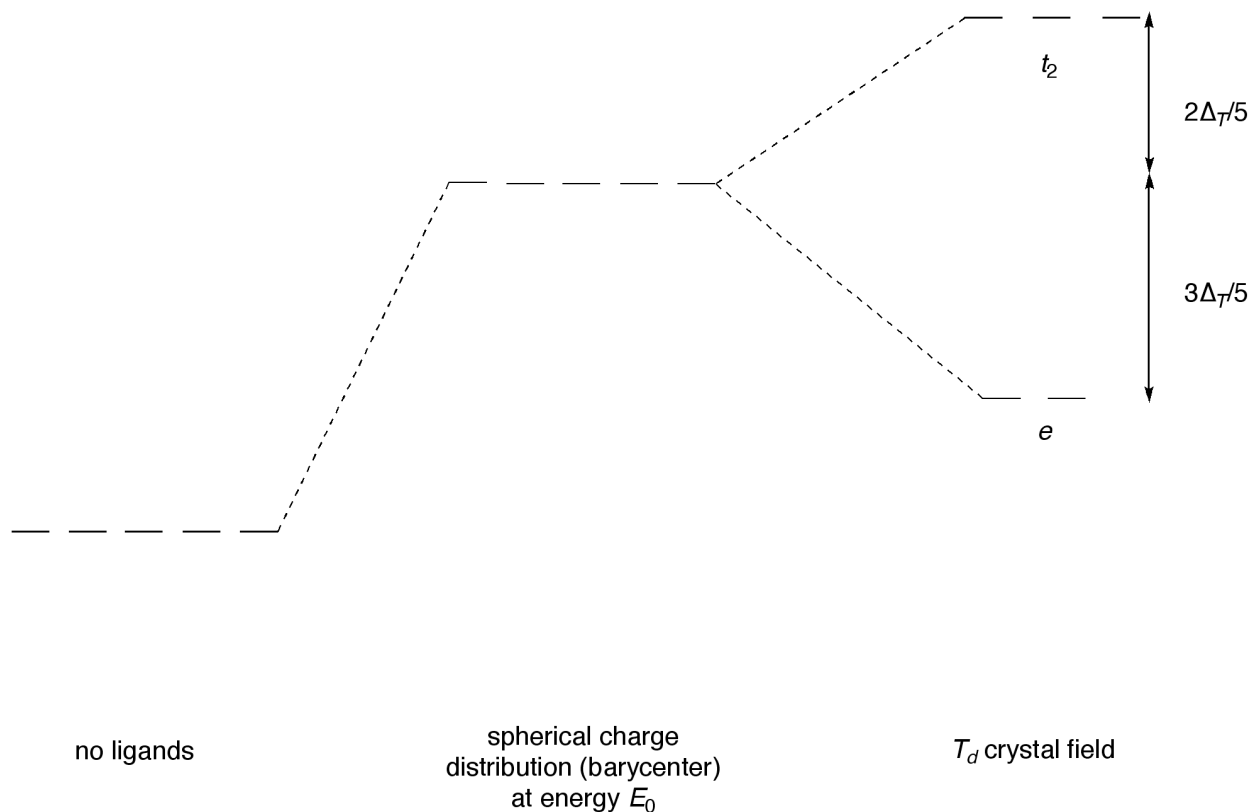


Figure 8.2. Splitting of d AOs in a crystal field of O_h symmetry.

As with the O_h problem, we can deduce the symmetry species of the d AOs in T_d by examining the rightmost column of the T_d character table, shown as Table 8.2 below.

Table 8.2. The character table for the T_d point group.

T_d	$\hat{E}$	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

In general, T_d complexes have their d AOs perturbed less than O_h complexes do. E_0 , the extent to which d AO energies are raised in a hypothetical spherical field of negative charge, is smaller for T_d than for O_h . If the metal, ligands and metal-ligand distances are the same between O_h ML_6 and T_d ML_4 , then

$$E_0(T_d) = E_0(O_h)$$

This makes sense, since, for the same type of ligand, a T_d complex with 4 ligands has only $\frac{4}{6} = \frac{2}{3}$ the negative charge around it than an O_h complex with 6 ligands does. The degree to which the fivefold degeneracy is broken is similarly less in T_d than in O_h : again assuming that the metal, ligands, and bond distances remain the same, we have

$$\Delta_T = \frac{4}{9} \Delta_O$$

The factor of $\frac{4}{9}$ is obtained through calculation, but it qualitatively makes sense that the energetic differentiation of d AOs in T_d should be less significant than in O_h , since in T_d none of the lobes of the AOs point directly at the ligands the way the e_g AOs in O_h do. It is also important not to take the factor of $\frac{4}{9}$ too literally. It is derived assuming that the metal, oxidation state, ligands, and metal-ligand bond distances are exactly the same between O_h ML_6 and T_d ML_4 complexes, and the chances that a single metal and set of ligands would form stable complexes of both geometries is quite low. Even if such a pair of ML_6 and ML_4 complexes existed, the $\frac{4}{9}$ factor still depends on the assumption underlying CFT, namely, that there is zero covalent interaction between the metal and ligands. Nonetheless, this result

correctly indicates that most spectroscopically-measured Δ_T values are considerably smaller than most Δ_O values.

While O_h and T_d are the most common point groups for homoleptic TM complexes, they are far from the only one. To see how the d AOs of the central TM will split (lose degeneracy) in a complex of any symmetry, you can simply examine the rightmost column of the character table for the complex's point group to see how the products of Cartesian vectors corresponding to the d AOs transform. For example, a square planar complex ML_4 (the third most common coordination geometry) belongs to D_{4h} if it is homoleptic. From the D_{4h} character table, we see that the d AOs lose almost all of their degeneracy, transforming as a_{1g} (d_{z^2}), b_{1g} ($d_{x^2-y^2}$), b_{2g} (d_{xy}), and e_g (d_{xz} , d_{yz}). The relative energies of the d AOs can only be ascertained by a calculation involving the evaluation of matrix elements and the solution of a secular determinantal equation of perturbation theory. However, one can often make a reasonable guess as to at least the ordering of the d AO energies by looking at which d AOs will have lobes closer to the negatively charged (or dipolar) ligands. The CFT energy ordering of d AOs in various coordination geometries can be found in various tables,⁶⁶ but it is often easier to reckon based on an MO approach that reflects covalent bonding, as we will see in Sections 8.3 through 8.5.

8.2. Electron Configurations of TM Complexes

The CFT which we considered in the preceding section implicitly assumed that we were dealing with a d^1 TM complex, that is, that in the ground state only one electron was present in the d -type AOs. While many d^1 TM complexes do exist, the majority of TM complexes have a d electron count of d^2 or higher. To understand the chemical and spectroscopic behavior of such complexes, we need to be able to determine their d AO configurations, that is, the number of electrons in each d -type AO or degenerate set of AOs.

⁶⁶ See, for instance, page 91 of *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, 2nd edition, by Isaac B. Bersuker, John Wiley & Sons: Hoboken, NJ, 2010.

We have seen that, in an O_h ML_6 complex, the d AOs of the central TM are split into a lower-energy t_{2g} set and a higher-energy e_g set, while in a T_d ML_4 complexes, they are split into a lower-energy e set and a higher-energy t_2 set. Before using CFT to determine the d electron configuration of a complexes, we must first determine the d electron count. This quantity is equal to the group number of the TM minus its oxidation state. For instance, the $FeCl_4^-$ complex anion can be considered to arise from an Fe^{3+} cation and four Cl^- anions as ligands, so the oxidation state of Fe is +3, and we describe $FeCl_4^-$ as an Fe(III) species. Since Fe is in Group 8 of the Periodic Table, its d electron count is $8 - 3 = 5$, so $FeCl_4^-$ is a d^5 species. Similarly, CoF_6^{3-} can be considered to arise from a Co^{3+} cation and six F^- anions as ligands, so the oxidation state of Co is +3, and we describe CoF_6^{3-} as a Co(III) species. Since Co is in Group 9 of the Periodic Table, its d electron count is $9 - 3 = 6$, so CoF_6^{3-} is a d^6 species.

As we saw when drawing MO diagrams for main-group molecules, one generally fills lower-energy orbitals first. Let us begin by considering O_h complexes. A d^1 complex will have the ground-state electron configuration $(t_{2g})^1(e_g)^0$, a d^2 complex will have $(t_{2g})^2(e_g)^0$, and a d^3 complex will have $(t_{2g})^3(e_g)^0$. For a d^4 complex, however, we have two possible options for the ground state. The fourth d electron might go into the t_{2g} set, thus making one of the t_{2g} orbitals doubly occupied, giving the configuration $(t_{2g})^4(e_g)^0$. Alternatively, this electron might go into the e_g set instead, giving the configuration $(t_{2g})^3(e_g)^1$. There is an energetic cost to each of these configurations. It makes sense that, for $(t_{2g})^3(e_g)^1$, there is an energetic cost to placing an electron into one of the e_g orbitals, each of which lies higher in energy than the t_{2g} trio by Δ_o . However, in the $(t_{2g})^4(e_g)^0$ configuration, one of the t_{2g} orbitals is doubly occupied, and this pairing of electrons leads to a Coulombic repulsion. We can associate this Coulombic repulsion with a quantity called the pairing energy Π (this is essentially equivalent to the Coulomb energy Π_c in Section 1.7). If $\Pi > \Delta_o$, then it is energetically more favorable to place the fourth electron in an e_g orbital, avoiding the pairing energy, so the ground-state configuration will be $(t_{2g})^3(e_g)^1$. This is called a high-spin ground state, since there are four unpaired electrons for a net spin of $S = 4 \left(\frac{1}{2}\right) = 2$. In contrast, if $\Pi < \Delta_o$, it is energetically more favorable to place the fourth electron in a t_{2g} orbital, to avoid the crystal field splitting Δ_o , so the ground-state configuration will be $(t_{2g})^4(e_g)^0$. This is called a low-

spin ground state, since there are only two unpaired electrons, for a net spin of $S = 2\left(\frac{1}{2}\right) = 1$. It turns out that, for the d electron counts d^4 , d^5 , d^6 , and d^7 , both high- and low-spin ground states are possible; which is lower in energy for a particular complex depends on the metal, oxidation state, and ligands. A table of possible ground-state d electron configurations for O_h ML_6 complexes is shown in Table 8.3 below. (See the following text for explanations of the spin-only magnetic moment μ_S and the term symbol.)

Table 8.3. Possible ground-state d electron configurations for O_h complexes.

d^n	d electron configuration	Number of unpaired electrons	$\frac{\mu_S}{\mu_B}$	Term symbol
d^0	$(t_{2g})^0(e_g)^0$	0	0	$^1A_{1g}$
d^1	$(t_{2g})^1(e_g)^0$	1	$\sqrt{3} \approx 1.73$	$^2T_{2g}$
d^2	$(t_{2g})^2(e_g)^0$	2	$2\sqrt{2} \approx 2.83$	$^3T_{1g}$
d^3	$(t_{2g})^3(e_g)^0$	3	$\sqrt{15} \approx 3.87$	$^4A_{2g}$
d^4 (high-spin)	$(t_{2g})^3(e_g)^1$	4	$2\sqrt{6} \approx 4.90$	^5E_g
d^4 (low-spin)	$(t_{2g})^4(e_g)^0$	2	$2\sqrt{2} \approx 2.83$	$^3T_{1g}$
d^5 (high-spin)	$(t_{2g})^3(e_g)^2$	5	$\sqrt{35} \approx 5.92$	$^6A_{1g}$
d^5 (low-spin)	$(t_{2g})^5(e_g)^0$	1	$\sqrt{3} \approx 1.73$	$^2T_{2g}$
d^6 (high-spin)	$(t_{2g})^4(e_g)^2$	4	$2\sqrt{6} \approx 4.90$	$^5T_{2g}$
d^6 (low-spin)	$(t_{2g})^6(e_g)^0$	0	0	$^1A_{1g}$
d^7 (high-spin)	$(t_{2g})^5(e_g)^2$	3	$\sqrt{15} \approx 3.87$	$^4T_{1g}$
d^7 (low-spin)	$(t_{2g})^6(e_g)^1$	1	$\sqrt{3} \approx 1.73$	^2E_g
d^8	$(t_{2g})^6(e_g)^2$	2	$2\sqrt{2} \approx 2.83$	$^3A_{2g}$
d^9	$(t_{2g})^6(e_g)^3$	1	$\sqrt{3} \approx 1.73$	^2E_g
d^{10}	$(t_{2g})^6(e_g)^4$	0	0	$^1A_{1g}$

High-spin complexes are sometimes known as weak-field complexes, since the crystal field splitting Δ_o is small (weak) compared to the pairing energy Π . Conversely, low-spin complexes are sometimes known as strong-field complexes. The values of Δ_o for different complexes can be measured by UV-visible spectroscopy. In general, complexes of TMs from the second transition series (Y-Cd) and third transition series (Lu-Hg) have larger Δ_o values than those from the first transition series (Sc-Zn), assuming the same ligands and oxidation state. For a given metal and set of ligands, an increase in metal oxidation state leads to a

larger value of Δ_o . For instance, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, an Fe(II) species, has $\Delta_o = 9350 \text{ cm}^{-1}$, while $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, an Fe(III) species, has $\Delta_o = 14000 \text{ cm}^{-1}$. For a given metal and oxidation state, certain ligands tend to give higher values of Δ_o than others. A list of ligands in increasing typical order of Δ_o is commonly known as a spectrochemical series, and a spectrochemical series for some common ligands is $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{OH}^- < \text{RCO}_2^- < \text{F}^- < \text{H}_2\text{O} < \text{NCS}^- < \text{NH}_3 < \text{en} < \text{PPh}_3 < \text{CO}, \text{CN}^-, \text{H}^- < \text{SnCl}_3^-$. The relative positions of different ligands in the spectrochemical series cannot be adequately explained with CFT, but when we discuss MO theory for TM complexes, we will see why some ligands are strong-field and others are weak-field.

In principle, T_d complexes with d electron counts d^3 through d^6 can have either high- or low-spin ground states. However, almost all T_d complexes known with these d electron counts are high-spin, since Δ_T values are, in general, considerably smaller than Δ_o values, so they are almost always smaller than the pairing energy Π . A table of ground-state d electron configurations for $T_d \text{ ML}_4$ complexes is shown in Table 8.4 below. (See the following text for explanations of the spin-only magnetic moment μ_s and the term symbol.)

Table 8.4. Ground-state d electron configurations for T_d complexes (low-spin states not given).

d^n	d electron configuration	Number of unpaired electrons	$\frac{\mu_s}{\mu_B}$	Term symbol
d^0	$(e)^0(t_2)^0$	0	0	$^1A_1$
d^1	$(e)^1(t_2)^0$	1	$\sqrt{3} \approx 1.73$	^2E
d^2	$(e)^2(t_2)^0$	2	$2\sqrt{2} \approx 2.83$	$^3A_2$
d^3	$(e)^2(t_2)^1$	3	$\sqrt{15} \approx 3.87$	$^4T_1$
d^4	$(e)^2(t_2)^2$	4	$2\sqrt{6} \approx 4.90$	$^5T_2$
d^5	$(e)^2(t_2)^3$	5	$\sqrt{35} \approx 5.92$	$^6A_1$
d^6	$(e)^3(t_2)^3$	4	$2\sqrt{6} \approx 4.90$	^5E
d^7	$(e)^4(t_2)^3$	3	$\sqrt{15} \approx 3.87$	$^4A_2$
d^8	$(e)^4(t_2)^4$	2	$2\sqrt{2} \approx 2.83$	$^3T_1$
d^9	$(e)^4(t_2)^5$	1	$\sqrt{3} \approx 1.73$	$^2T_2$
d^{10}	$(e)^4(t_2)^6$	0	0	$^1A_1$

8.3. Symmetry of Electronic States

We have seen that the atomic and molecular orbitals of any chemical system must transform as irreps in that system's point group. It turns out that the total *electronic state* of any system, that is, the electronic wavefunction that can be approximated as a Slater determinant (or as a linear combination of a few Slater determinants), must also transform as one of the point group's irreps. We have seen that free atoms and monatomic ions have a series of possible electronic states denoted by term symbols of the form ^{2S+1}L . In fact, the notations S, P, D, F , etc. are themselves labels of irreps in the point group K_h , to which systems with spherical symmetry (such as free atoms and monatomic ions) belong. We will now see how we can assign symmetry labels (irreps) for electronic states of a TM complex using CFT.

There are two starting points that we can choose for the determination of electronic state symmetry. One is the so-called weak-field limit, in which the splitting of atomic terms based on the crystal field is a small perturbation compared to the energy differences between *atomic* terms due to interelectronic interactions. This approach involves taking an atomic term such as ^2D or ^3H and seeing how it is split in a crystal field. The other is the strong-field limit, in which energy differences in terms of interelectronic interactions (such as the pairing energy) are small compared to the splitting of orbital energies in terms of a crystal-field splitting parameter such as Δ_o . This approach involves deducing the symmetries of states that arise from an electron configuration such as $(t_{2g})^3(e_g)^1$.

Considering the weak-field limit first, it turns out that a term denoted by a given value of the total angular momentum quantum number L (such as S for $L = 0$, P for $L = 1$, etc.) transforms as the same set of irreps as a set of atomic orbitals represented by a given angular momentum quantum number l . For instance, inspection of the O_h character table shows that a set of p AOs transform together as the triply degenerate irrep T_{1u} , as the second to rightmost column shows (x, y, z) transforming as T_{1u} . Thus, a P state of a free TM ion becomes a T_{1u} state in O_h symmetry.

While we can easily find the irreps corresponding to s AOs and S terms (always the totally symmetric irrep), p AOs and P terms, and d AOs and D terms, the character tables in most

sources do not list how f AOs and F terms transform. Furthermore, while there exist no known elements that use g , h , or i AOs in bonding, many atoms and ions do have G , H , or I terms. Table 8.5 below lists how S , P , D , F , G , H , and I terms are split in the most common coordination geometries for homoleptic TM complexes: octahedral ML_6 (O_h), tetrahedral ML_4 (T_d), and square planar ML_4 (D_{4h}).

Table 8.5. Splitting of atomic terms in the O_h , T_d , and D_{4h} point groups.

L	Free-atom or free-ion term symbol	O_h irreps	T_d irreps	D_{4h} irreps
0	S	A_{1g}	A_1	A_{1g}
1	P	T_{1u}	T_2	$A_{2u} + E_u$
2	D	$E_g + T_{2g}$	$E + T_2$	$A_{1g} + B_{1g} + B_{2g} + E_g$
3	F	$A_{1u} + T_{1u} + T_{2u}$	$A_2 + T_1 + T_2$	$A_{2u} + B_{1u} + B_{2u} + 2E_u$
4	G	$A_{1g} + E_g + T_{1g} + T_{2g}$	$A_1 + E + T_1 + T_2$	$2A_{1g} + A_{2g} + B_{1g} + B_{2g} + 2E_g$
5	H	$E_g + 2T_{1u} + T_{2u}$	$E + T_1 + 2T_2$	$A_{1u} + 2A_{2u} + B_{1u} + B_{2u} + 3E_u$
6	I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$	$A_1 + A_2 + E + T_1 + 2T_2$	$2A_{1g} + A_{2g} + 2B_{1g} + 2B_{2g} + 3E_g$

In the weak-field limit, crystal field splitting will not change the spin multiplicity of a term. (After all, “weak-field” means that the splitting is smaller than the pairing energy.) Thus, the ground-state term for a d^3 free ion is ^4F , which will give rise to the terms $^4A_{1g} + ^4T_{1u} + ^4T_{2u}$ in O_h symmetry. The possible states of a metal complex with a given symmetry is determined by how all of its possible free-ion terms split in the crystal field that it is in. So, to determine all the possible symmetries and multiplicities of a d^3 ion in an O_h complex, you would determine the possible term symbols (either by calculation or, more likely, by looking them up in a table⁶⁷) for the free ion as ^4F , ^4P , ^2H , ^2P , ^2G , ^2F , ^2D , and ^2D (this means two ^2D terms with different energies). Then, you would see how each of these terms splits in the O_h crystal field by examining Table 8.5.

⁶⁷ For instance, that on page 37 of *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, 2nd edition, by Isaac B. Bersuker, John Wiley & Sons: Hoboken, NJ, 2010.

The above procedure for determining how free-ion terms split in a crystal field is straightforward, but it has the disadvantage that it does not tell you which terms correspond to which electron configurations. This means that you could list all the possible terms of an $O_h d^3$ complex, but you would not know which correspond to the different possible electron configurations $(t_{2g})^3(e_g)^0$, $(t_{2g})^2(e_g)^1$, $(t_{2g})^1(e_g)^2$, and $(t_{2g})^0(e_g)^3$. To determine which terms correspond to which electron configurations, we approach the problem instead from the strong-field limit, in which the differences between the energies of the different d AOs (Δ_o , in the O_h case) are significantly larger than the pairing energy. Thus, we here consider interelectronic interactions to be a perturbation to the crystal field splitting, rather than *vice versa*. We can find the electronic states corresponding to a set of irreps from the electron configuration in a straightforward manner when (a) either all orbitals are empty or doubly occupied, (b) the only singly occupied orbitals are nondegenerate, or (c) only one set of degenerate orbitals is partially filled, and it either has only one electron in it or is only one electron away from being completely filled. When there are multiple unpaired electrons in degenerate orbitals, the analysis is more complicated, as we will see. The following procedures will show you how to derive electronic state symmetry from electron configurations.

(1) If all orbitals are either full (2 electrons) or empty (0 electrons), the electronic state is a singlet belonging to the totally symmetric irrep. For instance, a $d^{10} O_h$ complex, with electron configuration $(t_{2g})^6(e_g)^4$, has the electronic state $^1A_{1g}$, while a $d^{10} T_d$ complex, with electron configuration $(e)^4(t_2)^6$, has electronic state $^1A_1$. Note that a TM complex need not be either d^0 or d^{10} to have a totally symmetric, singlet electronic state. For instance, a low-spin d^6 complex with O_h symmetry, such as $\text{Cr}(\text{CO})_6$ or $\text{Fe}(\text{CN})_6^{4-}$, has electron configuration $(t_{2g})^6(e_g)^0$. Each of its three t_{2g} orbitals is doubly occupied, and each of its two e_g orbitals is empty. It, too, will have the electronic state $^1A_{1g}$.

(2) If there is only one unpaired electron, the electronic state will transform as the same irrep as the singly occupied orbital, and its spin multiplicity will be 2 (a doublet). For instance, our MO treatment of H_2O (see Section 3.3) gave rise to the ground-state valence electron configuration $(1a_1)^2(1b_1)^2(2a_1)^2(1b_2)^2(3a_1)^0(2b_1)^0$. Suppose an H_2O molecule was

irradiated with a sufficiently high-energy photon to remove an electron from the $1b_2$ HOMO, leaving an H_2O^+ radical cation with the electron configuration $(1a_1)^2(1b_1)^2(2a_1)^2(1b_2)^2(3a_1)^0(2b_1)^0$. This electron configuration corresponds to an electronic state with symmetry level ${}^2B_2$.

If only one electron is unpaired, this analysis does not depend on whether the singly occupied orbital is part of a degenerate set or not. For instance, a d^1 O_h complex has the ground-state electron configuration $(t_{2g})^1(e_g)^0$, which corresponds to a ${}^2T_{2g}$ electronic state. Similarly, a d^9 O_h complex has the ground-state electron configuration $(t_{2g})^6(e_g)^3$, which corresponds to a ${}^2E_g$ electronic state, since the only singly occupied orbital is one of the e_g set.

(3) If there are two unpaired electrons in nondegenerate orbitals, the symmetry of the electronic state is given by the direct product of the irreps corresponding to the singly occupied orbitals. Consider the first excited electron configuration of H_2O , which is $(1a_1)^2(1b_1)^2(2a_1)^2(1b_2)^1(3a_1)^1(2b_1)^0$. The electronic states corresponding to this configuration belong to the irrep which is the direct product of the irreps B_2 and A_1 in point group C_{2v} , which is B_2 . The unpaired electrons in $1b_2$ and $3a_1$ can either have parallel spin, giving rise to the triplet state ${}^3B_2$, or they can have antiparallel spin (and thus no net spin), giving rise to the singlet state ${}^1B_2$. Thus, this electron configuration gives rise to two electronic states, ${}^1B_2$ and ${}^3B_2$.

If the singly occupied orbitals are part of degenerate sets, but not part of the *same* degenerate set, the same procedure applies. Consider an excited state configuration of a d^2 O_h complex, $(t_{2g})^1(e_g)^1$. The symmetries of the electronic states arising from this configuration are given by the direct product of T_{2g} and E_g in point group O_h : $T_{1g} \times E_g = T_{1g} + T_{2g}$. Both singlet and triplet states are possible: if the t_{2g} and e_g electrons have parallel spin, they give rise to the triplet states ${}^3T_{1g}$ and ${}^3T_{2g}$, while if they have antiparallel spin, they give rise to the singlet states ${}^1T_{1g}$ and ${}^1T_{2g}$. Thus, the electron configuration $(t_{2g})^1(e_g)^1$, which does not, as written, specify the relative spins of the electrons, gives rise to four different electronic states: ${}^1T_{1g}$, ${}^1T_{2g}$, ${}^3T_{1g}$, and ${}^3T_{2g}$.

(4) If there are two unpaired electrons in the *same* set of degenerate orbitals, the situation is somewhat more difficult. Consider the ground-state electron configuration of a $d^2 O_h$ complex, $(t_{2g})^2(e_g)^0$. As the first step in tackling this problem, we calculate the direct product $T_{2g} \times T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$. These are indeed the symmetries of the electronic states that we will obtain from this electron configuration. One might suppose that, because the electrons in the $(t_{2g})^2(e_g)^0$ configuration can either have parallel spins (triplet) or antiparallel spins (singlet), the configuration leads to both singlet *and* triplet states belonging to each irrep: $^1A_{1g}$, ^1E_g , $^1T_{1g}$, $^1T_{2g}$, $^3A_{1g}$, ^3E_g , $^3T_{1g}$, and $^3T_{2g}$. In fact, however, this is *not* correct, and some of these states will *not* arise from the $(t_{2g})^2(e_g)^0$ configuration. The reason for this is that the spins of the two t_{2g} electrons are not independent. If they are in different t_{2g} orbitals, they can have either parallel or antiparallel spins, but if they are in the same t_{2g} orbital, their spins must be antiparallel, so as not to violate the Pauli exclusion principle. In fact, each of the states with symmetry A_{1g} , E_g , T_{1g} , and T_{2g} is either singlet *or* triplet.

We determine which states are singlets and which are triplets as follows: first, we note that the Pauli antisymmetry principle requires that any suitable wavefunction (including approximate wavefunctions such as Slater determinants) for a system with more than one electron must be antisymmetric upon the exchange of two electrons, *i.e.* exchanging two electrons takes the wavefunction to the negative of itself. A system with only two electrons, whose wavefunction can be represented by a 2×2 Slater determinant, can be written as the product of a spatial part and a spin part. (Note that this factorization of a wavefunction into spatial and spin parts is not possible for systems with more than two electrons, which are represented by higher-order determinants.) If the spatial part of the wavefunction is antisymmetric upon the exchange of two electrons, then the spin part must be symmetric for the entire wavefunction to be antisymmetric. In contrast, if the spatial part is symmetric upon the exchange of two electrons, then the spin part must be antisymmetric. It turns out that, for a system with only two unpaired electrons, a singlet state has an antisymmetric spin function, and a triplet state has a symmetric spin function. Thus, a singlet state must have a symmetric spatial wavefunction, and a triplet state must have an antisymmetric spatial wavefunction. The irrep labels that we obtain from our direct product calculation define the symmetry of the spatial part of the wavefunction. While the total direct product

$T_{2g} \times T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$ gives us the symmetries of the spatial wavefunctions, it does not tell us whether each is symmetric or antisymmetric with respect to electron exchange. This information is given by two other formulae, each of which takes the characters under each symmetry operation for the direct product, and takes them to the characters of a new reducible representation: one reducible representation for the terms symmetric with respect to electron exchange, and another for the terms antisymmetric with respect to electron exchange. For each symmetry operation $\hat{R}$, the characters of the parts of the direct product corresponding to symmetric and antisymmetric terms are given as follows:

$$\chi_{\text{symmetric}}(\hat{R}) = \chi_{\text{singlet}}(\hat{R}) = \frac{1}{2} \{ [\chi(\hat{R})]^2 + \chi(\hat{R}^2) \}$$

$$\chi_{\text{antisymmetric}}(\hat{R}) = \chi_{\text{triplet}}(\hat{R}) = \frac{1}{2} \{ [\chi(\hat{R})]^2 - \chi(\hat{R}^2) \}$$

Here $\chi(\hat{R})$ means the character of the direct product under $\hat{R}$, while $\chi(\hat{R}^2)$ means the character of the direct product under the operation $\hat{R}$ applied twice in a row, which must itself also be an operation of the group (because any mathematical group has the property of closure). For instance, in O_h , $\hat{C}_4^2 = \hat{C}_2$ and $\hat{S}_6^2 = \hat{C}_3$.

These formulae are useful, and their use is conceptually straightforward, but also tedious and lengthy. Fortunately, there exist direct product tables for various point groups, which show the direct products of any two irreps in the groups, and, for direct products that are sums of irreps, they indicate which terms are symmetric and which are antisymmetric. The direct product table for T_d and O_h is shown below (Table 8.6), and each antisymmetric term is enclosed in [square brackets].

Table 8.6. Direct product table for the T_d and O_h point groups.

T_d and O_h	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2		A_1	E	T_2	T_1
E			$A_1 + [A_2] + E$	$T_1 + T_2$	$T_1 + T_2$
T_1				$A_1 + E + [T_1] + T_2$	$A_2 + E + T_1 + T_2$
T_2					$A_1 + E + [T_1] + T_2$

Table 8.6 might seem appropriate for T_d , but incomplete for O_h . After all, there are 10 irreps in O_h , compared to 5 in T_d . However, the irreps in O_h have the same notation as those in T_d , except for a designation of each as g or u (symmetric or antisymmetric, respectively, with respect to inversion). The direct product of a g irrep and another g irrep is g , and the direct product of a u irrep and another u irrep is also g . However, the direct product of a g and a u irrep is u . This is somewhat analogous to the fact that the simple arithmetic product of two positive numbers is positive, as is the product of two negative numbers, but the product of one positive and one negative number is negative.

To see how to use this table, we note that we previously considered a $(t_{2g})^2$ electron configuration by taking the direct product $T_{2g} \times T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$. This is consistent with $T_2 \times T_2 = A_1 + E + [T_1] + T_2$ from Table 8.6. Since $g \times g = g$, this means that $T_{2g} \times T_{2g} = A_{1g} + E_g + [T_{1g}] + T_{2g}$, so the T_{1g} term is antisymmetric to electron exchange, and thus represents a triplet state, while the other terms are symmetry with respect to electron exchange, and are thus singlets. We conclude that a $(t_{2g})^2$ electron configuration gives rise to the terms $^1A_{1g}$, ^1E_g , $^1T_{2g}$, and $^3T_{1g}$.

As another example of how to use Table 8.6, consider an O_h d^8 species, with electron configuration $(t_{2g})^6(e_g)^2$. The t_{2g} orbitals are completely filled, so we need not consider them in our analysis of state symmetry. Thus, we take the direct product $E_g \times E_g$. Table 8.6 gives $E \times E = A_1 + [A_2] + E$, or $E_g \times E_g = A_{1g} + [A_{2g}] + E_g$, so the terms generated by this electron configuration are $^1A_{1g}$, ^1E_g , and $^3A_{2g}$.

Some electron configurations, such as $(t_{2g})^3$, involve three electrons in a set of triply degenerate orbitals. Such a configuration can lead to double terms (two electrons are spin-up, one is spin-down) or quartet terms (all three electrons are spin-up). Once one takes the direct product, the characters of the reducible representations corresponding to doublet and quartet states are given by

$$\chi_{\text{doublet}}(\hat{R}) = \frac{1}{3} \{ [\chi(\hat{R})]^3 + \chi(\hat{R}^3) \}$$

$$\chi_{\text{quartet}}(\hat{R}) = \frac{1}{6} \{ [\chi(\hat{R})]^3 - 3\chi(\hat{R})\chi(\hat{R}^2) + 2\chi(\hat{R}^3) \}$$

These equations are even more cumbersome, and I do not ask my students to perform calculations using them, but they are provided as a reference.

8.4. MO Theory for Octahedral TM Complexes

While CFT gives results with the correct symmetry, it is not quantitatively correct, since it does not account for covalent bonding between the TM and its ligands. We will now explore MO theory for TM complexes using the same general strategy that we used to develop MO theory for main-group molecules, namely, the formation of SALCs for ligand orbitals (where the ligands are atoms, ions, or molecules bound to the TM center), and the interaction of these SALCs with AOs of like symmetry on the TM. We will now be considering valence *d* AOs on the central TM, in addition to *s* and *p* AOs, and we will also be considering ligand-based orbitals that can form π bonds, as well as σ bonds, with the TM.

We will begin with the most common coordination geometry for TM complexes, octahedral coordination, in which the TM is at the origin of a Cartesian coordinate system and the ligands all lie along the *x*, *y*, and *z* axes. If all the ligands *L* are of the same type, then they define the vertices of a regular octahedron, and the point group of the complex ML_6 will be O_h . If there is more than one type of ligand, the resulting heteroleptic complex will belong to a point group of lower symmetry than O_h , but the coordination geometry is still said to be octahedral, just not *regular* octahedral.

Initially, we will assume that each ligand interacts with the TM in only a σ fashion. In this model, each ligand has a filled orbital (which could be a *p* AO, a hybrid orbital, or a roughly nonbonding MO like the “lone pair” of NH_3) pointing towards the metal. The geometry is shown in Figure 8.3 on the following page, with the ligand orbitals labeled σ_1 through σ_6 .

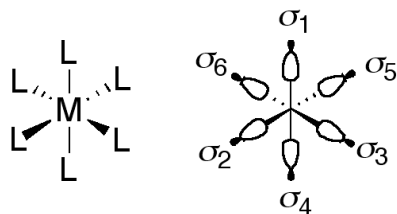


Figure 8.3. An O_h ML_6 complex and the ligand orbitals to be used to construct SALCs.

We now construct a reducible representation for the ligand orbitals in O_h , denoted Γ_σ , and shown in Table 8.7 below. (Another reducible representation, Γ_π in the final row, will be discussed later.) Note that the characters of Γ_σ are exactly the same as those of Γ_{SALC} in Table 3.7 in Section 3.6, in which we developed an approximate model for bonding in SF_6 by constructing SALCs from F 2p AOs pointing towards S. Thus, $\Gamma_\sigma = A_{1g} + E_g + T_{1u}$.

Table 8.7. The character table for the O_h point group.

O_h	$\hat{E}$	$8\hat{C}_3$	$6\hat{C}_2$	$6\hat{C}_4$	$3\hat{C}_2$ ($=\hat{C}_4^2$)	$\hat{i}$	$6\hat{S}_4$	$8\hat{S}_6$	$3\hat{\sigma}_h$	$6\hat{\sigma}_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	0	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	0	-1		
Γ_σ	6	0	0	2	2	0	0	0	4	2		
Γ_π	12	0	0	0	-4	0	0	0	0	0		

Looking at the rightmost two columns of Table 8.7, we see that the s AO of the TM transforms as A_{1g} , its p_x , p_y , and p_z AOs transform together as T_{1u} , its d_{xy} , d_{xz} , and d_{yz} AOs transform together as T_{2g} , and its $d_{x^2-y^2}$ and d_{z^2} AOs transform together as E_g . This means that we will form a bonding and an antibonding MO of A_{1g} symmetry, a bonding pair and an antibonding pair of MOs of E_g symmetry, and a bonding trio and an antibonding trio of MOs of T_{1u}

symmetry. As no ligand SALC has T_{2g} symmetry, the TM its d_{xy} , d_{xz} , and d_{yz} AOs are nonbonding.

To obtain the forms of the SALCs, we can, for the most part, use the pictorial method, rather than the more formal method of projection operators. The A_{1g} SALC simply has all the ligand orbitals in phase. Each of the T_{1u} SALCs is available for interaction with a TM p AO, so each consists of an out-of-phase combination of two ligand orbitals *trans* to each other. The E_g SALCs are the trickiest to visualize. We see that one must interact with the TM $d_{x^2-y^2}$ AO. IF the orbitals σ_2 , σ_3 , σ_5 , and σ_6 lie in the xy plane, they will interact with this AO, with zero contribution from σ_1 and σ_4 . The Gram-Schmidt algorithm allows us (rather tediously) to find the other E_g SALC, which can interact with the TM d_{z^2} AO. Pictorial depictions of the SALCs are shown in Figure 8.4 below, followed by the algebraic expressions for them.

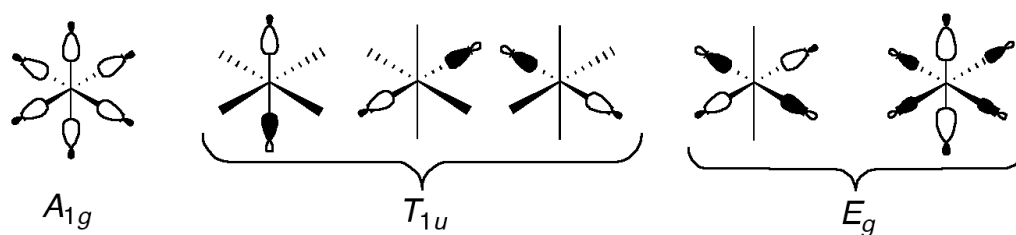


Figure 8.4. Ligand-based σ SALCs for O_h ML_6 .

$$\phi_{A_{1g}}^{\text{SALC}} = \frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$

$$\phi_{T_{1u,x}}^{\text{SALC}} = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_5)$$

$$\phi_{T_{1u,y}}^{\text{SALC}} = \frac{1}{\sqrt{2}}(\sigma_3 - \sigma_6)$$

$$\phi_{T_{1u,z}}^{\text{SALC}} = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_4)$$

$$\phi_{E_g, x^2-y^2}^{\text{SALC}} = \frac{1}{2}(\sigma_2 - \sigma_3 + \sigma_5 - \sigma_6)$$

$$\phi_{E_g, z^2}^{\text{SALC}} = \frac{1}{2\sqrt{3}}(2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6)$$

An MO diagram for this σ -only case is shown in Figure 8.5 on the following page, for a first-series TM (so its valence AOs are $3d$, $4s$, and $4p$). We have six bonding MOs: $1a_{1g}$, $1e_g$, and $1t_{1u}$. They all have more ligand than TM character, as the ligand lone pairs are lower in energy than the TM AOs,⁶⁸ but they do also have some TM s , d , and p character, respectively. The $1t_{2g}$ set of MOs is nonbonding, and they are just d_{xy} , d_{xz} , and d_{yz} for the TM, since there are no ligand SALCs with T_{2g} symmetry for them to interact with. There are six antibonding MOs: $2e_g$, $2a_{1g}$, and $2t_{1u}$, with some ligand character, but primarily TM d , s , and p character, respectively. Assuming that each ligand contributes two electrons, in a d^0 TM complex six bonding MOs are filled and every antibonding MO is empty, so the total M–L bond order is 6, and the average M–L bond order is 1.

It is instructive to compare the MO picture in Figure 8.4 with the CFT picture in Figure 8.1. According to CFT, all TM d AOs have their energy raised, but one set (t_{2g}) has its energy lowered from the barycenter, while the other set (e_g) has its energy raised from the barycenter. According to MO theory, the t_{2g} MOs should have the same energy as the TM d AOs, since they are nonbonding, while the $2e_g$ MOs, at higher energy, correspond to the e_g orbitals of CFT. Unlike in CFT, we see that the $2e_g$ MOs have both TM d and ligand lone-pair character, although they are still primarily TM d . The CFT splitting parameter Δ_o can be considered, in MO theory, as the energy difference between nonbonding $1t_{2g}$ and antibonding $2e_g$. For ligands that are σ -donors only, the better σ -donors will lie higher in the spectrochemical series (larger Δ_o), as the greater orbital interaction will lead to $1e_g$ being lower in energy (more bonding) and $2e_g$ being higher in energy (more antibonding). H^- and NH_3 are both σ -donors only, but as H^- , with its spherically symmetrical $1s$ AO, forms better overlap with TM d AOs, it is higher in the spectrochemical series than NH_3 is.

For d^1 , d^2 , d^3 , low-spin d^4 , low-spin d^5 , and low-spin d^6 complexes, the total M–L bond order is still 6, as the electrons in the “ d -type” MOs ($1t_{2g}$ and $2e_g$) all lie in nonbonding $1t_{2g}$, leaving

⁶⁸ In general, when two basis orbitals of different energies interact to form bonding and antibonding MOs, the bonding MO has a larger LCAO coefficient from the lower-energy basis orbital, and the antibonding MO has a larger LCAO coefficient from the higher-energy basis orbital.

the bond order unchanged. However, for d^7 and above complexes, and high-spin d^4 through d^6 , some electrons occupy the antibonding $2e_g$ MOs, so the formal M–L bond order is lower. For instance, high-spin d^4 , d^5 , and d^6 have total M–L bond orders of $\frac{11}{2}$, 5, and $\frac{9}{2}$, respectively.

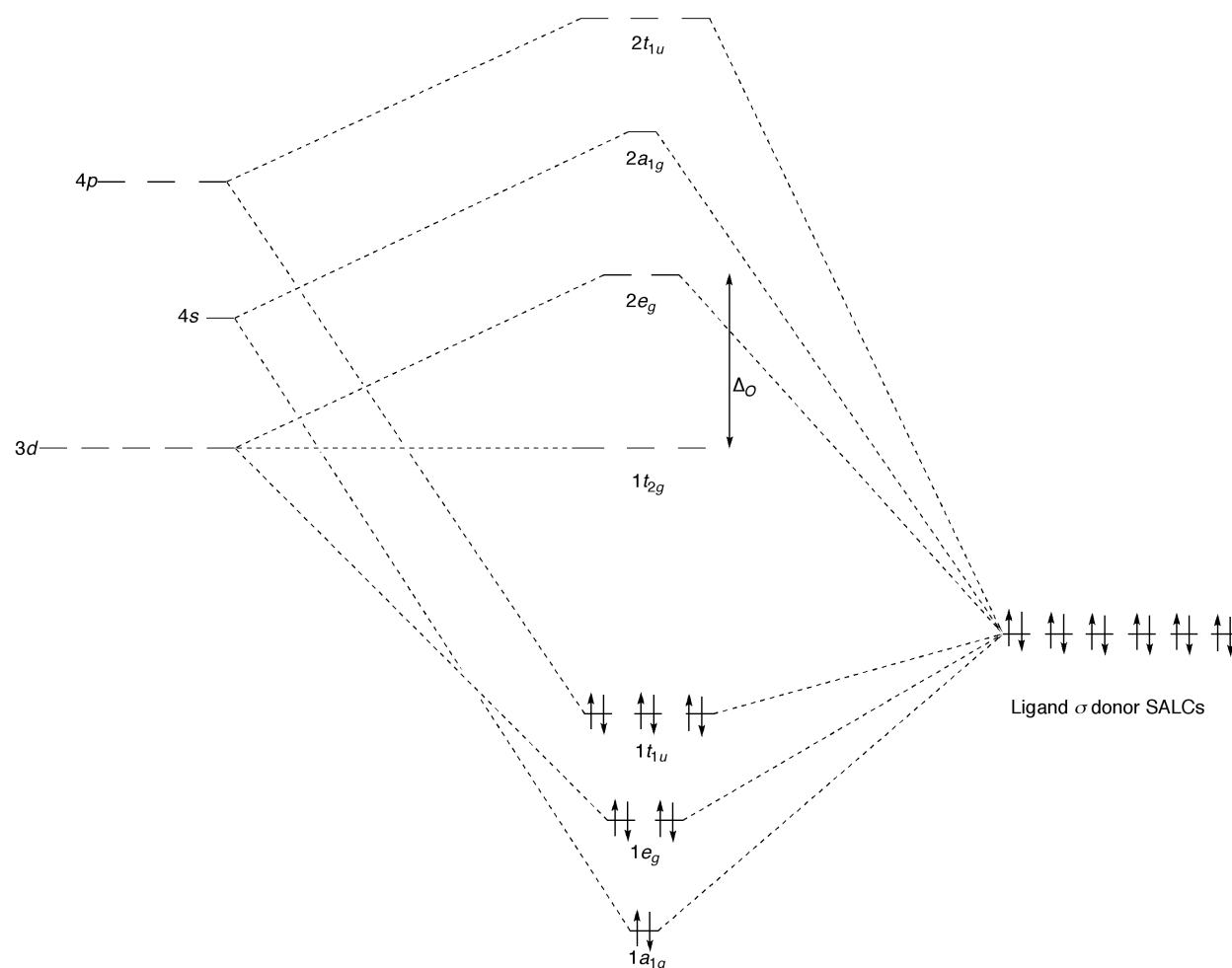


Figure 8.5. Qualitative MO diagram for O_h ML_6 , with only σ interactions between the metal and ligands.

We will now complicate things by asking what happens if the ligands have π orbitals with which they can engage in bonding. These π orbitals can be filled, and fairly low in energy, like the lone pairs of F^- or OH^- , or they can be empty, and higher in energy, like the C–O π antibonding orbitals of CO or the C–N π antibonding MOs of CN^- . The SALCs we form from these π orbitals will belong to the same irreducible representations in either case, but their energies compared to those of the TM d AOs will differ. To construct a reducible

representation Γ_π , we imagine two p AOs (or two π MOs) on each ligand, each perpendicular to the M–L bond axis. To simplify the diagram, we can simply draw vectors as shown in Figure 8.6 below, since these vectors have all the necessary symmetry properties. For the sake of argument, consider each ligand to be at the center of its own Cartesian coordinate system, with the z axis along the M–L bond axis, and the x and y axes perpendicular.

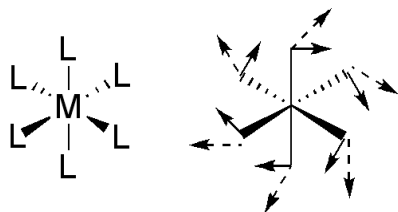


Figure 8.6. Vector picture used to derive a reducible representation for ligand-based π orbitals.

The characters of Γ_π are shown in Table 8.7, and decomposition of this representation *via* the usual formula gives $\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$. The SALCs with T_{1g} and T_{2u} symmetry have no match among the TM AOs, so they remain nonbonding.⁶⁹ The T_{1u} SALC has the same symmetry as the TM p AOs and one of the σ SALCs, so it mixes in: we now have three sets of t_{1u} MOs, rather than two. However, as π interactions are generally weaker than σ ones, we can view the t_{1u} MO derived from π -type SALCs ($2t_{1u}$) as roughly (though not rigorously) nonbonding, with the bonding t_{1u} MOs ($1t_{1u}$) being primarily σ -bonding, and the antibonding t_{1u} MOs ($3t_{1u}$) being primarily σ -antibonding.

What is most relevant for our qualitative discussion of bonding is the fact that there is now a set of π -type SALCs of T_{2g} symmetry, which can form bonding and antibonding t_{2g} MOs with the T_{2g} -symmetry TM d AOs, which were strictly nonbonding in the σ -only case. We need not be concerned with the forms of the T_{1g} and T_{2u} SALCs, which become strictly nonbonding MOs, but the forms of the π -type T_{1u} and T_{2g} SALCs are shown in Figure 8.7 below (one of each degenerate trio; the others have identical shapes, but are shifted in space). You can see

⁶⁹ Here, “nonbonding” means nonbonding with respect to the metal-ligand interactions. The SALCs may still have bonding or antibonding character within the ligands.

how the T_{2g} SALCs are set up to interact with TM d_{xy} , d_{xz} , and d_{yz} AOs, while the T_{1u} SALCs are set up to interact with TM p AOs.

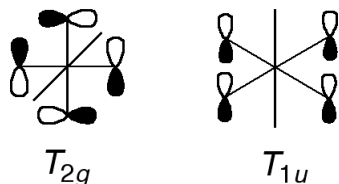


Figure 8.7. The shapes of π -type ligand SALCs with T_{2g} and T_{1u} symmetry.

When it comes to MO diagrams, let us first consider the case in which the π -type SALCs are fairly low in energy (lower in energy than the TM AOs) and filled. This will be the case with π -type SALCs derived from lone pairs of ligands such as F^- or OH^- . Ligands of this sort are referred to as π -donor ligands, since they have filled π -type orbitals whose electrons can be donated to the metal in a Lewis-base fashion. A real example of a homoleptic, O_h π -donor complex is TiF_6^{2-} . A qualitative MO diagram for a d^0 complex with π -donor ligands is shown in Figure 8.8 on the following page.

If we compare Figure 8.8 with Figure 8.5 (the σ -only case), the most important difference is that we now have bonding and antibonding MOs of t_{2g} symmetry. The bonding set, $1t_{2g}$, is closer in energy to the ligand π SALCs, so it is more ligand than metal in character, while the antibonding set, $2t_{2g}$, is closer in energy to the TM d AOs, so it is more metal than ligand in character. Now, the MOs corresponding to the pure TM d AOs in the CFT model are $2t_{2g}$ and $2e_g$, both antibonding. Since π donation from ligands makes the predominantly metal t_{2g} orbitals antibonding, bringing them closer in energy to the σ -antibonding e_g set, it lowers Δ_o . This is why π -donor ligands such as the halides and OH^- are low in the spectrochemical series. If we consider $2t_{1u}$ to be roughly nonbonding, then the total M–L bond order in a d^0 complex with π -donor ligands is 9, for an average M–L bond order of $\frac{3}{2}$. Since both sets of d -type MOs, $2t_{2g}$ and $2e_g$, are now M–L antibonding, adding more d electrons to a complex with π -donor ligands lowers the M–L bond order.

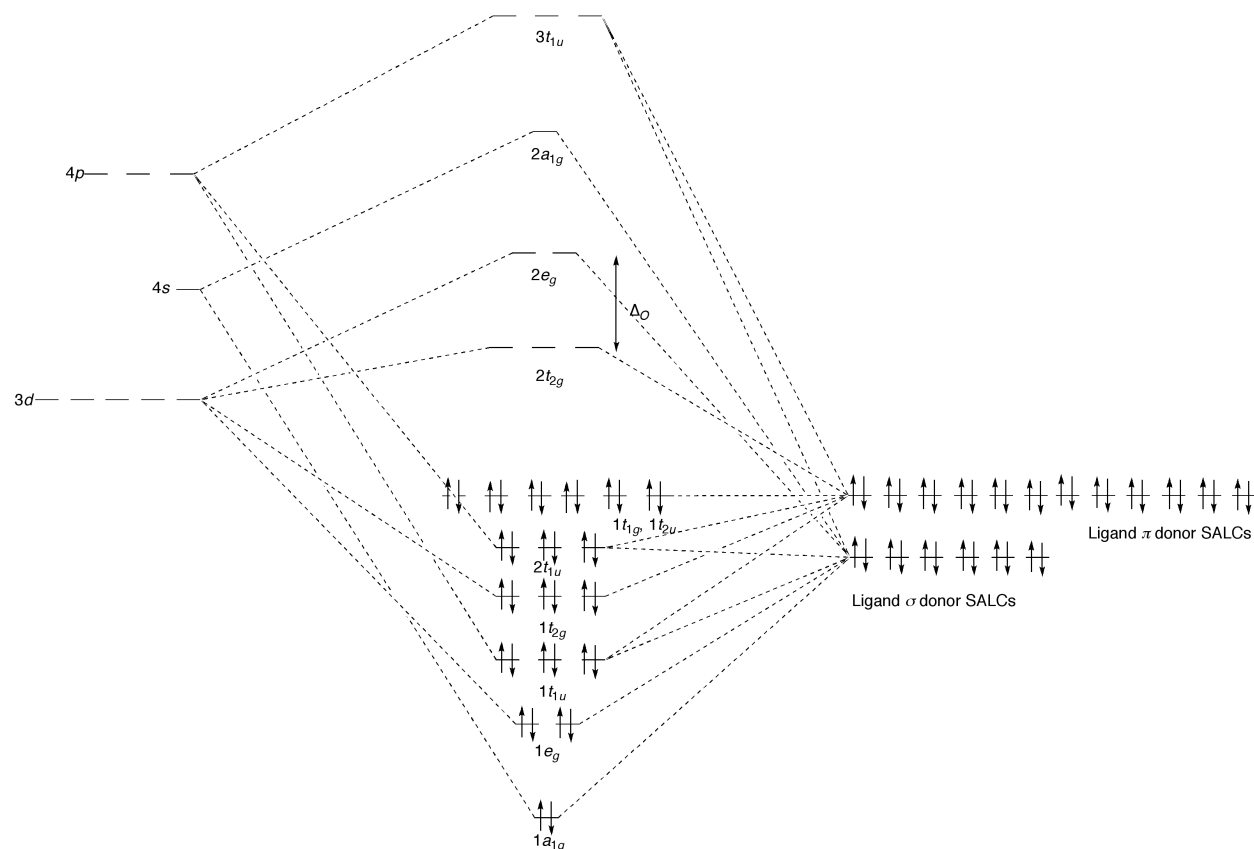


Figure 8.8. Qualitative MO diagram for O_h ML_6 with π -donor ligands.

Let us now consider the case where the ligands have empty, high-energy orbitals for π bonding. Common ligands of this sort include CO and CN^- , each of which has as its LUMOs a degenerate pair of π antibonding MOs (antibonding between C and O or between C and N). Ligands of this sort are known as π -acceptors, since they have empty π orbitals than can accept some electron density from filled TM AOs. Another term sometimes used for such ligands is “ π -acids,” since they are Lewis bases (electron pair donors) in a σ sense, but Lewis acids (electron pair acceptors) in a π sense. This bonding is also sometimes called “backbonding” or “back-donation,” because the ligands donate electron density *to* the metal in a σ sense, but the metal donates electron density *back* to the ligands in a π sense. A qualitative MO diagram for an O_h complex with π -acceptor ligands is shown in Figure 8.9 below.

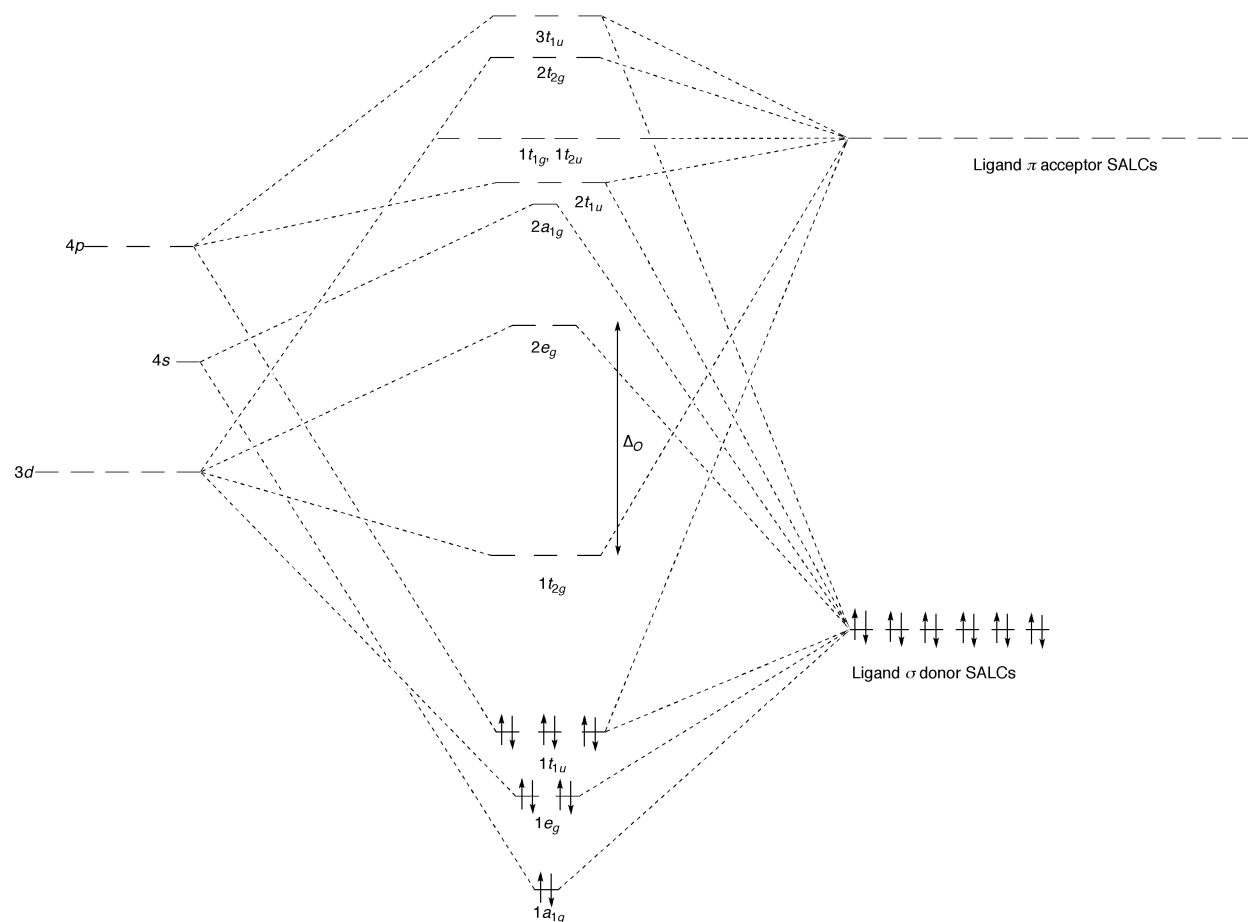


Figure 8.9. Qualitative MO diagram for ML_6 with π -acceptor ligands.

In complexes of π -acceptor ligands, the bonding t_{2g} set, $1t_{2g}$, is predominantly composed of TM d AOs, since the d AOs are lower in energy than the ligand π antibonding MOs. While the $1t_{2g}$ MOs are commonly described as “bonding,” it is more accurate to characterize them as being bonding with respect to the M–L interaction, but antibonding with respect to interactions between atoms within the ligands. Nevertheless, they can reasonably be considered bonding in the sense that they are lower in energy than the basis orbitals from which they were derived. The antibonding set, $2t_{2g}$, is predominantly ligand π antibonding MO in character, as it is closer in energy to the SALCs derived from ligand π antibonding MOs. These MOs are antibonding both with respect to the M–L interaction *and* with respect to interactions within the ligands. Because the predominantly TM d -type t_{2g} MOs, $1t_{2g}$, are M–L bonding and thus lowered in energy, the Δ_O values of complexes of π -acceptor ligands are greater than those of σ -only complexes. This is why π -acceptor ligands such as CO and CN^-

are so high in the spectrochemical series. (Ligands such as NH_3 and H^- , which are σ -donors only, are usually intermediate in the spectrochemical series, though H^- is actually comparable to CO and CN^- because it is an *extremely* good σ -donor.)

In contrast to the π -donor case, addition of up to 6 d electrons to a π -acceptor complex (assuming, as is very likely, a low-spin ground state) will *increase* the M–L bond order, up to a total M–L bond order of 9 for a d^6 π -acceptor complex, with an average M–L bond order of $\frac{3}{2}$. While Figure 8.9 shows a hypothetical d^0 complex for comparison with Figures 8.5 and 8.8, d^0 complexes of π -acceptor ligands are in fact quite rare, as much of the stability of such complexes comes from the strength of the π -backbonding interactions. In contrast, d^6 complexes of π -acceptor ligands are very common. Well-known examples of this class of complexes include $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $\text{V}(\text{CO})_6^-$, and $\text{Fe}(\text{CN})_6^{4-}$. Because they draw electron density away from the metal, π -acceptor ligands are often able to stabilize rather low metal oxidation states. One might generally expect metals, as electropositive elements, to prefer significantly positive oxidation states. However, in $\text{Cr}(\text{CO})_6$ and $\text{V}(\text{CO})_6^-$, the oxidation states of Cr and V are 0 and -1 , respectively. While salts of $\text{V}(\text{CO})_6^-$ are oxygen-sensitive, $\text{Cr}(\text{CO})_6$ can be handled on the benchtop, in stark contrast to finely-ground elemental Cr, which is pyrophoric. While the Cr atoms in $\text{Cr}(\text{CO})_6$ are in the same formal oxidation state as those in elemental Cr, they have considerably less electron density due to π -backbonding, making them less vulnerable to air oxidation.

It is worth noting that the distinction between σ and π MOs is only rigorously defined in linear molecules, based on whether the internuclear axis does or does not contain a nodal plane. While it is still often useful to talk about the interaction between a particular ligand and a TM as being either σ or π (as we have been doing), a delocalized MO scheme will often give rise to orbitals with some σ and some π character, as we saw with the t_{1u} MOs of an O_h ML_6 complex when π -donor or π -acceptor ligands are present. For nonlinear molecules, one often characterizes an MO as $[\sigma + \pi]$ bonding or $[\sigma + \pi]$ antibonding. We will see more of this σ vs. π ambiguity in our discussion of MO theory for T_d ML_4 complexes, in the following section.

8.5 MO Theory for Tetrahedral TM Complexes

The second most common coordination geometry for TM complexes is ML_4 (four-coordinate) with a tetrahedral arrangement of ligands, *i.e.* the four ligands define the vertices of a tetrahedron. If all ligands L are the same, then ML_4 belongs to point group T_d , with the symmetry of a regular tetrahedron. We take the TM to be at the center of a tetrahedron (the origin of our coordinate system), and we imagine that each ligand has a σ -type “lone pair” orbital pointing towards the metal, as shown in Figure 8.10 below.

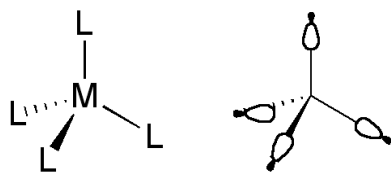


Figure 8.10. A T_d ML_4 complex and the ligand orbitals to be used to construct SALCs.

We now construct a reducible representation for the ligand orbitals in T_d , denoted Γ_σ , and shown in Table 8.8 below. (Another reducible representation, Γ_π in the final row, will be discussed later.) Note that the characters of Γ_σ are exactly the same as those of Γ_{SALC} in Table 3.6 in Section 3.5, in which we developed an approximate model for bonding in CH_4 . As in that case, reduction of Γ_σ gives $\Gamma_\sigma = A_1 + T_2$.

Table 8.8. The character table for the T_d point group.

T_d	$\hat{E}$	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
Γ_σ	4	1	0	0	2		
Γ_π	8	-1	0	0	0		

Just as in the case of CH_4 , the A_1 SALC can interact with the central atom s AO (here, of course, the central atom is a TM, not C), and the T_2 SALCs can interact with the TM p AOs. The difference from the CH_4 cases is that the central TM has valence d AOs, while C does not. In

section of the rightmost column of the character table shows that the d_{xy} , d_{xz} , and d_{yz} AOs transform as T_2 , just like the p AOs, while the $d_{x^2-y^2}$ and d_{z^2} AOs transform as E . This means that we will have bonding and antibonding MOs of a_1 symmetry, nonbonding MOs of e symmetry (these are the TM $d_{x^2-y^2}$ and d_{z^2} AOs, with no symmetry match among the ligand SALCs), and three sets of MOs with t_2 symmetry. Because of the d - p missing, this is another three-orbital problem (really, a three-energy-level problem, with three sets of triply degenerate orbitals). However, since the ligand SALCs are likely closer in energy to the TM d AOs than to the TM p AOs, it is reasonable to consider most of the TM contribution to the bonding $1t_2$ MOs to be from d , rather than p . The σ -only MO scheme for T_d ML_4 complexes is shown in Figure 8.11 on the following page.

Here we have the bonding MOs $1a_1$ and $1t_2$, which will be filled by the 8 electrons contributed by the four ligands' lone pairs. If the TM and oxidation state are such that the complex is not d^0 , the d electrons will fill the strictly nonbonding $1e$ MOs (which are still pure d AOs, as in CFT) and the roughly nonbonding $2t_2$ MOs, which are mostly d AOs, but with some ligand and some TM p character. The gap between $1e$ and $2t_2$ is the ligand field splitting parameter Δ_T , which is likely to be fairly small, since both sets of MOs are (either strictly or roughly) nonbonding. This is why the vast majority of T_d complexes are high-spin (if both high-spin and low-spin ground states are possible): for instance, a d^3 complex will almost certainly have electron configuration $(1e)^2(2t_2)^1$, rather than $(1e)^3(2t_2)^0$. The significantly antibonding MOs are $2a_1$, which is chiefly TM s in character with some ligand contribution, and $3t_2$, which is chiefly TM p in character with some TM d and ligand contribution. A d^0 , σ -only T_d ML_4 complex has a total M-L bond order of 4, and an average M-L bond order of 1. The addition of d electrons does not change the M-L bond order, assuming that the $2t_2$ MOs can be considered roughly nonbonding.

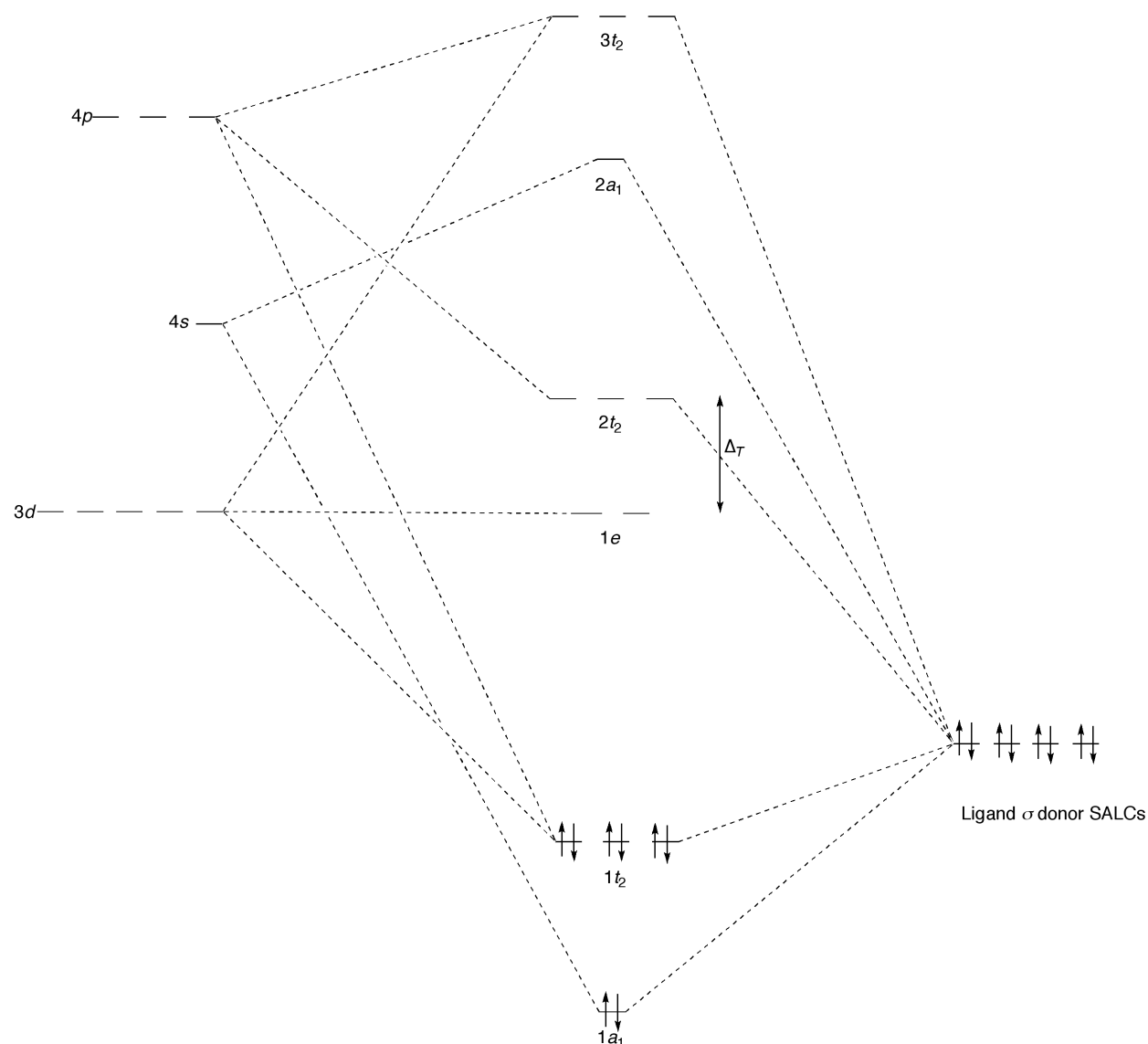


Figure 8.11. Qualitative MO diagram for T_d ML_4 , with only σ interactions between the metal and ligands.

We now consider ML_4 complexes in which the ligands have π orbitals with which they can engage in bonding. These orbitals can be filled, and fairly low in energy, like the lone pairs of a halide, or they can be empty, and high in energy, like the C–O π antibonding MOs of CO. The SALCs we form from these π orbitals will belong to the same irreps in either case, but their energies compared to the TM AOs will differ. To construct a reducible representation Γ_π , we imagine two p AOs (or π MOs) on each ligand, each perpendicular to the M–L bond axis. To simplify the diagram, we can simply write vectors like this, since they have all the necessary

symmetry properties, as shown in Figure 8.12 below. For the sake of argument, consider each ligand to be at the center of its own Cartesian coordinate system, with the z axis along the M–L bond axis, and the x and y axes perpendicular.

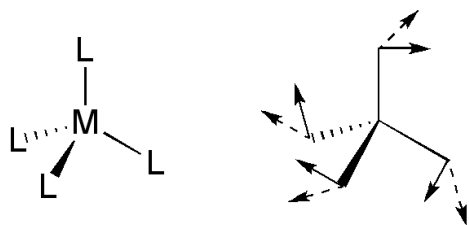


Figure 8.12. Vector picture used to derive a reducible representation for ligand-based π orbitals.

We derive the characters of Γ_π as follows: $\hat{E}$ leaves all 8 vectors unchanged, so $\chi = 8$. $\hat{C}_2$, $\hat{S}_4$, and $\hat{\sigma}_d$ all involve interchanging all the atoms, which also interchanges all the vectors, so each operation in any of these classes has $\chi = 0$. The character under $\hat{C}_3$ is more complicated. Each C_3 axis contains an M–L bond. The other three ligands are all interchanged with each other, along with their associated vectors, by a $\hat{C}_3$ operation, so we need only to consider what happens to the vectors on the ligand that lies along the C_3 axis. If the x and y vectors represent the p AOs or π MOs on that ligand, we see that a $\hat{C}_3$ rotation does the following, as shown in Figure 8.13 below.

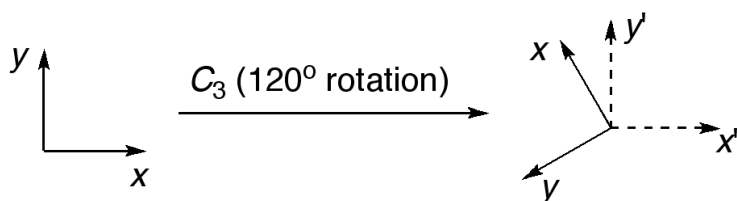


Figure 8.13. Effect of a $\hat{C}_3$ rotation on ligand-based π orbitals.

So far, we have used the rules that every vector that remains unchanged contributes +1 to the character, every vector taken into the negative of itself contributes –1, and every vector completely interchanged with another contributes 0. We see here, however, that a $\hat{C}_3$ rotation takes x and y into a new set of vectors, x' and y' , each of which is a mixture (a linear

combination) of x and y . To determine the character for this operation, we must look at the matrix representation of the operation. Recall that, when a set of coordinates (x, y, z) is rotated by some angle θ counterclockwise about the z axis, the transformation involving the rotation matrix is

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \cos \theta - y \sin \theta \\ x \sin \theta + y \cos \theta \\ z \end{bmatrix}$$

In this case, we need not concern ourselves with z (since the vector along the M-L bond's z axis is accounted for in Γ_σ), so we need only consider the transformation of x and y by a two-dimensional rotation matrix:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x \cos \theta - y \sin \theta \\ x \sin \theta + y \cos \theta \end{bmatrix}$$

For a $\hat{C}_3$ rotation, $\theta = 120^\circ = \frac{2\pi}{3}$, so the transformation in this case is

$$\begin{aligned} \begin{bmatrix} x' \\ y' \end{bmatrix} &= \begin{bmatrix} \cos\left(\frac{2\pi}{3}\right) & -\sin\left(\frac{2\pi}{3}\right) \\ \sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x \cos\left(\frac{2\pi}{3}\right) - y \sin\left(\frac{2\pi}{3}\right) \\ x \sin\left(\frac{2\pi}{3}\right) + y \cos\left(\frac{2\pi}{3}\right) \end{bmatrix} \\ &= \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ \frac{\sqrt{3}}{2}x - \frac{1}{2}y \end{bmatrix} \end{aligned}$$

The character under $\hat{C}_3$ is thus $-\frac{1}{2} - \frac{1}{2} = -1$. All the characters of Γ_π are shown in Table 8.8.

Decomposition of Γ_π using the usual formula yields $\Gamma_\pi = E + T_1 + T_2$. This gives us a pair of E SALCs that can interact with the TM d AOs of e symmetry, so these d -type orbitals are no longer strictly nonbonding. We also have another set of T_2 salts, turning our previous three-energy-level problem into a four-energy-level problem, with four sets of triply degenerate MOs with t_2 symmetry. The T_1 SALC is strictly nonbonding (with respect to metal-ligand interactions; it may be bonding or antibonding within the ligands), as the TM has no valence AOs with T_1 symmetry.

An MO scheme for a $d^0 T_d ML_4$ complex with π -donor ligands is shown in Figure 8.14 below. A real example of such a complex is one of the titanium(IV) alkoxides $Ti(OR)_4$ ($R = Me, Et, etc.$).

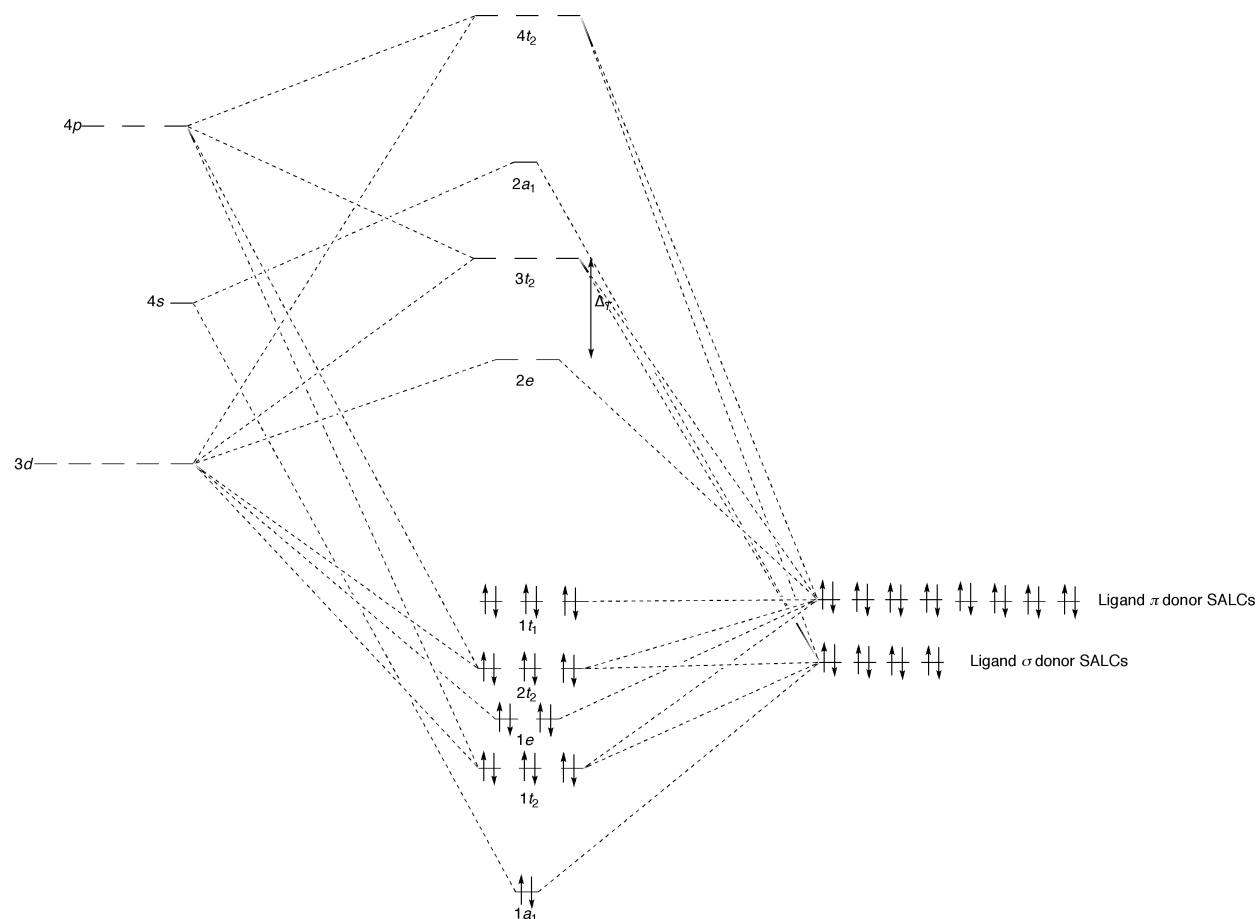


Figure 8.14. Qualitative MO diagram for $T_d ML_4$ with π -donor ligands.

Here the bonding MOs are $1a_1$ (TM s and ligand σ -bonding), $1t_2$ (mostly TM d and ligand σ -bonding, with some contribution from TM p and ligand π SALCs), $1e$ (TM d and ligand π -bonding), and $2t_2$ (mostly TM d and p and ligand π -bonding, with some contribution from ligand σ SALCs). The $1t_1$ MOs are ligand-only nonbonding MOs. The antibonding MOs are $2e$ (TM d and ligand π -antibonding), $3t_2$ (mostly TM d and p and ligand π -antibonding, with some contribution from ligand σ SALCs), $2a_1$ (TM s and ligand σ -antibonding), and $4t_2$ (mostly TM p and ligand σ antibonding, with some contribution from TM d and ligand π SALCs).

This MO diagram is significantly more complicated than the σ -only case shown in Figure 8.10, but the key change from the point of view of metal d AOs (*e.g.* when considering $d \rightarrow d$ electronic transitions in spectroscopy) is that the MOs with the most metal d character, $2e$ and $3t_2$, are now both metal-ligand antibonding. The d -type MOs with e symmetry ($2e$) are now π -antibonding, rather than nonbonding (as in the σ -only case). The d -type MOs with t_2 symmetry ($3t_2$) are now both σ -antibonding *and* π -antibonding, as opposed to merely σ -antibonding (as in the σ -only case). Thus, both sets of predominantly TM d -type MOs are raised in energy. It is difficult to predict whether Δ_T , the energy difference between these MOs, will increase or decrease compared to the σ -only case, and this will depend on the complex. The important point, however, is that Δ_T will not change *dramatically* the way that Δ_O decreases dramatically when going from a σ -only O_h ML_6 complex to an O_h ML_6 complex with π -donor ligands.

For a d^0 T_d ML_4 complex with π -donor ligands, the total M–L bond order is 9, and the average M–L bond order is $\frac{9}{4}$. The addition of d electrons decreases the M–L bond order, as the d -type MOs $2e$ and $3t_2$ are both M–L antibonding. For example, the common d^7 complex ion $CoCl_4^{2-}$ has a total M–L bond order of $\frac{11}{2}$, and an average M–L bond order of $\frac{11}{8}$. This does not, however, mean that T_d ML_4 complexes with π -donor ligands and several d electrons are uncommon or unstable. $CoCl_4^{2-}$ is the main cobalt-containing species formed when cobalt(II) salts are dissolved in concentrated HCl, and the d^5 , iron(III) complex anion $FeCl_4^-$ (total Fe–Cl bond order $\frac{13}{2}$, average Fe–Cl bond order $\frac{13}{8}$) is similarly common and stable. It is important to remember that most metal-ligand bonds are covalent, but often strongly polar (especially when the ligand binds *via* an electronegative atom like N, O, or a halide), so the electrostatic attraction between electronegative ligands and an electropositive metal contributes substantially to the overall bond energy, in addition to the covalent contributions.

Let us now consider $Ni(CO)_4$, a T_d ML_4 complex whose ligands have empty, high-energy π orbitals. This complex was the first transition metal carbonyl complex discovered (see Section 12.3 for some historical details), and its ligand π orbitals are C–O π antibonding MOs.

While these form SALCs of $E + T_1 + T_2$ symmetry, just as in the π -donor case, the fact that these basis orbitals start at higher energy and are empty in the free ligands changes the energy levels of the MOs of the resulting TM complex. An MO scheme for a $d^0 T_d ML_4$ complex with π -acceptor ligands is shown in Figure 8.15 on the following page.

The main difference from the σ -only case is that the TM d -type MOs, $1e$ and $2t_2$, are now lower in energy. The $1e$ MOs, formerly strictly nonbonding, are now M–L π bonding (though π antibonding within the ligands), and the $2t_2$ MOs, formerly roughly nonbonding, are now M–L bonding, with $[\sigma + \pi]$ character. There is no general way to easily predict whether the presence of π acceptor ligands will make Δ_T larger or smaller; this will depend on the ligand and the metal. However, the presence of π -acceptor ligands will not cause Δ_T to increase dramatically in the way that Δ_o increases dramatically in O_h , ML_6 complexes with π -acceptor ligands.

In a d^0 complex, the total M–L bond order is 4 and the average M–L bond order is 1, just as in the σ -only case. However, d^0 complexes with π -acceptor ligands are very rare for both octahedral and tetrahedral complexes. Since the d -type MOs, $1e$ and $2t_2$, are now distinctly M–L bonding, the addition of d electrons increases the M–L bond order. $Ni(CO)_4$ is a d^{10} complex: the CO ligands are taken to be neutral (since neutral CO is a stable, closed-shell molecule), so the Ni center is thus Ni(0) and d^{10} . The total Ni–C bond order in $Ni(CO)_4$, with valence electron configuration $(1a_1)^2(1t_2)^6(1e)^4(2t_2)^6$, is 9, with an average Ni–C bond order of $\frac{9}{4}$, the same as that of a $d^0 T_d$ complex with π -donor ligands. Just as with O_h complexes, T_d complexes with π -acceptor ligands are common for metal/oxidation state combinations with several d electrons. Another common d^{10} species is $Pd(PPh_3)_4$, often used as a catalyst precursor in synthetic organic chemistry.⁷⁰

⁷⁰ You may be wondering how a phosphine can be a π -acceptor ligand. The traditional explanation was that the empty $3d$ AOs of phosphorus accepted electron density from the metal *via* π -backbonding. A more modern explanation is that the metal back-donates, in a π fashion, into a phosphine MO which is σ -antibonding with respect to phosphorus and its substituents. Such phosphine MOs would be broadly similar to the $2e$ MOs of NH_3 shown in Figure 3.6, albeit with a more complicated form, since the phenyl substituents involve more basis orbitals than H.

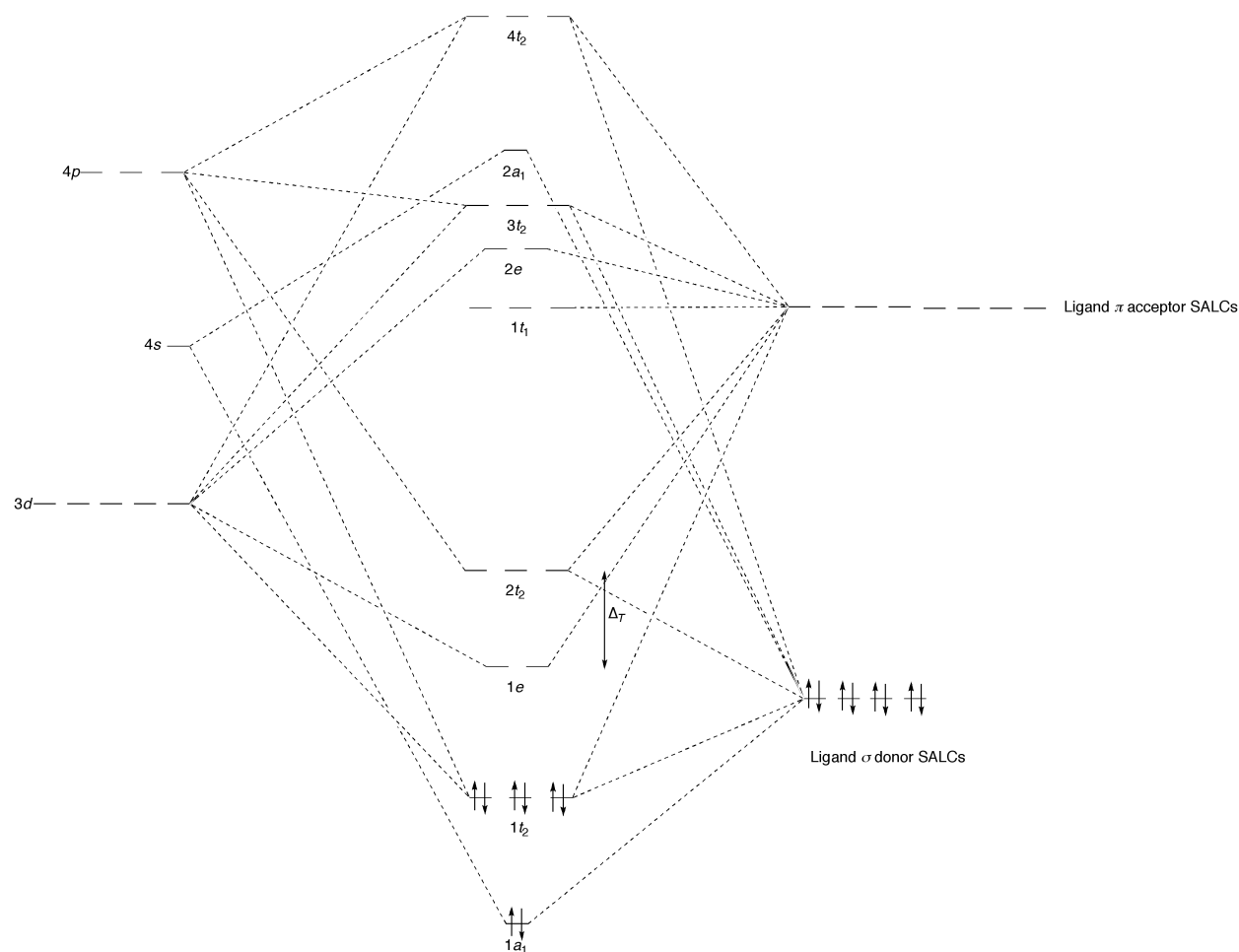


Figure 8.15. Qualitative MO diagram for T_d ML_4 with π -acceptor ligands.

8.6. Dependence of the Ligand Field Splitting Parameter (Δ_o or Δ_T) on the Metal

We have seen that the spectrochemical series can be rationalized by noting that π -donor ligands tend to be weak-field, π -acceptor ligands tend to be strong-field, and σ -only ligands tend to be intermediate. (This is particularly true for O_h complexes.) When discussing CFT, we also noted that, with the ligands and the oxidation state of the TM held constant, Δ_o values were higher for metals of the second (Y-Cd) and third (Lu-Hg) transition series than for those of the first (Sc-Zn). For instance, Δ_o for $Mo(CO)_6$ is greater than that for $Cr(CO)_6$ (though both complexes are low-spin). This can be rationalized on MO theory grounds by noting that a metal's 3d AOs, which are valence orbitals for first-series TMs, are poorly shielded by the inner electrons, and experience a high effective nuclear charge. The electrons in these AOs are thus pulled tightly towards the nucleus, causing the orbitals to be fairly contracted. This

means that the overlap integrals $S_{3d,SALC}$ between $3d$ AOs and ligand SALCs are rather small, since the $3d$ AOs do not extend very far out into space. In contrast, a $4d$ AO (valence for a second-series TM) or a $5d$ AO (valence for a third-series TM) is better shielded by core electrons, and has more significant electron density farther from the nucleus. This means that such orbitals can overlap with SALCs much better, making both bonding and antibonding interactions stronger. As the energy difference Δ_o between the t_{2g} and e_g d -type MOs of an O_h complex is one between a nonbonding, π -bonding, or π -antibonding set of MOs (t_{2g}) and a strongly σ -antibonding set of MOs (e_g), the stronger the bonding and antibonding interactions are, the greater the resulting energy difference is.

8.7. The 18-Electron Rule

In main-group chemistry, especially organic chemistry, we frequently invoke the octet rule: in a stable molecule, each atom (other than H and He) will have eight valence electrons around its nucleus, counting both lone pairs and electrons in covalent bonds. This tendency is commonly rationalized by the fact that each main-group atom has four valence AOs (one s and three p), which can be filled by eight electrons. This rationalization is heuristic, and a useful memory aid, but it is not rigorous. However, we have seen that the MO diagrams for some common main-group molecules, such as H_2O , NH_3 , and CH_4 , which follow the octet rule indicate that they have all bonding and nonbonding MOs filled, and all antibonding MOs empty.

Similarly, many (though by no means all!) stable TM complexes, particularly organometallic TM complexes, have 18 valence electrons around the TM center. The crudest way to rationalize this (or at least to help you remember the pattern) is to note that a TM atom has nine valence AOs (five d , one s , three p), which can be filled by 18 electrons. Looking at the MO picture, we can reason that, in an octahedral complexes with six σ -only ligands, each ligand donates two electrons to a bonding, mostly ligand-based MO, accounting for 12 electrons. The remaining six electrons occupy the lower-energy, nonbonding TM d -type MOs, labeled t_{2g} , while the higher-energy, antibonding e_g set remains unoccupied. The same is true when the six ligands are π -acceptors, only now the d -type t_{2g} MOs are bonding. We see that

$d^6 O_h$ complexes often satisfy this 18-electron rule (the “18e rule,” for short). Examples include $M(CO)_6$ ($M = Cr, Mo, W$) and $Fe(CN)_6^{4-}$. Note that the 18e rule implicitly assumes that the complex is low-spin, in order to avoid populating the antibonding e_g MOs. In high-spin complexes, however, the electrons occupy the e_g MOs in preference to pairing up in t_{2g} MOs. Thus, the 18e rule simply does not apply to high-spin complexes, and it should not be used as a guideline for predicting whether a given high-spin complex is or is not likely to be stable.

In general, the 18e rule also does not apply to complexes of π -donor ligands. A $d^0 O_h$ complex with six π -donor ligands has 36 valence electrons, all in bonding or antibonding MOs. Even if we exclude the strictly nonbonding $1t_{1g}$ and $1t_{2u}$ MOs, we still have 24 electrons in bonding MOs. Complexes with π -donor ligands and d electron counts greater than zero have some antibonding MOs occupied, but many such complexes are, nevertheless, stable.

For T_d complexes, the 18e rule is often followed in complexes of π -acceptor ligands, in which each ligand donates two electrons for eight total, and there are 10 d electrons, all occupying bonding d -type MOs. Thus, d^{10} species such as $Ni(CO)_4$, $Co(CO)_4^-$, and $Pd(PPh_3)_4$ are all 18e complexes, with all bonding MOs filled and all antibonding MOs empty.

Many TM complexes of various geometries have MO diagrams that suggest that the 18e rule under some circumstances (depending on whether the ligands are σ -only, π -donors, or π -acceptors), and it is a rule of thumb well worth remembering. Nonetheless, you should be aware that there are many more exceptions to the 18e rule among stable species than there are exceptions to the octet rule among stable main-group molecules. One major such exception will be discussed in the following section on square-planar TM complexes.

8.8. MO Theory for Square-Planar TM Complexes

The third most common coordination geometry for TM complexes is ML_4 (four-coordinate) with a square-planar arrangement of ligands, *i.e.* the metal and the Lewis-basic donor atoms of four ligands all lie in a plane, with the ligand donor atom defining the points of a quadrilateral. If all ligands L are the same, then the donor atoms define the points of a square,

and ML_4 belongs to point group D_{4h} . On steric grounds, we would expect a square-planar coordination geometry to be less stable than a tetrahedral one due to repulsion between the ligands, but we will see that some complexes adopt this geometry for electronic reasons. The presence of valence d AOs is key to the existence of square-planar TM complexes; we should never expect to find an organic compound with a square-planar geometry at a carbon atom. To develop bonding theory for these complexes, we take the TM to be at the center of the square (the origin of a Cartesian coordinate system), and we imagine that each ligand has a σ -type “lone pair” orbital pointing towards the metal, as shown in Figure 8.16 below. The ligands are taken to lie along the x and y axes, while the z axis is perpendicular to the plane of the molecule, and it is also the molecule’s C_4 proper rotation axis. A real example of a σ -only D_{4h} ML_4 complex is the Pt(II) complex cation $Pt(NH_3)_4^{2+}$.

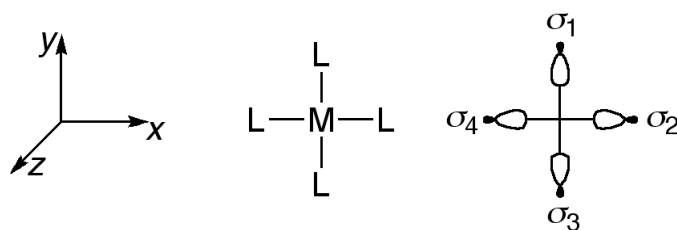


Figure 8.16. A D_{4h} ML_4 complex and the ligand orbitals to be used to construct SALCs.

We construct a reducible representation Γ_σ in Table 8.9 on the following page. (The reducible representations Γ_{par} and Γ_{perp} , which are used to account for π bonding between the TM and the ligands, will be discussed later.)

Table 8.9. The character table for the D_{4h} point group.

D_{4h}	$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$2\hat{C}_2'$	$2\hat{C}_2''$	$\hat{i}$	$2\hat{S}_4$	$\hat{\sigma}_h$	$2\hat{\sigma}_v$	$2\hat{\sigma}_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	
Γ_σ	4	0	0	2	0	0	0	4	2	0		
Γ_{par}	4	0	0	-2	0	0	0	4	-2	0		
Γ_{perp}	4	0	0	-2	0	0	0	-4	2	0		

Reduction of Γ_σ by the usual formula gives $\Gamma_\sigma = A_{1g} + B_{1g} + E_u$. Pictures of the SALCs are shown in Figure 8.17 below, followed by algebraic expressions for each.

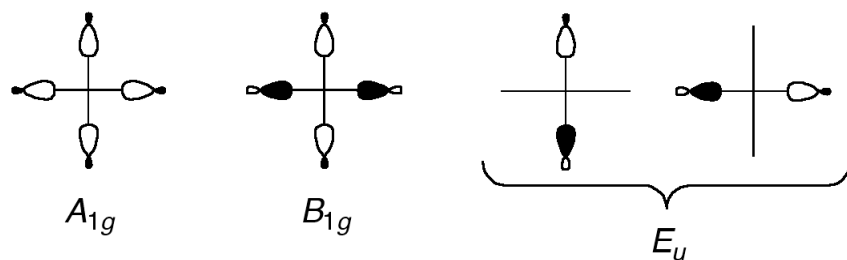


Figure 8.17. Ligand-based σ SALCs for D_{4h} ML_4 .

$$\phi_{A_{1g}}^{\text{SALC}} = \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

$$\phi_{B_{1g}}^{\text{SALC}} = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

$$\phi_{E_{u,x}}^{\text{SALC}} = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)$$

$$\phi_{E_{u,y}}^{\text{SALC}} = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3)$$

Comparing the symmetries of the SALCs with the rightmost two columns of the D_{4h} character table, we see that the TM s and d_{z^2} AOs transform as A_{1g} , setting up a three-orbital problem with the A_{1g} SALC. The metal $d_{x^2-y^2}$ AO transforms as B_{1g} , forming bonding and antibonding MOs with the B_{1g} SALC. The metal p_x and p_y AOs transform together as E_u , forming twofold-degenerate sets of bonding and antibonding MOs with the E_u SALCs. Several metal AOs remain nonbonding in the σ -only case, with no symmetry matches among the SALCs: d_{xy} transforms as B_{2g} , d_{xz} and d_{yz} transform together as E_g , and p_z transforms as A_{2u} . An MO diagram for the σ -only case is shown in Figure 8.18 on the following page.

Here the bonding MOs are $1a_{1g}$, $1e_u$, and $1b_{1g}$, predominantly ligand-based and each doubly occupied by electrons from the ligands, even in a d^0 complex. The predominantly TM d -type MOs are $1b_{2g}$ and $1e_g$ (strictly nonbonding), $2a_{1g}$ (roughly nonbonding, mostly TM d with some s contribution), and $2b_{1g}$ (strongly antibonding). Higher-energy MOs are $1a_{2u}$ (strictly nonbonding, TM p), $3a_{1g}$ (antibonding, mostly TM s with some d contribution), and $2e_u$ (antibonding, mostly TM p).

If the TM is d^0 , then the total M–L bond order is 4, and the average M–L bond order is 1. If we consider the $2a_{1g}$ MO to be roughly nonbonding, then adding d electrons up to d^8 does not change the M–L bond order. Past d^8 , however, the addition of further electrons lowers the bond order, due to the occupation of the strongly antibonding $2b_{1g}$ MO.

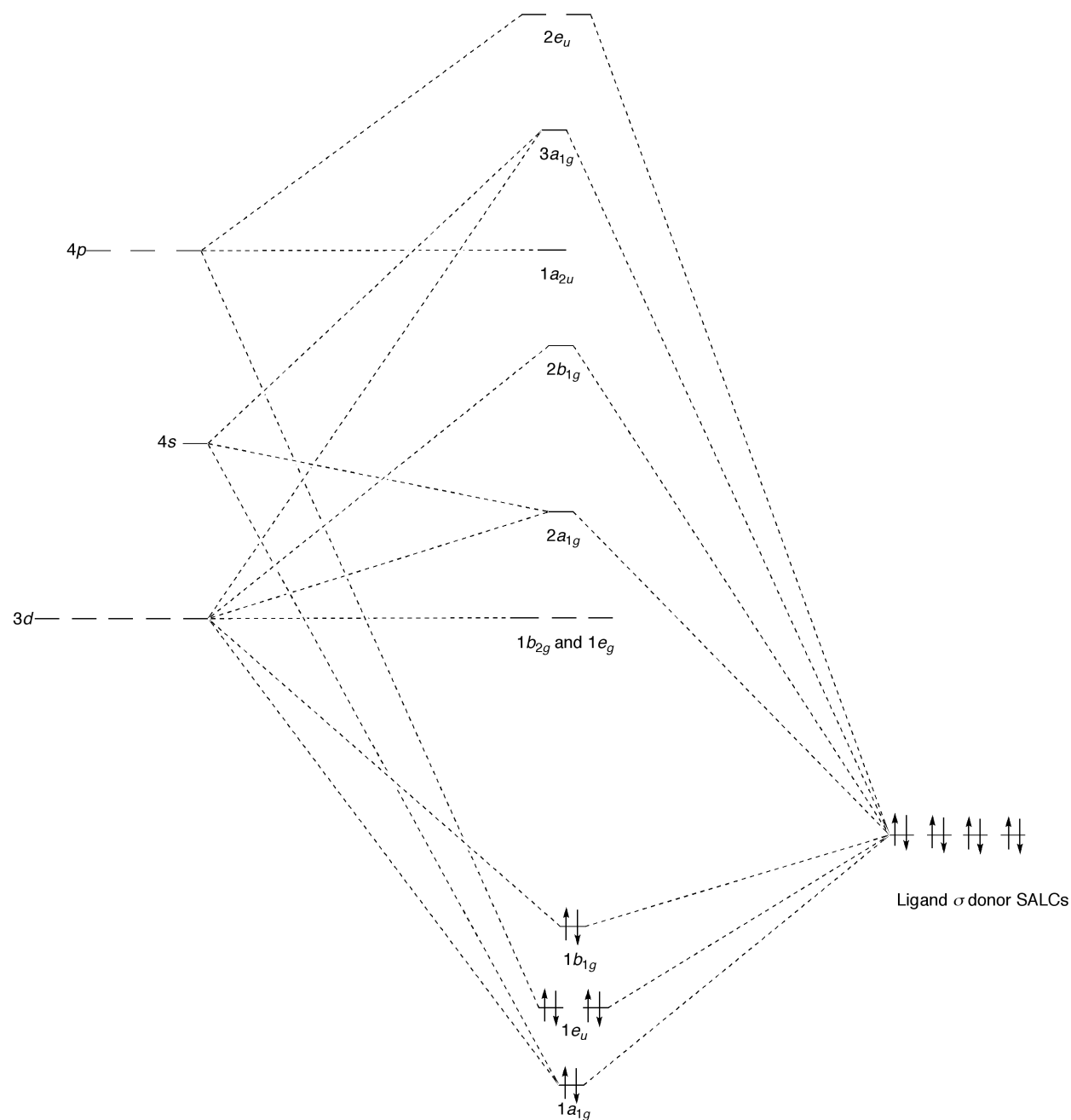


Figure 8.18. Qualitative MO diagram for D_{4h} ML_4 , with only σ interactions between the metal and ligands.

Next, we consider π bonding. We assume that each ligand has two AOs or MOs apiece that are suitable for π bonding, but in the lower-symmetry environment of D_{4h} , these orbitals come in two sets which are *not* equivalent by symmetry. One set lies in (parallel to) the molecular plane (which is the xy plane), and one is perpendicular to the molecular plane

(each of these orbitals is parallel to the z axis). Since an orbital in one of these sets cannot be converted to an orbital in the other by any symmetry operation in D_{4h} , we must derive two reducible representations: Γ_{par} , for the parallel orbitals, and Γ_{perp} , for the perpendicular orbitals. These reducible representations apply equally well to a set of filled lone pair orbitals, such as those on a halide ligand, and to a set of empty, higher-energy antibonding ligand MOs, such as the π -antibonding MOs of a π -acceptor ligand like CO or CN^- . Each reducible representation is shown in Table 8.9 above, and reduction of these representations using the usual formula gives $\Gamma_{\text{par}} = A_{2g} + B_{2g} + E_u$ and $\Gamma_{\text{perp}} = A_{2u} + B_{2u} + E_g$. Diagrams of the π -type B_{2g} , E_u , A_{2u} , and E_g SALCs are shown in Figure 8.19 below.

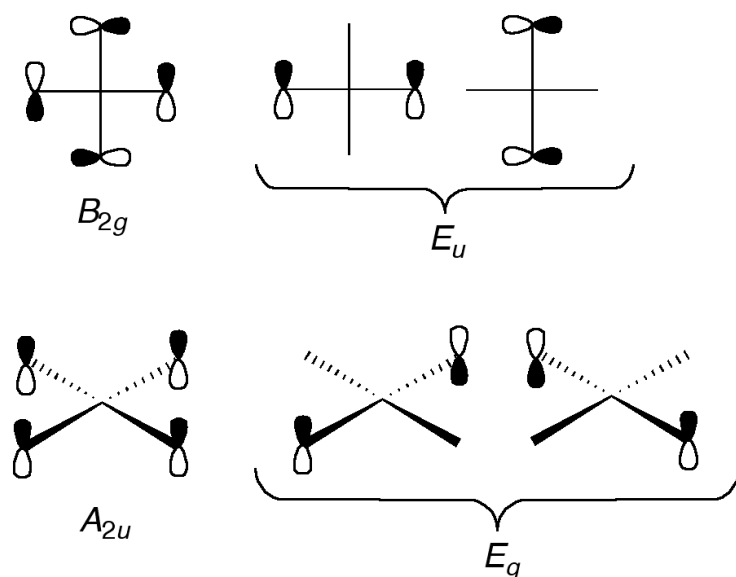


Figure 8.19. The π -type B_{2g} , E_u , A_{2u} , and E_g SALCs of a D_{4h} ML_4 complex.

Examining the symmetries of the SALCs from Γ_{par} and Γ_{perp} , we note that the A_{2g} and B_{2u} SALCs have no match among the TM AOs, so each of these SALCs constitutes a nonbonding MO. The A_{2u} SALC forms bonding and antibonding interactions with the metal p_z AO, so this AO is no longer nonbonding. The E_u SALCs mix with the metal p_x and p_y AOs and the σ -type E_u SALCs, resulting in three sets of MOs with E_u symmetry, each with mixed σ and π character. Finally, and most importantly from a view of TM chemistry focusing on d AOs, the B_{2g} and E_g SALCs form bonding and antibonding interactions with the metal d_{xy} and (d_{xz}, d_{yz}) AOs, respectively. Thus, when π interactions are taken into account, none of the TM's d AOs is

rigorously nonbonding. An MO diagram for the π -donor case is shown in Figure 8.20 below. A real example of a square-planar TM complex with π -donor ligands is PtCl_4^{2-} .

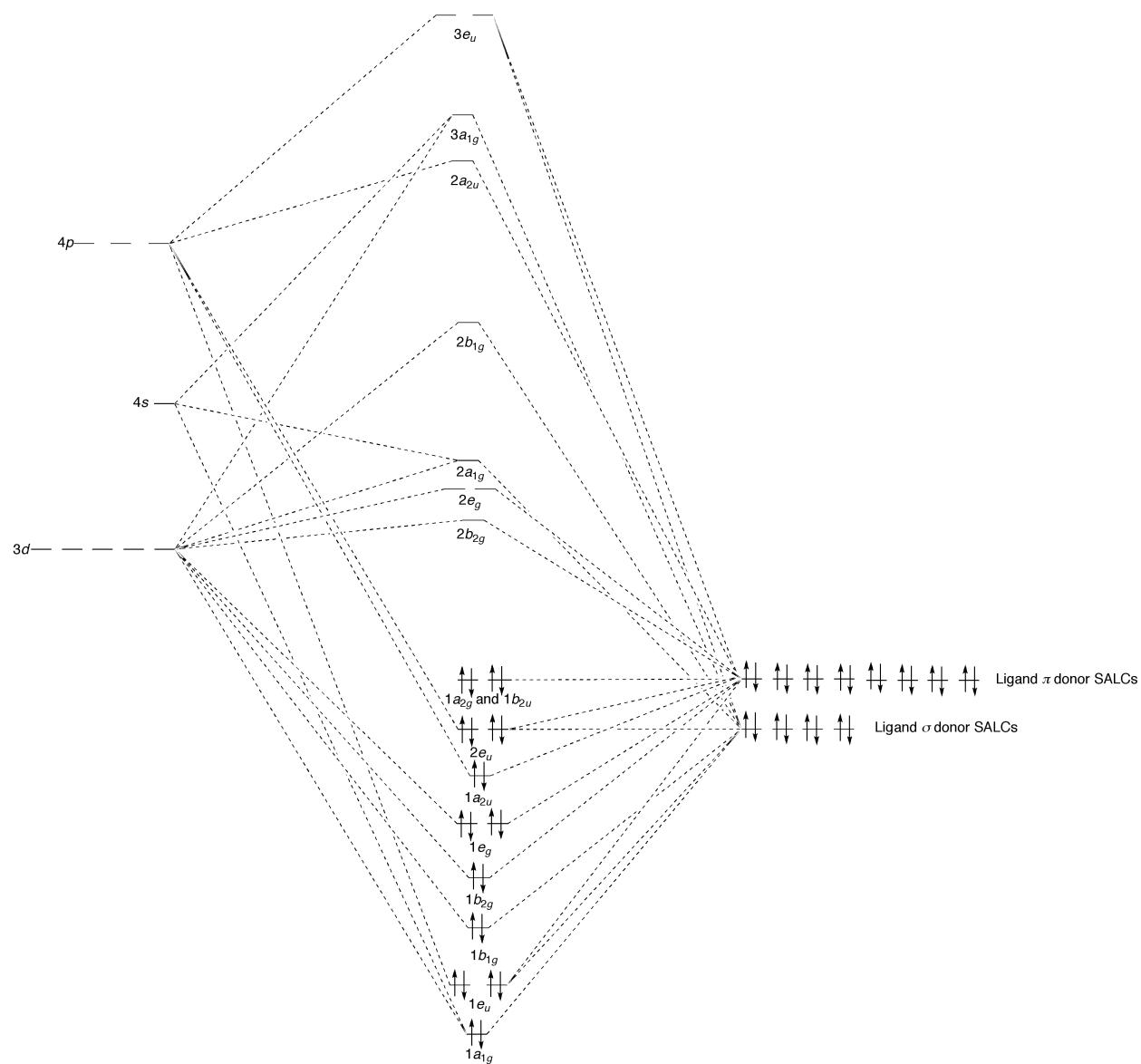


Figure 8.20. Qualitative MO diagram for D_{4h} ML_4 with π -donor ligands.

Figure 8.20 is, without question, a complicated diagram. The MOs $1a_{1g}$, $1e_u$, $1b_{1g}$, $1b_{2g}$, $1e_g$, and $1a_{2u}$ are all bonding, and predominantly located on the ligands. The $2e_u$ MOs are slightly bonding and mostly ligand-based, but it is reasonable to consider them as *roughly* nonbonding, as this is the intermediate energy level in a three-energy-level problem. The

$1a_{2g}$ and $1b_{2u}$ MOs are ligand-based and strictly nonbonding in terms of metal-ligand interactions.

The mostly TM d -type MOs are $2b_{2g}$ and $2e_g$, which are π -antibonding, $2a_{1g}$, which is roughly nonbonding but which consists of a mixture of TM d and TM s character, and $2b_{1g}$, which is strongly σ -antibonding. The relative energies of $2b_{2g}$, $2e_g$, and $2a_{1g}$ are difficult to predict, and in fact, their relative energies may vary based on the metal and the ligands. The key point, however, is that $2b_{1g}$ remains higher in energy than the other d -type MOs (by a considerable margin), just as in the σ -only case. This is because there is a good energy match between the d AOs and the ligand orbitals, and excellent σ -type overlap between this d AO ($d_{x^2-y^2}$) and the ligands, since it points directly towards the ligands along the x and y axes. These factors combine to make $1b_{1g}$ strongly σ -bonding and $2b_{1g}$ strongly σ -antibonding. The MOs of higher energy than $2b_{1g}$ are all predominantly TM s or p in character.

Considering $2e_u$ as roughly nonbonding, the total M–L bond order in a d^0 complex with π -donor ligands is 8, and the average M–L bond order is 2. The addition of d electrons will lower the bond order, as $2b_{2g}$, $2e_g$, and $2b_{1g}$ are antibonding (though $2a_{1g}$ is roughly nonbonding). However, $2b_{2g}$ and $2e_g$ are fairly weakly π -antibonding, while $2b_{1g}$ is strongly σ -antibonding, so a d electron count above d^8 , in which $2b_{1g}$ is occupied, will weaken the M–L bonds substantially.

After having considered the π -donor case, we now consider a D_{4h} ML_4 complex whose ligands have empty, high-energy π orbitals. A real example of such a complex is $Ni(CN)_4^{2-}$, in which case the ligand π orbitals are C–N π -antibonding MOs. The symmetries of the π -type SALCs are precisely the same as in the π -donor case, but their energies are higher. An MO diagram for such a case is shown in Figure 8.21 on the following page.

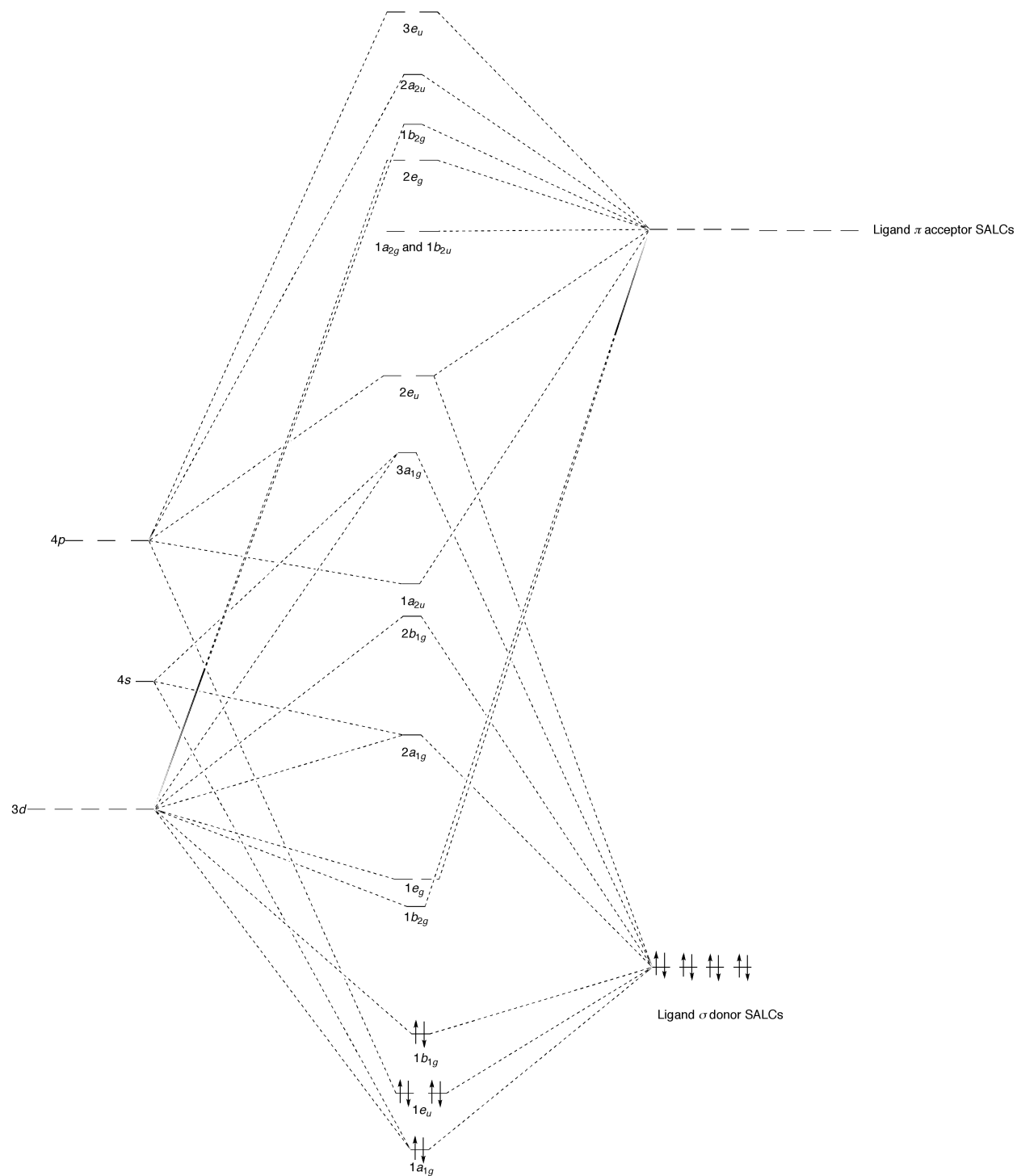


Figure 8.21. Qualitative MO diagram for D_{4h} ML_4 with π -acceptor ligands.

This is another very complicated MO diagram, but the key feature of it is the fact that, since the ligand π orbitals are now significantly *higher* in energy than the TM d AOs, the TM d -type

MOs $1b_{1g}$ and $1e_g$ will now be π -bonding, as opposed to π -antibonding. As in the σ -only case, the other TM d -type MOs are $2a_{1g}$ (roughly nonbonding, with some contribution from TM s) and $2b_{1g}$ (strongly σ -antibonding). As in the π -donor case, the relative energies of $1b_{2g}$ and $1e_g$ may be reversed from what is shown in the figure, depending on the TM and the ligands. Still, since $1b_{2g}$ and $1e_g$ are significantly π -bonding, they will be clearly lower in energy than $2a_{1g}$, and much lower in energy than $2b_{1g}$.

In a d^0 square-planar complex with π -acceptor ligands, the total M–L bond order is 4 and the average M–L bond order is 1, just as in the σ -only case. However, d^0 complexes of this sort are not at all common. Addition of d electrons up to d^6 increases the M–L bond order, and a further increase up to d^8 leaves the M–L bond order unchanged (since the seventh and eighth d electrons will occupy the nonbonding $2a_{1g}$). Another increase past d^8 will cause a decrease in M–L bond order, since $2b_{1g}$ is strongly antibonding. The complex $\text{Ni}(\text{CN})_4^{2-}$ is d^8 , and its total Ni–C bond order is 7, with an average Ni–C bond order of $\frac{7}{4}$.

8.9. The 16-Electron Rule for Square-Planar Complexes

Regardless of whether the ligands are σ -only, π -donors, or π -acceptors, we see that, in all square-planar, D_{4h} complexes, the $2b_{1g}$ MO is considerably higher in energy than any of the other TM d -type MOs. Thus, a d electron count of d^8 fills all the relatively low-energy d -type MOs, leaving the strongly antibonding $2b_{1g}$ empty. (In the case of π -donor ligands, $2b_{2g}$ and $2e_g$ are also antibonding, but they are less strongly antibonding than $2b_{1g}$.) For this reason, d^8 is the most common d electron count for square-planar complexes, and a great many d^8 square planar complexes are known, such as the anticancer drug *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, better known as cisplatin. Square planar geometry is particularly common among Ni(II), Pd(II), and Pt(II) complexes, although a fair number of tetrahedral and octahedral Ni(II) complexes are also known. Square planar geometry is also quite commonly seen among Rh(I) and Ir(I) complexes, and sometimes, but less often, among Co(I) complexes.⁷¹

⁷¹ For example, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, a widely used catalyst for the homogeneous hydrogenation of alkenes, is square-planar at Rh, while $\text{Co}(\text{PPh}_3)_3\text{Cl}$ has a distorted tetrahedral geometry at Co.

We have previously discussed the fact that, for O_h and T_d complexes with π -acceptor ligands (and sometimes with σ -only ligands, if the O_h complexes are low-spin), the 18e rule is often followed, so there are 18 valence electrons around the TM center. Since each ligand is taken to provide two electrons toward this total, we see that d^6 (low-spin) O_h complexes and d^{10} T_d complexes are often found. The 18e rule does *not*, however, apply in general to square-planar complexes. If the ligands are π -acceptors or σ -only, they together donate 8 valence electrons. If the TM is d^8 , as is common for square-planar complexes, then the total valence electron count is 16. It is sometimes said that a “16e rule” applies to square-planar complexes, since addition of two more electrons would fill the $2b_{1g}$ MO, which is much higher in energy. It should be noted that a 16e square-planar complex can undergo *oxidative addition*⁷² of a species X_2 (such as H_2 or an elemental halogen) to form an octahedral complex with two new ligands (each formally considered as X^- for the purposes of assigning oxidation state), an octahedral coordination geometry, and a d^6 d electron count (because the TM has been oxidized by two units). While the TM has two fewer d electrons, each new X^- ligand contributes two electrons, so we have two more valence electrons in the complex overall: it is a d^6 octahedral complex with 18 valence electrons around the TM. Since 18e octahedral and 16e square-planar complexes are both stable coordination geometries, many such complexes are involved in TM-catalyzed reactions of organic compounds, in which the catalytic cycle involves the TM alternating between 18e octahedral and 16e square-planar complexes. Such catalytic cycles will be discussed in depth in several of the following chapters.

Finally, it should be noted that π -donor ligands can be considered to donate more than two electrons to a TM center. A halide ion, for instance, can donate one lone pair to a TM in a σ fashion and up to two lone pairs in a π fashion. Thus, complexes such as $PtCl_4^{2-}$ and $Pt(NH_3)_2Cl_2$ are not really 16 e complexes. Nevertheless, they are stable as d^8 square-planar complexes.

⁷² This type of reaction will be discussed in detail in chapter 13.

Chapter 9: Further Topics in the Electronic Structure of Transition Metal Complexes

9.1. Vibronic Coupling

In Section 4.1, we made use of the Born-Oppenheimer approximation, which assumes that, since nuclei are much more massive than electrons, electronic motion can be analyzed assuming fixed positions of nuclei. Thus, we can assume that a molecule's overall wavefunction Ψ can be considered as the simple product of an electronic wavefunction ψ_{elec} and the vibrational wavefunction ψ_{vib} , or $\Psi = \psi_{\text{elec}}\psi_{\text{vib}}$. This approximation, however, is not exact, and the interaction between electronic and nuclear motion, known as *vibronic coupling*, must sometimes be considered in order to accurately understand molecular structure and spectroscopy.

In the operator notation of quantum mechanics, the vibronic coupling operator $\hat{W}$ is an energy term that shows the change in potential energy U for a molecule as a result of the movement of the nuclear distances $q_\alpha = |\mathbf{q}_\alpha - \mathbf{q}_{\alpha,0}|$ away from the reference distances $q_\alpha = 0$. $\hat{W}$ is given approximately⁷³ by the following expression.

$$\hat{W} \approx \sum_{\alpha} \left(\frac{\partial U}{\partial q_{\alpha}} \right)_0 q_{\alpha} + \frac{1}{2} \sum_{\alpha} \sum_{\beta} \left(\frac{\partial^2 U}{\partial q_{\alpha} \partial q_{\beta}} \right)_0 q_{\alpha} q_{\beta}$$

This expression can be rewritten in a useful fashion by using symmetrized normal coordinates Q , as follows.

$$\hat{W} \approx \sum_{\Gamma\gamma} \left(\frac{\partial U}{\partial Q_{\Gamma\gamma}} \right)_0 Q_{\Gamma\gamma} + \frac{1}{2} \sum_{\Gamma\gamma} \sum_{\Gamma'\gamma'} \left(\frac{\partial^2 U}{\partial Q_{\Gamma\gamma} \partial Q_{\Gamma'\gamma'}} \right)_0 Q_{\Gamma\gamma} Q_{\Gamma'\gamma'}$$

Here Γ represents the irreps of the molecule's point group, and γ represents the different members of a degenerate set of irreps. Thus, a nondegenerate (A or B) irrep would have only one value of γ , a doubly degenerate (E) irrep would have two, and a triply degenerate (T) irrep would have three. The first summation in the expression for $\hat{W}$ is a sum of linear terms,

⁷³ This expression is approximate, rather than exact, because it is a power-series expansion in q_α which has been truncated after the second term. The exact expression would have infinitely many terms, but it is assumed that terms following the ones given are small and become successively smaller.

since each is linearly dependent on a given normal coordinate Q , while the second summation is a sum of quadratic terms, since each is dependent on the product of two normal coordinates (or on the square of a single coordinate, if $\Gamma\gamma = \Gamma'\gamma'$).

When vibronic coupling effects are not too large, $\widehat{W}$ can be considered as a perturbation to the purely electronic Hamiltonian. Consider two electronic state wavefunctions, Ψ_Γ , which transforms as the irrep Γ , and $\Psi_{\Gamma'}$, which transforms as the irrep Γ' . When solving the perturbation theory equations for vibronic coupling, one often encounters matrix elements $W_{\Gamma,\Gamma'} = \langle \Psi_\Gamma | \widehat{W} | \Psi_{\Gamma'} \rangle$, which describes the vibronic coupling interaction between Ψ_Γ and $\Psi_{\Gamma'}$. Each $W_{\Gamma,\Gamma'}$ can be expanded as follows.

$$\begin{aligned} W_{\Gamma,\Gamma'} &= \left\langle \Psi_\Gamma \left| \sum_{\Gamma^*\gamma^*} \left(\frac{\partial U}{\partial Q_{\Gamma^*\gamma^*}} \right)_0 Q_{\Gamma^*\gamma^*} + \frac{1}{2} \sum_{\Gamma^*\gamma^*} \sum_{\Gamma^\dagger\gamma^\dagger} \left(\frac{\partial^2 U}{\partial Q_{\Gamma^*\gamma^*} \partial Q_{\Gamma^\dagger\gamma^\dagger}} \right)_0 Q_{\Gamma^*\gamma^*} Q_{\Gamma^\dagger\gamma^\dagger} \right| \Psi_{\Gamma'} \right\rangle \\ &= \sum_{\Gamma^*\gamma^*} \left\langle \Psi_\Gamma \left| \left(\frac{\partial U}{\partial Q_{\Gamma^*\gamma^*}} \right)_0 \right| \Psi_{\Gamma'} \right\rangle Q_{\Gamma^*\gamma^*} \\ &\quad + \frac{1}{2} \sum_{\Gamma^*\gamma^*} \sum_{\Gamma^\dagger\gamma^\dagger} \left\langle \Psi_\Gamma \left| \left(\frac{\partial^2 U}{\partial Q_{\Gamma^*\gamma^*} \partial Q_{\Gamma^\dagger\gamma^\dagger}} \right)_0 \right| \Psi_{\Gamma'} \right\rangle Q_{\Gamma^*\gamma^*} Q_{\Gamma^\dagger\gamma^\dagger} \end{aligned}$$

Note that all the normal coordinates Q can be pulled outside of the integrals, since the purely electronic wavefunctions Ψ_Γ and $\Psi_{\Gamma'}$ have the nuclear coordinates as *parameters*, and the electronic coordinates as *variables*.

The evaluation of these (admittedly complicated) matrix elements requires the evaluation of a series of quantities called *linear vibronic constants*, which take the form $F_{\Gamma^*}^{\Gamma,\Gamma'} = \left\langle \Psi_\Gamma \left| \left(\frac{\partial U}{\partial Q_{\Gamma^*}} \right)_0 \right| \Psi_{\Gamma'} \right\rangle$. If Ψ_Γ and $\Psi_{\Gamma'}$ are both nondegenerate, then $F_{\Gamma^*}^{\Gamma,\Gamma'} \neq 0$ if (and only if) $\Gamma \times \Gamma' = \Gamma^*$. If either or both of Ψ_Γ and $\Psi_{\Gamma'}$ are degenerate, and $\Gamma \neq \Gamma'$, then the linear vibronic constant has the form $F_{\Gamma^*\gamma^*}^{\Gamma\gamma,\Gamma'\gamma'} = \left\langle \Psi_\Gamma \left| \left(\frac{\partial U}{\partial Q_{\Gamma^*\gamma^*}} \right)_0 \right| \Psi_{\Gamma'} \right\rangle$, and it is nonzero if (and only if) the direct product $\Gamma \times \Gamma'$ contains Γ^* . We have a useful table for the direct products of irreps in the T_d and O_h point groups, which is shown again in Table 9.1 on the following page.

When using this table, please remember that $g \times g = u \times u = g$, $g \times u = u$, and antisymmetric terms are enclosed in square brackets.

Table 9.1. Direct product table for the T_d and O_h point groups.

T_d and O_h	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2		A_1	E	T_2	T_1
E			$A_1 + [A_2] + E$	$T_1 + T_2$	$T_1 + T_2$
T_1				$A_1 + E + [T_1] + T_2$	$A_2 + E + T_1 + T_2$
T_2					$A_1 + E + [T_1] + T_2$

For example, the ground electronic state of a d^2 O_h TM complex is $^3T_{1g}$, and the first excited electronic state with the same spin multiplicity is $^3T_{2g}$. Since $T_{1g} \times T_{2g} = A_{2g} + E_g + T_{1g} + T_{2g}$, any vibrational mode that transforms as A_{2g} , E_g , T_{1g} , or T_{2g} can serve to couple these two electronic states. An O_h ML_6 complex with monatomic ligands has vibrational modes $A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$. Of these, vibrations along the E_g or T_{2g} normal coordinates can couple $^3T_{1g}$ and $^3T_{2g}$.

If $\Gamma = \Gamma'$ and Ψ_Γ is degenerate, then the linear vibronic constant is called the *diagonal linear*

coupling constant. It has the form $F_{\Gamma^*\Gamma^*}^{\Gamma Y} = \left\langle \Psi_\Gamma \left| \left(\frac{\partial U}{\partial Q_{\Gamma^*\Gamma^*}} \right)_0 \right| \Psi_\Gamma \right\rangle$, and it is nonzero if (and only if)

the symmetric part of the direct product $\Gamma \times \Gamma$ contains Γ^* . The symmetric part of the direct product of two irreps, each of which is degenerate, can be determined by the equation

$\chi_{\text{symmetric}}(\hat{R}) = \frac{1}{2} \{ [\chi(\hat{R})]^2 + \chi(\hat{R}^2) \}$ or from Table 9.1. For example, the ground electronic

state of a low-spin O_h d^7 complex is ^2E_g . Can this ground state be vibronically coupled with an electronic excited state that is also ^2E_g ? We see that $E_g \times E_g = A_{1g} + [A_{2g}] + E_g$. This means that the two ^2E_g states can be coupled by vibrations with either A_{1g} or E_g symmetry. Assuming the complex has monatomic ligands, there are indeed both A_{1g} and E_g vibrational modes, so vibronic coupling of these two states is possible.

There is a specific physical meaning to the diagonal linear coupling constants. A molecule in a state Ψ_Γ will tend to undergo distortion along a normal coordinate whose irrep is contained

in the symmetrical part of $\Gamma \times \Gamma$. One such irrep will *always* be present, namely, the totally symmetric irrep (*e.g.* A_1 in T_d molecules, A_{1g} in O_h molecules). This “distortion” will not change the symmetry (point group) of the molecule: a totally symmetric vibration consists simply of stretching or compressing all bonds by the same amount. However, distortion along a normal coordinate that does *not* transform as the totally symmetric irrep will actually change the molecule’s shape and point group during the distortion. Note that two electronic states belonging to the same nondegenerate irrep can only couple through a totally symmetric vibration, since the direct product of any nondegenerate irrep with itself is just the totally symmetric irrep. Thus, vibronic coupling between two nondegenerate electronic states belonging to the same irrep may alter the bond lengths in a molecule, but it will not change the molecule’s point group. In contrast, vibronic coupling between two degenerate electronic states belonging to the same irrep can lead to vibrations that change the molecule’s point group.

There also exist quadratic vibronic constants, which are derived from the quadratic terms of $\hat{W}$ and its matrix elements. They are usually smaller in magnitude than the linear vibronic constants. From the linear and quadratic vibronic constants combined, one can calculate the value of the overall Hooke’s law-type force constant for displacement of nuclei along some normal coordinate Q .

9.2. The Jahn-Teller Effect

When we study chemistry, or any other physical science, it often appears that nature favors symmetry. Often, though not always, when multiple isomers are possible for a given molecular formula, the isomer with the most symmetrical structure is the most thermodynamically stable. Sometimes, however, the observed structure of a molecule or ion exhibits distortions from the symmetrical structure we might expect. For homoleptic ML_6 complexes with octahedral geometry, there is sometimes evidence that the ligands coordinate to the metal as a *nonregular* octahedron, leading to a structure that belongs to a point group with lower symmetry than O_h .

For instance, consider the ion $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Assuming rapid rotation about the Cu–O bonds, we would likely expect this complex to have O_h symmetry, with all six Cu–O bonds being of equal length. However, the structures of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ salts, measured using single-crystal X-ray diffraction, indicate that this complex cation has two aqua ligands, *trans* to each other, for which the Cu–O bonds are longer than those for the other aqua ligands. Such a *trans* double elongation lowers the cation's symmetry from O_h to D_{4h} . Similarly, one would expect only one signal in the UV-visible absorption spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in the region corresponding to $d \rightarrow d$ electronic transitions: since the d -type MO electron configuration is $(t_{2g})^6(e_g)^3$, one would expect only one signal, corresponding to the excitation of one of the electrons in the t_{2g} MOs into the e_g MO that is singly occupied. Experimentally, however, two closely spaced signals are observed in this region. While the energy difference between these absorptions is not especially large, it is still significant. What is going on here?

In 1937, Hermann Arthur Jahn (1907-1979) and Edward Teller (1908-2003)⁷⁴ proved an important theorem in the application of group theory to chemical bonding and molecular structure. The so-called Jahn-Teller theorem, as given in their seminal paper,⁷⁵ states that “All non-linear nuclear configurations are therefore unstable for an orbitally degenerate electronic state.” This sounds cryptic, but it can be helpfully illustrated by example. The d electron configuration of O_h $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is $(t_{2g})^6(e_g)^3$, which means that one of the two degenerate e_g orbitals is doubly occupied (two electrons), while the other is singly occupied (only one electron). Since the e_g orbitals are degenerate, it should not matter, energetically, which of the two is doubly occupied and which is singly occupied. Thus, the configuration $(t_{2g})^6(e_g)^3$ describes two degenerate electronic states: one in which the first of the two e_g orbitals is doubly occupied and the second is singly occupied, and the other, in which the reverse is true. In general, one can determine from an electron configuration whether an electronic state is degenerate as follows: the state is degenerate if (and only if) a set of degenerate orbitals is *unequally* occupied. In the case of the $(t_{2g})^6(e_g)^3$ configuration, the ground electronic state is the doubly degenerate ${}^2E_g$. Table 9.1 allows for the rapid

⁷⁴ Known more infamously as the “father of the hydrogen bomb.”

⁷⁵ *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **1937**, 161, 220-235.

determination of the state symmetry for a given electron configuration, but if no set of degenerate orbitals is unequally occupied, you can conclude immediately that the electronic state is nondegenerate without consulting a table or performing any calculations.

The Jahn-Teller theorem tells us that perfectly O_h complexes of Cu^{2+} must be unstable, *i.e.* the equilibrium geometry will not belong to the O_h point group. This means that, at equilibrium, the structure will undergo some distortion to lower its symmetry, resulting in a nondegenerate electronic ground state. The Jahn-Teller theorem alone does not tell us what the nature of this distortion will be (but *vide infra* on vibronic coupling), only that there will be a distortion in the ground state. In the case of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, two aqua ligands, *trans* to each other, move away from the $\text{Cu}(\text{II})$ center to equal extents, resulting in a new structure with D_{4h} symmetry, and two different Cu–O bond lengths: a longer one for the two axial ligands and a shorter one for the equatorial ligands. The d -type MOs of Cu split further from the octahedral case as shown in Figure 9.1 below, taking the z axis to be the axis containing the elongated Cu–O bonds.

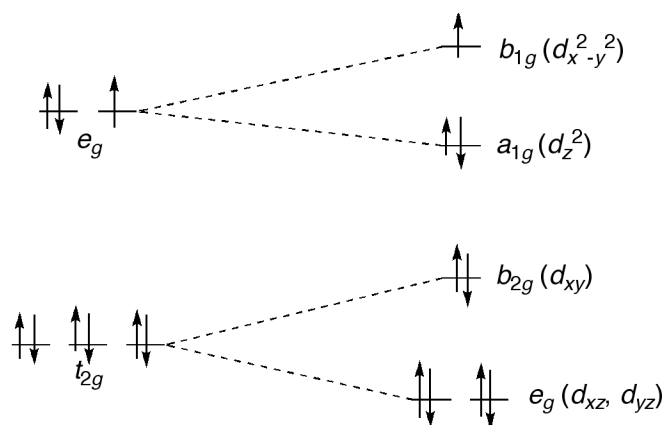


Figure 9.1. The change in d -type MO energies of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ upon Jahn-Teller distortion.

Here the lower-energy t_{2g} set splits into e_g and b_{1g} , and the higher-energy e_g set splits into a_{1g} and b_{1g} . The new state is not electronically degenerate, because the only singly-occupied MO, b_{1g} , is nondegenerate. From the (qualitative) energy level diagram in Figure 9.1 we can also see intuitively what the Jahn-Teller theorem proves mathematically, namely, that the d -type

electrons in the new geometry have a lower average energy than those in the old one. For the six t_{2g} electrons, two are raised in energy and four are lowered, and for the three e_g electrons, two are lowered in energy, while only one is raised. This lowers the electronic energy of the system overall.

We can understand the Jahn-Teller effect further in terms of vibronic coupling. If a diagonal linear vibrational coupling constant $F_{\Gamma^* \gamma^*}^{\Gamma \gamma} = \left\langle \Psi_{\Gamma} \left| \left(\frac{\partial U}{\partial Q_{\Gamma^* \gamma^*}} \right)_0 \right| \Psi_{\Gamma} \right\rangle$ is nonzero and Γ is degenerate, this means that the adiabatic potential energy surface (APES) for the molecule has no local minimum with respect to the normal coordinate with symmetry Γ^* . An equilibrium geometry is one that lies at a *global* minimum of potential energy with respect to all internuclear coordinates. If there is not even a *local* minimum with respect to some coordinate, this means that, at equilibrium, the molecule will adopt a shape with a different point group, and it will do so by internuclear motion along a coordinate with symmetry Γ^* . In the case of O_h $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, since $E_g \times E_g = A_{1g} + [A_{2g}] + E_g$, there is no minimum of potential energy with respect to coordinates with E_g symmetry. Thus, the system is distorted from O_h via a vibration with E_g symmetry. This leads to the observed tetragonal distortion to D_{4h} .

The structural Jahn-Teller distortion of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ can also explain its more complicated UV-visible spectrum. Electrons can undergo an $e_g \rightarrow b_{1g}$ or an $b_{2g} \rightarrow b_{1g}$ transition, and since b_{2g} and b_{1g} have somewhat different energies, these transitions are caused by the absorption of light of two different wavelengths. There is a third possible transition, $a_{1g} \rightarrow b_{1g}$, which indeed occurs, but its corresponding absorption signal does not appear in the UV-visible region, since the energy difference between a_{1g} and b_{1g} is so small compared to the other MO energy differences. This transition would occur by absorption of lower-energy light, with a longer wavelength than any in the UV or visible regions.

The group-theoretic treatment of MO theory and electronic states presented in this text can tell us that two MOs will have different energies, but it does not tell us how large this energy difference will be. Similarly, the Jahn-Teller theorem can tell us that a distortion will occur

in a molecule's ground state, but not how large that distortion will be. The magnitude of the distortion depends on the bonding, antibonding, or nonbonding character of the unequally occupied degenerate orbitals, not merely on the simple fact of their degeneracy. Jahn and Teller noted in their original paper that the distortion is not expected to be large if the unequally occupied degenerate orbitals are those "having no great influence on the binding of the molecule." This means that we will generally observe only small distortions for degenerate states arising from MOs that are either nonbonding or only weakly bonding or antibonding. In O_h TM complexes, the higher-energy e_g MOs are strongly σ -antibonding, so if they are unequally occupied, the Jahn-Teller effect will be significant, and we should expect to see a significant distortion in the complex's structure, as is indeed the case for the $O_h \rightarrow D_{4h}$ distortion of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$.

The t_{2g} MOs, however, are a different story. In complexes with ligands that are σ -donors only, they are rigorously nonbonding, while in complexes with π -donor or π -acceptor ligands, they are π -antibonding or π -bonding, respectively. However, since π interactions are generally weaker than σ ones, t_{2g} orbitals are usually *less significantly* bonding or antibonding than e_g orbitals, even if π interactions are present. This means that, in O_h complexes with unequal occupation of the t_{2g} set, but not of the e_g set, a Jahn-Teller distortion will occur, but it is likely to be small. Consider a low-spin d^5 complex, such as the iron(III) species ferricyanide, or $\text{Fe}(\text{CN})_6^{3-}$, with the d -type electron configuration $(t_{2g})^5(e_g)^0$. The ground state is ${}^2T_{2g}$. Taking the direct product $T_{2g} \times T_{2g} = A_{1g} + E_g + [T_{1g}] + T_{2g}$, we see that the complex's APES will have no minimum with respect to distortions with E_g or T_{2g} symmetry.

What does it mean that $O_h \text{Fe}(\text{CN})_6^{3-}$ will be subject to a Jahn-Teller distortion? It means that, if our experimental techniques could deliver numerical results to infinitely many significant digits, we would find that the structure of $\text{Fe}(\text{CN})_6^{3-}$ would deviate to some extent from a regular octahedron. However, because only the t_{2g} MOs are unequally occupied, the complex may well exhibit such small distortions that they cannot be observed experimentally. If the structure of a salt like $\text{Na}_3\text{Fe}(\text{CN})_6$ is determined *via* X-ray crystallography, any distortions in bond length or bond angle due to the Jahn-Teller effect may well be smaller than the

uncertainties in these values from experimental error in the crystal structure. If a UV-visible spectrum is obtained, multiple peaks due to the distortion may be so close together that they appear as only one peak, within the resolution of the spectrometer. In fact, crystallographic measurements of $\text{Na}_3\text{Fe}(\text{CN})_6$ show an apparently O_h $\text{Fe}(\text{CN})_6^{3-}$ anion. The moral of the story is that Jahn-Teller distortions that theory predicts must exist may not be experimentally observable.

The Jahn-Teller effect is usually taught in inorganic chemistry courses, but it can apply to organic compounds, as well. It is more often observed in TM complexes than in organic molecules, as a degenerate electronic state requires at least one unpaired electron, and organic radicals tend to be short-lived relative to some very stable paramagnetic TM complexes (particularly those of the metals of the first transition series). Stevenson and Kim,⁷⁶ however, have demonstrated that the radical monoanion C_8H_8^- , ideally with D_{8h} symmetry (a regular octagon), is indeed subject to a Jahn-Teller distortion. Recall that, if neutral C_8H_8 were planar (D_{8h}) and conjugated, it would be a highly unstable, antiaromatic diradical (*cf.* the Hückel $4n$ rule with 8π electrons, $n = 2$). Thus, it adopts a boat-shaped conformation with D_{2d} symmetry, which is neither aromatic nor antiaromatic, since the lack of planarity disrupts the conjugation of the C–C π bonds. The doubly reduced form $\text{C}_8\text{H}_8^{2-}$, however,⁷⁷ has D_{8h} symmetry, and it is closed-shell and aromatic (*cf.* the Hückel $4n + 2$ rule with 10π electrons, $n = 2$). The radical monoanion C_8H_8^- , if D_{8h} , would be in an electronically degenerate state, with a single electron in one of a pair of degenerate π MOs. It thus undergoes a distortion to an equilibrium structure with D_{4h} symmetry, in which the C–C bonds are not all equal and in which the singly-occupied MO is nondegenerate.

9.3. The Pseudo-Jahn-Teller Effect

We have seen that, when a nonlinear molecule or ion has a degenerate electronic state, such as O_h $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, with its ${}^2E_g$ ground state, the diagonal vibronic coupling constant

⁷⁶ *Journal of the American Chemical Society* **2000**, *122*, 3211-3215.

⁷⁷ Which can be found as a ligand for large metal centers, most famously in $\text{U}(\eta^8\text{-C}_8\text{H}_8)_2$, commonly known as uranocene.

$F_{\Gamma^*\gamma^*}^{\Gamma\gamma} = \left\langle \Psi_{\Gamma} \left| \left(\frac{\partial U}{\partial Q_{\Gamma^*\gamma^*}} \right)_0 \right| \Psi_{\Gamma} \right\rangle$ is nonzero. Here Ψ_{Γ} is the electronic wavefunction belonging to the irrep Γ . In this case, the APES has no minimum with respect to vibration along a mode belonging to the irrep Γ^* , where Γ^* is in the symmetrical part of the direct product $\Gamma \times \Gamma$. Thus, the molecule will distort along one of these vibrational modes, and it will adopt a structure belonging to a lower-symmetry point group, in which its electronic ground state is no longer degenerate. This is the famous Jahn-Teller Effect.

The Jahn-Teller effect thus predicts that molecules with an electronically degenerate ground state will be unstable with respect to a distortion with the proper symmetry. However, distortion of a highly symmetrical molecule is sometimes observed even when the electronic ground state is *nondegenerate*. The reason for this is vibronic coupling between the electronic ground state and an electronic excited state of *different* symmetry. This phenomenon is known as the pseudo-Jahn-Teller effect.

Consider now a nondiagonal linear vibronic coupling constant $F_{\Gamma^*\gamma^*}^{\Gamma,\Gamma'} = \left\langle \Psi_{\Gamma} \left| \left(\frac{\partial U}{\partial Q_{\Gamma^*\gamma^*}} \right)_0 \right| \Psi_{\Gamma'} \right\rangle$, where a nondegenerate electronic ground state Ψ_{Γ} interacts with an excited state $\Psi_{\Gamma'}$ (which can be either degenerate or nondegenerate). This coupling constant is nonzero if the symmetry Γ^* of a vibrational mode is equal to or part of the direct product $\Gamma \times \Gamma'$. Thus, vibronic coupling allows the energy of a nondegenerate electronic state to be altered by mixing (*via* vibration) with an excited electronic state of *different* symmetry.

Just because a linear nondiagonal vibronic coupling constant is nonzero does not mean that the ground state will be unstable with respect to distortion. If the energy gap between Ψ_{Γ} and $\Psi_{\Gamma'}$ is ΔE , and the force constant for motion along the symmetry-appropriate coordinate Q is K_0 without vibronic coupling, then the ground electronic state will be unstable with

respect to distortion if and only if $\Delta E < \frac{(F_{\Gamma^* \Gamma'}^{\Gamma, \Gamma'})^2}{K_0}$ (the “strong pseudo-Jahn-Teller effect”).⁷⁸ If the coupling constant is nonzero, but this inequality does not hold (the “weak pseudo-Jahn-Teller effect”), then the effect of the vibronic coupling is to reduce K , the force constant for the ground electronic state, making the quadratic potential “shallower” without making the ground state unstable with respect to distortion. The quantitative calculations of ΔE , K_0 , and $F_{\Gamma^* \Gamma'}^{\Gamma, \Gamma'}$ must be done using computational chemistry software, and, unfortunately, there is no easy “back of the envelope” method for obtaining even their relative values. Group theory can tell us whether $F_{\Gamma^* \Gamma'}^{\Gamma, \Gamma'}$ is exactly zero or not, but if it is nonzero, it cannot tell us its magnitude. Thus, from group theory alone, we will not be able to predict whether or not a molecule will experience a distortion due to the pseudo-Jahn-Teller effect, only whether it *might*.

An actual example of the pseudo-Jahn-Teller effect in action concerns the structure of the d^9 , Cu(II) complex CuCl_5^{3-} . If this ion had a trigonal-bipyramidal geometry with D_{3h} symmetry, like $\text{Fe}(\text{CO})_5$, then its d -type electron configuration would be $(e'')^4(e'')^4(a_1'')^1$, with the electronic ground state ${}^2A_1'$. Now consider an electronic excited state with the d -type electron configuration $(e'')^4(e'')^3(a_1'')^2$, which corresponds to the electronic term ${}^2E'$. To see if these states can interact, we take the direct product $A_1' \times E' = E'$, which shows us that vibrations of E' symmetry can mix these states. In the case of CuCl_5^{3-} , a strong pseudo-Jahn-Teller effect is operative, so the ion distorts along an E' vibrational mode to achieve a C_{4v} , square-pyramidal coordination geometry, which turns out to be the lowest-energy structure for this species.

9.4. Electronic Spectroscopy and the Laporte Rule

Electronic spectroscopy consists of measuring the energy differences between the electronic states of a molecule or ion by exposing a solution of that molecule (or a salt of the ion) to radiation of that energy. The energy differences between electronic states usually

⁷⁸ This expression assumes that the force constants K_0 for both electronic states, neglecting vibronic coupling, are equal, which is an assumption that may not be precisely correct.

correspond to photons of visible or ultraviolet light, so UV-visible spectroscopy is electronic spectroscopy. (In contrast, the energy differences between vibrational states correspond to infrared radiation, and those between rotational states correspond to microwave radiation.) The probability of a transition from state i to state j is proportional to the square of the transition moment integral $M_{ji} = \langle \Psi_j | \hat{M} | \Psi_i \rangle$, where $\hat{M}$ is the operator reflecting the interaction of radiation with the material. This operator is actually a vector operator, with components along the x, y , and z axes, so $\hat{M} = \hat{M}_x \mathbf{i} + \hat{M}_y \mathbf{j} + \hat{M}_z \mathbf{k}$, and there are really three transition moment integrals, $M_{ji}^x = \langle \Psi_j | \hat{M}_x | \Psi_i \rangle$, $M_{ji}^y = \langle \Psi_j | \hat{M}_y | \Psi_i \rangle$, and $M_{ji}^z = \langle \Psi_j | \hat{M}_z | \Psi_i \rangle$. If one or more of these integrals is nonzero, then absorption of light will occur and the spectroscopic transition is allowed. The components of the operator, $\hat{M}_x$, $\hat{M}_y$, and $\hat{M}_z$, have the same symmetries (belong to the same irreps) as x, y , and z , respectively. (This is the same result as what we saw in Section 4.4 for the absorption of infrared radiation in vibrational spectroscopy. We are still dealing with electromagnetic radiation, just radiation with different energy, which does not change the symmetry properties.)

Let us assume that we can write each wavefunction as (approximately) a product of an electronic wavefunction and a vibrational wavefunction, or $\Psi = \psi_{\text{elec}} \psi_{\text{vib}}$. The transition moment integral along an arbitrary axis is thus $M_{ji} = \langle \psi_j^{\text{elec}} \psi_j^{\text{vib}} | \hat{M} | \psi_i^{\text{elec}} \psi_i^{\text{vib}} \rangle$. If there is no vibronic coupling, then, since the transition operator applies to photons of energy that effects electronic states, we can write $M_{ji} = \langle \psi_j^{\text{elec}} | \hat{M} | \psi_i^{\text{elec}} \rangle \langle \psi_j^{\text{vib}} | \psi_i^{\text{vib}} \rangle$. At most temperatures, the majority of molecules will be in the ground vibrational state (even if some are in an electronic excited state due to absorption of UV or visible light). If the light absorbed is of the correct energy to excite the ground vibrational state of the ground electronic state i to the ground vibrational state of the excited electronic state j , then the factor $\langle \psi_j^{\text{vib}} | \psi_i^{\text{vib}} \rangle$ will be nonzero, since all ground-state vibrational wavefunctions belong to the totally symmetric irrep of their molecule's point group. Thus, we consider the purely electronic part of the transition moment integral, $M_{ji}^{\text{elec}} = \langle \psi_j^{\text{elec}} | \hat{M} | \psi_i^{\text{elec}} \rangle$. If the direct product of the irreps corresponding to ψ_i^{elec} and ψ_j^{elec} is equal to, or contains, the irrep(s) corresponding to x, y , and/or z , then the transition is spectroscopically "allowed," and we will observe a peak in our spectrum.

The various “selection rules” derived using group theory will label many transitions as “forbidden” that do, in fact, occur and lead to observable peaks in an experimental spectrum. This seeming mismatch of theory and experiment is due to the approximations used in deriving the selection rules. The “strongest” selection rule is the conservation of spin: only transitions between electronic states of the same multiplicity are allowed. For example, a low-spin d^6 complex like $\text{Co}(\text{NH}_3)_6^{3+}$ has a $^1A_{1g}$ ground state, and transitions to singlet excited states such as $^1T_{1g}$ or $^1T_{2g}$ are allowed by spin conservation, whereas transitions to triplet excited states such as $^3T_{2g}$, or quintet excited states like ^5E_g , are forbidden.

Now consider a high-spin, d^5 , O_h complex, with d electron configuration $(t_{2g})^3(e_g)^2$. A real example of such a complex is $\text{Mn}(\text{H}_2\text{O})_6^{2+}$. The ground state, with all 5 electrons unpaired (one electron in each of the d -type MOs), all with parallel spin, is $^6A_{1g}$. All excited states have at least one orbital doubly occupied, so they all have spin multiplicities less than 6. Thus, *all* electronic transitions from the ground state of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ are spin-forbidden. Such transitions can still occur because of spin-orbit coupling, in which the angular momentum of electron spin is coupled to the angular momentum due to the electron orbital motion. Thus, non-conservation of spin need not correspond to a (physically impossible) non-conservation of overall angular momentum. However, spin-orbit coupling is weak for first-series transition metals, so for a complex like $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, the transition is unlikely (and therefore infrequent). If you prepare an aqueous solution of a soluble Mn(II) salt such as MnCl_2 , you will obtain a solution with only a very pale pink color, in contrast to the strong colors displayed by many TM complexes in solution. The faintness of this color is due to the fact that absorption of visible light by the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ion formed is spin-forbidden, and thus infrequent.

Now let us consider spin-allowed $d \rightarrow d$ transitions of TM complexes. For a low-spin d^6 complex like $\text{Fe}(\text{CN})_6^{4-}$ (commonly known as ferrocyanide), the lowest-energy spin-allowed transition is $^1A_{1g} \rightarrow ^1T_{1g}$. Consulting Table 9.1, we see that $A_{1g} \times T_{1g} = T_{1g}$. But in the O_h character table, we see that (x, y, z) transform together as T_{1u} . The direct product $T_{1g} \times T_{1u} = A_{1u} + E_u + T_{1u} + T_{2u}$. Since this direct product does not contain A_{1g} , so the transition is forbidden, according to the selection rule we have derived so far. In fact, all electronic

states of O_h TM complexes belong to *gerade* (g) irreps, and thus the direct product of any two of them will contain only g irreps. But since (x, y, z) transform as an *ungerade* (u) irrep, the direct product of the irreps of two O_h electronic states and T_{1u} will *always* contain only u irreps, and will *never* contain the totally symmetric irrep A_{1g} .

An important consequence of this result is that *all* purely electronic $d \rightarrow d$ transitions of O_h TM complexes are forbidden! In general, for any point group, such as O_h , that contains an inversion center i , all d -type MOs and all electronic states are g , and x, y , and z are always u . so all purely electronic $d \rightarrow d$ transitions of TM complexes with an inversion center are forbidden. This result is often known as the Laporte rule, after the physicist Otto Laporte (1902-1971). The Laporte rule may seem absurd to anyone with much experience handling TM complexes in the laboratory, since such complexes (including O_h ones!) are famous for displaying a wide range of vivid colors. We will see in the following section that vibronic coupling provides a way around the Laporte rule that makes apparently “forbidden” transitions allowed.

9.5. Vibronic Coupling in Electronic Spectroscopy of O_h Complexes

Let us now return to our expression for the transition moment integral corresponding to absorption of light along a particular axis: $M_{ji} = \langle \psi_j^{\text{elec}} \psi_j^{\text{vib}} | \hat{M} | \psi_i^{\text{elec}} \psi_i^{\text{vib}} \rangle$. If vibronic coupling is operative, then it is no longer mathematically justifiable to pull the vibrational wavefunctions out of the inner product containing the electronic wavefunctions and the operator. Our new condition for an allowed transition is if the direct product of all the irreps corresponding to both the vibrational wavefunctions *and* the electronic wavefunctions *and* the operator is equal to, or contains, the totally symmetrical irrep (A_{1g} in O_h), or

$$A_{1g} \in \Gamma(\psi_j^{\text{elec}}) \times \Gamma(\psi_j^{\text{vib}}) \times \Gamma(\hat{M}) \times \Gamma(\psi_i^{\text{elec}}) \times \Gamma(\psi_i^{\text{vib}})$$

Now we consider the fact that, at moderate temperatures, most molecules are in the ground vibrational state, with the vibrational quantum number $\nu = 0$. Thus, $\psi_i^{\text{vib}} = \psi_0^{\text{vib}}$. The most likely vibrational transition is from $\nu = 0$ to the first excited vibrational state ($\nu = 1$), so $\psi_j^{\text{vib}} = \psi_1^{\text{vib}}$. The condition for an allowed vibronic transition is now

$$A_{1g} \in \Gamma(\psi_j^{\text{elec}}) \times \Gamma(\psi_1^{\text{vib}}) \times \Gamma(\hat{M}) \times \Gamma(\psi_i^{\text{elec}}) \times \Gamma(\psi_0^{\text{vib}})$$

But the ground-state vibrational wavefunction ψ_0^{vib} always has the symmetry of A_{1g} in O_h (and of the corresponding totally symmetric irrep in other point groups). Additionally, the first excited vibrational wavefunction ψ_1^{vib} has the same symmetry as the normal coordinate Q along which the vibration occurs. Taking the direct product of *any* representation (reducible or irreducible) with the totally symmetric irrep leaves the first representation unchanged. Thus, if a vibronic transition, involving a vibrational transition (from $v = 0$ to $v = 1$) along a normal coordinate Q , is allowed, the symmetry requirement is

$$A_{1g} \in \Gamma(Q) \times \Gamma(\psi_j^{\text{elec}}) \times \Gamma(\hat{M}) \times \Gamma(\psi_i^{\text{elec}})$$

As an example of how forbidden electronic transitions can become allowed vibronic transitions, consider again the first spin-allowed electronic transition of a low-spin d^6 complex such as $\text{Co}(\text{NH}_3)_6^{3+}$ or $\text{Fe}(\text{CN})_6^{4+}$, which is ${}^1A_{1g} \rightarrow {}^1T_{1g}$. Recall that a purely electronic transition here is forbidden, since in O_h (x, y, z) transform as T_{1u} . To see which vibrations could make this transition allowed by vibronic coupling, we take the triple direct product $T_{1g} \times T_{1u} \times A_{1g} = A_{1u} + E_u + T_{1u} + T_{2u}$. This means that any vibrational mode with symmetry A_{1u} , E_u , T_{1u} , or T_{2u} will allow this electronic transition to occur concomitant with excitation to the first excited vibrational state along that coordinate. We have already seen that, for an O_h ML_6 complex with monatomic ligands, $\Gamma_{\text{vib}} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$. More vibrations are possible in a complex with larger ligands, but these should still be present, and we see that the $2T_{1u} + T_{2u}$ vibrations are suitable for this vibronic coupling.

Another example, for which the electronic ground state has a symmetry lower than ${}^1A_{1g}$, is a d^8 complex such as $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. The ground electronic state is ${}^3A_{2g}$, and the lowest-energy spin-allowed transition is ${}^3A_{2g} \rightarrow {}^3T_{2g}$. To find out which vibrations make this transition allowed, we take the triple direct product $T_{2g} \times T_{1u} \times A_{2g} = A_{1u} + E_u + T_{1u} + T_{2u}$. So any vibrations of A_{1u} , E_u , T_{1u} , or T_{2u} symmetry, such as the $2T_{1u} + T_{2u}$ vibrations mentioned above, allow this electronic transition to occur *via* vibronic coupling.

9.6. The Nephelauxetic Effect

For various d electron counts of O_h complexes, plots are available of the energies (and symmetry labels) of the possible electronic states (relative to the ground state) as a function of the ligand field splitting parameter Δ_o . The details of these plots, known as Tanabe-Sugano diagrams (after Yukito Tanabe and Satoru Sugano, the scientists who prepared them), are beyond the scope of this text,⁷⁹ but it should be noted that both the state energies and Δ_o are given in units of the Racah parameter B , which is a definite integral whose value reflects the repulsion between electrons. If you obtain a UV-visible absorption spectrum of an O_h TM complex and obtain several bands corresponding to the energies of more than one spin-allowed electronic transitions, you can match these bands to their corresponding transitions and use the Tanabe-Sugano diagrams to calculate both Δ_o and B for the complex in question. The values of B for free TM ions can be calculated using some rather laborious quantum mechanics,⁸⁰ but it is often found that, when the B values for complexes (B_{complex}) are experimentally obtained, they tend to be smaller than those calculated for free TM ions (B_{ion}) with the same number of d electrons. A parameter β , called the nephelauxetic ratio, is defined as $\beta = \frac{B_{\text{complex}}}{B_{\text{ion}}}$, and it is invariably found that $\beta < 1$, though the precise value of β varies from complex to complex. This phenomenon is known as the nephelauxetic effect.

The nephelauxetic effect occurs because the “ d orbitals” in a TM complex are not the pure d AOs of the central TM. Rather, they are MOs whose contributions from the d AOs are larger than those from the ligand orbitals, but which still have some contribution from the ligands. These MOs are thus delocalized over more of the molecule than the “pure” d AOs would be, so they experience less Coulombic repulsion between the electrons. The word “nephelauxetic” comes from classical Greek⁸¹ and essentially means “cloud-expanding.” Keeping in mind the quantum-mechanical result according to which electrons may be

⁷⁹ These diagrams can be found on pages 116-122 of *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, 2nd edition, by Isaac B. Bersuker, John Wiley & Sons: Hoboken, NJ, 2010.

⁸⁰ *Ibidem*, pages 42-46.

⁸¹ νεφέλη, “cloud” + αύξησις, “growth”

viewed as probability clouds “smeared out” over space, the nephelauxetic effect leads to these clouds being more diffuse.

Different ligands lead to a stronger or weaker nephelauxetic effect. The following is a list of common ligands in order of decreasing values of β for their complexes (remember that a *smaller* value of β corresponds to a *more* significant nephelauxetic effect): $\text{F}^- > \text{H}_2\text{O} > (\text{H}_2\text{N})_2\text{CO}$ (urea) $> \text{NH}_3 > \text{C}_2\text{O}_4^{2-}$ (oxalate) $> \text{NCS}^- > \text{Cl}^- \approx \text{CN}^- > \text{Br}^- > (\text{EtO})_2\text{PS}_2^- \approx \text{S}^{2-} \approx \text{I}^- > (\text{EtO})_2\text{PSe}_2^-$. Those ligands with a low nephelauxetic effect tend to be those with more electronegative donor atoms, such that a large part of their bonding to TM ions is electrostatic (ion-ion or ion-dipole interactions). While these TM-ligand bonds have *some* covalent character, they are strongly polar covalent. In contrast, ligands with a high nephelauxetic effect tend to have less electronegative donor atoms with more diffuse orbitals, so they form less polar, and more highly covalent, bonds to TMs. If you recall Pearson’s concept of hard and soft Lewis acids and bases (Sections 5.9-5.11), you may notice that ligands that are softer Lewis bases tend to have a greater nephelauxetic effect (lower β).

9.7. Electronic Spectroscopy of Tetrahedral Complexes

The Laporte rule does not apply to T_d complexes, since molecules with T_d symmetry lack inversion centers. While Tanabe-Sugano diagrams found in the literature are labeled for O_h complexes, it turns out that they can be used for T_d complexes as well, using the following rule: the Tanabe-Sugano diagram for an O_h, d^n TM complex also serves for a T_d, d^{10-n} complex. Of course, the horizontal axis should be taken as Δ_T , rather than Δ_O . (Note that there are essentially no low-spin T_d complexes.) Additionally, the electronic states for T_d complexes have no g or u labels: the irreps of T_d are A_1, A_2, E, T_1 , and T_2 .

As an example, consider the T_d, d^8 complex ion NiCl_4^{2-} . Its ground state, which can be determined from the Tanabe-Sugano diagram for O_h, d^2 complexes, is $^3T_1$, and the lowest-energy spin-allowed electronic transition is $^3T_1 \rightarrow ^3T_2$. In $T_d, (x, y, z)$ transform together as T_2 . To see if any of the transition moment integrals are nonzero, we examine the triple direct

product $T_2 \times T_2 \times T_1 = A_1 + A_2 + 2E + 4T_1 + 3T_2$. Since this direct product contains the totally symmetric irrep A_1 , the pure electronic transition is allowed.

The fact that T_d complexes have electronic transitions which are allowed without vibrational coupling being necessary means that they usually absorb light more strongly than O_h complexes. The $d \rightarrow d$ transitions of O_h complexes usually have molar absorptivities (a.k.a. extinction coefficients) at their maximum absorption wavelengths $\lambda_{\max}$ of between 5 and 50 $M^{-1} \cdot \text{cm}^{-1}$, while those of T_d complexes are usually much greater.

9.8. Charge-Transfer Bands

Many of the strong colors associated with TM complexes are due to $d \rightarrow d$ transitions, but not all of them. The permanganate ion MnO_4^- is a deep purple color (its potassium salt KMnO_4 is a common oxidizing agent in synthetic chemistry, as well as a stain for thin-layer chromatography plates), but it is a Mn(VII) complex. Since Mn(VII) complexes are d^0 , $d \rightarrow d$ transitions cannot be responsible for its color. Instead, the relevant electronic transitions are from MOs that are largely ligand-based (“lone pair”-type SALCs from the O atoms) to Mn-centered d -type MOs. This type of electronic transition is called “charge transfer,” since an electron, with its negative charge, moves from a ligand-based MO to a TM-based MO. This particular type of charge transfer is known as ligand-to-metal charge transfer, or LMCT.

In contrast, some complexes display electronic transitions in which an electron is excited from a TM d -type MO to a weakly antibonding ligand-based MO. This type of transition is known as metal-to-ligand charge transfer, or MLCT. A well-known example of a complex that displays MLCT is $\text{Ru}(\text{bpy})_3^{2+}$, which is a Ru(II) complex in the ground state, and can be thought of as $(\text{Ru}^{2+})(\text{bpy})_3$. When MLCT occurs, an electron moves from a d -type MO on Ru to a π -antibonding MO on one of the bpy ligands, yielding an excited state that formally contains a Ru(III) center, two neutral bpy ligands, and one bpy^- radical anion, or $(\text{Ru}^{3+})(\text{bpy})_2(\text{bpy}^-)$. Charge transfer transitions are important not only in spectroscopy but also in chemical reactivity, such as photochemistry and catalysis.

9.9. Basics of Magnetism

Subatomic particles such as electrons and some nuclei (NMR-active nuclei, such as ^1H , ^{13}C , ^{19}F , and ^{31}P) have magnetic moments, and those magnetic moments are responsible for the *net* magnetic moments of molecules and bulk materials as a whole. The magnetic field inside a material is a vector quantity known as the magnetic induction $\mathbf{B}$, and it is dependent on the external magnetic field present $\mathbf{H}$ (be careful not to confuse this with the Hamiltonian operator $\hat{H}$). An additional important quantity is the magnetization $\mathbf{M}$ of a sample, which is the sum of the magnetic moments from all of its individual atoms or molecules, divided by the sample volume. These quantities are related by $\mathbf{B} = \mathbf{H} + \mu_0\mathbf{M}$, where the proportionality constant μ_0 is equal to $4\pi \times 10^{-7} \text{ N}\cdot\text{A}^{-2}$.

The magnetization itself is also dependent on the external magnetic field. The dependence of $\mathbf{M}$ on $\mathbf{H}$ can be rather complicated for some systems, but for an isotropic material (one in which the magnetic properties are the same along the x , y , and z axes) and external magnetic fields of relatively low intensities, the relation $\mu_0\mathbf{M} = \chi\mathbf{H}$ holds, where χ is a dimensionless quality called the magnetic susceptibility. Using this relation, the equation for the magnetic induction can be written as $\mathbf{B} = \mathbf{H} + \chi\mathbf{H} = \mathbf{H}(1 + \chi)$. This equation helps explain why χ is known as the magnetic susceptibility: it indicates how *susceptible* a material is to having magnetization induced by an external magnetic field.

The magnetization is a measure of how much the individual magnetic moments of atoms and molecules in the material are aligned with each other along the external magnetic field. Magnetic moment is a vector quantity, so if each magnetic moment in one direction is accompanied by an equally large antiparallel magnetic moment, those moments overall contribute nothing to the overall magnetization. Magnetization, in which at least some individual magnetic moments are aligned with each other, is a form of order, and as such it is a decreasing function of temperature, since at higher temperatures there is more disorder due to the thermal motion of particles (greater entropy). The physicist and human rights activist Paul Langevin (1872-1946) proposed the following equation relating magnetic susceptibility to temperature:

$$\chi = \frac{N\mu_0\mu^2}{3k_{\text{B}}T}$$

Here N is the number of individual magnetic moments per volume, μ is the *magnitude* of each particle's magnetic moment, $k_{\text{B}} = 1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ is Boltzmann's constant, and T is the absolute temperature. Langevin's equation is important for studying the magnetism of molecules: one can measure magnetic susceptibility experimentally, by measuring the magnetic induction of a sample as a function of the applied magnetic field. One then uses Langevin's equation to relate the measured magnetic susceptibility to the *individual* magnetic moment of each molecule or ion.

It should be noted that the magnetic susceptibility χ is an extensive quantity, *i.e.* its magnitude is proportional to the amount of material in the sample. It is often more convenient to discuss intensive quantities. *i.e.* properties whose value depends on the identity of the material, but not how much of it there is. The molar magnetic susceptibility χ_{mol} is such an intensive quantity, defined by

$$\chi_{\text{mol}} = \frac{M\chi}{\rho}$$

where M is the compound's molar mass and ρ is its density.

The magnetism described thus far is paramagnetism. For a paramagnetic substance, the magnetic moments tend to be aligned with an external magnetic field, and the substance is attracted to that field. A common demonstration of this phenomenon involves the fact that the ground state of O_2 is paramagnetic. Thus, when some liquid O_2 is poured between the poles of an electromagnet (a region with a very high magnetic field strength), it will remain suspended there until it evaporates. Paramagnetism is not possible in materials whose atoms or molecules have no net magnetic moment. However, *all* substances display another type of magnetic behavior called diamagnetism, in which an external magnetic field induces a circular current in the material. This circular current leads to an induced magnetic field opposite to the external field, so diamagnetism causes a material to be repelled by, rather than attracted to, an external magnetic field. However, in a paramagnetic material, the effect of paramagnetism is *much* greater (by orders of magnitude) than that of diamagnetism, so

all paramagnetic materials are attracted to an external magnetic field. A diamagnetic material is one which displays no paramagnetism, only diamagnetism, and it will thus be repelled by an external magnetic field. However, this repulsion will usually be quite small in magnitude, and of little practical consequence in many cases.

9.10. Magnetism of Molecules and Unpaired Electrons

The net magnetic moment of an atom, molecule, or ion is primarily due to the magnetic moments of its electrons, rather than its nucleus or nuclei. Thus, it is usually an excellent approximation to consider only electrons when predicting atomic or molecular magnetic moments. For a free atom or ion, the magnetic moment operator $\hat{\mu}$ is given by

$$\hat{\mu} = \mu_B(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})$$

where $\hat{\mathbf{L}}$ is the vector operator corresponding to the total orbital angular momentum of the electrons, $\hat{\mathbf{S}}$ is the vector operator corresponding to the total spin angular momentum of the electrons, and $\mu_B = 9.274 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$ is a physical constant called the Bohr magneton, defined in terms of other physical constants by

$$\mu_B = \frac{e\hbar}{2m_e}$$

The average magnetic moment (expectation value) of an atom along the total angular momentum vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$ (whose magnitude is J) is given by the following formula:

$$\mu_J = g\mu_B\sqrt{J(J+1)}$$

In this formula, the quantity g , called the gyromagnetic ratio, Landé factor (after Alfred Landé, 1888-1976), or simply the g -factor, is given in terms of L , S , and J , the magnitudes of the orbital angular momentum, the spin angular momentum, and the total angular momentum, respectively, by the Landé formula:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

For a free electron, $L = 0$ and $J = S = \frac{1}{2}$, so the Landé formula predicts that $g = 2$. In fact, due to effects in quantum electrodynamics not accounted for in Landé's derivation, the true value of g is very slightly higher (to five significant digits, $g = 2.0023$). For most purposes, it is an

excellent approximation to set $g = 2$. Additionally, the Landé formula is derived based on the assumption that spin-orbit coupling is strong, so that atomic states with the same values of L and S , but with different values of J , are separated by enough energy that only the lowest-energy state is significantly populated at room temperature. For first-series TMs, however, spin-orbit coupling is fairly weak, so a better approximation ignores the splitting between states with the same L and S values by different J values, so the states with different J values are about equally populated. Under this approximation, the magnitude of the effective magnetic moment μ_{eff} is given by

$$\mu_{\text{eff}} = 2\mu_B \sqrt{S(S+1) + L(L+1)}$$

The above formula for μ_{eff} applies to free atoms and ions. When measurements are made on TM complexes with n unpaired electrons and a net spin $S = \frac{n}{2}$ (assuming that all unpaired electrons are parallel, in accordance with Hund's rule), it is found that the effective magnetic moment is approximately that which would be obtained by assuming that $L = 0$, or

$$\mu_{\text{eff}} = 2\mu_B \sqrt{S(S+1)} = \mu_B \sqrt{n(n+2)}$$

Thus, it is often said that the orbital angular momentum of a free TM atom or ion is “quenched” by complex formation. A qualitative rationale for this phenomenon is the fact that the total orbital angular momentum quantum number L is really a feature of atomic states with spherical symmetry (point group K_h), and when some degeneracy is broken by the formation of complexes belonging to lower-symmetry point groups (such as O_h or T_d), arguments based on L are no longer valid.

We can use symmetry arguments to see, in more precise terms, why orbital angular momentum is sometimes quenched. The average orbital angular momentum of a complex with electronic state Ψ is given by $\langle \mathbf{L} \rangle = \langle \Psi | \hat{\mathbf{L}} | \Psi \rangle$, and this integral is nonzero if and only if $\Gamma(\hat{\mathbf{L}}) \in \Gamma(\Psi) \times \Gamma(\Psi)$. The x , y , and z components of the orbital angular momentum operator transform as the rotations R_x , R_y , and R_z , respectively. In O_h , they transform together as T_{1g} , and in T_d , they transform as T_1 . Use of Table 9.1 shows that there will be nonzero orbital angular momentum for T_d complexes with T_1 or T_2 electronic states, and for O_h complexes

with T_{1g} , T_{2g} , T_{1u} , or T_{2u} states. (However, no O_h ML_6 complexes whose only unpaired electrons are d -type give rise to T_{1u} or T_{2u} terms.)

Tables 9.2 below and 9.3 on the following page give the d -type electron configurations of O_h and T_d TM complexes with different electron counts, along with their ground-state electronic terms and predicted magnetic moments using the spin-only formula $\mu_{\text{eff}} = \mu_B \sqrt{n(n+2)}$. Only the high-spin configurations of T_d complexes are given, because low-spin T_d complexes are so rare. Based on the terms, we can see that, for example, $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ (d^8 , $^3A_{2g}$) would be expected to have no orbital angular momentum contribution to its magnetic moment, while $\text{Fe}(\text{CN})_6^{3-}$ (low-spin d^5 , $^2T_{2g}$) would have some orbital angular momentum contribution.

Table 9.2. Electronic and magnetic properties of O_h ML_6 complexes.

d^n	d electron configuration	Number of unpaired electrons	$\frac{\mu_{\text{eff}}}{\mu_B}$	Ground-state electronic term
d^0	$(t_{2g})^0(e_g)^0$	0	0	$^1A_{1g}$
d^1	$(t_{2g})^1(e_g)^0$	1	$\sqrt{3} \approx 1.73$	$^2T_{2g}$
d^2	$(t_{2g})^2(e_g)^0$	2	$2\sqrt{2} \approx 2.83$	$^3T_{1g}$
d^3	$(t_{2g})^3(e_g)^0$	3	$\sqrt{15} \approx 3.87$	$^4A_{2g}$
d^4 (high-spin)	$(t_{2g})^3(e_g)^1$	4	$2\sqrt{6} \approx 4.90$	^5E_g
d^4 (low-spin)	$(t_{2g})^4(e_g)^0$	2	$2\sqrt{2} \approx 2.83$	$^3T_{1g}$
d^5 (high-spin)	$(t_{2g})^3(e_g)^2$	5	$\sqrt{35} \approx 5.92$	$^6A_{1g}$
d^5 (low-spin)	$(t_{2g})^5(e_g)^0$	1	$\sqrt{3} \approx 1.73$	$^2T_{2g}$
d^6 (high-spin)	$(t_{2g})^4(e_g)^2$	4	$2\sqrt{6} \approx 4.90$	$^5T_{2g}$
d^6 (low-spin)	$(t_{2g})^6(e_g)^0$	0	0	$^1A_{1g}$
d^7 (high-spin)	$(t_{2g})^5(e_g)^2$	3	$\sqrt{15} \approx 3.87$	$^4T_{1g}$
d^7 (low-spin)	$(t_{2g})^6(e_g)^1$	1	$\sqrt{3} \approx 1.73$	^2E_g
d^8	$(t_{2g})^6(e_g)^2$	2	$2\sqrt{2} \approx 2.83$	$^3A_{2g}$
d^9	$(t_{2g})^6(e_g)^3$	1	$\sqrt{3} \approx 1.73$	^2E_g
d^{10}	$(t_{2g})^6(e_g)^4$	0	0	$^1A_{1g}$

Table 9.3. Electronic and magnetic properties of T_d ML_6 complexes (only high-spin cases shown).

d^n	d electron configuration	Number of unpaired electrons	$\frac{\mu_{\text{eff}}}{\mu_B}$	Ground-state electronic term
d^0	$(e)^0(t_2)^0$	0	0	$^1A_1$
d^1	$(e)^1(t_2)^0$	1	$\sqrt{3} \approx 1.73$	^2E
d^2	$(e)^2(t_2)^0$	2	$2\sqrt{2} \approx 2.83$	$^3A_2$
d^3	$(e)^2(t_2)^1$	3	$\sqrt{15} \approx 3.87$	$^4T_1$
d^4	$(e)^2(t_2)^2$	4	$2\sqrt{6} \approx 4.90$	$^5T_2$
d^5	$(e)^2(t_2)^3$	5	$\sqrt{35} \approx 5.92$	$^5A_1$
d^6	$(e)^3(t_2)^3$	4	$2\sqrt{6} \approx 4.90$	^5E
d^7	$(e)^4(t_2)^3$	3	$\sqrt{15} \approx 3.87$	$^4A_2$
d^8	$(e)^4(t_2)^4$	2	$2\sqrt{2} \approx 2.83$	$^3T_1$
d^9	$(e)^4(t_2)^5$	1	$\sqrt{3} \approx 1.73$	$^2T_2$
d^{10}	$(e)^4(t_2)^6$	0	0	$^1A_1$

When one measures χ_{mol} for a TM complex using a magnetic susceptibility balance, and then calculates the magnetic moment μ , the experimental value of μ will invariably be different from the value of μ_{eff} calculated using the simple, spin-only formula. This is partly because of orbital angular momentum contributions in complexes with electronic wavefunctions of the appropriate symmetry, and partly because of spin-orbit coupling. In general, it is most reliable to relate experimental μ to calculated μ_{eff} for complexes of first-series TMs, for which spin-orbit coupling is relatively small in magnitude, and considerably less reliable for complexes of second- and third-series TMs, for which spin-orbit coupling is greater. It is still a very useful technique for the analysis of first-series TM complexes. If one matches the experimentally obtained μ to the closest calculated μ_{eff} , this can allow for reasonable confidence that the complex has the number of unpaired electrons corresponding to that calculated μ_{eff} value. For example, a high-spin O_h d^5 complex has calculated $\mu_{\text{eff}} = 5.92 \mu_B$, while a low-spin O_h d^5 complex has calculated $\mu_{\text{eff}} = 1.73 \mu_B$. The high-spin $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ should have an experimental μ value closer to $5.92 \mu_B$, while the low-spin $\text{Fe}(\text{CN})_6^{3-}$ should have an experimental μ value closer to $1.73 \mu_B$.

Chapter 10: Fundamentals of Chemical Kinetics

10.1. Reaction Rates: Definition and Notation

Having explored some of the basics of structure and bonding in transition metal complexes, we will now review some of the important principles of chemical kinetics (from Greek κινεῖν, “to move”), the study of the rates of chemical reactions. Kinetics experiments are very important in the study of reaction mechanisms, whether organic, inorganic, or organometallic.

The rate of a chemical reaction is both the rate of formation of the products and the rate of consumption of the reactants. Imagine a general reaction $a A + b B \rightarrow p P + q Q$. The reaction rate r is given by

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt} = \frac{1}{q} \frac{d[Q]}{dt}$$

In general, if we denote the stoichiometric coefficient of any species X in the balanced reaction equation by ν_X and consider reactants to have a negative stoichiometric coefficient, then the rate can be written in terms of any one of the reactants or products according to

$$r = \frac{1}{\nu_X} \frac{d[X]}{dt}$$

Empirically, the reaction rate is often equal to a constant⁸² (the rate constant k) multiplied by the product of various concentrations raised to various powers, *e.g.* $r = k[A]^m[B]^n$. Here m and n are called the orders of the reaction with respect to the reactants A and B, respectively, and the total order of the reaction is equal to $m + n$. It is important to note that m and n are *not* generally equal to the stoichiometric coefficients a and b ; they must be determined experimentally. An equation relating r to the concentrations of reactants is called a rate law. Some rate laws are not simple products as shown above, containing sums and differences of

⁸² The rate constant k does not change over the course of a reaction (assuming that the reaction takes place at a constant temperature), but it *does* change as a function of temperature. In this respect, it is like an equilibrium constant K , which is no longer constant when the temperature changes.

terms. For such rate laws, the order of the reaction is not defined. We will see shortly how such rate laws can arise.

10.2. First-Order Kinetics

Many reactions obey a rate law in which the reaction rate is directly proportional to the concentration of one of the reactants, or

$$-\frac{d[A]}{dt} = k[A]$$

This reaction is both first-order in the reactant A and first-order overall. If we denote the initial concentration of A as $[A]_0$, this differential rate law can be transformed to the integrated rate law,

$$\ln[A] = \ln[A]_0 - kt$$

or

$$[A] = [A]_0 e^{-kt}$$

Thus, for a reaction that obeys first-order kinetics, a plot of $\ln[A]$ vs. time⁸³ will have a slope of $-k$ and an intercept of $\ln[A]_0$. Another quantity commonly tabulated for first-order reactions is the half-life $t_{1/2}$, the time at which point half of the initial amount of the reactant A has been consumed. Setting $[A] = [A]_0/2$ in the integrated rate law and solving for $t = t_{1/2}$ yields

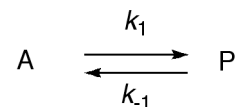
$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k}$$

Note that the half-life is independent of initial concentration *for a first-order reaction*. Nuclear decay processes follow first-order kinetics, which is why the half-life of a radioactive isotope is a commonly tabulated quantity in nuclear physics and chemistry.

In the discussion above, we have implicitly assumed that the reaction in question is irreversible, that is, its equilibrium constant is so large that the reverse reaction need not be

⁸³ Strictly speaking, this should be $\ln([A]/\text{concentration unit})$, since the argument of a logarithm must be unitless. For reactions conducted in solution (which are the type of reactions that we will focus on in this course), the common unit of concentration is molar ($\text{mol}\cdot\text{L}^{-1}$ or M).

considered. This is not always true. Imagine the following reversible reaction, with forward rate constant k_1 and reverse rate constant k_{-1} :



The forward reaction rate, namely minus the rate of change of $[A]$, is given by

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[P]$$

If one uses the appropriate material balance expressions, and denotes the equilibrium concentration of A as $[A]_{\text{eq}}$, then the integrated rate law is given by

$$\ln\left(\frac{[A] - [A]_{\text{eq}}}{[A]_0 - [A]_{\text{eq}}}\right) = -(k_1 + k_{-1})t$$

A plot of $\ln([A] - [A]_{\text{eq}})$ vs. time will have slope $-(k_1 + k_{-1})$ and intercept $\ln([A]_0 - [A]_{\text{eq}})$. In practice, data analysis for reversible reactions can be difficult, because $[A]_{\text{eq}}$ is often difficult to measure precisely.

10.3. Second-Order Kinetics

There are two commonly encountered ways in which a reaction obeys second-order kinetics. In the first, the reaction rate is simply proportional to the square of a reactant concentration, or

$$-\frac{d[A]}{dt} = k[A]^2$$

Thus, the reaction is both second-order in A and second-order overall. Integrating this rate law gives

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

or

$$[A] = \frac{[A]_0}{1 + [A]_0 kt}$$

For a reaction that obeys this type of second-order kinetics, a plot of $1/[A]$ vs. time will have a slope of k and an intercept of $1/[A]_0$. The half-life of such a reaction is given by

$$t_{1/2} = \frac{1}{k[A]_0}$$

Note that the half-life is dependent on the initial concentration $[A]_0$, unlike in the case of first-order kinetics. Thus, half-lives are rarely tabulated for second-order reactions. The other commonly encountered type of second-order kinetics is one in which the reaction is second-order overall, but first-order in each of two reactants, *i.e.*

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

The corresponding integrated rate law (whose derivation is considerably more difficult) is as follows (assuming $[A]_0 \neq [B]_0$):

$$\frac{1}{[A]_0 - [B]_0} \ln \left(\frac{[A][B]_0}{[B][A]_0} \right) = kt$$

The analysis of data using this equation can be difficult, since it requires that the initial concentrations $[A]_0$ and $[B]_0$ each be measured quite accurately in order for an accurate value of k to be obtained, *e.g.* from the slope of a plot of $\frac{1}{[A]_0 - [B]_0} \ln \left(\frac{[A][B]_0}{[B][A]_0} \right)$ vs. time. Fortunately, there are ways to avoid this type of analysis when analyzing reactions with nonzero order in more than one reagent.

10.4. The Method of Initial Rates

There are various experimental strategies for determining the differential rate law of a reaction, but the method of initial rates is one of the most useful. If we have a differential rate law of the form $r = k[A]^m[B]^n$, we can write this explicitly as a differential equation, namely, as

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^m[B]^n$$

where we have assumed, for simplicity, that the stoichiometric coefficients of A and B are both equal to 1.

We now measure the initial reaction rate r_0 , that is, the rate at the time $t = 0$ (when we first start the experiment), which is related to the initial concentrations $[A]_0$ and $[B]_0$ by

$$r_0 = k[A]_0^m[B]_0^n$$

While a reaction rate is an instantaneous rate – a derivative of concentration with respect to time – it can be approximated as a difference quotient, if the change in time Δt is small:

$$r_0 = -\frac{d[A]}{dt}\bigg|_{t=0} \approx -\frac{\Delta[A]}{\Delta t}$$

where $\Delta t = t - 0$, and t is small. If $[A]$ can be measured (for instance, by spectroscopy) at the beginning of the reaction and at a very short time afterwards, an approximate value of r_0 can thus be obtained.

To determine the order of the reaction in each reactant, one performs two (or more) experimental runs in which the initial concentration of one reactant is varied, but those of all the others are held constant. Suppose run 1 has initial concentrations $[A]_{0,1}$ and $[B]_{0,1}$ and initial rate $r_{0,1}$, while run 2 has initial concentrations $[A]_{0,2}$ and $[B]_{0,2}$ and initial rate $r_{0,2}$. The ratio of the initial rates will thus be

$$\frac{r_{0,2}}{r_{0,1}} = \frac{[A]_{0,2}^m [B]_{0,2}^n}{[A]_{0,1}^m [B]_{0,1}^n}$$

Now suppose we only change $[A]_0$ between run 1 and run 2, so that $[B]_{0,1} = [B]_{0,2}$. The ratio of initial rates will now be

$$\frac{r_{0,2}}{r_{0,1}} = \frac{[A]_{0,2}^m}{[A]_{0,1}^m} = \left(\frac{[A]_{0,2}}{[A]_{0,1}}\right)^m$$

Taking the natural logarithm of both sides and using the properties of logarithms to solve for m yields

$$\ln\left(\frac{r_{0,2}}{r_{0,1}}\right) = \ln\left(\frac{[A]_{0,2}}{[A]_{0,1}}\right)^m = m \ln\left(\frac{[A]_{0,2}}{[A]_{0,1}}\right)$$

$$m = \frac{\ln\left(\frac{r_{0,2}}{r_{0,1}}\right)}{\ln\left(\frac{[A]_{0,2}}{[A]_{0,1}}\right)}$$

Similarly, if $[A]_0$ is held constant, so that $[A]_{0,1} = [A]_{0,2}$, and only $[B]_0$ is varied between run 1 and run 2, then n is calculated in an analogous manner:

$$n = \frac{\ln\left(\frac{r_{0,2}}{r_{0,1}}\right)}{\ln\left(\frac{[B]_{0,2}}{[B]_{0,1}}\right)}$$

It should be noted that the above analysis using logarithms may not be necessary if initial concentrations are varied by factors of small whole numbers. For instance, if $[A]_0$ is doubled

with $[B]_0$ held constant, and r_0 is doubled, we can decide “by inspection” that $m = 1$ (the rate is proportional to $[A]$). If $[B]_0$ is double with $[A]_0$ held constant, and r_0 is quadrupled, then we can readily see that $n = 2$ (the rate is proportional to $[B]^2$).

10.5. Pseudo-Lower-Order Kinetics

As we have just seen, if a reaction is non-zero-order in each of two reactants A and B, the integrated rate law will likely be complicated, and it will not be easy to determine the value of k from concentration and time data. In contrast, data analysis for a reaction that is non-zero-order in only one reactant is relatively simple. The technique of pseudo-lower-order kinetics allows us to use the data analysis techniques for reactions that are non-zero-order in only one reactants to analyze reactions that are nonzero-order in two reactants.

Suppose we have a generic reaction $A + B \rightarrow \text{products}$, and we assume that the rate law has the form

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^m[B]^n$$

We could use the method of initial rates to determine m and n , but sometimes a reaction proceeds quickly enough that it is difficult to obtain a truly “initial” rate. We would instead like to use concentration and time data from a wider range of times. The trick here is to set up a reaction with a very large excess of one reactant (here, B) compared to the other (here, A), or $[B]_0 \gg [A]_0$. The concentration of B will, of course, decrease over time, since B is a reactant, just like A. But if the initial concentration of B is large enough relative to that of A, then $[B]$ will not decrease *very much* from $[B]_0$ during a reasonable amount of time during which we can measure $[A]$ at several points. Thus, we say that, for a reasonable amount of time, $[B] \approx [B]_0$, and thus

$$-\frac{d[A]}{dt} = k_{\text{obs}}[A]^m$$

where the observed rate constant (sometimes called the pseudo-rate constant) k_{obs} is given by

$$k_{\text{obs}} = k[B]_0^n$$

By measuring $[A]$ at several different time points, we can determine m : if a plot of $\ln [A]$ vs. time is linear, $m = 1$, if a plot of $\frac{1}{[A]}$ vs. time is linear, $m = 2$, and so on, and once m is known, k can be obtained from the relevant plot. To determine n , we can measure k_{obs} for several different values of $[B]_0$, as long as $[B]_0 \gg [A]_0$ in all cases. The equation for k_{obs} can be usefully rearranged by taking the logarithm of both sides⁸⁴:

$$k_{\text{obs}} = k[B]_0^n$$

$$\ln k_{\text{obs}} = \ln(k[B]_0^n)$$

$$\ln k_{\text{obs}} = n \ln[B]_0 + \ln k$$

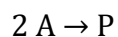
Thus, a plot of $\ln k_{\text{obs}}$ vs. $\ln [B]_0$ will have a slope of n and an intercept of $\ln k$.

10.6. Rate Laws for Concerted Reactions

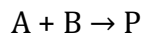
In general, for a reaction $a A + b B \rightarrow p P + q Q$, we cannot determine the reaction order in A and B from their stoichiometric coefficients. If a reaction is *concerted*, however (that is, it occurs in only one step, with only one transition state),⁸⁵ then the stoichiometric coefficients of the reagents *are* equal to the reaction orders. Thus, if the following reactions are concerted, their rate laws are given as follows:



$$r = -\frac{d[A]}{dt} = k[A]$$



$$r = -\frac{1}{2} \frac{d[A]}{dt} = k[A]^2$$



$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

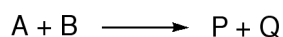
⁸⁴ To be perfectly correct, one must divide k_{obs} by its appropriate unit before taking the logarithm. In the interest of avoiding algebraic clutter, I am not including these units in the relevant equations.

⁸⁵ Concerted reactions are also sometimes called *elementary*, or “elementary steps” that make up a full mechanism. The rate constants of elementary steps are often called “microscopic rate constants,” in contrast to the experimental or observed rate constants (sometimes denoted k_{exp} or k_{obs}) obtained from fitting data to a rate law.

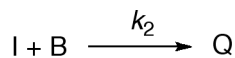
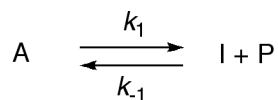
This sort of analysis becomes more complicated for a multistep mechanism involving reactive intermediates. In principle, we can write a rate law for each elementary step from the stoichiometric coefficients of each species (including reaction intermediates). These multiple rate laws constitute a series of coupled differential equations which will, more often than not, have no analytical or “closed-form” solution (though they can often be “solved” numerically with a computer). However, we can get useful equations with analytical solutions by applying certain reasonable approximations.

10.7. The Steady-State Approximation

The first of the approximations that we will discuss is the steady-state approximation, often abbreviated as the SSA. The SSA is generally used for mechanisms involving very unstable, short-lived reactive intermediates. An example of such an intermediate that will likely be familiar to you from your organic chemistry classes is the carbocation intermediate in an S_N1 reaction. The central idea of the SSA is that, since the concentration of a reactive intermediate is never very high, the rate of change of its concentration is never very large; that is, for an intermediate I, the time derivative $\frac{d[I]}{dt} \approx 0$. This may or may not seem intuitively obvious to you, but the SSA can be used to fit experimental data quite well for many reactions. Let us see how we would, mathematically, use the SSA to derive an approximate differential rate law for a reaction. Assume our net reaction is



and the mechanism is believed to consist of the following elementary steps:



Note that the overall reaction is irreversible due to the second step, but the first step, in which the unstable intermediate I is formed, is reversible. We can write the reaction rate in terms of the final, irreversible step:

$$r = \frac{d[Q]}{dt} = k_2[I][B]$$

This expression is true as far as it goes, but it is not useful for comparison with experimental data. Since I is a reactive intermediate, it is far too unstable to be isolated, so we certainly cannot set up an experiment with a precisely measured initial concentration of I. The utility of the SSA is that it allows us to derive an approximate expression for [I] in terms of the concentrations of stable species, which can be easily handled, and solutions of which with precisely known concentrations can be prepared. We write the expression for $\frac{d[I]}{dt}$, assume that it is equal to zero, and solve for [I] as follows:

$$\begin{aligned}\frac{d[I]}{dt} &= k_1[A] - k_{-1}[I][P] - k_2[I][B] = 0 \\ k_{-1}[I][P] + k_2[I][B] &= k_1[A] \\ (k_{-1}[P] + k_2[B])[I] &= k_1[A] \\ [I] &= \frac{k_1[A]}{k_{-1}[P] + k_2[B]}\end{aligned}$$

Next, we plug our approximate expression for [I] into the rate law:

$$\begin{aligned}r &= k_2[I][B] \\ r &= \frac{k_1 k_2 [A][B]}{k_{-1}[P] + k_2[B]}\end{aligned}$$

We now have an equation that expresses the reaction rate in terms of the concentrations of stable, measurable species: the reactants A and B, and one of the products P. Note that we can say that the reaction is first-order in A and zeroth-order in Q, but we cannot specify the orders in B or P, due to the sum of terms in the denominator of the rate law.

It is instructive to see how the reaction rate behaves in certain limiting cases, when one species is present in vastly greater concentration than another. First, let us imagine that the reactant B is present in a large excess over the reactant A or product P, so that $k_2[B] \gg k_{-1}[P]$. Under these conditions, we can write $k_{-1}[P] + k_2[B] \approx k_2[B]$, and the rate law can be simplified to

$$r = \frac{k_1 k_2 [A][B]}{k_{-1}[P] + k_2[B]} \approx \frac{k_1 k_2 [A][B]}{k_2[B]} = k_1[A]$$

Under these circumstances, the reaction will be both first-order in A and first-order total. In an organic S_N1 reaction in which the entering nucleophile (B) is present in large excess over the alkyl halide or sulfonate (A) or leaving group (P) the standard first-order kinetics are observed. (This is why we have a “1” in the notation “S_N1.”)

Now consider what happens if little B is present, but a substantial amount of the product P is present even at the start of the reaction, so that $k_2[B] \ll k_{-1}[P]$ and $k_{-1}[P] + k_2[B] \approx k_{-1}[P]$. Under these conditions, the rate law is simplified to

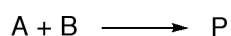
$$r = \frac{k_1 k_2 [A][B]}{k_{-1}[P] + k_2[B]} \approx \frac{k_1 k_2 [A][B]}{k_{-1}[P]} = \frac{k_1 k_2 [A][B]}{k_{-1}[P]} = k_{\text{obs}} \frac{[A][B]}{[P]}$$

Now, the reaction will be first-order in both A and B, but *inverse* first-order in P (the order of the reaction in P is -1) This means that the reaction will be inhibited by P, since it is the product of a reversible reaction. The observed rate constant k_{obs} is, in terms of the microscopic rate constants, given by

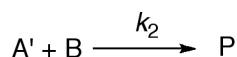
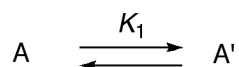
$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1}}$$

10.8. The Rapid-Equilibrium Approximation

In addition to the steady-state approximation, another useful approximation for deriving rate laws is the rapid-equilibrium approximation. Imagine that the net reaction is



and that the mechanism is



Here the reactant A is in equilibrium with an isomer A', and it is A' which undergoes the (irreversible) reaction to form the product (or products). One can easily confuse the rapid-equilibrium approximation with the SSA, but the key difference is that in the SSA, the intermediate is taken to have a very small concentration, while in the rapid-equilibrium approximation, the “intermediate” A' may have a significant concentration, perhaps even

greater than that of A, if $K_1 > 1$. The key assumption is that the first elementary step is not only reversible, but that it has reached equilibrium early in the reaction. This cannot be exactly correct, since the irreversible second reaction keeps driving the first reaction to the right as per Le Châtelier's principle, but it is a useful assumption for the derivation of an approximate rate law.

First, we write the reaction rate as the rate of the final step:

$$r = k_2[A'][B]$$

Now we use the equilibrium constant to solve for $[A']$ in terms of $[A]$:

$$K_1 = \frac{[A']}{[A]}$$

$$[A'] = K_1[A]$$

Substituting this expression into our initial rate equation yields

$$r = K_1 k_2[A][B]$$

The above rate law is useful if we can measure out pure A, that is, if K_1 is quite small. The reaction will thus be first-order in both A and B, and second-order overall, with observed rate constant $k_{\text{obs}} = K_1 k_2$. However, we may have a situation in which K_1 is on the order of 1, so that the concentrations of A and A' are comparable. In this case, we can usefully define $[A]_{\text{total}} = [A] + [A']$. This allows us to do some algebraic manipulation, as follows, to obtain a more useful approximate rate law:

$$K_1 = \frac{[A']}{[A]}$$

$$\frac{1}{K_1} = \frac{[A]}{[A']}$$

$$\frac{1}{K_1} + 1 = \frac{[A]}{[A']} + 1 = \frac{[A]}{[A']} + \frac{[A']}{[A']} = \frac{[A] + [A']}{[A']} = \frac{[A]_{\text{total}}}{[A']}$$

$$[A'] = \frac{[A]_{\text{total}}}{K_1^{-1} + 1}$$

$$r = k_2[A'][B] = \frac{k_2[A]_{\text{total}}[B]}{K_1^{-1} + 1} = k_{\text{obs}}[A]_{\text{total}}[B]$$

where

$$k_{\text{obs}} = \frac{k_2}{K_1^{-1} + 1}$$

Under these conditions, the rate law is first order in both B and A and A' taken together. This form of the rate law is useful if we cannot obtain either A or A' pure, but we can prepare solutions in which the sum of their concentrations is known.

10.9. The Arrhenius equation

As mentioned earlier, rate constants are only constant when the temperature is constant. The dependence of rate constants on temperature was first studied by Svante Arrhenius, who proposed the following equation (now well-known as the Arrhenius equation) to fit the experimental data:

$$k = Ae^{-E_a/RT}$$

Here A is the so-called pre-exponential factor, with the same units as k , and E_a is the activation energy, with units of $\text{J}\cdot\text{mol}^{-1}$ or $\text{kJ}\cdot\text{mol}^{-1}$. Both of these parameters are taken to be characteristic of a given reaction, and temperature-independent. T is the absolute temperature and R is the ideal gas constant ($8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). Taking the natural logarithm of both sides of the Arrhenius equation⁸⁶ yields a useful linearized form:

$$\begin{aligned}\ln k &= \ln A - \frac{E_a}{RT} \\ \ln k &= -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A\end{aligned}$$

so a plot of $\ln k$ vs. $\frac{1}{T}$ (a so-called Arrhenius plot) has slope $-\frac{E_a}{R}$ and intercept $\ln A$.

Arrhenius interpreted E_a as a measure of the kinetic energy that a molecule or molecules must have in order to reach the transition state, which is a relative maximum on the curve of energy vs. reaction progress. If the molecule(s) do not have at least E_a , they cannot surmount the “barrier” consisting of the energy difference between the transition state and the reactant(s). He interpreted the A factor as a measure of the sensitivity of the orientation of

⁸⁶ Strictly speaking, one must divide k and A by their units before taking their logarithms.

collision of two or more molecules, where collision with the wrong orientation would not lead to reaction. (Consider the “back-side attack” geometry of an organic S_N2 reaction: if a nucleophile approaches the alkyl halide or sulfonate from the direction of the leaving group, no reaction will occur). A reaction with a *larger* A factor would thus be *less* sensitive to the relative orientation of the reactants.

Despite the heuristic usefulness of these interpretations, the form of the Arrhenius equation does not have a sound theoretical foundation; Arrhenius simply proposed its functional form by analogy with the equilibrium constant expression $K = e^{-\Delta G^\circ/RT}$. Transition state theory, the successor to Arrhenius’ approach, introduces a firmer theoretical basis for the temperature dependence on rate constants.

10.10. Transition state theory and the Eyring equation

Nearly all chemistry students will learn, in their introductory courses, the key difference between kinetics and thermodynamics of a chemical reaction. For instance, the formation of water from the elements, $2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l)$, is very thermodynamically favorable, with an enormous equilibrium constant: with a spark, it occurs explosively. Yet, in the absence of a spark or catalyst, a mixture of H_2 and O_2 at room temperature will be indefinitely *kinetically* stable (or metastable). Thus, many thermodynamically favored reactions are nevertheless very slow at a given temperature. Nonetheless, one might think that, since both kinetics and thermodynamics deal with the energies of molecular systems, there must be *some* connection. Transition state theory (TST), developed by Henry Eyring (1901-1981), Michael Polanyi (1891-1976), and Meredith Gwynne Evans (1904-1952), relates the rate of a chemical reaction to the thermodynamic parameters of the reaction’s transition state.

Consider an elementary, bimolecular reaction $A + B \rightleftharpoons [A-B]^\ddagger \rightarrow P$, where $[A-B]^\ddagger$ is the transition state of the reaction. TST imagines an “equilibrium” of sorts between the reactants A and B and the transition state. This cannot be quite correct, since a transition state is a relative maximum on the reaction coordinate diagram, while a reactive intermediate, however unstable or short-lived, is still a relative minimum. Nevertheless, assuming

something like an equilibrium, statistical mechanics can be used to derive the Eyring equation for rate constants:

$$k = \frac{k_B T}{h c^\circ} e^{-\Delta G^\ddagger / RT}$$

where k_B is Boltzmann's constant, $h = 6.6261 \times 10^{-34}$ J·s is Planck's constant, and $\Delta G^\ddagger$, the Gibbs energy of activation or free energy of activation, is the Gibbs energy (free energy) difference between the transition state and the reactants. The term c° is the standard-state concentration, which is usually 1 M for reactions occurring in the solution phase. The Gibbs energy of activation can be broken up into enthalpy and entropy terms by

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Substituting this expression into the Eyring equation yields

$$k = \frac{k_B T}{h c^\circ} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

which can be linearized as

$$\ln\left(\frac{k h c^\circ}{k_B T}\right) = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \frac{\Delta S^\ddagger}{R}$$

An Eyring plot of $\ln\left(\frac{k h c^\circ}{k_B T}\right)$ vs. $\frac{1}{T}$ will thus be linear, with a slope of $-\frac{\Delta H^\ddagger}{R}$ and an intercept of $\frac{\Delta S^\ddagger}{R}$. Note that the Arrhenius equation and the Eyring equation have different temperature dependences, with a pre-exponential factor proportional to T in the Eyring equation but not the Arrhenius equation. In practice, this temperature dependence is much smaller than the exponential temperature dependence, so for a great many reactions, both Arrhenius and Eyring plots are very close to linear.

Comparing the Arrhenius and Eyring equations allows for the expression of Arrhenius' parameters in terms of Eyring's thermodynamic quantities of activation:

$$E_a = \Delta H^\ddagger + 2RT$$

$$A = \frac{e^2 k_B T}{h c^\circ} e^{\Delta S^\ddagger / R}$$

Thus, we see that Arrhenius' empirical E_a is related to the enthalpy of activation, whereas his A , reflecting the requirements for collision geometry and thus a certain measure of transition state disorder, is related to the entropy of activation.

You may wonder whether the Eyring equation is useful for unimolecular reactions, as well as bimolecular reactions. The answer is yes, even though it was derived for bimolecular reactions. The reason for this is that many apparently unimolecular reactions are still believed to involve a molecular collision, in which the reacting species collides with an *unreactive* molecule (such as a solvent molecule in a solution-phase reaction, or an inert gas molecule or atom in a gas-phase reaction). This collision transfers energy (as kinetic energy) to the reactive molecule, giving it enough energy to overcome the activation barrier, while slowing down the unreactive molecule. This type of unimolecular reaction by way of collision is known as the Lindemann mechanism, after Frederick Lindemann (1886-1957). For a multi-step reaction, parameters from an Eyring plot can be interpreted in terms of the rate-limiting step of the reaction.

Chapter 11: Ligand Substitution Reactions

11.1. The Hammond Postulate

We have already seen that transition state theory and the Eyring equation are used to draw a connection between the kinetics of a reaction and the thermodynamics of its transition state. A qualitative argument that is also useful for connecting kinetics and thermodynamics is the Hammond postulate, proposed in 1955 by the organic chemist George Hammond (1921-2005). Hammond phrased his postulate as follows:

“If two states, as for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structures.”⁸⁷

The Hammond postulate thus applies to intermediates that are close in energy to the transition states leading to them. It is often valid to assume such a closeness in energy. Although a transition state is a local maximum in a plot of energy vs. reaction progress and a reactive intermediate is a local minimum, the intermediate is still very likely a high-lying local minimum, far from the global minimum of energy. The Hammond postulate then says that a high-energy intermediate will have a similar structure to the transition state leading to it. If the rate-limiting step of a multistep reaction is the formation of a reactive intermediate from a comparatively low-energy reactant, then any feature of the reactant that will lead to a more stable intermediate will also likely lead to a lower-energy transition state and thus a faster reaction (larger value of k). A familiar example of the utility of the Hammond postulate can be found in the organic S_N1 mechanism, in which the reactive intermediate is a carbocation R^+ : the more stable the carbocation (due to greater substitution, the presence of a π -donor substituent, *etc.*), the lower-energy the transition state leading to its formation and the faster the reaction. The Hammond postulate is very useful when we qualitatively $\alpha\beta\delta$ intuitively think about reaction rates and reaction mechanisms, and it provides an heuristic

⁸⁷ *Journal of the American Chemical Society* **1955**, 77, 334-338.

backdrop for linear free energy relationships, a more quantitative way of relating molecular structure and reaction rate.

11.2. Linear Free Energy Relationships (LFERs)

Linear free energy relationships, or LFERs for short (somewhat humorously pronounced as “elfers”) are relationships that describe the rate constant for a particular type of reaction as a function of substituents on the reactant(s). The assumption is that the fundamental mechanism of the reaction does not change as a function of the substituents (this assumption is not always valid), and the sensitivity of the value of the rate constant to the change in substituents can tell us something about the mechanism.

One of the earliest LFERs was proposed by the physical organic chemist Louis Hammett (1894-1987), and early LFER work was done largely on organic systems. We will now consider Hammett’s work as a good “textbook example” of LFERs, and later in this course we will see LFER experiments that are useful for the analysis of transition metal systems. Hammett developed a parameter denoted σ (not to be confused with σ bonds) as a measure of how electron-withdrawing a substituent is, based on its effect on the acidity of a substituted benzoic acid. For the ionization reaction of a benzoic acid with a substituent in the *meta* position, shown in Figure 11.1 below, the Hammett parameter is defined as $\sigma_{meta} = \log_{10} \left(\frac{K_X}{K_H} \right)$. Similarly, when the substituent is in the *para* position, as shown in Figure 11.2 on the following page, the Hammett parameter is defined as $\sigma_{para} = \log_{10} \left(\frac{K_X}{K_H} \right)$. In both cases, K_H is just K_a for benzoic acid itself, while K_X is K_a for the substituted benzoic acid.

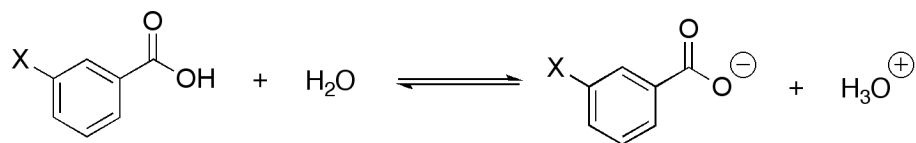


Figure 11.1. The ionization reaction used to define σ_{meta} .

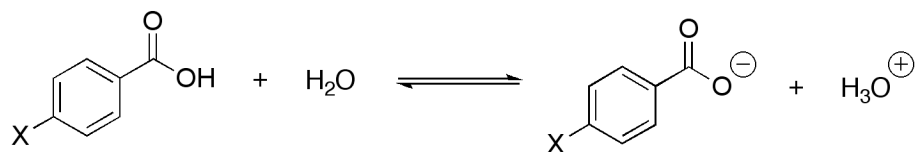


Figure 11.2. The ionization reaction used to define σ_{para} .

In general, electron-withdrawing substituents X have $\sigma > 0$, as they make it more favorable for negative charge to build up on the benzoate anion. The more electron-withdrawing the substituent, the larger the value of σ . Conversely, electron-donating substituents have $\sigma < 0$, as they make this negative charge buildup less favorable. The reason two sets of parameters, σ_{meta} and σ_{para} , are defined is that substituents in the *para* position can participate in resonance with the σ systems of the benzoic acid and benzoate, whereas those in the *meta* position cannot.

You might, quite reasonably, be asking yourself what in the world the relative acidities of benzoic acid derivatives have to do with the wider world of chemical reactions. It turns out that the σ substituent parameters defined in terms of the ionization of benzoic acids can also affect the thermodynamics and/or the kinetics of other chemical reactions in which the substituents on the reactant(s) can be varied. The equilibrium constants for many reactions with a variable substituent X will often (at least roughly) obey the following equation:

$$\log_{10} \left(\frac{K_X}{K_H} \right) = \rho \sigma_X$$

This equation means that a so-called Hammett plot of $\log_{10} \left(\frac{K_X}{K_H} \right)$ vs. σ_X for different X will be linear with a slope of ρ . If $\rho > 0$, this is usually interpreted as meaning that there is a net buildup of negative charge when going from the reactant containing X to the product with X. If $\sigma < 0$, this suggests a net buildup of positive charge when going from reactant to product. For reactions with $\sigma > 0$, $\rho > 1$ suggests that there is more negative charge buildup than in the case of the deprotonation of a benzoic acid, so the reaction thermodynamics are more sensitive to the electron-withdrawing ability of X, while $0 < \sigma < 1$ suggests that there is less negative charge buildup than in the deprotonation of a benzoic acid, so the thermodynamics are less sensitive to the electron-withdrawing ability of X.

It turns out that Hammett plots can be made for rate constants, as well as equilibrium constants. Measuring the experimental rate constant k for a series of related reactions with different substituents X on a reactant often yields data which fit the following equation:

$$\log_{10} \left(\frac{k_X}{k_H} \right) = \rho \sigma_X$$

This equation means that a kinetic Hammett plot of $\log_{10} \left(\frac{k_X}{k_H} \right)$ vs. σ_X for different X will be linear with a slope of ρ . Here the sign and magnitude of ρ tell us something about the buildup of negative or positive charge in the transition state of the reaction's rate-determining step: $\rho > 0$ suggests a buildup of negative charge, while $\rho < 0$ suggests a buildup of positive charge. By the Hammond postulate, we can (at least tentatively) conclude that, for a multistep reaction, the sign and magnitude of ρ tell us something about the nature of a reactive intermediate, as well. For example, an organic S_N1 reaction would be expected to have $\rho < 0$, due to the positively charged carbocation intermediate, while a nucleophilic aromatic substitution (S_NAr) reaction would be expected to have $\rho > 0$, due to the role of a carbanion intermediate. It should be noted that a strongly nonlinear kinetic Hammett plot is often indicative of a change in mechanism, or a change of the rate-limiting step in the same mechanism, occurring as a result of a change in X.

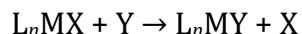
We have spent some time discussing Hammett's σ parameters as a classic example of how LFERs are used in the analysis of kinetic data. There have been many different LFERs proposed for organic reactions,⁸⁸ and we will see some "inorganic" examples shortly when we discuss ligand substitution reactions on square-planar platinum(II) complexes.

11.3. Definition of Ligand Substitution Reactions

A very important type of reaction undergone by transition metal complexes is ligand substitution, the replacement of one ligand (the leaving ligand, leaving group, or nucleofuge)

⁸⁸ For a good discussion of LFERs in mechanistic organic chemistry, see Chapter 8 of *Modern Physical Organic Chemistry*, by Eric V. Anslyn and Dennis A. Dougherty, University Science Books: Sausalito, CA, 2006.

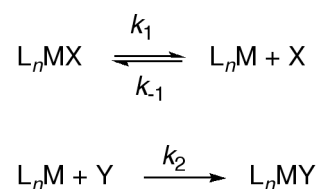
by another (the entering ligand or nucleophile). In its most general form, the net reaction equation is



where the ligands X and Y are here written without charges for simplicity, but can be neutral, anionic, or (rarely) even cationic in actual cases. (The metal complexes can also be neutral, cationic, or anionic.) The L_n simply denote the other ligands in the metal's coordination sphere. They are sometimes known as spectator ligands or ancillary ligands, because they undergo no net change, but their identity can still have a significant effect on the rate and mechanism of the ligand substitution (*e.g.* by their steric or electronic character). Overall, one can think of ligand substitution as the analog for metals of nucleophilic substitution reactions at carbon.

11.4. Dissociative (*D*) Ligand Substitution

One possible mechanism for ligand substitution is the dissociative mechanism, often denoted *D* for short. It is akin to the S_N1 mechanism for nucleophilic substitution at carbon. As shown below, the *D* mechanism involves initial loss of the leaving ligand X, giving an intermediate L_nM with lower coordination number than the reactant, which then reacts with the entering ligand Y:



We can predict the rate law for this mechanism as follows: first we note that we can write $r = k_2[L_nM][Y]$, but this is not experimentally useful, since the intermediate L_nM is usually too unstable to be isolated, or for stock solutions of precisely known concentrations to be prepared. Instead, we use the SSA for L_nM to yield the following rate law:

$$r = \frac{k_1 k_2 [L_nMX][Y]}{k_{-1}[X] + k_2[Y]}$$

We see that under the condition of a large excess of the entering ligand Y, $k_2[Y] \gg k_{-1}[X]$, the rate law reduces to

$$r = k_1[L_nMX]$$

which is the first-order result. This is exactly analogous to the first-order result often seen for organic S_N1 reactions in which the entering nucleophile is present in significant excess. If, instead, the leaving ligand X is present in large excess, $k_{-1}[X] \gg k_2[Y]$, then the rate law reduces to

$$r = \frac{k_1 k_2 [L_nMX][Y]}{k_{-1}[X]} = k_{\text{obs}} \frac{[L_nMX][Y]}{[X]}$$

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1}}$$

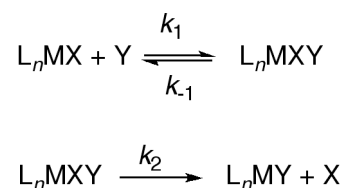
Under first-order conditions, with Y present in large excess, the observed rate constant k (which will be k_1 under the first-order conditions) should, for a dissociative mechanism, be independent on the nature of Y, since that ligand is not involved in the rate-determining dissociation step. In practice, there is often significant experimental error associated with the measurement of rate constants, so if k values for a series of different entering ligands span less than a factor of 10, the rate is often considered “independent” of the ligand. In contrast, k is highly dependent on the nature of the leaving group X. Dissociative substitution is also suggested by a strong dependence of k on the sterics of the spectator ligands L in L_nMX : for instance, if L = an amine NR₃ or a phosphine PR₃ with large R groups, dissociative substitution often proceeds faster than for amines or phosphines with smaller R, as some of the steric congestion in L_nMX is relieved in the lower-coordinate L_nM intermediate (and in the transition state leading up to it).

It is often said that Eyring analysis of a reaction that proceeds *via* a *D* mechanism will yield a negative value for the entropy of activation $\Delta S^\ddagger$. After all, in the rate-determining step, one molecule, L_nMX , goes to two molecules, L_nM and X, so this step (and its transition state) should be accompanied by an increase in freedom of motion and thus entropy. It is not necessarily the case, however, that $\Delta S^\ddagger > 0$ for a *D* reaction. This is because, for a reaction taking place in solution, the solvation of intermediates (and transition states) can be considerably different than the solvation of the reactants. If the dissociation step is accompanied by substantially stronger solvation, the overall entropy of the system might

decrease, leading to $\Delta S^\ddagger < 0$. This is more likely to be true if the dissociation is associated with charge separation (such as the case where a negatively charged ligand leaves a neutral complex, $L_nMX \rightarrow L_nM^+ + X^-$) and the solvent is strongly polar. In such cases, the strong ion-dipole interactions can lower entropy upon dissociation. Nevertheless, many *D* reactions do have $\Delta S^\ddagger > 0$, and if a ligand substitution reaction has a $\Delta S^\ddagger$ value which is greater than $10 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ($41.84 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), it is very likely dissociative. If, on the other hand, $-10 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} < \Delta S^\ddagger < +10 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, one cannot be confident whether the reaction is dissociative or not.

11.5. Associative (A) Ligand substitution

The opposite of the dissociative mechanism is the associative mechanism, often symbolized *A*. In this mechanism, *Y* reversibly adds to L_nMX to form the intermediate L_nMXY , of greater coordination number, which then loses *X* to form the product L_nMY . This is analogous to nucleophilic acyl substitution in organic chemistry, such as the addition of an alkoxide $R'O^-$ to an acyl chloride $RC(O)Cl$ to form an ester $RC(O)OR'$ and Cl^- , or to a nucleophilic aromatic substitution (S_NAr) reaction.⁸⁹



As with the dissociative case, we can write $r = k_2[L_nMXY]$, but since L_nMXY is a transient intermediate, we cannot measure out a known concentration of it to run a kinetics experiment. We can use the SSA for L_nMXY to yield

$$r = \frac{k_1 k_2 [L_nMX][Y]}{k_{-1} + k_2} = k_{\text{obs}} [L_nMX][Y]$$

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1} + k_2}$$

⁸⁹ Many textbooks state that *A*-type ligand substitution is akin to the S_N2 reaction in organic chemistry. This is incorrect, since the carbon atom undergoing substitution in an S_N2 reaction has an increased coordination number in the transition state, but not in the reactive intermediate – after all, an S_N2 reaction is concerted, so there is no intermediate!

For an associative mechanism, we expect the rate law to be second order overall, first order in both reactants, L_nMX and Y , regardless of their initial concentrations. We expect Eyring analysis to yield a negative entropy of activation, as in the rate-determining first step, two molecules are becoming one, though if charge neutralization occurs ($L_nMX^+ + Y^- \rightarrow L_nMXY$) in a polar solvent, less tight solvation of the intermediate and transition state may occur, so $\Delta S^\ddagger$ may be small but positive. In general, $\Delta S^\ddagger < -10 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is strongly suggestive of an A mechanism.

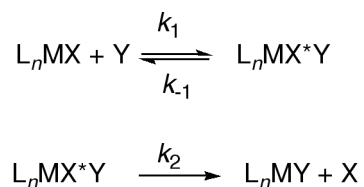
We expect the observed rate constant $k_{\text{obs}} = \frac{k_1 k_2}{k_{-1} + k_2}$ to depend strongly on the incoming ligand Y , in addition to the leaving ligand X and the ancillary ligands L . Larger (more sterically encumbering) ancillary ligands L will generally lead to slower reactions if the A mechanism is operative, in contrast to the D mechanism, where larger L speed dissociation. For an octahedral reactant L_5MX , an A mechanism would proceed *via* a seven-coordinate intermediate L_5MXY . This behavior is rare due to the highly sterically hindered nature of a seven-coordinate species (and the transition state leading to it). However, for a square-planar reactant L_3MX , an A mechanism would involve a five-coordinate intermediate L_3MXY . This is much less sterically hindered, and we will see shortly that the A mechanism is most common for ligand substitution reactions of square-planar complexes.

11.6. Interchange (I) mechanisms of ligand substitution

Both the D and A mechanisms for ligand substitution involve an intermediate with a coordination number different from that of the reactant and product metal complexes (lower in the D case, higher in the A case). In contrast, the interchange, or I , mechanism involves no intermediate with a different coordination number. In the simplest type of I mechanism, Y displaces X from L_nMX in a concerted fashion, with no intermediates and only one transition state and one rate constant k . $L_nMX + Y \rightarrow [L_nMXY]^\ddagger \rightarrow L_nMY + X$. This is analogous to the S_N2 reaction in organic chemistry.

For a reaction that proceeds by the simple *I* mechanism, the rate law is simple: $r = k[\text{ML}_5\text{X}][\text{Y}]$. This has the same form as the rate law for an associative mechanism, so simple kinetic studies cannot distinguish between an *A* and a simple *I* mechanism based on the rate law alone.

Some reactions proceed by a more complex type of interchange mechanism than that discussed previously. One such possibility is the Eigen-Wilkins mechanism for ligand substitution, shown below:



At first glance, this may seem to you like an *A*-type mechanism. However, the intermediate species $\text{L}_n\text{MX}\cdots\text{Y}$, often called the encounter complex, does *not* have an increased coordination number at M like L_nMXY in the *A* mechanism. Instead, the entering Y ligand is engaged in *noncovalent* interactions with L_nMX , so it is in the secondary, or outer, coordination sphere of M, not the primary one (the primary, or inner, coordination sphere consists of those ligands covalently bound to M, in this case n L and X). If L_nMX is a cation and Y is an anion, then the encounter complex is an ion pair, but even if one or both of L_nMX and Y are neutral, an encounter complex can still form through attractive ion-dipole or dipole-dipole interactions.

In some cases, k_1 and k_{-1} are both significantly larger than k_2 , so $\text{L}_n\text{MX}\cdots\text{Y}$ will be present in significant concentration, and might be detectable spectroscopically. Often, however, $\text{L}_n\text{MX}\cdots\text{Y}$ will be a typical reactive intermediate, present in only very low concentration, though the first step is at equilibrium (this means that k_1 and k_{-1} are both of comparable magnitude to k_2). Under such conditions, and when the reaction is run with a significant excess of Y (that is, $[\text{Y}] \gg [\text{L}_n\text{MX}]$), we can derive a rate law for the Eigen-Wilkins mechanism. Since step 2 is rate-limiting, we write $r = k_2[\text{L}_n\text{MX}\cdots\text{Y}]$. To recast $[\text{L}_n\text{MX}\cdots\text{Y}]$ in terms of experimentally measurable quantities, we use the SSA once again:

$$\frac{d[L_nMX \cdot Y]}{dt} = k_1[L_nMX][Y] - k_{-1}[L_nMX \cdot Y] - k_2[L_nMX \cdot Y] \approx 0$$

At this point, we note that since Y is present in much greater concentrations than ML_5X , its concentration will not change very much during the course of the experiment, that is, $[Y] \approx [Y]_0$. We also define the quantity $[M]_0 = [L_nMX] + [L_nMX \cdot Y]$, or $[L_nMX] = [M]_0 - [L_nMX \cdot Y]$. Making these substitutions in our SSA expression yields

$$\begin{aligned} k_1[L_nMX][Y] - k_{-1}[L_nMX \cdot Y] - k_2[L_nMX \cdot Y] &= 0 \\ k_1[Y]_0([M]_0 - [L_nMX \cdot Y]) - (k_{-1} + k_2)[L_nMX \cdot Y] &= 0 \\ k_1[M]_0[Y]_0 - (k_1[Y]_0 + k_{-1} + k_2)[L_nMX \cdot Y] &= 0 \\ [L_nMX \cdot Y] &= \frac{k_1[M]_0[Y]_0}{k_1[Y]_0 + k_{-1} + k_2} \\ r = k_2[L_nMX \cdot Y] &= \frac{k_1k_2[M]_0[Y]_0}{k_1[Y]_0 + k_{-1} + k_2} \end{aligned}$$

Dividing both numerator and denominator of the rate law by k_{-1} , and denoting the equilibrium constant for encounter complex formation as $K_1 = \frac{k_1}{k_{-1}}$ yields

$$r = \frac{k_2K_1[M]_0[Y]_0}{K_1[Y]_0 + 1 + \frac{k_2}{k_{-1}}}$$

The ratio $\frac{k_2}{k_{-1}}$ is usually much smaller than either of the terms $K_1[Y]_0$ or 1, so we can often neglect it for the more simplified rate law

$$r = \frac{k_2K_1[M]_0[Y]_0}{K_1[Y]_0 + 1}$$

Our derivation of the Eigen-Wilkins rate law rests on the assumption that the reaction is run with a large excess of [Y], or $[Y]_0 \gg [M]_0$. If enough Y is used that the product $K_1[Y]_0 \gg 1$, then the rate law will be first-order in the metal complex: $r \approx \frac{k_2K_1[M]_0[Y]_0}{K_1[Y]_0} = k_2[M]_0$. Thus, a *D* mechanism and an Eigen-Wilkins interchange mechanism may each give a first-order rate law, just as an *A* mechanism and a simple *I* mechanism will each give a second order rate law (first-order in both ML_5X and Y). It is often, however, the case that $K_1[Y]_0$ is close to 1, in which case the more complicated rate law holds for the Eigen-Wilkins interchange mechanism.

As mathematically messy as the Eigen-Wilkins rate law can be, one can simplify experimental interpretation of results by theoretical estimation of K_1 , the equilibrium constant for encounter complex formation. According to the Fuoss-Eigen equation, $K_1 = \frac{4}{3}\pi a^3 N_A e^{-V/RT}$. In this equation, a is the closest distance between L_nMX and Y in $L_nMX \cdots Y$, and V is the potential energy of interaction between them. If L_nMX and Y are both charged species, with charges q_1 and q_2 , respectively, then V is given by $V = \frac{q_1 q_2 e^2}{4\pi\epsilon a}$. Here e is the electronic charge, *not* Euler's number, and ϵ is the permittivity of the solvent (for a vacuum, $\epsilon = \epsilon_0$). If either or both of L_nMX and Y are uncharged, then a different equation for V must be used, reflecting an ion-ion or ion-dipole interaction. Using this approach, K_1 is estimated by theory, and the experimental data are fit using this value to determine k_2 .

11.7. Dissociative and Associative Interchange Mechanisms

Let us now return to the simple I mechanism (which I will just call the I mechanism from now on, not to be confused with the more complicated Eigen-Wilkins mechanism). It turns out that different reactions proceeding *via* this mechanism can have interestingly different types of transition state. The classification of ligand substitution reactions into those proceeding by D , A , I , or Eigen-Wilkins mechanisms is said to specify the *stoichiometric* mechanism, that is, it tells us the number of steps in the mechanism, and the stoichiometry of each. It does not, however, tell us what the transition state geometries look like. The *intimate* mechanism, on the other hand, describes not only the number and stoichiometry of the steps, but also the nature of the transition states. While we cannot actually observe transition states, we can calculate their structures using computational techniques. Experimental measurements can, however, tell us something about the nature of transition states in lieu of direct observation.

To illustrate this, we consider that the I mechanism involves no intermediate of increased coordination number, but that the transition state L_nMXY *does* formally have an increased coordination number, with the M - Y bond forming as the M - X bond breaks. Thus, in the transition state, there is some level of bonding between M , X , Y , and all n spectator ligands L . However, at the transition state itself – the maximum on the curve of free energy vs. reaction

coordinate – it need not be the case that the M–Y bond has formed to the exact same extent as the M–X bond has broken. We might have a transition state in which the M–X bond has significantly weakened, with only slight M–Y interaction. In such a case, the transition state would resemble that of a *D* mechanism, even though the reaction's stoichiometric mechanism, and its corresponding rate law, will be that for *I*, not *D*. We call this dissociative interchange, or *I_d*. Conversely, we might have a transition state in which the M–X bond has been weakened only slightly, but in which there are already substantial M–Y bonding interactions. This transition state is more similar to that of an *A* mechanism, and so we say that this reaction proceeds by associative interchange, or *I_a*. As with the *I_d* case, this is still an *I* mechanism in terms of the rate law and the stoichiometry of each step. This variation in intimate mechanisms is possible for organic S_N2 reactions, as well. In some S_N2 reactions, the transition state involves the leaving group departing more than the nucleophile bonding, while in others the nucleophile is bonding more than the leaving group is leaving in the transition state.

How can we use kinetics to probe *I_d* vs. *I_a* mechanisms for ligand substitution in octahedral complexes? Simply measuring the rate law is not sufficient, since any simple *I* mechanism will have $r = k[L_nMX][Y]$. We can, however, gain insight by seeing how *k* varies with temperature and with incoming ligand Y. If the rate law includes [Y], consistent with an *I* mechanism, but *k* is similar for a range of entering ligands Y, then this suggests that the involvement of Y in the transition state is small, and that the intimate mechanism is *I_d*. If *k* varies significantly with different Y, then there is likely substantial M–Y interaction in the transition state, and the intimate mechanism can be assigned as *I_a*. For instance, the replacement of water by an anionic ligand in Cr(H₂O)₆³⁺ varies tremendously, with $k = 8 \times 10^{-10} \text{ M}^{-1}\cdot\text{s}^{-1}$ when I[–] is the entering ligand, but $k = 1.8 \times 10^{-6} \text{ M}^{-1}\cdot\text{s}^{-1}$ when the entering ligand is NCS[–]. Thus we can say with confidence that Cr(H₂O)₆³⁺ undergoes substitution by *I_a* (if we rule out *A* due to steric crowding). Similarly, Eyring analysis of *k* vs. *T* for an *I_d* reaction will yield an entropy of activation that is not highly negative, and may even be slightly positive, while that of an *I_a* reaction will more likely be highly negative, like that of an *A*

reaction (but see discussion above about how solvation changes can pose a difficulty in the interpretation of $\Delta S^\ddagger$ values).

11.8. Ligand Substitution Mechanisms with Two-Term Rate Laws

It is sometimes observed that a ligand substitution mechanism $L_nMX + Y \rightarrow L_nMY + X$ will follow a rate law of the form

$$r = k[L_nMX] + k'[L_nMX][Y]$$

with a sum of two terms: one apparently first-order, with rate constant k , and one apparently second-order, with rate constant k' . Such behavior is most commonly observed experimentally by using pseudo-first-order conditions, with Y present in such large excess that $[Y] \approx [Y]_0$ over the course of a reaction, in which case the rate law can be written as

$$r = k_{\text{obs}}[L_nMX]$$

$$k_{\text{obs}} = k + k'[Y]_0$$

If the pseudo-first-order observed rate constant k_{obs} is measured at several different values of $[Y]_0$, then a plot of k_{obs} vs. $[Y]_0$ will be linear with a slope of k' and an intercept of k .

There is more than one possible interpretation of such rate behavior. One possibility is that L_nMX undergoes ligand substitution *via* two mechanisms, each operating at the same time: a D mechanism with a first-order rate law and rate constant k , and an A or I mechanism with a second-order rate law and rate constant k' . Another possibility, often observed in coordinating solvents (solvents that are themselves Lewis bases that can act as ligands, such as water, alcohols, ethers, ketones, *etc.*) is that two different A or I mechanisms are proceeding in tandem. One is a simple A or I mechanism with entering ligand Y and rate constant k' , and another involves substitution of X by the solvent S : $L_nMX + S \rightarrow L_nMS + Y$, followed by substitution of S by Y : $L_nMS + Y \rightarrow L_nMY + S$. If this mechanism is either A or I with respect to solvent, and if substitution of X by S is slower (rate-determining) than the following substitution of S by Y , then the rate law will have the form

$$r = k_S[L_nMX][S] + k'[L_nMX][Y]$$

reflecting two A or I mechanisms operating in tandem. However, the solvent will be present in such large excess that its concentration $[S]$ will be very nearly constant over the course of

the reaction, so that $k_s[S]$, the product of a second-order rate constant and a concentration, will appear to be a first-order rate constant k , giving rise to a rate law suggesting both a first-order and a second-order reaction. A standard operational test for whether an apparently first-order term in the rate law is truly dissociative or involves solvent is to run the reaction in several different solvents and measure k for each. If k varies considerably with solvent, the mechanism involving solvent displacement of X is likely.

11.9. Ligand Substitution Reactions on Square-Planar Platinum(II) Complexes

One can think of ligand substitution reactions as the transition metal analog of the nucleophilic substitution reactions on carbon discussed in organic chemistry classes. The rates, scope, mechanisms, and stereochemistry of ligand substitution are more widely varied than those of substitution on carbon, as they encompass substitutions on a large number of elements, rather than just one, and there are more possible coordination geometries about transition metals than about a central carbon atom. While octahedral metal complexes are the most common coordination number and geometry, we will begin our in-depth study of ligand substitution reactions with substitution on square-planar metal complexes, since the patterns for these reactions seem to be some of the most regular.

Recall from our discussion of structure and bonding that metal/oxidation state combinations with a d^8 electron count commonly give rise to square-planar coordination geometry. Square-planar complexes of Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), and Au(III) are all well known. Much of the seminal work on square-planar substitution reactions was conducted in the 1920s by Ilya Ilyich Chernyaev (1893-1966) who studied the chemistry of Pt(II) complexes in great detail, and it is thus with Pt(II) complexes where we will begin. A general substitution reaction at Pt(II) can be written as shown in Figure 11.3 below: please note the symbol T for the ligand that lies *trans* to the leaving ligand (this will be important later).

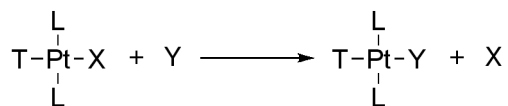


Figure 11.3. A generic ligand substitution reaction on a square-planar Pt(II) complex.

A hallmark of substitution on square-planar Pt(II) complexes is retention of stereochemistry: the leaving ligand X is *trans* to T in the reactant, and the entering ligand Y is *trans* to T in the product. When the kinetics of such reactions are studied, the following two-term rate law is usually observed:

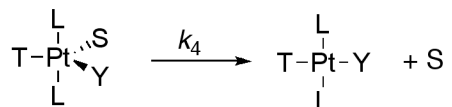
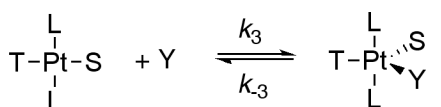
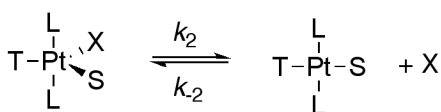
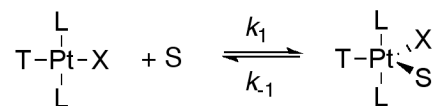
$$r = k[\text{L}_2\text{TPtX}] + k'[\text{L}_2\text{TPtX}][\text{Y}]$$

The apparently first-order term, with rate constant k , is generally believed to correspond to a solvent-dependent *A* mechanism (see Section 11.8), not a truly first-order *D* mechanism. This conclusion is based on the fact that for reactions of this sort, the value of the “first-order” rate constant k varies tremendously when the solvent is changed. For instance, for the reaction $\text{Pt}(\text{NO}_2)(\text{py})_2\text{Cl} + \text{py} \rightarrow \text{Pt}(\text{NO}_2)(\text{py})_3^+ + \text{Cl}^-$, where py = pyridine), $k = 6 \times 10^{-6} \text{ s}^{-1}$ when the reaction is conducted in dichloromethane (only a weakly coordinating solvent), while $k = 0.31 \text{ s}^{-1}$ in acetone (a strongly coordinating solvent). Based on observations such as these, the mechanism for ligand substitution reactions on most square-planar Pt(II) complexes is believed to consist of the following two *A* mechanisms operating in tandem, as shown in Figure 11.4 on the

Here we assume that the first step (attack of solvent on L_2TPtX) of the k mechanism is rate-limiting, giving the “first-order” term $k_1[\text{L}_2\text{TPtX}][\text{S}] = k[\text{L}_2\text{TPtX}]$ in the rate law (since the concentration of solvent is essentially constant, $k = k_1[\text{S}]$), while the k' mechanism is a standard *A* mechanism, giving rise to the second-order term. In principle, the ligand substitution steps shown above could proceed by an I_a mechanism, instead of the *A* mechanism shown. An *A* mechanism is generally favored, based on the fact that the d^8 , square-planar complex $\text{Ni}(\text{CN})_4^{2-}$, in the presence of excess CN^- , is in equilibrium with the five-coordinate, trigonal-bipyramidal complex $\text{Ni}(\text{CN})_5^{3-}$, which can be viewed as a model for a trigonal-bipyramidal intermediate in an *A*-type substitution mechanism. Additionally, Eyring plots show that for substitution on Pt(II) complexes, both the k and k' terms have

$\Delta S^\ddagger < -10 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is usually considered strong evidence for the *A* mechanism. However, it may well be the case that some substitution reactions on square-planar complexes proceed *via* an *I_a* mechanism instead, with *A* vs. *I_a* depending on the metal and ligands.

Solvent-dependent (*k*) mechanism:



Solvent-independent (*k'*) mechanism:

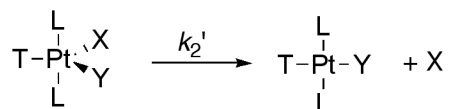
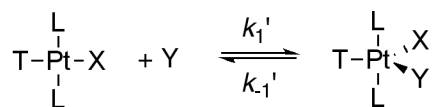


Figure 11.4. Proposed mechanism for ligand substitution reactions on square-planar Pt(II) complexes.

11.10. The *Trans* Effect

Chernyaev and others found that which ligand X is replaced by an incoming ligand Y was highly dependent on the ligand *trans* to the ligand to be replaced (this *trans* ligand will be symbolized as T in general). For instance, either the *cis* or *trans* isomer of Pt(PEt₃)₂Cl₂ may

be formed depending on whether one uses $\text{Pt}(\text{PEt}_3)_4^{2+}$ or PtCl_4^{2-} as the Pt-containing starting material, as shown in Figure 11.5 below.

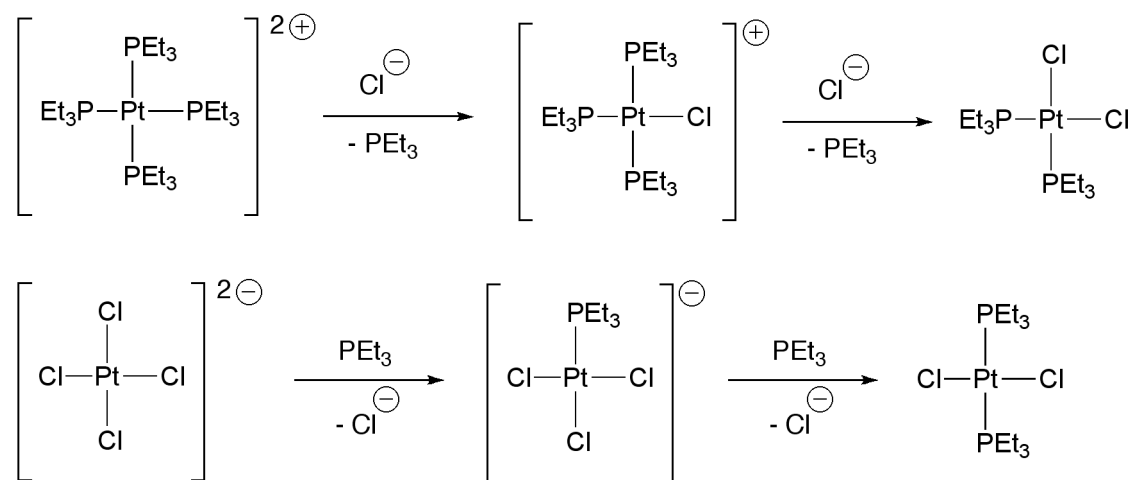


Figure 11.5. Preparation of the *cis* and *trans* isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.

Consider first the reaction sequence in which *cis*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ is formed from $\text{Pt}(\text{PEt}_3)_4^{2+}$. When the first equivalent of Cl^- replaces a PEt_3 ligand, it does not matter which PEt_3 is replaced; all are equivalent in the molecule. When the second equivalent of Cl^- replaces another PEt_3 in $\text{Pt}(\text{PEt}_3)_3\text{Cl}^+$, however, two different types of PEt_3 can be replaced: the one *trans* to Cl , or one of the two *cis* to Cl and *trans* to another PEt_3 . We see that the PEt_3 that is *trans* to PEt_3 , rather than Cl , is more easily replaced. This yields the *cis* isomer of the product. Similarly, when we start with PtCl_4^{2-} , the first equivalent of PEt_3 replaces one of four equivalent Cl^- ligands. When the second equivalent of PEt_3 reacts with $\text{Pt}(\text{PEt}_3)\text{Cl}_3^-$, however, it displaces the Cl^- *trans* to PEt_3 , not one of those *trans* to another Cl . This yields the *trans* isomer of the product.

We thus see that certain ligands *labilize* other ligands that are *trans* to them, where a ligand is considered labilized if it is more easily replaced by an incoming ligand. This is known as the *trans* effect, and ligands that more strongly labilize others *trans* to them are said to have a stronger *trans* effect. From the above example, it is clear that PEt_3 has a stronger *trans* effect than Cl^- . This is clearly an overall kinetic, rather than a thermodynamic, phenomenon. The *cis* and *trans* isomers of $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ will not have identical free energies, so at equilibrium,

one will be favored over the other. But the kinetic product of this reaction depends on the starting material.

The kinetic dependence on the ligand *trans* to the leaving ligand has been studied in reactions such as the one in Figure 11.6 below.

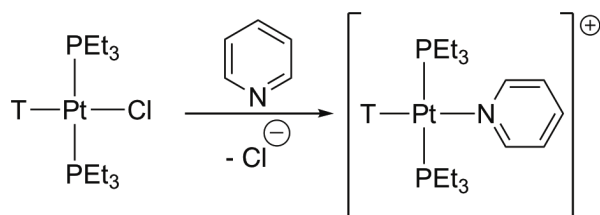


Figure 11.6. A series of experiments designed to determine the relative *trans* effects of different ligands.

It was found that both k (the pyridine-independent term reflecting solvent involvement) and k' (the pyridine-dependent term) were strongly affected by the *trans* ligand T. For instance, if $\text{T} = \text{H}^-$, then $k = 1.8 \times 10^{-2} \text{ s}^{-1}$ and $k' = 4.2 \text{ M}^{-1} \cdot \text{s}^{-1}$, while if $\text{T} = \text{CH}_3^-$, then $k = 1.7 \times 10^{-4} \text{ s}^{-1}$ and $k' = 6.7 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$. From experiments like this one and many others, an ordering of the *trans* effect strength of ligands can be prepared, which is applicable to reactions of square-planar Pt(II) complexes in general: $\text{O}, \text{CN}^-, \text{C}_2\text{H}_4 > \text{PR}_3, \text{H}^- > \text{CH}_3^- > \text{C}_6\text{H}_5^-, \text{NO}_2^-, \text{I}^-, \text{SCN}^- > \text{Br}^-, \text{Cl}^- > \text{py}, \text{NH}_3, \text{OH}^-, \text{H}_2\text{O}$.

To explain the *trans* effect, we consider the two fundamental ways in which a change in molecular structure can lower activation energy and increase reaction rate: such a change can 1) raise the energy of the reactants (the ground state) and 2) lower the energy of the transition state. Note that either of these things will lower the activation energy, which is the energy *difference* between the transition state and the reactants. Considering effect 1, raising the energy of the reactants, first, we would predict that more strongly σ -bonding ligands would exert a greater *trans* effect. To see why this should be so, imagine that the ligands T and X both lie along the x -axis (or the y -axis; the z -axis is generally taken to be perpendicular to the plane of the molecule). They are both involved in σ -bonding with the metal's p_x valence

AO ($6p_x$, if the metal is Pt), If T and X are the same ligand, then the bonding is symmetrical, as shown in the first part of Figure 11.7. However, if T and X are *not* the same, and T is a better σ -bonding ligand, then the metal p_x AO will be polarized towards T, forming a stronger bond with it and a weaker bond with X, as shown in the second part of Figure 11.7. In effect, T and X compete for bonding to the same metal p AO, and the better T is at this competition, the weaker the metal–X bond.

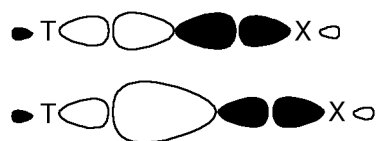


Figure 11.7. σ -bonding involving a metal p AO, for a pair of equivalent ligands (top) and nonequivalent ligands (bottom).

The five-coordinate, trigonal-bipyramidal intermediate in Figure 11.4 (and the transition state leading to it, recalling the Hammond postulate) has a Pt–X bond than the reactant. The weaker the Pt–X bond is in the reactant to start with, the lower the activation energy needed to reach this transition state. An approximate order of σ -bonding strength for some common ligands is as follows: $\text{H}^- > \text{PR}_3 > \text{SCN}^- > \text{I}^-$, CH_3^- , CO , $\text{CN}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 > \text{OH}^-$. There are some similarities between this ranking and the overall experimental *trans* effect order. However, this order does not account for the experimentally observed fact that CO and CN^- have a very large *trans* effect. Thus, the *trans* effect arising from weakening of a bond in the reactant complex (sometimes called the *trans* influence or the thermodynamic *trans* effect⁹⁰) is only part of the explanation.

The fact that CO and CN^- have such a large *trans* effect is believed to be due to their ability to act as π -acceptor ligands (see Sections 8.4, 8.5, and 8.8). In the five-coordinate intermediate

⁹⁰ The “thermodynamic *trans* effect,” while frequently invoked, is an unfortunate piece of terminology in that it may give the (incorrect) impression that there is no kinetic consequence to it. This is not so: raising the reactant energy while leaving the transition state energy roughly the same will certainly lower the activation energy, increasing reaction rate (a kinetic phenomenon).

(and, again, the transition state leading to it), there is additional electron density near the metal due to donation from the entering ligand Y. In the intermediate, the ligands T, X, and Y all occupy equatorial positions in which substantial π -bonding is possible (this is borne out by MO calculations). If T is a good π -acceptor, the increase in electron density is more delocalized, leading to a more stable intermediate, a lower-energy transition state leading to that intermediate, a lower activation energy, and a faster reaction rate.

So far, we have not considered the effect on reaction rate of the ligands *cis* to that being replaced. It turns out that, while the *cis* ligands do have some effect, that effect is drastically smaller than the *trans* effect. If the ligand(s) *cis* to that being replaced are varied, the rate constants generally vary by no more than a factor of 3 or so (compare to hundredfold differences in rate constants due to the *trans* effect). What *cis* effect there is appears to be largely steric, rather than electronic, with larger *cis* ligands leading to slower reactions. This can be rationalized by realizing that, in the trigonal-bipyramidal intermediate, the *cis* ligands lie in axial positions, each of which has an angle of about 90° with the three ligands T, X, and Y. Thus, large *cis* ligands give rise to energetically unfavorable steric crowding in the transition state.

11.11. Nucleophilicity and Nucleofugacity of Ligands

So far, in discussing the rates of ligand substitution on square-planar complexes, we have primarily considered the effects of ancillary ligands, especially that ligand *trans* to the ligand being replaced. To draw an analogy with organic chemistry, this is akin to discussing the relative tendencies of methyl, primary, secondary, and tertiary alkyl halides to undergo S_N1 or S_N2 reactions, without considering the nucleophile or leaving group. In organic chemistry, of course, the strength of the nucleophile and the readiness with which a leaving group departs are of tremendous importance for the rates of nucleophilic substitution reactions. We will see that the identities of the entering ligand (nucleophile) and leaving ligand (leaving group) do affect the rates of ligand substitution reactions, as well.

First, we consider the relative abilities (nucleofugacity⁹¹) of different ligands to leave the Pt center. Studies of this phenomenon can be difficult due to the fact that the identity of the *trans* ligand, not the ligand to be replaced, can often determine which ligand is replaced. To surmount this, studies were conducted on complexes of type Pt(dien)X⁺, where X⁺ is the ligand to be displaced and dien⁹² is shorthand for diethylenetriamine (H₂NCH₂CH₂NHCH₂CH₂NH₂), a tridentate ligand that binds to a metal such as Pt at three sites. Because dien is a chelating ligand, namely one that bonds a metal through more than one atom, it is unlikely to be replaced in a ligand substitution reaction (we will discuss this feature of chelating ligands later on). Thus, X⁺ is generally the only ligand replaced in reactions such as that shown in Figure 11.8 below.

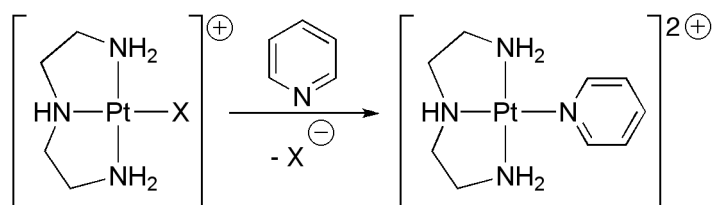


Figure 11.8. Ligand substitution by pyridine on a Pt(dien)X⁺ complex.

The reaction rate is strongly dependent on the identity of X⁺, spanning over three orders of magnitude. For instance, the displacement of Cl⁺ by py proceeds about 1750 times as fast as replacement of CN⁺. In general, the following order of nucleofugacity is observed: NO₃⁺ > H₂O > Cl⁺ > Br⁺ > I⁺ > N₃⁺ > SCN⁺ > NO₂⁺ > CN⁺. This is rather different from the order of nucleofugacity observed in organic nucleophilic substitution reactions. For example, in organic chemistry, I⁺ > Br⁺ > Cl⁺, whereas the opposite is true here. One way to understand this is to realize that, in both S_N1 and S_N2 reactions on carbon, the nucleofuge leaves in the rate-determining step. In contrast, in the A mechanism generally proposed for ligand substitution on Pt(II) complexes, the rate-determining step is generally believed to be

⁹¹ From Latin *nucleus* + *fugax*, “fleeing.” A good nucleophile (“nucleus-lover”) readily forms a new bond to the central atom, while a good nucleofuge (“nucleus-fleeer”) readily leaves. “Nucleofuge” is a good \$5 way of saying “leaving group.”

⁹² Please be sure not to confuse the abbreviation “dien” with a diene, that is, an organic compound containing two carbon-carbon double bonds.

addition of the entering ligand, rather than the loss of the departing ligand. While the departing ligand does not leave in this step, the bond between X and Pt is weakened in the pentacoordinate intermediate (and its corresponding transition state) compared to the reactant. This weakening is more energetically unfavorable for ligands that bind Pt strongly (either as good σ -donors or good π -acceptors), which raises the activation energy and lowers the rate constant. Thus, ligands with a stronger *trans* effect tend to be poorer nucleofuges.

To consider the effect of the entering ligand on the rate of ligand substitution, we must consider both steric and electronic effects. Because the addition of this ligand is the rate-determining step, we expect that more sterically hindered ligands will add more slowly than electronically similar, but smaller, ligands. Consider reactions of the type shown in Figure 11.9 below, where L is an amine (either an aliphatic amine or an aromatic amine like pyridine).

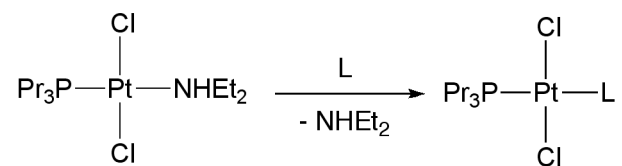


Figure 11.9. Ligand substitution by a variety of entering ligands.

The reaction proceeds much more slowly when L is a more highly substituted amine, or when it bears bulkier substituents. In terms of sterics, this is akin to the observation in organic chemistry that bulky nucleophiles react more slowly in $\text{S}_{\text{N}}2$ processes.

The effect of the entering ligand's electronic properties is rather similar to the *trans* effect order, though not exactly the same. In decreasing order of reactivity, we have the following: $\text{PR}_3 > \text{I}^-$, SCN^- , $\text{N}_3^- > \text{NO}_2^- > \text{Br}^- > \text{py} > \text{NH}_3$, $\text{Cl}^- > \text{H}_2\text{O} > \text{OH}^-$. The fact that this list is similar, though not identical, to the order of decreasing *trans* effect is perhaps not so surprising, given that, in the five-coordinate, trigonal bipyramidal transition state, the *trans* ligand, departing ligand (nucleofuge) and entering ligand (nucleophile) all occupy an equatorial position, and will engage in similar bonding interactions with the central Pt.

In organic chemistry, the nucleophilicity and nucleofugacity of species is often related to their Brønsted basicity, that is, their basicity towards H^+ . However, we can see from the list of nucleophile strength above that more Brønsted-basic ligands do not, in general, add to Pt centers faster. For instance, phosphines PR_3 are quite weak Brønsted bases, but add to Pt centers quickly, while the strong Brønsted base OH^- adds slowly. The hard and soft acid and base (HSAB) theory discussed in Section 5.9 helps explain patterns like this. The hydrogen ion H^+ is one of the hardest Lewis acids around (it does not have a high charge, but it is very small), so it readily reacts with hard bases such as OH^- . In contrast, Pt(II) compounds are soft Lewis acids: Pt atoms are large, and +2 is not a terribly high oxidation state, so Pt(II) more readily forms bonds with soft Lewis bases like PR_3 and I^- . Thus, those species that are better nucleophiles for associative substitution on Pt are thus generally soft bases.⁹³

We can put the trends in entering ligand strength in a more quantitative form with an LFER. Consider the following general reaction of the complex *trans*-Pt(py)₂Cl₂, conducted in methanol (the charges assume that Y is neutral: if Y is a monoanion, the product Pt complex will be neutral, not a cation), shown in Figure 11.10 below.

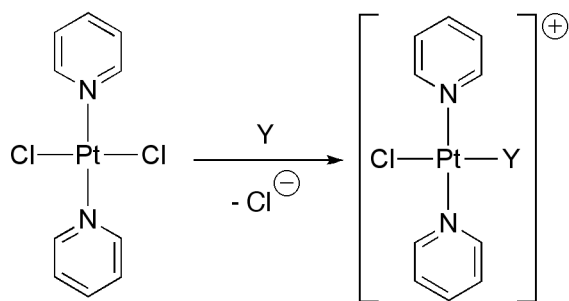


Figure 11.10. Ligand substitution of *trans*-Pt(py)₂Cl₂.

⁹³ We must be careful with this argument. Pearson derived his HSAB theory to rationalize *thermodynamic* trends, as did others, such as Drago and Wayland, who extended the HSAB ideas in quantitative form. We are here using HSAB theory to rationalize *kinetic* trends (rates of substitution reactions) on the grounds that, according to the Hammond postulate, stabilization of the trigonal bipyramidal reaction intermediate will also stabilize the transition state leading to it.

If the entering ligand Y is just the solvent methanol itself, the reaction is a solvolysis with rate constant k_S . Methanol is not a particularly strongly nucleophilic entering ligand, so the nucleophilic reactivity constant n_{Pt} for each ligand Y is determined by comparing the rate constant k_Y with the solvolysis rate constant k_S :

$$n_{Pt} = \log_{10} \left(\frac{k_Y}{k_S} \right)$$

When ligand substitution reactions of many other Pt(II) complexes are conducted in solvents other than methanol, a plot of $\log_{10} k_Y$ vs. n_{Pt} for that entering ligand Y is linear with a slope other than 1, or $\log_{10} k_Y = sn_{Pt} + \log_{10} k_S$. The slope s is called the nucleophilic discrimination factor, and it tells, for a given Pt(II) complex in a given solvent, how sensitive the rate of ligand substitution is to the entering ligand. If $s > 1$, then the substitution is more sensitive to the identity of Y than *trans*-Pt(py)₂Cl₂ in methanol, and if $s < 1$, it is less sensitive. For instance, $s = 1.43$ for *trans*-Pt(PEt₃)₂Cl₂, but only 0.44 for Pt(dien)(H₂O)²⁺.

We have seen that most ligand substitution reactions of square-planar Pt(II) complexes proceed *via* an associative (*A*) mechanism. However, there are a comparatively small number of cases in which the reaction appears to proceed *via* a dissociative (*D*) mechanism instead. The substitution reaction *cis*-PtMe₂S₂ + 2 S' → *cis*-PtMe₂S'₂ + 2 S, where S and S' are sulfur-containing ligands (Me₂S or Me₂SO) is believed to follow a *D* mechanism. The rate law is consistent with the *D* mechanism, being first-order at high [S'], the rate constant is independent of the identity of the entering ligand S', and the entropy of activation $\Delta S^\ddagger$ is large and positive. The ability of this reaction to proceed *via* a *D* mechanism has been proposed to be due to the strong σ -donor nature of the methyl ligands, weakening the bonds between Pt and the S ligands *trans* to them. This can reasonably be viewed as a case in which the thermodynamic *trans* effect (or *trans* influence) is strong enough that it promotes actual dissociation, rather than merely weakening of the bond to the departing ligand in the transition state for an *A* or *I_a* mechanism. In general, most Pt(II) complexes undergo substitution by the *A* (or possibly *I_a*) mechanism, but the possibility of a *D* mechanism should not be discounted.

11.12. Ligand Substitution on Square-Planar Complexes of Other Metals

As we discussed earlier in the course, combinations of metal and oxidation state leading to a d electron count of d^8 are often found in square-planar, 16-electron complexes. Square-planar complexes of Rh(I), Ir(I), Ni(II), Pd(II), and Au(III) are all well known. While the most thorough investigations of ligand substitution mechanisms have been performed on Pt(II) complexes, it is worthwhile to compare these trends with what has been observed for other d^8 complexes.

Perhaps the most closely analogous metal center is Pd(II). Ligand substitution (and other reactions) at Pd(II) centers are very important in catalysis, as an enormous number of organic reactions can be (homogeneously) catalyzed by soluble Pd(II) complexes; we will return to this topic later in the course. Square-planar Pd(II) complexes appear to undergo ligand substitution by a broadly similar mechanism to Pt(II) complexes: an *A* mechanism involving direct attack of the entering ligand, coincident with initial replacement of the departing ligand with solvent, followed by replacement of solvent by the entering ligand. The solvent-dependent pathway, which leads to the apparently first-order term in the rate law $r = k[\text{L}_3\text{PdX}] + k'[\text{L}_3\text{PdX}][\text{Y}]$, appears to be relatively more important in substitution on Pd(II) complexes. In general, Pd(II) complexes undergo ligand substitution *much* faster than their Pt(II) analogs, up to 10^5 times as fast, but the qualitative dependences of the rate constant on entering ligand, departing ligand, and ligand *trans* to the departing ligand are similar to the Pt(II) case.

The slower rates of substitution on Pt(II) complexes as opposed to Pd(II) complexes is generally attributed to stronger bonds between Pt and the ligands, making the weakening of some Pt-ligand bonds in the transition state less favorable. This comparative sluggishness is one reason why Pd-catalyzed organic reactions are much less common than Pt-catalyzed ones (though there are some organic reactions known that can be efficiently catalyzed by Pt). Pd complexes with *cis* and *trans* isomers tend to undergo isomerization quickly; this can be catalyzed by a free ligand such as a phosphine or even the solvent, if the solvent is capable of coordination. Thus, a pure sample of either the *cis* or *trans* isomer will usually reach a thermodynamic equilibrium with the other isomer quickly. The comparative kinetic stability

of isomers of Pt(II) complexes is very important in medicine: *cis*-Pt(NH₃)₂Cl₂, commonly known as cisplatin, is a very effective drug in the treatment of many cancers, but its *trans* isomer is both ineffective as an anticancer drug and toxic to the patient.

We will have more to say about Rh(I) and Ir(I) complexes later in the course, when we discuss catalytic hydrogenation and C–H activation reactions. It is worth noting that while Au³⁺ is isoelectronic to Pt²⁺, and there do exist square-planar complexes of Au(III), their reactivity towards ligand substitution is often difficult to study kinetically, because Au(III) species tend to be highly oxidizing: thus ligand substitution reactions must compete with reactions in which Au(III) is reduced to Au(I) or Au(0).

11.13. Werner-Type complexes

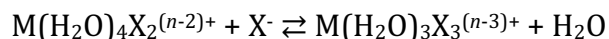
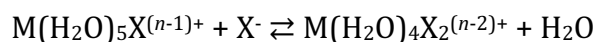
The Swiss chemist Alfred Werner (1866-1919) is widely known as the father of modern coordination chemistry. The Nobel Prize in Chemistry awarded to him in 1913 was the only Nobel Prize awarded for work in inorganic chemistry until 1973, when Ernst Otto Fischer (1918-2007) and Geoffrey Wilkinson (1921-1996) were awarded their prize for work on organometallic compounds such as ferrocene. Most of the octahedral transition metal complexes that Werner studied feature ligands that bind the metal through highly electronegative atoms, such as oxygen, nitrogen, and the halogens. In this chapter, we will consider ligand substitution reactions on such “classical” or “Werner-type” complexes. In chapter 13, we will discuss complexes in which the metal is bound to less electronegative atoms such as carbon, hydrogen, and phosphorus.

11.14. Ligand Substitution on Octahedral Complexes

Much modern inorganic chemistry is conducted in nonaqueous solvents, often with traces of moisture rigorously excluded. The early work of Werner and others, however, was predominantly focused on reactions occurring in aqueous solution, since many transition metal salts are conveniently quite soluble in water. In general chemistry courses, a metal ion dissolved in water is often written simply as Mⁿ⁺ (*aq*), *e.g.* Cr³⁺ (*aq*), Co²⁺ (*aq*). This notation, while it is a convenient shorthand, can be misleading. A transition metal cation in water is

not a more or less “naked” ion only weakly solvated: instead, a certain number of water molecules (usually six) are covalently bound to the metal *via* their oxygen atoms, leading to the formation of molecular orbitals as we discussed when we reviewed ligand field theory. Thus M^{n+} (aq) really refers to ions of the form $M(H_2O)_6^{n+}$, which is itself solvated by noncovalent interactions with other water molecules outside its primary coordination sphere. Such complex ions, which are homoleptic with water as the only ligand, are known as aqua complexes.⁹⁴

We saw in our discussion of ligand field theory and the spectrochemical series that water is a fairly weak-field ligand. It is frequently replaced in ligand substitution reactions by ligands which bind a metal more strongly. Replacement of coordinated H_2O by ammonia has frequently been observed, as well as replacement by anionic ligands X^- , known as anation. The sequential replacements of water on an aqua ion with an anion X^- may be represented in the following reactions:



etc.

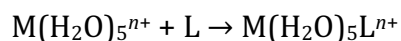
The equilibrium constant for the replacement of the n th water molecule by another ligand is denoted K_n , so the equilibrium constants for the three reactions above are K_1 , K_2 , and K_3 , respectively. (These equilibrium constants are sometimes called formation constants.) Additionally, chemists sometimes discuss cumulative formation constants, denoted by β_m , which are the equilibrium constants for the replacement of m water molecules with m other ligands. Consider the reaction $M(H_2O)_6^{n+} + 3 X^- \rightleftharpoons M(H_2O)_3X_3^{(n-3)+} + 3 H_2O$. The equilibrium constant would be denoted β_3 , and it is equal to $K_1K_2K_3$, the product of the individual formation constants. In general, the m th formation constant is given by

$$\beta_m = \frac{[M(H_2O)_{6-n}X_m^{(n-m)+}]}{[M(H_2O)_6^{n+}][X^-]^m} = \prod_{i=1}^m K_i$$

⁹⁴ Recall from Table 7.1 that water is called “aqua” when it is a ligand.

Regardless of the thermodynamic favorability of a ligand substitution reaction, one can characterize the kinetic stability of a TM complex by its half-life under conditions of excess entering ligand. The great mechanistic inorganic chemist Henry Taube (1915-2005, Nobel Prize in Chemistry 1983) studied formally the rates of water exchange between aqua ions $M(H_2O)_6^{n+}$ and isotopically labeled solvent water $H_2^{18}O$ (recall that the vast majority of oxygen atoms in unlabeled water are ^{16}O , not ^{18}O). This reaction, which is represented as $M(H_2O)_6^{n+} + H_2^{18}O \rightleftharpoons M(H_2O)_5(H_2^{18}O)^{n+} + H_2O$, is useful for studying kinetics without thermodynamics, since ^{16}O and ^{18}O , as different isotopes of the same element, have chemically almost identical behavior, so the equilibrium constant for this reaction will be almost exactly 1. Taube defined aqua complexes with $t_{1/2} < 1$ min for water exchange as “labile” and those with $t_{1/2} > 1$ min as “inert.” While this choice of cutoff is, of course, arbitrary, it will be a useful metric for us to use when we discuss the effect of oxidation state and d electron count on ligand substitution rates.

A great many TMs form octahedral complexes that can undergo ligand substitution, and the mechanisms for ligand substitution can vary depending on the TM, oxidation state, entering ligand, departing ligand, and ancillary ligands. Thus, when considering the mechanisms of ligand substitution on octahedral complexes of TMs in general, we should not expect the mechanistic behavior to be as regular as that of square-planar Pt(II) complexes. Some generalizations can be drawn, however, and most ligand substitution reactions of aqua ions are believed to proceed by either a pure dissociative (D) mechanism or an dissociative interchange (I_d) mechanism of the Eigen-Wilkins type, with rapid-equilibrium formation of an encounter complex. The D mechanism would be as follows:

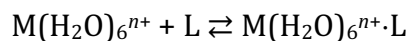


with the first step having forward and reverse rate constants k_1 and k_{-1} , and the second step having forward rate constant k_2 . As we have seen, the expected rate law will be

$$r = \frac{k_1 k_2 [M(H_2O)_6^{n+}][L]}{k_{-1}[H_2O] + k_2[L]}$$

where $[H_2O]$ will be essentially constant over the course of the reaction. (For a dilute aqueous solution at or near room temperature, $[H_2O] \approx 55.5$ M.)

The Eigen-Wilkins I_d mechanism would be as follows:



with the first step in rapid equilibrium with equilibrium constant K_1 and the second step having forward rate constant k_2 . As previously discussed, the expected rate law will be

$$r = \frac{K_1 k_2 [M(H_2O)_6^{n+}] [L]}{K_1 [L] + 1}$$

Many experimental observations support a D or Eigen-Wilkins I_d mechanisms. The rates of substitution on aqua ions usually depend only weakly on the identity of the incoming ligand L and its concentration; from the rate laws, we see that both of these mechanisms reduce to a first-order expression with no $[L]$ dependence when L is present in large excess. Ligand substitution reactions are generally slower when the metal's oxidation state is higher, consistent with rate-determining dissociation: as metal-ligand bonding in Werner-type complexes is highly polar-covalent, negatively charged or dipolar ligands would be expected to leave more slowly from more highly charged metal centers. Complexes with larger (more sterically bulky) ancillary ligands undergo substitution faster, consistent with a relief of steric crowding upon the rate-determining dissociation step. Eyring analysis of these reactions generally give $\Delta S^\ddagger$ values between -10 and $+10$ $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is generally most suggestive of an I mechanism rather than either D or A .

If the ligand to be replaced is *not* water, the rate of ligand substitution increases with the thermodynamic favorability of the substitution. Consider the following reaction of a series of Co(III) complexes (often termed an aquation, as a ligand other than water is replaced with water): $\text{Co}(\text{NH}_3)_5\text{X}^{2+} + \text{H}_2\text{O} \rightarrow \text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+} + \text{X}^-$. An LFER can readily be constructed for these reactions, with a plot of $\ln k$ vs. $\ln K$ being approximately linear with a positive slope. Thus, the more thermodynamically favorable the reaction is (larger K), the faster its rate (larger k). Since the only variable changed between reactions is the identity of the departing ligand X^- (*e.g.* F^- vs. NO_3^-), the observation of such an LFER suggests rate-determining dissociation, with less strongly coordinating ligands X^- leaving more quickly. In general, reaction rates as a function of departing ligand decrease in the following order: $\text{NO}_3^- > \text{I}^- > \text{Br}^-, \text{H}_2\text{O} > \text{Cl}^-, \text{SO}_4^{2-} > \text{CH}_3\text{COO}^- > \text{N}_3^-, \text{NCS}^-, \text{NH}_3 > \text{NO}_2^-, \text{OH}^-$.

The fundamental difference between a *D* or an Eigen-Wilkins *I_d* mechanism is the nature of the intermediate: a five-coordinate intermediate in a *D* mechanism vs. an Eigen-Wilkins encounter complex. Direct observation of either intermediate (*e.g.* by spectroscopy of a reaction mixture) would enable a fairly definitive choice between the possible mechanisms, but an intermediate that genuinely occurs may not be directly detectable if it is too short-lived, present at too low a concentration, or both. There have been experimental observations of Eigen-Wilkins encounter complexes in octahedral ligand substitution reactions, and fewer observations of five-coordinate intermediates, suggesting that *I_d* mechanisms are more common than *D*, though one cannot simply look at a net reaction equation and declare with confidence that it will be *I_d*, rather than *D*.

11.15. Volumes of Activation

One experimentally determined parameter that has been proposed to distinguish *D* vs. *I* vs. *A* mechanisms is the volume of activation $\Delta V^\ddagger$, which is the volume of the transition state minus the volume of the reactants. It is determined by measuring the effect of pressure *P* on the rate constant while holding temperature constant, and calculated from the equation

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT}$$

If $\Delta V^\ddagger$ is (approximately) independent of pressure over the pressure range investigated, then a plot of $\ln k$ vs. *P* with, *T* constant, should be linear with slope $-\frac{\Delta V^\ddagger}{RT}$. It is often argued that a *D* or *I_d* mechanism will have $\Delta V^\ddagger > 0$ (as dissociation will increase the transition state volume), while an *A* or *I_a* mechanism will have $\Delta V^\ddagger < 0$ (as association will decrease the transition state volume). Unfortunately, $\Delta V^\ddagger$ values can be ambiguous for much the same reason that $\Delta S^\ddagger$ values can be, since the depiction of dissociation or association of species in a stoichiometric mechanism on paper does not indicate whether the reactants or transition state will be more strongly solvated (a phenomenon known as solvent electrostriction). Thus, interpretation of $\Delta V^\ddagger$ values is most reliable when those values are large in magnitude. Water exchange of $\text{Ti}(\text{H}_2\text{O})_6^{2+}$ with isotopically labeled H_2^{17}O was found to have an unusually negative $\Delta V^\ddagger = -12.4 \text{ cm}^3\cdot\text{mol}^{-1}$, which may indicate an *A* mechanism, rare for octahedral complexes.

11.16. The Kinetic Chelate Effect

In Section 7.4, we saw that ligands such as ethylenediamine (en, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) that can bind a metal through more than one Lewis-basic atom, are known as chelating ligands. Thermodynamically, we saw that the replacement of monodentate ligands by an electronically similar chelating ligand is favored due to entropic reasons.

There exists a kinetic chelate effect, as well as a thermodynamic one. The replacement of a chelating ligand with monodentate ligands tends to be significantly slower than replacement of a pair of electronically similar monodentate ligands, even if the replacement is overall thermodynamically favorable (due to enthalpically stronger bonding by the entering ligands than by the departing chelating ligand). Consider, in Figure 11.11 below, a general scheme for the aquation of an en complex by a dissociative pathway (with an NH_2 group written as N for simplicity), showing replacement of one nitrogen by water.

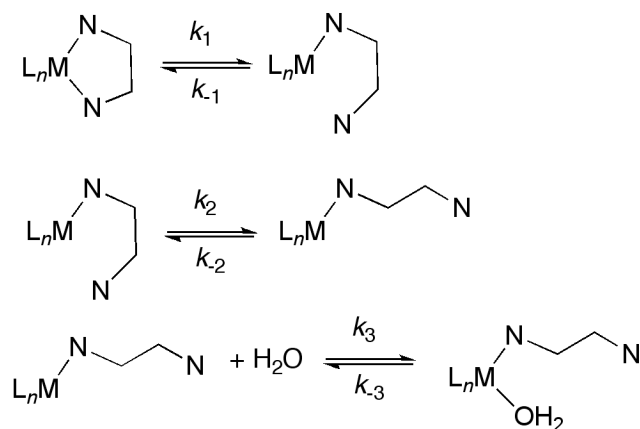


Figure 11.11. Replacement of one “arm” of a chelating ethylenediamine ligand by water.

The first step, dissociation of one Lewis-basic N atom, is more readily reversible than the dissociation of a monodentate ligand. This can be understood as follows: when a monodentate ligand X dissociates from L_nMX , the rate of the reverse reaction is proportional to the concentration of X in solution: $r_{-1} = k_{-1}[\text{L}_n\text{M}][\text{X}]$. But in the above case, the “effective concentration” of the departing ligand near the metal is quite high, since it is attached to

another Lewis basic atom already coordinated to the metal. Additionally, the second step, a conformational change in the en ligand when it is bound by only one N, is necessary for the addition of water for steric reasons: if the conformational change did not occur, the entering water ligand would clash sterically with the N group that has dissociated, but is still near the metal. This required conformational change increases the $\Delta H^\ddagger$ value of the reaction. Depending on the chelating ligand and the comparable monodentate ligand, the kinetic chelate effect can slow a ligand substitution reaction anywhere from a factor of about 10 to a factor of about 10^5 .

11.17. Ligand Field Stabilization Energy (LFSE) and Ligand Substitution Rates

An important quantity in transition metal chemistry is the ligand field stabilization energy, or LFSE (sometimes known as the crystal field stabilization energy of CFSE). The LFSE is the total energy of the d -type electrons in the complex, relative to the barycenter defined by crystal field theory (*cf.* Section 8.1). That is, it is the difference between the d electron energy of a complex *vs.* the d electron energy of the free ion or atom. In an O_h complex, each electron in a t_{2g} orbital contributes $-\frac{2}{5}\Delta_o$ to the LFSE, and each electron in an e_g orbital contributes $+\frac{3}{5}\Delta_o$. Thus, for an O_h complex with d electron configuration $(t_{2g})^p(e_g)^q$, we have

$$\text{LFSE} = \left(-\frac{2}{5}p + \frac{3}{5}q\right)\Delta_o$$

In a T_d complex, each electron in an e orbital contributes $-\frac{3}{5}\Delta_T$, and each electron in a t_2 orbital contributes $+\frac{2}{5}\Delta_T$. Thus, for a T_d complex with d electron configuration $(e)^x(t_2)^y$, we have

$$\text{LFSE} = \left(-\frac{3}{5}x + \frac{2}{5}y\right)\Delta_T$$

By convention, LFSE is not considered to take into account pairing energy terms Π compared to the free ion or atom with fivefold degenerate d orbitals. You need only consider orbital energies when calculating LFSE.

You might (quite reasonably) wonder why LFSE is a relevant quantity: after all, the value of Δ_o (or Δ_T) varies from complex to complex, often quite significantly. Furthermore, LFSE

values are defined relative to the barycenter of crystal field theory, which is not really a physically meaningful quantity in the more accurate, MO-based ligand field theory. It turns out, however, that LFSE, as imprecise a measure as it is, helps us to both rationalize and predict relative rates of ligand substitution based on the d electron configuration of the TM complex undergoing substitution.

How is LFSE relevant to ligand substitution? First, we note that while an increase in metal oxidation state is often associated with a slower rate of dissociative (D or I_d) ligand substitution, this is not the only factor at play. Consider the series of aqua ions $M(H_2O)_6^{2+}$, where $M = Mn, Fe, Co, \text{ or } Ni$: the (first-order) rate constant k for water exchange decreases from $2.1 \times 10^7 \text{ s}^{-1}$ for Mn to $3.2 \times 10^4 \text{ s}^{-1}$ for Ni. This can be understood in terms of d electron count. Mn(II), Fe(II), Co(II), and Ni(II) are d^5 , d^6 , d^7 , and d^8 , respectively, and since water is a weak-field (π donor) ligand, each of these aqua complexes is high-spin. $Mn(H_2O)_6^{2+}$ has the d -electron configuration $(t_{2g})^3(e_g)^2$, which corresponds to zero LFSE. Going from d^5 to d^8 involves placing more electrons in the lower-energy t_{2g} MOs, giving greater (more negative) LFSE values for the Fe, Co, and Ni complexes: $-\frac{2}{5}\Delta_o$, $-\frac{4}{5}\Delta_o$, and $-\frac{6}{5}\Delta_o$, respectively.

Why will a greater (more negative) LFSE value correspond to a slower reaction? In a dissociative process, an octahedral metal complex goes to a square-pyramidal, five-coordinate intermediate. One can use LFT or CFT to calculate energy levels and LFSE values for square-pyramidal complexes, but for our purposes, we will simply note that d electrons in a square-pyramidal complex generally experience less stabilization than those in an octahedral complex. Thus, the loss of some of the favorable LFSE in the rate-determining dissociation step corresponds to an increase in activation energy for the reaction, a phenomenon often known as ligand field activation energy or LFAE. (The term crystal field activation energy or CFAE is also seen, and it means the same thing, just based on a different level of theory.)

We can use LFAE arguments to explain the fact that certain d electron counts are often associated with inert complexes (by Taube's definition of inertness). Both d^3 complexes, such

as those of Cr(III), and low-spin d^6 complexes, such as some Co(III) species, have all their d electrons in the lower-energy t_{2g} MOs, so they have large negative LFSE values, and tend to be inert. It is no surprise that much of Werner's seminal work on coordination chemistry focused on Cr(III) and low-spin Co(III) complexes; their inertness allowed for more ready synthesis and isolation than that which would be possible for more labile species. On the other hand, high-spin d^5 complexes like $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ are exceptionally labile, as they have all five d -type MOs (both t_{2g} and e_g) equally occupied, and zero LFSE. While high-spin d^6 , high-spin d^7 , and d^8 complexes like $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, $\text{Co}(\text{H}_2\text{O})_6^{2+}$, and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ have electrons in both the t_{2g} and e_g MOs, the fact that they have *more* electrons in the t_{2g} than in the e_g MOs make them less labile than $\text{Mn}(\text{H}_2\text{O})_6^{2+}$.

It is often observed that lability of transition metal complexes decreases as one moves down a column of the periodic table. This is often true for two reasons. One is that Δ_o values are larger for elements of the second (Y-Cd) and third (Lu-Hg) transition series than for the first (Sc-Zn). Thus, if a first-row complex and a second- or third-row complex have the same LFSE in units of Δ_o , the LFSE in joules or calories will be greater (more negative) for the second- or third-row complex. The other reason is that these greater Δ_o values can cause a given d electron count and set of ligands to yield high-spin complexes of a first-row transition metal, but low-spin complexes of a second- or third-row metal. For instance, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is high-spin, with electron configuration $(t_{2g})^3(e_g)^2$, zero LFSE, and a water-exchange rate constant of 160 s^{-1} . In contrast, $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ is low-spin, with electron configuration $(t_{2g})^5(e_g)^0$, a LFSE of $-2\Delta_o$, and a water-exchange rate constant of $3.5 \times 10^{-6} \text{ s}^{-1}$, a decrease by a factor of almost 10^8 .

The Jahn-Teller effect is another result of d electron configuration with significant effects on complex lability. Both $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ have very fast rate constants for water exchange: $7 \times 10^9 \text{ s}^{-1}$ and $8 \times 10^9 \text{ s}^{-1}$, respectively. This is because both high-spin d^4 and d^9 octahedral complexes are subject to a strong Jahn-Teller distortion due to unequal occupation of their high-energy (strongly antibonding) e_g MOs. This distortion most often takes the form of elongation of a pair of mutually *trans* metal–oxygen bonds, thus weakening the bonding of two water ligands and increasing their rate of dissociation.

11.18. Brønsted Acid and Base Catalysis in Ligand Substitution

Many common ligands in TM chemistry have more than one lone pair, enabling them to be protonated while still attached to the metal. Often, protonation of the ligand makes the ligand a better leaving group, increasing the rate of dissociative substitution. Thus, many ligand substitution reactions are acid-catalyzed, proceeding more quickly at lower pH. The acid-catalyzed aquation of $\text{Cr}(\text{H}_2\text{O})_5\text{F}^{2+}$ is proposed to occur by the following mechanism, as shown in Figure 11.12 below.

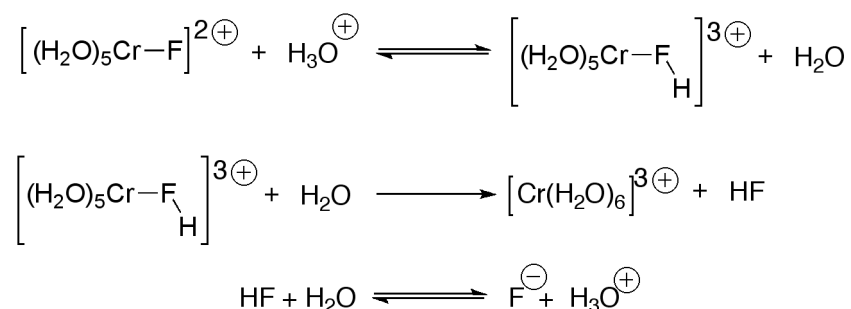
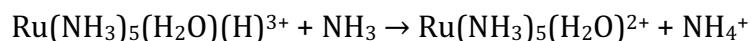
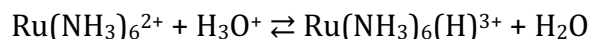


Figure 11.12. Acid-catalyzed aquation of $\text{Cr}(\text{H}_2\text{O})_5\text{F}^{2+}$.

Acid catalysis occurs because HF is a better leaving group than F^- . Similar acid catalysis is observed for aquation of complexes of N_3^- and CN^- , both of which are weakly Brønsted-basic ligands with more than one lone pair. This is very much analogous to the fact that $\text{S}_{\text{N}}1$ or $\text{E}1$ reactions of tertiary alcohols will not proceed at any significant rate under neutral conditions, since OH^- is a very poor leaving group, but they will proceed under acidic conditions, in which the OH group is first protonated and then leaves as H_2O , which is an excellent leaving group.

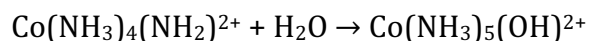
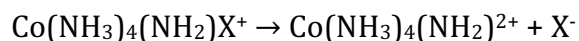
Most ammine complexes (complexes of NH_3) do *not* undergo aquation faster under acidic conditions. This makes sense in light of the fact that NH_3 has a single lone pair, donated to the metal in a σ fashion; while coordinated, it cannot be protonated. However, the aquation of $\text{Ru}(\text{NH}_3)_6^{2+}$, with net reaction $\text{Ru}(\text{NH}_3)_6^{2+} + \text{H}_2\text{O} \rightarrow \text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+} + \text{NH}_3$, is found to be acid-promoted, with rate law $r = k[\text{Ru}(\text{NH}_3)_6^{2+}][\text{H}_3\text{O}^+]$. This reaction is proposed to proceed by protonation not of a ligand, but of the Ru, which, as a low-spin d^6 species, has roughly

nonbonding t_{2g} electrons that can react like lone pairs on a main-group element. The following mechanism accounts for the rate law:



In this mechanism, the intermediate $\text{Ru}(\text{NH}_3)_6(\text{H})^{3+}$ undergoes faster ligand substitution than $\text{Ru}(\text{NH}_3)_6^{2+}$. Note that the complexes in which Ru is protonated are seven-coordinate intermediates, which we have previously stated are rare. However, hydride (formally H^- for the assignment of oxidation states) is a very small ligand, and Ru, as a second-row transition metal, is larger than first-row metals and can thus accommodate a higher coordination number. Note that this reaction is correctly termed acid-promoted, rather than acid-catalyzed, since the H_3O^+ is not regenerated in the reaction mechanism, as a catalyst would be.

Some ligand substitution reactions have mechanisms in which ancillary ligands are deprotonated by a Brønsted base. The reaction $\text{Co}(\text{NH}_3)_5\text{X}^{2+} + \text{OH}^- \rightarrow \text{Co}(\text{NH}_3)_5(\text{OH})^{2+} + \text{X}^-$ has the rate law $r = k[\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$. This rate law is consistent with an *A* mechanism of ligand substitution, but such a mechanism may seem unlikely, given the unlikelihood of forming a seven-coordinate intermediate with a first-row transition metal. Instead, the following mechanism is proposed, in which one of the ammine ligands is temporarily deprotonated to form an amido (NH_2^-) ligand:



It is believed that X^- leaves more rapidly from $\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{X}^+$ than from $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ because the five-coordinate intermediate $\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+}$ (and the transition state leading to it) is stabilized by π -donation from the amido ligand, which can be sketched in shorthand as $[\text{H}_2\text{N}=\text{Co}(\text{NH}_3)_4]^{2+}$. In this square-pyramidal intermediate, the amido ligand occupies the axial (rather than an equatorial) position.

Chapter 12: Fundamentals of Organometallic Chemistry

12.1. Coordination chemistry and Organometallic Chemistry

The following three chapters will focus on organometallic chemistry, a field of study that lies on the border between inorganic and organic chemistry. Organometallic chemistry is a subfield of coordination chemistry, the study of the complexes of metals with ligands. Much of the seminal work on transition-metal coordination chemistry was done by scientists like Alfred Werner, who studied isomerism in octahedral complexes, and Ilya Ilich Chernyaev, who studied the ligand substitution reactions of square-planar Pt(II) complexes. Much of the “classical” coordination chemistry of Werner’s and Chernyaev’s day focused on complexes of metal ions with highly electronegative ligands, such as Cl^- , NH_3 , H_2O , and OH^- . Although the metal-ligand bonds in these complexes are covalent, they are polar covalent, with the electron density polarized toward the Cl, N, or O atom. We have already discussed aspects of this chemistry in chapters 7-11.

In contrast to “classical” coordination complexes, an organometallic compound is one containing at least one metal-carbon covalent bond. That is, an organometallic complex has at least one ligand bound to the metal through carbon. So, for instance, titanium(IV) isopropoxide, $\text{Ti}(\text{OiPr})_4$, is both an organic compound (because isopropoxide is an organic ligand) and a coordination compound, but it is *not* an organometallic compound, since isopropoxide binds to titanium through its oxygen atom, not a carbon atom. True organometallic complexes include, for example, complexes of CO, cyanide, alkyl, and aryl groups.

Much of the early work on organometallic chemistry was done with main-group organometallic compounds. If one considers arsenic to be a metal as opposed to a semimetal or metalloid, then the first organometallic compound made in the laboratory was cacodyl oxide, $\text{Me}_2\text{As-O-AsMe}_2$, prepared in 1757 by Louis-Claude Cadet de Gassicourt (1731-1799). Its common name is derived from the Greek word $\kappa\alpha\kappa\acute{\omega}\delta\eta\varsigma$, “foul-smelling,” which should give you some idea of how pleasant it is to work with. The organoarsenic drug Salvarsan, an

equilibrium mixture of the trimer $\{\text{As}(\text{3-NH}_2\text{-4-OH-C}_6\text{H}_3)\}_3$ and the pentamer $\{\text{As}(\text{3-NH}_2\text{-4-OH-C}_6\text{H}_3)\}_5$, was the first effective, relatively safe treatment for syphilis. Paul Ehrlich (1854-1915), who developed it, won the Nobel Prize in Physiology or Medicine for his work in 1908.

Moving on to true metals, early main-group organometallics include the alkyllithium compounds RLi and the alkylmagnesium halides RMgX (commonly known as Grignard reagents), which you have learned about in your organic chemistry courses. These compounds behave, essentially, as highly nucleophilic stabilized carbanions, attacking electrophiles such as carbonyl carbons to make, for example, tertiary alcohols from ketones and secondary alcohols from aldehydes. These carbon atoms are also nucleophilic toward H^+ (that is, they are strong bases), so they must be used in rigorously dry solvents, or else they will react with moisture to yield the hydrocarbon and oxides or hydroxides of the metal. The Nobel committee recognized the importance of this work, awarding the Nobel Prize in Chemistry in 1912 to Victor Grignard (1871-1935), for the discovery of his eponymous reagents, and in 1963 to Karl Ziegler (1898-1973), an early investigator of organolithium compounds, and Giulio Natta (1903-1979), for their related work on the use of organoaluminium compounds in polymer synthesis.

The carbanion-like nature of organolithium and Grignard reagents is not surprising when you compare the Allen electronegativities of carbon (2.554) and Li and Mg (0.912 and 1.293, respectively). While there is some covalent character to C–Li and C–Mg bonds, these bonds are still *strongly* polar. In this course, we will primarily focus on organometallic compounds of transition metals, rather than main-group elements. The electronegativities of TMs span quite a significant range, and for the more electronegative TMs, a metal-carbon bond is *much* less polar than an Li–C or Mg–C bond. TMs toward the left of the *d*-block (“early metals”) are more electropositive (Ti and Nb, for instance, have electronegativities of 1.38 and 1.41, respectively), but those toward the right of the *d*-block (“late metals”) are more electronegative (sample electronegativities include Co: 1.84, Ni: 1.88, Cu: 1.85, Rh: 1.56, Pd: 1.58, Ag: 1.87, Ir: 1.68, Pt: 1.72, Au: 1.92). Early-metal organometallic compounds are often moisture-sensitive, similar to organolithium and Grignard reagents, but late metal

organometallics have less polar metal-carbon bonds, and are often moisture-stable. One important example of a water-stable late-metal organometallic compound is vitamin B₁₂, which contains a methyl ligand on Co; it is a rare example of an organotransition metal compound produced by living systems.

There is nothing magic about carbon, but its low electronegativity for a nonmetal, compared with the high electronegativity of elements present as donor atoms in “classical” TM complexes, leads to organometallic complexes having different reactivity than the “classical” complexes. Some of these reactivity patterns are shared by complexes of other ligands with donor atoms of modest electronegativity. Examples of such ligands include H⁻, H₂ itself, and phosphines PR₃ (where R = H or an organic group). Organometallic chemists often study complexes of these ligands, and they are often considered to be honorary organometallic ligands of a sort. Additionally, while N is a quite electronegative donor atom, the bonding in N₂ and NO is quite similar to the bonding in the organometallic ligand CO, so N₂ and NO complexes are also often studied in organometallic chemistry. In addition, many important organometallic complexes contain one or more electronegative ligands such as R₃N, R₂N⁻, RO⁻, or O²⁻ in addition to organic ligands.

12.2. Electron Counting and the 18e Rule

In your general chemistry and organic chemistry courses, you often made use of the octet rule, which states that an atom of a main-group element (other than H or He) in a stable compound will usually have 8 electrons around it, either as covalent bonds or lone pairs. There are certainly exceptions to the octet rule: many short-lived intermediates are electron-deficient (such as carbocations), and even some stable compounds are either electron-deficient, such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), or exceed the octet rule, such as PF₅, SF₆, and various Xe compounds (see the discussion of SF₆ in Section 3.6). In TM chemistry, it is common to find that TM atoms in stable species have 18 valence electrons in their coordination sphere. This 18-electron rule (or 18e rule for short) is not infallible, and in fact it is violated more frequently than the octet rule. Section 8.7 gives a rationale for the 18e rule in terms of bonding theory for some octahedral and tetrahedral complexes. We now

consider how to count the valence electrons around a TM when considering the formula or structure of a complex.

When counting electrons donated from ligands, we first identify what sorts of ligand electrons are used in bonding. Most ligands donate nonbonding electrons to a metal, that is, electrons either in lone pairs or in singly occupied nonbonding (or roughly nonbonding) orbitals. However, sometimes a pair of electrons already involved in a bond in the ligand can themselves interact with AOs of the metal. These electrons can be in π bonds, as shown in the ethene and butadiene examples in Figure 12.1 below, or in a σ bond, as shown in the H_2 example below. These bonding interactions involve a delocalized sharing of electrons between the metal and the carbons in an alkene or diene or the hydrogens in H_2 .

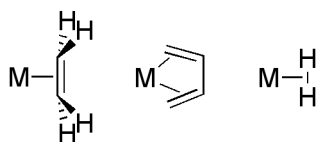


Figure 12.1. Examples of ligands binding TMs using already-bonding electron pairs.

There are two main methods of electron counting: the donor pair method and the neutral ligand method. In the donor pair method, each ligand is considered to donate an even number of electrons to the metal, that is, a whole number of electron pairs. This means that we do not consider any ligands as radicals. To do this, we assign charges to each ligands, the charges that they would have as closed-shell species. Generally, “closed-shell” means that all the main-group atoms in the ligand follow the octet rule. Thus, CO, an amine R_3N , and a phosphine R_3P are all closed-shell when neutral. Each of these molecules has one lone pair, so each is a two-electron (2e for short) ligand. A halogen like Cl needs a negative charge to be closed-shell, so it is considered Cl^- . This ligand is then considered to donate 2e, namely, one of its lone pairs. Other monoanionic closed-shell ligands are H^- , R^- (R = alkyl), Ar^- (Ar = aryl). Now consider the fragments O or NR (R = H, alkyl, aryl). Each of these must have a 2- charge to be closed-shell, so they are considered as O^{2-} or NR^{2-} . Each of these closed-shell ions is considered to donate two of its lone pairs, 4e total, to a metal, so O^{2-} and NR^{2-} are 4e

ligands. This is reflected in that we usually draw double bonds in complexes of these ligands: $M=O$, $M=NR$.

To get the total electron count using the donor pair method, one first calculates the oxidation state of the metal. This is done by seeing what charge the metal must have in order to balance out the (mostly) negative charges of the closed-shell ligands in order to obtain the overall charge of the complex. For instance, $Cr(CO)_6$ is a Cr atom with 6 CO ligands. Since CO is neutral when closed-shell, Cr contributes zero to the overall neutral complex, so it is in the zero oxidation state, or Cr(0). The number of electrons the metal contributes to the count is simply its number of valence electrons, adjusted for oxidation state. Neutral Cr has 6 valence electrons, so Cr(0) contributes 6e. Each CO ligand contributes 2e, so the total electron count is $6e + 6(2e) = 18e$.

As an example of electron counting with a non-zero metal oxidation state, consider the classical coordination complex $[CoCl_6]^{3-}$. Each Cl ligand is considered to be closed-shell Cl^- . This means that the Co center must be akin to a Co^{3+} ion, or Co(III), for the complex to have an overall 3- charge. Each Cl^- contributes 2e, for 12e total. Neutral Co has 9 valence electrons, so Co(III) contributes $9 - 3 = 6e$. The total electron count is thus $6e + 12e = 18e$.

The neutral ligand method is, in contrast, exactly what it sounds like: each ligand is considered as a neutral molecule, atom, or molecular fragment, even if it is not closed-shell. If the neutral ligand has a lone pair, it donates the two electrons from that lone pair to the metal. Thus, CO and PR_3 are 2e ligands in the neutral ligand electron-counting method, as well as in the donor pair method. In the case of ligands with unpaired electrons when neutral, each unpaired electron is donated to the metal. Thus, according to the neutral ligand method, H, F, Cl, Br, I, R, and Ar are all 1e ligands, since each has one unpaired electron to donate. On the other hand, a free O atom or a free NR fragment has two unpaired electrons, so each is a 2e ligand by the neutral ligand method.

One advantage of the neutral ligand method is that one need not calculate the metal's oxidation state. Instead, each metal contributes the number of valence electrons that a

neutral metal atom would have. Finally, with the neutral ligand method, one accounts for the complex's charge at the end of the calculation, subtracting 1e for each positive charge and adding 1e for each negative charge. (In the donor pair method, one would have accounted for this when calculating the metal's oxidation state).

Considering $\text{Cr}(\text{CO})_6$ once again, each CO contributes 2e as a neutral ligand (it is a 2e ligand by both methods, as it is neutral when closed-shell). Cr contributes 6e, and the complex has no net charge, so the count is $6e + 6(2e) = 18e$. Each of the two methods of electron counting is a formalism, but they must always give the same answer. As an example of accounting for charge, by the neutral ligand method, each Cl in $[\text{CoCl}_6]^{3-}$ contributes 1e, Co contributes 9e, and the 3- charge represents another 3e. Thus, the count is $9e + 6(1e) + 3e = 18e$, as before.

When considering the side-on bonding of a σ system like H_2 or a π system like C_2H_4 , each bond whose electron pair is donated to a metal is considered to contribute 2e to the electron count, using *either* method. A diene like butadiene contributes 4e, 2e for each double bond. The two counting systems differ when we have an unsaturated hydrocarbon ligand that is a radical when neutral. Consider first allyl, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2$. The allyl ligand can bind to a metal atom in one of two ways. It can bind only through one of the terminal carbons, with the double bond not interacting with the metal: this mode is denoted η^1 , where the superscript 1 on the letter eta indicates the number of carbon atoms interacting with the metal. On the other hand, it can also bind through one of the terminal atoms as a “classical” metal-ligand bond, and through the other two as donation from a π bonding electron pair. It turns out that in this latter case (denoted η^3 , as three carbons are interacting with the metal), the interactions are delocalized, as per the resonance structures in Figure 12.2 below.

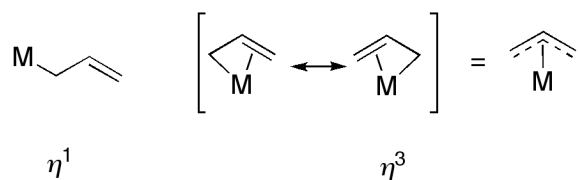


Figure 12.2. Binding of an allyl ligand to a TM center.

Electron counting for the η^1 binding mode is the same as that for a saturated alkyl ligand like methyl or ethyl: by the donor pair method, closed-shell $[\text{H}_2\text{C}-\text{CH}-\text{CH}_2]^-$ donates 2e, while by the neutral ligand method, the allyl radical donates 1e. For the η^3 binding mode, the π bond electron pair donates 2e by either method, while the terminal CH_2 group donates 1e by the neutral ligand method, and 2e by the donor pair method, which assumes $[\text{H}_2\text{C}-\text{CH}-\text{CH}_2]^-$. So η^3 -allyl is 3e by the neutral ligand method, and 4e by the donor pair method.

Unsaturated cyclic ligands with formula C_mH_m (annulenes) are handled in a straightforward manner by the neutral ligand method. Assuming that they are bound in a η^m fashion (each carbon is interacting with the metal), each is an *me* ligand by the neutral method, consisting of $\frac{m}{2}$ C=C double bonds if *m* is even, and $\frac{m-1}{2}$ C=C double bonds and 1 unpaired electron if *m* is odd. The donor pair method is somewhat more awkward here, as it is dependent on what counts as “closed-shell.” Normally, we consider the closed-shell form of a ligand to be the one in which all atoms have an octet of electrons. However, for annulenes, the closed-shell charge is defined to be the one in which the ligand is aromatic according to the Hückel $4n + 2$ rule. Benzene, C_6H_6 , is of course aromatic when neutral, so it is a 6e ligand by both the donor pair method and the neutral ligand method. For C_5H_5 (commonly abbreviated Cp as a ligand, short for cyclopentadienyl), the closed-shell form is the aromatic (6 π electrons) anion C_5H_5^- . In this ion, the octet rule is satisfied for every carbon in addition to its being aromatic. By the donor pair system, it is a 6e ligand, since each resonance form has one lone pair and two C=C π bonds. It is, of course, 5e by the neutral ligand method.

Now consider cyclobutadiene, C_4H_4 . It is a 4e ligand by the neutral method, but not by the donor pair method. Although we can draw resonance structures of C_4H_4 that follow the octet rule, MO theory tells us that neutral, planar C_4H_4 is antiaromatic, with 4 π electrons. The dianion $\text{C}_4\text{H}_4^{2-}$, however, is aromatic (6 π electrons). Thus, by the donor pair method, the closed-shell form is $\text{C}_4\text{H}_4^{2-}$, a 6e ligand. Similarly, C_7H_7 is 7e by the neutral ligand method, but the octet-rule satisfying C_7H_7^- anion would be antiaromatic, with 8 π electrons. The cation C_7H_7^+ is aromatic, with 6 π electrons. It is stable enough that its salt $[\text{C}_7\text{H}_7^+][\text{BF}_4^-]$ can be stored in a bottle in the absence of moisture, and it has the common name tropylium. It is

considered closed-shell as an aromatic cation, and thus a 6e ligand, even though each of the 7 resonance forms of the cation has one carbon lacking an octet.

The important molecule ferrocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, or Cp_2Fe for short, is an 18e species. By the donor pair method, each Cp^- is a 6e ligand, and Fe(II) contributes 6e, so the count is $6e + 2(6e) = 18e$. By the neutral ligand method, each Cp is a 5e ligand and Fe contributes 8e, so the count is $8e + 2(5e) = 18e$.

While C_4H_4 is not a stable molecule on its own (two molecules of it will undergo an extremely rapid Diels-Alder reaction with each other), it is synthetically useful to be able to generate it transiently from a stable molecule. The complex $(\eta^4\text{-C}_4\text{H}_4)\text{Fe(CO)}_3$ will release C_4H_4 when treated with salts of the highly oxidizing cation Ce^{4+} . By the donor pair method, this complex contains 3 CO ligands (2e each, 6e total), a $\text{C}_4\text{H}_4^{2-}$ ligand (6e) and Fe(II) (6e), for 18e total. By the neutral ligand method, the 3 CO still contribute 6e together, C_4H_4 contributes 4e, and Fe contributes 8e, again for 18e total.

As a final example of electron counting in annulene complexes, we consider the mixed annulene complex $\text{Cp}(\eta^7\text{-C}_7\text{H}_7)\text{Cr}$. By the donor pair method, Cp^- contributes 6e, as does C_7H_7^+ , and Cr(0) contributes 6e as well for 18e total. By the neutral ligand method, Cp contributes 5e, C_7H_7 contributes 7e, and Cr contributes 6e, again for 18e total.

One simple ligand whose electron counting can be ambiguous is nitric oxide, NO, which can bind to a metal in either a linear or a bent fashion. (NO is known as nitrosyl when it acts as a ligand) By the donor pair method, linear NO is considered to be the closed-shell NO^+ ligand (isoelectronic to CO), donating 2e with a lone pair set up for a linear M-N-O angle. Bent NO, on the other hand, is considered to be the (also closed-shell) NO^- ligand, donating 2e with a lone pair set up for bent coordination. By the neutral ligand method, bent NO is a 1e ligand, in a σ fashion, while linear NO is a 3e ligand, 1e in a σ fashion and another 2e in a π fashion, as shown in Figure 12.3 on the following page.

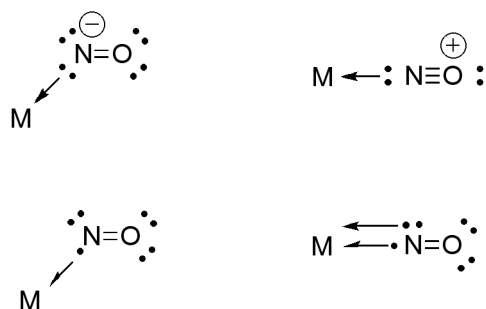


Figure 12.3. Bonding modes of the nitrosyl ligand.

An interesting example of a nitrosyl complex is $\text{Cr}(\text{lin-NO})_4$, as yet one of only two homoleptic nitrosyl complexes known; the other is $\text{Co}(\text{NO})_3$. By the donor pair method, we have 4 NO^+ , each of which contributes 2e each for 8e total, and $\text{Cr}(\text{-IV})$, contributing 10e, for an electron count of 18e. By the neutral ligand method, each linear NO contributes 3e (12e between the four of them), and Cr contributes 6e, giving us 18e total again.

Both the donor pair and neutral ligand methods of electron counting are widely used, and you are welcome to use whichever one you find most intuitive. I personally prefer the neutral ligand method, as it allows for a simpler assignment for unsaturated hydrocarbon ligands, *e.g.* an $\eta^m\text{-C}_m\text{H}_m$ ligand contributes m electrons. Furthermore, one need not assign oxidation states that are wildly different from actual charge: for instance, while $\text{Cr}(\text{lin-NO})_4$ is technically a $\text{Cr}(\text{-IV})$ complex, there is not actually a buildup of negative charge on Cr, since Cr is much *less* electronegative than N and O. I primarily use the neutral ligand method in my lecture classes. Table 12.1 on the following page lists common ligands in organometallic chemistry and their electron counts using both counting schemes. You can use these same counting schemes to account for the 16e rule in d^8 , square-planar complexes (see Sections 8.8 and 8.9).

One important note on electron counting occurs when there is a direct metal-metal covalent bond, as in compounds such as the stable, commercially available $\text{Co}_2(\text{CO})_8$, with structure $(\text{CO})_4\text{Co}-\text{Co}(\text{CO})_4$. The electrons in the metal-metal bond are considered to “belong” to both metals, so the presence of an M–M bond gives each metal one additional electron. The $\text{Co}(\text{CO})_4$ fragment has 8e from the four 2e CO ligands, and 9e from Co, for 17e total. When

two such fragments combine to form $\text{Co}_2(\text{CO})_8$, the Co-Co bond gives each Co center one additional electron, so $\text{Co}_2(\text{CO})_8$ is 18e at both cobalt centers. This is closely analogous to how a CH_3 fragment has 7e around carbon, but formation of a C-C single bond in the formation of ethane means that each C has 8e around it, and it thus obeys the octet rule.

Table 12.1. Common ligands in organometallic chemistry and their electron counts.

Neutral form	Electron count (neutral ligand method)	Closed-shell form	Electron count (donor pair method)	Name as ligand	Notes
H	1	H^-	2	hydrido	
F	1	F^-	2	fluoro	
Cl	1	Cl^-	2	chloro	
Br	1	Br^-	2	bromo	
I	1	I^-	2	iodo	
H_2O	2	H_2O	2	aqua	
OH	1	OH^-	2	hydroxo	
O	2	O^{2-}	4	oxo	
NH_3	2	NH_3	2	ammine	
NR_3	2	NR_3	2	amine	
NR_2	1	NR_2^-	2	amido	
NR	2	NR^{2-}	4	imido	
N	3	N^{3-}	6	nitrido	
R	1	R^-	2	alkyl	
Ar	1	Ar^-	2	aryl	
CO	2	CO	2	carbonyl	
CS	2	CS	2	thiocarbonyl	
Linear NO	3	NO^+	2	nitrosyl	
Bent NO	1	NO^-	2	nitrosyl	
R_2O	2	R_2O	2	ether	
ROH	2	ROH	2	alcohol	
RO	1	RO^-	2	alkoxo	
PR_3	2	PR_3	2	phosphine	
PR_2	1	PR_2^-	2	phosphido	
RCN	2	RCN	2	nitrile	
RNC	2	RNC	2	isonitrile	
CR_2 , R = alkyl	2	CR_2^{2-}	4	carbene (Schrock-type)	

The π -donor ability of some ligands means that their electron count can be greater than that listed in the handout I have provide. For each additional lone pair used in π -donation, an additional 2e is donated. A good example is that of amido ligands NR_2 . By the neutral ligand method, NR_2 is a 1e donor (since a free NR_2 fragment has one unpaired electron). We expect a trigonal pyramidal geometry around nitrogen in this case, with room for a sterically active lone pair. If that lone pair is used in π donation, however, NR_2 becomes a 3e ligand, and we expect the N atom, R groups, and the metal all to lie in a plane. Similarly, imido ligands NR are normally 2e donors (neutral ligand method), with a nonlinear M-N-R bond angle to make room for the lone pair on N. If this lone pair is donated to the metal, however, NR becomes a 4e ligand, and the M-N-R connection will be linear (M-N-R bond angle of about 180°). An analogous situation holds for alkoxo ligands OR , which are 1e ligands (neutral ligand method). Each OR ligand has two lone pairs: if one participates in π bonding, the M-O-R angle increases to around 120° , and it is a 3e ligand, and if both are used in π bonding, we have a 5e ligand and expect an M-O-R bond angle of about 180° .

Because of these potential ambiguities, electron counting is less useful for complexes with a high-oxidation state metal and multiple π -donor ligands. For instance, $\text{W}(\text{OMe})_6$ has W in the +6 oxidation state (the highest W can be), and it is a 12e complex if each OMe is taken to be a 1e ligand. However, since each OMe ligand has two lone pairs that could potentially engage in π bonding, there are 24 additional electrons that could, in principle, interact with the W center.

Since we have classified some MOs as basically metal d in character, it is important to be able to calculate the d electron count, usually written as d^n , for the metal center of a complex. This is done by calculating the metal's oxidation state, and then counting the number of d electrons for a free atom or ion with the oxidation state as its charge. Since the number of valence electrons in a free atom is the same as the group number, one can get d electron count simply by subtracting oxidation state from group number.

There is one caveat: recall that, in a free metal atom, the 4s AOs are generally filled before the 3d, so the electron configuration of an Fe atom is $[\text{Ar}](4s)^2(3d)^6$, not $[\text{Ar}](4s)^0(3d)^8$. In a

free metal ion, however, the $3d$ AOs lie *below* the $4s$ in energy, so Fe^{3+} is $[\text{Ar}](4s)^0(3d)^5$, not $[\text{Ar}](4s)^2(3d)^3$. Similar rules apply for second-row transition metals, with $5s$ and $4d$ AOs, and third-row transition metals, with $6s$ and $5d$ AOs. In transition metal complexes, the valence d orbitals are lower in energy than the valence s even if the oxidation state is zero or negative. Thus, since a free Fe atom has 8 valence electrons, the $\text{Fe}(0)$ complex $\text{Fe}(\text{CO})_5$ is d^8 , not d^6 , even though a free (uncomplexed) Fe atom is $(4s)^2(3d)^6$. This phenomenon may be understood as resulting from the fact that, even if the metal has a zero or negative oxidation state, more electron density will lie on the ligands, since the donor atoms will almost certainly be more electronegative than the metal. Thus, there is some positive ion character to Fe in $\text{Fe}(\text{CO})_5$, even if its oxidation state is the same as elemental Fe metal.

Compounds with metal-metal bonds are an exception: in $(\text{CO})_4\text{Co}-\text{Co}(\text{CO})_4$, each Co is $\text{Co}(0)$. A $\text{Co}(0)$ complex with only one Co atom would be d^9 , since Co is a group 9 element. Each metal-metal bond, however, is considered to give an additional d electron to each metal, just as it gives an additional electron to each metal's electron count. So each Co in $\text{Co}_2(\text{CO})_8$ is best considered d^{10} .

12.3. Carbonyl Complexes

$\text{Ni}(\text{CO})_4$, the first carbonyl complex known, was discovered by accident by the chemist and engineer Ludwig Mond (1839-1909). Mond noticed that nickel pipes through which CO gas was flowing were being corroded. The intentional reaction of Ni powder with CO yielded the tetrahedral complex $\text{Ni}(\text{CO})_4$, which is a liquid with a low boiling point (43°C) and a substantial vapor pressure at room temperature. Mond extended this chemistry to carbonyl complexes of other transition metals, prompting William Thomson, Lord Kelvin (the namesake of the temperature unit) to marvel that Mond "gave wings to heavy metals"). This discovery led to considerable wealth for Mond, as he was able to use it to develop a process for the isolation of elemental nickel with very high purity. The so-called Mond process relies on the fact that nickel is the only metal that reacts with CO at fairly low temperatures to form a carbonyl complex. Thus, treatment of *impure* nickel with CO yields volatile $\text{Ni}(\text{CO})_4$, which can be distilled away, leaving the other metals behind as solids. Further heating of the

Ni(CO)_4 obtained causes dissociation of the CO, yielding very pure elemental nickel. Unfortunately, the Mond process is hazardous due to the extreme toxicity of Ni(CO)_4 , which is one of the most poisonous substances known. When inhaled, it gradually decomposes to release CO, which is bad enough given the toxicity of CO. Worse, however, is the fact that this decomposition deposits a thin layer of metallic nickel, essentially nickel-plating the inside of one's lungs. The human body has no way to effectively clear elemental metals from tissues, so Ni(CO)_4 poisoning is extremely damaging and often fatal. Nevertheless, thin-layer metal plating is often accomplished by the thermal decomposition of metal carbonyls onto the surface to be plated.

The MO picture of the bonding in carbonyl complexes was discussed in Sections 8.4 and 8.5. Recall that CO is a π -acceptor ligand with valence MOs that are C–O π antibonding. If the metal has d electrons, the MOs arising from this type of π bonding are occupied and bonding in an M–C sense. One can think of this as a transfer of electron density from metal to CO ligand, strengthening the M–C bond while weakening the C–O bond (since the MO populated is M–C bonding, but C–O antibonding). This phenomenon can be depicted with resonance structures, as shown for Cr(CO)_6 in Figure 12.4 below.

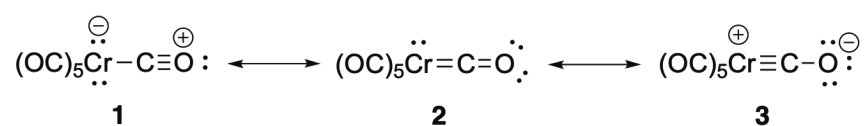


Figure 12.4. Resonance structures of Cr(CO)_6 showing the effects of π backbonding.

The π -acceptor nature of CO makes resonance structure 2 quite important: there is significant Cr–C double-bond character, but the C–O bond is closer to a double bond than the triple bond present in free CO. This is why, when CO is a ligand, it is known as “carbonyl,” in analogy with carbonyl groups in organic molecules, with C–O double bonds.

The decrease in C–O bond order (moving from a triple bond towards a double bond) can be experimentally measured using IR spectroscopy. Recall that the frequency in the IR spectrum corresponding to stretching of a bond is greater for stronger bonds, as long as the bonds are

between the same pairs of atoms. Free CO has a very strong triple bond, and its IR spectrum shows a C-O stretching frequency of $\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$. The isoelectronic metal carbonyl species $\text{Ti}(\text{CO})_6^{2-}$, $\text{V}(\text{CO})_6^-$, $\text{Cr}(\text{CO})_6$, $\text{Mn}(\text{CO})_6^+$, and $\text{Fe}(\text{CO})_6^{2+}$ have ν_{CO} values of 1748, 1859, 2000, 2100, and 2204 cm^{-1} , respectively. The greater the negative charge (or the lower the positive charge) on a metal carbonyl complex, the more able the metal is to engage in $\text{M} \rightarrow \text{CO}$ back-donation, thus decreasing the C-O bond order and the value of ν_{CO} . Organic compounds with a carbonyl ($\text{C}=\text{O}$) functional group (*e.g.* ketones) usually have ν_{CO} values of 1700-1850 cm^{-1} . The fact that ν_{CO} values of metal carbonyl complexes can extend into this region is another reason why CO is known as “carbonyl” when acting as a ligand.

The ν_{CO} value of $\text{Fe}(\text{CO})_6^{2+}$ is interesting, since it is *greater* than that observed for free CO. In the case of this species, there is very little backbonding (which would tend to lower ν_{CO}) due to the complex's positive charge: the *d* electrons of Fe are tightly held, and reluctant to be donated to the ligands. At the same time, the positive charge of Fe strongly draws electron density from C in a σ sense. This, in turn, makes C pull electron density away from O lone pairs into the C-O bonding region, strengthening the C-O bond, in this case, relative to free CO itself! This phenomenon is not restricted to $\text{Fe}(\text{CO})_6^{2+}$: the carbonyl cations $\text{Os}(\text{CO})_6^{2+}$ and $\text{Ir}(\text{CO})_6^{3+}$ have ν_{CO} values of 2190 and 2254 cm^{-1} , respectively, both greater than that for free CO.

As we have noted before, complexes with π -acceptor ligands tend to obey the 18e rule. (In octahedral complexes, the t_{2g} *d* orbitals become bonding, rather than nonbonding, MOs). Thus, almost all binary carbonyl complexes (complexes containing only a metal and CO ligands) obey the 18e rule. The list of isoelectronic complexes whose ν_{CO} values were previously provided are all 18e, as are the non-octahedral 18e species $\text{Fe}(\text{CO})_5$, $\text{Ru}(\text{CO})_5$, and $\text{Os}(\text{CO})_5$ (trigonal bipyramidal) and $\text{Ni}(\text{CO})_4$ and $\text{Pd}(\text{CO})_4$ (tetrahedral, as previously noted). The vanadium complex $\text{V}(\text{CO})_6$ is an isolable species, even though it is only 17e. However, it is readily reduced to the 18e $\text{V}(\text{CO})_6^-$. This is a good example of how species that violate the 18e rule may be stable enough to be isolated, but their redox reactivity often tends to lead to 18e products.

It is notable that V is in the -1 oxidation state in $\text{V}(\text{CO})_6^-$, which you may find surprising, since V, as a metal, is not very electronegative. There are several other 18e binary carbonyl complexes with metals in negative oxidation states, such as $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Co}(\text{CO})_4^-$. Such complexes are sometimes termed “carbonylate anions,” and their stability is due to the fact that the metal *d* electrons are extensively delocalized over the ligands through back-bonding, leaving the central metal less electron-rich than its negative oxidation state might indicate. The neutral complex $\text{HCo}(\text{CO})_4$ is actually a reasonably strong acid, since its deprotonation leads to the highly delocalized $\text{Co}(\text{CO})_4^-$ anion. CO is also able to stabilize the zero oxidation state for many metals, in comparison to the elemental metal or zerovalent complexes with more electron-donating ligands. For example, powdered elemental Mo is pyrophoric (spontaneously ignites in air), but powdered $\text{Mo}(\text{CO})_6$ is air-stable and can be handled without special techniques.

Metals with an even number of valence electrons can reach 18e in neutral CO complexes, with each CO a 2e ligand as usual, such as $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Ni}(\text{CO})_4$. Neutral, 18e CO complexes of metals with an odd number of valence electrons also exist, with the 18e rule being satisfied by metal-metal bonding. The fragments $\text{Mn}(\text{CO})_5$ and $\text{Co}(\text{CO})_4$ are 17e each, but the bimetallic complexes $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$ are 18e at each metal: each contains a metal-metal σ bond, so their formulae might be better written as $(\text{OC})_5\text{Mn-Mn}(\text{CO})_5$ and $(\text{OC})_4\text{Co-Co}(\text{CO})_4$. This metal-metal bonding gives each metal an extra electron in its coordination sphere. Two molecules of $\text{V}(\text{CO})_6$ could, on paper, pair up to form a V-V bond in $\text{V}_2(\text{CO})_{12}$, but this is not experimentally observed, probably because each V atom is too small to accommodate this bond in addition to six CO ligands.

The x-ray crystal structure of $\text{Co}_2(\text{CO})_8$ is interesting, in that only six of its eight CO ligands are bound to only one Co atom apiece. The two other CO ligands bridge both Co atoms through carbon as shown in Figure 12.5 on the following page.

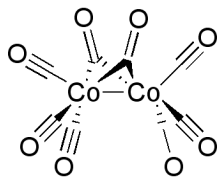


Figure 12.5. Structure of $\text{Co}_2(\text{CO})_8$, in the solid state, with bridging carbonyl ligands.

While a terminal carbonyl ligand (one bound only to one metal atom) is considered a 2e ligand by either electron counting scheme, a bridging carbonyl ligand is considered to be a 2e ligand total, but only a 1e ligand to each metal. When two terminal CO ligands in a bimetallic complex become bridging, there is no change in the electron count at either metal. If $\text{Co}_2(\text{CO})_8$ had all-terminal ligands, each Co has 9e from its own valence electrons, 8e from 4 CO ligands (2e each) and 1e from the Co-Co bond, for 18e total. In the doubly bridged structure, each Co has 9e from its own valence electrons, 6e from 3 terminal CO ligands (2e each), 2e from 2 bridging CO ligands (1e each) and 1e from the Co-Co bond, for 18e total once again. In formulae, the Greek letter mu (μ) and a hyphen is listed before a bridging ligand, so the solid-state structure of $\text{Co}_2(\text{CO})_8$ could be written as $\text{Co}_2(\text{CO})_6(\mu\text{-CO})_2$, or as $[\text{Co}(\text{CO})_3(\mu\text{-CO})]_2$.

In drawing Lewis structures for carbonyl complexes, a terminal CO can, at least formally, be drawn with a C-O triple bond, as per resonance structure 1 in Figure 12.4, though there is considerable contribution from the “metalla-ketene” structure 2, especially in electron-rich metal complexes. For bridging CO ligands, each having two C-M single bonds, we naturally draw a C-O double bond, akin to an organic carbonyl compound. As it happens, IR spectra of compounds with bridging CO ligands tend to bear out a lowered C-O bond order for bridging CO, with ν_{CO} values generally falling in the range 1700-1860 cm^{-1} , comparable to organic carbonyl stretches with unambiguous C-O double bonds.

The energy differences between bimetallic structures with bridging CO ligands and those without is often small. In the solid state, $\text{Co}_2(\text{CO})_8$ has two bridging CO ligands, as confirmed by its crystal structure, but spectroscopic measurements of $\text{Co}_2(\text{CO})_8$ in solution indicate that all CO ligands are terminal, with each Co having trigonal bipyramidal geometry, as shown in

Figure 12.6 below. The Group 7 carbonyl complexes $M_2(CO)_{10}$ ($M = Mn, Tc, Re$) have all terminal carbonyl groups in both the solid and solution phases. Since the electron count is unchanged when two terminal carbonyl groups become bridging, one cannot reliably predict whether a given bimetallic complex will have bridging carbonyls or not; experimental measurements must be done.

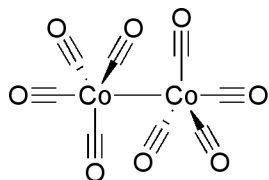


Figure 12.6. Structure of $Co_2(CO)_8$ in solution, with all CO ligands terminal.

Moving from the formal, Lewis structure depiction of a carbonyl bridge, with an M-M single bond and two M-C single bonds, to a discussion of the orbital interactions involved, we see that a CO lone pair can donate, in a σ sense, to an empty metal-based MO of σ bonding character. Similarly, a filled metal-based MO of σ -antibonding character can donate to the empty π antibonding MOs of a bridging CO, as shown in Figure 12.7 below.

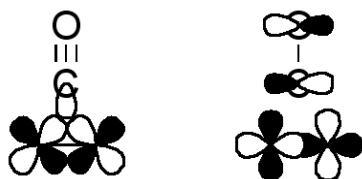


Figure 12.7. Interactions of CO MOs with metal-metal bonding and antibonding MOs.

This more delocalized picture suggests that a discrete metal-metal bond is probably not the most accurate representation, since the interactions between the metal centers are a mix of bonding or antibonding. Instead, bridging carbonyl groups serve as an example of highly delocalized σ bonding, like the bridging hydrogen atoms in diborane, B_2H_6 (see Section 3.7). Nonetheless, the metal-metal bonds are useful in terms of electron-counting bookkeeping, and in complexes without bridging CO ligands, such as $Mn_2(CO)_{10}$, there is unambiguous metal-metal bonding. Another example of clear metal-metal bonding, though not an

organometallic one, is Cotton's famous anion $\text{Re}_2\text{Cl}_8^{2-}$, which has an Re-Re quadruple bond. (Metal-metal bonding will be discussed in more detail in Chapter 16.) We will draw structures with metal-metal bonds in this course, even when carbonyl ligands are bridging, but be aware that these graphical representations may not be exactly correct from a theoretical point of view.

A σ -delocalized picture of bonding is absolutely necessary in cases where a carbonyl C bridges three metal centers, as opposed to two. (In formulae, this is denoted by $\mu^3\text{-CO}$.) In these cases, each M-C bond should not be considered to represent two entire electrons. Instead, CO may be considered to contribute 2e to the cluster as a whole, but at this point the delocalization is widespread enough that it no longer makes sense to count electrons around any individual atom. In $\mu^3\text{-CO}$ complexes, ν_{CO} values generally lie within the range of 1600-1700 cm^{-1} , reflecting additional lowering of the C-O bond order.

There is another way in which a CO ligand can bridge two metals. When a CO ligand is bound to only one metal, the donor atom is invariably C, rather than O: this is because both the π -donor HOMO (roughly nonbonding, corresponding to the C lone pair) and the π -acceptor LUMO (C-O π -antibonding) have their largest lobes on carbon. This reflects the strongly covalent nature of transition metal-CO bonding. In some TM carbonyl complexes, however, the oxygen atom can also engage in bonding to a more electropositive main-group metal. These bonds, while having some covalent character, are significantly more polar. In such cases, electron density is depleted from CO, lowering ν_{CO} . An example with W as the TM and Al as the main-group metal is shown in Figure 12.8 below.

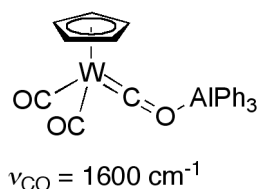
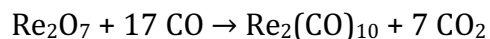
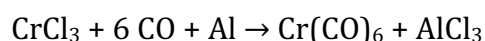


Figure 12.8. A complex with a CO ligand bridging a TM and a main-group metal.

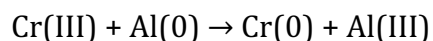
We will discuss some general types of organometallic reactivity later in the next chapter, but at this point, it is worth noting what some of the standard methods are for preparing carbonyl complexes, as well as some of the standard reactions that said complexes can undergo.

Conceptually, the simplest strategy for carbonyl complex synthesis is simply the reaction of an elemental metal with CO. The reaction $\text{Ni} + 4 \text{CO} \rightarrow \text{Ni}(\text{CO})_4$ was, after all, what led to Ludwig Mond's key insight. This reaction is less generally useful than you might think, however. For one thing, Ni is the only transition metal that reacts with CO at room temperature: formation of other homoleptic carbonyls in this fashion requires elevated temperature and often high pressures of CO. For another thing, elemental metals are not the most convenient materials to work with. If the metals are present as large chunks, then the reaction will proceed slowly: the reaction occurs at the surface of the metal, and large pieces of metal have a low surface area/volume ratio. One can achieve a superior surface/volume ratio by using a powdered form of the metal, but such powders are unfortunately often pyrophoric, since their high surface/volume ratio leads to rapid reaction with O_2 in the air.

Since the π -accepting CO ligand stabilizes metals in low (often zero) oxidation states, another general strategy is to start with the metal in a positive oxidation state (such as in a salt), and to treat it with a reducing agent under a CO atmosphere. This type of reaction is called reductive carbonylation, and some examples are as follows:



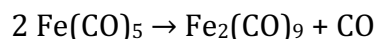
In the first reaction, elemental Al is the reducing agent, with the redox process being



This is favored by the fact that Cr is more electronegative than Al. In the second reaction, CO is both the reducing agent, abstracting O atoms to form CO_2 , and the ligand for the reduced Re(0) .

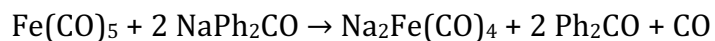
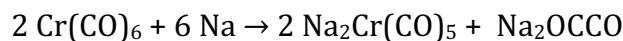
Finally, a good way to make bimetallic or polymetallic CO complexes is by heating monometallic ones: dissociation of CO ligands leads to coordinatively unsaturated metals,

which regain an 18e configuration by forming metal-metal bonds (with or without bridging CO ligands). Depending on how vigorous the reaction conditions are, different levels of unsaturation can be obtained:



As for reactions of carbonyl complexes, one of the most common is the replacement of CO by another ligand. For most 18e CO complexes, the reactions proceed by the dissociative mechanism. One example is $\text{Cr}(\text{CO})_6 + \text{PPh}_3 \rightarrow \text{Cr}(\text{CO})_5(\text{PPh}_3) + \text{CO}$. Since CO is strongly bound, at least to electron-rich metal centers like Cr(0), these reactions usually require elevated temperatures to proceed. Alternatively, high-energy light can provide the activation energy necessary (photolysis).

As we discussed previously, the π -accepting nature of CO allows it to stabilize metals in negative oxidation states. Thus, many zerovalent metal complexes of CO can be reduced to carbonylate anions, as in the following examples:



The second of these reactions involves two notable compounds. The carbonylate salt $\text{Na}_2\text{Fe}(\text{CO})_4$, known as Collman's reagent (after chemist James Collman, b. 1932) is useful as a nucleophile and reducing agent in many areas of chemical synthesis. The salt $\text{Na}[\text{Ph}_2\text{CO}]$ involves the radical anion of benzophenone, $\text{Ph}_2\text{CO}^\cdot$, which is a synthetically useful reducing agent (It is also an excellent indicator for whether a sample of deoxygenated solvent in a glovebox is truly air-free: the $\text{Ph}_2\text{CO}^\cdot$ anion is an intense purple color, but it turns yellow almost instantly upon exposure to O_2 .)

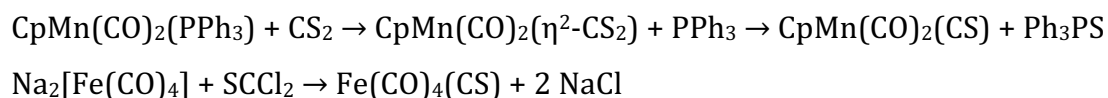
There are many other reactions that CO complexes can undergo, generally involving the CO ligand changing to a different ligand. We will discuss these reactions later in the course.

12.4. Ligands Analogous to CO

A variety of ligands exist which are similar to CO in important respects. Perhaps the most obviously similar is cyanide, CN^- , which is isoelectronic to CO, and which has a generally similar set of MOs. Like CO, CN^- binds through C, and is capable of very strong attachment to Fe in a variety of coordination environments. In fact, both CO and CN^- are poisonous because of their ability to bind to heme, an iron complex attached to many naturally occurring proteins. CO strongly binds to the heme group in hemoglobin, preventing hemoglobin from doing its job transporting O_2 in the body. CN^- , on the other hand, binds to the heme in cytochrome *c*, an enzyme involved in the mitochondrial electron-transport chain, inhibiting its function. Lethal amounts of either CO or CN^- cause death by suffocation: CO prevents O_2 from being transported between organs, and CN^- prevents it from being used by cells.

Elemental nitrogen, N_2 , is also isoelectronic with CO, and it is, in some respects, analogous as a ligand. However, its similarity with CO is less than that of CN^- , because the homonuclear nature of N_2 means that none of its MOs is polarized toward either N atom. In both CO and CN, both the HOMO and the LUMO are polarized toward C, leading to efficient orbital overlap when binding to a transition metal. Because of the lack of such polarization in N_2 , transition metals bind it much less strongly as a ligand. The coordination chemistry of N_2 is still an active research area, because some organisms are able to “fix” atmospheric nitrogen, reducing it to bioavailable NH_3 , using iron- and molybdenum-containing enzymes called nitrogenases. It would be of tremendous economic importance to develop a synthetic catalyst capable of enabling the reaction $2 \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$ to proceed at modest temperatures and pressures.

Other analogous ligands are those in which the oxygen has been replaced by another chalcogen, namely, CS, CSe, and CTe, which are known as thiocarbonyl, selenocarbonyl, and tellurocarbonyl, respectively, when present as ligands. Chemistry with these ligands is more difficult than CO chemistry, since unlike CO, neither CS, CSe, nor CTe is stable as a free molecule. To obtain complexes, one must start with another reagent and have it become CS, CSe, or CTe once bound. This is more readily done for CS than for the others, with CS_2 and SCCl_2 as useful synthons, as in the following two examples:



In addition to the isoelectronic CN^- and N_2 ligands, and the congeners CS, CSe, and CTe, another ligand that is somewhat analogous to CO is nitric oxide,⁹⁵ NO, known as nitrosyl when bound as a ligand (analogous to CO as carbonyl). It is an interesting molecule in part because of its stability, despite being a main-group radical species: while it forms the closed-shell dimer $\text{O}=\text{N}-\text{N}=\text{O}$ at low temperatures in the solid phase, as a gas it exists essentially entirely of NO monomers. It is also interesting for its biological activity: while NO is toxic in significant concentrations, it is used in small amounts as a signaling molecule in living systems, with its release leading to the process of vasodilation (the widening of blood vessels). Its ability to coordinate to transition metals is crucial for this activity, since it conveys the signal by binding to a heme Fe atom in the enzyme guanylate cyclase, activating the enzyme and allowing it to continue the signaling pathway. The 1998 Nobel Prize in Physiology or Medicine was awarded to Robert Furchgott (1916-2009), Louis Ignarro (b. 1941), and Ferid Murad (1936-2023) for their discovery of this rôle for NO.

While NO is not, strictly speaking, an organometallic ligand, its complexes are often studied by organometallic chemists, given their similarity to complexes of CO. The chief difference between NO and CO is the fact that NO has one more electron, which resides in one of the two (degenerate) antibonding MOs of the molecule. The highest-energy doubly filled MO is a slightly bonding (roughly nonbonding) σ MO with high amplitude on N, analogous to the C-based “lone pair” of CO. These are the “frontier orbitals” of NO, which are involved in bonding to transition metals.

The principal difference between CO and NO as ligands is the ability of NO to bind to a metal in either a linear or a bent fashion, as mentioned in Section 12.2. The linear fashion is perhaps easier to envision in orbital terms. If we consider NO to be neutral, it donates 2e to the metal

⁹⁵ General chemistry textbooks will tell you that its systematic name is “nitrogen monoxide,” and so it is, but practicing chemists call NO this name not much more often than they call water “dihydrogen monoxide.”

in a σ fashion *via* the “lone pair.” At the same time, a π interaction occurs in which 1e comes from the singly occupied π antibonding MO, and another from a metal d AO with suitable symmetry. Thus, using the neutral-ligand counting scheme, linear NO is 3e. Alternatively, according to the donor pair method, linear NO can be considered as NO^+ , isoelectronic to CO, donating only 2e (in a σ sense), with the π antibonding MOs empty on the ligand, accepting electron density through backbonding just like in the case of CO. As in the case of CO, in linear NO complexes there is substantial M-N double bond character. These orbital interactions are sketched in Figure 12.9 below.

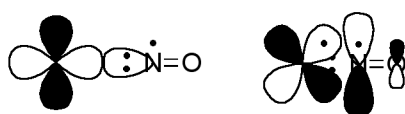


Figure 12.9. Key orbital interactions in the binding of linear NO to a TM center.

The situation is different for bent NO. If we consider the ligand as neutral NO, the singly occupied π antibonding MO can donate 1e into a metal d AO that also contains 1e. The resulting bond is σ -bonding between the metal and N, even though it is N-O π antibonding. In valence bond terms, one might consider the N atom of bent NO to be sp^2 -hybridized, whereas it is sp -hybridized in linear NO. Thus, linear NO is a 1e ligand by the neutral ligand counting scheme. Alternatively, by the donor pair method, linear NO is considered as NO^- , a 2e donor through a doubly occupied π MO. These orbital interactions are sketched in Figure 12.10 below.

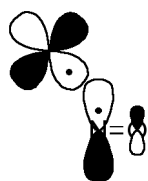


Figure 12.10. The key orbital interaction in the binding of bent NO to a TM center.

In a given complex, the energy difference between linear and bent NO is sometimes small; in such cases, molecules with the linear geometry can be in equilibrium with those in the bent geometry, as in the example shown below in Figure 12.11.

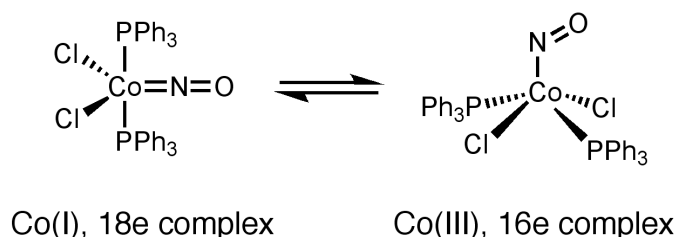


Figure 12.11. An equilibrium involving a linear or bent NO ligand.

Note that, when a bent NO ligand becomes linear, this corresponds to a decrease of 2e in the electron count at the metal (from 18e with linear NO to 16e with bent NO, in this case). Concomitantly, the metal's formal oxidation state increases by 2, since linear NO is counted as NO⁺ and bent NO as NO⁻. The linear → bent geometrical change can be thought of as a transfer of electron density from the metal to NO, and for this reason NO, with its variable geometry, is often described as a redox-active or “non-innocent” ligand.

In addition to its two possible terminal binding modes, NO can also bridge two metal centers, analogously to CO, as in Figure 12.12 below:

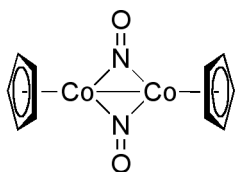


Figure 12.12. A cobalt complex with bridging NO ligands.

In terms of electron counting, bridging NO (μ -NO) is considered a 3e ligand overall, donating 2e to one metal and 1e to the other. In most cases, the bridging is symmetrical, so the bonding is delocalized, without one metal-N bond having any more electron density than the other. This can be represented in resonance forms as in Figure 12.13 on the following page, with

the arrow representing 2e donation and the straight bond line representing 1e from NO and 1e from Co:

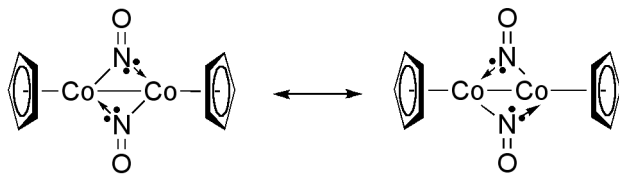
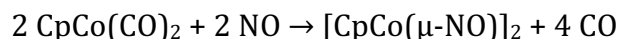
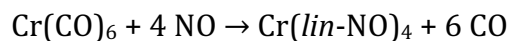
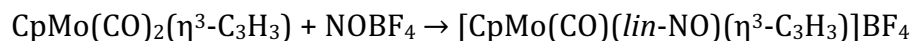


Figure 12.13. Resonance depiction of the bonding between bridging NO ligands and TM centers.

NO complexes can be synthesized in a variety of ways. Often, CO complexes are treated with NO gas bubbled through solution, with NO replacing CO as a ligand substitution. Because NO is a 3e ligand and CO is a 2e ligand, however, the substitution will not be one NO per every CO lost, and metal-metal bonding may occur.



Another approach to ligand substitution involves replacement of CO by the isoelectronic NO^+ unit. Salts of the NO^+ cation (known as nitrosonium) can be isolated, and NOBF_4 is both commercially available and stable in the absence of moisture. One example of a monosubstitution of NO^+ in place of CO is the following reaction:



The nitrite anion, NO_2^- , can also react with CO complexes to yield NO complexes, with oxygen transfer to a leaving CO ligand, so that it leaves as CO_2 :



There are complexes known of the ligands NS (thionitrosyl) and NSe (selenonitrosyl), but they are few and far between. Since neither NS nor NSe is stable as a free molecule, the syntheses involve treatment of a complex with a nitrido (N^{3-}) ligand with elemental S or Se. To the best of my knowledge, no complex of the NTe ligand has thus far been prepared.

12.5 Ligands Bound Through Organic π Systems

Moving on from complexes of carbonyl, nitrosyl, and related ligands, we will now consider complexes of unsaturated organic ligands, bound to a metal by their π systems. The first such π complex prepared was $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$, commonly known as Zeise's salt, after its discoverer, the Danish chemist William Christopher Zeise (1789-1847), who prepared it 1827 and proposed that it contained an ethene (C_2H_4) group. Most other chemists of Zeise's time doubted this claim, but Zeise was vindicated in 1967, when x-ray diffraction analysis of a crystal of Zeise's salt established that the anion has the structure shown in Figure 12.14 below.

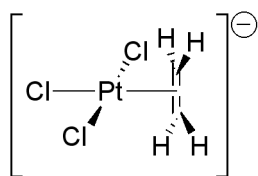


Figure 12.14. Structure of $\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)^-$, the anion of Zeise's salt.

Unlike most of the ligands of “classical” (non-organometallic) coordination chemistry, ethene does not use nonbonding electrons to attach to a metal; rather, it uses the electron density of its π system. This type of bonding was discussed in orbital terms by Michael J. S. Dewar (1918-1997), Joseph Chatt (1914-1994), and L. A. Duncanson. According to the so-called Dewar-Chatt-Duncanson or DCC model, the electrons in the filled π bonding MO of ethene are donated in a π sense to an empty metal d AO, while a filled metal d AO back-donates, in a π sense, electrons to the empty π^* antibonding LUMO of ethene. The orbital interactions and a resonance picture are sketched in Figure 12.15 below.

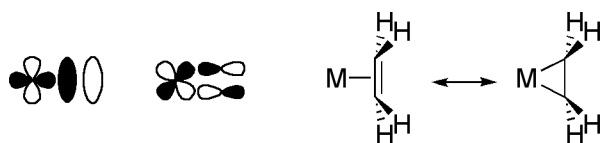


Figure 12.15. Orbital and resonance picture of the binding of ethene to a TM center, according to the DCC model.

The metal, taking electron density from the bonding π MO of ethene and adding electron density to the empty π antibonding MO, lowers the C-C bond order in the ethene ligand, lengthening the C-C bond to somewhere between the typical values for a C-C single bond and a C-C double bond. This can be represented in resonance terms by the “metallacyclopropane” resonance structure shown on the right of Figure 12.15. Where a particular alkene complex lies on this continuum depends on the substituents on the alkene, as well as the electron-rich or electron-poor nature of the metal (oxidation state, charge, other ligands). In complexes with significant metallacyclopropane character, the substituents on the alkene are often bent out of the plane, reminiscent of the geometry of an sp^3 -hybridized, rather than an sp^2 -hybridized, carbon atom. This is very much analogous to the decrease in C-O bond order in carbonyl complexes due to backbonding. Because alkenes are 2e ligands, their complexes can often be synthesized by the displacement of other 2e ligands, such as



We can describe the bonding in other complexes of acyclic π systems in a similar fashion, but we must recognize that we have more π MOs of the ligand to consider. The allyl ligand, C_3H_5 , can bind *via* one terminal carbon (η^1), in a purely σ fashion, much like a simple alkyl ligand, *e.g.* methyl or ethyl. Alternatively, it can bind using the delocalized π system *via* all three carbon atoms (η^3). Some examples of nonzero overlap between allyl π MOs and metal AOs are shown in Figure 12.16 on the following page. Which of these interactions are considered forward bonding and which are backbonding depends on how you apportion electrons between the reacting metal fragment and the allyl ligand before complex formation: if you think of L_nM^+ and $C_3H_5^-$, then the interactions with ψ_1 and ψ_2 of allyl would be forward donation and that with ψ_3 would be back-donation. On the other hand, if you think of L_nM^- and $C_3H_5^+$, then the ψ_1 interaction would still be forward donation, and the others back-donation.

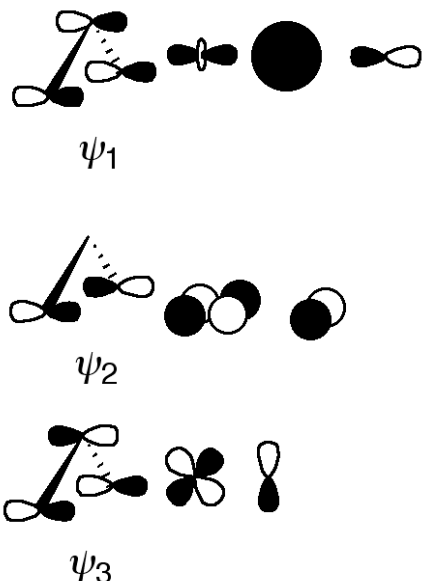


Figure 12.16. Orbital interactions between allyl π MOs and the appropriate TM AOs.

Allyl is a 1e ligand when η^1 , but a 3e ligand when η^3 , so if a 2e ligand leaves an 18e complex with an η^1 allyl ligand, the complex can remain 18e by changing the allyl hapticity to η^3 , as in the reaction $(\eta^1\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_5 \rightarrow (\eta^3\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_4 + \text{CO}$, which readily proceeds under heating or photolysis.

Similar interactions can be imagined between the MOs of butadiene and metal AOs, as shown in Figure 12.18 on the following page. Neutral butadiene has ψ_2 , which is C1-C2 and C3-C4 bonding and C2-C3 antibonding, as its HOMO, and ψ_3 , which is C2-C3 bonding and C1-C2 and C3-C4 antibonding, as its LUMO. Assuming $\text{L} \rightarrow \text{M}$ “forward” donation by ψ_2 into metal d , and $\text{M} \rightarrow \text{L}$ back-donation by metal d into ψ_3 , we can envision the resonance picture of a butadiene complex shown in Figure 12.17 below.

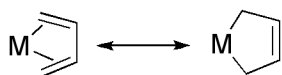


Figure 12.17. Resonance picture of the bonding of butadiene to a TM center.

These principles can readily be extended to larger acyclic systems.

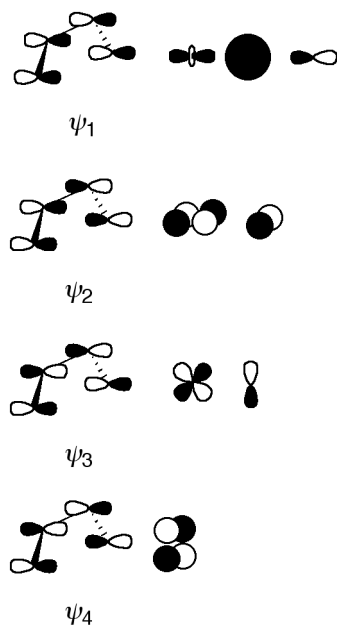


Figure 12.18. Orbital interactions between butadiene π MOs and the appropriate TM AOs.

Moving on from metal complexes of acyclic π systems, we now consider the binding of metals by cyclic, delocalized π systems. The prototypic example of such a complex is the famous molecule ferrocene, Cp_2Fe , which has the possible structures shown in Figure 12.19 below.

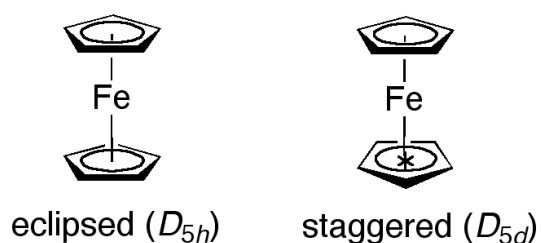


Figure 12.19. Possible structures of ferrocene.

There have been debates over the years about which structure, the eclipsed or the staggered, is the ground-state geometry of ferrocene. Current experimental and theoretical work seems to indicate that the eclipsed geometry is lowest in energy, although the energy difference between eclipsed and staggered is small. Thus, our discussion of bonding will focus on the

eclipsed geometry, although the MO diagram for the staggered case is qualitatively quite similar.

To understand the bonding in ferrocene, we construct group orbitals from the two Cp rings. The π MOs of Cp are constructed using group theory,⁹⁶ and we can divide them into those with 0 nodes, 1 node, and 2 nodes (not counting the node in the plane of the ring), as shown in Figure 12.20 below.

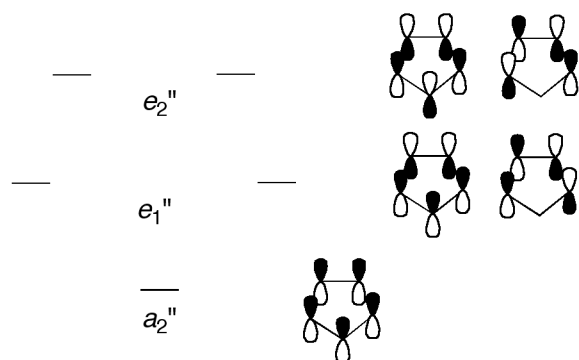


Figure 12.20. π MOs for cyclopentadienyl.

Now, we simply have π MOs with the same number of nodes form in-phase and out-of-phase combinations. For instance, the 0-node MOs can form an in-phase combination (a_1') or an out-of-phase one (a_2''), as shown in Figure 12.21 on the following page. These combinations of Cp MOs can interact with the Fe AOs as shown in Figure 12.22 on the following page.

⁹⁶ A fairly rapid method for the construction of MOs for cyclic conjugated π systems is described in Section 7.3 of *Chemical Applications of Group Theory*, 3rd edition, by F. Albert Cotton, John Wiley & Sons, Inc.: New York, 1990.

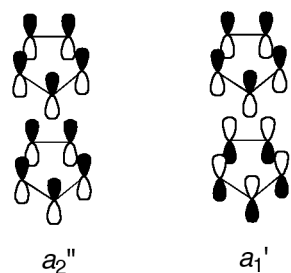


Figure 12.21. An example of in-phase and out-of-phase combinations of MOs for a pair of cyclopentadienyl rings.

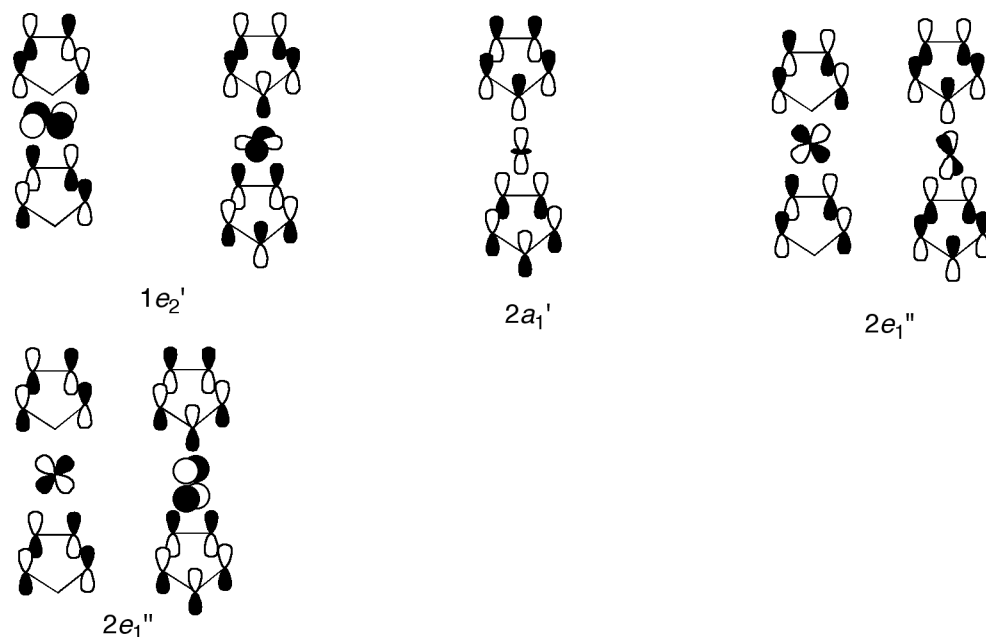


Figure 12.22. MOs of ferrocene arising from interactions between cyclopentadienyl π MOs and Fe AOs.

The MO diagram of ferrocene is shown in Figure 12.23 on the following page. While it may seem horribly complex, we can gain a good qualitative understanding by focusing on the MOs that are predominantly metal d in character: $1e_2'$, which are $3d_{xy}$ and $3d_{x^2-y^2}$ based and bonding, $2a_1'$, which is $3d_{z^2}$ based (with some mixture of $4s$) and roughly (though not rigorously) nonbonding, and $2e_1''$, which are $3d_{xz}$ and $3d_{yz}$ based and antibonding.

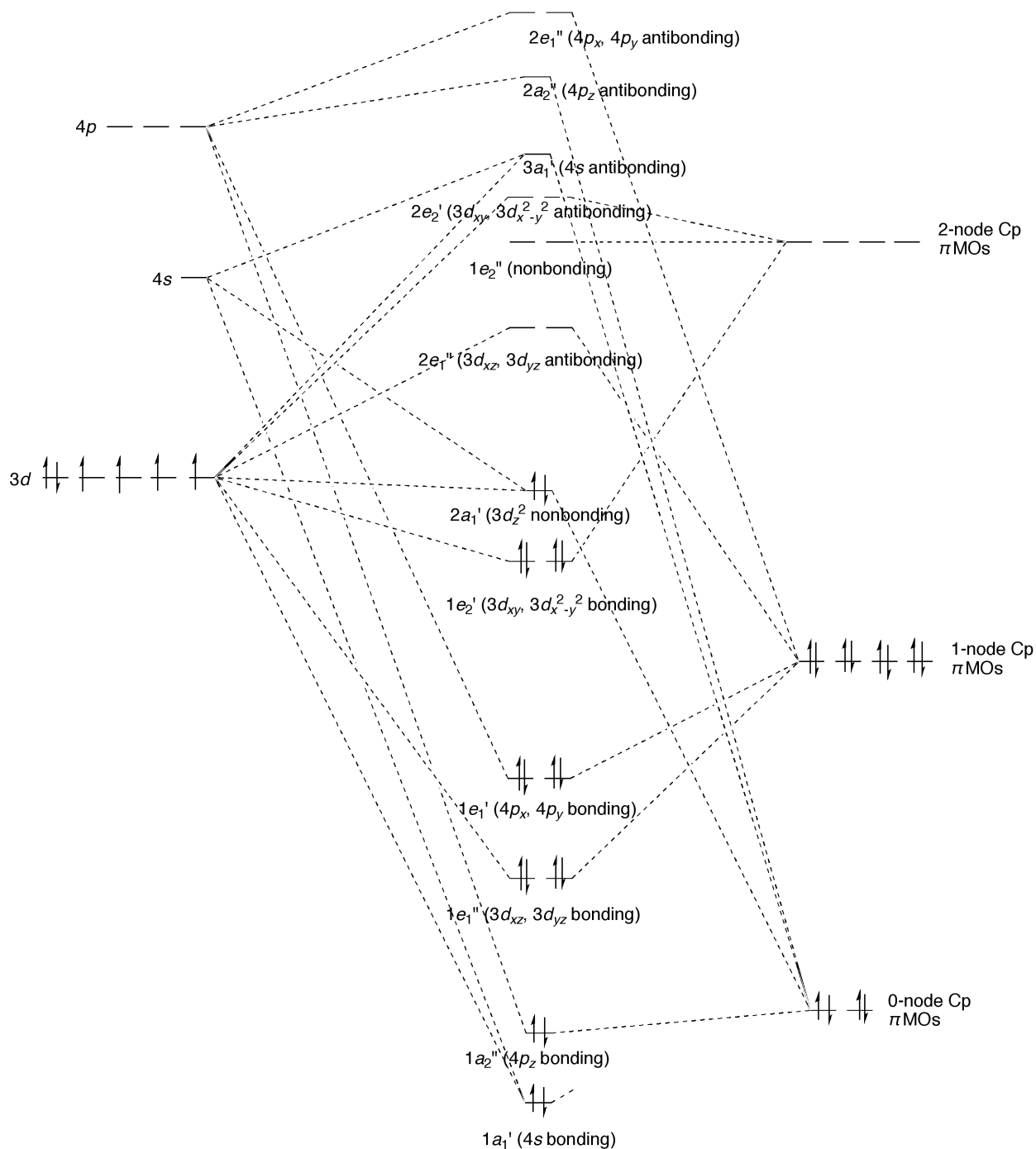


Figure 12.23. Qualitative MO diagram for ferrocene.

If we consider Cp^- to be an anionic ligand (which makes sense, because C_5H_5^- is aromatic, with a Hückel number of 6 π electrons), then the Fe center of ferrocene is Fe(II) and thus d^6 . This means that the lower energy d -based MOs, $1e_2'$ and $2a_1'$, are filled, while the higher-

energy, antibonding d -based MOs, $2e_1''$, are empty. Though the geometry of ferrocene is different from that of an octahedral transition metal complex, we see that once again an 18e configuration leads to all low-energy MOs being occupied, and all high-energy MOs being empty.

Complexes with formula Cp_2M are known as metallocenes, and are a subclass of “sandwich compounds,” complexes in which a metal is “sandwiched” between two parallel cyclic π systems. We have seen that ferrocene is a metallocene that obeys the 18e rule. The other group 8 metallocenes, ruthenocene (Cp_2Ru) and osmocene (Cp_2Os), are also stable, 18e complexes. Also known, however, are metallocenes which do *not* obey the 18e rule, such as cobaltocene (Cp_2Co , 19e) and nickelocene (Cp_2Ni , 20e). Cobaltocene has one unpaired electron, in one of the metal-ligand antibonding $2e_1''$ MOs, and nickelocene has two unpaired electrons, one in each of the antibonding $2e_1''$ MOs. The partial occupation of antibonding MOs is reflected in the structures of the metallocenes: in ferrocene, each metal-carbon distance is 206.4 pm, while the metal-carbon distances in cobaltocene and nickelocene are 211.9 and 219.6 pm, respectively. Clearly, the population of antibonding MOs weakens and lengthens the M-C bonds.

The reactivity differences between ferrocene and metallocenes with over 18e are also dramatic. As we saw with homoleptic metal carbonyl complexes, while a complexes without an 18e count may be stable enough to isolate, it will often be liable to undergo redox reactions that yield an 18e product. The 18e ferrocene is chemically very stable, and can be stored on the benchtop, in air, without fear of decomposition. In contrast, the 19e cobaltocene and 20e nickelocene are good reducing agents, and they must be stored and handled under inert gas (N_2 or Ar), as they will readily react with O_2 in the air. The cobaltocenium cation (Cp_2Co^+), however, is 18e and isoelectronic with ferrocene, and it is also air-stable.

Cp is not the only annulene capable as acting as a ligand for transition metal complexes. The three-membered rings C_3R_3 , classified as C_3R_3^+ for oxidation state purposes (since cyclopropenium cations are aromatic), can act as ligands much like Cp can. Such complexes

are comparatively rare, however, due to the severe ring strain in three-membered rings. Examples include $[(\eta^3\text{-C}_3\text{Ph}_3)\text{Ni}(\text{CO})(\mu\text{-Br})]_2$ and the sandwich complex $\text{CpNi}(\eta^3\text{-C}_3\text{Ph}_3)$.

One recurring feature of organometallic chemistry is the ability of transition metals to stabilize organic ligands that are unstable (to the point of not being isolable) as free molecules. Cyclobutadienes C_4R_4 are classic examples of antiaromatic, 4π electron systems, and the parent cyclobutadiene molecule C_4H_4 will, if formed, immediately react with itself in a Diels-Alder fashion. Several metal complexes with $\eta^4\text{-C}_4\text{R}_4$ ligands have been prepared, and they are generally quite stable: the ligand is best thought of as aromatic $\text{C}_4\text{R}_4^{2-}$. Examples include the chloride-bridged dimers $[(\eta^4\text{-C}_4\text{R}_4)\text{M}(\text{Cl})(\mu\text{-Cl})]_2$ ($\text{M} = \text{Ni}$, $\text{R} = \text{Me}$, or $\text{M} = \text{Pd}$, $\text{R} = \text{Ph}$). Cyclobutadiene itself can be found as a ligand in the complex $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_3$. This complex is a useful reagent in organic synthesis, as oxidation with cerium(IV) salts leads to the loss of C_4H_4 , which can react (as a short-lived intermediate) with other organic molecules in the reaction mixture.

Moving to larger rings than Cp, another classic sandwich complex is bis(benzene)chromium, $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$. This $\text{Cr}(0)$ species is prepared using a reaction analogous to reductive carbonylation: $3 \text{CrCl}_3 + 2 \text{Al} + \text{AlCl}_3 + 6 \text{C}_6\text{H}_6 \rightarrow 3 (\eta^6\text{-C}_6\text{H}_6)_2\text{Cr} + 3 \text{AlCl}_4^-$.

This only reduces $\text{Cr}(\text{III})$ down to $\text{Cr}(\text{I})$; the final reduction to $\text{Cr}(0)$ is accomplished with dithionite ($\text{S}_2\text{O}_4^{2-}$), a common reducing anion.

While the most common binding mode of C_5R_5 ligands is η^5 , as in ferrocene, η^3 and η^1 binding modes are also possible. This is generally seen when $\eta^5\text{-C}_5\text{R}_5$ binding would cause the complex to exceed 18e at the metal. An important example is $(\eta^1\text{-C}_5\text{H}_5)\text{CpFe}(\text{CO})_2$, which is 18e with $\eta^1\text{-C}_5\text{H}_5$ as a 1e ligand, just like a simple alkyl.

An interesting thing is observed when the ^1H NMR spectrum of $(\eta^1\text{-C}_5\text{H}_5)\text{CpFe}(\text{CO})_2$ is taken at room temperature: only two signals are seen, in a 1:1 ratio. Examination of the structure of this compound, however, would suggest that four signals should be seen in a 5:1:2:2 ratio, 5H from the Cp ligand, 1H from the Fe-bound carbon in $(\eta^1\text{-C}_5\text{H}_5)$, and 2H from each of the vinylic positions in $(\eta^1\text{-C}_5\text{H}_5)$. However, it turns out that at room temperature, the Fe moves

from carbon to carbon in the (η^1 -C₅H₅) ligand, in a process somewhat whimsically known as “ring whizzing.” At room temperature, this process occurs more quickly than the acquisition of an NMR spectrum, so we see one signal for Cp and another signal for (η^1 -C₅H₅) that is an average of all the types of carbon in this ligand, since they interchange so quickly. If a ¹H NMR spectrum is obtained at low temperatures, however, the ring whizzing is slower than the spectral acquisition, and the 5:1:2:2 ratio of signals is seen.

Ring whizzing is an example of a general phenomenon called fluxionality. A molecule is considered fluxional if two (or more) chemically nonequivalent groups interchange with each other at appropriate temperatures. An example from organic chemistry is *N,N*-dimethylformamide, HC(O)NMe₂. At room temperature, two methyl signals are observed in the ¹H NMR spectrum of this compound, as they are on different sides of a C-N bond with partial double-bond character. At 100 °C, however, rotation about the C-N bond is faster than spectral acquisition, so an average signal for both methyl groups together is seen. This process is called coalescence. Molecules with five identical substituents in a trigonal bipyramidal geometry are often fluxional, as well. Examples include PF₅ and Fe(CO)₅. We have two different types of substituent (F or CO) in these molecules: axial and equatorial. At low temperatures, we would see two different signals in the ¹⁹F or ¹³C NMR spectrum, but at room temperature, we only see an average, as the two types of substituent are interchanged by a process with a square pyramidal transition state. This process is called the Berry pseudorotation, after its discoverer, R. Stephen Berry (1931-2020).

Returning to cyclopentadienyl complexes, even Cp, or (η^5 -C₅H₅), ligands can exhibit fluxionality. Though each carbon is bound to the metal, rotation of the ligand about the centroid-metal connection is generally rapid at room temperature. As an example, ferrocene can be acetylated much like benzene in the presence of AlCl₃ as a catalyst, according to the reaction $\text{Cp}_2\text{Fe} + \text{MeC(O)Cl} \rightarrow \text{Cp}(\eta^5\text{-C}_5\text{H}_4\text{COMe})\text{Fe} + \text{HCl}$. The resulting acetylferrocene shows only four signals in the room temperature ¹H NMR: one from the methyl, one from each of the types of aromatic proton in the C₅H₄COMe ligand, and one from the unsubstituted Cp protons, which are on average equivalent to each other.

12.6. Metal Alkyl and Carbene Complexes

Thus far, we have considered a variety of organic ligands in which more than one carbon atom binds to a metal through a carbon-based π system. However, many ligands (other than CO and CN $^-$) bind to a metal through just one carbon atom. The simplest such ligands are alkyl groups: methyl, ethyl, *etc.* You have seen main-group metal alkyl species in your organic chemistry classes, since alkyllithium and alkylmagnesium compounds are widely used in synthesis. TM alkyl complexes, however, were thought to be inherently unstable for quite some time, as many attempts to prepare them were unsuccessful. In 1973, however, Geoffrey Wilkinson (1921-1996, Nobel Prize in Chemistry 1973) prepared tetramethyltungsten(VI), WMe $_6$, a complex with an interesting trigonal prismatic coordination geometry, as opposed to the octahedral coordination that might be expected. The W-C bond strength in this compound was found to be an impressive 163 kJ $\cdot$ mol $^{-1}$. We now know that the early failures to prepare metal alkyl complexes was not, in general, due to thermodynamic instability, but to kinetic instability, instead. If an alkyl ligand has at least one hydrogen atom at its beta (β) position, this hydrogen can move from the ligand to the metal, yielding a hydrido ligand and an alkene, in a process known as β -hydrogen elimination or β -hydride elimination, sketched in Figure 12.24 below. This reaction often occurs quite quickly, making the alkyl complex difficult to isolate.

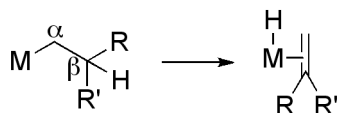


Figure 12.24. A generic example of β -hydrogen elimination.

We will discuss β -hydrogen elimination in more detail in the next chapter, but, given that it is perhaps the most common mode of decomposition for alkyl complexes, it is often easier to prepare alkyl complexes whose alkyl ligands have no β -hydrogens. Examples include neopentyl (CH $_2$ -CMe $_3$), benzyl (CH $_2$ Ph) and 2,2,2-trifluoroethyl (CH $_2$ CF $_3$),⁹⁷ in addition, of course, to methyl itself, which has no β -carbon. As it stands, homoleptic alkyl complexes such

⁹⁷ One can “push arrows” on paper to propose β -halogen elimination, but in practice such reactions very seldom occur.

as WMe_6 are fairly uncommon, but alkyl ligands are common in heteroleptic complexes, such as 18e MeMn(CO)_5 and $16\text{e Pt(Et)(Cl)(PEt}_3)_2$.

The bonding in alkyl complexes is fairly simple: an sp^3 type nonbonding orbital on the carbon interacts with a metal d AO in a σ fashion. In fact, if one uses the donor pair method, one recognizes that methyl anion (CH_3^-) is isoelectronic with ammonia (NH_3), one of the prototypic σ -only ligands. Thus an alkyl ligand is a 2e donor anion (R^-) by the donor pair method, and a 1e ligand ($\text{R}\cdot$) by the neutral ligand method.

The bonding situation is more complicated for species with metal-carbon multiple bonds, known as metal carbene complexes, metal carbenoids, or just “metal carbenes” for short. If we consider complexes with metal-carbon double bonds, we find two main types of complexes, listed as Fischer carbenes and Schrock carbenes in Figure 12.24 below. Here E symbolizes a heteroatom group with at least one lone pair, like an alkoxy group OR or a dialkylamino group NR_2 .

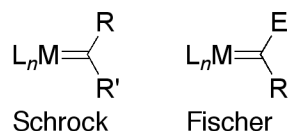


Figure 12.24. Generic structures of Schrock and Fischer carbenes.

These complexes are known as metal carbenes because they contain a carbene as a ligand. A carbene is any electron-deficient species CR_2 , with two single bonds and a lone pair around carbon. The simplest carbene is methylene, CH_2 . In Schrock carbenes, named after Richard Schrock (b. 1945, Nobel Prize in Chemistry 2005), both substituents on carbon, R and R' , are either a hydrocarbyl group (alkyl, alkenyl, aryl) or hydrogen. As free CRR' would have only 6e around carbon, we formally consider it a 2^- ligand: CH_2^{2-} would have an octet around C, being isoelectronic to H_2O . It is thus a 4e dianionic ligand by the donor pair method, and a 2e ligand by the neutral ligand method, somewhat analogous to the oxo (O) ligand. As such, the metal-carbon bonds in Schrock carbene complexes tend to be heavily polarized toward

carbon, with important contribution from the charge-separated resonance structure in Figure 12.25 below.

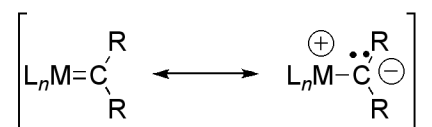


Figure 12.25. Important resonance structures for a Schrock carbene.

Because of this bond polarity, Schrock carbene complexes are usually nucleophilic at carbon, often even reacting with H^+ from moisture, requiring their handling under rigorously dry conditions. In general, metals in Schrock carbene complexes tend to be in high oxidation states (often the highest possible oxidation state for that metal, leading to a d^0 configuration), with the other ligands being σ -only or π -donors, but not π -acceptors. Some important Schrock carbenes are shown in Figure 12.26 below.

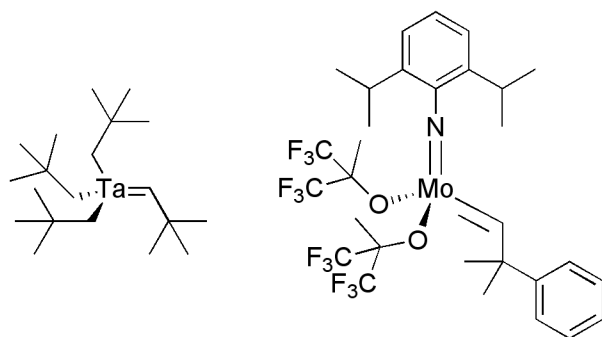


Figure 12.26. Representative Schrock carbenes.

Fischer carbene complexes, named after Ernst Otto Fischer (1918-2007, Nobel Prize in Chemistry 1973),⁹⁸ on the other hand, have as one of their substituents on carbon a group with an electronegative heteroatom bearing at least one lone pair, usually an alkoxy (OR') or

⁹⁸ Fischer's Nobel Prize was not awarded for his work on carbene complexes, but shared with Geoffrey Wilkinson for their independent, but roughly simultaneous, work on metallocenes. His name should not be confused with that of Emil Fischer (1852-1919), who was awarded the 1902 Nobel Prize in chemistry for his work in carbohydrate chemistry. (He lends his name to Fischer projections, used to indicate stereochemistry in the acyclic forms of sugars.)

dialkylamino (NR'_2) group. If we consider a free carbene species $\text{CR}(\text{OR}')$, we can write a resonance structure in which every atom has an octet, as shown in Figure 12.27 below.

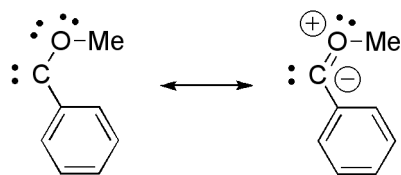


Figure 12.27. Resonance structures for a free carbene with an π -donor substituent.

Because there exists a “closed-shell” (octet rule-satisfying) resonance structure for the free carbene, these carbenes are considered neutral ligands, 2e donors, where the metal-carbon double bond comes from backbonding, as represented by the resonance structures of the Fischer carbene $(\text{OC})_5\text{CrC}(\text{OMe})(\text{Ph})$, shown in Figure 12.28 below.

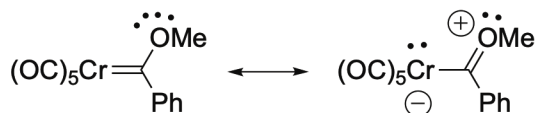


Figure 12.28. Resonance structures for $(\text{OC})_5\text{CrC}(\text{OMe})(\text{Ph})$.

Comparing these resonance structures to the standard resonance structures for a Schrock carbene, we expect that, while Schrock carbenes are nucleophilic at carbon, Fischer carbenes will be electrophilic at carbon. This is, in fact, the reactivity trend generally observed experimentally. The partial double-bond character of the C-O bond in Fischer’s complex is attested by the fact that, at low temperatures, C-O bond rotation is sufficiently slow that one can observe two different methyl signals in the ^1H NMR spectrum of this compound, from the *cis* and *trans* isomers of the C-O bond. In general, while Schrock carbenes have metals in high oxidation states, often with π -donor ligands, Fischer carbenes tend to have metals in low oxidation states (often zero), with π -acceptor ligands such as CO. In fact, Fischer carbene ligands are often prepared from carbonyl ligands, *via* nucleophilic attack by an alkyllithium or aryllithium reagent to form a complex anion, followed by alkylation, as in the example reactions shown in Figure 12.29 on the following page.

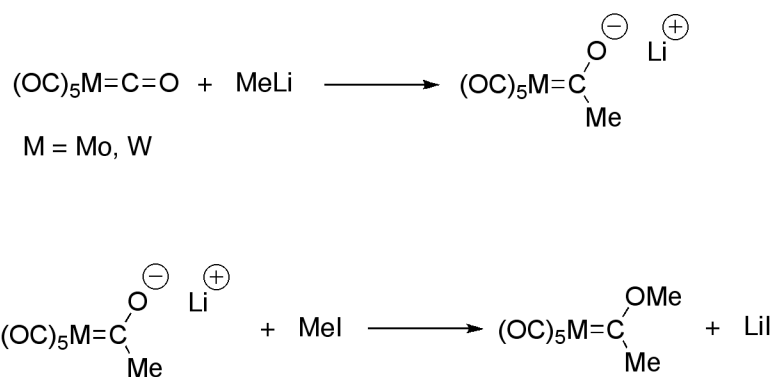


Figure 12.29. Example synthesis of a Fischer carbene complex from a carbonyl complex.

In addition to carbene complexes, with metal-carbon double bonds, there also exist metal carbyne complexes, with metal-carbon triple bonds. One way of preparing a carbyne complex is from a carbene complex, by abstracting one of the substituents on the carbene carbon. Such a synthesis was first accomplished by Fischer, using the Fischer carbene $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})(\text{Me})$ as the starting material, as shown in Figure 12.30 below.

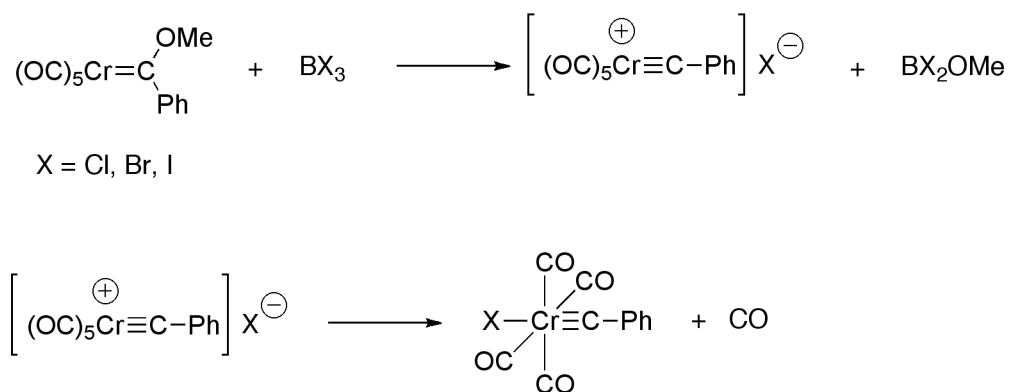


Figure 12.30. Synthesis of a carbyne complex.

In the above reaction, the Lewis-acidic boron trihalide abstracts methoxide (MeO^-) from the carbene, yielding a cationic carbyne complex and halide. A neutral carbyne complex is then formed *via* displacement of CO by halide.

12.7. Complexes with Metal-Hydrogen Bonds

While organometallic chemistry is defined by the presence of metal-carbon bonds, metal-hydrogen covalent bonds are very important as well. We will see that species with metal-hydrogen covalent bonds are very important in organic reactions catalyzed by transition metal complexes. The simplest case of a metal-hydrogen covalent bond is that of the hydrido ligand (sometimes known as a hydride ligand), which is simply a single H atom attached to a metal. It is a 1e ligand by the neutral ligand method, akin to alkyl, and by the donor pair method it is considered the 2e anionic H^- (hydride), assuming that H will be (at least slightly) more electronegative than most transition metals. In practice, the polarity of an M-H bond can go either way. Hydrido complexes of electropositive early metals such as Sc and Zr tend to have substantial H^- character (*e.g.* $\text{Cp}^*_2\text{ZrH}_2$), reacting with water to release H_2 gas just as main-group hydride salts such as NaH and CaH_2 do. In contrast, hydrido complexes with more electronegative late metals and π -acceptor ligands can actually have substantial H^+ character. For instance, HCo(CO)_4 behaves as a Brønsted acid in water, though it is not very water-soluble.

The bonding between a hydrido ligand and a metal is as simple as can be: an H 1s AO interacts with metal AOs in a σ fashion. A more complicated bonding arrangement is present when dihydrogen (H_2), rather than H, acts as a ligand. The first such complexes were prepared in 1984 by the group of Gregory Kubas: *mer-trans*- $\text{M(CO)}_3(\text{PR}_3)_2(\eta^2\text{-H}_2)$, where M = Mo or W and R = cyclohexyl or isopropyl. The structure of this type of complex is shown in Figure 12.31 below.

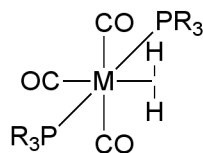


Figure 12.31. Kubas' dihydrogen complexes.

The H_2 ligand is akin to an alkene ligand in that, rather than donating a lone pair of electrons to a metal, it uses a pair of electrons in a bonding MO. The difference is that an alkene donates

electrons from a π bonding MO, whereas H_2 donates from a π bonding MO. There is also backbonding into the σ antibonding MO of the H_2 ligand, as shown in Figure 12.32 below.



Figure 12.32. Orbital interactions in the bonding of H_2 to a TM center.

Both the forward bonding and the backbonding decrease the H–H bond order. If the metal with its other ligands is electron-rich enough, the backbonding will cause the H_2 σ antibonding MO to be occupied enough that the H–H bond breaks, and a dihydrido complex is formed, as in Figure 12.33 below.

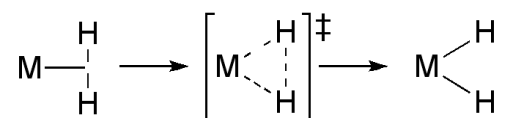


Figure 12.33. Oxidative addition of H_2 to form a pair of hydrido ligands.

If this occurs, it is an example of a reaction type called oxidative addition: since H_2 is a neutral ligand, and H is considered to be H^- for the assignment of TM oxidation states, the TM will have increased its oxidation state by two units. H_2 gas will react with a variety of electron-rich metal fragments to form dihydrido complexes, while it will form dihydrogen complexes with more electron-poor fragments. For instance, while $\text{Mo}(\text{CO})_3(\text{P}^i\text{Pr}_3)_2(\eta^2\text{-H}_2)$, with three electron-withdrawing CO ligands, is a dihydrogen complex, $\text{Mo}(\text{PMe}_3)_5(\text{H})_2$, with five strongly σ -donating ligands and no π -acceptors, is a dihydrido species. Other complexes with σ bonds as donors are known, especially C–H examples.

12.8. Phosphines and Related Ligands

The final general class of “honorary organometallic” ligands that we will consider in detail are the phosphines, PR_3 , where $\text{R} = \text{H}$, an organic group, or a heteroatom. Strictly speaking, molecules PX_3 where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ are usually called phosphorus trihalides, and molecules $\text{P}(\text{OR})_3$ are called phosphites, but we will consider them together with phosphines *per se*, as

their bonding to transition metals is similar in many respects. Phosphines are σ -donor ligands much like ammonia and amines, donating a pair of electrons from a roughly nonbonding, sp^3 -hybrid orbital on phosphorus. In another respect, however, phosphines are more akin to CO than to amines: they are π -acceptors.

How can phosphines act as π -acceptors? Traditionally, their π -acceptor ability was explained by invoking the use of $3d$ atomic orbitals on phosphorus. While the $3s$ and $3p$ AOs are used in the lone pair and the bonding of phosphorus to its substituents, the empty $3d$ AOs were assumed to accept electron density from metal d AOs *via* π -backbonding. This traditional model has been called into severe question, however, by more recent computational results. These results indicate that, while P $3d$ AOs have the appropriate symmetry to interact with metal d orbitals, the *energy* of P $3d$ orbitals is simply too high for this interaction to be significant.⁹⁹ Instead, the currently prevailing view is that the π -backbonding occurs by donation of electron density from filled metal d orbitals into empty phosphine MOs that are P-R σ -antibonding in character, as shown in Figure 12.34 below.



Figure 12.34. A schematic of TM $\rightarrow$ phosphine backbonding that does not require the participation of P $3d$ AOs.

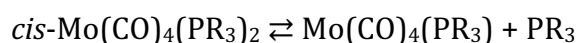
This type of interaction strengthens the M-P bond while weakening each of the P-R bonds. Experimental support for this model comes from the fact that in the cation $[\text{CpCo}(\text{PEt}_3)_2]^+$, the Co-P distance is 223.0 pm and the P-C distances are 182.9 pm, while in the neutral complex $\text{CpCo}(\text{PEt}_3)_2$, where more electron density is available for backbonding, the Co-P distance decreases to 221.8 pm, while the P-C distances increase to 184.6 pm. The degree of backbonding depends greatly on the electron-withdrawing ability of the substituents on P:

⁹⁹ The fact that the interaction is symmetry-allowed means that the contribution of P $3d$ AOs to the bonding cannot be precisely zero, to infinitely many significant digits. Qualitatively, however, it is not the primary mechanism of backbonding.

while there is little backbonding to trialkylphosphine ligands like PMe_3 and PEt_3 , there is heavy backbonding to phosphites and PF_3 . In fact, PF_3 is about as good of a π -acceptor as CO, and $\text{Ni}(\text{PF}_3)_4$, analogous to $\text{Ni}(\text{CO})_4$, is a well-known, stable compound. Triarylphosphines like PPh_3 are intermediate: they are better acceptors than trialkylphosphines due to the fact that sp^2 carbons are more electronegative than sp^3 ones, but they are still much poorer acceptors than PF_3 or $\text{P}(\text{OR})_3$.

Phosphines are very useful ligands because they are available with a wide variety of substituents, that differ in both their steric and electronic properties. Larger R groups lead to bulkier ligands, which can have strong effects on complex reactivity. One measure of phosphine bulkiness is called the Tolman cone angle θ , after Chadwick Tolman (1938-2024). This is the apex angle formed by a metal-bound phosphine and its substituents, with the apex being at the metal atom, not P. Relatively small phosphines include PH_3 , PF_3 , and PMe_3 ($\theta = 87^\circ$, 104° , and 118° , respectively), while some common bulky phosphines include PPh_3 (145°), PtBu_3 (182°), and $\text{P}(\text{mesityl})_3$ (212°).

Though the Tolman θ parameter is not a rigorous quantity (Tolman originally obtained the values by measurements on wooden models of molecules!), it is very useful in rationalizing reactivity differences. For instance, consider the following ligand substitution reaction: $\text{cis-Mo}(\text{CO})_4(\text{PR}_3)_2 + \text{CO} \rightarrow \text{Mo}(\text{CO})_5(\text{PR}_3) + \text{PR}_3$. This reaction has been shown to proceed by a dissociative mechanism, with the first (dissociative) step being rate-determining:



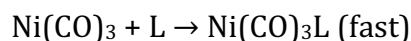
The reaction is much faster with bulkier phosphines, which dissociate more readily in the rate-determining first step, relieving steric strain. With PMePh_2 ($\theta = 136^\circ$), $k = 1.3 \times 10^{-5} \text{ s}^{-1}$, while with the larger PPhCy_2 ($\theta = 162^\circ$, Cy = cyclohexyl), $k = 6.4 \times 10^{-2} \text{ s}^{-1}$, an increase by a factor of over 4900.

It is worth noting that the only stable isotope of phosphorus is ^{31}P , with 100% natural abundance (^{32}P , a β -emitter with a half-life of 14.3 days, is often used by biochemists and

molecular biologists in radiolabeling experiments). Since ^{31}P has a nuclear spin of $\frac{1}{2}$, like ^1H and ^{13}C , phosphorus-containing compounds are commonly characterized by ^{31}P NMR in tandem with ^1H and ^{13}C NMR.

12.9. Ligand Substitution on Carbonyl Complexes and Related Species

Many homoleptic carbonyl complexes behave similarly to Werner-type coordination complexes in that they undergo dissociative substitution. Mond's complex $\text{Ni}(\text{CO})_4$ reacts with 2e ligands L such as phosphines, according to the reaction $\text{Ni}(\text{CO})_4 + \text{L} \rightarrow \text{Ni}(\text{CO})_3\text{L} + \text{CO}$. The rate law for this reaction is found to be $r = k[\text{Ni}(\text{CO})_4]$, the value of k does not vary significantly when L is changed from PPh_3 , to AsPh_3 , to SbPh_3 , and the entropy of activation $\Delta S^\ddagger$ is greater than $+10 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. These experimental observations are all consistent with the following *D* mechanism involving a rate-determining (slow) dissociation step and the 16e intermediate $\text{Ni}(\text{CO})_3$:



Note that the first, dissociative step is written with a simple forward arrow, *not* equilibrium arrows ($\rightleftharpoons$). This is because, since CO is a gas, it will likely leave the reaction mixture, making the first step effectively irreversible, unless the reaction is conducted in a tightly sealed vessel under a considerable pressure of CO.

Some carbonyl substitution reactions proceed with a two-term rate law, indicating that the reaction proceeds by two different mechanisms, both of which occur to some extent. For example, the reaction $\text{Cr}(\text{CO})_6 + \text{L} \rightarrow \text{Cr}(\text{CO})_5\text{L} + \text{CO}$, where L is a 2e ligand such as a phosphine, has the experimentally observed rate law $r = k[\text{Cr}(\text{CO})_6] + k'[\text{Cr}(\text{CO})_6][\text{L}]$. Angelici proposed¹⁰⁰ that this reflects a *D* mechanism as previously discussed (the first-order term) occurring concomitantly with an *A* mechanism (the second-order term). On the other hand, the reaction $\text{Mo}(\text{CO})_5\text{A} + \text{L} \rightarrow \text{Mo}(\text{CO})_5\text{L} + \text{A}$, where A is an amine (also a 2e ligand) and L is an amine, phosphine, phosphite, or arsine, also has a two-term rate law, with the form

¹⁰⁰ Graham, J. R.; Angelici, R. J. *Inorganic Chemistry* **1967**, 6, 2082-2085.

$r = k[\text{Mo}(\text{CO})_5\text{A}] + k'[\text{Mo}(\text{CO})_5\text{A}][\text{L}]$. Brown interpreted¹⁰¹ this rate law not in terms of competing *D* and *A* mechanisms, but instead in terms of competing *D* and *I_d* mechanisms. This avoids having to invoke a seven-coordinate *A* intermediate in the mechanism represented by the second-order term. Despite these two-term rate laws sometimes observed, however, it does appear that many ligand substitution reactions of carbonyl complexes and similar species with low metal oxidation states do proceed *via* genuine *D* mechanisms.

It is reasonable to wonder if ligand substitution reactions on carbonyl complexes proceed according to similar trends as Werner-type complexes in terms of metal, *d* electron count, charge, solvent, *etc.* It turns out that many of these trends do *not* carry over. For octahedral Werner-type metal complexes, *d* electron count has a very significant effect on the rate of substitution, due to considerations of LFSE, LFAE, and the Jahn-Teller effect. There is less of a clear pattern for organometallic complexes. This can be understood by recognizing that a great many stable organometallic complexes are 18e species. We have seen that octahedral complexes follow the 18e rule only if they are low-spin *d*⁶. But an 18e system can occur with different *d* electron counts if the geometry is different, as we see with *d*⁸, trigonal-bipyramidal Fe(CO)₅ and *d*¹⁰, tetrahedral Ni(CO)₄. Thus, LFSE and LFAE are not predictable by a simple formula, because the coordination geometries of the starting complex and intermediate vary much more than among octahedral complexes with square-pyramidal intermediates. In terms of substitution rates, it is generally observed that lability increases in the order Fe(CO)₅ < Cr(CO)₆ < Ni(CO)₄, but this is difficult to rationalize with any simple theory.

Ligand substitution on Werner-type coordination complexes tends to be slower the more highly charged the complex is. This makes sense, since the ligands in these complexes tend either to be anionic (*e.g.* halides) or neutral but strongly dipolar (*e.g.* water, ammonia). Thus, there is a Coulombic disadvantage to loss of a negatively charged ligand (or the negative end of a neutral one). In contrast, CO is not a strongly polar molecule, and phosphines PR₃

¹⁰¹ Covey, W. D.; Brown, T. L. *Inorganic Chemistry* **1973**, *12*, 2820-2825.

generally have much smaller dipole moments than amines NR_3 . Because of this, the charge of carbonyl and phosphine complexes does not have a great effect on their rates of substitution. The isoelectronic species $\text{V}(\text{CO})_6^-$, $\text{Cr}(\text{CO})_6$, and $\text{Mn}(\text{CO})_6^+$ all react fairly slowly, and $\text{Ni}(\text{CO})_4$ actually undergoes *faster* substitution than the isoelectronic $\text{Co}(\text{CO})_4^-$, the *opposite* to what one would expect for Werner-type complexes. For Werner-type complexes, rates of substitution of a given type of complex ML_6^{n+} tend to decrease down a column of the Periodic Table (*e.g.* $\text{Fe} > \text{Ru} > \text{Os}$). For carbonyl and phosphine complexes, however, the second-row metal is often the most reactive, and it varies whether the first-row metal reacts faster than the third-row metal, or *vice versa*. For instance, in terms of ligand substitution reaction rates, $\text{Mo}(\text{CO})_6 > \text{Cr}(\text{CO})_6 > \text{W}(\text{CO})_6$, but $\text{Pd}\{\text{P}(\text{OEt})_3\}_4 > \text{Pt}\{\text{P}(\text{OEt})_3\}_4 > \text{Ni}\{\text{P}(\text{OEt})_3\}_4$. Solvent effects are small for ligand substitution on carbonyl and phosphine complexes due to the dissociation of less polar, neutral molecules, so there is unlikely to be a significant difference between the reactant and transition state in terms of polarity and differential solvation.

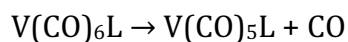
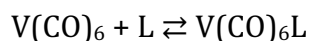
Many heteroleptic carbonyl complexes (complexes with CO and at least one other type of ligand) undergo replacement of CO with an incoming ligand. In such cases, the other (ancillary) ligands can have an effect on the rate of dissociative substitution of CO. For reactions of the sort $\text{Cr}(\text{CO})_5\text{L} + \text{L}' \rightarrow \text{Cr}(\text{CO})_4\text{LL}' + \text{CO}$, the rates increase depending on the identity of the ancillary ligand L according to $\text{CO}, \text{H}^- < \text{P}(\text{OPh})_3 < \text{PPh}_3 < \text{I}^- < \text{py} < \text{Br}^-, \text{MeCN} < \text{Cl}^- < \text{MeCO}^- < \text{NO}_3^-$. In general, good donor ligands (both σ and π) speed dissociation of CO by providing more electron density to the 16e $\text{Cr}(\text{CO})_4\text{L}$ intermediate (and the transition state leading to it). If L is not a π -acceptor ligand, then the CO that leaves is usually one that is *cis*, rather than *trans*, to L, leading to a product $\text{Cr}(\text{CO})_4\text{LL}'$ with *cis* stereochemistry.

There are also significant ligand effects when a ligand other than CO dissociates. For reactions of the sort $\text{NiL}_4 + \text{L}' \rightarrow \text{NiL}_3\text{L}' + \text{L}$, or *cis*- $\text{Mo}(\text{CO})_4\text{L}_2 + \text{CO} \rightarrow \text{Mo}(\text{CO})_5\text{L} + \text{L}$, where L is a phosphorus ligand, the reaction rates were generally faster for bulkier ligands L, with larger Tolman cone angles θ . This makes sense for a ligand substitution process with rate-determining dissociation: the larger the departing ligand is, the more steric strain will be relieved when it dissociates, leading to a lower activation energy. Note that ordering rates

according to the sterics of the departing ligand is only reliable when the ligands being compared are electronically similar. Phosphites P(OR)_3 may dissociate more slowly than trialkylphosphines PR_3 , even if the phosphites are larger, because phosphites are better π -acceptors, and tend to be more strongly bound for that reason.

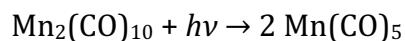
12.10. Ligand Substitution on Odd-Electron Organometallic Complexes

While most metal carbonyl complexes studied are diamagnetic, 18e species, paramagnetic (usually 17e) species can display striking differences in reactivity. For instance, the 18e complex anion V(CO)_6^- is quite inert to ligand substitution: it does not react in molten PPh_3 at 80 °C. In contrast, the neutral, 17e complex V(CO)_6 undergoes ligand substitution much more rapidly than 18e carbonyl complexes. More striking still, it does so *via* an associative mechanism. For reactions of the sort $\text{V(CO)}_6 + \text{L} \rightarrow \text{V(CO)}_5\text{L} + \text{CO}$, in which L is a 2e ligand, the rate law has the form $r = k[\text{V(CO)}_6][\text{L}]$, and entropies of activation $\Delta S^\ddagger$ are between -23 and -28 $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, suggesting an A mechanism:

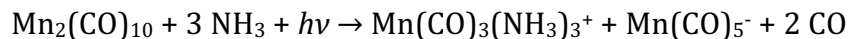


While the intermediate $\text{V(CO)}_6\text{L}$ is seven-coordinate, it is only 19e, rather than 20e, and is believed to be much lower in energy than a 20e seven-coordinate intermediate. In this intermediate, there may be a weak, three-electron bond (with a bond order of approximately $\frac{1}{2}$) involving an unpaired electron in a *d*-type MO on V and the two electrons donated by L. One can, roughly, think of this “half-bond” as corresponding to two electrons in a bonding MO and one electron in an antibonding MO.

V(CO)_6 is unusual in that it is a 17e species that is kinetically stable enough to isolate. One can, however, generate less stable 17e species transiently, as reaction intermediates. One way to do this is to start with a bimetallic complex $\text{M}_2(\text{CO})_n$, 18e at each metal, and cleave the M–M bond in a homolytic fashion *via* photolysis (exposure of the reaction mixture to high-energy photons of the appropriate wavelength), yielding two 17e radicals. For instance, Mn(CO)_5 can be generated from photolysis of $\text{Mn}_2(\text{CO})_{10}$:

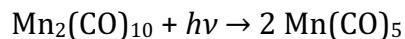


These $\text{Mn}(\text{CO})_5$ radicals can then undergo both ligand substitution and electron transfer, as in the following reaction, which proceeds *via* a radical chain mechanism:

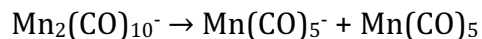
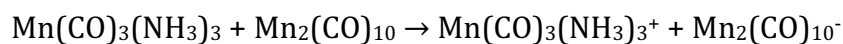
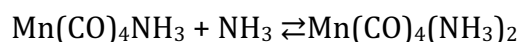
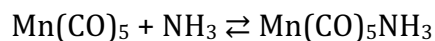


A plausible chain mechanism for this reaction is as follows:

Initiation:



Propagation:



Photolysis of monometallic 18e carbonyl complexes can also increase the rates of ligand substitution. The excited state will have an electron promoted from a weakly bonding MO (t_{2g} for an octahedral complex) to a strongly antibonding MO (e_g for an octahedral complex), thus weakening the M–CO bonds, promoting dissociation. Catalytic amounts of a single-electron oxidizing or reducing agent can also promote ligand substitution, by temporarily forming either a 17e complex (which readily undergoes substitution by the *A* mechanism) or a 19e complex (which readily undergoes substitution by the *D* mechanism).

12.11. Ligand substitution on Bimetallic Complexes

Ligand substitution can occur on bimetallic complexes as well as on monometallic ones. The Group 7 carbonyl species $\text{M}_2(\text{CO})_{10}$, where $\text{M} = \text{Mn}, \text{Tc},^{102} \text{ or Re}$, as well as the

¹⁰² Technetium has no stable isotopes. However, it is possible to do synthetic chemistry with it, since its longest-lived isotope, ⁹⁷Tc (which decays to ⁹⁷Mo *via* electron capture) has a half-life of 4.21 million years, plenty of time to run chemical reactions. Tc chemistry is very important in medicine: the metastable nuclear isomer ^{99m}Tc has a half-life of 6 hours and decays *via* γ -ray emission to ⁹⁹Tc. (⁹⁹Tc itself decays *via* β -emission to ⁹⁹Ru, with a half-life

heterobimetallic complex $\text{MnRe}(\text{CO})_{10}$, have been most thoroughly studied. Substitution generally occurs *trans* to the metal-metal bonds, and if two CO ligands are replaced, one CO is usually replaced at each metal, as shown in Figure 12.35 below.

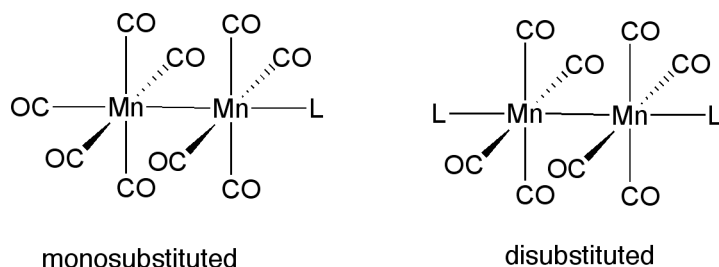


Figure 12.35. Structures of mono- and disubstituted derivatives of $\text{Mn}_2(\text{CO})_{10}$.

For substitution reactions of the type $\text{M}_2(\text{CO})_{10} + \text{L} \rightarrow \text{M}_2(\text{CO})_9\text{L} + \text{CO}$, where L is a 2e ligand a two-term rate law is observed: $r = k[\text{M}_2(\text{CO})_{10}] + k'[\text{M}_2(\text{CO})_{10}][\text{L}]$ This is generally taken to reflect solvent-dependent and solvent-independent I_d mechanisms operating in parallel, as in the case of substitution on $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_5(\text{amine})$. One cannot, however, rule out parallel D and A mechanisms as an alternative.

It is reasonable to ask whether such substitution reactions involve homolytic cleavage of the metal-metal bond and formation of 17e $\text{M}(\text{CO})_5$ radical species. As we have discussed above, 17e species undergo substitution *via* the A mechanism considerably faster than 18e species substitute by the D or I_d pathways. A clever isotopic labeling experiment by Muetterties,¹⁰³ however, indicates that such a metal-metal bond cleavage does *not* occur when $\text{M} = \text{Re}$. The two common isotopes of Re are ^{185}Re and ^{187}Re .¹⁰⁴ Muetterties prepared isotopically pure $^{185}\text{Re}_2(\text{CO})_{10}$ and $^{187}\text{Re}_2(\text{CO})_{10}$ and had a mixture of these two species react with PPh_3 . Mass spectral analysis of the reaction products showed the presence of the monosubstituted

of 2.11×10^5 years.) When $^{99\text{m}}\text{Tc}$ is given to a patient, the γ -rays that it emits allow for imaging of various organs and tissues.

¹⁰³ Stolzenberg, A. M.; Muetterties, E. L. *Journal of the American Chemical Society* **1983**, *105*, 822-827.

¹⁰⁴ While ^{185}Re is stable, ^{187}Re is not, since it decays *via* β^- -emission. However, it can be considered stable for most practical purposes, since its half-life is 4.16×10^{10} years.

products $^{185}\text{Re}_2(\text{CO})_9\text{PPh}_3$ and $^{187}\text{Re}_2(\text{CO})_9\text{PPh}_3$, as well as the disubstituted products $^{185}\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ and $^{187}\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$. However, no products of the form $^{185}\text{Re}^{187}\text{Re}(\text{CO})_9\text{PPh}_3$ or $^{185}\text{Re}^{187}\text{Re}(\text{CO})_8(\text{PPh}_3)_2$ were observed. If Re–Re bond cleavage occurred, one would expect to see a statistical distribution of Re isomers in the products, as 17e ReL_5 radicals recombined with each other: 25% $^{185}\text{Re}_2$, 25% $^{187}\text{Re}_2$, and 50% $^{185}\text{Re}^{187}\text{Re}$. The fact that no mixed-isotope dimers were found is thus strong evidence against Re–Re bond cleavage. This is an example of a general strategy in mechanistic study known as a crossover experiment, where one expects to find mixtures of groups from the reactants among the products if one mechanism is operative, and not if another is. Crossover experiments can use different isotopes of the same element, as in the above case, or different, but fairly similar groups (*e.g.* methyl vs. ethyl).

The fluxionality of carbonyl ligands, namely, their ability to rapidly interconvert between terminal and bridging geometries, has significant consequences in bimetallic ligand substitution. It is known that $\text{Mn}_2(\text{CO})_{10}$ is more reactive toward ligand substitution than $\text{Re}_2(\text{CO})_{10}$, that is, reactions of the form $\text{Mn}_2(\text{CO})_{10} + \text{L} \rightarrow \text{Mn}_2(\text{CO})_9\text{L} + \text{CO}$ are faster than those of the type $\text{Re}_2(\text{CO})_{10} + \text{L} \rightarrow \text{Re}_2(\text{CO})_9\text{L} + \text{CO}$. However, Atwood found that reaction of the heterobimetallic species $\text{MnRe}(\text{CO})_{10}$ with PPh_3 primarily gave substitution at Re, rather than Mn, that is, the major product was $(\text{OC})_5\text{Mn}-\text{Re}(\text{CO})_4\text{PPh}_3$, with $\text{Ph}_3\text{P}(\text{OC})_4\text{Mn}-\text{Re}(\text{CO})_5$ present only as a minor product. How can this result be explained? Note that cleavage of the Mn–Re bond is ruled out by the fact that no species with Mn–Mn or Re–Re bonds were observed among the products; the formation of such species would be expected if the 17e species $\text{Mn}(\text{CO})_5$ and $\text{Re}(\text{CO})_5$ were present.

Atwood proposed¹⁰⁵ the mechanism shown in Figure 12.36 on the following page, in which CO initially dissociates from the more labile Mn, but then a CO from Re migrates to Mn *via* a bridging (μ -CO) intermediate, opening up an empty coordination site on Re, to which PPh_3

¹⁰⁵ Sonnenberger, D.; Atwood, J. D. *Journal of the American Chemical Society* **1980**, *102*, 3484–3489.

adds. The intermediate with an empty coordination site on Mn occasionally reacts with PPh_3 before the CO migration occurs, accounting for the Mn-substituted minor product.

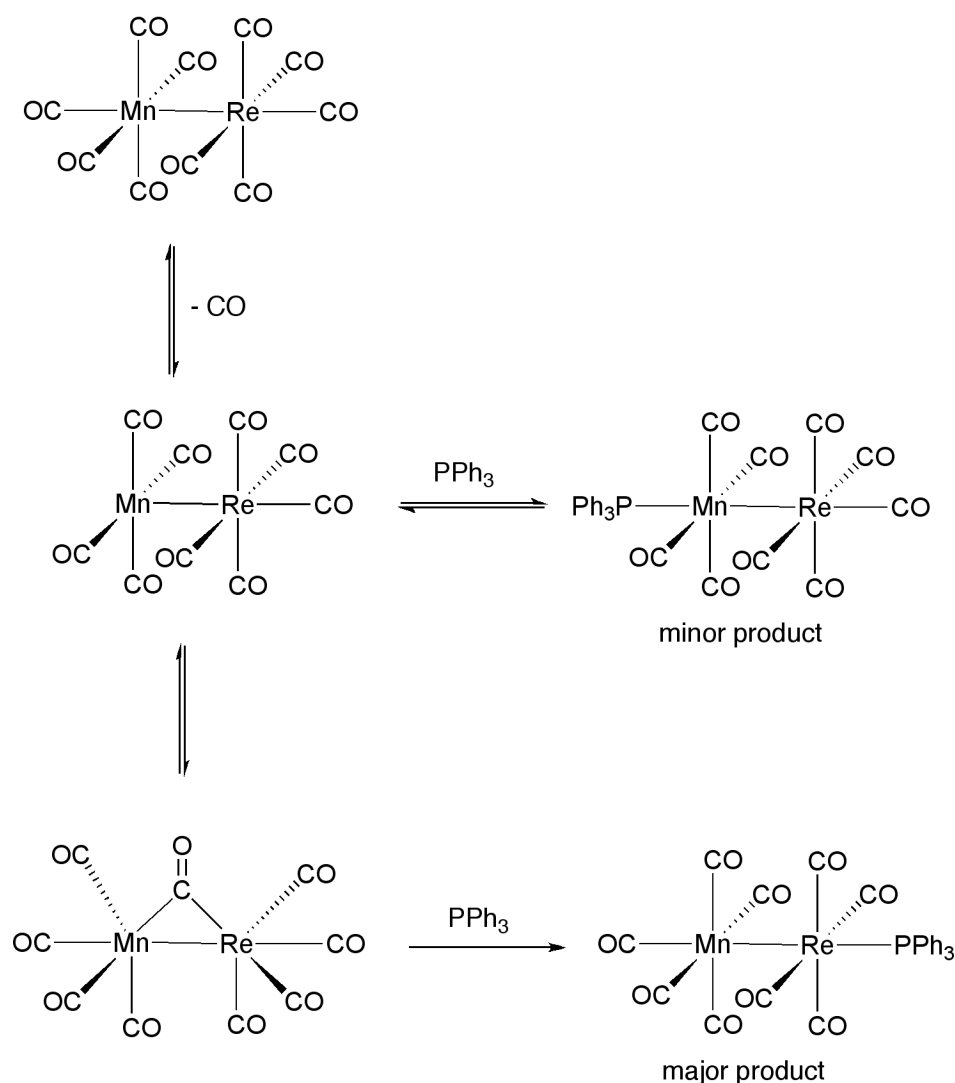


Figure 12.36. Proposed mechanism for ligand substitution on MnRe(CO)_{10} .

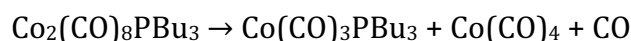
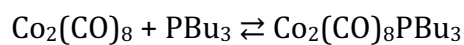
The reactivity of bimetallic species toward substitution does depend on the metal. The Group 9 dimer $\text{Co}_2(\text{CO})_8$ undergoes some substantially different reactions than $\text{Mn}_2(\text{CO})_{10}$ and its congeners, and the reactions are notably ligand-dependent. $\text{Co}_2(\text{CO})_8$ undergoes simple ligand substitution with AsPh_3 (the arsenic analog of PPh_3 , which binds to metals in similar fashion): $\text{Co}_2(\text{CO})_8 + \text{AsPh}_3 \rightarrow \text{Co}_2(\text{CO})_7\text{AsPh}_3 + \text{CO}$. Based on the rate law $r = k[\text{Co}_2(\text{CO})_8]$ and the entropy of activation $\Delta S^\ddagger = +10 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, this reaction appears to proceed *via* a

straightforward *D* mechanism. When a phosphine such as PBu_3 is used as the incoming ligand, however, the net reaction is considerably different:

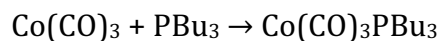
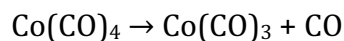
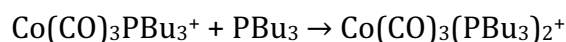
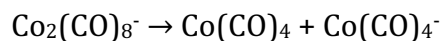
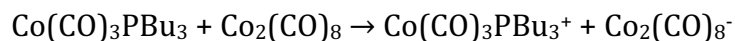


Note that this is a disproportionation reaction with respect to cobalt: $\text{Co}_2(\text{CO})_8$ is a $\text{Co}(0)$ species, while the cation $\text{Co}(\text{CO})_3(\text{PBu}_3)_2^+$ is $\text{Co}(\text{I})$ and the anion $\text{Co}(\text{CO})_4^-$ is $\text{Co}(-\text{I})$. The rate law had a noninteger order in $[\text{Co}_2(\text{CO})_8]$, whose value varied depending on the temperature and $[\text{PBu}_3]$. Noninteger reaction orders are often observed for reactions that proceed *via* radical chain mechanisms, and Brown proposed the following mechanism for this reaction.¹⁰⁶

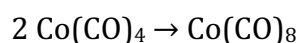
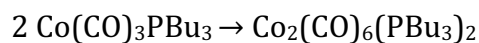
Initiation:



Propagation:



Termination:



In general, phosphines are stronger nucleophiles than arsines, which is probably why the first initiation step, an associative reaction between $\text{Co}_2(\text{CO})_8$ and a ligand, occurs with PBu_3 but not with AsPh_3 .

¹⁰⁶ Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *Journal of the American Chemical Society* **1980**, 102, 6248-6254.

Chapter 13: Fundamental Organometallic Reactions

13.1. Oxidative Addition and Reductive Elimination

One of the most important types of reactions in organometallic chemistry is oxidative addition (often abbreviated as OA and sometimes as “oxad”), which takes (very generally) the form $L_nM + X-Y \rightarrow L_nM(X)(Y)$. Oxidative addition thus consists of the *formal* insertion of a metal (with ancillary ligands) into a single bond of another reagent, breaking that bond and forming two new metal-ligand bonds: M-X and M-Y. It is called oxidative addition because X and Y are both 1e ligands (by the neutral ligand method) and anionic as closed-shell species (X^- and Y^-), so if the metal center has oxidation state m prior to the addition, it will have oxidation state $m + 2$ after. This means that no d^0 metal complex may undergo oxidative addition: the d electron count must be d^2 or greater. Since both X and Y are 1e ligands, oxidative addition results in an increase of electron count by 2, so the starting metal L_nM will almost certainly be 16e (or sometimes 14e), not 18e, so as not to give a 20e product. Often an 18e complex will undergo oxidative addition after dissociation of a 2e ligand (*e.g.* CO or PR_3) to form a coordinatively unsaturated, 16e intermediate. Common reagents that can oxidatively add to metals include Cl_2 , Br_2 , H_2 , HCl, HBr, HI, RCl, RBr, RI, ArCl, ArBr, ArI, RH, and ArH, where R refers to an alkyl group and Ar to an aryl group. It is important to emphasize at this point that oxidative addition refers to a net reaction, *not* its mechanism. Just as a nucleophilic substitution reaction in organic chemistry can proceed by an S_N1 , S_N2 , radical, or other mechanism, oxidative addition can proceed by any of several different mechanisms.

The reverse of oxidative addition is known as reductive elimination (often abbreviated RE), and can be represented generally as $L_nM(X)(Y) \rightarrow L_nM + X-Y$. Reductive elimination decreases the electron count at the metal by 2, as well as decreasing the metal's oxidation state by 2. Because of the principle of microscopic reversibility, the mechanism of any reductive elimination reaction will be the reverse of that of the corresponding oxidative addition.

The first mechanism of oxidative addition that we will consider is often called the “concerted mechanism,” though we will see that this term is sometimes a misnomer. Let us consider the oxidative addition of H_2 to the 16e, square planar iridium complex *trans*- $\text{Ir}(\text{PEt}_3)_2(\text{CO})\text{Cl}$, shown in Figure 13.1 below. The first step is coordination of H_2 as a ligand, as we have previously discussed, with the electrons in the H-H bond being donated to the metal. Back donation into the H-H antibonding MO, from the electron-rich Ir(I) center, then causes the H-H bond to break, resulting in the 18e Ir(III) complex $\text{Ir}(\text{PEt}_3)_2(\text{CO})\text{Cl}(\text{H})_2$, with the new hydride ligands *cis* and the phosphines still *trans*. Because of the three-membered ring transition state, in which an H-H bond is broken and two Ir-H bonds are formed, the H ligands must end up *cis* in the product.

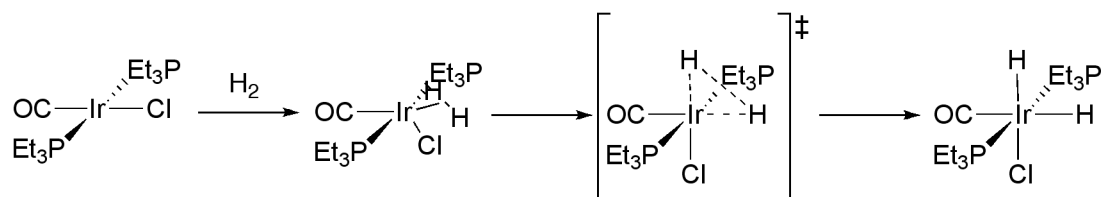


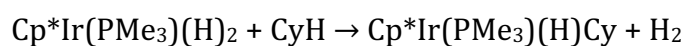
Figure 13.1. Oxidative addition of H_2 to *trans*- $\text{Ir}(\text{PEt}_3)_2(\text{CO})\text{Cl}$.

While this is not, strictly speaking, a concerted reaction, since it has an intermediate dihydrogen complex, the two H ligands do assume their final positions as the metal is oxidized. Some oxidative additions of H_2 , however, are believed to be genuinely concerted, with the η^2 coordination of H_2 present in a transition state (a local maximum of free energy vs. reaction progress) as opposed to a reactive intermediate (a local minimum). One cannot predict which will be the case simply from the reaction equation.

A similar “concerted” pathway generally applies for the oxidative addition of other reagents with fairly nonpolar bonds: R-H, Ar-H, Si-H, B-B. Most of these reactions are believed to proceed *via* an intermediate containing a σ -bond ligand (*e.g.* $\eta^2\text{-RH}$), rather than being truly concerted. Oxidative addition of Ar-Cl and Ar-Br usually also proceed by this mechanism, even though those bonds are significantly polar.

The oxidative addition of C-H bonds is commonly known as “C-H bond activation” or simply “C-H activation,” and it is critically important in the use of organometallic chemistry in organic synthesis. Most C-H bonds in organic compounds are relatively unreactive, with exceptions when they are significantly acidic, such as in cyclopentadiene or C-H bonds α to a carbonyl or nitro group. Thus, a C-H bond is not a very useful organic “functional group” for further synthesis. A simple alkane will not undergo very many chemical reactions, besides combustion. A metal-carbon single bond, however, will often be quite reactive, and easily converted to any one of a wide variety of organic functional groups. Thus, C-H activation can lead to interesting transformations of an organic molecule that would be difficult, if not impossible, to accomplish with “traditional” organic chemistry reagents (*i.e.* no transition metals). A good example of C-H oxidative addition is the following reaction, done under photolytic conditions: $\text{Cp}^*\text{Ir}(\text{CO})_2 + \text{CMe}_4 \rightarrow \text{Cp}^*\text{Ir}(\text{CO})(\text{H})(\text{CH}_2^t\text{Bu}) + \text{CO}$. Initial loss of CO (due to photolysis) yields the 16e intermediate $\text{Cp}^*\text{Ir}(\text{CO})$, which oxidatively adds neopentane.

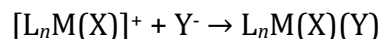
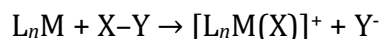
Many reactions involve OA followed by RE, or RE followed by OA, resulting in no net change in the metal’s oxidation state, but involving an intermediate with a higher or lower oxidation state. Bergman showed that the following reaction proceeds under photolytic conditions:



The Ir(III) reactant undergoes reductive elimination of H_2 to form the transient Ir(I) species $\text{Cp}^*\text{Ir}(\text{PMe}_3)$, which then oxidatively adds cyclohexane as a C-H activation.

Just as concerted OA results in a *cis* addition of the two new ligands, concerted RE requires that the ligands to be eliminated are *cis* before RE can occur. Stille studied the rates of RE of ethane (Me–Me) from the *cis* and *trans* isomers of square planar $\text{Pd}(\text{PPh}_3)_2\text{Me}_2$, and found that the *cis* isomer underwent RE much more quickly. The *trans* isomer must first isomerize to the *cis* before RE can occur. For square planar complexes like these, isomerization probably occurs *via* coordination of a polar solvent molecule (such as Et_2O or THF) to form a trigonal bipyramidal intermediate, which then undergoes pseudorotation to make the two methyl ligands *cis*. It is notable that OA and RE of C-H bonds, by the concerted mechanism, proceed with retention of configuration at the carbon, if it is a stereocenter.

In contrast to the concerted mechanism of OA and RE, some reactants X-Y undergo OA by an ionic mechanism. In an ionic OA, an electron-rich, and thus, nucleophilic, metal complex reacts with X-Y as follows:



Thus, the first step is nucleophilic attack *by the metal* to abstract the unit X^+ , followed by association of Y^- as a ligand to the intermediate, positively charged metal complex $[L_nM(X)]^+$ to form the final product. This type of mechanism is favored for reagents in which the Y^- anion is at least reasonably stable as an uncoordinated species.

TM complexes often react with methyl, primary, or secondary alkyl halides, tosylates, or triflates by this mechanism, adding R^+ , then halide or tosylate. In this type of reaction, the first step is an S_N2 reaction of the alkyl halide, with the metal atom as the nucleophile. Figure 13.2 below shows, as an example, the reaction of *trans*-Ir(PEt₃)₂(CO)Cl with bromomethane.

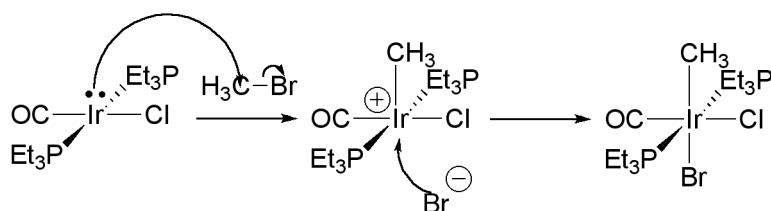


Figure 13.2. Oxidative addition of bromomethane to *trans*-Ir(PEt₃)₂(CO)Cl.

In this case, the methyl and bromo ligands end up *trans* in the product: initial transfer of CH_3^+ forms a square-pyramidal intermediate with one sterically unhindered open face *trans* to the methyl; Br^- attacks the Ir at this site to form the octahedral product. However, many transition metal complexes are stereochemically nonrigid, and can rapidly undergo *cis/trans* isomerization. Thus, the *cis* or *trans* arrangement of added ligands in an octahedral OA product is not a reliable indication of the mechanism of its formation.

In keeping with the S_N2 nature of this mechanism, alkyl species with a given leaving group react in the order $\text{methyl} > 1^\circ > 2^\circ \gg 3^\circ$, with this mechanism almost never proceeding with

a 3° alkyl group, just as fully organic S_N2 reactions almost never proceed with 3° alkyl halides or sulfonates. Also in keeping with organic S_N2 reactions, for a given alkyl group the reaction proceeds faster with better anionic leaving groups: TfO⁻ > I⁻ > TsO⁻ > Br⁻ > Cl⁻. (Here TfO⁻ = triflate = F₃CSO₃⁻ and TsO⁻ = tosylate = *p*-MeC₆H₄SO₃⁻.) If the alkyl group is 2° and a chiral center, it will experience inversion of configuration upon OA by this mechanism, as one would expect from an S_N2 pathway. This is shown in the stereochemical results of the reactions in Figure 13.3 below; in all of these reactions OA is followed by loss of phosphine ligands to give 16e Pd(II) or Pt(II) products.

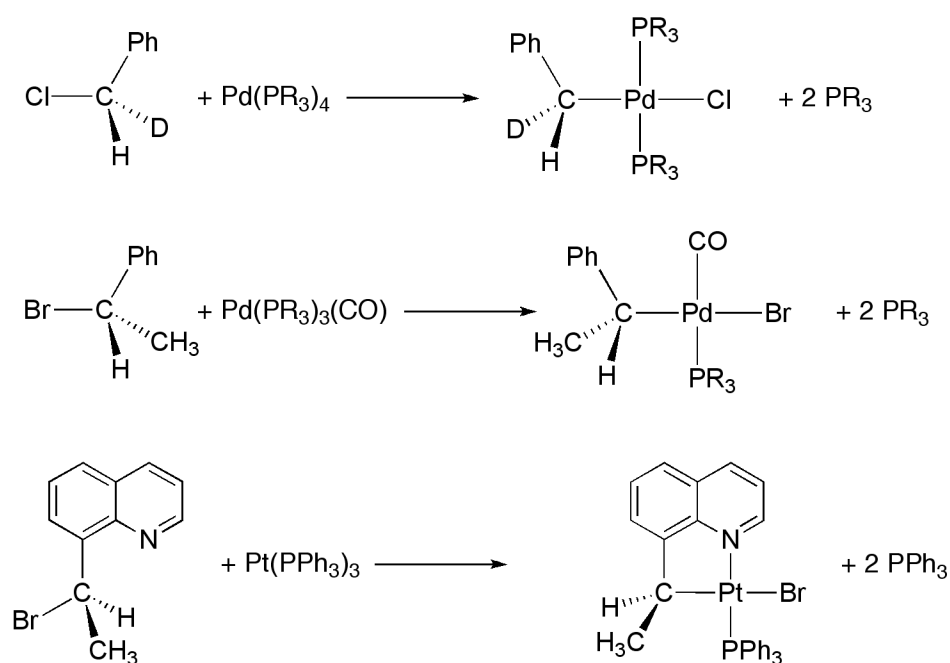


Figure 13.3. S_N2 oxidative addition reactions and their stereochemical consequences.

Finally, while normally the ion pair [L_nMR⁺][X⁻] is a reactive intermediate, they can be isolated in some cases: reaction of CpIr(CO)(PPh₃) with RI where R = methyl or benzyl yields the salt [CpIr(CO)(PPh₃)R⁺][I⁻], which is stable enough to be isolated and characterized. Coordination of I⁻ to the Ir complex cation would yield a 20e species, and presumably in this case I⁻ cannot displace the strongly bonding ligands CO or PPh₃.

It should be noted that aryl halides and sulfonates are similar to alkyl halides and sulfonates in that they contain polar bonds between carbon and a leaving group. However, aryl halides and sulfonates do not undergo OA by the S_N2 mechanism, since S_N2 reactions on an aromatic ring are not kinetically plausible. Thus, despite the polar bond, aryl halides and sulfonates generally undergo oxidative addition by the “concerted” mechanism, perhaps involving an intermediate in which there is π coordination to the metal *via* the aromatic ring.

Reductive elimination of alkyl halides and sulfonates usually proceeds by an S_N2 mechanism, as well. For example, the Pt(IV) species *fac*-Pt(dppe)(Me)₃(I) can reductively eliminate MeI: this proceeds *via* the dissociation of I[−] followed by nucleophilic attack on the Me ligand of [Pt(dppe)(Me)₃]⁺ that had been *trans* to I. This is thus an S_N2 reaction with the Pt(II) complex Pt(dppe)(Me)₂ as leaving group. Again, reductive elimination of R–X, if R is a chiral center, will proceed with inversion of configuration.

Other reagents that can add by ionic mechanisms are the hydrohalic acids HCl, HBr, and HI and the elemental halogens Cl₂ and Br₂. One can treat these mechanisms as amounting to S_N2 attack by the metal on H or a halogen, rather than on carbon, followed by attack of the released halide. Because H is such a sterically small ligand, we do not always see H and the new halide *trans* in the product. For instance, OA of HI to *trans*-Ir(PEt₃)₂(CO)Cl gives a product with H and I ligands *cis* to each other, as shown in Figure 13.4 below.

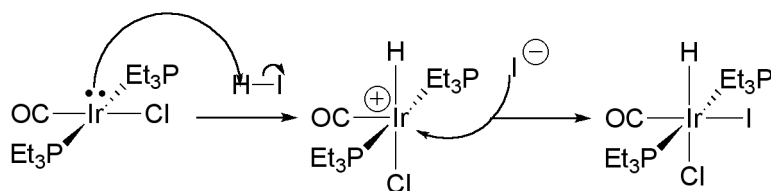


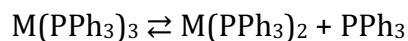
Figure 13.4. Oxidative addition of HI to *trans*-Ir(PEt₃)₂(CO)Cl *via* the ionic mechanism.

Metal complexes both a hydrido and a halogen ligand will often undergo RE upon treatment with a Brønsted base such as a bulky (noncoordinating) amine or a carboxylate anion: loss of the hydrido ligand as H⁺ and dissociation of X[−] occur to yield the reduced metal complex.

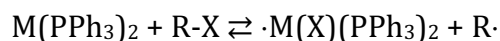
One of the steps of the Mizoroki-Heck reaction, an important catalytic process, involves the reaction of *trans*-PdL₂(H)(X), a Pd(II) species where L = a phosphine, with a base such as Et₃N to yield PdL₂ and [Et₃NH⁺][X⁻].

Halogen ligands are larger than H, of course, and are more likely to end up *trans* to one another in the final product. For instance, *trans*-Ir(PPh₃)₂(CO)(Cl), commonly known as Vaska's complex after Lauri Vaska (1925-2015), reacts with X₂ (where X = Cl, Br, I) to form *trans,trans*-Ir(PPh₃)₂(CO)(Cl)(X)₂.

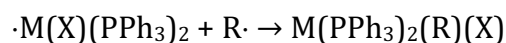
Some R-X species will oxidatively add to a metal by a radical, rather than an S_N2, reaction. Radical mechanisms can be either chain or non-chain. An example of a non-chain radical reaction is M(PPh₃)₃ + R-X → M(PPh₃)₂(R)(X) + PPh₃, where M = Pd or Pt. The first step of the mechanism is dissociation of a phosphine ligand to yield a reactive, coordinatively unsaturated 2-coordinate species:



Next, this metal species abstracts a halogen *atom* to make a paramagnetic M(I) complex and an alkyl radical:



Finally, the two radicals rapidly recombine to yield the final product:

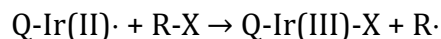
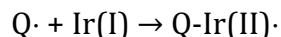


As one might expect, for a given halide X, this type of reaction proceeds faster with more substituted alkyl groups, since they give more stable radicals. Thus, the reaction order is 3° > 2° > 1° > methyl, the opposite of the S_N2 case. Additionally, heavier halogens are easier for the metal to abstract, and halogens are easier than sulfonates, so, for a given R group, RI > RBr > RCl > ROTs. If R is a chiral center, we expect that its configuration will be randomized in a reaction of this sort, since alkyl radicals racemize rapidly.

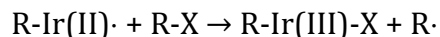
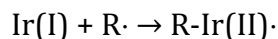
A chain radical mechanism is also possible, and it is sometimes observed for the OA of alkyl halides to Ir(I) compounds such as Vaska's complex *trans*-Ir(PPh₃)₂(CO)(Cl), as long as the alkyl group is not methyl, allyl, or benzyl. For a radical chain mechanism to occur, a radical

initiator $Q\cdot$ must be present, such as O_2 (recall that O_2 is a triplet diradical in its ground state).

The initiation steps are as follows:



The propagation steps, which when summed constitute the net reactions, are



Some net transition metal reactions may initially appear to proceed by OA followed by RE, but they cannot. Consider the reaction of a scandium complex shown in Figure 13.5 below.

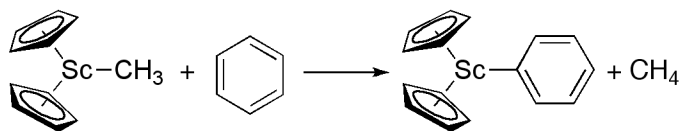


Figure 13.5. Reaction of Cp_2ScCH_3 with benzene.

One might suspect that the reaction would proceed *via* initial OA of benzene to yield $Cp_2Sc(CH_3)(H)(Ph)$, then RE of methane to yield Cp_2ScPh . But this is impossible, since the scandium complex is $Sc(III)$, and d^0 . The scandium cannot be further oxidized without using its core electrons, which would be energetically prohibitive, so the $Sc(V)$ species $Cp_2Sc(CH_3)(H)(Ph)$ cannot form, even as a transient reactive intermediate. Instead, this reaction proceeds through a process known as σ -bond metathesis (SBM for short): benzene binds to Sc through a C-H bond, then a switching of σ -bonds, called a metathesis, yields the products *via* a four-membered cyclic transition state. The general mechanism for SBM is shown in Figure 13.6 below.

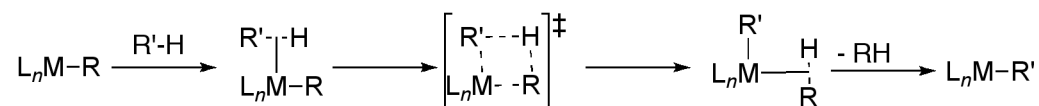
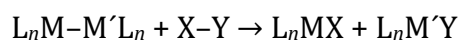


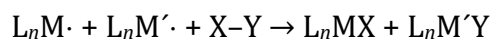
Figure 13.6. The general mechanism for σ -bond metathesis.

In some SBM reactions, there may not be any σ -complex intermediates, and the reaction may be truly concerted. When a d^0 complex undergoes a reaction that is equivalent to OA followed by RE, the mechanism must be SBM, but when a d^2 or above complex undergoes the same net reaction, OA followed by RE is usually assumed to occur. One cannot be sure of this, however, without experimental and/or computation support, and theoretical work suggests that some d^2 or greater species may also react by SBM.

Thus far, all of the OA and RE reactions that we have discussed have been “mononuclear,” with only one metal atom changing oxidation state. Another possible type of reaction is binuclear oxidative addition,¹⁰⁷ in which each of two metal atoms increases its oxidation state and electron count by +1, rather than +2. This can occur when a species contains a metal-metal bond, or when the metal complex in question is paramagnetic with 17e or fewer.

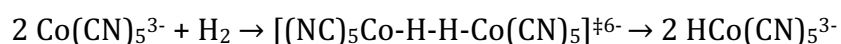


or

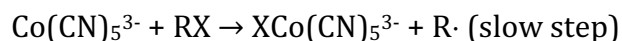


Often the first step of binuclear oxidative addition to a metal-metal bonded species is breakage of the metal-metal bond to yield a pair of radical complexes. From there, different mechanisms are possible for the actual X-Y bond cleavage.

For example, the 17e species $\text{Co}(\text{CN})_5^{3-}$ is believed to react with H_2 in a concerted mechanism, with the H-H bond broken at the same time both H-Co bonds are formed:



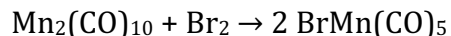
Support for this concerted mechanism comes from the observed third-order rate law, $r = [\text{Co}(\text{CN})_5^{3-}]^2[\text{H}_2]$. On the other hand, $\text{Co}(\text{CN})_5^{3-}$ is believed to react with alkyl halides *via* a radical, nonconcerted pathway:



¹⁰⁷ The terms “mononuclear” and “binuclear” are perhaps unfortunate because the molecules in question do, of course, contain more than one or two nuclei. The names refer to whether one or two TM nuclei undergo a change in oxidation state.

The radical mechanism is suggested by the facts that the halide preference is $\text{RI} > \text{RBr} \gg \text{RCl}$ and the alkyl preference is $3^\circ > 2^\circ > 1^\circ > \text{methyl}$.

Examples of complexes with metal-metal bonds undergoing binuclear OA include the following, in each of which the first step is presumably the homolytic cleavage of the Mn–Mn bond in $\text{Mn}_2(\text{CO})_{10}$.



13.2. Insertion and Elimination

Another fundamental type of organometallic reaction is migratory insertion (sometimes just called insertion). The reverse of this reaction is called elimination (not to be confused with reductive elimination). Very generally, insertion consists of the reaction of two ligands that are already bound to a metal, one of which is a 2e neutral ligand (L) and one of which is a 1e anionic ligand (X), to make a new 1e, anionic ligand LX, as shown in Figure 13.7 below.

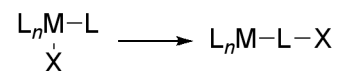


Figure 13.7. A generic insertion reaction.

These reactions have been termed insertions because, formally, the L ligand has inserted itself between the metal and the X ligand. I say “formally” here, because this is not usually the actual mechanism. Since reactions of this type begin with a 2e ligand and a 1e ligand on the metal, and end with only a 1e ligand, insertion is commonly followed by association of another 2e ligand to the metal, such as a phosphine or CO, to maintain the same electron count at the metal, especially if the 18e rule is to be followed. Note that, while an insertion results in a 2e decrease in the valence electron count of the metal, the metal’s oxidation state generally does not change.

There are many types of insertion reactions known, but there are two general types that are the most common and most important synthetically. In one, the 2e neutral ligand is CO, and

the 1e ligand is an alkyl group R, so a metal alkyl carbonyl complex becomes a metal acyl complex, as shown generally in Figure 13.8 below.

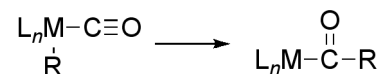


Figure 13.8. A general insertion involving alkyl and carbonyl ligands.

This type of insertion is often referred to as a 1,1-insertion, because in the final metal acyl complex product, the metal and the alkyl group are both bound to the *same* atom in the CO ligand, namely, carbon, which we may label as position 1, with oxygen as position 2.

In the other most common type of insertion, the 2e neutral ligand is an alkene bound in η^2 fashion, and the 1e anionic ligand is either an alkyl group R or simply H. This results in a metal alkyl complex (with a larger alkyl group than one started with), as shown in Figure 13.9 below.

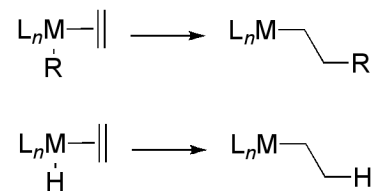


Figure 13.9. A general insertion involving alkyl (or hydrido) and alkene ligands.

This type of insertion is termed a 1,2-insertion, since in the final product the metal and alkyl group or hydrogen are bound to adjacent atoms (positions 1 and 2) in the alkene ligand.

As mentioned before, while the term “insertion” implies that the 2e ligand L actually inserts itself into the M–X bond, this is not how most insertion reactions are actually believed to proceed. Carbonyl insertion is the most thoroughly studied class of insertion reaction, with particular attention paid to the reaction of the well-known complex $\text{Mn}(\text{CO})_5\text{CH}_3$ with CO to form $\text{Mn}(\text{CO})_5(\text{COCH}_3)$, as shown in Figure 13.10 on the following page.

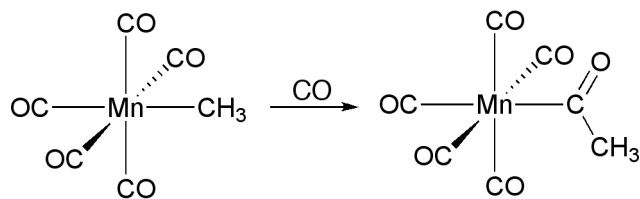


Figure 13.10. Insertion reaction of $\text{Mn}(\text{CO})_5\text{CH}_3$ with CO.

The generally accepted mechanism for this reaction is one in which the methyl ligand first migrates to a *cis* CO ligand to form a 16e, square-pyramidal intermediate with an acetyl ligand. Another molecule of CO then adds to the open coordination site, *cis* to the newly-formed acetyl. This mechanism is shown in Figure 13.11 below. Because the reaction is believed not to proceed by a direct insertion of CO, these reactions are often termed “migratory insertion,” or sometimes just “alkyl migration.”

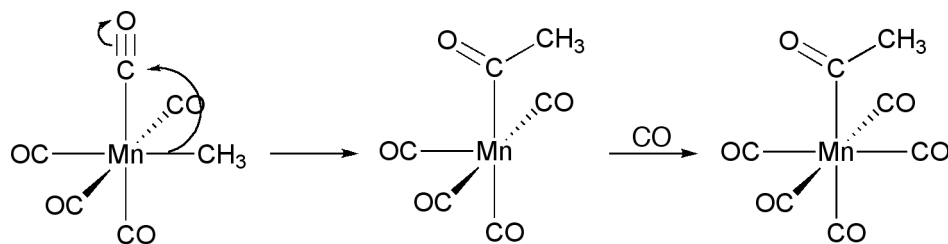
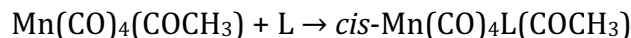
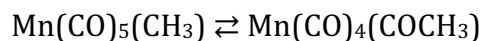


Figure 13.11. The accepted mechanism for the reaction of $\text{Mn}(\text{CO})_5\text{CH}_3$ with CO.

This mechanism can be written schematically as the following two steps:



with rate constants k_1 and k_{-1} for the (reversible) first step and k_2 for the second. Use of the SSA for the 16e intermediate $\text{Mn}(\text{CO})_4(\text{COCH}_3)$ yields the predicted rate law

$$r = \frac{k_1 k_2 [\text{Mn}(\text{CO})_5(\text{CH}_3)] [\text{L}]}{k_{-1} + k_2 [\text{L}]}$$

which becomes simple first-order, $r = k_1 [\text{Mn}(\text{CO})_5(\text{CH}_3)]$ if the entering 2e ligand (which can be CO) is in large excess, and first-order in entering ligand when the entering ligand concentration is low. This is indeed what is observed experimentally. The formally 16e intermediate $\text{Mn}(\text{CO})_4(\text{COCH}_3)$ may be stabilized by coordination of solvent, making it 18e

and lowering the barrier to its formation. This reaction occurs 50 times as quickly in DMF (*N,N*-dimethylformamide), a strongly coordinating solvent, than in mesitylene (1,3,5-trimethylbenzene), a poorly coordinating solvent.

An important labeling experiment whose results support this mechanism involved treatment of $\text{Mn}(\text{CO})_5\text{CH}_3$ with ^{13}CO , that is, CO with all its carbon atoms being ^{13}C . (The natural abundance of ^{13}C in compounds not specifically labeled is about 1.07%, with the vast majority being ^{12}C , and trace amounts present of the radioisotope ^{14}C , which is used in radiocarbon dating.) When this experiment is run, the ^{13}C in the product is always present in a CO ligand *cis* to the acetyl ligand, *never* in the acetyl ligand itself, as shown in Figure 13.12 below. If free CO directly inserted itself into the Mn-Me bond, we would expect to see ^{13}C in the acetyl carbonyl.

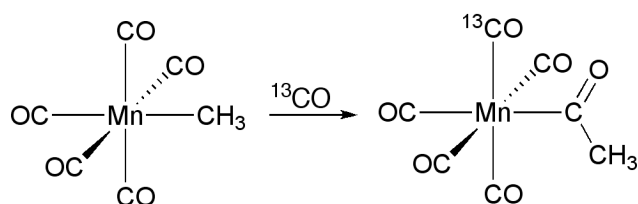


Figure 13.12. Results of the treatment of $\text{Mn}(\text{CO})_5\text{CH}_3$ with ^{13}CO .

The labeling experiment discussed above clearly establishes that *free* CO does not directly insert into the Mn-CH₃ bond. However, we must also consider the possibility that an already coordinated CO ligand *cis* to methyl inserts into the Mn-CH₃ bond.

Another important labeling experiment involves the reverse reaction: $\text{Mn}(\text{CO})_5(\text{COCH}_3) \rightarrow \text{Mn}(\text{CO})_5(\text{CH}_3) + \text{CO}$. The reverse of an insertion reaction is called elimination, deinsertion, or extrusion. Because of the principle of microscopic reversibility, the mechanism of the deinsertion reaction must be the same as that of the insertion reaction, just in reverse, so any experiment that tells us about the mechanism of deinsertion tells us just as much about the mechanism of insertion. Figure 13.13 on the following page shows

the distribution of products that the alkyl migration mechanism predicts will be formed when $cis\text{-Mn(CO)}_4(^{13}\text{CO})(\text{COCH}_3)$ is heated to drive off CO.

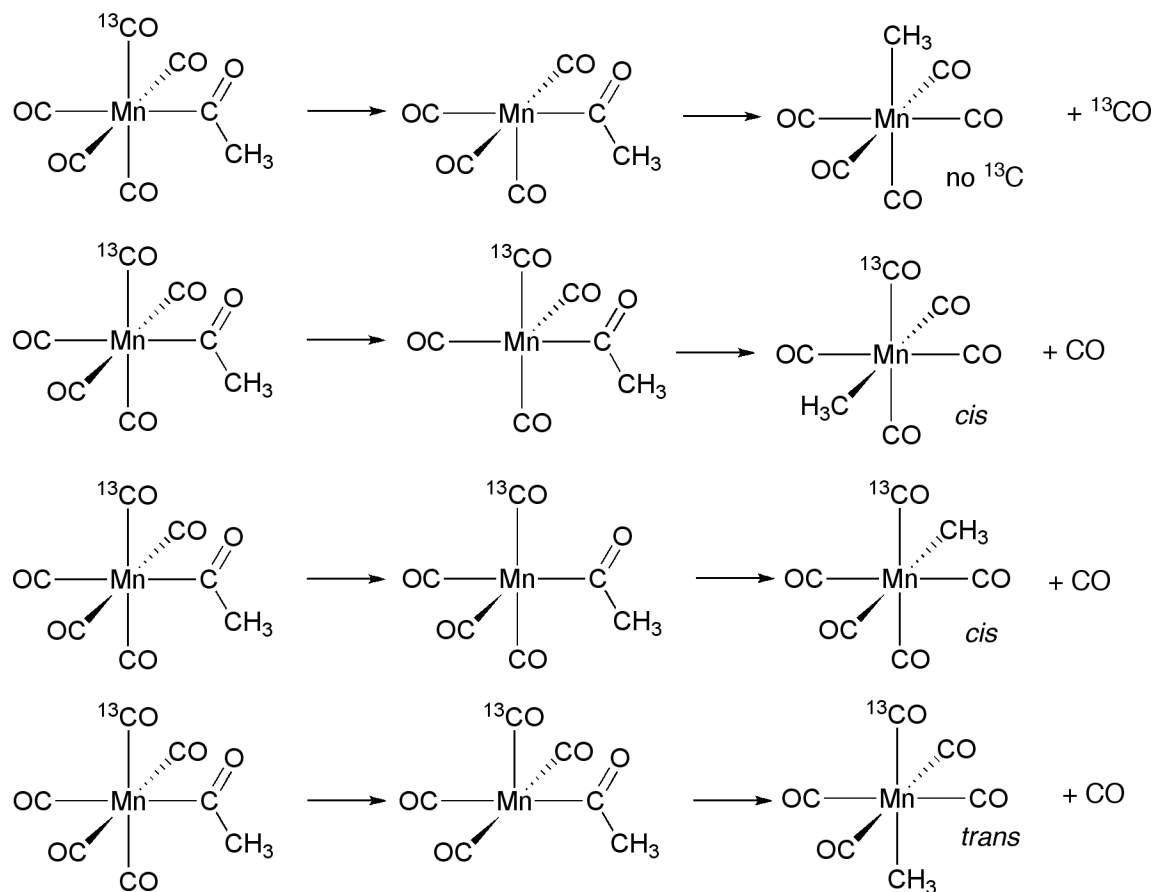


Figure 13.13. Product distribution for the deinsertion reaction of $cis\text{-Mn(CO)}_4(^{13}\text{CO})(\text{COCH}_3)$ predicted by the alkyl migration mechanism.

There are four CO ligands *cis* to acetyl, one of which is ^{13}CO . One must be lost for CO deinsertion to occur. If the ^{13}CO is lost, then we have an unlabeled $\text{Mn(CO)}_5(\text{CH}_3)$ product. The other possibilities lead to two CO ligands whose loss leads to *cis*- $\text{Mn(CO)}_4(^{13}\text{CO})(\text{CH}_3)$, and one CO ligand whose loss leads to *trans*- $\text{Mn(CO)}_4(^{13}\text{CO})(\text{CH}_3)$. When this experiment is actually run, the labeled Mn products $\text{Mn(CO)}_4(^{13}\text{CO})(\text{CH}_3)$ are present in a 2:1 *cis:trans* ratio, just as would be predicted by this mechanism.

Now consider the product distribution for the deinsertion that would be expected if, in the forward reaction, a CO ligand *cis* to methyl directly inserted into the Mn–CH₃ bond. In this case, a CO *cis* to the acetyl ligand would dissociate, and the CO portion of the acetyl ligand would migrate into its coordination site, with the possibilities shown in Figure 13.14 below.

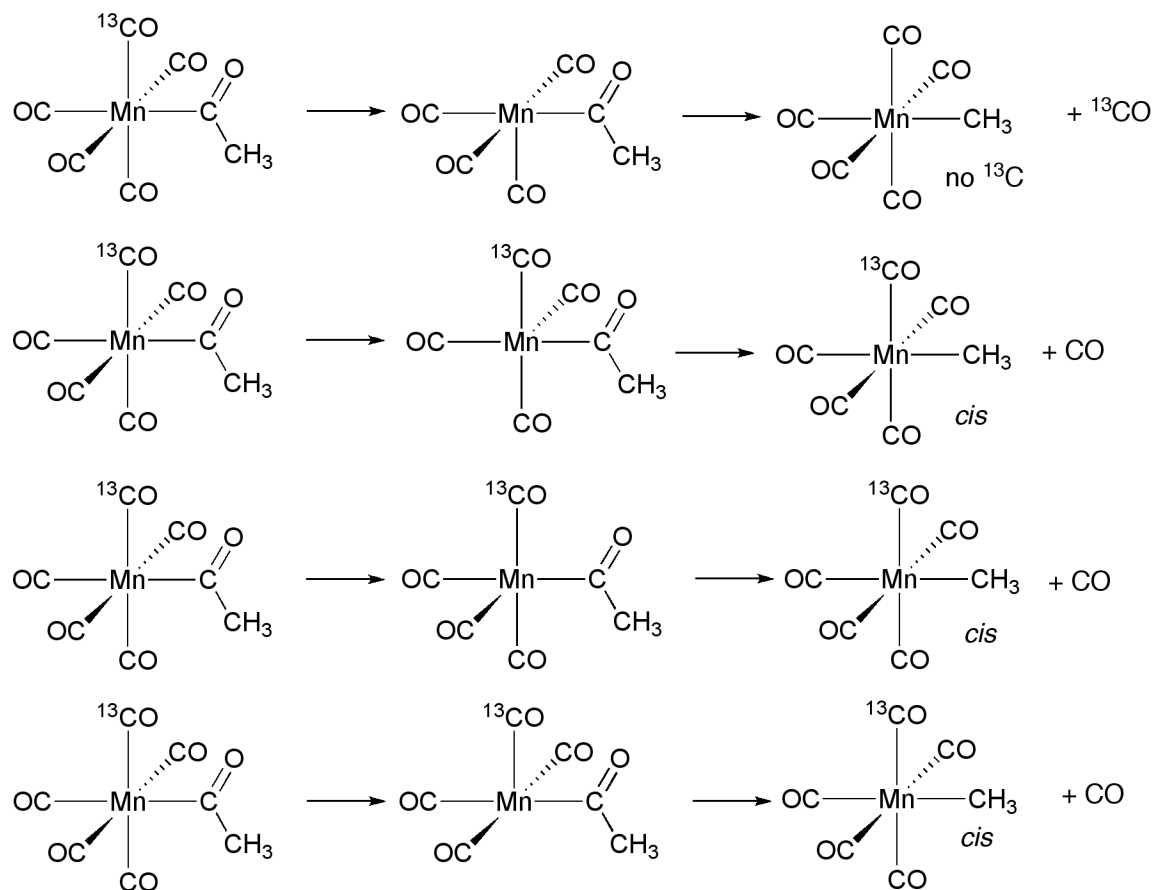


Figure 13.14. Product distribution for the deinsertion reaction of *cis*-Mn(CO)₄(¹³CO)(COCH₃) predicted by the intramolecular CO migration mechanism.

This intramolecular CO migration mechanism predicts that all the molecules of Mn(CO)₅(CH₃) formed which contain ¹³CO will have methyl and ¹³CO *cis* to each other, which is *not* what is experimentally observed. Thus, observed results are consistent with the accepted alkyl migration mechanism, in which a methyl ligand with its pair of electrons (H₃C⁻) migrates onto a CO ligand *cis* to it.

Some trends in CO insertion are worth mentioning. Alkyl migration onto CO ligands to form acyl ligands is common, but hydride migration to form complexes of the formyl ligand (COH) is not, probably due to the thermodynamic fact that M–H bonds are generally stronger than M–C bonds. For a given set of ligands and column of the periodic table, CO insertion is usually slower for the third-series transition metal than for the first- and second-series metals, probably because third-series M–C bonds are stronger. The presence of Lewis acids such as AlCl_3 that coordinate to a CO oxygen speeds up CO insertion reactions, and when the alkyl group is a chiral center, its configuration is retained. These observations suggest an analogy with 1,2-alkyl shifts in the isomerization of carbocations: an alkyl group moves, with its pair of electrons, onto an (at least partly) electron-deficient carbon, with retention of configuration.

When 1,2-insertion occurs with alkene ligands, the apparent insertion is also in fact a migratory process, with either H or R migrating (just as R migrates in a CO “insertion”). In general, the transition states for such reactions involve four-membered rings, in which a metal-carbon σ -bond is being formed and a metal-hydrogen or metal-alkyl σ -bond is being broken, while a carbon-carbon or carbon-hydrogen σ -bond is being formed and a carbon-carbon π bond is being broken, as shown for the reaction of *cis*- $\text{Pt}(\text{PEt}_3)_2(\text{H})(\text{Cl})$ with ethene in Figure 13.15 below. As with alkyl migration in CO “insertion,” retention of configuration is observed when a chiral R group moves.

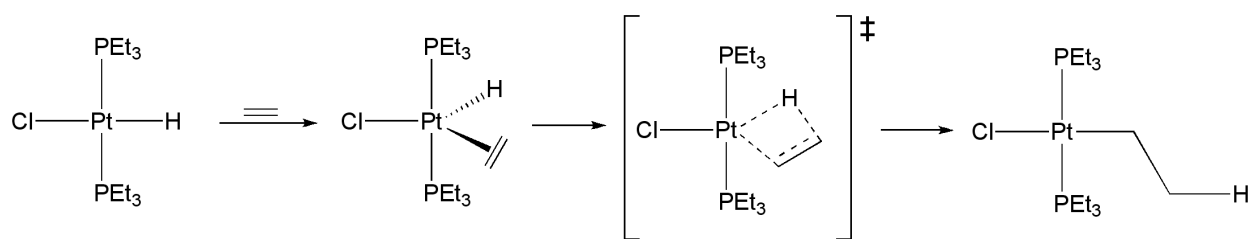


Figure 13.15. Migratory insertion reaction of *cis*- $\text{Pt}(\text{PEt}_3)_2(\text{H})(\text{Cl})$ with ethene.

Migratory insertion of alkenes into M–H bonds is often reversible. Many metal alkyl complexes whose alkyl ligands have at least one hydrogen at the β position (the α position is the carbon attached to the metal, and the β position is the next carbon out) are thus

kinetically unstable, and can decompose by β -hydrogen elimination (also called β -hydride elimination), the reverse of insertion, as shown for $[\text{CpRh}(\text{PMe}_3)(\text{Et})]^+$ in Figure 13.16 below. Note that β -alkyl elimination almost never occurs.

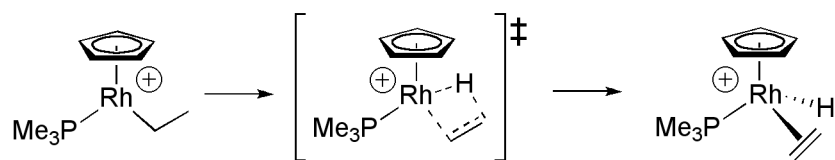


Figure 13.16. The β -hydrogen elimination reaction of $[\text{CpRh}(\text{PMe}_3)(\text{Et})]^+$.

Most kinetically stable metal alkyl complexes have alkyl ligands with no β hydrogen atoms (the neopentyl group, $-\text{CH}_2\text{CMe}_3$, is often used), or they have d^0 TM centers. β -hydrogen elimination results in an alkene ligand, and π backbonding from a TM d orbital into an alkene π^* LUMO is an important contribution to the ability of alkenes to coordinate. Because of this latter fact, alkenes tend to bind very weakly to d^0 TMs (as do other strongly π -accepting ligands such as CO), and thus β -hydrogen elimination is energetically not as favorable for d^0 alkyl complexes, though it can occur in multistep mechanisms to form unstable d^0 alkene complex intermediates. The d^0 species $(\text{dmpe})\text{TiCl}_3(\text{CH}_2\text{CH}_3)$, where $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, is stable for this reason. One way to understand this is to look at the metallacyclopropane resonance form of an η^2 alkene complex, in which the alkene is drawn as a dianionic “diyl” ligand. Using this convention, the Rh example shown in Figure 13.16 can instead be viewed as in Figure 13.17 below.

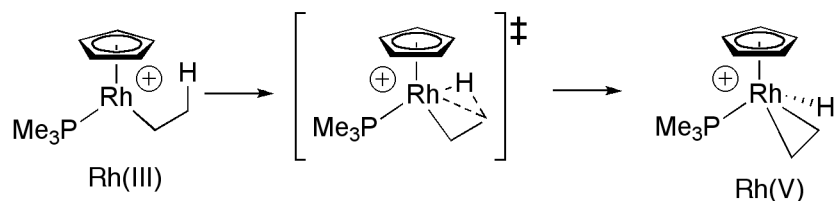


Figure 13.17. The β -hydrogen elimination reaction of $[\text{CpRh}(\text{PMe}_3)(\text{Et})]^+$, with the ethene ligand treated as a dianionic diyl ligand.

Viewed this way, β -hydrogen elimination is akin to C-H oxidative addition to form a three-membered metallacyclopropane. Thus, it is unlikely to occur for a d^0 complex, just as d^0 complexes will not undergo oxidative addition. In addition, β -H elimination converts a 1e ligand (alkyl) to a 1e ligand (H) and a 2e ligand (alkene), so 18e complexes cannot undergo β -H elimination without prior dissociation of a 2e ligand, if they are to remain 18e. The 18e complex salt $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2\text{Et}^+][\text{BF}_4^-]$ is fairly stable with respect to β -H elimination, since neither of the 2e, strongly σ -donating PMe_3 ligands are likely to dissociate from this positively charged complex to free up a coordination site.

The geometry of the transition state, in which the metal, alkene carbons, and migrating group (H or R) form a four-membered ring, is important. 1,2-insertion is always a *syn* addition across an alkene double bond, just like hydroboration of an alkene with BH_3 . Since the transition state for β -hydrogen elimination must have the same shape, metal alkyl complexes that are d^2 or above, with β hydrogens present, can still be stable, if the required transition state geometry cannot be achieved. For instance, while *cis*- $\text{Pt}(\text{PPh}_3)_2\text{Bu}_2$ is kinetically unstable with respect to β -elimination, *cis*- $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$ is quite stable. Sequential 1,2-addition of an alkene into an M-R bond, followed by β -H elimination, can lead to the stereospecific formation of larger alkenes, as shown for a Pt example in Figure 13.18 below.

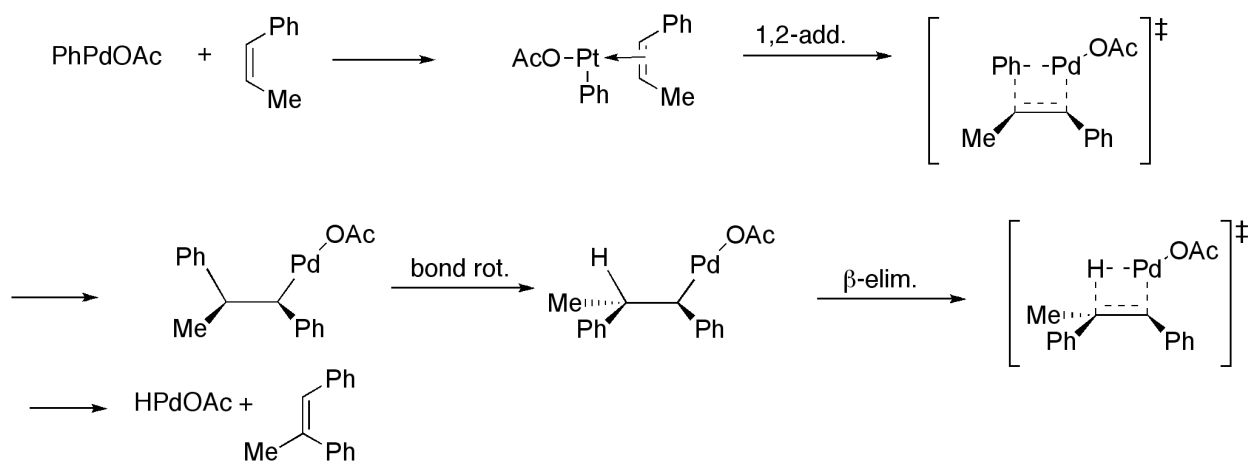


Figure 13.18. Stereospecificity of β -hydrogen elimination.

In terms of regioselectivity, 1,2-insertion often proceeds in an anti-Markovnikov fashion, with the bulky metal (with its ancillary ligands) attached to the less substituted carbon. However, metals do seem to prefer to add to carbons with phenyl groups bound, giving rise to benzylic alkyl complexes.

Methyl complexes cannot decompose *via* β -H elimination, since they have no β -hydrogen atoms to eliminate. They can, however, decompose by α -H elimination to yield a methylene ($=CH_2$) complex, which can often be trapped by other reagents. An example with a molybdenum complex is shown in Figure 13.19 below.

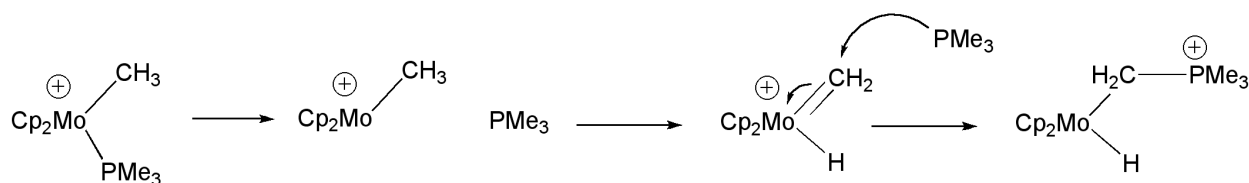


Figure 13.19. An example of α -hydrogen elimination.

Note that, unlike β -H elimination, α -H elimination involves a formal increase by 2 in the metal's oxidation state. In the molybdenum example shown in Figure 13.19, the elimination is a $Mo(IV) \rightarrow Mo(VI)$ change.

Another important type of reaction of unsaturated hydrocarbons is oxidative coupling, where two alkenes or alkynes form a diyl ligand, formally increasing the metal oxidation state by +2, as shown for iron in Figure 13.20 below.

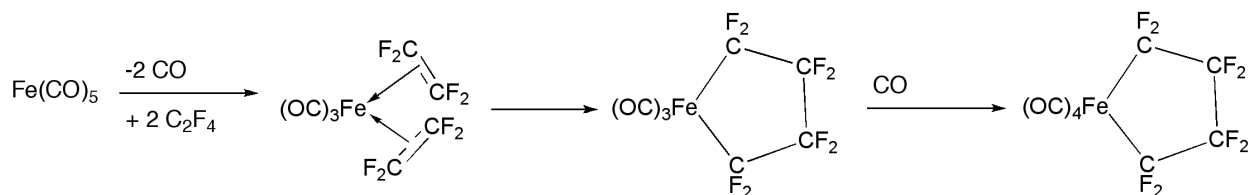


Figure 13.20. An example of an oxidative coupling reaction.

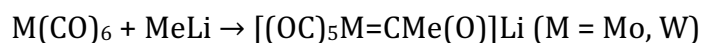
The reverse of oxidative coupling is known as reductive fragmentation or reductive cleavage, but it is rarely observed compared to the oxidative coupling direction.

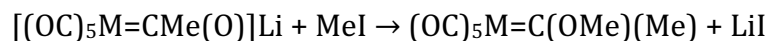
13.3. Nucleophilic Attack on Coordinated Ligands

So far, we have discussed organometallic reactions involving coordination changes at the metal center (ligand substitution, oxidative addition, reductive elimination), and those involving the reaction of one ligand with another ligand (1,1- and 1,2-insertion). Now let us examine the reaction of a coordinated ligand with an external reagent, either a nucleophile or an electrophile. We will see that the reactivity of organic ligands, when coordinated, is often very different from that of the free organic molecules.

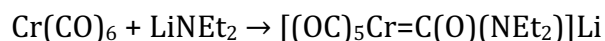
Our initial focus will be on the attack of external nucleophiles on unsaturated organic ligands, such as CO, alkenes, polyenes/polyenylys, and arenes. At this point it is worthwhile to go over an important concept in synthetic chemistry called *umpolung*. *Umpolung* is a German word meaning “reversal of polarity,” and it refers to a modification of a molecule such that an atom (usually carbon) that was either electrophilic or nucleophilic in the initial molecule becomes nucleophilic or electrophilic, respectively, in the new molecule. A classic organic example of *umpolung* is the Corey-Seebach reaction of aldehydes, in which an aldehyde, with an electrophilic carbonyl carbon, condenses with propane-1,3-dithiol to form a 1,3-dithiane, which is now sufficiently Brønsted-acidic at the former carbonyl carbon that it can be lithiated and add as a nucleophile to alkyl halides. When external nucleophiles react with unsaturated organic ligands, this is also an example of *umpolung*: free CO, alkenes, arenes, *etc.* are electron-rich, and generally react with electrophiles in classical organic chemistry. Once they are bound to a TM center, however, they donate enough of their electron density to the metal that they become less electron-rich themselves, and thus electrophilic.

We have already seen that nucleophilic attack on a carbonyl ligand by an organolithium or organomagnesium reagent, followed by alkylation of the resulting anion, is a good way to prepare a Fischer carbene, as in the following two reactions.

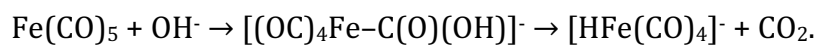




A Fischer carbene with both alkoxy and amino substituents on the carbene C can be prepared by treatment of a metal carbonyl complex with an amide salt, followed by alkylation, as follows.

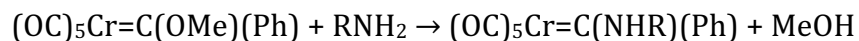


Nucleophilic attack on a carbonyl complex by hydroxide can lead to initial formation of a metallacarboxylic acid, which undergoes β -H elimination from oxygen, rather than carbon, to yield CO_2 and a metal hydride anion, as in the following reaction:



Attack by an alkoxide instead would lead to the formation of a metallaester, which is more stable, since it lacks β -H atoms.

An alkoxy Fischer carbene can be transformed into an amino Fischer carbene in a reaction analogous to the formation by nucleophilic acyl substitution of a carboxylic acid amide from a carboxylic acid ester:



Nucleophilic attack on hydrocarbon ligands bound through their π systems is common. If a metal complex has more than one organic π ligand, it is often the case that one site is preferentially attacked. The chemists Stephen Davies (b. 1950), Malcolm Green (1936-2020), and Michael Mingos (b. 1944) devised a set of rules, now known as the Davies-Green-Mingos or DGM rules, for predicting which of two (or more) organic π ligands will be more susceptible to nucleophilic attack. Like most reactivity rules in chemistry, the DGM rules are not always followed, but they are a sufficiently reliable predictive tool to be worth discussion. They are as follows:

(1) Organic π ligands with an even number of conjugated carbons (polyenes) are more susceptible to nucleophilic attack than those with an odd number of conjugated carbons (polyenylys).

(2) Open polyenes or polyenyls (those with interrupted conjugation) undergo nucleophilic attack more readily than closed polyenes or polyenyls (those with cyclic conjugation, like benzene or Cp).

(3) Open, even (polyene) ligands undergo nucleophilic attack at their terminal positions.

(4) Open, odd (polyenyl) ligands undergo nucleophilic attack at their terminal positions, if the metal fragment is strongly electron-withdrawing, but at a nonterminal position if the metal fragment is more electron-donating.

The rules should be applied in order: 1, 2, then (3 or 4). Rules 1 and 2 can be summarized as “even before odd, open before closed.” It is worth noting that a ligand is considered “open” if the conjugation is not cyclic, even if the ligand itself is cyclic: the ligand in Figure 13.21 below is considered open and odd. Similarly, the “terminal” position of an open ligand refers to one of the ends of the conjugated system.



Figure 13.21. A cyclic ligand considered to be open by the DGM rules, since it is not conjugated around the ring.

Some examples of reactions that follow the DGM rules are shown in Figure 13.22 on the following page. The rhodium reaction in this figure is worth noting for its stereochemistry: the methoxide ion attacks the ligand in an *exo* fashion (opposite the metal), rather than *endo* (on the same side of the ring as the metal). This can be understood as a function of steric hindrance: the *endo* side of the ligand, with the Rh center (and its Cp spectator ligand), is much more sterically crowded than the *exo* side.

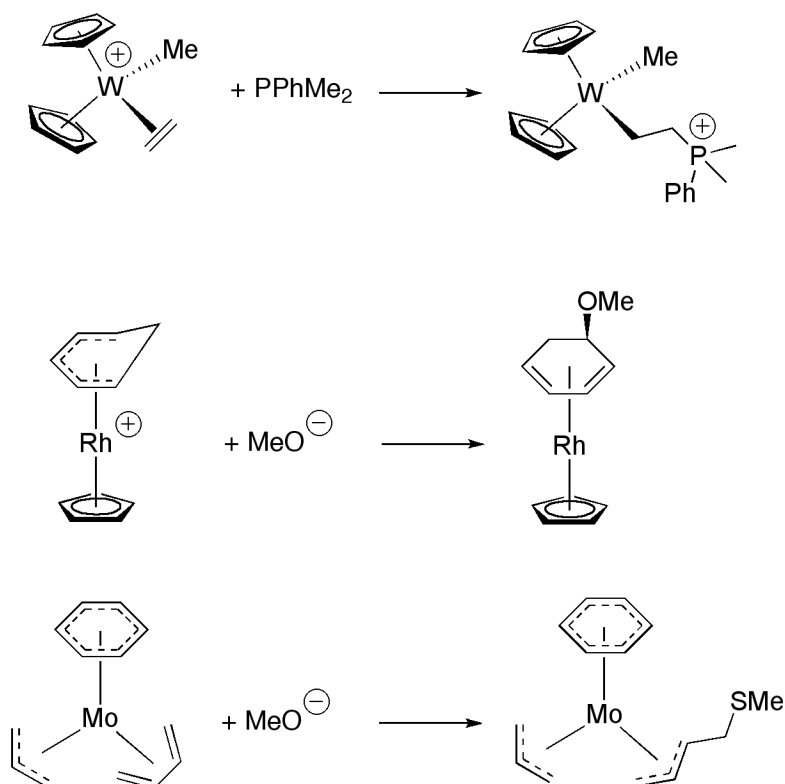


Figure 13.22. Examples of reactions whose products are those predicted by the DGM rules.

The DGM rules were empirically developed, but they can be rationalized in terms of concepts of chemical bonding. In terms of rule 1 (even before odd), we note that we usually think of even (polyene) ligands as neutral, but odd (polyenyl) ligands as anionic, when we assign oxidation states to the metal. While formal oxidation states should not be taken too literally, it is reasonable to suppose that there is more negative charge (or less positive charge) built up on odd ligands, making them *less* susceptible to further electron donation *via* nucleophilic attack. Rule 2 (open before closed) can be rationalized by reasoning that charge distribution in a closed (cyclic) conjugated system is more evenly distributed than in an open one due to symmetry, making it less likely that there will be a given position on the ligand that is especially (partially) positively charged and thus vulnerable to nucleophilic attack. Another way to think of this is to realize that cyclic conjugated systems have considerable aromatic character when coordinated to a metal (*cf.* C_3H_3^+ vs. $\text{C}_4\text{H}_4^{2-}$ vs. C_5H_5^- vs. C_6H_6 vs. C_7H_7^+ when assigning oxidation states), and nucleophilic attack breaks that aromaticity.

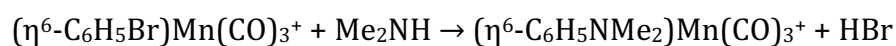
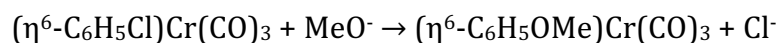
Rules 3 and 4, sometimes considered together as just one Rule 3, are the most complicated, and require consideration of the HOMO and LUMO of the ligand. For Rule 3, considering 1,3-butadiene as an example, calculations shown that its LUMO, ψ_3 , has larger coefficients on the terminal carbons (1 and 4) than on the internal ones (2 and 3). Thus, there is greater orbital overlap between the nucleophile HOMO and the ligand LUMO if terminal attack occurs, lowering the transition state energy and thus increasing the reaction rate. For Rule 4, the favored product can be difficult to predict if the metal is neither especially electron-rich nor especially electron-poor. We can consider the extreme cases, however, with allyl as an example. If the metal fragment is especially electron-withdrawing, the allyl ligand might behave as a cation, with the LUMO, ψ_2 , having a zero coefficient at the central carbon, but nonzero coefficients at the terminal ones. If the metal is very electron-donating, however, the LUMO will be ψ_3 , with a larger coefficient at the center carbon. For the allyl ligand, it turns out that nucleophiles attack at the terminal carbons the vast majority of the time. For internal attack to be favored, the metal fragment must be very electron-donating indeed. This is the case for $\text{Cp}_2\text{Mo}(\eta^3\text{-allyl})^+$ in its reaction with allylmagnesium chloride, and for $\text{Cp}^*(\text{PMe}_3)\text{Rh}(\eta^3\text{-allyl})^+$ in its reaction with lithium triethylborohydride. Both of these metal fragments have ligands that are excellent σ -donors, and lack any strongly π -accepting ligands like CO, NO, or PF_3 .

In general, for complexes with substituted allyl ligands whose metal fragments are not highly electron-donating, nucleophiles will attack the more substituted terminal position, unless the substituents are very sterically hindering indeed. This can be thought of as something of an allyl version of Markovnikov's rule in organic chemistry: there is more cationic character (or less anionic character) at the terminal carbon with more substitution. This has been shown experimentally with complexes of the form $\text{Pd}(\text{PR}_3)_2(\text{R}^1\text{R}^2\text{C-CH-CH}_2)^+$.

For coordinated alkenes, Markovnikov's rule generally predicts the favored site of nucleophilic attack, if the metal is considered analogous to the H^+ in Markovnikov's rule. The level of selectivity can vary widely, however. For the reaction of the complexes $\text{CpFe}(\text{CO})_2(\eta^2\text{-H}_2\text{C=CHR})$ ($\text{R} = \text{Me, Ph}$) with the enolate $\text{Li}[\text{CH}(\text{CO}_2\text{Me})_2]$, Markovnikov selectivity was only 2:1 for $\text{R} = \text{Me}$, while it was completely selective for $\text{R} = \text{Ph}$. The

stereochemistry of nucleophilic attack on coordinated alkenes was demonstrated to be *anti* to the metal in studies of the attack of $\text{H}_2\text{NCH}_2\text{Ph}$ on $\text{CpFe}(\text{CO})_2(\eta^2\text{-MeCH=CHMe})$, where the alkene ligand could be either *cis* or *trans*.

The effect of coordination on the reactivity of substituted benzenes is profound, and it is an excellent illustration of *umpolung*. Free arenes are electron-rich, and more prone to undergo electrophilic aromatic substitution ($\text{S}_{\text{E}}\text{Ar}$) than nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$). While $\text{S}_{\text{N}}\text{Ar}$ reactions do occur on aryl halides with very π -withdrawing substituents, such as *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-Cl}$, simple chlorobenzene will not undergo nucleophilic substitution with nucleophiles such as methoxide ion. On the other hand, the following reactions proceed readily:



Sometimes, nucleophiles do not add to a ligand, but rather abstract it, removing it from the metal's coordination sphere. In this case, a pair of electrons from the nucleophile adds to the ligand, and the electrons in the ligand-metal bond revert to the metal. Nucleophilic abstraction thus results in the lowering of the metal's oxidation state by 2 units. Consider the reductive elimination of MeI from the $\text{Pt}(\text{IV})$ complex *fac*- $\text{Pt}(\text{dppe})(\text{Me})_3\text{I}$ by the ionic mechanism: first I^- dissociates, forming the square pyramidal $[\text{Pt}(\text{dppe})(\text{Me})_3]^+$, which is still $\text{Pt}(\text{IV})$. The I^- ion then attacks one of the methyl ligands in an $\text{S}_{\text{N}}2$ reaction with the reduced $\text{Pt}(\text{II})$ species $\text{Pt}(\text{dppe})(\text{Me})_2$ as the leaving group. One way to understand why this process reduces the metal is to realize that we consider the methyl ligand as Me^- when assigning metal oxidation states, but I^- removes the components of Me^+ in order to eliminate neutral MeI .

Another form of nucleophilic abstraction is the deprotonation of metal hydride complexes. Reaction of the $\text{Co}(\text{I})$ complex $\text{HCo}(\text{CO})_4$ with a Brønsted base gives the $\text{Co}(-\text{I})$ complex anion $[\text{Co}(\text{CO})_4]^-$. Again, this is a reduction by 2 oxidation state units: H is considered H^- when we conclude that $\text{HCo}(\text{CO})_4$ is $\text{Co}(\text{I})$, but it is removed as H^+ .

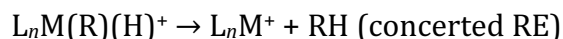
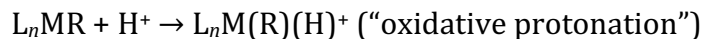
13.4. Electrophilic Attack on Coordinated Ligands

Ligands which are nucleophilic as free species are often instead electrophilic when coordinated to a metal, being less electron-rich due to donation of electron density to the metal center. This *umpolung* often leads to their reaction with external nucleophiles. However, some ligands can also react, when coordinated, with external electrophiles. A generic electrophile E^+ can either add to a ligand to form a new ligand (electrophilic addition) or abstract a ligand from the metal's coordination sphere (electrophilic abstraction).

The reaction of some metal hydrocarbyl complexes L_nM-R with electrophiles involves the abstraction of the hydrocarbyl ligand as R^- by E^+ , yielding L_nM^+ and $R-E$. When E^+ is H^+ (or a hydrogen in a somewhat acidic molecule such as water), the hydrocarbon $R-H$ is liberated, according to $L_nM-R + H^+ \rightarrow L_nM^+ + R-H$. The common laboratory jargon for such a reaction is that the hydrocarbyl ligand is “protonated off” the metal. If the conjugate base of the acid is a sufficiently good nucleophile, it may then coordinate to the metal, so, for instance, reaction of a metal hydrocarbyl with water might give the hydroxo complex L_nM-OH as a product. The more electropositive the metal, the more polar the $M-R$ bond, and the more easily R^- will be protonated off. (One way to understand this is to think of the R ligand as being a better Brønsted base.) Thus, hydrocarbyl complexes of electropositive “early” transition metals, such as Cp_2TiMe_2 and $Cl_2Ta(CH_2^tBu)_3$, are often highly moisture-sensitive, similar to the moisture-sensitivity of electropositive main-group metal hydrocarbyl compounds (Li, Mg, Al). Hydrocarbyl complexes of the less electropositive “late” transition metals, such as Fe or Ni, are often not sensitive to moisture, but will react with stronger acids than water, such as HCl or H_2SO_4 . Similarly, metal hydrido complexes L_nM-H will often react with Brønsted acids to protonate off H_2 : as with the hydrocarbyl case, electropositive early metal hydrides have more negative, “hydridic” character and are often moisture-sensitive, whereas late-metal hydrides have less Brønsted-basic hydrido ligands. Some late-metal hydrides, such as $H_2Fe(CO)_4$ and $HCo(CO)_4$, are actually Brønsted acids, with the hydrido ligand more prone to behave as H^+ than H^- (*cf.* our discussion of nucleophilic abstraction in Section 13.3).

One possible mechanism for electrophilic hydrocarbyl abstraction first involves protonation at the metal, consisting of an increase in metal oxidation state by two units (like the first step

of the ionic oxidative addition of HCl or HBr). Next, concerted reductive elimination of the hydrocarbon returns the metal to its initial oxidation state:



This mechanism is, of course, only possible if the metal is d^2 or above, since the initial protonation is like an oxidative addition. A concerted mechanism, involving a three-membered $M \cdots H \cdots R$ transition state is also possible. This is akin to σ -bond metathesis, and it is believed to be the operative mechanism for protic hydrocarbyl abstraction from d^0 early-metal complexes. When the hydrocarbyl ligand has a stereocenter bound to the metal (either an alkyl with *R* or *S* stereochemistry, or an alkenyl with *E* or *Z* stereochemistry), retention of configuration is invariably observed upon protic abstraction, whether the metal complex is d^0 or d^2 or above: this has been demonstrated in experiments using labeled Brønsted acids that donate D^+ , instead of H^+ , as shown in Figure 13.23 below.

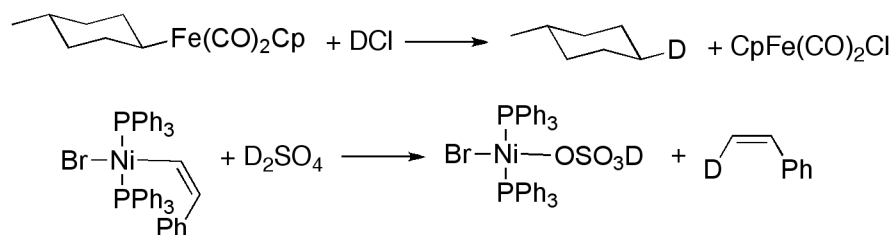
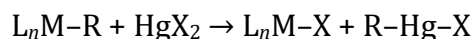
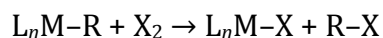


Figure 13.23. Stereochemical results of deuteration of alkyl or alkenyl ligands.

Hydrocarbyl abstraction can also be accomplished with elemental halogens X_2 or mercury(II) halides HgX_2 ($X = Cl$ or Br), as follows:



Unlike the protonolysis reactions, though, these reactions can give either retention or inversion of stereochemistry, depending on the metal fragment and the hydrocarbyl ligand. Different mechanisms are believed to be operative with different metal fragments and ligands.

In addition to the electrophilic abstraction of hydrocarbyl ligands, many unsaturated organic ligands can be subject to electrophilic addition. One way to prepare a cationic Fischer carbene complex is *via* treatment of a metal acyl complex with an alkyl halide or sulfonate, as shown in Figure 13.24 below.

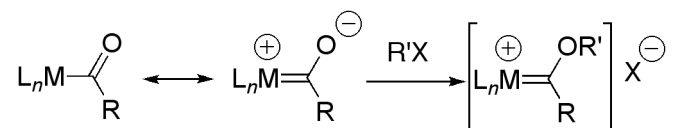
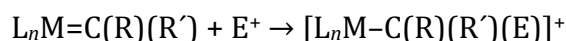


Figure 13.24. Alkylation of an acyl complex to form a cationic Fischer carbene complex.

As we have discussed, Schrock carbenes are nucleophilic at the carbene carbon, and they can react with electrophiles to form cationic alkyl complexes:



Here E^+ could be H^+ , from an acidic molecule (including H_2O , since Schrock carbenes tend to be moisture-sensitive) or R''^+ from an alkyl halide or sulfonate.

Organic ligands with extended π systems undergo some very interesting electrophilic addition reactions. For example, ferrocene was shown, shortly after its synthesis, to be able to undergo electrophilic aromatic substitution ($\text{S}_{\text{E}}\text{Ar}$) reactions much like those of benzene, as shown in Figure 13.25 below.

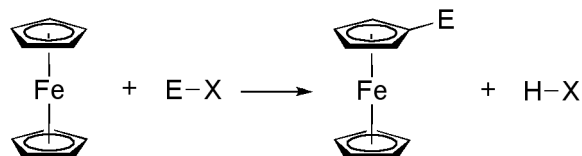


Figure 13.25. Generic electrophilic aromatic substitution of ferrocene.

Unlike organic $\text{S}_{\text{E}}\text{Ar}$ reactions, which always proceed *via* an arenium ion intermediate, the mechanism of electrophilic substitution on ferrocene depends on the electrophile. When ferrocene reacts with acetic anhydride to form acetylferrocene, the first step is attack of the

acylium ion on one of the rings. Next, the *endo* proton of the substituted ring migrates to the *endo* position of the unsubstituted ring, from which a proton is removed from the *exo* position by acetate. This proton transfer probably occurs so that acetate can approach the less sterically hindered *exo* position of the compound. This mechanism is shown in Figure 13.26 below.

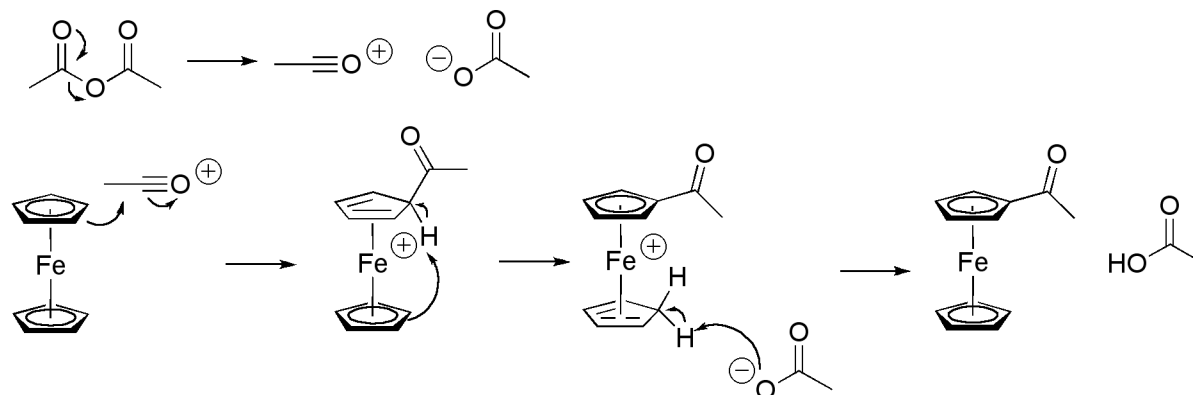


Figure 13.26. Mechanism of acylation of ferrocene.

On the other hand, mercury(II) acetate reacts with ferrocene to yield ferrocenylmercury(II) acetate. In this reaction, the iron actually behaves as a nucleophile to mercury, expelling acetate to form an intermediate with an iron-mercury bond. The HgOAc^+ moiety then moves to the *endo* position of one of the rings, which acetate deprotonates from the *exo* position to yield the final product. The mechanism is shown in Figure 13.27 below.

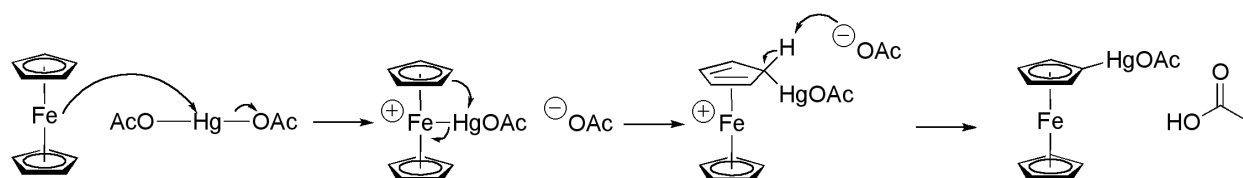


Figure 13.27. Mechanism for the mercuration of ferrocene.

While the mechanisms of acetylation and mercuration of ferrocene are different, they share the common feature that the final step of each involves the deprotonation of a substituted cyclopentadiene ligand from the less sterically hindered *exo* face.

While Cp ligands can undergo electrophilic substitution, many organic π ligands undergo electrophilic *addition*, instead. The γ position of η^1 -allyl ligands is often nucleophilic, as shown in the reactions in Figure 13.28 below. Here Fp is an abbreviation for the common 17e metal fragment $\text{CpFe}(\text{CO})_2$.

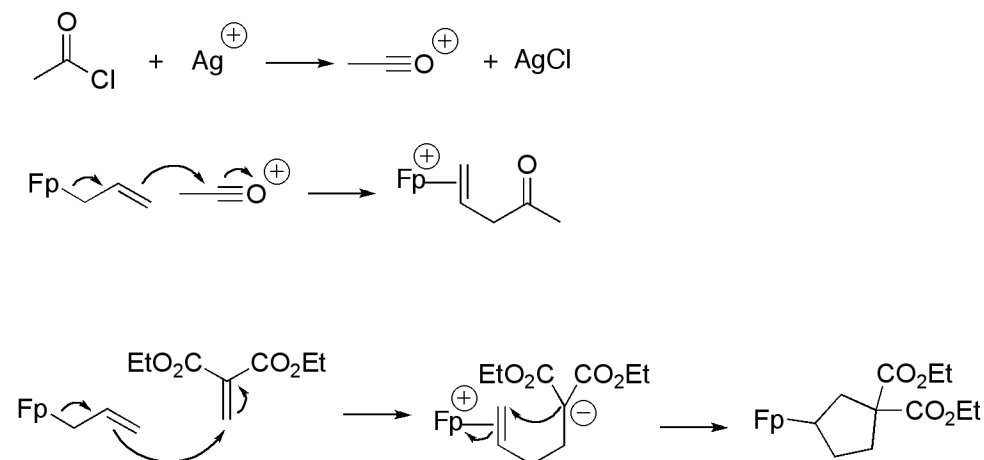


Figure 13.28. Examples of electrophilic addition to unsaturated ligands.

In addition to electrophilic substitution and addition, electrophilic abstraction from ligands is also possible. This reaction type can be thought of as the reverse of nucleophilic addition. For example, many π ligands can undergo addition of H^- by a nucleophilic hydride source such as BH_4^- or AlH_4^- . Similarly, a saturated ligand can undergo *abstraction* of H^- by a hydride abstractor such as triphenylmethyl cation, Ph_3C^+ , commonly called “trityl” for short. While this is a carbocation with no canonical resonance form that satisfies the octet rule for all atoms, it is still very stable, as carbocations go, due to the delocalization of the positive charge, and salts such as $[\text{Ph}_3\text{C}^+][\text{BF}_4^-]$ are commercially available and stable in the absence of moisture. Hydride abstraction from alkyl ligands involves an *anti* stereochemical relationship between the metal and the hydride to be lost, as shown by the stereochemical results of the experiment shown in Figure 13.28 on the following page.

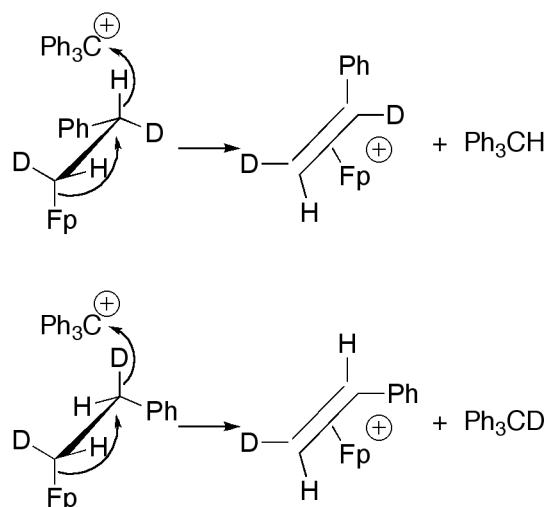


Figure 13.28. Stereochemical results of hydride abstraction from an alkene ligand by trityl cation.

Just as an alkyl ligand can undergo hydride abstraction to become an alkene ligand, increasing its hapticity from 1 to 2, an η^3 -allyl ligand can undergo hydride abstraction to form a conjugated diene ligand, increasing its hapticity from 3 to 4, as shown in Figure 13.29 below.

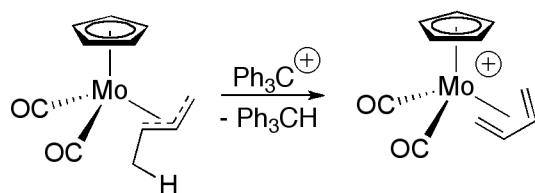


Figure 13.29. Hydride abstraction by trityl cation from an η^3 allyl ligand.

Chapter 14: Catalysis of Organic Reactions by Transition Metal Complexes

14.1. Introduction to Catalysis

Now that we have discussed the major classes of fundamental organometallic reactions, we are ready to move on to a discussion of how these reactions can be put together in organic reactions which are *catalytic* in the transition metal. Organometallic complexes can be used to catalyze many organic reactions, allowing them to proceed under mild conditions. Attempting to run many of these reactions without a catalyst would require harsh conditions (such as very high temperatures and/or pressures) that would be unsafe, energetically too costly, or which might lead to unwanted side reactions. We can draw a “catalytic cycle” in which we follow what happens to the transition metal: as a catalyst, it must be regenerated after effecting the desired organic reaction. Catalytic cycles often involve several different types of fundamental organometallic reactions occurring in one reaction vessel.

14.2. Catalytic Hydrogenation and Hydroformylation

The first reaction we will discuss is the rhodium-catalyzed hydrogenation of alkenes. The net reaction is shown for a *cis* disubstituted alkene in Figure 14.1 below.

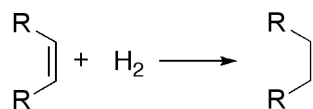


Figure 14.1. Hydrogenation of a *cis*-disubstituted alkene.

You may be familiar with catalytic hydrogenation reactions from your organic chemistry courses. The hydrogenation of alkenes to form alkanes is thermodynamically favorable, but slow on its own. When a solution of alkene with hydrogen gas is stirred over finely ground Ni, Pd, or Pt, however, the hydrogenation proceeds rapidly. These reactions are examples of *heterogeneous* catalysis: the reactants (alkene and hydrogen) are dissolved in a solvent, while the catalyst (the Group 10 TM) is present as a solid, and only its surface area comes in contact with the reactants. This is why heterogeneous catalysts are usually finely ground: to maximize the surface area/volume ratio and thus the number of reactive sites. In contrast to

these reactions, we will primarily be discussing *homogeneous* catalysis in this chapter, where “homogeneous” means that the catalyst is dissolved in solution along with reactants. Homogeneous catalysis has the practical disadvantage that it is more difficult to separate the catalyst from the reaction products, making product purification and catalyst reuse more difficult. For this reason, many large-scale industrial processes use heterogeneous catalysts. Mechanistic investigation, however, is *much* easier for homogeneous catalytic reactions, since one can do kinetics with precisely known initial catalyst concentrations. In contrast, the “concentration” of a heterogeneous catalyst, active only at its surface, is not well-defined.

The hydrogenation of alkenes is readily catalyzed by the soluble rhodium(I) complex $(\text{Ph}_3\text{P})_3\text{RhCl}$, commonly known as Wilkinson’s catalyst (after Geoffrey Wilkinson, who won the Nobel Prize for his work on metallocenes). Mechanistic studies have worked out the catalytic cycle for this process, which is shown in Figure 14.2 on the following page, with triphenylphosphine (PPh_3) abbreviated as L. Strictly speaking, Wilkinson’s catalyst is better termed a precatalyst, in that it undergoes two reactions to form the active catalyst, which will be regenerated during each “turn” of the catalytic cycle. First, the Rh(I) precatalyst (16e and d^8) undergoes concerted, *cis* OA of H_2 (step 1) to form the coordinatively saturated *cis,mer*-Rh(H) $_2$ Cl(PPh_3) $_3$ complex, which is Rh(III), d^6 and 18e. One of the PPh_3 ligands then dissociates (step 2) to give the much more reactive, square pyramidal 16e species Rh(H) $_2$ Cl(PPh_3) $_2$, which is the active catalyst.

In the catalytic cycle proper, an 18e species is formed *via* coordination of the alkene (step 3), and migratory insertion occurs to yield a 16e alkyl complex (step 4). At this point, reductive elimination of the alkyl and H ligands would give the alkane product. However, nonpolar bonds such as C-H are formed by reductive elimination in a concerted fashion, requiring the H and alkyl to be *cis*. Thus, isomerization occurs to make these ligands *cis* (step 5), followed by the actual reductive elimination (step 6) to yield the organic alkane product and the coordinatively unsaturated 14e Rh(I) species, $(\text{Ph}_3\text{P})_2\text{RhCl}$, which undergoes OA of H_2 (step 7) to regenerate the active catalyst.

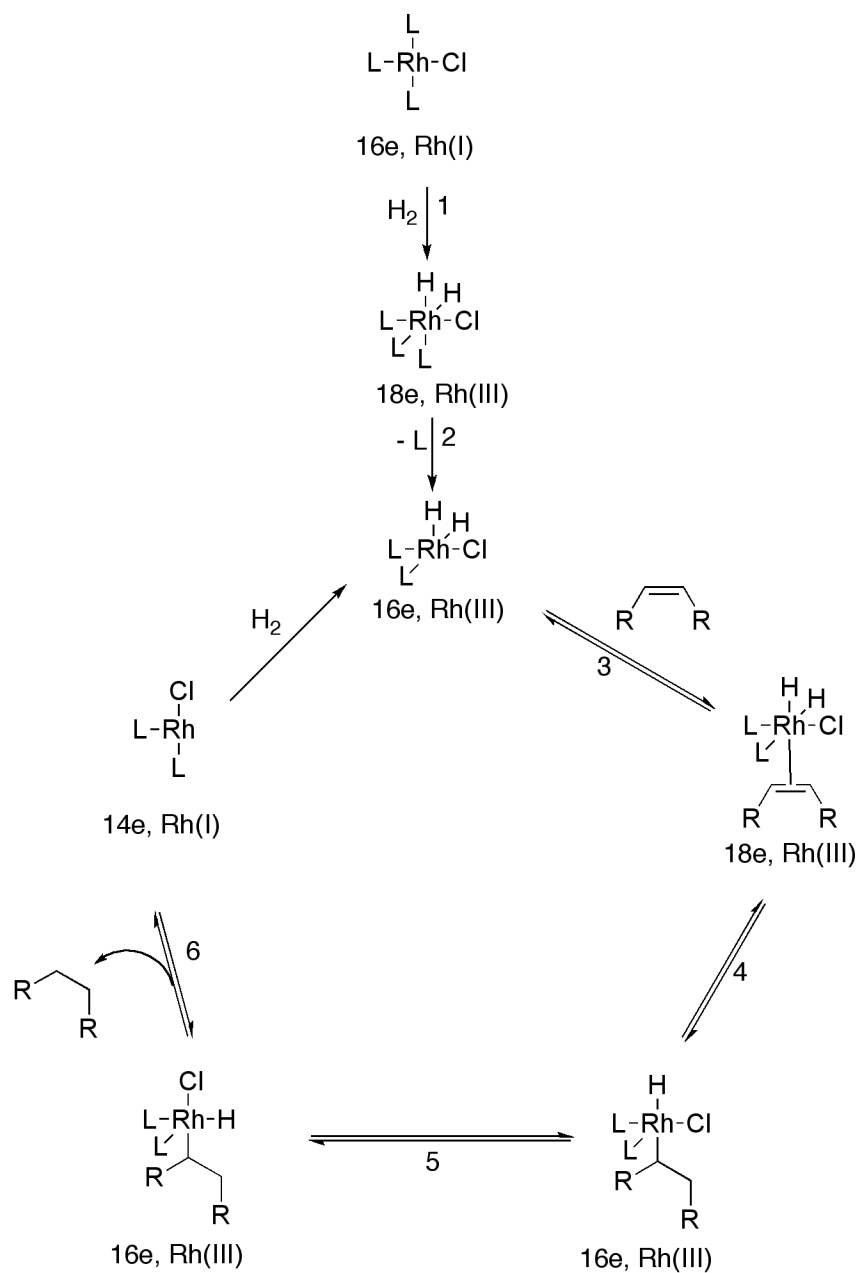


Figure 14.2. Catalytic cycle for alkene hydrogenation catalyzed by $\text{RhCl(PPh}_3)_3$.

It is important to note that the 1,2-migratory insertion of step 4 is really a 1,2-*syn* addition of Rh and H across the carbon-carbon double bond. The stereochemistry at the carbon bound to Rh is preserved during the concerted RE of step 6. This net *syn* addition of H_2 makes the reaction stereoselective in cases where *syn* and *anti* addition of H_2 would give rise to

different diastereomers. For example, 1,2-dimethylcyclohexene would be hydrogenated to give *cis*-1,2-dimethylcyclohexane, not (*R*)- or (*S*)-*trans*-1,2-dimethylcyclohexane.

Closely related to catalytic hydrogenation is the cobalt-catalyzed hydroformylation of alkenes, also known as the “oxo process,” which was developed in 1938 by the industrial chemist Otto Roelen (1897-1993) of Ruhr Chemie. It consists of the reaction of an alkene with CO and H₂ to form an aldehyde product, as shown in Figure 14.3 below.

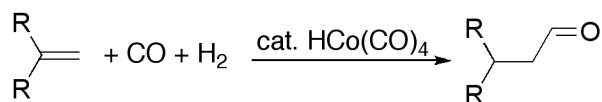


Figure 14.3. Generic equation for the hydroformylation of a 1,1-disubstituted alkene.

The catalytic cycle is shown on Figure 14.4 on the following page. First, the “catalyst,” HCo(CO)₄, is an 18e species, and loses CO to become the active catalyst, the 16e, coordinatively unsaturated species HCo(CO)₃. Again, we see that the stable species added as the catalyst is really a precatalyst or catalyst precursor, and undergoes a reaction (here dissociation of CO) in order to form a less stable, often not isolable, species that is the active catalyst. The precursor HCo(CO)₄ is a trigonal pyramidal complex with axial H, and the active species HCo(CO)₃ is believed to be square planar, resulting from the loss of an equatorial CO ligand. The CO is replaced by the alkene substrate to form a new 18e complex (step 1), which then undergoes migratory insertion with the hydride ligand to form a 16e alkyl complex (step 2). Association of another molecule of CO (step 3) yields an 18e complex which then undergoes migratory insertion with the CO and the alkyl ligand to yield a 16e acyl complex (step 4). The acyl complex then undergoes oxidative addition of H₂ to form the 18e, Co(III) dihydride complex (step 5). Finally, reductive elimination to form a C-H bond and release the aldehyde final product regenerates the 16e, Co(I) catalyst HCo(CO)₃.

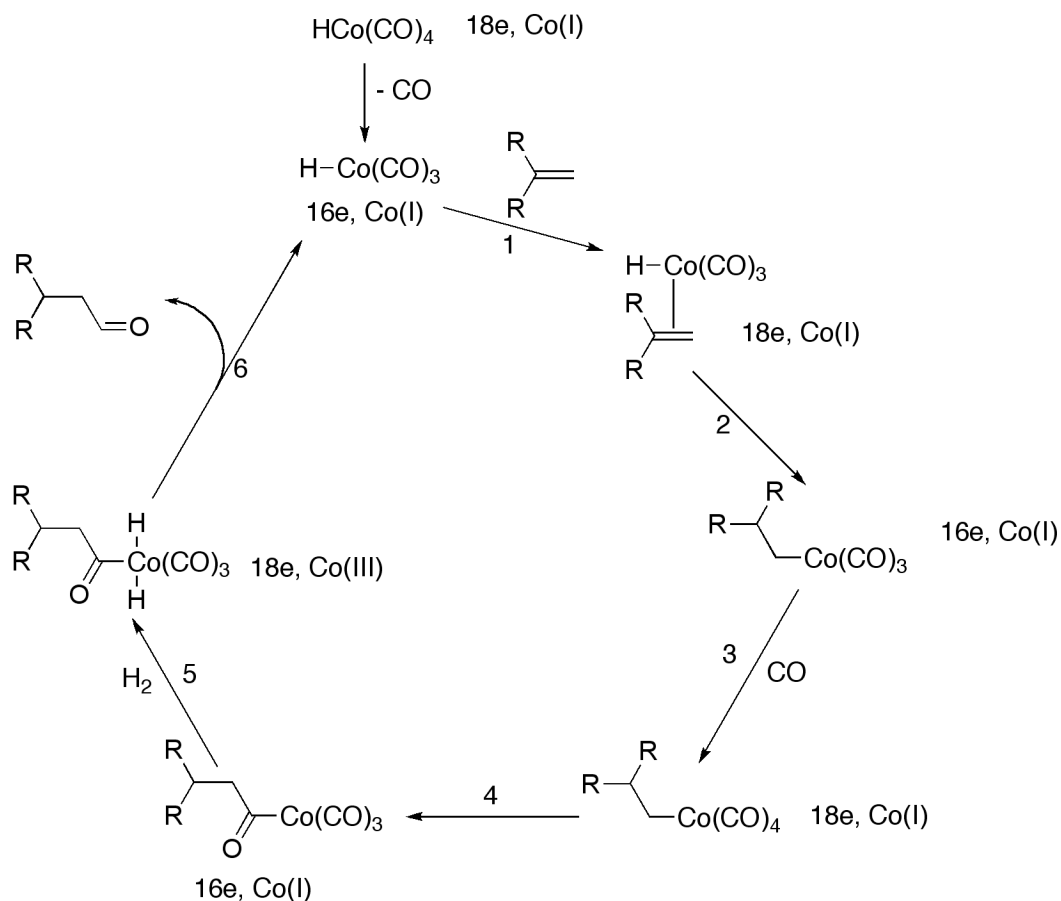


Figure 14.4. Catalytic cycle for the hydroformylation of a 1,1-disubstituted alkene.

The catalytic cycle as drawn shows the formation of the “linear” aldehyde product, in which the formyl group (CHO) has been added to the less substituted alkene carbon. The “branched” aldehyde, in which the more substituted carbon has the formyl group attached, can also be formed, depending on the regioselectivity of the migratory insertion in step 2. Kinetically, the linear product is formed preferentially to the branched, probably because of the greater steric hindrance involved in the addition of the Co(CO)_3 moiety to the more substituted carbon. However, this regioselectivity is not great, with the ratio of linear:branched aldehyde products being around 4:1, depending on the alkene. Later work on hydroformylation involved the substitution of some of the carbonyl ligands of HCo(CO)_4 with bulky phosphines, increasing the steric preference for formation of linear aldehydes, often leading to linear/branched ratios of about 9 to 1. This is advantageous economically,

since linear aldehydes are precursors to linear alcohols, which have a wide variety of industrial applications.

The hydrogenation of alkenes catalyzed by $(\text{Ph}_3\text{P})_3\text{RhCl}$ is often said to proceed through a “dihydride mechanism,” since its catalytic cycle involve transition metal species with two hydrido ligands, such as $\text{Rh}(\text{PPh}_3)_2\text{Cl}(\text{H})_2$. The hydroformylation of alkenes by $\text{HCo}(\text{CO})_4$ can also be considered to proceed through a dihydride mechanism, with the involvement of the intermediate $\text{Co}(\text{CO})_3(\text{H})_2(\text{acyl})$. In contrast, some transition metal complexes can catalyze the homogeneous hydrogenation of alkenes by a different type of mechanism, called the “monohydride mechanism” since its catalytic cycle involves transition metal species with one hydrido ligand, but none with two. One catalyst that operates by this type of mechanism is the 16e, five-coordinate Ru(II) species $\text{Ru}(\text{H})(\text{Cl})(\text{PPh}_3)_3$.¹⁰⁸ A plausible catalytic cycle for the hydrogenation of *cis*-2-butene catalyzed by this complex is shown in Figure 14.5 on the following page, with PPh_3 abbreviated as L.

Step **1** of the catalytic cycle consists of coordination of the alkene to the catalyst in an η^2 fashion, to form an 18e intermediate. In step **2**, migratory insertion (really hydride migration) forms an alkyl ligand from the alkene and hydride ligands, dropping the electron count back down to 16e. In step **3**, η^2 coordination of H_2 forms an 18e alkyl/dihydrogen intermediate, which undergoes σ -bond metathesis in step **4** to release the alkane product and regenerate the catalyst.

In both Rh-catalyzed hydrogenation by the dihydride mechanism and Co-catalyzed hydroformylation, the metal changes oxidation state during the catalytic cycle, alternating between Rh(I) and Rh(III) or Co(I) and Co(III). This is because each mechanism involves both OA and RE steps, each of which changes a metal's oxidation state by two units. Similarly, we will see later that cross-coupling reactions catalyzed by Pd involve both OA and RE, and an

¹⁰⁸ This is not a stable, isolable species. It is formed *in situ* from the precatalyst $\text{RuCl}_2(\text{PPh}_3)_3$, to which H_2 coordinates to form $\text{RuCl}_2(\text{PPh}_3)_3(\eta^2\text{-H}_2)$. Triethylamine present in the reaction mixture deprotonates the $\eta^2\text{-H}_2$ ligand to form a hydrido ligand concomitant with the release of Cl^- . Thus, every molecule of the precatalyst leads to the formation of one formula unit of Et_3NHCl .

alternation between Pd(0) and Pd(II) oxidation states. In contrast, note that, in the mechanism for Ru-catalyzed hydrogenation by the monohydride mechanism, the oxidation state of Ru does not change, instead remaining Ru(II) throughout. This is consistent with the fact that Ru(II) is a common oxidation state, while Ru(IV) is rare. In contrast, both Rh(I) and Rh(III) are common oxidation states, as are both Pd(0) and Pd(II).

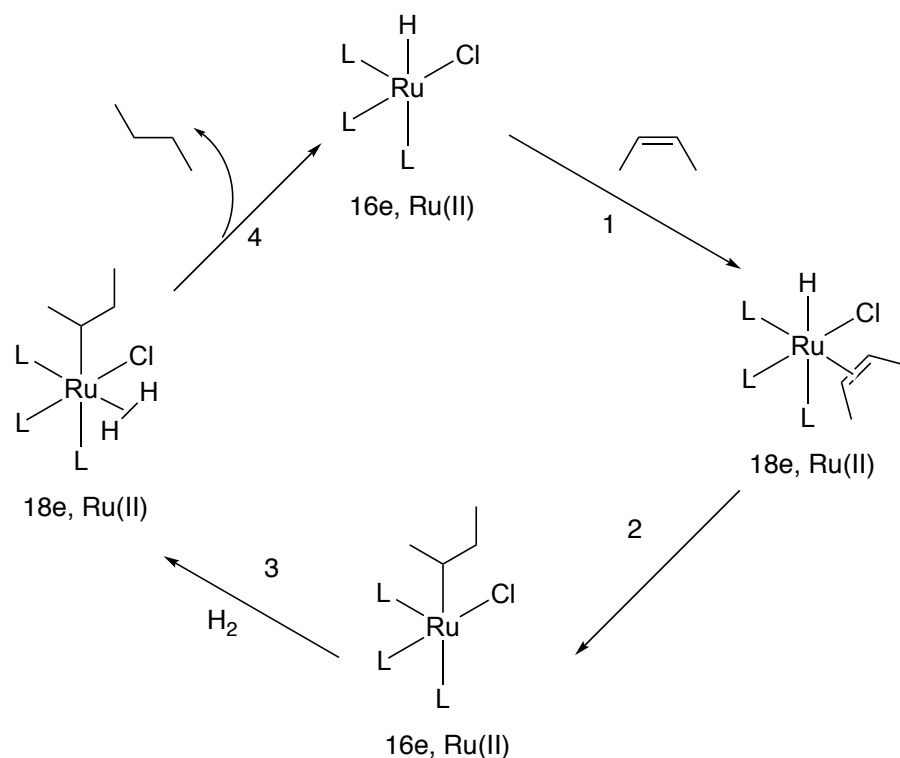


Figure 14.5. Catalytic cycle for homogeneous alkene hydrogenation catalyzed by $\text{Ru(H)(Cl)(PPh}_3)_3$.

14.3. The Monsanto Acetic Acid Process

It turns out that some reactions are catalytic both in a transition metal species *and* in a main-group species. Main group catalysis should not be new to you – recall the many reactions of organic chemistry which are catalyzed by a Brønsted acid – but here we will see a reaction in which a transition metal and main group species *both* act as catalysts, namely, the Monsanto acetic acid process.

Acetic acid, CH_3COOH , and its dehydration product acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$, are widely useful compounds. In your organic chemistry classes, you learned that ethanol can be oxidized to acetic acid: $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2$, a reaction that proceeds readily in the presence of many oxidizing agents that can act as hydrogen acceptors. In fact, ethanol in alcoholic beverages can be oxidized to acetic acid when stored improperly: this is what is meant when one talks about old wine “turning to vinegar.” The Monsanto acetic acid process, however, starts not with ethanol, but with methanol, adding an additional carbon atom from carbon monoxide: $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$. This reaction thus consists, formally, of the insertion of a CO carbon into the C–O bond of methanol. It is catalyzed by the transition-metal species $\text{Rh}(\text{CO})_2\text{I}_2^-$, an Rh(I) complex anion, and the main-group Brønsted acid HI. Thus, a complete catalytic cycle for this reaction must really consist of *two* cycles: one showing the behavior of the Rh catalyst, and one showing that of HI. The reaction is also performed in the presence of some water, and we will see that acidic hydrogen atoms alternated between being present in water and in HI. The mechanism of the Monsanto process is believed to be as shown in Figure 14.6 below.

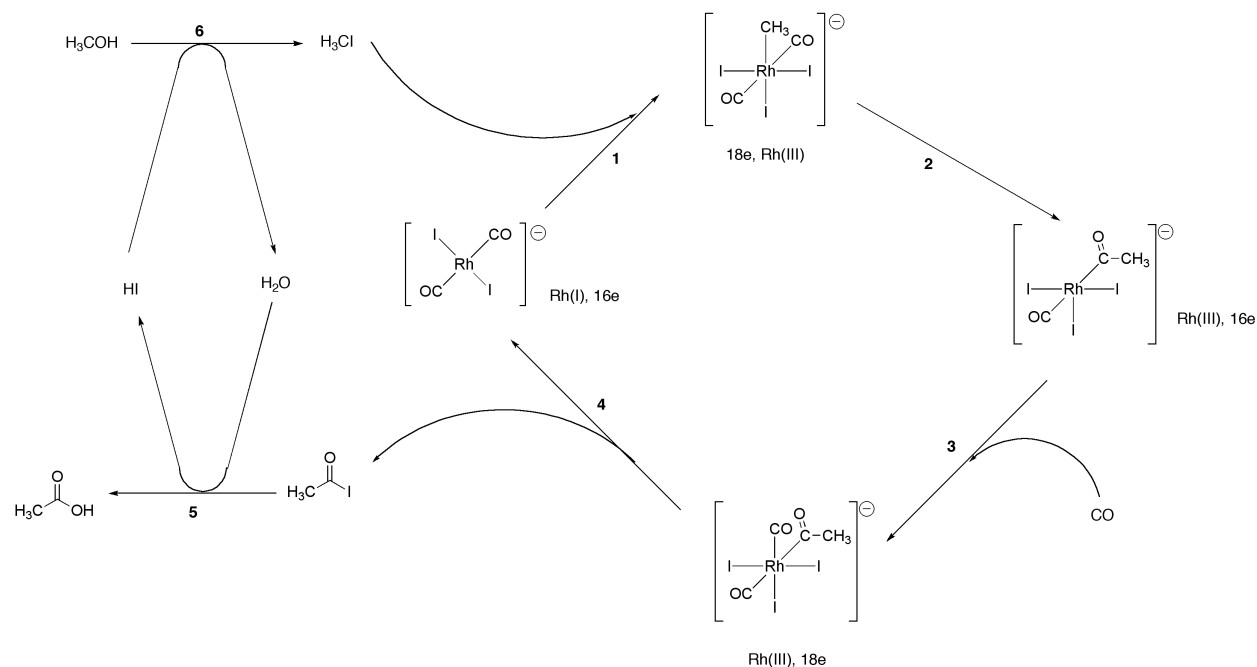


Figure 14.6. Catalytic cycles for the Monsanto acetic acid process.

Step **1** of the process is the oxidative addition (ionic mechanism) of iodomethane to the Rh catalyst. This is believed to be the rate-limiting step of the whole mechanism. Step **2** is a 1,1-migratory insertion of CO, that is, a migration of methyl to a CO ligand to form an acetyl ligand. Step **3** is ligand association of another molecule of CO, making the Rh(III) species **18e** again. In step **4**, reductive elimination (probably by an ionic mechanism) of acetyl iodide regenerates the Rh(I) starting catalyst.

Acetyl chloride is readily hydrolyzed to form acetic acid and HCl, and acetyl iodide is hydrolyzed even faster. In step **5**, acetyl iodide reacts with water present in the reaction mixture to give acetic acid, the reaction's organic product, and HI. Finally, in step **6**, HI reacts with methanol, the starting material, to reform iodomethane (which oxidatively adds to Rh in step **1**) and water.

14.4. *N*-Heterocyclic Carbenes (NHCs)

We have already discussed, in the previous chapter, the distinction between Schrock and Fischer carbene ligands. There is one additional class of carbene ligands of high importance in organometallic chemistry: *N*-heterocyclic carbenes, or NHCs for short. The basic structure of an NHC, and its relevant resonance forms, are shown in Figure 14.7 below.

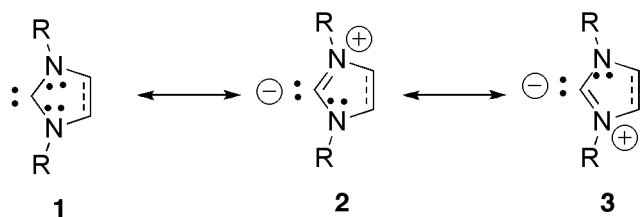


Figure 14.7. Generic structure of an *N*-heterocyclic carbene.

While resonance structure **1** emphasizes the carbene nature of this type of species, resonance structures **2** and **3** are the major contributors, due to the fact that every heavy atom in each has an octet. Thus NHCs, like Fischer carbenes in general, are considered neutral ligands when figuring metal oxidation state. While “normal” Fischer carbenes like C(OMe)(Me) have octet rule-satisfying resonance structures, they are not stable as free

species: when not bound to a metal center, they would dimerize to form an alkene. Many NHCs, on the other hand, especially those with large R groups on nitrogen, can be isolated as free species. For instance, the carbene shown in Figure 14.7 below, prepared by Anthony Arduengo (b. 1952),¹⁰⁹ is stable in the absence of O₂ and moisture, and can be handled easily in a nitrogen- or argon-filled glovebox:

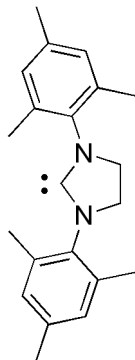


Figure 14.7. Arduengo's stable NHC.

Free NHCs are stable because they have two, rather than one, resonance structures each with octets on every heavy atom. Because they are stable, closed-shell species, they generally behave as excellent σ -donors, but very poor π -acceptors when bound to a metal center. Thus, the canonical “metal carbene” resonance form **4** shown in Figure 14.8 below, with an M–C double bond, contributes very little to the actual electronic structure of a metal-NHC complex, while structures **5** and **6**, each with an M–C single bond, are the major contributors:

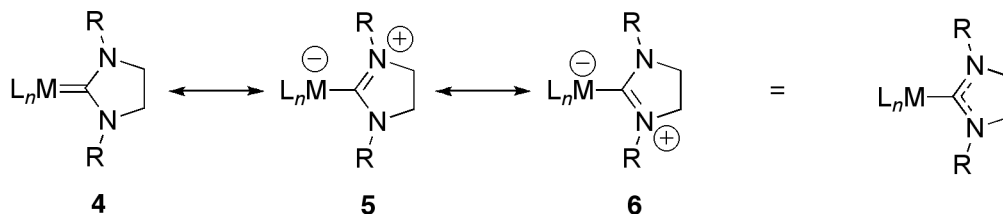


Figure 14.8. Resonance structures of a generic NHC complex.

¹⁰⁹ Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J. *Journal of the American Chemical Society* **1995**, *117*, 11027-11028.

We have already seen some reactions of Schrock and Fischer carbenes (and we will soon see more) in which the carbenes are *actor* ligands: their bonding topology changes during the course of a reaction. NHCs, in contrast, more often behave as *spectator* or *ancillary* ligands: they do not undergo bond formation or bond-breaking, but their steric and electronic properties influence the behavior of other ligands on the metal to which they are bound. In this sense, they are somewhat analogous to phosphines, which are usually spectator ligands. NHCs are also like phosphines in being readily tunable: NHCs can be prepared with a wide range of R groups which differ in their steric and electronic properties, and the R groups of an NHC ligand can have a significant effect on the chemistry of an NHC complex.

14.5. More Reactions of Fischer and Schrock Carbene Complexes

Moving back to Fischer and Schrock carbenes, we have already seen that a very common strategy for synthesis of Fischer carbene complexes consists of nucleophilic attack on CO ligands, and that alkoxy Fischer carbene complexes can be converted to amino Fischer carbenes by reaction with a free amine, analogous to aminolysis of a carboxylic acid ester. Let us now discuss some techniques for the synthesis of Schrock carbene complexes. We have already discussed α elimination, in which a metal alkyl complex becomes a metal carbene hydrido complex. A different kind of α elimination can occur when the metal center is d^0 : in such a case, the electron density necessary to “deprotonate” the alkyl ligand at its α position cannot come from the metal, but it *can* come from another ligand.

This type of reactivity was observed by Schrock himself when he attempted to prepare homoleptic Group 5 complexes of the neopentyl ($\text{Np} = \text{CH}_2\text{CMe}_3 = \text{CH}_2^t\text{Bu}$) ligand, $\text{M}(\text{CH}_2\text{CMe}_3)_5$, where $\text{M} = \text{Nb}$ or Ta . The treatment of *trans*- $\text{MCl}_2(\text{CH}_2\text{CMe}_3)_3$ with two equivalents of $\text{LiCH}_2\text{CMe}_3$ did *not* give the homoleptic alkyl complex as intended, but a carbene complex instead, as shown in Figure 14.9 on the following page.

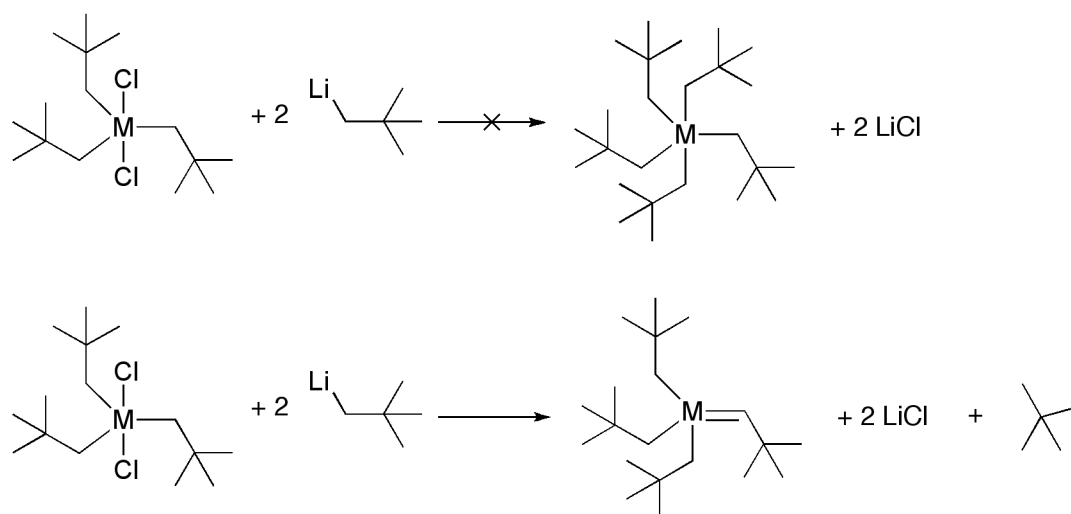
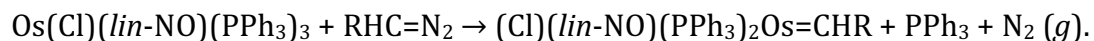


Figure 14.9. Schrock's synthesis of $\text{Np}_3\text{M}=\text{CH}^t\text{Bu}$ ($\text{M} = \text{Nb}, \text{Ta}$).

The mechanism for this reaction, shown in Figure 14.10 on the following page, is believed to begin with initial substitution of one $\text{Me}_3\text{CCH}_2^-$ for Cl^- as Schrock intended. At this point, the second equivalent of $\text{Me}_3\text{CCH}_2^-$ may deprotonate one of the neopentyl ligands, eliminating Cl^- and forming an $\text{M}-\text{C}$ double bond, reminiscent of an elimination in organic chemistry by the E2 mechanism. Alternatively, an already coordinated neopentyl ligand in $\text{MCl}(\text{CH}_2\text{CMe}_3)_4$ may deprotonate another, liberating free neopentane and forming the $\text{M}-\text{C}$ double bond. A second equivalent of $\text{Me}_3\text{CCH}_2^-$ then does the final ligand substitution, yielding the product. Whichever of these mechanisms is operative, the driving force for carbene formation appears to be the relief of steric hindrance: since the neopentyl ligand is so bulky, Schrock's initially desired product $\text{M}(\text{CH}_2\text{CMe}_3)_5$ would simply be too sterically crowded to form.

Schrock carbene ligands are not stable as free species, but diazoalkanes $(\text{R})(\text{R}')\text{C}=\text{N}_2$ are often used in synthetic chemistry as sources of the carbene $\text{C}(\text{R})(\text{R}')$. They are often so reactive as to be dangerous: diazomethane, $\text{H}_2\text{C}=\text{N}_2$, is highly toxic, since it can be protonated to form the strongly carcinogenic methylating agent methyldiazonium, H_3CN_2^+ . It is also explosive, being so shock-sensitive that the friction of a ground glass stopper placed into a flask can cause it to detonate! Nevertheless, it can be synthetically useful when appropriate precautions are taken, and heavier diazoalkanes are often less sensitive and thus safer.

Reaction of a diazoalkane with a metal complex can often yield a Schrock carbene complex, as in the following osmium case:



Here R = H, Me, or *p*-tolyl, and the product has the PPh₃ ligands axial and *trans* to each other.

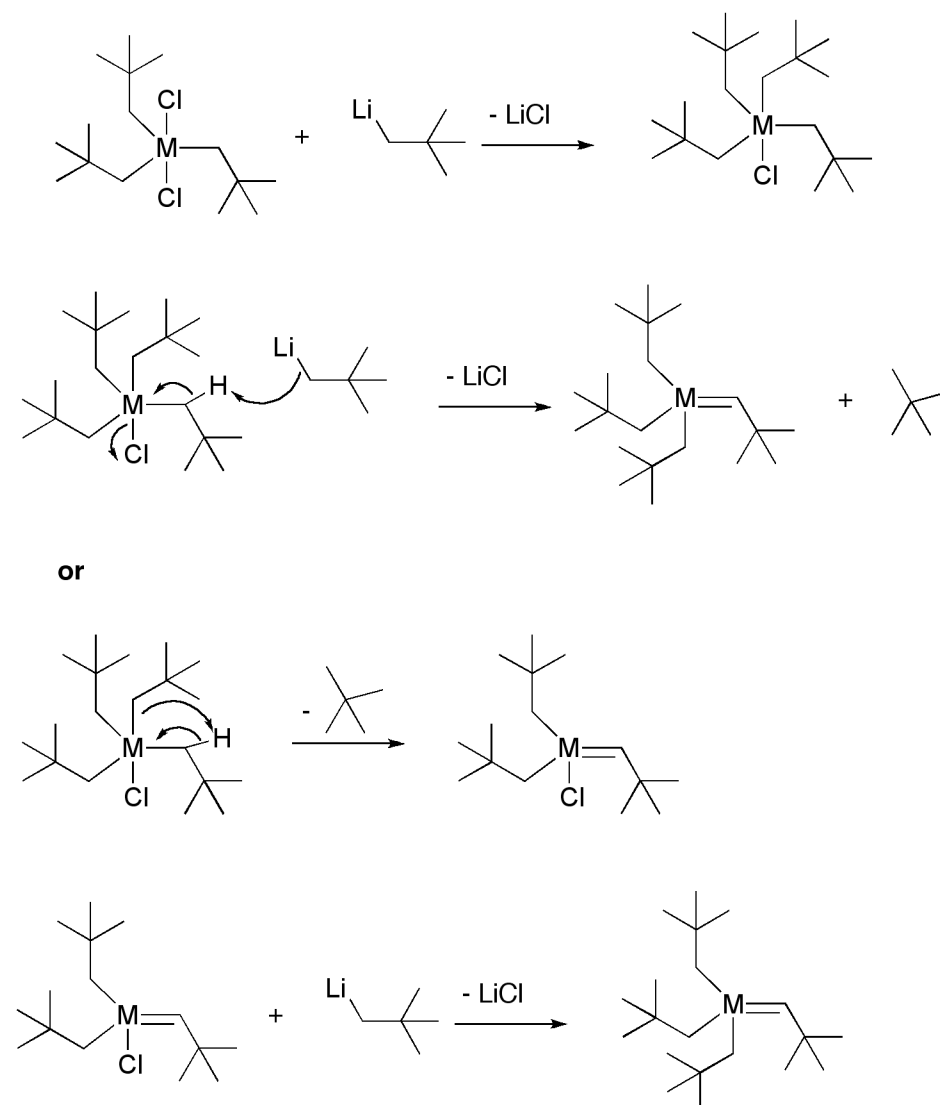


Figure 14.10. Possible mechanisms for the formation of $\text{Np}_3\text{M}=\text{CH}^t\text{Bu}$ ($\text{M} = \text{Nb}, \text{Ta}$).

A certain degree of steric hindrance often stabilizes Schrock carbene complexes, with complexes of unsubstituted methylene (CH_2) ligands often being unstable. The methylene complex $\text{Cp}_2\text{Ti}=\text{CH}_2$ cannot be isolated for this reason. However, it can be generated *in situ*

by treating a bimetallic Ti/Al complex, $\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{AlMe}_2$, known as Tebbe's reagent after Frederick Tebbe (1935-1995), with a Lewis base such as pyridine to abstract Me_2AlCl : $\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{AlMe}_2 + \text{C}_5\text{H}_5\text{N} \rightarrow \text{Cp}_2\text{Ti=CH}_2 + \text{C}_5\text{H}_5\text{N-AlMe}_2\text{Cl}$. The $\text{Cp}_2\text{Ti=CH}_2$ thus formed can then react with other molecules in the reaction mixture.

We have already discussed some reactions of Fischer carbene complexes with external nucleophiles. An additional, important mode of reactivity is based on the analogy between a Fischer carbene $\text{L}_n\text{M}=\text{C(R)(OR)}$ and a carboxylic acid ester $\text{O}=\text{C(R)(OR)}$. Just as hydrogen atoms on a carbon α to an organic carbonyl group are somewhat acidic, so are hydrogens on a carbon α to a Fischer carbene carbon, so Fischer carbene complexes can be deprotonated to form species analogous to enolates and then alkylated, as shown in Figure 14.11 below.

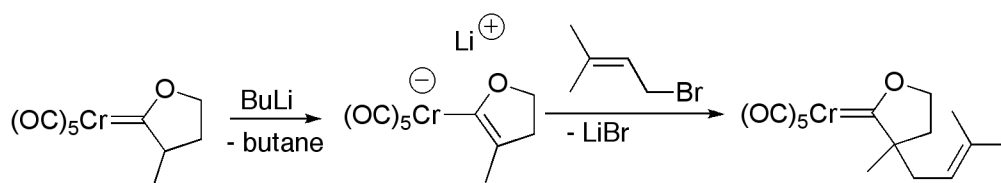


Figure 14.11. Deprotonation and alkylation of a Fischer carbene complex.

Free carbenes, generated as reactive intermediates *in situ*, react with alkenes to form cyclopropanes, preserving the stereochemistry of the alkene. For instance, treatment of chloroform with *t*-butoxide generates dichloromethylene, which reacts with alkenes to form *gem*-dichlorocyclopropanes, as shown in Figure 14.12 on the following page. The mechanism is a concerted [2+1] cycloaddition, a pericyclic reaction governed by the Woodward-Hoffmann orbital symmetry rules.

Some metal carbene complexes will react with alkenes to form cyclopropanes. However, the mechanism does *not* consist of a concerted transfer of the carbene from the metal to the alkene. If the alkene is fairly electron-rich, the mechanism shown in Figure 14.13 on the following page is generally believed to be operative.

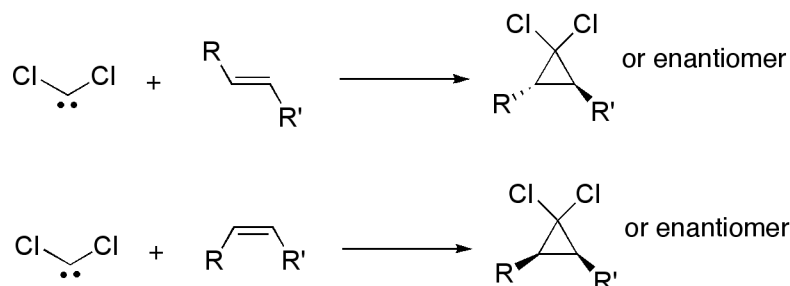
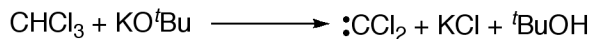


Figure 14.12. Reaction of a free carbene with alkenes.

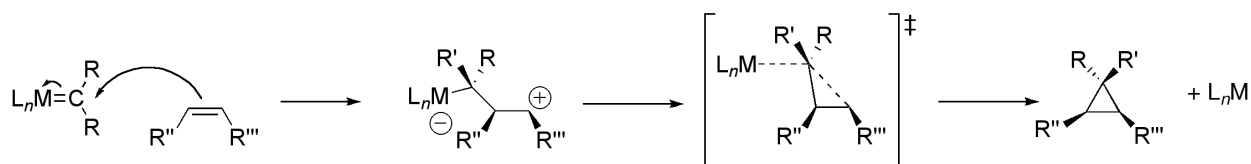


Figure 14.13. Reaction of an electron-rich alkene with a metal carbene complex.

The mechanism for metal-promoted cyclopropanation shown in Figure 14.13 involves the temporary formation of a carbocation center. Electron-poor alkenes, with electron-withdrawing substituents such as CO_2R or NO_2 , are highly unlikely to undergo cyclopropanation by this mechanism, since formation of the carbocation center would be energetically highly unfavorable. However, such alkenes can still be cyclopropanated by suitable metal carbene complexes, but in these case the mechanism consists of a [2+2] cycloaddition to form a metallacyclobutane, followed by reductive elimination of the cyclopropane product, as shown in Figure 14.14 on the following page. We will see shortly how such a [2+2] cycloaddition is thermally allowed.

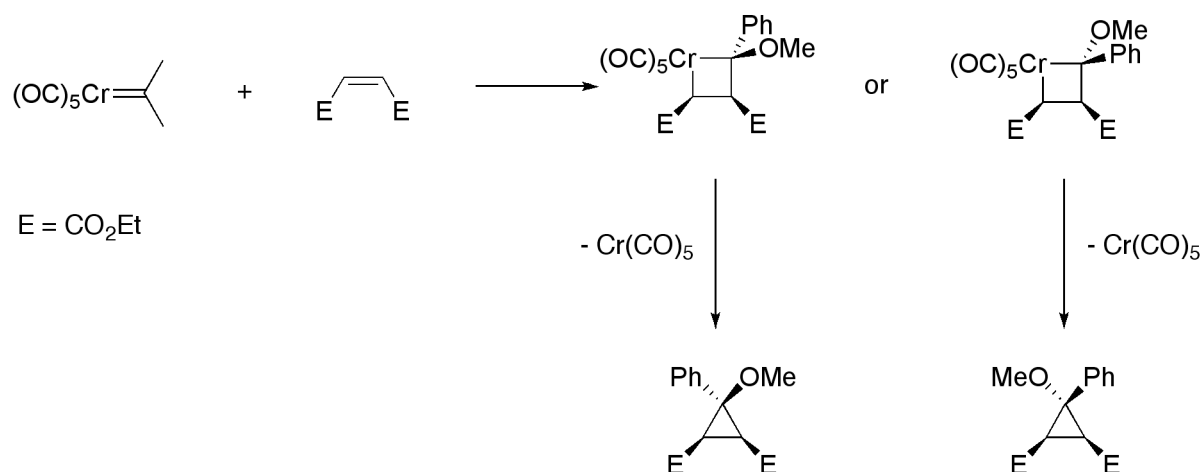


Figure 14.14. Cyclopropanation of an alkene by [2 + 2] cycloaddition followed by RE.

14.6. Alkene Metathesis

We have seen that some TM-promoted or -catalyzed cyclopropanation reactions proceed *via* a [2+2] cycloaddition of a TM carbene complex to an alkene, forming a metallacyclobutane intermediate. It turns out that this type of mechanistic step is quite commonly observed in the reactions of metal carbene complexes, both Fischer-type and Schrock-type, with main-group compounds containing double bonds. One example, with a useful analog in purely main-group chemistry, is the formation of alkenes from carbonyl compounds, as shown in Figure 14.15 below in the reaction of a lactone with $Cp_2Ti=CH_2$ derived from Tebbe's reagent.

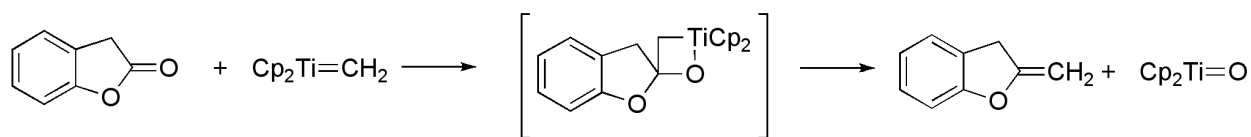


Figure 14.15. Reaction of a lactone with Tebbe's reagent.

The metallaoxacyclobutane intermediate in this reaction is quite closely analogous to the phosphaoxacyclobutane formed in the famous Wittig reaction between a ketone and a phosphorus ylide (Wittig reagent), named for its discoverer, Georg Wittig (1897-1987, Nobel Prize in Chemistry 1979). An example of the Wittig reaction is shown in Figure 14.16 on the following page.

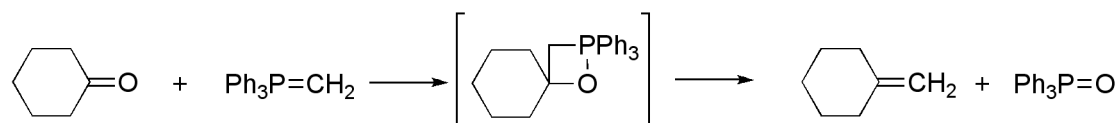


Figure 14.16. An example of the Wittig reaction.

In either case, the thermodynamic driving force for the reaction is the oxophilicity of the non-carbon atom (titanium or phosphorus).

The most important and widely used reactions of carbene complexes, however, involve [2+2] cycloadditions between metal carbene complexes and alkenes to form a metallacyclobutane. For some metal fragments, this reaction is followed by reductive elimination of cyclopropane, but for many, it is instead followed by a [2+2] *retrocycloaddition* or *cycloreversion* to yield a new metal carbene complex and a new alkene, as shown in Figure 14.17 below.

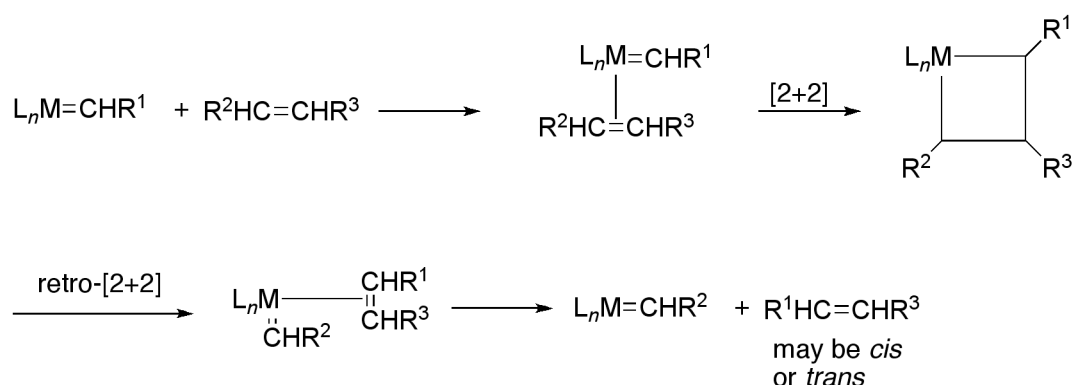
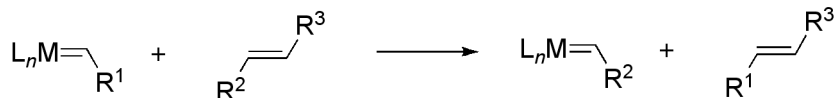


Figure 14.17. The basic mechanism of double-bond metathesis.

This reaction is called a double-bond metathesis, from Greek μετά, “besides” and θέσις, “setting.” The metal fragment L_nM and the carbene fragments CHR^1 , CHR^2 , and CHR^3 swap places, just as in σ -bond metathesis, which we have already discussed, a reaction type in which groups bound to each other by σ -type single bonds swap places.

Now let us see what might happen when a metal carbene complex $L_nM=CHR^1$ is treated with an excess of the alkene $R^2HC=CHR^3$, in Figure 14.18 below.

Initiation



Propagation

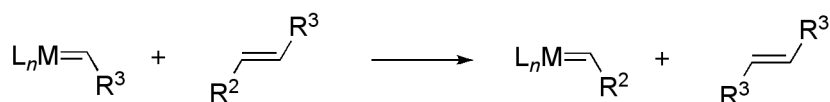
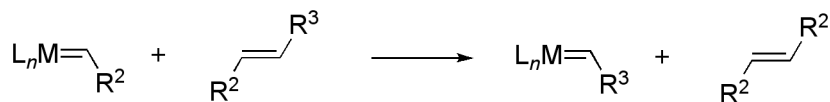


Figure 14.18. Initiation and propagation of alkene metathesis.

The initial metal carbene species has a substituent R^1 that is not present in the alkene, but after an “initiation” step in which the CHR^1 group is exchanged with CHR^2 , we can write a pair of “propagation” steps whose net reaction equation is shown in Figure 14.19 below.

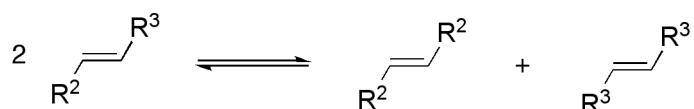


Figure 14.19. The net reaction of alkene metathesis.

This net reaction, an exchange of carbene moieties between two molecules of an alkene, can be termed alkene metathesis (sometimes called olefin metathesis; “olefin” is an old-fashioned word for an alkene). Alkene metathesis is often said to be catalyzed by metal carbene complexes, but it is more strictly correct to say that $L_nM=CHR^1$ in the above reaction scheme is an initiator or precatalyst, not a catalyst itself. After all, in the reaction scheme above, one molecule of the starting alkene is converted to $R^1HC=CHR^3$, which contains a substituent *not* present in the starting alkene. However, many metathesis reactions are run with only a few percent (by mole) of metal carbene compared to the alkene, so only a few

alkene molecules out of every hundred have a “non-native” substituent attached. Thus, very high yields are often possible for metal-catalyzed metathesis reactions.

The [2+2] cycloaddition and retrocycloaddition steps are notable in that they superficially resemble a type of reaction that is generally considered “forbidden” (that is, possessing a high activation energy for electronic reasons) in organic chemistry, namely, the concerted cycloaddition of two alkenes to form a cyclobutane. The reason this purely organic [2+2] cycloaddition is forbidden by the Woodward-Hoffmann rules is that the transition state must involve interaction of the HOMO (π bonding MO) of one alkene with the LUMO (π antibonding MO) of the other. One can see in Figure 14.20 below that this leads, in the case of two molecules of ethene, to exactly zero net overlap. If the alkenes are less symmetric than ethene, the overlap may not be rigorously zero, but it will still be quite small.

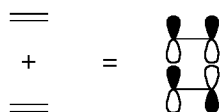


Figure 14.20. Orbital diagram showing why the [2 + 2] cycloaddition of a pair of alkenes is forbidden.

In the case of [2+2] cycloaddition of a metal carbene complex and an alkene, however, the π HOMO or π antibonding LUMO of the metal-carbene will have an additional node due to the presence of a metal d orbital in the bonding scheme, so the overlap with the LUMO or HOMO, respectively, of the alkene will be significantly greater, lowering the transition state energy and increasing the reaction rate. The relevant orbitals are shown in Figure 14.21 below.

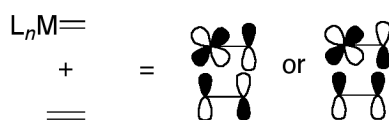


Figure 14.21. Orbital diagram showing why the [2 + 2] cycloaddition of an alkene and a TM carbene complex is allowed.

The alkene metathesis reaction is of tremendous importance in synthetic chemistry, both in large-scale industrial processes and in the synthesis of complex organic molecules such as natural products. The importance of this reaction was recognized by the awarding of the 2005 Nobel Prize in Chemistry to Yves Chauvin (1930-2015, French Institute of Petroleum), Robert Grubbs (1942-2021, Caltech) and Richard Schrock (b. 1945, MIT), for their seminal work in determining the mechanism of alkene metathesis and developing its synthetic utility.

A wide variety of catalysts (or precatalysts) for alkene metathesis are known. Early work on metathesis by industrial chemists used heterogeneous catalyst mixtures, such as $\text{Re}_2\text{O}_7/\text{Me}_4\text{Sn}/\text{Al}_2\text{O}_3$, $\text{MoO}_3/\beta\text{-TiO}_2/\text{Me}_4\text{Sn}$, and $\text{W}(\text{CO})_6/\text{Me}_4\text{Sn}/\text{PhOH}$. Though heterogeneous catalysis was (and still is) widely used in industrial-scale processes due to the ease of separating the product from the catalyst, the mechanisms of such reactions are very difficult to determine experimentally. Thus, most of the mechanistic work on alkene metathesis has been done with soluble, molecular metal carbene complexes, which are also readily tunable by the substitution of ligands and substituents on ligands. Some of the most effective homogeneous metathesis catalysts, developed by Schrock and Grubbs, are shown in Figure 14.22 below.

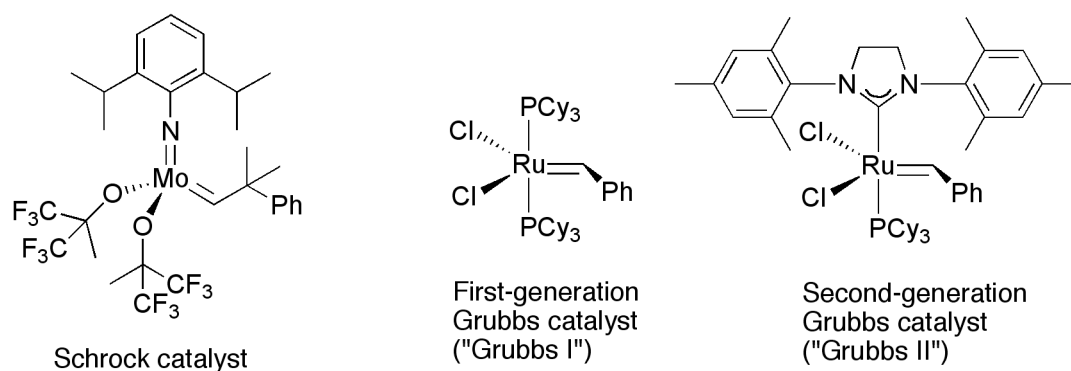


Figure 14.22. Commonly used alkene metathesis catalysts.

The Schrock catalyst (and others like it) is a classic example of a Schrock carbene complex. It has an early metal in a high (d^0) oxidation state, Mo(VI), with highly electronegative, π -donor ligands (alkoxides, imide). The Grubbs catalysts have somewhat more Fischer carbene character, though they are, in a sense, intermediate between Fischer and Schrock. Their

carbene ligands do not have any π -donor heteroatom substituents, as do classical Fischer carbene complexes like $(OC)_5Cr=(OMe)(Me)$, but the phenyl substituent, while it would not give the free carbene any resonance forms with an octet, would still have the electron-deficiency highly delocalized. Additionally, Ru is a late metal, in the low Ru(II), d^6 oxidation state if CHPh is considered a neutral, Fischer carbene ligand, but in the higher Ru(IV), d^4 oxidation state if it is considered a dianionic, Schrock carbene ligand. Note that the NHC in Grubbs II is not an active “carbene” in the mechanism of metathesis: while its steric and electronic properties are surely important for reactivity, it is still a spectator or ancillary ligand. In general, the Schrock catalyst and similar species is often more reactive than the Grubbs catalysts, allowing reactions to occur that would be catalyzed sluggishly, or not at all, by the Grubbs species. However, its strongly polar Mo–O, Mo–N, and Mo=C bonds make it vulnerable to hydrolysis (protonation of the ligands by trace water), necessitating the use of inert-atmosphere glove box or Schlenk line methods for its handling. Additionally, the oxophilicity of Mo can cause undesired side reactions between the catalyst and alkene substrates that also contain oxygen functional groups. The Grubbs catalysts, in contrast, are air-stable, and can be handled on the benchtop without any special precautions. They are also more tolerant of functional groups than the Schrock catalysts. Some metathesis reactions, nevertheless, will not proceed readily under Grubbs catalyst conditions, with the Schrock catalyst required.

It is often useful to classify alkene metathesis reactions by type, depending on the substrate(s) involved. The basic mechanism involving [2+2] cycloadditions and cycloreversions is assumed to be generally applicable. Perhaps the conceptually simplest type of alkene metathesis is self-metathesis, the reaction of one alkene under metathesis conditions to yield two different alkene products, as shown in Figure 14.23 below.

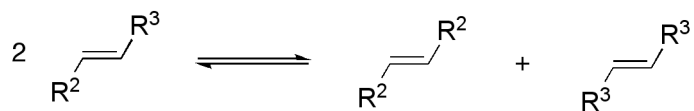


Figure 14.23. General equation for self-metathesis.

In general, one would not expect a self-metathesis reaction like that of Figure 14.23 to give an especially high yield. Since the number of C=C double bonds is the same in both the reactants and products, the reaction will likely not be very thermodynamically favored in either the forward or the reverse direction, so we expect that K will have a value fairly close to 1. Catalysts can speed a reaction system's approach to equilibrium, but cannot change thermodynamic quantities like K or ΔG° . Self-metathesis reactions can proceed in high yield, however, when one of their products is ethene and the other is a significantly larger alkene. Consider the reaction shown in Figure 14.24 below.

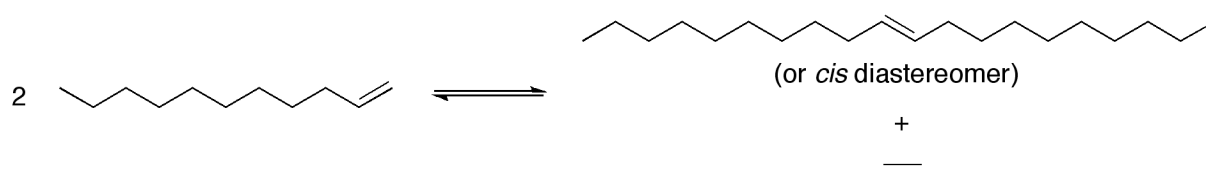


Figure 14.24. A self-metathesis reaction with a very volatile product alkene.

While this reaction may not have a large value of K , both the 11-carbon reactant and the 20-carbon product will definitely have higher boiling points than the two-carbon product ethene (whose boiling point is only 103.7 °C). If the reaction is not run in a tightly sealed vessel, then ethene will continuously be removed from the reaction mixture by evaporation, driving the reaction to the right according to Le Châtelier's principle. Thus, self-metathesis reactions of terminal alkenes, with ethene as a product, can often give very high yields.

When a mixture of two alkenes are subjected to metathesis conditions, the reaction is known as cross metathesis, as shown in Figure 14.25 on the following page. Again, this type of reaction would not, in general, be predicted to proceed in high yield, instead resulting in a statistical mixture of alkenes. However, as with self-metathesis, if both reacting alkenes are terminal, ethene will be expelled as a product, so yields can be high, as shown in Figure 14.26 on the following page.

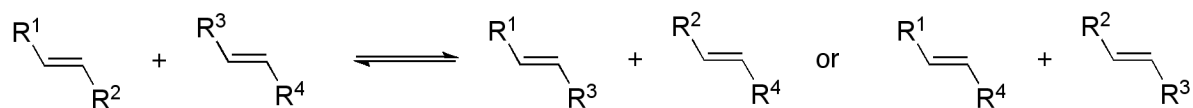


Figure 14.25. A generic example of cross metathesis.

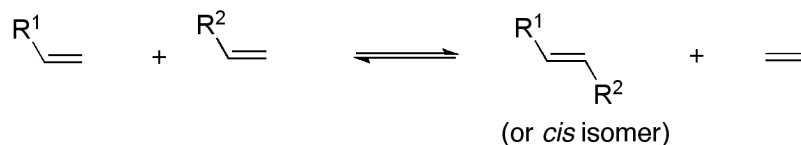


Figure 14.26. Cross metathesis with ethene as a stoichiometric product

A special kind of cross metathesis consists of reactions in which alkene functional groups are present at each end of a large molecule. Metathesis in such a case will result in the formation of a new, cyclic alkene and extrusion of an acyclic one, in a reaction known as ring-closing metathesis, or RCM for short. A general example of RCM is shown in Figure 14.27 below.

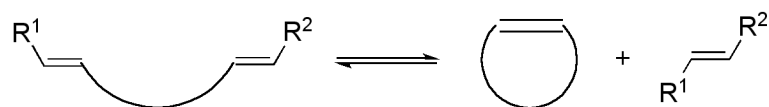


Figure 14.27. A generic example of ring-closing metathesis (RCM).

If the acyclic alkene extruded is ethene ($\text{R}^1 = \text{R}^2 = \text{H}$) or another low-boiling alkene, RCM can proceed in excellent yield. RCM is often used by organic chemists in the synthesis of complex natural products. The example in Figure 14.28 on the following page, from the group of Stephen Martin of the University of Texas at Austin, demonstrates the utility of RCM in a key step of the total synthesis of manzamine A, an alkaloid with antitumor activity derived from sea sponges. This reaction is notable because it proceeds well (67% yield) with Schrock's catalyst, despite the presence of ketone, ester, and amide functional groups and the oxophilicity of Mo(VI). It is notable that the terminal alkene functionalities react in preference to the alkene in conjugation with the ester.

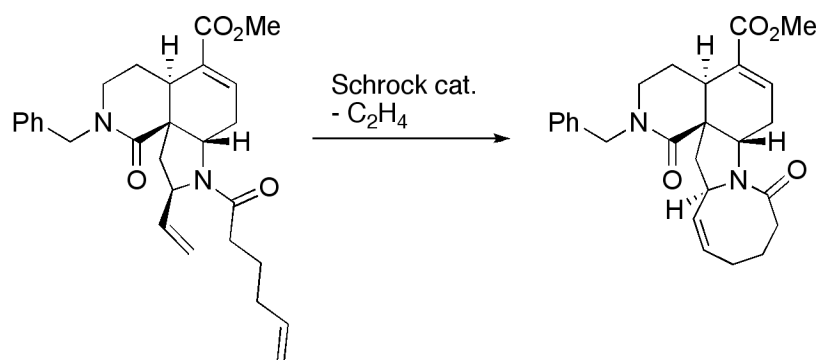


Figure 14.28. RCM in a key step of the synthesis of manzamine A.

The reverse of RCM is ring-opening metathesis (ROM), which can be accomplished by treating a cyclic alkene with excess ethene under high pressure. Again, no catalyst can overcome thermodynamics, so the high pressure and excess amounts of ethene are required to make the reaction proceed in the desired direction as per Le Châtelier's principle. Perhaps more interesting than simple ROM is what happens when a cyclic alkene, especially a relatively strained one, is heated at high concentration under metathesis conditions. The scheme of Figure 14.29 on the following page shows the reaction of excess 1-methylcyclobutene with a catalytic amount of the metathesis catalyst $(OC)_5W=CPh_2$. We see in this reaction that the series of cycloadditions and cycloreversions leads to a polymer of 1-methylcyclobutene, with the CPh_2 group from the catalyst (strictly speaking, a polymerization initiator, not a catalyst, in this case) at one end, and the metal carbene at the other. This reaction is known as ring-opening metathesis polymerization or ROMP. A notable feature of ROMP is that the resulting polymer has an active metal carbene moiety at one end, so if more monomer is added, the polymerization will continue. Alternatively, if a different cyclic alkene monomer is added, a so-called "block copolymer" will form, with the new monomer repeating in a "block" after the old one. Because of the ability of ROMP polymers to react with further alkene, they are often referred to as "living polymers."

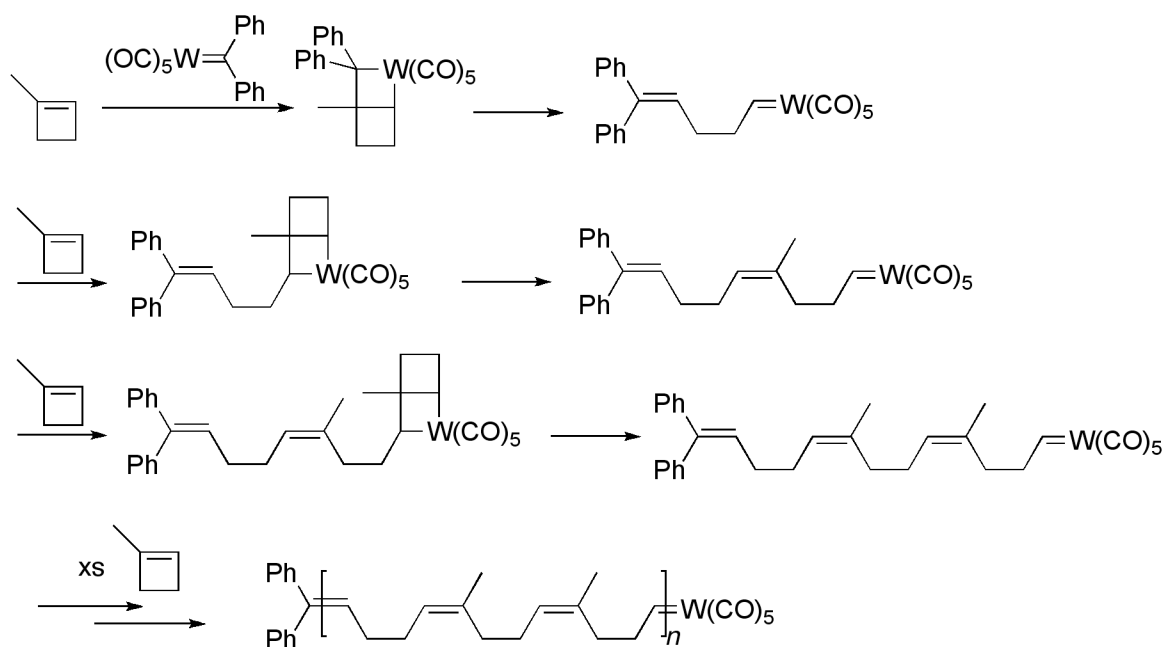


Figure 14.29. Ring-opening metathesis polymerization (ROMP) of 1-methylcyclobutene.

An additional type of polymerization occurs when high concentrations of acyclic terminal dienes are subjected to metathesis conditions. At low concentrations, a metal carbene intermediate formed on one end will be most likely to react with the other end of the molecule, leading to cyclization (RCM). At high concentrations, however, it will react with another molecule of monomer, leading to a type of polymerization known as acyclic diene metathesis polymerization or ADMET (**A**cylic **D**iene **M**ETathesis polymerization). An example of ADMET is shown in Figure 14.30 on the following page.

14.7. Alkyne and Enyne Metathesis

We have seen that transition metal carbene complexes, with M-C double bonds, can serve as catalysts (or precatalysts/initiators) for the double-bond metathesis of alkenes. Similarly, transition metal carbyne complexes can catalyze/initiate the triple-bond metathesis of alkynes. The general mechanism, shown in Figure 14.31 on the following page, is very similar to that of alkene metathesis, with each metathesis step involving a [2+2] cycloaddition to

form a metallacyclobutadiene intermediate (as opposed to a metallacyclobutane), followed by a [2+2] cycloreversion.

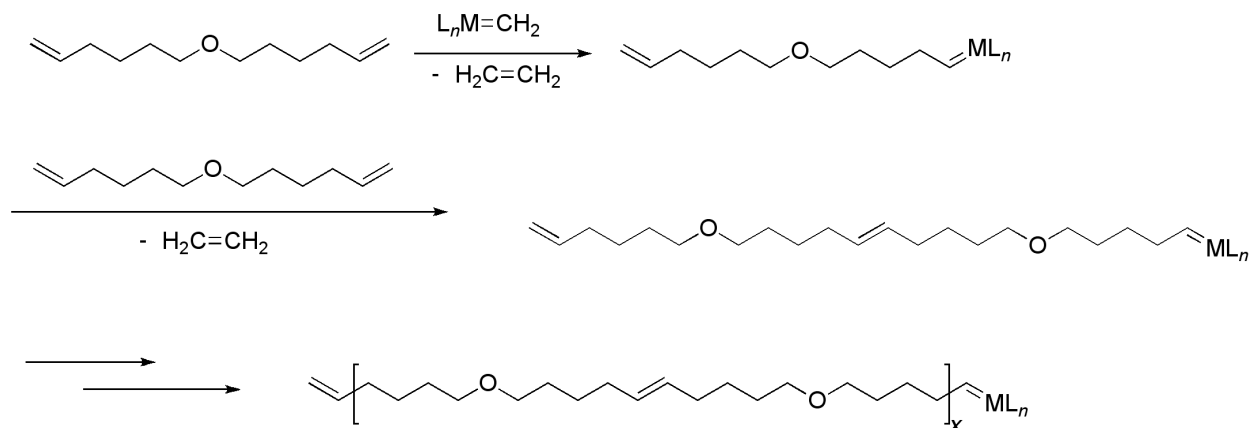


Figure 14.30. An example of ADMET polymerization.

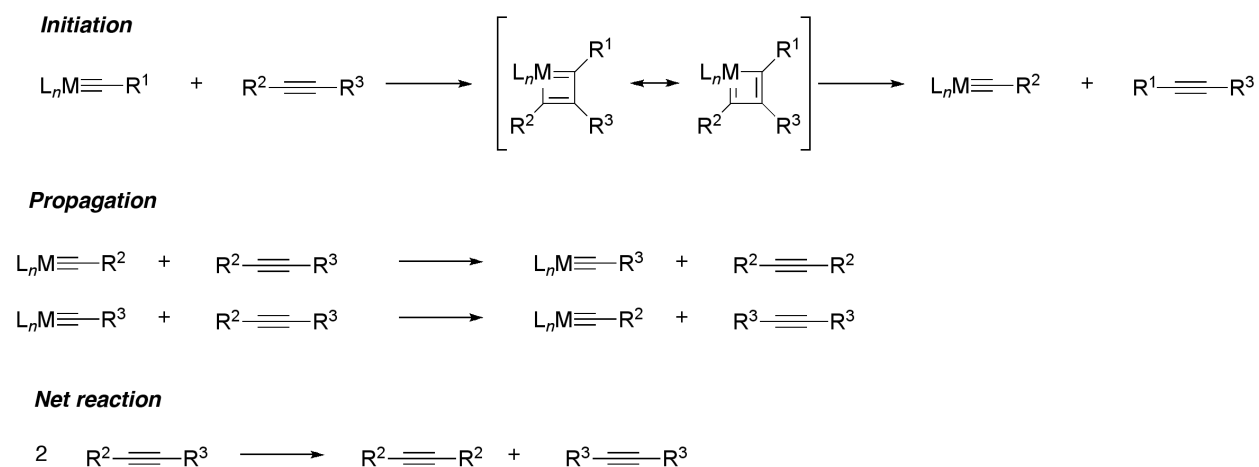


Figure 14.31. The basic mechanism of alkyne metathesis.

As with alkene metathesis, an equilibrium mixture of product alkynes may be reached, but the reaction may be driven in the forward direction if a volatile small alkyne is produced and removed from the reaction mixture. The example in Figure 14.32 on the following page shows a ring-closing alkyne metathesis (RCAM) reaction that is an important step in the total synthesis of the natural product prostaglandin E₂-1,15-lactone. The alkyne formed in addition to the desired complex product is 2-butyne, whose boiling point is only 27 °C.

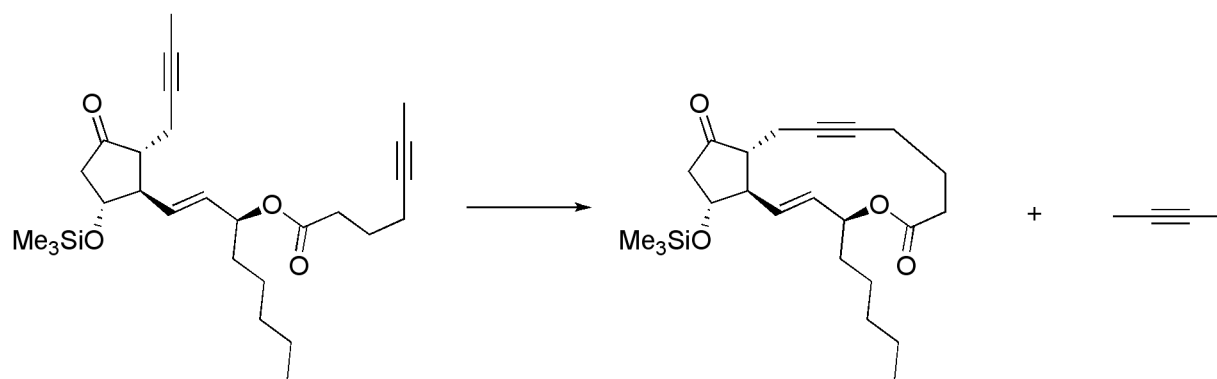
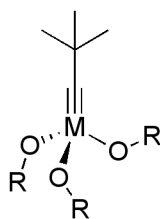


Figure 14.32. A ring-closing alkyne metathesis in the synthesis of prostaglandin E₂-1,15-lactone.

Quite a few metal carbyne complexes have been prepared, and some that are widely used as alkyne metathesis catalysts, developed by Schrock, are shown in Figure 14.33 below.



M = W: R = C(CH₃)₃ (= ^tBu)

M = Mo: R = C(CH₃)(CF₃)₂

Figure 14.33. Schrock's alkyne metathesis catalysts.

Metal carbene complexes may catalyze (or initiate) reactions involving a combination of alkene and alkyne metathesis; such reactions are commonly termed enyne metathesis. In most enyne metathesis reactions, the alkene and alkyne are part of the same molecule, as shown in the example catalytic cycle in Figure 14.34 on the following page, giving an intramolecular reaction.

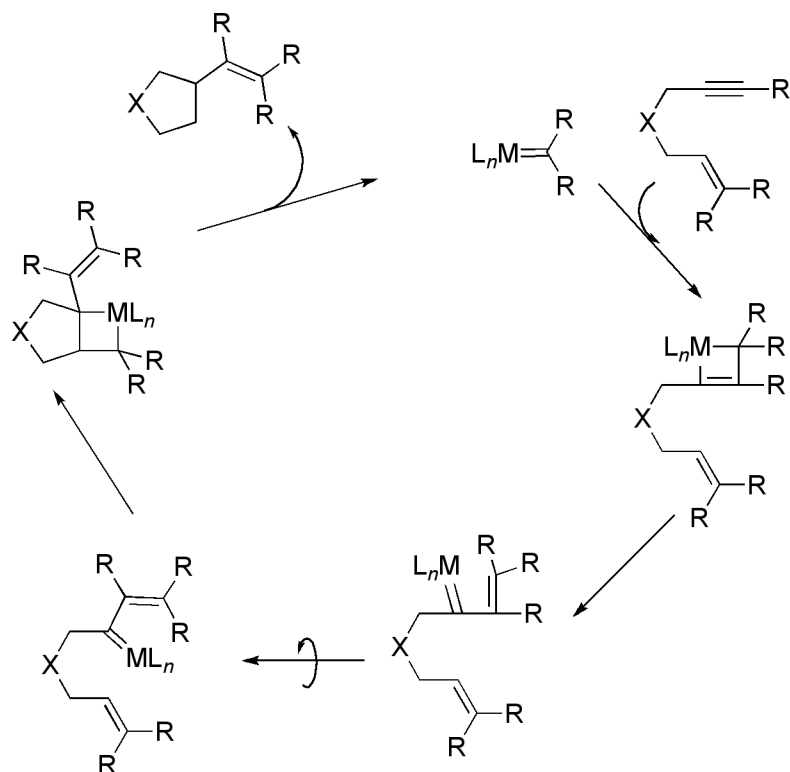


Figure 14.34. An example of an intramolecular enyne metathesis reaction.

However, some intermolecular enyne metathesis reactions have been performed with an alkyne and ethene as the reactants, as shown in Figure 14.35 below.

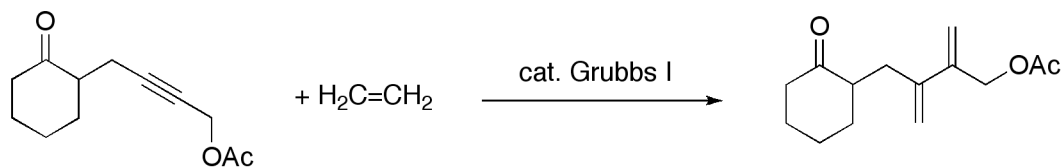


Figure 14.35. An example of an intermolecular enyne metathesis reaction.

The “Grubbs I” and “Grubbs II” alkene metathesis catalysts have been successfully used for a variety of enyne metathesis reactions.

14.8. Cross-Coupling Reactions

As we have discussed with regards to alkene metathesis, reactions that enable the formation of a new carbon-carbon bond are of tremendous importance in organic synthesis. Another

class of such reactions, known as cross-coupling reactions, consists of the reaction of an organic halide or triflate with an organometallic complex of an electropositive metal or semimetal. Such reactions have the general form $R-X + R'-M \rightarrow R-R' + M-X$. In this type of reaction, the R groups are sometimes alkyl, but are more commonly either aryl, alkenyl (vinyl) or alkynyl. M is either a main-group element (B or Sn) or a transition metal in an oxidation state with a d^{10} electron configuration, such as Zn(II) or Cu(I). These reactions are catalyzed by late transition metals, in the vast majority of cases Pd. The importance of these reactions was exemplified by the awarding of the 2010 Nobel Prize in Chemistry to Richard Heck (1931-2015), Ei-ichi Negishi (1935-2021) and Akira Suzuki (b. 1930) for their work in palladium-catalyzed cross-coupling reactions.

The first cross-coupling reaction we will discuss is known as the Stille coupling or Stille reaction, after John Stille of Colorado State University (1930-1989). Stille almost certainly would have had a share of the 2010 Nobel Prize, had he not died in a plane crash in 1989. The Stille reaction consists of the coupling of an aryl or alkenyl bromide, iodide, or triflate with a trialkylalkenyltin or trialkylaryl tin compound (stannane), shown for the aryl example as $Ar-X + Ar'-SnR_3 \rightarrow Ar-Ar' + R_3Sn-X$, where R is usually methyl or *n*-butyl.

Clearly, this reaction will not proceed at any reasonable rate without catalysis: the aryl halide or triflate is often not activated to nucleophilic aryl substitution (S_NAr) reactions with a π -acceptor substituent such as nitro or carbonyl, and besides, aryl tin compounds do not have especially nucleophilic aryl groups (the Pauling electronegativities of C and Sn are 2.55 and 1.96, respectively, so a C-Sn bond is not terribly polar). The generally accepted catalytic cycle for the Stille coupling is shown in Figure 14.36 on the following page, starting from a Pd(0) species such as $Pd(PPh_3)_4$.

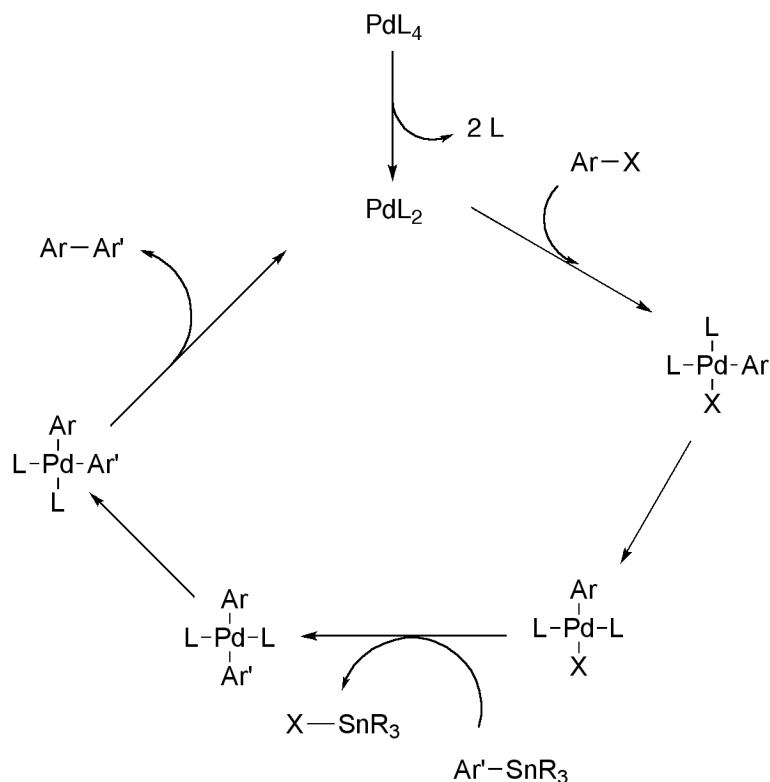
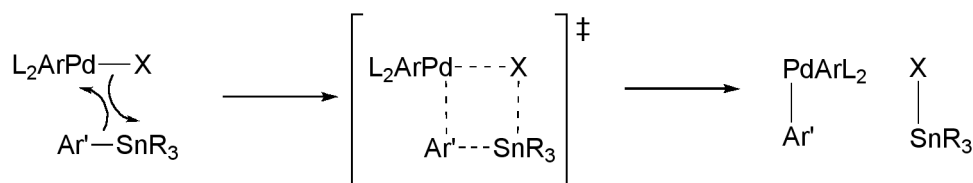


Figure 14.36. A general catalytic cycle for the Stille coupling.

The 18e PdL₄ species (where often L = PPh₃) is really a precatalyst, not the active catalyst: dissociation of 2 L forms the 14e Pd(0) species PdL₂. This undergoes concerted oxidative addition of the aryl halide (remember, this OA is concerted, since an S_N2 reaction on an aryl group is impossible) to yield a 16e Pd(II) complex with *cis* stereochemistry. This complex is less stable than its *trans* isomer, and it usually undergoes *cis-trans* isomerization before the next step. After the isomerization, a reaction called transmetalation (also spelled transmetalation) occurs, replacing the halide with the other aryl group and yielding one of the reaction products, a trialkyltin halide. The resulting *trans* Pd(II) diaryl complex (16e) then undergoes *trans-cis* isomerization so that the aryl ligands can be *cis*, as is required for the concerted reductive elimination that yields the organic biaryl product and regenerates PdL₂.

This reaction is shown for the coupling of two aryl groups. Alkenyl (vinyl) groups also work well, either on the organic halide or triflate and on the trialkyltin compound. In such cases,

We have already discussed the oxidative addition, reductive elimination, and *cis-trans* isomerization steps of this catalytic cycle, but not transmetallation. The precise mechanism of transmetallation depends on the group on Sn being transferred to Pd. If this group is bound by an sp^2 -hybridized C atom, such as an aryl or alkenyl group, the transmetallation is believed to be concerted, with a four-membered ring transition state, essentially a σ -bond metathesis, as shown in Figure 14.37 below.



The retention of configuration at alkenyl groups is what would be expected of a σ -bond metathesis mechanism. This is sometimes still observed for the transfer of alkyl groups (without β -hydrogens, of course) from Sn to Pd if the solvent is a weakly coordinating one such as toluene or dichloromethane; retention of configuration is seen at the alkyl group.

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shown below have been called S_E2 (substitution, electrophilic, bimolecular): it is essentially the electrophilic version of an S_N2 reaction, with a similar “umbrella in the wind” transition state, leading to inversion of configuration. In Figure 14.38 below, S is the coordinating solvent.

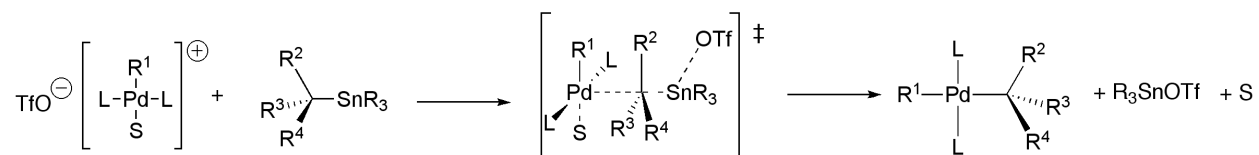


Figure 14.38. The S_E2 mechanism for transmetalation.

If a Stille coupling is run under a carbon monoxide atmosphere, ketones are formed: the net reaction (showing aryl groups) is $\text{Ar-X} + \text{Ar}'\text{-SnR}_3 + \text{CO} \rightarrow (\text{Ar})(\text{Ar}')\text{C=O} + \text{R}_3\text{Sn-X}$. This reaction is commonly known as the carbonylative Stille coupling, as a carbonyl group is added to the biaryl product that would otherwise be formed. The catalytic cycle is shown in Figure 14.39 on the following page. The mechanism for carbonylative Stille coupling is broadly similar to that for regular Stille coupling, with the key difference being that the aryl group from the aryl halide migrates to a CO ligand.

The Stille reaction is reliable and has good scope in terms of its organic substrates. The organotin compounds used are advantageous in that they are far less moisture-sensitive than organometallic compounds of more electropositive main-group elements (such as organolithium or organomagnesium species). However, the organotin halide or triflate byproducts can be difficult to separate from the organic coupling product, causing purification difficulty. Organotin compounds are also quite neurotoxic. While they are perfectly safe to use on a small scale, in a laboratory equipped with a good fume hood, their use on an industrial scale is far more hazardous. If the desired product of a Stille coupling is a drug, then the difficulty in purification, combined with the toxicity of organotin compounds, can make the Stille reaction unattractive.

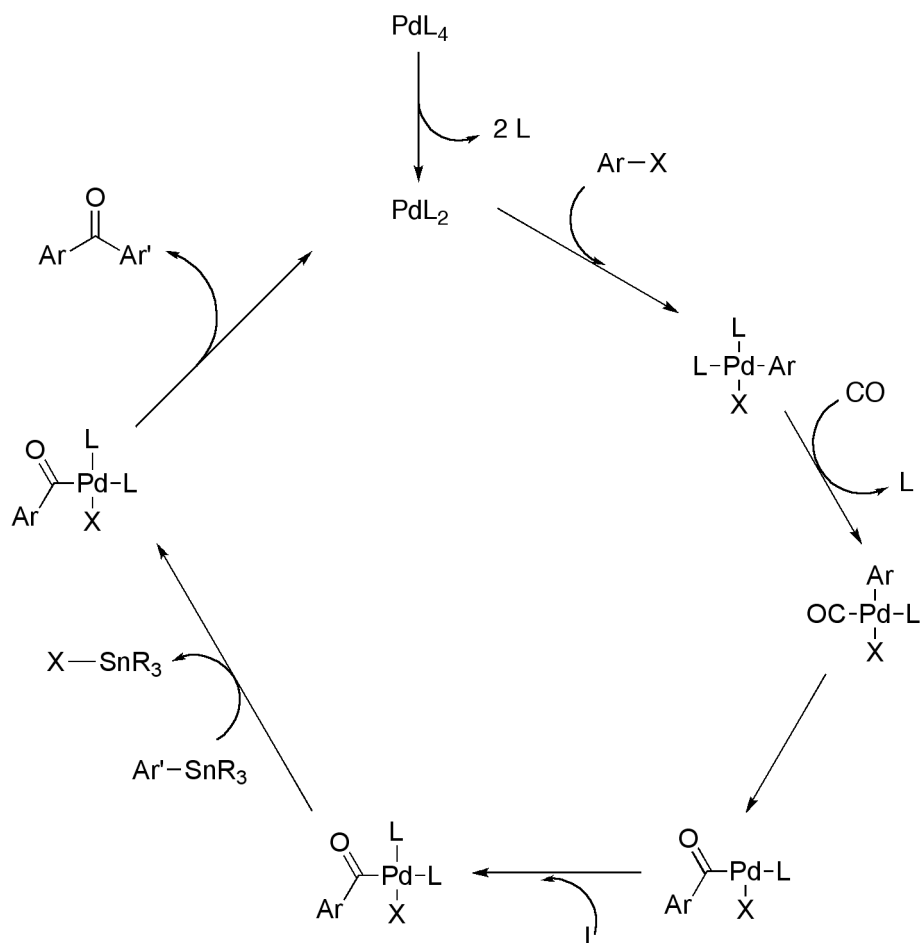


Figure 14.39. The catalytic cycle for the carbonylative Stille coupling.

Another important cross-coupling reaction is the Suzuki-Miyaura coupling (sometimes known just as the Suzuki coupling), after Akira Suzuki and Norio Miyaura (b. 1946). It is akin to the Stille coupling, but an aryl- or alkenylboronic acid or ester is used in place of an organotin compound, so the reaction is $\text{Ar-X} + \text{Ar'-B(OR)}_2 \rightarrow \text{Ar-Ar'} + (\text{RO})_2\text{B-X}$. Additionally, a stoichiometric amount of a base which is nucleophilic at oxygen is required for the reaction to proceed. These bases can be metal hydroxides MOH ($\text{M} = \text{Na}, \text{Li}$), carbonates M_2CO_3 ($\text{M} = \text{Na}, \text{K}, \text{Cs}$), NaOMe , or K_3PO_4 .

The catalytic cycle for the Suzuki coupling is shown in Figure 14.40 on the following page, with the added base shown as hydroxide.

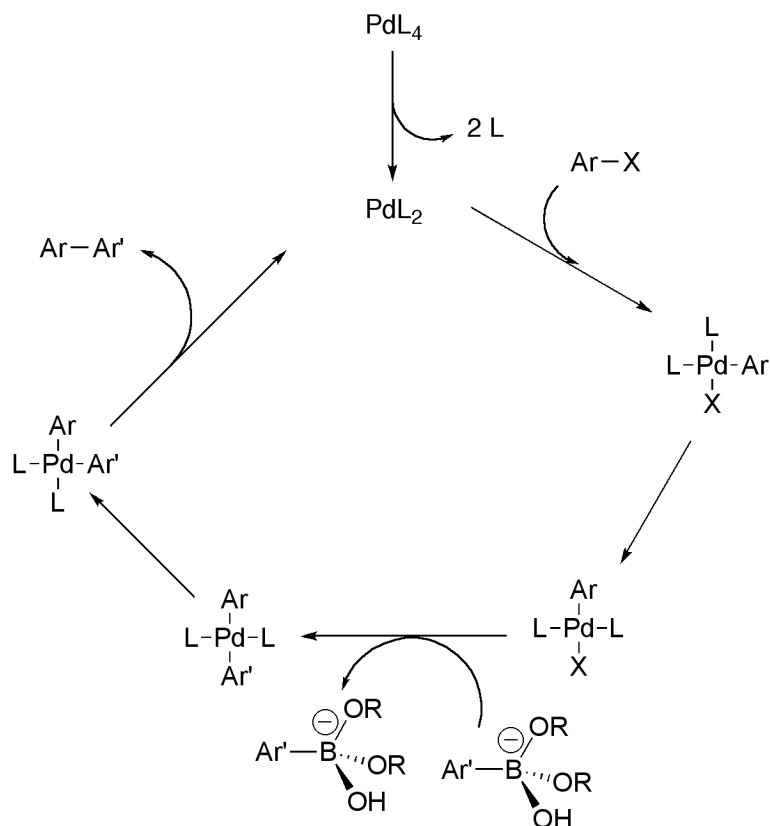


Figure 14.40. The catalytic cycle for the Suzuki-Miyaura coupling.

The base is necessary for the transmetalation step.¹¹⁰ (If you wish to be pedantic, then, strictly speaking, this isn't truly a transmetalation since boron is a nonmetal or semimetal, but this reaction is widely referred to as a transmetalation anyway.) The transfer of the second aryl group from B to Pd is much faster when the boron is present in an anionic borate species. Because of this, perhaps the stoichiometric reaction should instead be written as $\text{Ar-X} + \text{Ar'-B(OR)}_2 + \text{MOH} \rightarrow \text{Ar-Ar'} + \text{M}[(\text{RO})_2(\text{HO})\text{B-X}]$. Less work has been done on the details of the transmetalation mechanism in this reaction than on that in the Stille coupling.

The boron-containing products of the Suzuki coupling are generally easier to separate from the desired organic product than are the tin-containing products of the Stille coupling. Thus,

¹¹⁰ If you wish to be pedantic, then, strictly speaking, this step is not truly a transmetalation, since boron is usually considered to be a nonmetal or a semimetal. Nevertheless, this reaction is widely referred to as a transmetalation.

the Suzuki coupling is widely used in industry for the synthesis of pharmaceutical agents. It has also been used in key steps in organic total synthesis projects. The reaction shown in Figure 14.41 on the following page, from the group of Clayton Heathcock (b. 1936) of the University of California, Berkeley, is the last step of the total synthesis of myxalamide A, a naturally occurring antibiotic produced by *Myxococcus xanthus*. It illustrates the utility of the Suzuki coupling in joining alkenyl carbons, as well as its remarkable functional group tolerance. In this reaction, the Heathcock group used the Pd(II) species Pd(OAc)₂, which is reduced to Pd(0) *in situ* by the phosphine ligand. This reaction also used a phosphine ligand salt, enabling the catalysis to occur in water. The diethylisopropylamine is here in place of the usual oxygen-centered base.

The third “straightforward” cross-coupling reaction that we will discuss is the Negishi coupling, devised by Ei-ichi Negishi, which involves an organozinc species in place of the organotin species of the Stille coupling or the organoboron species of the Suzuki coupling. The net reaction (for the aryl example) can be written as $\text{Ar-X} + \text{Ar}'\text{-ZnX} \rightarrow \text{Ar-Ar}' + \text{ZnX}_2$. The mechanism of the Negishi coupling is likely analogous to the Stille coupling, but with Zn in place of Sn, but much less mechanistic work has been done on it, so one cannot say for sure. Since Zn is quite electropositive (Pauling electronegativity 1.65), the organozinc reagents Ar'-ZnX are air- and moisture-sensitive like their Mg analogs, the Grignard reagents (Mg has electronegativity 1.31). In general, the scope of the Negishi coupling is narrower than that of the Stille or Suzuki couplings, due to the greater reactivity of the organozinc reagent with many functional groups. However, the reaction shown in Figure 14.42 on the following page did succeed, despite its functional groups present.

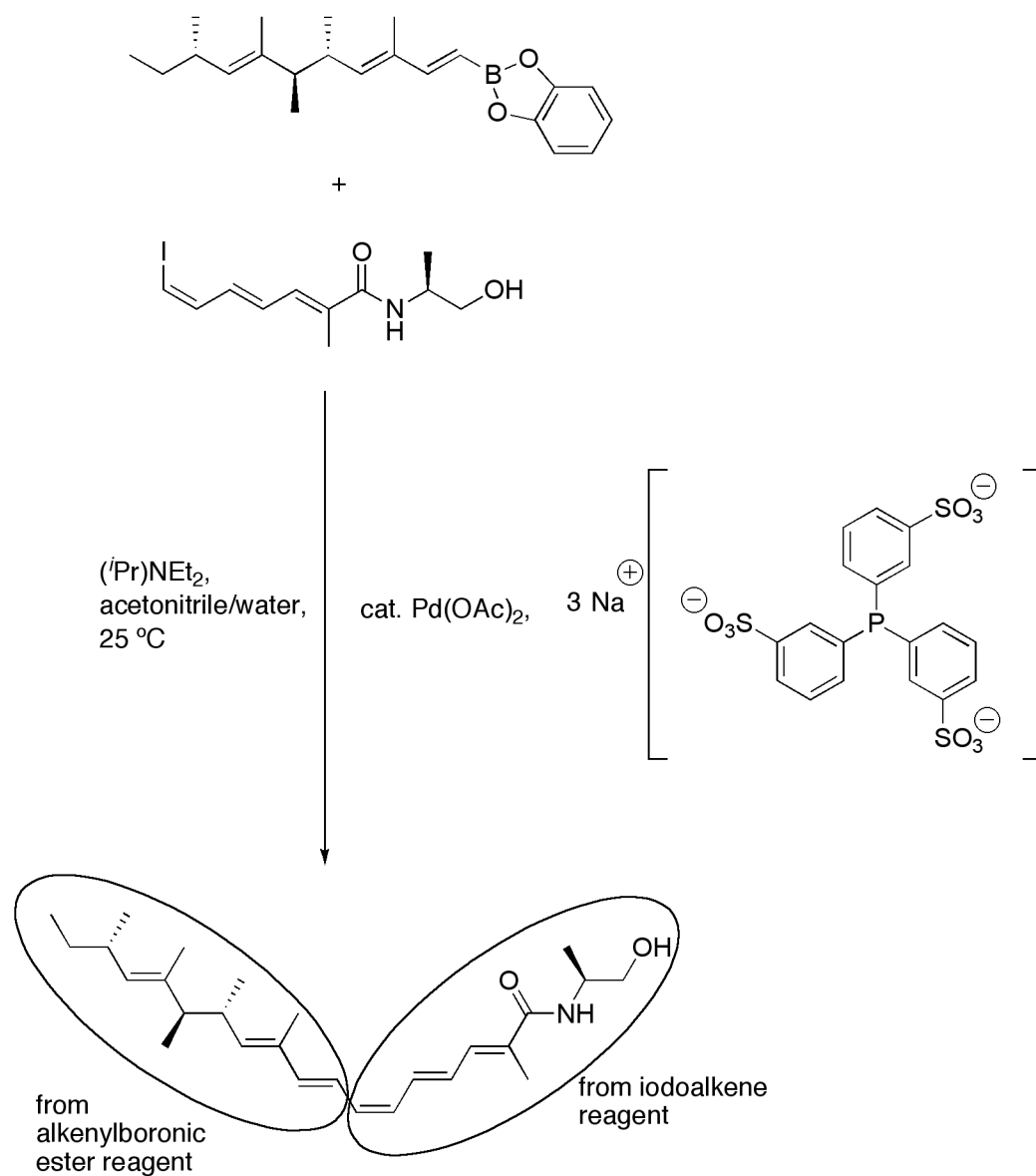


Figure 14.41. A Suzuki-Miyaura coupling in the final step of the synthesis of myxalamide A.

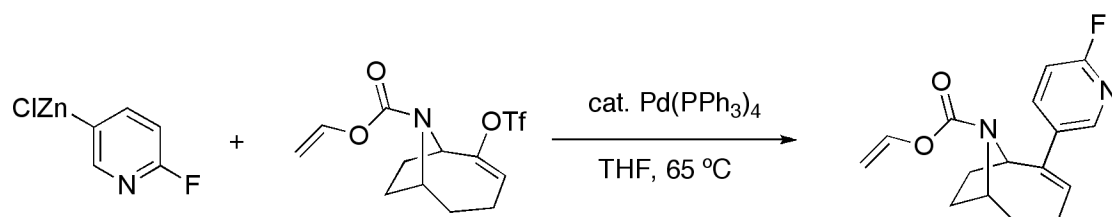


Figure 14.42. An example of a Negishi coupling with a range of functional groups present.

The final cross-coupling reaction that we will discuss is known as the Sonogashira coupling, after Kenkichi Sonogashira (b. 1931). The net reaction consists of the coupling of an aryl (or alkenyl) halide or triflate to a terminal alkyne, with a Brønsted-basic amine forming the ammonium halide or triflate: $\text{Ar-X} + \text{H-C}\equiv\text{C-R} + (\text{R}')_3\text{N} \rightarrow \text{Ar-C}\equiv\text{C-R} + [(\text{R}')_3\text{NH}^+][\text{X}^-]$. The mechanism of the Sonogashira coupling is more complicated than that of the Stille, Suzuki, or Negishi coupling, as it is catalyzed by *two* transition metals: a Pd(0) source as usual, and a Cu(I) source. Thus, two (linked) catalytic cycles are operative. The generally accepted mechanism for Sonogashira coupling is as shown in Figure 14.43 on the following page.

The Pd part of the catalytic cycle is basically the same as that of the Stille or Negishi couplings, with the transmetallation occurring from a copper(I) acetylide to give the palladium(II) aryl alkynyl complex and a copper(I) halide or triflate. The CuX species is then coordinated in an π^2 fashion by the terminal alkyne: deprotonation of the coordinated alkyne by the amine base regenerates the Cu(I) acetylide. This coordination of the alkyne to copper is essential to the deprotonation step: while free terminal alkynes are somewhat Brønsted-acidic ($\text{p}K_{\text{a}} \approx 20$ to 24), they are much less so than tertiary ammonium cations ($\text{p}K_{\text{a}} \approx 10$), so a tertiary amine is not basic enough to deprotonate a free terminal alkyne (remember that a $\text{p}K_{\text{a}}$ difference of 10 units corresponds to a factor of 10^{10} = ten billion difference in K_{a} values). Coordination of the alkyne by the Lewis-acidic Cu(I) thus increases its Brønsted acidity, making this an example of activation of a ligand to nucleophilic abstraction of H^+ . The fact that this reaction is catalytic in both Cu, as well as Pd, avoids the necessity of using stoichiometric amounts of copper(I) acetylides, which can be shock-sensitive explosives.

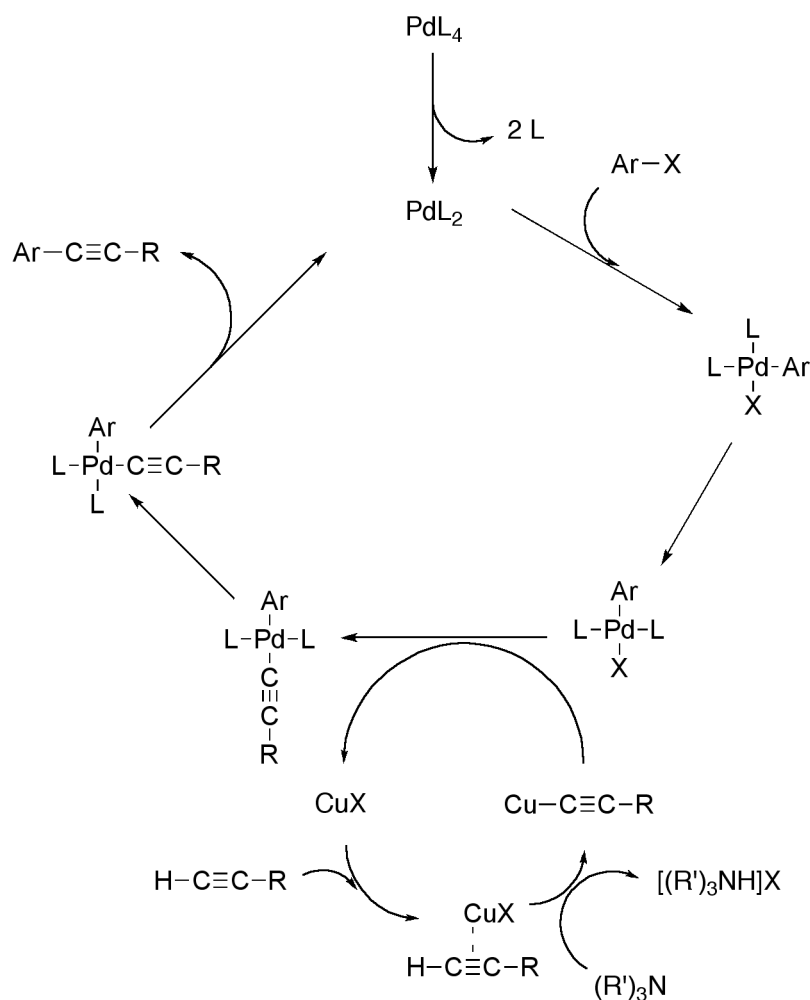


Figure 14.43. The linked catalytic cycles for the Sonogashira coupling.

14.9. The Mizoroki-Heck Reaction

The 2010 Nobel Prize in Chemistry was awarded to Akira Suzuki, Ei-ichi Negishi, and Richard Heck for their work on palladium-catalyzed cross-coupling reactions. The Suzuki coupling and Negishi coupling are standard textbook examples of cross-coupling reactions *per se*. On the other hand, the Heck reaction, sometimes called the Mizoroki-Heck reaction, after Tsutomu Mizoroki (1933-1980), who did early work on it, is not quite a cross-coupling reaction as we have discussed them, in that no stoichiometric metal or semimetal species (such as the Sn compounds of the Stille coupling or the Zn compounds of the Negishi coupling) are involved, and there is only one catalytic metal, palladium (as opposed to the Sonogashira coupling, which is catalytic in palladium *and* copper).

The Heck reaction has the general form $R^1-X + R^2HC=CR^3R^4 + B \rightarrow R^1R^2C=CR^3R^4 + [BH^+][X^-]$, where $X = Cl, Br, I, \text{ or } OTf$, $R^1 = \text{aryl, alkenyl, benzyl, or allyl}$, $R^2, R^3, \text{ and } R^4 = \text{hydrocarbonyl or H}$, and $B = \text{a neutral Brønsted base, often a trialkylamine}$. The net reaction is the replacement of a vinylic H atom with an organic group R^1 , or, alternatively, the addition of an alkenyl group to R^1 . Because of the addition of an alkene (olefin) functionality to R^1 , this reaction is sometimes known as the Heck olefination. The catalyst is usually a Pd(0) species such as $Pd(PPh_3)_4$ or a Pd(II) compound such as $Pd(OAc)_2$ that is reduced to Pd(0) *in situ*.

The generally accepted mechanism for the Heck reaction is shown in the catalytic cycle in Figure 14.44 on the following page, for a monosubstituted alkene. After formation of the PdL_2 active catalyst, the first step in the cycle is oxidative addition of the organic halide, much like the first step of a true cross-coupling reaction. Next, a ligand is replaced by the η^2 alkene. At this point, the alkene undergoes 1,2-migratory insertion into the Pd- R^1 bond (really, a *syn* addition of Pd and R^1 across the C=C double bond) to yield a new Pd alkyl complex, to which L recoordinates. This complex has an alkyl ligand with a β -hydrogen, so β -hydrogen elimination releases the product alkene. Finally, the base deprotonates Pd, causing the halide to dissociate and regenerating the active catalyst. This constitutes a reductive elimination of Pd by the ionic mechanism.

The regiochemistry and the stereochemistry of the Heck reaction are both worth mentioning. When a monosubstituted alkene is used, the product will be a 1,2-disubstituted alkene, not 1,1-disubstituted, since the R^1 group almost invariably adds to the *less* substituted position of the η^2 -alkene and the Pd to the more substituted part, as shown in Figure 14.47 on the following page. This selectivity is probably due to steric reasons: Heck reactions can be performed where the group R^1 is significantly larger than Pd and its ancillary ligands. Once the migratory insertion step has occurred, the *E* or *Z* stereochemistry of the product alkene is determined by the β -hydrogen elimination step, as shown in Figure 14.48 on the following page. The *E* isomer is formed in preference to the *Z*: this is the thermodynamic product (less steric clashing between R^1 and R^2), and it would also be expected to be the kinetic product, since in the β -hydrogen elimination step leading to it, R^1 and R^2 will be further apart in the transition state.

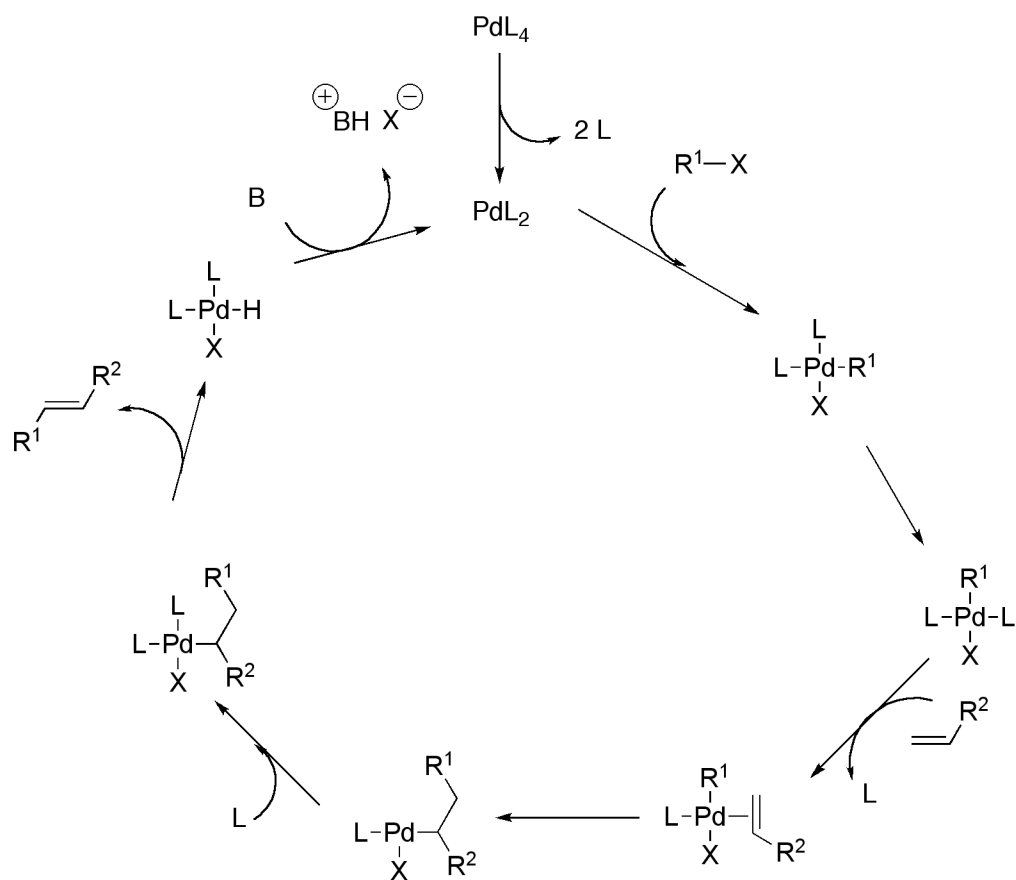


Figure 14.46. Catalytic cycle for the Mizoroki-Heck reaction.

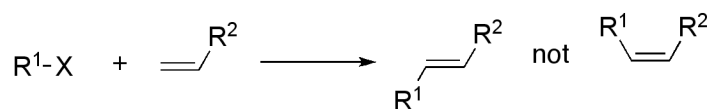


Figure 14.47. Regioselectivity of the Mizoroki-Heck reaction.

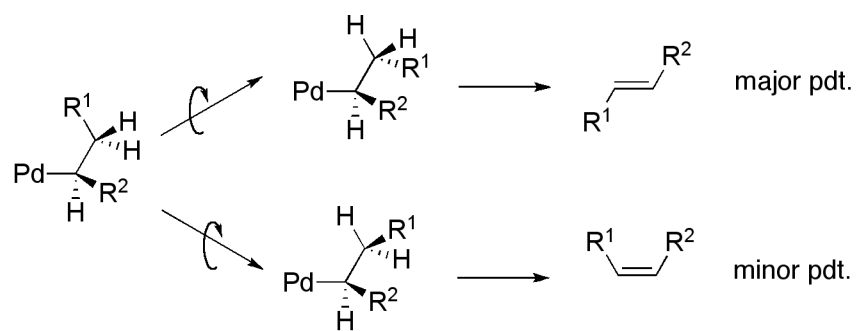


Figure 14.48 Stereoselectivity of the Mizoroki-Heck reaction.

The alkene in the Heck reaction may also be 1,2-disubstituted. In such cases, the Pd-bound R^1 group will add preferentially to the alkene carbon with the smaller substituent. In such cases, the stereochemistry of the resulting alkene depends on the stereochemistry of the reactant alkene, given the requirement of a *syn* transition state for β -hydrogen elimination, as shown in Figure 14.49 below. The upshot is that, for a Heck reaction with a 1,2-disubstituted alkene, the two groups that were *cis* to each other in the starting material will end up *trans* to each other in the product, or *vice versa*.

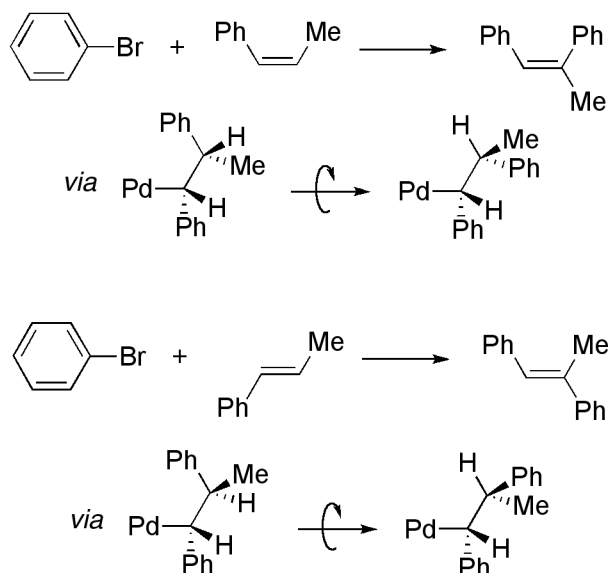


Figure 14.49. Stereoselectivity of the Mizoroki-Heck reaction on a 1,2-disubstituted alkene.

14.10. The Vollhardt Cyclotrimerization

There exist a number of transition metal-catalyzed reactions in which the product formed is a cyclic organic molecule. A good example of a net cyclization reaction is the reaction of three alkynes to form benzene or a substituted benzene. Such a reaction is known as a cyclotrimerization, and an example is shown in Figure 14.50 on the following page. While one could, “on paper,” imagine this reaction occurring as a concerted, termolecular pericyclic reaction [a [2+2+2] cycloaddition], this has never been observed: the reaction will not occur at any significant rate without a catalyst. Peter Vollhardt (b. 1946) of the University of California, Berkeley (and a member of this author’s dissertation committee) found that the

reaction is effectively catalyzed by the Co(I) species $\text{CpCo}(\text{CO})_2$, a nice example of catalytic utility from an inexpensive, first-row transition metal. Co(I) phosphine complexes $\text{CpCo}(\text{PR}_3)_3$ have also been used to catalyze this reaction, as have Rh(I) species.

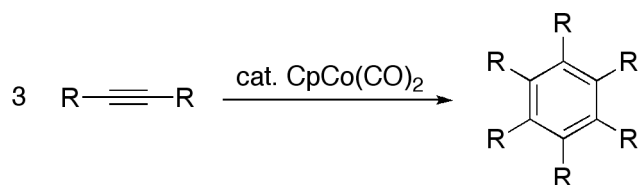


Figure 14.50. A cobalt-catalyzed cyclotrimerization of alkynes.

The mechanism that was initially proposed for the Vollhardt cyclotrimerization is displayed in the catalytic cycle of Figure 14.51 on the following page, shown with acetylene (ethyne) as the alkyne and $\text{CpCo}(\text{CO})_2$ as the catalyst. First, it turns out that $\text{CpCo}(\text{CO})_2$ is actually a precatalyst: it undergoes ligand substitution with two molecules of acetylene to form $\text{CpCo}(\eta^2\text{-C}_2\text{H}_2)_2$, still Co(I) and 18e. Oxidative coupling of the two acetylene ligands forms a Co(III), 16e cobaltacyclopentadiene, which coordinates another molecule of acetylene and undergoes 1,2-migratory insertion to form the ring-expanded cobaltacycloheptatriene, also Co(III) and 16e. This finally undergoes reductive elimination to yield the 18e, Co(I) complex $\text{CpCo}(\eta^4\text{-C}_6\text{H}_6)$, which undergoes ligand substitution with two acetylenes to yield benzene as the organic product and regenerate the active catalysts. Unfortunately, while this mechanism looks elegant and plausible at a first glance, a more formal theoretical analysis has indicated that the reductive elimination step from the cobaltacycloheptatriene is “forbidden” by orbital symmetry rules, suggesting that it will have a very high-energy transition state and that it will thus be kinetically very slow, much too slow to explain the observed catalysis.

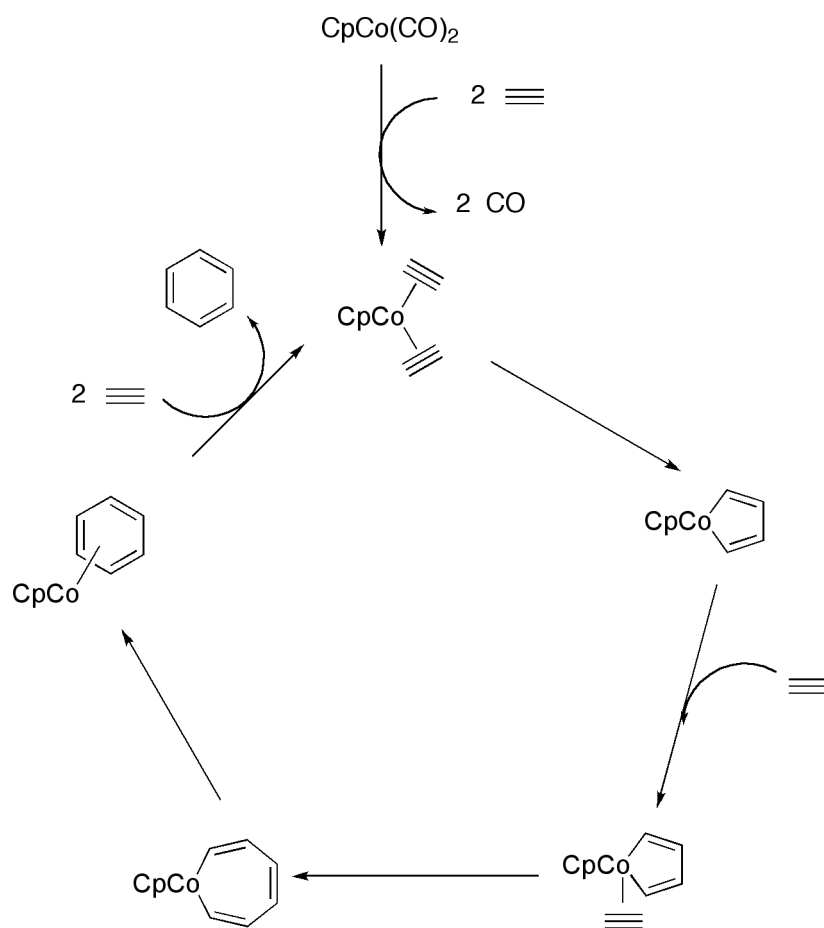


Figure 14.51. The initially proposed mechanism for the Vollhardt cyclotrimerization.

An alternative catalytic cycle was proposed, whose steps were all allowed according to an orbital symmetry analysis, and this now-accepted mechanism is shown in Figure 14.52 on the following page. This mechanism differs from the first one proposed only in terms of how the third alkyne is incorporated. In this mechanism, the cobaltacyclopentadiene undergoes a Diels-Alder reaction (a [4+2] cycloaddition) to the coordinated acetylene, to form a cobaltanorbornadiene. The reaction of cyclopentadiene itself with alkynes to yield all-organic norbornadienes is well known. The cobaltanorbornadiene then undergoes a [4 + 1] retrocycloaddition, which also constitutes a reductive elimination at Co, to yield the Co(I) species $\text{CpCo(}\eta^4\text{-C}_6\text{H}_6\text{)}$, as shown in the original mechanism. A [4 + 1] retrocycloaddition that expels carbon monoxide from 7-oxonorbornadiene is well known, as shown in Figure 14.53 on the following page, and one can think of CO as behaving analogously to the CpCo fragment.

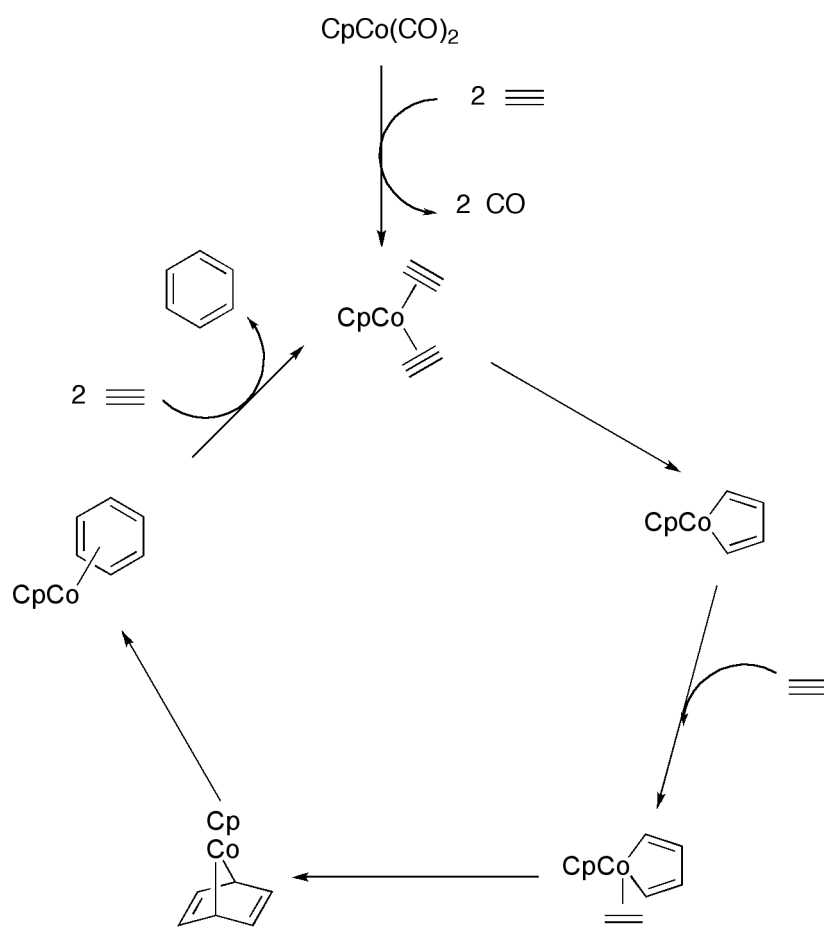


Figure 14.52. The revised mechanism for the Vollhardt cyclotrimerization.

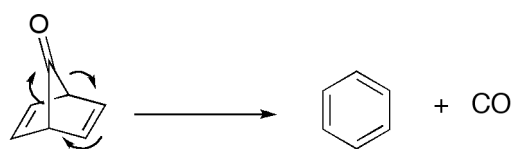


Figure 14.53. Retro-[4 + 2] cycloaddition of 7-oxanorbornadiene to yield CO and benzene.

There are synthetic difficulties that can occur with the Vollhardt cyclotrimerization. It is a good way to form symmetrically hexasubstituted arenes from symmetrical alkynes, but if the alkyne to be trimerized is asymmetric, a mixture of products may result due to imperfect regioselectivity. A generic example of how this reaction can lead to a mixture of products is shown in Figure 14.54 on the following page.

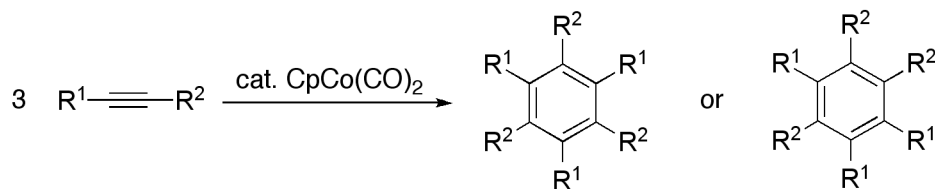


Figure 14.54. A product mixture formed from the cyclotrimerization of asymmetrically disubstituted alkynes.

So far, we have discussed true cyclotrimerizations, that is, three molecules of the same alkyne coming together to form an arene. If a mixture of alkynes is used, there can be chemoselectivity problems with the Vollhardt reaction. However, if the three different alkynes are all present in the same molecule, a Vollhardt reaction can occur with quite good regio- and chemoselectivity. This feature was used by Vollhardt and his group in their synthesis of the sex hormone estrone, with a key step being the reaction shown in Figure 14.55 below.

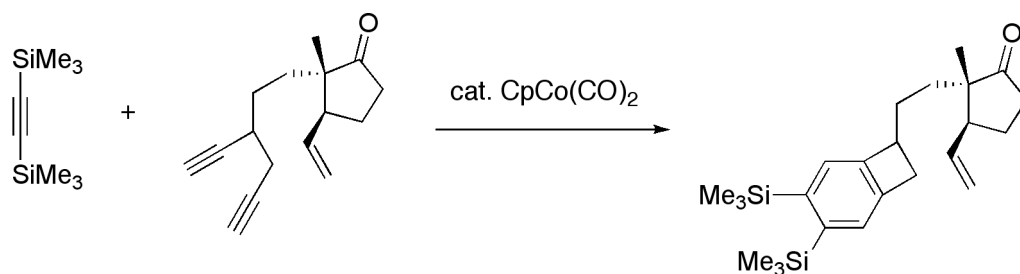


Figure 14.55. A Vollhardt cyclotrimerization in the synthesis of estrone.

Chapter 15: Electron-Transfer Reactions

15.1. Electron Transfer Between Transition Metals

We have already encountered some oxidation and reduction reactions in this course. Oxidative addition and reductive elimination, two very common reaction types of transition metal complexes, involve oxidation and reduction, respectively, of the relevant transition metal, just as their names imply. There also exist a wide variety of main-group reducing agents that can reduce transition metal complexes, including elemental main-group metals (*e.g.* Li, Na, K, Mg, Al), organic radical anions (*e.g.* the benzophenone ketyl radical anion, Ph_2CO^-), and main-group hydrides and hydrido anions (*e.g.* B_2H_6 , BH_4^- , R_2AlH , AlH_4^- , R_3SnH , N_2H_4). Here, in contrast, we will consider redox reactions *between* transition metal complexes, in which one transition metal increases in oxidation state (is oxidized) while another decreases in oxidation state (is reduced).

In introductory chemistry, this type of reaction is often represented in chemical equations simply by a change in oxidation state of two ions, for instance, in a simple redox reaction like $\text{Cu}^+ (\text{aq}) + \text{Fe}^{3+} (\text{aq}) \rightarrow \text{Cu}^{2+} (\text{aq}) + \text{Fe}^{2+} (\text{aq})$. In considering the mechanisms of electron-transfer reactions, however, we must think about the ligands around each metal, which often have profound effects on both the thermodynamics and kinetics of electron-transfer processes. For example, $\text{Co}^{3+} (\text{aq})$, really $\text{Co}(\text{H}_2\text{O})_6^{3+}$, is not stable: Co(III) with only aqua ligands will actually oxidize water: $4 \text{Co}(\text{H}_2\text{O})_6^{3+} + 6 \text{H}_2\text{O} \rightarrow 4 \text{Co}(\text{H}_2\text{O})_6^{2+} + 4 \text{H}_3\text{O}^+ + \text{O}_2$. In contrast, $\text{Co}(\text{NH}_3)_6^{3+}$, also a Co(III) complex, is stable in aqueous solution: the NH_3 ligands are apparently better donors to Co^{3+} , making it less electron-deficient and not as strongly oxidizing.

15.2 Outer-Sphere Electron-Transfer Reactions

The mechanistically simplest electron-transfer reactions between transition metal complexes involve no change in which ligands are bound to which metal. Such reactions occur in one step, with only one transition state, and are known as outer-sphere reactions, for reasons we will discuss shortly. A straightforward example of an outer-sphere electron-

transfer reaction is $\text{Co}(\text{NH}_3)_6^{3+} + \text{Ru}(\text{NH}_3)_6^{2+} \rightarrow \text{Co}(\text{NH}_3)_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$. In this reaction, Co(III) is reduced to Co(II), and Ru(II) is oxidized to Ru(III). Since the mechanism is one step, the rate law is second-order: $r = k[\text{Co}(\text{NH}_3)_6^{3+}][\text{Ru}(\text{NH}_3)_6^{2+}]$, with $k = 1.1 \times 10^{-2} \text{ M}^{-1}\cdot\text{s}^{-1}$ at 25 °C. In outer-sphere reactions like this, the electron moves from one metal to the other *via* the quantum-mechanical phenomenon of *tunneling*, in which an electron moves through a potential-energy barrier that it does not have enough energy to surmount. As you might expect, the rate constants for reactions involving tunneling depend strongly on both the metal and the ligand: the reaction $\text{Co}(\text{NH}_3)_5(\text{I})^{2+} + \text{Ru}(\text{NH}_3)_6^{2+} \rightarrow \text{Co}(\text{NH}_3)_5(\text{I})^+ + \text{Ru}(\text{NH}_3)_6^{2+}$ has $k = 6.7 \times 10^3 \text{ M}^{-1}\cdot\text{s}^{-1}$ at 25 °C. Thus, the replacement of one NH_3 ligand by I^- led to the rate increasing by a factor of over 10^5 , a striking change indeed!

15.3. Self-Exchange Reactions and Marcus-Hush Theory

The simplest possible electron-transfer reaction, known as a self-exchange reaction, is one between two species that differ by only one electron. Such a reaction is degenerate ($\Delta G^\circ = 0$, $K = 1$), since no net chemical change occurs. Two such self-exchange reactions are as follows: the cobalt reaction $\text{Co}(\text{NH}_3)_6^{3+} + \text{Co}(\text{NH}_3)_6^{2+} \rightarrow \text{Co}(\text{NH}_3)_6^{2+} + \text{Co}(\text{NH}_3)_6^{3+}$ and the ruthenium reaction $\text{Ru}(\text{NH}_3)_6^{3+} + \text{Ru}(\text{NH}_3)_6^{2+} \rightarrow \text{Ru}(\text{NH}_3)_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$. The rate of such reactions can be measured by radiolabeling: either the oxidized or reduced species may be prepared with a radioactive isotope of the metal present, such as radioactive ^{60}Co in place of stable ^{59}Co . Under such circumstances, the self-exchange reaction will have a ΔG° value that is not strictly zero, and an equilibrium constant K value that is not strictly unity, due to equilibrium isotope effects, but these isotope effects are quite small compared with the free energy changes and equilibrium constants due to a net chemical change. You might wonder what the source of the activation barrier for a self-exchange reaction is, *i.e.* why k for such a reaction is not infinite. The answer lies in the fact that the values of Δ_o and the metal-ligand bond lengths both change as a function of oxidation state. For instance, the Co–N bond lengths in $\text{Co}(\text{NH}_3)_6^{3+}$ will be shorter than those in $\text{Co}(\text{NH}_3)_6^{2+}$, in these species' vibrational ground states.

The Franck-Condon principle, after James Franck (1882-1964, Nobel Prize in Physics 1925) and Edward Condon (1902-1974), states that, in chemical reactions (including photochemical reactions), the motion of electrons, which have very low mass, is considerably faster than the motion of nuclei, which are much more massive. When $\text{Co}(\text{NH}_3)_6^{3+}$ (with shorter Co–N bond lengths) accepts an electron from $\text{Co}(\text{NH}_3)_6^{2+}$ (with longer Co–N bond lengths), the $\text{Co}(\text{NH}_3)_6^{2+}$ initially formed has shorter bond lengths than it does at vibrational equilibrium, and the $\text{Co}(\text{NH}_3)_6^{3+}$ formed has longer ones.¹¹¹ Both product molecules are formed, initially, in vibrational excited states, as a result of electrons moving much faster than nuclei. After the electron transfer, they relax to their vibrational ground states. However, activation energy is required to lead to the formation of vibrationally excited products due to the initial nonequilibrium bond lengths. This part of the activation energy is sometimes referred to as reorganization energy, and often symbolized by λ .

It turns out that the Gibbs free energy of activation $\Delta G^\ddagger$ of outer-sphere electron-transfer reactions is particularly amenable to theoretical calculation using some reasonable approximations. These approximations and the resulting calculations were done by Rudolph Marcus (b. 1923, Nobel Prize in Chemistry 1992) and Noel Hush (1924-2019), and their results are known as Marcus-Hush theory. While in many cases thermodynamics and kinetics are not closely related (for instance, a strongly thermodynamically favorable reaction may still be quite slow), for outer-sphere electron-transfer reactions $\Delta G^\ddagger$ is dependent both on the reorganization energy λ and on the standard-state Gibbs free energy of reaction ΔG° :

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda}$$

If we take the linearized form of the Eyring equation for rate constants,

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta G^\ddagger}{RT}$$

¹¹¹ This bond length difference can be understood in terms of ligand field theory as follows: $\text{Co}(\text{NH}_3)_6^{2+}$ is high-spin d^7 , with d electron configuration $(t_{2g})^5(e_g)^2$, while $\text{Co}(\text{NH}_3)_6^{3+}$ is low-spin d^6 , with d electron configuration $(t_{2g})^6(e_g)^0$. Since the e_g MOs are Co–N antibonding, the Co(II) complex, in which they are occupied, has longer Co–N bond lengths than does the Co(III) complex, in which they are empty.

and use the Marcus-Hush expression for $\Delta G^\ddagger$, we get the following equation for the rate constant of an outer-sphere electron-transfer reaction:

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{(\lambda + \Delta G^\circ)^2}{4\lambda RT}$$

Let us now look at the mathematical implications of Marcus-Hush theory. The right side of the equation is always negative or zero. The quantities λ , R , and T are always positive, and while the standard-state Gibbs energy of reaction ΔG° can be positive, negative, or zero, the term $(\lambda + \Delta G^\circ)^2$ is always positive because of the square. Thus, for a given temperature, the reaction is fastest (k is largest) when the right side of the equation is equal to zero, or $(\lambda + \Delta G^\circ)^2 = 0$. This implies that the reaction is fastest when ΔG° and the reorganization energy are equal in magnitude but opposite in sign, or $\Delta G^\circ = -\lambda$. Thus, the reaction will slow down when ΔG° is *either* less negative than λ *or* more negative than $-\lambda$. This result is very much out of line with much of our qualitative chemical intuition. While thermodynamics and kinetics are not always simply related, we nevertheless, as chemists, tend to expect that, *ceteris paribus*, a more thermodynamically favored chemical reaction will be faster. But Marcus-Hush theory tells us that the reaction rate will increase as ΔG° gets more negative (the “normal region”) up until $\Delta G^\circ = -\lambda$, and when $\Delta G^\circ < -\lambda$, the reaction rate will *decrease* as ΔG° gets more negative (the “Marcus inverted region”).

One might, quite reasonably, wonder whether perhaps the prediction of the Marcus inverted region is simply an artifact of the approximations made by Marcus-Hush theory, without physical significance. However, in 1984, Miller, Calcaterra, and Closs demonstrated¹¹² the existence of the Marcus inverted region experimentally, in the class of organic, intramolecular electron-transfer reactions shown in Figure 15.1 on the following page. Here we have an organic radical anion with a negative charge (and unpaired electron) located on a biphenyl portion, and this electron migrates to an acceptor group A (which is also an unsaturated cyclic substituent). This is truly a transfer of electrons, not merely a different resonance structure, as A and the biphenyl portion are not conjugated (the steroid bridge

¹¹² Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047-3049.

connecting them is a σ -bonding network only). Miller *et al.* varied the identity of A, which changed both the rate constant k and free energy of reaction ΔG° , and a plot of k vs. $-\Delta G^\circ$ had a clear maximum. The side of this maximum on which a more negative ΔG° corresponds to a *slower* reaction is a Marcus inverted region.

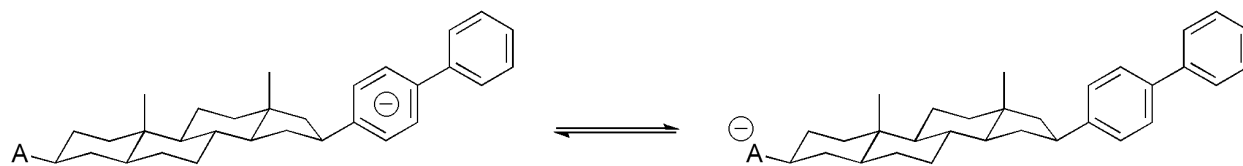


Figure 15.1. Organic, intramolecular electron-transfer reactions.

15.4. Outer-Sphere Cross Reactions

Marcus-Hush theory is generally useful for calculating the rate constants of outer-sphere electron-transfer reactions. Applying a few more approximations to the theory allowed Marcus to relate the rates of degenerate, self-exchange reactions to those of nondegenerate electron-transfer reactions, known as “cross reactions.” For instance, consider the following reaction: $\text{Co}(\text{NH}_3)_6^{3+} + \text{Ru}(\text{NH}_3)_6^{2+} \rightarrow \text{Co}(\text{NH}_3)_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$. This is an example of a cross reaction, since Co is being reduced and Ru is being oxidized. By assuming that the energetics of approaching complex ions is fundamentally similar between self-exchange reactions and cross reactions, Marcus derived a formula for estimating the rate constant k_{cross} of a cross reaction, when the equilibrium constant K_{cross} for the cross reaction and the rate constants k_1 and k_2 for the related self-exchange reactions are known. The Marcus cross relation, as this equation is known, is given by

$$k_{\text{cross}} = \sqrt{fk_1k_2K_{\text{cross}}}.$$

The quantity f , called the frequency factor, does vary somewhat between reactions, but for many electron-transfer reactions its value is close to 1. A notable feature of the Marcus cross relation is the dependence of k_{cross} on K_{cross} ; this is akin to the dependence of $\Delta G^\ddagger$ on ΔG° in the “parent” Marcus-Hush theory. Note, however, that the Marcus cross relation equation does not account for the Marcus inverted region.

15.5. Inner-Sphere Electron-Transfer Reactions and Mixed-Valence Complexes

In contrast to outer-sphere reactions, some electron-transfer reactions are termed inner-sphere. An inner-sphere electron-transfer reaction involves ligand substitution as part of its mechanism. Often, the products of an inner-sphere reaction reflect a net ligand exchange between metal centers, such as in the following reaction between a cobalt complex and a chromium complex: $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+} + [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$. In this reaction, note that Co(III) is reduced to Co(II), and Cr(II) is oxidized to Cr(III), but that a Cl^- ligand moves from Co to Cr and an H_2O ligand moves from Cr to Co. This reaction is believed to proceed by the mechanism shown in Figure 15.2 below.

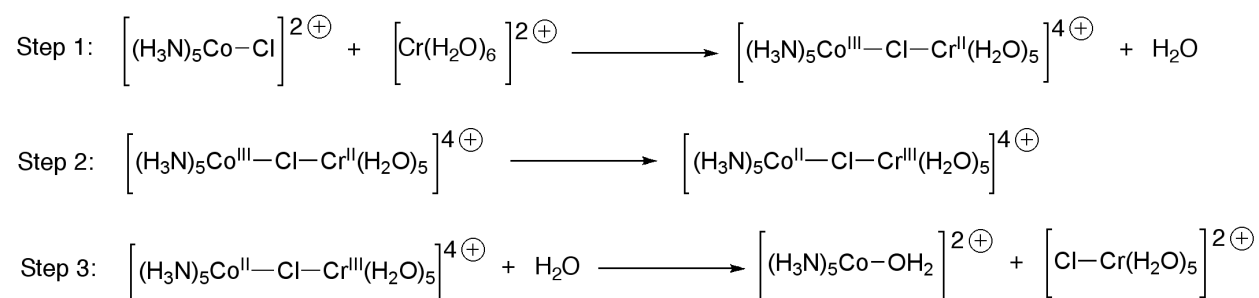


Figure 15.2. An example of an inner-sphere electron-transfer mechanism.

Steps 1 and 3 of this mechanism may not actually be concerted reactions: as ligand substitutions, they could plausibly proceed by any of a variety of mechanisms, as we have previously discussed in Chapter 11. Step 2, however, is what is notable as a hallmark of an inner-sphere electron transfer. In this step, an electron moves from Cr to Co *through* the bridging Cl^- ligand, rather than simply through space between two complexes. One can think of the bridging ligand as something like a “wire” through which electron density flows from one metal to another. The “inner sphere” of the mechanism name refers to the coordination spheres of the metals involved, in which electron transfer occurs.

You might look at step 2 and wonder why it is even considered a reaction at all, with a defined reactant and product, rather than merely a depiction of two resonance structures of the same bimetallic complex ion. The reason is that, in two different resonance structures, the atoms must stay in the same positions: bond lengths and bond angles cannot be different in

different resonance structures of the same species. Now consider that, when Co is reduced and Cr is oxidized, their metal-ligand bond lengths change, as discussed above. Thus, when the reaction of Step 2 occurs, the metal-to-metal electron transfer is accompanied by changes in bond lengths, making the reactant and product two distinct species, rather than different resonance structures of a single species.

In general, for an electron-transfer reaction to proceed *via* an inner-sphere mechanism, at least one of the reacting complexes must have at least one ligand with at least one additional lone pair, enabling it to bridge two metal centers. Halides, CN^- , water, OH^- , and O^{2-} can all engage in such bridging. Inner-sphere electron transfer can occur over rather long distances if the bridging ligand contains a conjugated π system. Ammonia, amines R_3N , and phosphines R_3P cannot bridge, since each has only one lone pair available for binding a metal. Thus, the reaction $\text{Co}(\text{NH}_3)_6^{3+} + \text{Ru}(\text{NH}_3)_6^{2+} \rightarrow \text{Co}(\text{NH}_3)_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$ must proceed by an outer-sphere mechanism, since the only ligand present is NH_3 , which cannot bridge two metals. The related reaction $\text{Co}(\text{NH}_3)_5(\text{F})^{2+} + \text{Ru}(\text{NH}_3)_6^{2+} \rightarrow \text{Co}(\text{NH}_3)_5(\text{F})^+ + \text{Ru}(\text{NH}_3)_6^{3+}$ also likely proceeds by an outer-sphere mechanism: although the F^- ligand in $\text{Co}(\text{NH}_3)_5(\text{F})^{2+}$ can certainly bridge two metals, it is unlikely to be able to rapidly displace an NH_3 ligand on $\text{Ru}(\text{NH}_3)_6^{2+}$. This is because $\text{Ru}(\text{NH}_3)_6^{2+}$, as an $\text{Ru}(\text{II})$ species, is d^6 and low-spin, making it inert to ligand substitution.

One cannot always identify an inner-sphere reaction based on a net transfer of ligands among its products. The reaction $\text{Fe}(\text{CN})_6^{3-} + \text{Co}(\text{CN})_5^{3-} \rightarrow \text{Fe}(\text{CN})_6^{4-} + \text{Co}(\text{CN})_5^{2-}$, in which $\text{Fe}(\text{III})$ is reduced to $\text{Fe}(\text{II})$, and $\text{Co}(\text{II})$ is oxidized to $\text{Co}(\text{III})$, involves no net ligand transfer, and thus cannot be said to *necessarily* be inner-sphere based on its stoichiometry. However, CN^- is an effective bridging ligand, and the electron-transfer step is likely to involve bimetallic species, as in $[(\text{NC})_5\text{Fe}^{\text{III}}-\text{CN}-\text{Co}^{\text{II}}(\text{CN})_5]^{6-} \rightarrow [(\text{NC})_5\text{Fe}^{\text{II}}-\text{CN}-\text{Co}^{\text{III}}(\text{CN})_5]^{6-}$.

It is worth noting that intramolecular electron transfer from one metal center to another cannot always be unambiguously defined. In the inner-sphere electron-transfer reactions we have discussed, the change in oxidation state, while something of a formalism, really does reflect a change in electron distribution within a molecule. Sometimes, however, in

complexes with more than one of the same metal atom, it is impossible to assign each one a distinct integer oxidation state. This is distinct from the phenomenon in which the *average* oxidation state of an element in a compound is not an integer. As an example of the latter case, consider the iron ore magnetite, with the formula unit Fe_3O_4 . If each O is considered to be an O^{2-} ion, then the average oxidation state of Fe in magnetite is $8/3$. However, crystallographic study of magnetite reveals that there are two nonequivalent types of Fe ions in the structure: each formula unit contains two Fe^{3+} ions and one Fe^{2+} ion, so the formula of magnetite might better be written as $(\text{Fe}^{3+})_2(\text{Fe}^{2+})(\text{O}^{2-})_4$. In this case, each Fe ion has a distinct, integer oxidation state, even if the *average* oxidation state of Fe is not an integer.

In contrast to the example of magnetite, genuinely non-integer oxidation states are observed in the bimetallic Ru complex ion shown in Figure 15.3 below, which contains the bridging ligand pyrazine (1,4-diazabenzene).

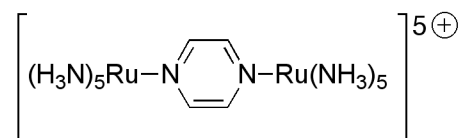


Figure 15.3. The Creutz-Taube ion.

This complex, which is known as the Creutz-Taube ion after Henry Taube and his Ph.D. student Carol Creutz (1944-2013), who first prepared its tosylate salt, poses a challenge for the assignment of oxidation states. The only ligands present are NH_3 and pyrazine, both of which are neutral as closed shell molecules. Thus, the *sum* of the oxidation states of the two Ru centers must equal +5, the overall charge of the complex. One might propose that one Ru is present as Ru(II) and the other as Ru(III), a reasonable proposal given the fact that +2 and +3 are both common oxidation states for Ru, each one observed in many stable compounds. However, crystallographic studies indicate that the two Ru centers are *equivalent*, without, for instance, shorter Ru- NH_3 bond lengths for the Ru(III) center. Thus, the oxidation state of each Ru is best assigned as $+5/2$. This may seem strange, but it is a result of the fact that the metal *d*-type electrons are delocalized between the two metals, with the π system of the aromatic pyrazine ligand connecting the two and allowing for this delocalization.

Fundamentally, non-integer oxidation states due to delocalization are closely analogous to non-integer bond orders arising from resonance structures: recall that the delocalization of benzene's π system makes each of its C–C bonds have a bond order of $\frac{3}{2}$, and each N–O bond in NO_3^- has a bond order of $\frac{4}{3}$.

The Robin-Day scheme is a useful method for classifying mixed-valence complexes. According to this scheme, a Class III mixed-valence complex is one with complete delocalization, like the Creutz-Taube ion. Class III complexes generally have a conjugated π system connecting the two metals, so that one can envision a set of π MOs with character from d orbitals on both metals. In contrast, a Class I mixed-valence complex is one in which the two metal centers are, more or less, electronically isolated from one another: their d -type MOs do not interact electronically through a conjugated π system. The type of organic radical anion shown in Figure 15.1 above, for which a Marcus inverted region was discovered, can be thought of as an organic analog of a Class I mixed-valence complex: electron transfer between the biphenyl group and the acceptor group A must proceed simply through space, rather than through the connecting backbone of the molecule, since this backbone is not a conjugated π system. Class II mixed-valence complexes are the intermediate case, with some delocalization, but not total delocalization. A Class II mixed-valence complex might have a metal–metal charge transfer band at fairly low energy (low frequency, high wavelength) in its visible absorption spectrum, reflecting the fact that electron migration from one metal center to the other occurs in an electronic excited state.

Chapter 16: Bonding Between Transition Metals

16.1. Metal-Metal Single Bonds

So far, our discussion of TM complexes has primarily been confined to molecules or ions containing only one TM each, with the ligands composed of atoms of main-group elements. There exist, however, many TM complexes containing more than one TM center. We will now consider bimetallic complexes, primarily those containing two of the same TM. We have briefly considered such complexes in light of electron counting (Sections 12.2 and 12.3) and bimetallic oxidative addition (Section 13.1). Now, we will consider bimetallic complexes from a more theoretical perspective.

Many bimetallic complexes have covalent bonding between the metals. A well-known example is dimanganese decacarbonyl, $\text{Mn}_2(\text{CO})_{10}$, with its Mn–Mn bond. It can be thought of as a dimer of the $\text{Mn}(\text{CO})_5$ fragment, with the equatorial CO ligands staggered, giving the molecule D_{4d} symmetry, as shown in Figure 16.1 below.

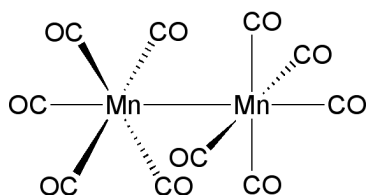


Figure 16.1. The structure of $\text{Mn}_2(\text{CO})_{10}$.

The two Mn centers are generally considered to be joined by a single σ bond. This can be predicted (very nonrigorously) using the 18e rule, by noting that each $\text{Mn}(\text{CO})_5$ fragment has 17e around Mn: Mn(0) contributes 7e (Mn is in Group 7) and 5 CO ligands contribute 2e each for 10e total. By the 18e rule, the two 17e $\text{Mn}(\text{CO})_5$ fragment, each with one unpaired electron on Mn, can have their unpaired electrons pair up to form an Mn–Mn single bond, where both electrons in the Mn–Mn bond can be considered to “belong” to each Mn. Thus, a metal-metal single bond contributes one additional electron to each metal when considering the 18e rule.

Moving beyond the heuristic 18e rule, we can explain the Mn–Mn bonding in $\text{Mn}_2(\text{CO})_{10}$ in a more theoretically justified manner by using MO theory. One way to approach this problem would be to derive irreducible representations in D_{4d} for the valence AOs on each Mn, as well as for the σ and π orbitals on all 10 CO ligands. However, it is easier to first derive an approximate MO diagram for a single square-pyramidal $\text{Mn}(\text{CO})_5$ fragment, and then see how the roughly nonbonding MOs in each of two such fragments can interact in D_{4d} . This is the approach that we will follow. (Note that we have already implicitly used this approach when considering the interaction of ligand MOs with TM AOs in TM complexes of ligands containing more than one atom each, like NH_3 , CH_3 , or CO.)

A square pyramidal $\text{Mn}(\text{CO})_5$ fragment has C_{4v} symmetry, with the z axis taken as being the C_4 rotation axis. Note that there are two sets of symmetry-nonequivalent CO ligands: four equivalent equatorial CO ligands, and one different axial ligand, through which the C_4 axis passes. A diagram of the $\text{Mn}(\text{CO})_5$ fragment is shown in Figure 16.2 below.

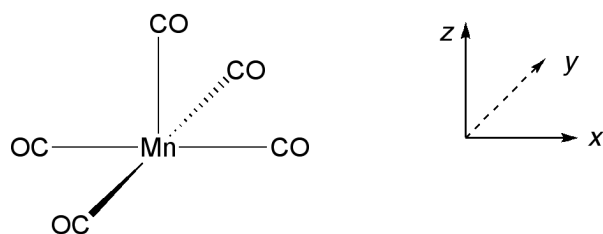


Figure 16.2. The $\text{Mn}(\text{CO})_5$ fragment and its coordinate system.

As a very approximate look at the bonding in this fragment, we will simplify things by considering the σ -bonding ability of the CO ligands only. We expect that the MOs that will be involved in Mn–Mn bonding will be predominantly Mn d in character, and since we have seen that π interactions are generally weaker than σ ones, we assume that the π interactions with the CO ligands may lower the energy of the d -type MOs, but that they are unlikely to do so drastically.

We derive representations for the σ orbitals on both the equatorial and axial CO ligands. Table 16.1 below shows the C_{4v} character table and, beneath it, the reducible representations Γ_{eq} and Γ_{ax} .

Table 16.1 The character table for the C_{4v} point group.

C_{4v}	$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$2\hat{\sigma}_4$	$2\hat{\sigma}_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1	(R_x, R_y, R_z)	xy
E	2	0	-2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)
Γ_{eq}	4	0	0	2	0		
Γ_{ax}	1	1	1	1	1		

Decomposition of Γ_{eq} , and recognition that Γ_{ax} is already an irreducible representation, gives $\Gamma_{\text{eq}} = A_1 + B_1 + E$ and $\Gamma_{\text{ax}} = A_1$. We see that the Mn $4s$, $4p_z$, and $3d_{z^2}$ AOs transform as A_1 , $3d_{x^2-y^2}$ transforms as B_1 , $3d_{xy}$ transforms as B_2 , and $(4p_x, 4p_y)$ and $(3d_{xz}, 3d_{yz})$ transform as E . Given the ligand SALCs, we thus have five MOs of A_1 symmetry, none of A_2 symmetry, two of B_1 symmetry, one of B_2 symmetry (a nonbonding d AO if we do not consider π bonding), and three pairs of MOs of E symmetry. An approximate, σ -only MO diagram of the $\text{Mn}(\text{CO})_5$ fragment is shown in Figure 16.2 on the following page.

The MOs $1a_1$, $1b_1$, $1e$, and $2a_1$ are all considerably bonding and primarily ligand-based. The d -type MOs are $1b_2$, $2e$, $3a_1$, and $2b_1$. Note that, except for $1b_2$ (which is nonbonding), all of the d -type MOs are antibonding, $2e$ have some p character, and $3a_1$ has some s and p character. The $2b_1$ MO is quite strongly antibonding, and thus the highest-energy d -type MO. The remaining (unoccupied) MOs are higher-energy, with predominant s and p character.

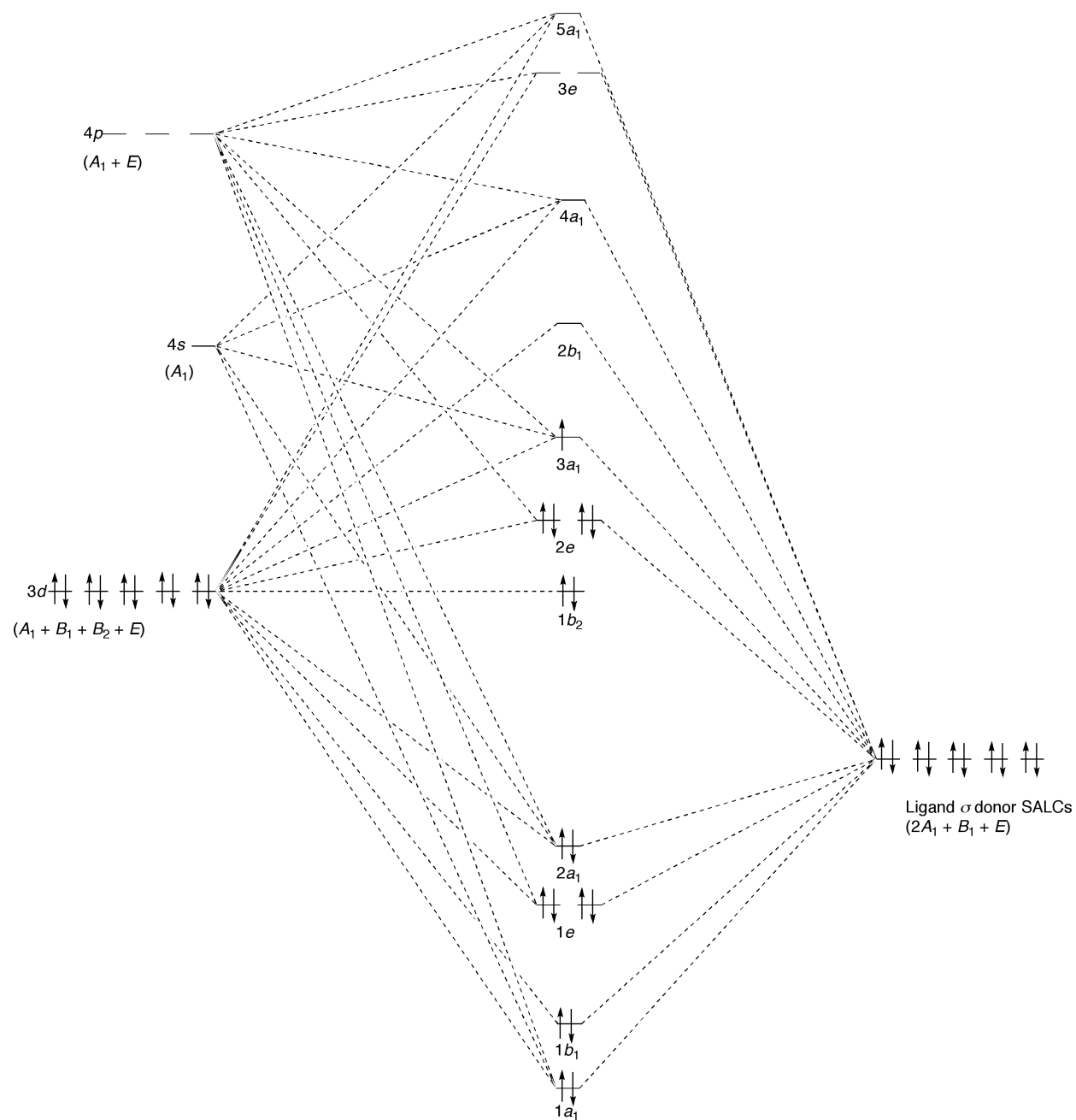


Figure 16.2. Qualitative MO diagram for $C_{4v} \text{Mn(CO)}_5$, with only σ interactions between the metal and ligands.

As the Mn(CO)_4 fragment is d^7 , the strongly antibonding $2b_1$ MO is empty, so the HOMO (which is also a singly-occupied MO or SOMO) is $3a_1$. It is primarily $3d_{z^2}$ in character, with a large lobe pointing away from the ligands, as shown in Figure 16.3 on the following page.



Figure 16.3. The SOMO of the C_{4v} $Mn(CO)_5$ fragment.

A SOMO of this symmetry on each $Mn(CO)_5$ fragment can interact to form a σ -bonding MO (a_1) and a σ -antibonding MO (b_2), as shown in Figure 16.4 below. The symmetries a_1 and b_2 refer to D_{4d} , which is the point group to which $Mn_2(CO)_{10}$ belongs. As the bonding MO is doubly occupied, and the antibonding MO is empty, we have an Mn–Mn single bond. In this case, the MO picture is (qualitatively) consistent with the Lewis structure and the 18e rule.

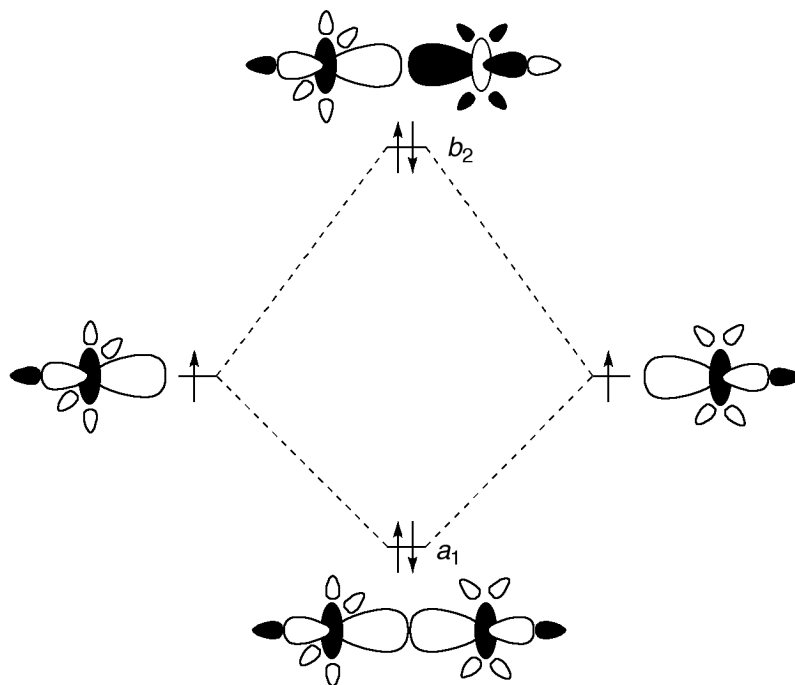


Figure 16.4. Interaction of two $Mn(CO)_5$ SOMOs to form Mn–Mn bonding and antibonding σ MOs.

You may be curious as to how the symmetries of the a_1 and b_2 MOs were obtained. One certainly could construct a reducible representation in D_{4d} for the two $Mn(CO)_5$ SOMOs and decompose it to its component irreps. However, one can also note that the σ -bonding MO has

the same symmetry as a d_{z^2} AO on a hypothetical atom between the Mn centers, and the σ -antibonding MO has the same symmetry as a p_z AO on the same hypothetical atom. Examination of the rightmost two columns of the D_{4d} character table shows that d_{z^2} transforms as A_1 and p_z transforms as B_2 , so the MOs in this example are assigned to those two irreps.

16.2. Metal-Metal Multiple Bonds

In main-group chemistry, the highest possible bond order between two atoms is three: such triple bonds can be found in N_2 , CO, CN^- , alkynes, and nitriles. (One can naïvely draw a Lewis structure for C_2 in which there is a C–C quadruple bond, but an MO treatment of C_2 shows that it actually has a double bond, with both of its bonding pairs of electrons in a degenerate pair of MOs with π symmetry; see any good undergraduate physical chemistry textbook for details.) In contrast, bonds between transition metal atoms can be single bonds, double bonds, triple bonds, quadruple bonds, and possibly even quintuple bonds. The field of metal-metal multiple bonds with bond orders greater than three began in 1964, when the great coordination chemist F. Albert Cotton (1930-2007) and C. B. Harris prepared (and characterized *via* X-ray diffraction) potassium octachlorodirhennate(III) ($K_2Re_2Cl_8$), whose structure is shown in Figure 16.5 below, and proposed that the rhenium centers in the $Re_2Cl_8^{2-}$ anion were held together by a Re–Re quadruple bond.

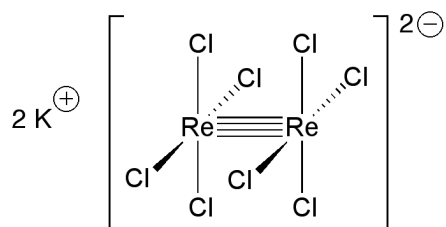


Figure 16.5. The structure of $K_2Re_2Cl_8$.

The Re–Re bond length in $Re_2Cl_8^{2-}$ is short (224.1 pm), about 85% of the average length of an Re–Re single bond. This complex ion also has D_{4h} symmetry, with the Cl $^-$ ligands eclipsed, rather than D_{4d} symmetry, with the Cl $^-$ ligands staggered, as in the case of the staggered equatorial CO ligands in $Mn_2(CO)_{10}$. The quadruple bonding between the Re centers is

responsible for this eclipsed geometry, as on steric grounds alone, one would expect a staggered geometry in order to minimize repulsion between the ligands.

Before considering in depth the MO picture of the Re–Re bond in $\text{Re}_2\text{Cl}_8^{2-}$, it is worth asking what types of bonds TM atoms can form between one another. In main-group chemistry, assuming that the z axis is the internuclear axis, σ bonds can be formed between s AOs, p_z AOs or combinations of the two, and π bonds can be formed between the p_x AOs or the p_y AOs. A σ MO has no nodal plane containing the internuclear axis, while a π MO has one nodal plane containing the internuclear axis. When d AOs are allowed to participate in the bonding, both σ bonds and π bonds can be formed between them, but so can a new type of bond, called a δ (delta) bond,¹¹³ where a δ MO has two nodal planes containing the internuclear axis. An MO scheme for a diatomic molecule M_2 , where M is a first-series transition metal and only the $3d$ AOs are used in bonding, is shown in Figure 16.6 on the following page, with z being the internuclear axis.

We see that the $3d_{z^2}$ AOs can interact with each other to form a bonding MO, δ_g , and an antibonding MO, δ_u . The $3d_{xz}$ AOs interact with each other, as do the $3d_{yz}$ AOs, to form a degenerate pair of bonding MOs, π_u , and a degenerate pair of antibonding MOs, π_g . Finally, the $3d_{x^2-y^2}$ AOs interact with each other, as do the $3d_{xy}$ AOs, to form a degenerate pair of bonding MOs, δ_g , and a degenerate pair of antibonding MOs, δ_u . Interactions with the $4s$ and $4p$ AOs are not shown in the diagram, but the $4s$ and $4p_z$ AOs can participate in σ MOs, and the $4p_x$ and $4p_y$ AOs can participate in π MOs. Interaction between the d AOs of TMs and the

¹¹³ A useful way to remember the labels for different types of bonds is as follows: s AOs can only form σ bonds, and σ is the equivalent of s in the Greek alphabet. Next, p AOs can form not only σ bonds, but π bonds as well, and π is the Greek equivalent of p . Finally, d AOs can form δ bonds in addition to σ and π bonds, and δ is the Greek equivalent of d . In principle, f AOs could form ϕ (phi) bonds, with three nodal planes containing the internuclear axis, in addition to σ , π , and δ bonds. (There is no Greek equivalent for f , but ϕ is usually transliterated as ph .) However, bonding between lanthanide and actinide atoms is rare, and thus far a ϕ bond has only been proposed to exist in the molecule U_2 , which exists only in the gas phase.

s and p AOs of main-group elements is, as we have already seen, common in complexes of TM atoms or ions with main-group ligands.

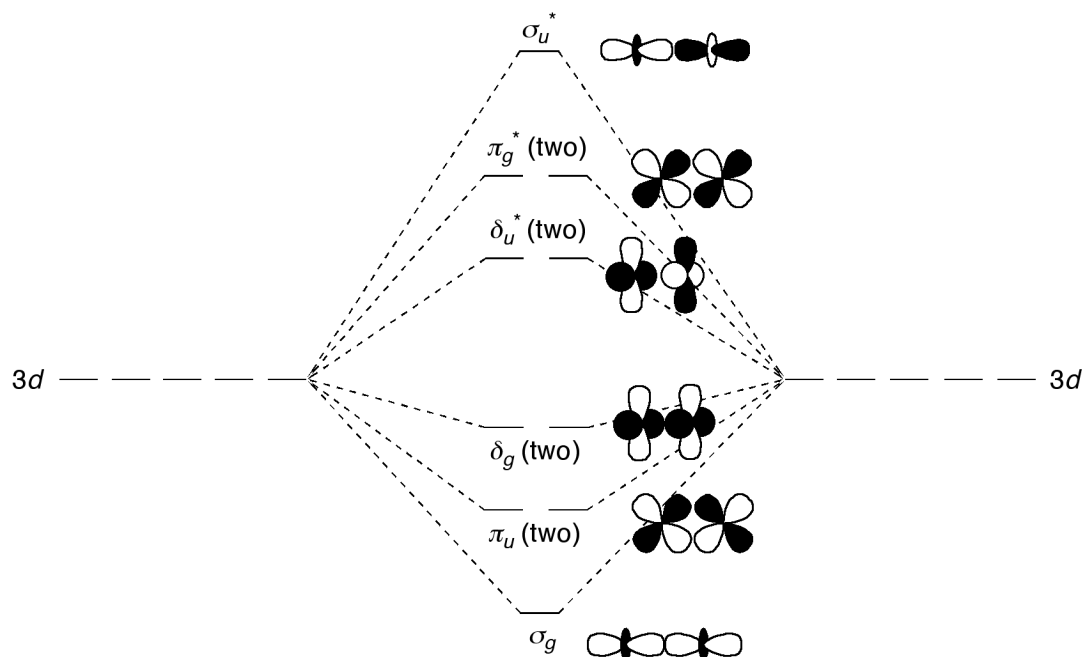


Figure 16.5. A *d*-only MO diagram for a hypothetical M_2 molecule.

If we consider the 3*d* AOs only, however, we obtain 5 bonding MOs and 5 antibonding MOs. Thus, a diatomic molecule with two Group 5 TM atoms, such as V_2 , and 10 *d* electrons total, would have the electron configuration $(\sigma_g)^2(\pi_u)^4(\delta_g)^4(\delta_u)^0(\pi_g)^0(\sigma_u)^0$, with five bonding MOs occupied and all antibonding MOs empty, corresponding to a bond order of 5 (a quintuple bond). Of course, diatomic molecules consisting of two TM centers are of limited chemical relevance: they may be generated at low pressure in the gas phase, but they will not be stable species in any of the solution-phase chemistry commonly practiced by synthetic inorganic chemists. A bimetallic TM complex containing both metal-metal bonds and metal-ligand bonds will have a different MO scheme, because the TM AOs are involved in bonding to the ligands, as well as bonding to each other.

To obtain a qualitative MO picture for the Re–Re bonding in Cotton and Harris' $Re_2Cl_8^{2-}$ ion, we use the same fragment approach that we did when considering the bonding between

Mn(CO)₅ fragments to make Mn₂(CO)₁₀, that is, we look at the MOs of two ReCl₄⁻ fragments and consider how they can interact. Since Re₂Cl₈²⁻ is a *D*_{4h} species with staggered Cl⁻ ligands, we consider a pair of *D*_{4h} ReCl₄⁻ fragments and see what their roughly nonbonding MOs look like.

A qualitative MO diagram for *D*_{4h} ReCl₄⁻ is shown in Figure 16.6 on the following page (see Section 8.8 for how it was derived). The MOs 1*a*_{1g} through 1*a*_{2g} and 1*b*_{2u} are predominantly ligand-based, and they would not be expected to participate significantly in Re–Re bonding. The Re *d*-type MOs are 2*b*_{2g} (mostly 5*d*_{xy}, some π-antibonding character), 2*e*_g (mostly 5*d*_{xz} and 5*d*_{yz}, some π-antibonding character), 2*a*_{1g} (mostly 5*d*_{z²}, with some 6*s* character) and 2*b*_{1g} (5*d*_{x²-y²} with strong σ-antibonding character).

Of the *d*-type MOs, 2*b*_{1g} is strongly Re–Cl antibonding, and much higher in energy than the others. We will not consider it as being important in the Re–Re bonding scheme. This leaves a roughly 5*d*_{z²} orbital (2*a*_{1g}) available for Re–Re σ-bonding, two roughly 5*d*_{xz} and 5*d*_{yz} orbitals (2*e*_g) available for Re–Re π-bonding, and a roughly 5*d*_{xy} orbital (2*b*_{2g}) available for Re–Re δ-bonding. We can form representations Γ_σ, Γ_π, and Γ_δ for these orbitals in *D*_{4h}, corresponding to SALCs, as shown in Figure 16.7 on the page after the following one. In this case, the SALCS *are* the Re–Re bonding and antibonding MOs. There are 4 *d* electrons in each ReCl₄⁻ fragment, since Re is a Group 7 element in the +3 oxidation state.

Table 16.2 on the page after the following one shows the *D*_{4h} character table and the representations Γ_σ, Γ_π, and Γ_δ. For Γ_δ, it should be noted that $\hat{C}_4$ and $\hat{\sigma}_v$ take each orbital into the negative of itself ($\chi = -2$ overall), while $\hat{C}_2 = \hat{C}_4^2$ and $\hat{\sigma}_d$ take each orbital into itself ($\chi = 2$ total).

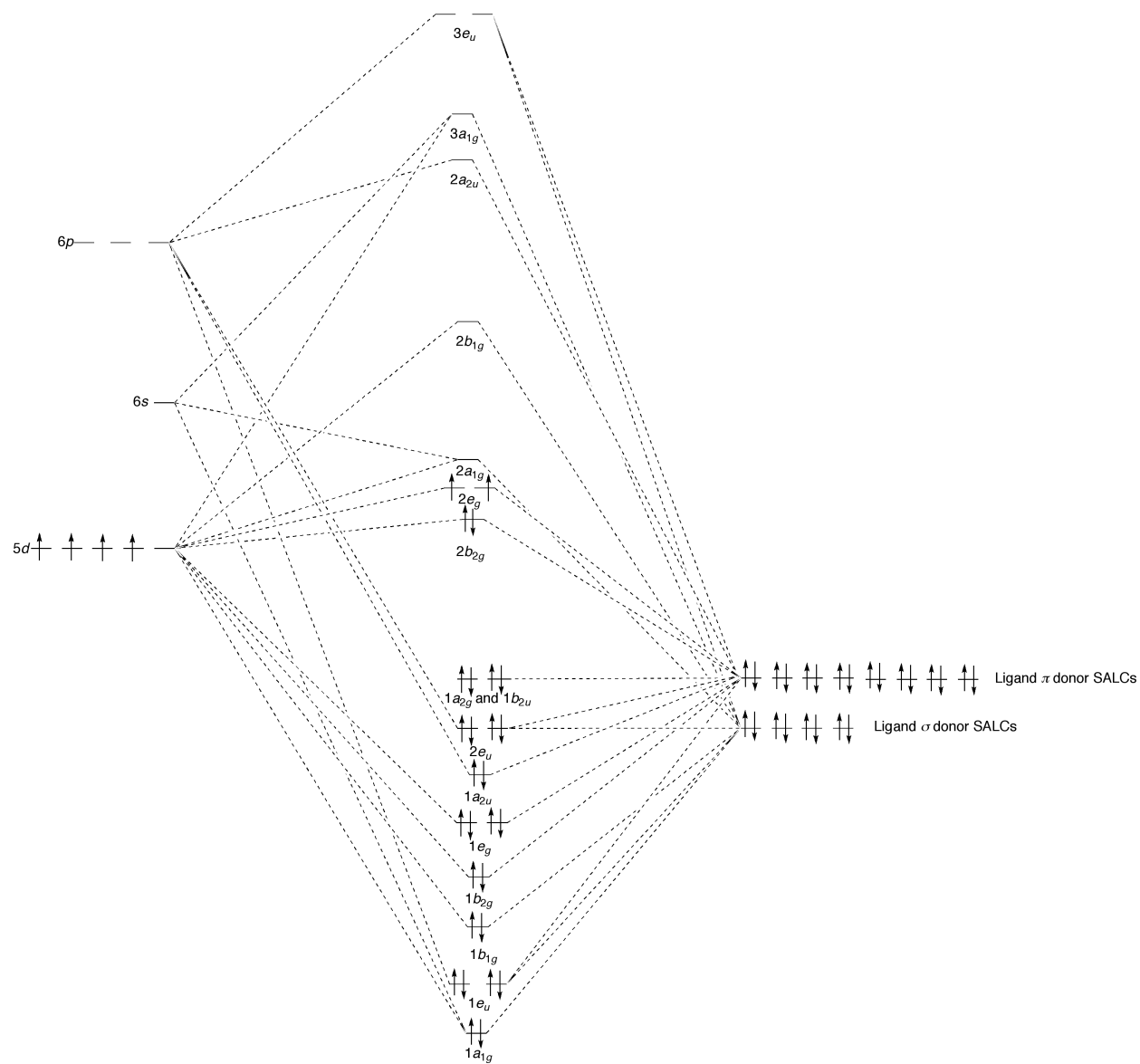


Figure 16.6. Qualitative MO diagram for ReCl_4^- .

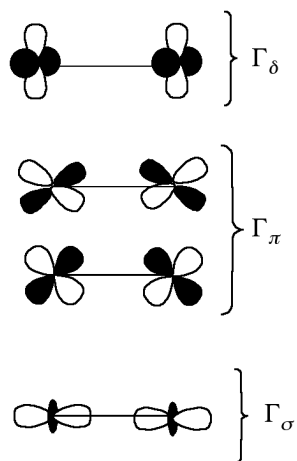


Figure 16.7. SALCs for d -type MOs in $\text{Re}_2\text{Cl}_8^{2-}$.

Table 16.2. The character table for the D_{4h} point group.

D_{4h}	$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$2\hat{C}_2'$	$2\hat{C}_2''$	$\hat{i}$	$2\hat{S}_4$	$\hat{\sigma}_h$	$2\hat{\sigma}_v$	$2\hat{\sigma}_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	
Γ_σ	2	2	2	0	0	0	0	0	2	2		
Γ_π	4	0	-4	0	0	0	0	0	0	0		
Γ_δ	2	-2	2	0	0	0	0	0	-2	2		

The reducible representations can be decomposed to $\Gamma_\sigma = A_{1g} + A_{2u}$, $\Gamma_\pi = E_g + E_u$, and $\Gamma_\delta = B_{2g} + B_{1u}$. A partial MO diagram for $\text{Re}_2\text{Cl}_8^{2-}$, showing the MOs involved in the Re–Re interactions only, is shown in Figure 16.8 on the following page.

It should be note that, just as π bonds are weaker, *ceteris paribus*, than σ bonds, δ bonds tend to be weaker than π bonds. Thus, while we can see from the Figure 16.8 that the formal Re–Re bond order in $\text{Re}_2\text{Cl}_8^{2-}$ is 4 (there are 8 electrons in Re–Re bonding MOs, and zero

electrons in Re–Re antibonding MOs), we should not expect an Re–Re quadruple bond to be twice as strong as an Re–Re double bond, or four times as strong as an Re–Re single bond.

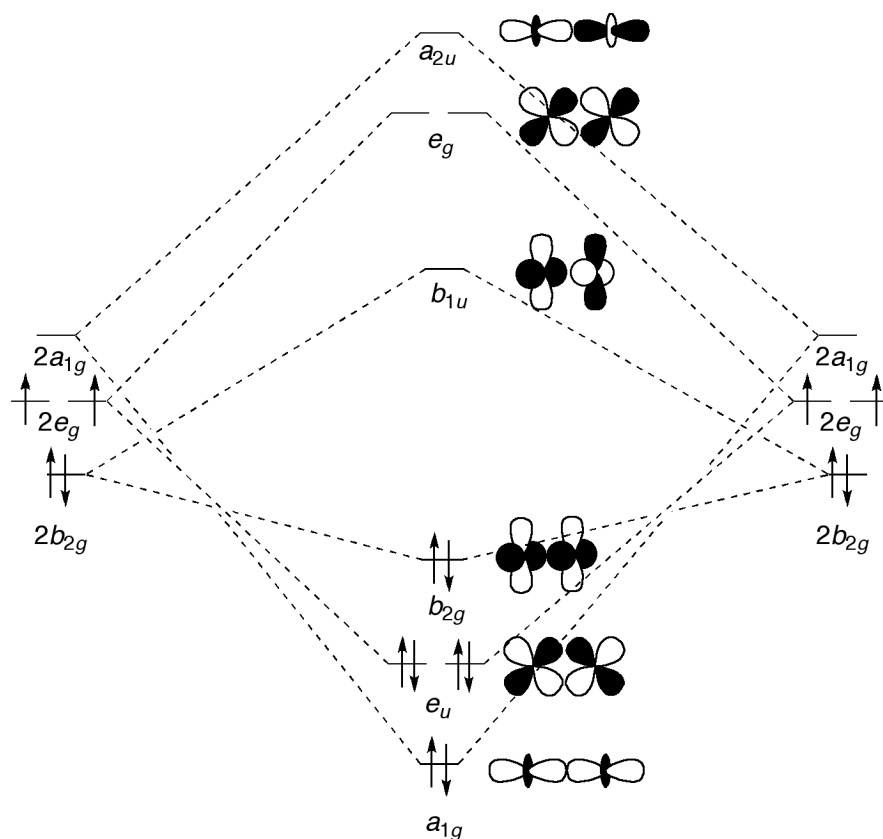


Figure 16.8. A partial (*d*-only) MO diagram showing the Re–Re bonding in $\text{Re}_2\text{Cl}_8^{2-}$.

The MO picture we derived for $\text{Re}_2\text{Cl}_8^{2-}$ can be extended to other D_{4h} complexes with formula M_2L_8^n . We see that a *d* electron count of d^4 at each metal gives a formal metal-metal quadruple bond. Examples include $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{W}_2(\text{CH}_3)_8^{4-}$. (Students in my upper-level inorganic lab course prepare beautiful, magenta crystals of $\text{K}_4\text{Mo}_2\text{Cl}_8$.) The presence of the δ bond, even if it is weak compared to σ and π bonds, explains the sterically more hindered eclipsed (D_{4h}) geometry of $\text{Re}_2\text{Cl}_8^{2-}$. You can see from Figure 16.8 that a twist of the ReCl_4^- units by $\frac{360^\circ}{8} = 45^\circ$, forming a staggered (D_{4d}) geometry, would break the δ interaction in the b_{2g} δ bonding MO. In contrast, consider the complex ion $\text{Os}_2\text{Cl}_8^{2-}$. It can be thought of as arising from a combination of OsCl_4^- fragments, each of which is d^5 (Os, a Group 8 element, is in the +3 oxidation state). If $\text{Os}_2\text{Cl}_8^{2-}$ had an eclipsed D_{4h} geometry, it would have only a triple

bond between the Os centers, since both the b_{2g} d bonding MO and the b_{1u} δ antibonding MO would be doubly occupied. In fact, since no net δ bonding is available, $\text{Os}_2\text{Cl}_8^{2-}$ has the less sterically-hindered D_{4d} structure, with staggered Cl^- ligands.

There exist bimetallic complexes that contain bridging ligands, *i.e.* ligands that are covalently bound to both TM centers. Common bridging ligands include the halides, OH^- , O^{2-} , RO^- , RS^- , S^{2-} , CO, and NO. One can analyze the metal-metal bonding in such complexes using a symmetry-based MO treatment, but the diagrams will be more complicated, as some of the bonding MOs holding the TM centers together will have significant contributions from the bridging ligand orbitals, in addition to the d AOs of the metals. Some bimetallic complexes are not believed to have *any* significant metal-metal bonding; in such cases, the TM centers are held together only by the bridging ligands. One can also extend the treatment of metal-metal bonding in bimetallic complexes to describe the bonding in cluster compounds, which are molecules or ions containing several TM centers. A hallmark of cluster compounds is the presence of highly delocalized σ -bonding MOs, a situation which has sometimes been described as “ σ -aromaticity,” in analogy to the highly delocalized π MOs in aromatic organic compounds. There are useful parallels to be drawn between the bonding in TM clusters such as $\text{Rh}_6(\text{CO})_{16}$ and borane clusters such as $\text{B}_6\text{H}_6^{2-}$, as will be discussed in Chapter 17.

Chapter 17: The Isolobal Analogy, Boranes, and Metal Clusters

17.1. The Isolobal Analogy

One of the most useful qualitative theoretical tools in chemistry is known as the isolobal analogy or isolobal principle. The isolobal analogy was devised by the great theoretical chemist Roald Hoffmann (b. 1937), who won the 1981 Nobel Prize in Chemistry for his use of orbital-symmetry arguments (the “Woodward-Hoffmann rules”) to predict which organic pericyclic reactions are electronically “allowed,” and which are “forbidden.” In his Nobel lecture, “Building Bridges Between Inorganic and Organic Chemistry,” Hoffman proposed the isolobal analogy as a way of focusing on important similarities between some transition-metal (“inorganic”) molecular fragments and main-group (“organic”) fragments.¹¹⁴

To motivate the isolobal analogy, consider the phenomenon of pseudohalides and pseudohalogens, which you may recall from general chemistry. The halides Cl^- , Br^- , and I^- all have oxidized dimers (Cl_2 , Br_2 , I_2), acidic halides (HCl , HBr , HI), and sparingly soluble silver(I) salts (AgCl , AgBr , AgI). Cyanide, CN^- , is often described as a pseudohalide (or the CN unit as a pseudohalogen) since the oxidized dimer $(\text{CN})_2$ ($\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$) exists, as does the acid HCN and the sparingly soluble AgCN . Perhaps more surprisingly, the 17e transition metal fragment $\text{Co}(\text{CO})_4$ can also be thought of as a pseudohalogen: the dimer $(\text{OC})_4\text{Co}-\text{Co}(\text{CO})_4$ exists, the hydride $\text{HCo}(\text{CO})_4$ is appreciably Brønsted acidic, since the negative charge of $\text{Co}(\text{CO})_4^-$ is delocalized over the CO ligands, and the salt $[\text{Ag}^+][\text{Co}(\text{CO})_4^-]$ is only sparingly soluble in water. We will see that the isolobal analogy predicts this behavior, and that it is not mere coincidence.

Similarly, you may already be familiar with the phenomenon of isoelectronic molecules and ions. One isoelectronic set is BH_4^- , CH_4 , and NH_4^+ , and another is H_2N^- , H_2O , and the rarely seen cation H_2F^+ . What about a comparison between H_2O and H_2S , however? These two compounds have the same shape, the same number of bonds and lone pairs, and some similar

¹¹⁴ The lecture can be read as a paper in Hoffmann, R. *Angewandte Chemie International Edition in English* **1982**, vol. 21, pp. 711-724. It remains a theoretical *tour de force* today.

reactivity. They are even sometimes described as being “isoelectronic,” but this is not exactly correct: H_2S has eight more electrons than H_2O , even though it has the same number of *valence* electrons. Similarly, CH_4 , NH_3 , H_2O , and HF all contain 10 electrons (and eight valence electrons) each, but most chemists would not describe them as isoelectronic, as their electrons are differently distributed between bonds and lone pairs. Thus while they are, in a sense, isoelectronic, their orbitals are differently arranged, making them not *isolobal*.

The use of Hoffmann’s isolobal analogy involves getting a qualitative sense of the frontier orbitals of a molecule fragment and comparing them with the frontier MOs of other fragments. As Hoffmann put it, “We will call two fragments *isolobal* if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar – not identical, but similar.”

What makes the orbitals of two fragment “similar” enough? This is perhaps best illustrated by example. Let us first consider some very simple hydrocarbon fragments. Methane, CH_4 , is a stable, closed-shell molecule, with 8 electrons (the standard main-group octet) around its central atom, carbon, and a tetrahedral stereochemistry. Now imagine we remove a hydrogen atom, with its one electron, from methane, to yield the methyl, CH_3 , fragment. Now, using the vocabulary of valence bond theory and hybrid orbitals developed by Pauling, we have a trigonal pyramidal radical with a single nonbonding, sp^3 hybrid orbital, singly occupied. Removing another hydrogen yields the methylene, CH_2 , fragment, with two nonbonding hybrids, each singly occupied. Removal of a third hydrogen gives the methine, CH , fragment, with three singly occupied, nonbonding hybrid orbitals. Each of these fragments will have a tendency to form as many bonds as needed to regain a tetrahedral arrangement of substituents, or ligands, around carbon: CH_3 will make one, CH_2 will make two, and CH will make three. (This holds if the bonds in question are single bonds. The carbon atoms can, of course, achieve octets *via* multiple bonds, and we will see later how to account for this in the isolobal analogy.) This simple hybrid orbital picture for CH_4 , CH_3 , CH_2 , and CH is shown in Figure 17.1 on the following page.

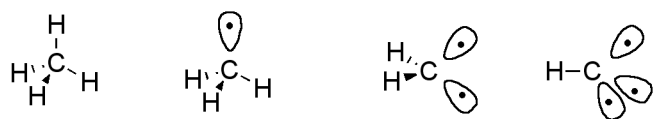


Figure 17.1. A simple hybrid orbital picture of CH_4 , CH_3 , CH_2 , and CH .

Now, let us consider transition metals. The 18e rule for transition metals is the analog of the octet rule for main-group elements, and the octahedron is the most common stereochemistry around transition metals, just as the tetrahedron is common for carbon. So the analog of CH_4 , as our closed-shell example, should be an 18e, octahedral complex, such as $\text{HMn}(\text{CO})_6$. For transition metals, we will have our “parent polyhedron” be the octahedron, while for carbon, it will be the tetrahedron. Now let us consider what happens when we remove a hydrogen from this compound. While a highly delocalized MO theory is often a better description of the bonding in transition metal complexes than valence bond theory, in this case, we may (qualitatively) view a singly occupied d^2sp^3 hybrid orbital resulting from the loss of H. We now have a 17e fragment (one electron short of 18e), with a singly occupied hybrid orbital pointing away from the remaining ligands. This is similar enough in shape to the singly occupied hybrid orbital of the 7e fragment CH_3 that we say that the $\text{Mn}(\text{CO})_5$ and CH_3 fragments are isolobal, which we indicate with a double-headed arrow with one lobe of an cartoon orbital below it, as in Figure 17.1 below.

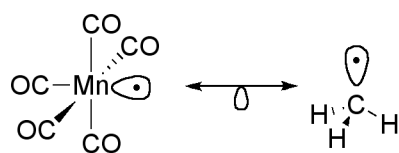


Figure 17.2. Isolobality of the $\text{Mn}(\text{CO})_5$ and CH_3 fragments.

Each of these fragments will have a tendency to form one single bond, such as with hydrogen, to form $\text{HMn}(\text{CO})_5$ and CH_4 , or a halogen, as in $\text{Mn}(\text{CO})_5\text{Cl}$ and CH_3Cl . Each fragment is also able to form a dimer with a single bond between fragments: $\text{H}_3\text{C}-\text{CH}_3$ (ethane) and $(\text{OC})_5\text{Mn}-\text{Mn}(\text{OC})_5$ (dimanganese decacarbonyl). Finally, these two isolobal fragments can form a single bond with each other, to form the organometallic complex $(\text{OC})_5\text{Mn}-\text{CH}_3$, a

well-known compound that we have already discussed in Section 13.2 in the context of methyl migration to CO.

We have seen that a 17e transition metal fragment, derived from an octahedron by the removal of a 1e ligand, is isolobal to methyl. Similarly, a 16e metal fragment, derived from the removal of two *cis* 1e ligands from an octahedron, is isolobal with methylene. Imagine removing two *cis* hydrogen atoms from $\text{H}_2\text{Fe}(\text{CO})_4$, yielding the seesaw-shaped $\text{Fe}(\text{CO})_4$ fragment. Just like methylene, it contains two hybrid orbitals, each with one electron in it, as shown in Figure 17.3 below.

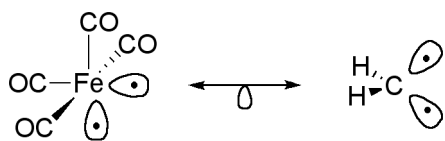


Figure 17.3. Isolobality of the $\text{Fe}(\text{CO})_4$ and CH_2 fragments.

Each of these fragments can trimerize: three CH_2 fragments form two more single bonds each to form cyclopropane, and three $\text{Fe}(\text{CO})_4$ fragments form triiron dodecacarbonyl, $\text{Fe}_3(\text{CO})_{12}$. The isolobal analogy is not perfect here: one of the Fe–Fe bonds in $\text{Fe}_3(\text{CO})_{12}$ has two bridging carbonyl ligands, rather than all terminal carbonyls, as shown in Figure 17.4 below. However, $\text{Ru}_3(\text{CO})_{12}$ has all terminal carbonyls, making it a true trimer of $\text{Ru}(\text{CO})_4$ fragments, and the all-terminal geometry of $\text{Fe}_3(\text{CO})_{12}$ is likely not too much higher in energy than the doubly-bridging ground state.

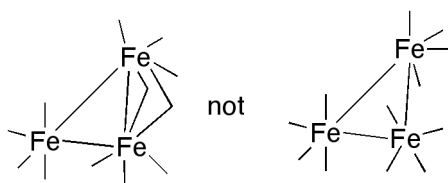


Figure 17.4. Skeleton drawing of bridging CO ligands in $\text{Fe}_3(\text{CO})_{12}$.

Moving on to methine, imagine removing three 1e ligands from an 18e octahedral complex. While *cis*- $\text{H}_3\text{Co}(\text{CO})_3$ is not, in fact, a stable compound, it would be 18e if it did exist, and we

can in principle remove three H ligands from this hypothetical molecule to yield the 15e, trigonal pyramidal $\text{Co}(\text{CO})_3$ fragment, with three singly occupied hybrid orbitals, isolobal to methine, as shown in Figure 17.5 below.

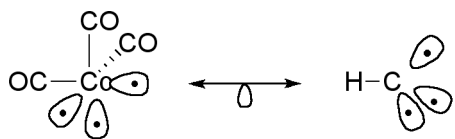


Figure 17.5. Isolobality of the $\text{Co}(\text{CO})_3$ and CH_3 fragments.

In principle, four CH groups can form a tetrahedron, each with three C–C bonds. The simple hydrocarbon C_4H_4 , known as tetrahedrane, has not yet been isolated, but derivatives C_4R_4 have, where $\text{R} = \text{tBu}$ or SiMe_3 . The tetrahedrane analog $[\text{Co}(\text{CO})_3]_4$ has been prepared, though three Co–Co bonds have one bridging CO ligand each. The congener $[\text{Ir}(\text{CO})_4]_4$, however, has all terminal CO ligands. The “mixed tetrahedranes” $\{(\text{RC})_2[\text{Co}(\text{CO})_3]_2\}$ and $\{(\text{RC})[\text{Co}(\text{CO})_3]_3\}$ are also known, as shown in Figure 17.6 below.

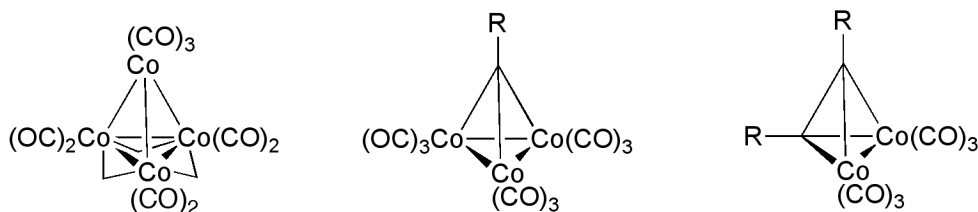


Figure 17.6. Mixed carbon and cobalt tetrahedrane structures.

At this point, we can extend the isolobal analogy in some useful ways.

(1) Perhaps most obviously, if the central atom in a fragment is replaced with another atom from the same group, the fragment is isolobal, since the number of valence electrons will be the same. Thus H_2O and H_2S are an isolobal pair, as are CH_3 and SiH_3 , $\text{Mn}(\text{CO})_5$ and $\text{Re}(\text{CO})_5$, and $\text{Co}(\text{CO})_3$ and $\text{Ir}(\text{CO})_3$.

(2) Two isoelectronic fragments with the same coordination number and geometry are isolobal. Thus $\text{Mn}(\text{CO})_5$ is isolobal to $\text{Cr}(\text{CO})_5^-$ and $\text{Fe}(\text{CO})_5^+$, and all three are isolobal to CH_3 .

(3) The substituents or ligands on a central atom in a fragment can be changed without altering isolobality, as long as they donate the same number of electrons. Thus R_3C (R = hydrocarbyl) is isolobal to H_3C , and $\text{Co}(\text{NH}_3)_3$ is isolobal to $\text{Co}(\text{CO})_3$, since both NH_3 and CO are 2e ligands. For the purposes of this extension, one considers a halogen X^- as a 2e ligand, though the neutral halogen is only a 1e ligand. Thus, CoCl_3^{3-} is isolobal to $\text{Co}(\text{CO})_3$ (each 2e CO is replaced by 2e Cl^-), but CoCl_3 is *not*.

(4) Since an alkene ligand, despite bonding in an η^2 fashion, is a 2e ligand, this means that it is isolobal to CO or another 2e ligand that binds through only one atom. One can think of cyclopentadienyl anion, C_5H_5^- , of consisting (in any one of its resonance structures) as being a 6e donor, and occupying three mutually *cis* coordination sites, just like three CO ligands. Thus, the $\text{CpFe}(\text{CO})_2$ fragment, commonly abbreviated as Fp, is isolobal to $\text{Fe}(\text{CO})_5^+$ (by mentally replacing Cp^- with 3 CO), which is isolobal to $\text{Mn}(\text{CO})_5$ and thus to CH_3 . This makes sense, since Fp is a 17e fragment that usually forms one more single bond, as in compounds such as $\text{CpFe}(\text{CO})_2\text{Cl}$, just as the 17e fragment CH_3 forms CH_3Cl .

There is another, very important, extension of the isolobal analogy that is worth considering in some detail. It has to do with the concept of the “parent polyhedron” that an isolobal fragment will react in order to form. So far, we have been careful to specify the tetrahedron and the octahedron as the parent polyhedra of main-group and transition-metal fragments, respectively. But a different reactivity might be implied when a different polyhedron is the result of a reaction.

To give a concrete example, consider again methylene, CH_2 . If we take the parent polyhedron to be the tetrahedron, then CH_2 will “want” to form two more single bonds, leading to compounds such as CH_4 , CH_2Cl_2 , *etc.*, all of which are tetrahedral (not necessarily regularly tetrahedral) at carbon. But a CH_2 or CR_2 unit could also form a double bond to one other fragment, rather than a single bond each to two. So CH_2 could form a double bond to an O

atom fragment to give formaldehyde, $\text{H}_2\text{C}=\text{O}$, or to another CH_2 fragment to form ethene, $\text{H}_2\text{C}=\text{CH}_2$. In each of these cases, the geometry about the carbon is trigonal planar, so a trigonal plane is the “parent polyhedron” of CH_2 in these cases.

Similarly, $\text{Fe}(\text{CO})_4$, which is isolobal to CH_2 , could form two single bonds at Fe, but it could also form one double bond. It could form a double bond with CO (using the resonance form for metal carbonyls with an $\text{M}=\text{C}$ double bond) to form $\text{Fe}(\text{CO})_5$, which is a stable, 18e complex with a trigonal bipyramidal geometry about Fe. It could also form a double bond to a CH_2 fragment to yield the carbene complex $(\text{OC})_5\text{Fe}=\text{CH}_2$; though this species is not itself stable, some derivatives of it of the form $(\text{OC})_5\text{Fe}=\text{CR}_2$ are. Finally, it could, in principle, dimerize to form $(\text{OC})_4\text{Fe}=\text{Fe}(\text{CO})_4$, though this molecule is not itself stable. However, two $\text{Fe}_2(\text{CO})_8$ units can be bridged by an Sn atom: since $\text{Fe}(\text{CO})_4$ is isolobal to CH_2 , and an Sn atom is isolobal to a C atom, the resulting compound is isolobal to spirocyclopentane, as shown in Figure 17.7 below.

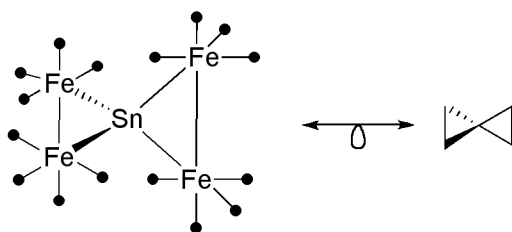


Figure 17.7. Isolobality of $[\text{Fe}(\text{CO})_4]_4\text{Sn}$ and spirocyclopentane.

In all the cases where an $\text{Fe}(\text{CO})_4$ fragment is engaged in a double bond, rather than two single bonds, the parent polyhedron should be considered a trigonal bipyramid, since it is now pentacoordinate, not hexacoordinate. This is why $\text{Co}(\text{CO})_4$ is a pseudohalogen, with a tendency to form one single bond: it is a 17e species, which joins with a 1e ligand like H to form the 18e, trigonal pyramidal species $\text{HCo}(\text{CO})_4$.

The fact that the methylene complex $(\text{OC})_4\text{Fe}=\text{CH}_2$ is not stable, nor is the dimer $(\text{OC})_4\text{Fe}=\text{Fe}(\text{CO})_4$, should not be taken to be too terrible a flaw in the isolobal analogy. Many “stable” compounds handled in the laboratory on a daily bases are, in fact,

thermodynamically unstable, but *kinetically* persistent. The hydrogenation of ethene by H_2 to yield ethane is thermodynamically favorable, but a mixture of ethene and H_2 at room temperature will not react at any significant rate in the absence of a catalyst. Kinetic “stability” (sometimes referred to as “persistence” or “metastability”) is a difficult property to predict: it can even be difficult to calculate using high-level computational methods, so we should not expect a qualitative tool like the isolobal analogy to be able to predict it reliably. If a hypothetical molecule can be shown to be isolobal to a compound that is known to be (at least kinetically) stable, that does not mean that the new molecule will necessarily be stable enough to isolate, but it does suggest that it *might* be, so its synthesis might well be worth a try. Note also that these “failures” of the isolobal analogy do not merely occur among the transition metals: CH_2 is, of course, isolobal with SiH_2 (silylene) and GeH_2 (germylene), but the double-bonded species disilylene, $\text{H}_2\text{Si}=\text{SiH}_2$, and digermylene, $\text{H}_2\text{Ge}=\text{GeH}_2$, are not stable enough to isolate. There is nothing “wrong” with the bonding in these molecules from the standpoint of the isolobal analogy, but it turns out, quantitatively, that π bonds between Si or Ge and other main-group elements are generally quite weak, so that compounds in which Si or Ge engage in multiple bonding are quite rare, and those that do exist are quite reactive and require special handling.

The tetrahedron can also be used as the parent polyhedron for transition metal species. After all, 18e, closed-shell tetrahedral transition metal complexes exist, such as $\text{Ni}(\text{CO})_4$ and $\text{Cr}(\text{lin-NO})_4$. The pseudohalide $\text{Co}(\text{CO})_4^-$ is tetrahedral, as it is isoelectronic to $\text{Ni}(\text{CO})_4$. Tetrahedral $\text{Co}(\text{CO})_4^-$ would best be considered isolobal with CH_4 , whereas $\text{Co}(\text{CO})_4^-$ with a see-saw geometry is better considered isolobal to CH_3^- : both fragments are closed shell (18e and 8e, respectively), but with a tendency to react with H^+ , a zero-electron reagent, to form the parent polyhedron (trigonal bipyramid and tetrahedron, respectively). Similarly, square pyramidal $\text{Mn}(\text{CO})_5^-$, which is 18e with a lone pair “hybrid” pointing away from the CO ligands, is isolobal with CH_3^- , but the ground state geometry of the $\text{Mn}(\text{CO})_5^-$ anion is likely to instead be trigonal bipyramidal, isoelectronic and isostructural with the stable $\text{Fe}(\text{CO})_5$ molecule. Thus, with the trigonal bipyramid as its parent polyhedron, $\text{Mn}(\text{CO})_5^-$ would be considered isolobal with CH_4 . In general, a species with a parent polyhedron involving a lone pair can be considered isolobal with CH_4 if that lone pair is unlikely to engage in bonding in

the circumstances in question. For instance, phosphines PR_3 , trigonal pyramidal with a lone pair on P, readily use their lone pairs in bonding with transition metals, as ligands, or in reaction with electrophilic alkylating agents like CH_3I or CH_3OTf . However, most phosphines are quite weak Brønsted bases. Thus, in the presence of no acids other than H^+ or an H^+ source, a PR_3 species may be considered isolobal with CH_4 , based on trigonal pyramidal parent geometry.

Transition metals, unlike main-group species, have a common tetracoordinate geometry other than the tetrahedron, namely, square planar. We can perfectly well treat square planar as a parent geometry for the purposes of the isolobal analogy, as long as we remember that square-planar metal complexes tend to be stable with 16e about the metal, not 18e. For example, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, “Wilkinson’s catalyst” for homogeneous hydrogenation reactions, is a stable, d^8 , 16e, square-planar, Rh(I) complex. If we remove a Cl atom, a 1e ligand, we get the 15e, T-shaped fragment $\text{Rh}(\text{PPh}_3)_3$, which is isolobal with CH_3 or $\text{Mn}(\text{CO})_5$ in its tendency to form one more single bond. If, on the other hand, we were to remove a Cl^- anion or PPh_3 , a 2e ligand, we would get 14e $\text{Rh}(\text{PPh}_3)_2\text{Cl}$ or $\text{Rh}(\text{PPh}_3)_3^+$, each of which is isolobal with CH_3^+ , the result of removing H^- from CH_4 or Cl^- from CH_3Cl . Similarly, *trans*- $\text{Ni}(\text{PPh}_3)\text{Cl}_2$ is also a stable, 16e, square planar compound: removing two Cl atoms (two 1e ligands) yields $\text{Ni}(\text{PPh}_3)_2$, which is isolobal with CH_2 .

Finally, it should be noted that there are some genuine exceptions to the isolobal analogy beyond the prediction of kinetically unstable molecules, that is, domains of chemistry where it simply does not apply. The isolobal analogy is based on the correspondence between the octet rule for main-group compounds and the 18e rule for transition-metal compounds, and it cannot readily account for transition metal compounds that exceed 18e, with antibonding MOs populated, such as 19e Cp_2Co and 20e Cp_2Ni . (These compounds are isolable, but they must be handled in the absence of O_2 , since the electron or electrons in antibonding MOs make them powerful reducing agents.) Similarly, it does not account for so-called “hypervalent” main-group species that exceed an octet around a main-group element, such as PF_5 or SF_6 . It also does not account for high-spin transition-metal complexes, in which some electrons will occupy MOs lying (somewhat) higher in energy, to avoid the greater

energetic cost of pairing in lower-energy MOs. Nevertheless, as a way of rationalizing surprising synthetic results and suggesting the synthesis of new compounds, the isolobal analogy is exceedingly useful, as long as one keeps in mind its fallibility.

17.2. Borane Cluster Compounds

In Chapter 16 and elsewhere in this text, we have already discussed some chemistry of bimetallic complexes with metal–metal covalent bonds. We can extend this discussion to one of structure and bonding in transition metal *clusters*, that is, complexes containing more than two metal centers involved in metal–metal covalent bonding. The catalysis of organic reactions by TM clusters, as well as by monometallic complexes, is an active research area. Before discussing TM clusters, however, it is useful to consider main-group cluster compounds, particularly those based on boron skeletons. The rules for electron counting and stable structures are simpler for these main-group species, and they can then be extended to approximate rules for TM clusters.

Boron chemistry is rarely discussed much in introductory chemistry courses, as boron is, among all the main-group elements, perhaps the most notable for its *frequent* disobedience of the “octet rule” used in writing Lewis structures of main-group compounds. There do exist boron species that are “closed-shell” by the Lewis structure formalism, such as borohydride (BH_4^-) and the tetraorganoborates (BR_4^- , R = alkyl or aryl) but the majority of boron compounds cannot be described accurately using the valence bond assumption that each atom-atom connection consists of an integer number of electron pairs (localized bonds). You may recall from your organic chemistry classes that borane (BH_3), a reagent used in the hydroboration of alkenes, undergoes dimerization to diborane (B_2H_6), a molecule with two bridging B–H–B groups. There are not two full bonds to hydrogen in each of these bridging groups; rather, each bridging H has essentially $\frac{1}{2}$ bond per boron. (See Section 3.7 for a discussion of the bonding in B_2H_6 in MO terms.)

A large group of stable boron species consist of anionic borane clusters, $\text{B}_n\text{H}_n^{x-}$, where $x = 2, 4, 6$, or 8 . The simplest (which is to say, most symmetrical) boron clusters have formulas of

the form $B_nH_n^{2-}$, and their structures are that of deltahedra, polyhedra whose faces are all equilateral triangles (after the Greek letter delta, whose capital form, Δ , is triangular). The vertices of the deltahedron consist of B–H units, with the hydrogens pointing away from the center of the cluster. Borane clusters with this type of structure are called *closo*, from Latin *closus*, “enclosed.”

Let us consider a shape very familiar from transition metal chemistry: the octahedron. The *closo* borane $B_6H_6^{2-}$ has an octahedral structure with a B–H unit at each vertex. It has the same shape as an octahedral metal complex, except there is no atom at the center of the octahedron. This structure is shown in Figure 17.8 below.

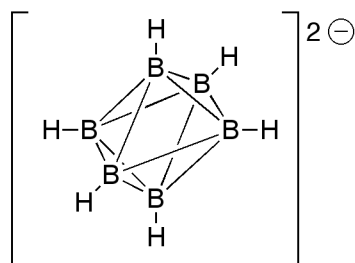


Figure 17.8. The structure of $B_6H_6^{2-}$.

Now, let us think about the valence electrons available for bonding in this cluster. A boron atom has 3 valence electrons, and a hydrogen atom has 1, so each B–H unit contributes 4 valence electrons. The 2- charge provides 2 more valence electrons, so the total number of valence electrons in the anion is $4(6) + 2 = 26$. In general, for a *closo* borane $B_nH_n^{2-}$, the number of valence electrons is $4n + 2$, for $2n + 1$ valence electron pairs. Now let us think about the orbitals involved in bonding. We will consider each B–H bond to be a “traditional” single bond, that is, each B–H connection consists of two electrons, fairly localized. If we consider the $2p_z$ AO on each boron to be that pointing towards (and away) from the center of the octahedron, then each boron is *sp* hybridized, with one *sp* orbital used in B–H bonding, another pointed toward the center of the octahedron, and the $2p_x$ and $2p_y$ AOs pointed along the sides of the octahedron, tangent to each vertex. The $2p_x$ and $2p_y$ AOs are often called the tangential orbitals for this reason, while the inward-pointing *sp* orbitals are sometimes

called the radial orbitals. Sketches of these orbital arrangements can be found in Figure 17.9 below.

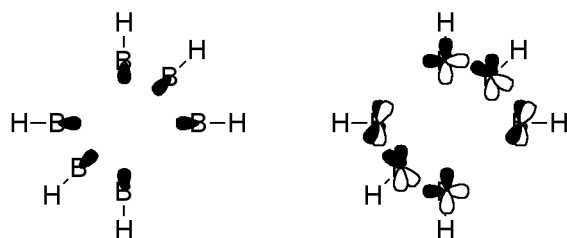


Figure 17.9. Radial and tangential orbitals in $B_6H_6^{2-}$.

How are the electrons apportioned between molecular orbitals? Since there are six B–H bonds, that accounts for 12 electrons, two for each bond. This leaves 14 valence electrons that can participate in what is called *framework* or *skeletal* bonding, that is, the bonding interactions that hold the framework or “skeleton” of boron atoms together, where the important orbital overlap is B–B, not B–H. For $B_nH_n^{2-}$ in general, the number of framework electrons is $2n + 2$, for $n + 1$ electron pairs.

Molecular orbital calculations show that, for $B_nH_n^{2-}$, there are $n + 1$ skeletal MOs that are bonding in character. They are exactly filled by the $n + 1$ electron pairs available in an ion of formula $B_nH_n^{2-}$, and all of the antibonding MOs are empty. This is why *closo* boranes with are so stable with a 2- charge: all bonding MOs are filled, and all antibonding MOs are empty. This can be thought of as something of a σ version of the Hückel rule for predicting the number of π electrons in an aromatic system, and the bonding pattern in borane clusters is sometimes called “ σ -aromaticity” in analogy. For $B_6H_6^{2-}$ in particular, there are $6 + 1 = 7$ skeletal bonding MOs. For every *closo* borane, the lowest-energy (most strongly bonding) MO is a totally symmetric, in-phase arrangement of B sp hybrid orbitals pointing toward the center of the polyhedron, and the other MOs are formed from mixtures of sp and tangential (p_x, p_y) AO. For $B_6H_6^{2-}$, the lowest energy MO is labeled a_{1g} , and the other bonding MOs consist of two triply degenerate sets, labeled t_{1u} and t_{2g} . The a_{1g} MO and example members of the t_{1u} and t_{2g} MO sets are shown in Figure 17.10 on the following page.

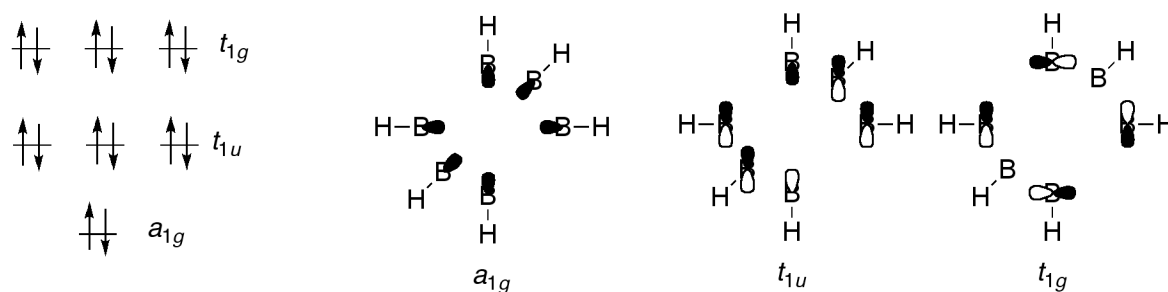


Figure 17.10. Some representative MOs of $B_6H_6^{2-}$.

As mentioned previously, for every *closo* $B_nH_n^{2-}$ species, there are $n + 1$ skeletal MOs that are bonding in character, filled by $n + 1$ pairs of electrons. The shapes and symmetry designations of these orbitals can be derived using group theory, and the details of the orbital arrangements (such as degeneracies) vary depending on n . For instance, not all $B_nH_n^{2-}$ will have triply degenerate MO sets as $B_6H_6^{2-}$ does. However, the lowest-energy (most strongly bonding) framework MO will always be nondegenerate and totally symmetric, with all B atoms having an *sp* hybrid orbital pointing toward the polyhedron center.

For *closo* boranes $B_nH_n^{2-}$, the deltahedral shapes are an octahedron, pentagonal bipyramid, dodecahedron, and icosahedron for $n = 6, 7, 8$, and 12 , respectively. There also exist boranes whose structures can be derived from a deltahedron by removal of one, two, or three vertices. Kenneth Wade (1932-2014) of Durham University studied the molecular orbitals of these structures. While the precise arrangement of MOs, and their degeneracies, varies between species, Wade was able to formulate a general strategy for predicting the closed-shell electron counts¹¹⁵ of such geometries. These electron-counting strategies are known as polyhedral skeletal electron pair theory (PSEPT) or simply “Wade’s rules.”

¹¹⁵ Here “closed-shell” does not refer to structures satisfying Lewis’ octet rule, but to a situation in which all low-energy MOs are doubly occupied, and all high-energy (antibonding) MOs are empty. It is analogous to saying that the cycloheptatrienyl cation ($C_7H_7^+$) is closed-shell because it is aromatic (6 π electrons in its ring), even though there is no resonance structure one can draw for it in which each carbon atom has 8 valence electrons around it.

Let us start with a *closo* borane $B_nH_n^{2-}$ and remove one B–H unit. This yields what is called a *nido* borane.¹¹⁶ Without considering charge, this leads to a formula of $B_{n-1}H_{n-1}$, or B_mH_m , where $m = n - 1$. It turns out that the number of low-energy MOs is still $n + 1$, where n is the number of vertices of the *parent* deltahedron, *not* the number of boron atoms m in the new cluster. Thus, for a closed-shell electron configuration, we need $n + 1$ framework electron pairs, or $2n + 2$ framework electrons. As before, each B–H unit contributes 2 electrons to the framework orbitals, for $2(n - 1) = 2n - 2$ framework electrons total. We need $2n + 2$ framework electrons to fill the bonding MOs, so we must add 4 more electrons with a 4- charge. So the formula of a closed-shell *nido* borane is $B_{n-1}H_{n-1}^{4-}$, or $B_mH_m^{4-}$, where again $m = n - 1$. The *nido* borane derived from *closo* $B_6H_6^{2-}$ is $B_5H_5^{4-}$, with a square pyramidal geometry: if you remove one vertex from an octahedron, you get a square pyramid.

Next, let us remove *two* B–H units from the *closo* borane $B_nH_n^{2-}$. This yields what is known as an *arachno* borane (from Greek ἀράχνη, “spider web”). Without charge, the new formula is $B_{n-2}H_{n-2}$, or B_pH_p , where $p = n - 2$. Wade showed that the number of low-energy MOs is again $n + 1$, based on the parent deltahedron, so again, we need $2n + 2$ framework electrons. The $n - 2$ B–H units contribute $2n - 4$ framework electrons, so we must add 6 more with a 6- charge. Thus, the formula of a closed-shell *arachno* borane is $B_{n-2}H_{n-2}^{6-}$ or $B_pH_p^{6-}$ with $p = n - 2$. The *arachno* borane derived from *closo* $B_6H_6^{2-}$ is $B_4H_4^{6-}$. Two isomers are possible: if the B–H units removed were adjacent to each other, we have a “butterfly” geometry (*not* a regular tetrahedron). If they were opposite each other, we have a square plane.

Finally, we could remove three B–H units from *closo* borane $B_nH_n^{2-}$. This yields what is known as an *hypho* borane (from Greek ὑφή, another word for a spider web). Without charge, the new formula is $B_{n-3}H_{n-3}$, or B_qH_q , where $q = n - 3$. Once again, Wade showed that the number of low-energy MOs is $n + 1$, based on the parent deltahedron, so once again, we need $2n + 2$ framework electrons. The $n - 3$ B–H units contribute $2n - 6$ framework electrons, so we must add 8 more with an 8- charge. Thus, the formula of a closed-shell *hypho* borane is $B_{n-3}H_{n-3}^{8-}$.

¹¹⁶ From Latin *nidus*, “nest.” Many *nido* boranes have something of a bird’s-nest appearance, at least to an imaginative eye.

or $B_qH_q^{8-}$ with $q = n - 3$. The *arachno* borane derived from *closo* $B_6H_6^{2-}$ would be $B_3H_3^{8-}$, though this species has not been isolated. It would have a trigonal planar geometry. Pure *hypho* boranes, without the substitution of some boron atoms by heteroatoms, are not yet known.

By this point, we have discussed some borane clusters with large negative charges. It is often difficult to form ions (at least relatively small ones) with such large charges (negative or positive). Thus, many neutral (or less anionic) borane clusters exist, and can be thought of as the result of protonation of these idealized anions. The additional hydrogen atoms (formally added as H^+) generally bridge two adjacent boron atoms, with delocalized bonding similar to that of the bridging H atoms in B_2H_6 . To classify a neutral borane as *closo*, *nido*, *arachno*, or *hypho*, we remove H^+ from the formula until the number of B and H atoms are equal, and then look at the charge.

Let us consider some examples. $B_{11}H_{13}^{2-}$ has two more H than B, so we remove two H^+ to get $B_{11}H_{11}^{4-}$. This has a formula of the type $B_mH_m^{4-}$, so it is *nido*. $B_5H_8^-$ has three more H than B, so we remove three H^+ to get $B_5H_5^{4-}$. This also has a formula of the type $B_mH_m^{4-}$, so it is *nido* as well. $B_7H_7^{2-}$ already has the same number of B and H, with a formula of the type $B_nH_n^{2-}$, so it is *closo*. $B_{10}H_{18}$ has eight more H than B, so we remove eight H^+ to get $B_{10}H_{10}^{8-}$, with a formula of the type $B_qH_q^{8-}$, so it is *hypho*.

17.3. Heteroboranes and Zintl Ions

Many clusters exist in which one or more boron atoms are replaced by those of another element. These species are known as heteroboranes, where the prefix “hetero-” means, in this case, different from boron.¹¹⁷ One of the most well-studied classes of heteroboranes is called the carboranes or carbaboranes, in which one or more boron atoms is replaced by carbon. To understand how PSEPT works when counting electrons for carborane structure, we consider that the B–H fragment is isoelectronic to both C– H^+ and just C (since H^+ has no

¹¹⁷ Note the difference from the organic chemists’ convention, in which a heteroatom is a heavy (non-hydrogen) atom other than carbon.

electrons). One can imagine a carbon atom at the vertex of a heteroborane having a “lone pair” in an *sp* hybrid-type orbital pointing away from the center. We can thus mentally replace C with B–H in a formula in order to decide whether a carborane is *closo*, *nido*, *arachno*, or *hypho*.

For instance, consider the well-known, stable molecule $C_2B_4H_6$. Replacing each C with B–H, we get the formula of the analogous borane, B_6H_8 . To make the numbers of B and H equal, we remove two H^+ to yield $B_6H_6^{2-}$, a *closo* borane. Thus, $C_2B_4H_6$ is a *closo* cluster, analogous to $B_6H_6^{2-}$. The actual structure has the carbon atoms opposite to other in the octahedron, rather than adjacent (if the two carbons were ligands around a central metal, they would be *trans*, not *cis*). Wade’s rules, for all their utility, cannot predict that this isomer is more stable than that with the carbon atoms adjacent (though it in fact is). It is often the case that more electronegative atoms are farther apart from one another in a cluster: given that C is more electronegative than B (though not by any great margin), it makes sense that the C atoms are on opposite vertices of the octahedron.

Other group 14 elements, like Si and Ge, behave the same way as C in heteroboranes. While they are not isoelectronic to C, they have the same number of *valence* electrons: in the terminology of Hoffmann, they are isolobal. Considering $GeC_2B_9H_{11}$, we replace the Ge and both C atoms with B–H to get the analogous borane $B_{12}H_{14}$, which can be derived from $B_{12}H_{12}^{2-}$. This is thus another *closo* cluster. Just as we can replace a Group 14 element with BH, we can replace a Group 15 element or pnictogen (such as N, P, or As) with BH_2 , and a Group 16 element (such as S or Se) with BH_3 . If we consider SB_9H_9 , we can see that it is analogous to $B_{10}H_{12}$, derived from $B_{10}H_{10}^{2-}$. This is another *closo* species. $SB_9H_{12}^-$, however, is analogous to $B_{10}H_{15}^-$, derived from $B_{10}H_{10}^{6-}$, so this is an *arachno* cluster.

The analogies used in heteroboranes show us that there can be surprising connections between seemingly unrelated areas of chemistry. Borane clusters may seem to be a very different beast from aromatic hydrocarbons, but it turns out that, when Wade’s rules are applied to heteroboranes with a two-dimensional structure, we get the electron counts expected by Hückel’s rule for aromaticity! We can actually treat aromatic hydrocarbon

species as being, essentially, two-dimensional carboranes, and use Wade's rules to predict the closed-shell charges.

Let us start with $C_5H_5^-$, the familiar Cp^- anion. $C_5H_5^-$ is analogous to $B_5H_{10}^-$, derived from $B_5H_5^{6-}$, an *arachno* cluster. The parent deltahedron ($n = 5$) is a pentagonal bipyramid; removing the top and bottom vertices gives the planar, pentagonal shape of $C_5H_5^-$. We can also consider benzene, the archetypal aromatic compound, in this manner. C_6H_6 is analogous to B_6H_{12} , derived from $B_6H_6^{6-}$, also *arachno*, with a parent deltahedron with $n = 6$. Though the standard shape for a *closo* deltahedron with 8 vertices is a dodecahedron, a hexagonal bipyramid will also work: removing the top and bottom vertices gives the planar hexagon shape of benzene.

There exist many cluster ions of main-group metals or semimetals, known as Zintl ions after Eduard Zintl (1898-1941) of the Darmstadt University of Technology. Most are polyanions, associated with alkali metal or alkaline earth metal cations. Examples include the square planar Se_4^{2-} and Sb_4^{2-} , and the trigonal bipyramidal Pb_5^{2-} and Sn_5^{2-} . Their structures can be understood using the isolobal analogy and Wade's rules. For instance, since Pb, like C, is in Group 14, Pb_5^{2-} is analogous to $B_5H_5^{2-}$, a *closo* borane. The argument for Sn_5^{2-} is exactly analogous. This fits with its structure: a trigonal bipyramid is a closed deltahedron. Se_4^{2-} is analogous to $B_4H_{12}^{2+}$, derived from $B_4H_4^{6-}$, an *arachno* cluster derived from the removal of two opposite vertices of an octahedron. By the same arguments, Sb_4^{2-} is analogous to $B_4H_8^{2-}$ and $B_4H_4^{6-}$, explaining its square planar geometry as well. Both Se_4^{2-} and Sb_4^{2-} can be thought of as analogous to the aromatic (by Hückel's rule) $C_4H_4^{2-}$ ion.

17.3. Transition Metal-Containing Cluster Compounds

There exist many metallaboranes, borane clusters in which one or more B-H group has been replaced by a TM and its ancillary ligands. Wade's rules can be extended to account for the structures of metallaboranes by drawing an analogy between the octet rule (an 8e rule) for main-group elements and the 18e rule for transition metals. Of course, this analogy only makes sense if the metals in question are low-spin, but metallaboranes usually contain

strong-field ligands, so assuming low-spin behavior is reasonable. Three examples of known metallaboranes are shown in Figure 17.10 below.

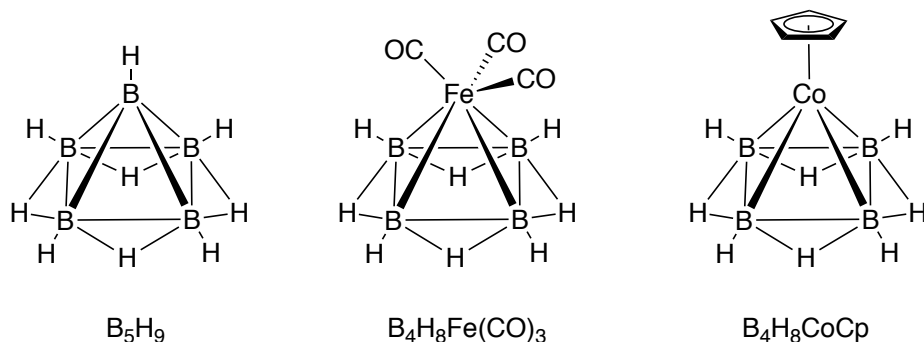


Figure 17.10. B_5H_9 and related metallaboranes.

B_5H_9 is a classic example of a *nido* borane: removing 4 H^+ to equalize the numbers of B and H atoms gives $B_5H_5^{4-}$, whose 4- charge allows us to classify it as *nido*. To see why these metallaboranes, in which a B–H has been replaced by $Fe(CO)_3$ or $CoCp$, we realize that a B–H group has 4e around boron, so it needs an additional 4e to satisfy the octet rule. (While our drawings of borane clusters do not obey the octet rule as is taught in general chemistry for the drawing of “good” Lewis structures, this is still a useful way of thinking about things.) A TM fragment analogous to B–H (isolobal by Hoffman’s definition) would thus also need 4e, but it will need 4e to satisfy the 18e rule. Thus, it should have 14e in the metal’s coordination sphere.

Considering $B_4H_8Fe(CO)_3$, we count electrons for the $Fe(CO)_3$ fragment: Fe gives us 8e and each CO gives us 2e for 14e total, so we can mentally “replace” $Fe(CO)_3$ with B–H to give B_5H_9 , which is *nido* by the preceding argument. Similarly, when considering B_4H_8CoCp , we count electrons for $CoCp$: Co gives us 9e and Cp (considered as the neutral radical) gives us 5e,¹¹⁸ for 14e total once again. Thus replacement of $CoCp$ by B–H gives *nido* B_5H_9 .

¹¹⁸ Some people prefer to count electrons starting with the metals as ions corresponding to their oxidation states. This would amount to considering $CoCp$ as Co^+ , with 8e (one electron fewer than neutral Co) and Cp^- , with 6e (the 6 π electrons that make Cp^- aromatic). The two electron-counting methods are completely equivalent, though I personally find easier the one that separates compounds into neutral fragments. You can use whichever you prefer.

There also exist cluster compounds *all* of whose framework atoms are TMs, very commonly with carbonyl ligands. $\text{Fe}_3(\text{CO})_{12}$, whose formula is perhaps more transparently written as $[\text{Fe}(\text{CO})_4]_3$, is an equilateral triangle of Fe atoms, each with four CO ligands. How can we understand its structure by analogy with boranes? First, we note that $\text{Fe}(\text{CO})_4$ is a 16e fragment: 8e from Fe and 8e from four 2e CO ligands. It thus needs 2e to attain an 18e configuration. The corresponding borane fragment is 6e BH_3 , which needs 2e to get an octet. So $\text{Fe}_3(\text{CO})_{12}$ can be thought of as analogous to $(\text{BH}_3)_3$ or B_3H_9 . Removing 6 H^+ to equalize the numbers of B and H atoms gives $\text{B}_3\text{H}_3^{6-}$, which is *arachno*. The parent deltahedron of an *arachno* structure has two more vertices: a trigonal pyramid. And, indeed, removing the two axial vertices of a trigonal pyramid yields an equilateral triangle.

The tetrahedral cluster $\text{Ir}_4(\text{CO})_{12}$, or $[\text{Ir}(\text{CO})_3]_4$, can be considered in a similar fashion, with something of an additional wrinkle. An $\text{Ir}(\text{CO})_3$ fragment is 15e: 9e from Ir and 6e from 3 CO. It needs 3e to attain 18e, so the analogous borane fragment is BH_2 with 5e. Mental replacement of $\text{Ir}(\text{CO})_3$ with BH_2 gives us the analogous borane cluster $(\text{BH}_2)_4$ or B_4H_8 , corresponding to the anion $\text{B}_4\text{H}_4^{4-}$. The 4- charge says this is a *nido* structure, and the parent deltahedron must thus have one more vertex: a trigonal bipyramid once again. Removal of one of the axial vertices from a trigonal bipyramid yields a tetrahedron, which is indeed the shape of $[\text{Ir}(\text{CO})_3]_4$. This is potentially confusing in one respect, namely, that a tetrahedron is itself a deltahedron: it has four faces, each of which is an equilateral triangle. So it might seem a bit confusing to think of it as derived from a separate “parent” structure. Nevertheless, when considering cluster compounds, it is most consistent to think of a tetrahedron as a *nido* derivative of a trigonal bipyramid, rather than as a “parent” deltahedron of its own.

So far, the analogy between boranes and transition metal clusters has been fruitful, but there are two problems. For one thing, it is somewhat cumbersome to figure out which BH_z fragment each TM fragment corresponds to, followed by analyzing the (perhaps hypothetical) analogous borane. It would be more convenient to have a simpler algorithm for structure prediction. Additionally, the borane analogy is not useful when we cannot write the cluster formula as a simple oligomer of a single metal fragment. For instance, $\text{Co}_6(\text{CO})_{16}$ is a *closo* cluster compound: its structure is an octahedron with a Co at each vertex. But it

cannot be a *regular* octahedron like $B_6H_6^{2-}$, because $\frac{16}{6}$ is not an integer: $Co_6(CO)_{16}$ is not a hexamer of $Co(CO)_z$ for some integer z . This is not a problem when it comes to the formation of the compound, since CO ligands regularly bridge two metal centers engaged in covalent bonding to each other. It does, however, pose a problem for simple electron-counting rules, since, while an H atom bridging two B atoms can be (at least conceptually) removed as H^+ , leaving the same number of electrons in the borane, no easy “electronless” hypothetical removal of bridging CO ligands is possible.

Wade extended his rules for metal carbonyl clusters by considering the total valence electron count (VEC for short) of a cluster. For a borane, each B contributes 3e and each H contributes 1e; adding the charge gives the total VEC. For example, $B_6H_6^{2-}$ has 18e from 6 B, 6e from 6 H, and an additional 2e from the 2- charge, for a VEC of 26e total. Not all of these 26 valence electrons are available for bonding in the deltahedron framework: since each “localized” B–H bond consists of two electrons, 12e are used in the terminal B–H bonds, leaving 14e in the framework. It is important to realize that these framework valence electrons are used in the bonding of additional H atoms that bridge two B centers. For example, $B_5H_5^{4-}$ has a VEC of $(5 B)(3e/B) + (5 H)(1e/H) + 4 = 15 + 5 + 4 = 24e$. Of these electrons, 10e are used in the five terminal B–H bonds, with 14e left in the framework. When $B_5H_5^{4-}$ binds 4 H^+ to form the neutral, stable compound B_5H_9 , it is using some of the framework electrons to bind the additional H^+ , which end up bridging.

Wade proposed the following analogy between the octet rule and the 18e rule: since a TM atom has five more valence AOs than a B atom, each of which can hold 2e, the total VEC for a TM cluster must be 10e greater than the corresponding borane cluster for each B replaced by a TM. Here it is important to consider the valence electron contribution by the ligands: for instance, each CO contributes 2e, as opposed to 1e per H. We have seen that *closo* $B_6H_6^{2-}$ has VEC = 26e. Since *closo* $Co_6(CO)_{16}$ has 6 Co in place of 6 B, it should have a VEC of $26e + 6(10e) = 86e$. And, indeed, it does: $(6 Co)(9e/Co) + (16 CO)(2e/CO) = 54e + 32e = 86e$. This argument works for metallaboranes, as well as pure boranes and pure TM carbonyl clusters. We have seen that *nido* B_5H_9 has VEC = 24e. The *closo* metallaborane $B_4H_8Fe(CO)_3$, with one B replaced

by Fe, should have a VEC of 34e, 10e greater. We figure its VEC as $(4 \text{ B})(3\text{e/B}) + (8 \text{ H})(1\text{e/H}) + (1 \text{ Fe})(8\text{e/Fe}) + (3 \text{ CO})(2\text{e/CO}) = 12\text{e} + 8\text{e} + 8\text{e} + 6\text{e} = 34\text{e}$, exactly as Wade's rules predict.

If some of these arguments strike you as a bit like numerology and seem lacking in rigor, they are. Simple rules like this for predicting structures are not, in the end, a substitute for detailed theory. But the octet rule for main-group molecules is not rigorous, either: it relies on the happy fact that MO models for many (but not all) such molecules end up with 8 valence MOs of fairly low energy. There exist many exceptions to Wade's rules, just as there are exceptions to the octet rule and 18e rules. It is nonetheless a good starting point for understanding this interesting and increasingly relevant class of compounds.

Chapter 18: Bioinorganic Chemistry and Medicinal Inorganic Chemistry

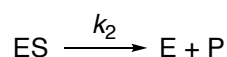
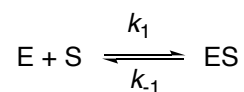
18.1. Bioinorganic Chemistry

Biochemistry is commonly thought of as an area of organic chemistry. After all, we are carbon-based, as are all other life forms known. Certainly, the well-known macromolecules of biochemistry, such as proteins, nucleic acids, carbohydrates, and lipids, are all organic compounds. Nonetheless, metal species are of paramount importance in the function of many biological systems, and changes in their levels can be associated with disease states. Main-group metals have significant roles in biology: for instance, Na^+ and K^+ are important for nerve signaling, Mg^{2+} is associated with the negatively charged phosphate groups of DNA, and the “mineral” part of bones is primarily $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (hydroxyapatite).

Transition metals are also widely used by life. Some biological roles of transition metal compounds are structural: for example, a group of mollusks called chitons (class Polyplacophora) have teeth coated with the iron ore magnetite (Fe_3O_4). In this course, however, I would like to focus on metalloproteins: proteins (including enzymes) containing transition metals necessary for their function. In introductory biology, proteins are described as polymers of amino acids, held together by amide (“peptide”) bonds between the amino group of one amino acid and the carboxyl group of another. However, many important proteins contain chemical groups that do *not* come from an amino acid residue. Glycoproteins have carbohydrate groups bound to the amino acid backbone, and metalloproteins contain at least one metal atom or ion. When discussing the structure of a metalloenzyme, one often refers to the polypeptide chain without the metal as the apoenzyme (from Greek *ἀπό*, “away from”), and the metal (and any non-amino acid ligands) as either a coenzyme or a prosthetic group. In general, coenzymes engage in noncovalent interactions with the apoenzyme, whereas prosthetic groups are covalently bound to the apoenzyme. The complete enzyme, containing both the apoenzyme and the coenzyme or prosthetic group, is called the holoenzyme (from Greek *ὅλος*, “whole” or “entire”). There exists a wide variety of metalloproteins, far more than can be discussed in a portion of a single course, but we will go over some representative, important examples.

18.2. Enzyme Kinetics and the Michaelis-Menten Equation

The full stoichiometric mechanisms by which enzymes catalyze reactions are often very complex, and difficult to determine in complete detail. However, the following rough outline of the mechanism of much enzyme catalysis is useful, in that it leads to the derivation of a useful formula for the rates of enzyme-catalyzed reactions.



In this outline of the mechanism, the enzyme E binds reversibly to the substrate (reactant) S to form the enzyme/substrate complex ES. Once this complex is formed, the reaction occurs in which the enzyme-bound substrate is converted to the product P, regenerating the free enzyme. This outline treats the actual reaction of enzyme-bound substrate as something of a “black box,” not specifying its elementary steps. In addition, the second, product-forming step is treated as irreversible. This is not always true, but one can ignore the reversibility of the product-forming step if one considers *initial* reactions rates r_0 .

Leonor Michaelis (1875-1949) and Maud Menten (1879-1960) assumed a rapid equilibrium between E, S, and ES, and derived the now-famous Michaelis-Menten equation for the initial rate of an enzyme-catalyzed reaction:

$$r_0 = \left. \frac{d[\text{P}]}{dt} \right|_{t=0} = \frac{k_2[\text{E}]_{\text{T}}[\text{S}]}{[\text{S}] + K_{\text{M}}} = \frac{V_{\text{max}}[\text{S}]}{[\text{S}] + K_{\text{M}}}$$

where

$$[\text{E}]_{\text{T}} = [\text{E}] + [\text{ES}]$$

$$K_{\text{M}} = K_{\text{S}} + \frac{k_2}{k_1} = \frac{k_{-1} + k_2}{k_1}$$

$$K_{\text{S}} = \frac{[\text{E}]_{\text{eq}}[\text{S}]_{\text{eq}}}{[\text{ES}]_{\text{eq}}} = \frac{k_{-1}}{k_1}$$

$$V_{\text{max}} = k_2[\text{E}]_{\text{T}}$$

The mathematical dependence of the initial rate r_0 on the substrate concentration is important to consider carefully. While r_0 is certainly an increasing function of $[\text{S}]$, as one

would expect, the more [S] increases, the more slowly r_0 increases with it. Taking derivatives of r_0 with respect to [S] while holding the total enzyme concentration constant, we see that

$$\frac{\partial r_0}{\partial [S]} = \frac{V_{\max} K_M}{([S] + K_M)^2} > 0$$

but

$$\frac{\partial^2 r_0}{\partial [S]^2} = -\frac{2V_{\max} K_M}{([S] + K_M)^3} < 0$$

Thus, while r_0 increases with increasing [S], it does not increase without bound, rather converging to a limiting highest reaction rate $r_0 = V_{\max}$ once $[S] \gg K_M$. The physical interpretation of this is that when [S] is very large, the enzyme is “saturated,” *i.e.* essentially all molecules of enzyme have a molecule of substrate bound and are in the process of catalyzing its reaction. At this point, increasing [S] further will not speed up the reaction any further, because there are no enzyme molecules left to engage in catalysis. Rate laws of this form are commonly known as “saturation kinetics” for this reason, and some synthetic catalysts, as well as enzymes, display them.

Many (though not all) enzymes are highly specific: they will catalyze the reaction of one substrate very efficiently, but they will catalyze the reaction of a related substrate much more slowly or not at all. In introductory biology, the specificity of many enzymes is rationalized in terms of the so-called “lock and key” model, according to which enzymes only catalyze the reaction of substrates that bind to it very favorably: the substrate is a very specific “key” that fits into the “lock” of the enzyme’s active site. However, an enzyme that binds a substrate strongly enough will *not* be an especially good catalyst, for a reason that is perhaps not obvious based on the Michaelis-Menten equation.

The Michaelis constant K_M , which appears in the denominator of this rate law, includes K_S , the equilibrium constant for $ES \rightleftharpoons E + P$, or the dissociation of substrate from enzyme. If K_S (and therefore K_M) is quite large (very weak enzyme-substrate binding), the reaction rate will thus be slow. But the value of K_S only indicates the stability of ES relative to E and S, *not* relative to the product P. If ES is thermodynamically stable enough relative to the *product*, there will not be a substantial “driving force” for conversion of substrate to product. We thus

must also consider k_2 , the rate constant for conversion of substrate to product once the substrate is bound: larger values of k_2 for some substrates as opposed to others lead to substantial specificity. It is often proposed that binding of substrate to enzyme is actually thermodynamically *destabilizing* to the substrate, thus lowering the activation energy for the actual catalysis (and increasing k_2). For this reason, k_2 is sometimes denoted as k_{cat} in the Michaelis-Menten equation. Reasonably small values of K_S for the substrate are necessary, however, for the enzyme to selectively catalyze a reaction of that substrate rather than another.

When studying an enzyme, one often wishes to determine the numerical values of the crucial constants K_M and k_2 . For this purpose, one can analyze enzyme kinetics data using a so-called Lineweaver-Burk plot,¹¹⁹ after Hans Lineweaver (1907-2009) and Dean Burk (1904-1988). Taking the reciprocal of the Michaelis-Menten equation yields

$$\frac{1}{r_0} = \frac{[S] + K_M}{V_{\text{max}}[S]} = \frac{1}{V_{\text{max}}} + \frac{K_M}{V_{\text{max}}[S]}$$

A plot of $\frac{1}{r_0}$ on the y -axis vs. $\frac{1}{[S]}$ on the x -axis should be linear (within experimental error), with a y -intercept of $\frac{1}{V_{\text{max}}}$, a slope of $\frac{K_M}{V_{\text{max}}}$, and an x -intercept of $-\frac{1}{K_M}$. If one knows $[E]_T$, which one usually does, the Lineweaver-Burk plot allows for the calculation of k_2 from V_{max} . It should be noted that a downside of the Lineweaver-Burk plot method is the fact that errors in directly measured quantities are increased when reciprocals are taken. There now exist methods for nonlinear curve-fitting of enzyme kinetics data, but the Lineweaver-Burk plot is worth describing due to its conceptual simplicity, and it is still commonly used in data analysis in biochemistry lab courses.

18.3. Porphyrins, Hemoglobin, and Cytochromes

One of the most common types of transition metal-containing prosthetic groups is the heme family (haem in British English), most famous for its presence in hemoglobin, the oxygen-carrying molecule in blood. (The words “heme” and “haem” comes from Greek αἷμα, “blood.”)

¹¹⁹ Also known as a “double reciprocal plot.”

Hemes are iron complexes of porphyrinate ligands, so it is worth giving a general outline of this important class of organic molecules. The simplest porphyrin is porphine, shown in Figure 18.1 below alongside octaethylporphyrin and tetraphenylporphyrin, common ligands in synthetic molecules used as model systems for metalloenzymes.

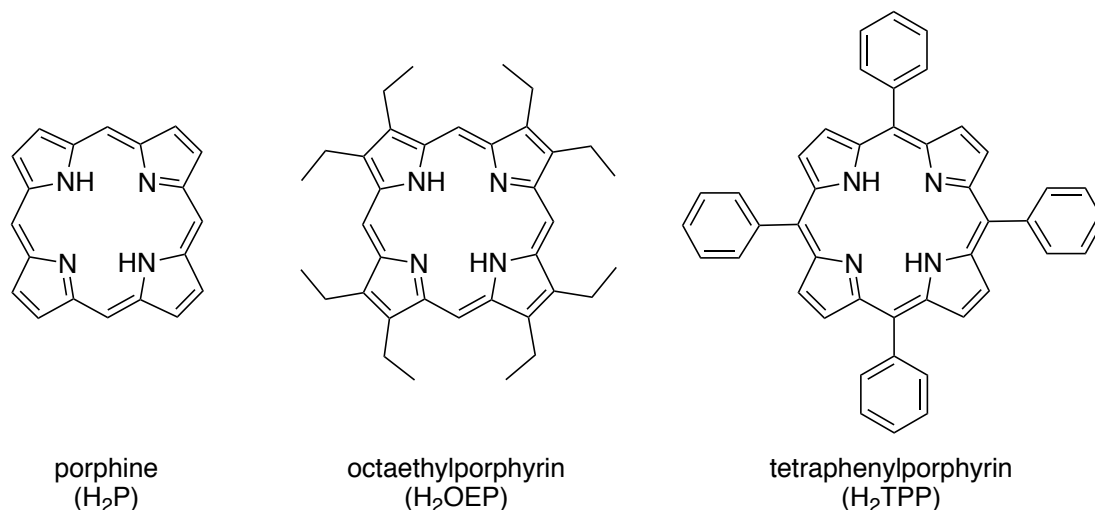


Figure 18.1. Structures of some simple porphyrins.

Going around the outer ring, one can count 18 π electrons in a porphyrin, making such systems aromatic. Once a porphyrin is deprotonated twice to form a porphyrinate, the resulting 2- charge is shared by all four N atoms, and in the symmetrical porphyrins shown above, all the N atoms in the porphyrinate are equivalent (as can be shown by sketching the various possible resonance structures) and the dianions have fourfold symmetry (they belong to the D_{4h} point group).

Heme b, the form of heme present in the O₂ transport proteins, contains a less symmetrical porphyrinate, and its structure is shown in Figure 18.2 on the following page. The iron in the center of the porphyrinate is actually five-coordinate, with a histidine residue from the apoenzyme binding it at an axial position.

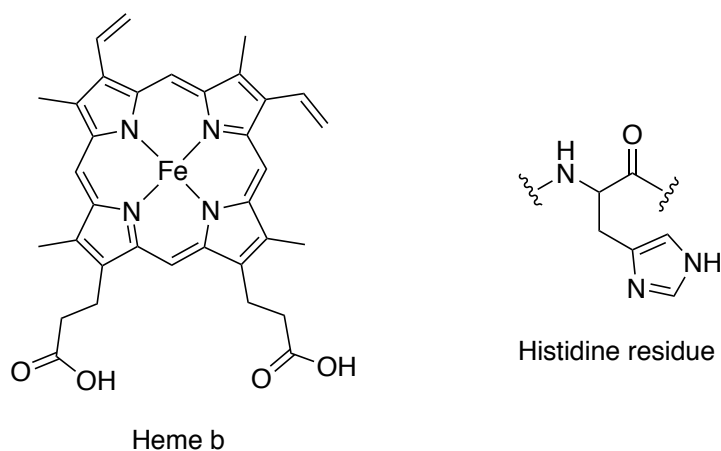
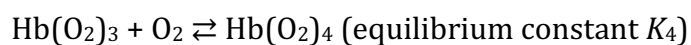
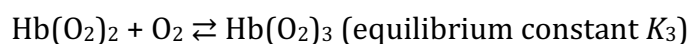
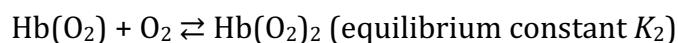
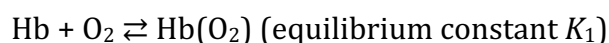


Figure 18.2. Heme b.

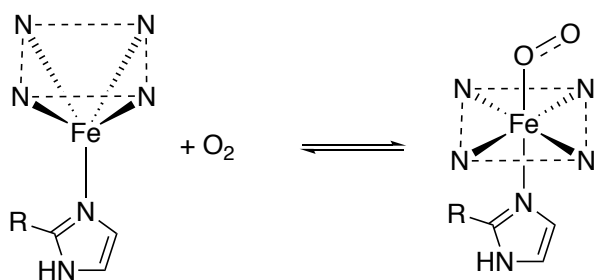
A single “molecule” of hemoglobin actually consists of four protein molecules, two of one type, labeled α , and two of another type, labeled β , noncovalently bound to each other. Thus, hemoglobin is a mixed tetramer of stoichiometry $\alpha_2\beta_2$. Each constituent protein (both α and β) has its own heme group, so there are four Fe centers per hemoglobin and thus four O_2 binding sites, since the O_2 is bound at Fe. The binding of O_2 by hemoglobin can be represented by four equilibria, with $Hb = \alpha_2\beta_2$ a shorthand for non-oxygenated hemoglobin:



What is striking about the binding of O_2 to hemoglobin is that each successive binding constant is larger than the last: $K_n > K_{n-1}$, so the more O_2 is bound to hemoglobin, the higher the affinity of hemoglobin for O_2 (up to the maximum number of four O_2 molecules bound). The exact amino acid sequence, (and thus the O_2 binding constants) of hemoglobin differs between species, but K_1 is usually between 5 and 60, and K_4 is usually between 3000 and 6000. Every time an O_2 molecule binds to hemoglobin, it induces conformational changes in the protein tetramer to make the next binding more favorable, a phenomenon known as cooperative binding. Such cooperative binding is well suited for hemoglobin’s biological role of transporting O_2 to tissues that need it the most. When a hemoglobin molecule is present

in a blood vessel flowing through highly oxygenated tissue, $[O_2]$ is high, and thus O_2 in hemoglobin tends to stay bound. When a hemoglobin molecule is in oxygen-deprived tissue, dissociation of bound O_2 is favored, and the tissue gets the oxygen it needs. Even without cooperative binding, this phenomenon would be expected to some extent due to Le Chatelier's principle, but the cooperativity strongly enhances this effect.

The conformational changes responsible for cooperative binding are certainly complicated, given what large molecules proteins (let alone protein tetramers) are. One intriguing structural change, however, involves the coordination geometry of the heme Fe center and its dependence on O_2 . In nonoxygenated hemoglobin, the Fe does *not* lie in the plane of the four porphyrinate N atoms. Instead, it is outside the plane in the direction of the histidine imidazole group. Once O_2 binds, however, the Fe atom moves into the porphyrinate N plane, adopting a basically octahedral coordination geometry, as shown in Figure 18.3 below.



R = rest of protein

Figure 18.3. The change in hemoglobin Fe coordination geometry upon binding of O_2 .

The oxidation state of Fe in hemoglobin is worth comment. Unoxygenated hemoglobin is an Fe(II) species, a straightforward assignment based on the facts that porphyrinates are 2- ligands and the histidine nitrogen is neutral. Upon the binding of oxygen, however, the Fe is considered to be Fe(III), with O_2 behaving as a coordinated superoxide (O_2^-) radical anion. This assignment may seem inconsistent with the usual rules for assignment of oxidation states, in which ligands are taken to have whatever charge leads to a closed-shell species: superoxide, after all, is not closed-shell. Spectroscopic data, however, do suggest that O_2 in hemoglobin is best described as bound O_2^- . This redox behavior is due in large part to the

tremendous steric bulk of the protein part of hemoglobin: the treatment of small-molecule Fe(II) porphyrinate model systems (as shown below, with L being a small 2e ligand like imidazole) with O₂ leads to the formation of bimetallic Fe(III) complexes, in which a single O₂ molecule is reduced to a peroxide (O₂²⁻) ligand that bridges two Fe centers, as shown in Figure 18.4 below.

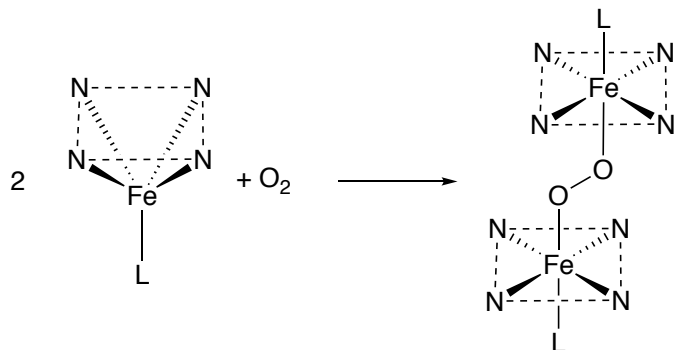


Figure 18.4. Formation of bridging peroxide ligands in synthetic Fe porphyrinate complexes.

In general, when a synthetic chemist is trying to avoid the formation of bimetallic complexes or clusters, a standard strategy is to use large, bulky ligands to provide enough steric hindrance that two (or more) metal centers cannot approach closely enough to form a larger molecule. In the case of hemoglobin, that criterion is more than met: it is difficult to imagine a ligand bulkier than an entire protein.

Hemoglobin (and the related protein myoglobin, which transports O₂ in muscle) is not an enzyme *per se*, as it transports a small molecule, rather than catalyzing a reaction. There exist many genuine enzymes, however, with a heme prosthetic group at their active sites. A very important group of such enzymes is the cytochrome P-450 family,¹²⁰ whose members are generally monooxygenase enzymes, catalyzing reactions of organic molecules with O₂ in which a single oxygen atom is added to the organic molecule. Many monooxygenase

¹²⁰ The “450” in the name comes from the fact that the UV-visible spectra of these enzymes all have a strong absorption peak at $\lambda = 450$ nm.

reactions consist of the conversion of a C–H bond to C–OH, a C–H activation reaction of the C–H oxidation type: $\text{R-H} + \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{R-OH} + \text{H}_2\text{O}$. The electrons written as e^- in the previous reaction are not truly free electrons, but they come from the common biological reducing agent NADPH. An enzyme called cytochrome P-450 reductase is necessary to transfer electrons from NADPH in this reaction, so monooxygenase reactions are actually catalyzed by two different enzymes: a cytochrome P-450, which accomplishes the hydroxylation, and the reductase which provides the P-450 catalytic cycle with electrons from NADPH.

The generally accepted mechanism for hydroxylation catalyzed by P-450 enzymes is shown in Figure 18.5 on the following page (with e^- coming from the activity of the reductase, not shown). The group R' represents the rest of the protein, bound to the heme Fe through a thiolate (deprotonated cysteine residue). Oxidation states of Fe are indicated by a Roman numeral superscript, *e.g.* Fe^{II} is shorthand for $\text{Fe}(\text{II})$.

Step **1** of this mechanism consists of the organic substrate (which is to be hydroxylated) displacing a coordinated water molecule. Because C–H bonds are not very good ligands, the substrate does not directly coordinate Fe, though it does take up space in the enzyme's active site. In step **2**, the heme Fe is reduced from $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ with the help of a reductase. This $\text{Fe}(\text{II})$ form then binds O_2 in step **3**, transferring an electron to the O_2 so that the resulting complex can be thought of as $\text{Fe}(\text{III})$ with an O_2^- ligand. Transfer of another electron and two protons in step **4** results in the loss of one oxygen from the O_2^- ligand as water, and the formation of an $\text{Fe}(\text{IV})$ oxo complex. (An oxo or oxido ligand is O^{2-} , which binds to a metal center with an M–O double or triple bond.) Interestingly, when the Fe center is oxidized to $\text{Fe}(\text{IV})$, the porphyrinate ligand is also oxidized by one electron, giving it radical character, as represented in the diagram by the unpaired electron and the + charge. This $\text{Fe}(\text{IV})$ /porphyrinate radical species is a strong H atom abstraction reagent, and removes H from the substrate in step **5** to yield an organic radical and an $\text{Fe}(\text{III})$ complex with an OH^- ligand. In step **6**, an OH group (*not* OH^-) is transferred to the organic radical to yield the alcohol product coordinated to an $\text{Fe}(\text{III})$ species that no longer has substantial porphyrinate

radical character. Finally, in step 7, another water molecule replaces the alcohol in the Fe center's coordination sphere, regenerating the enzyme.

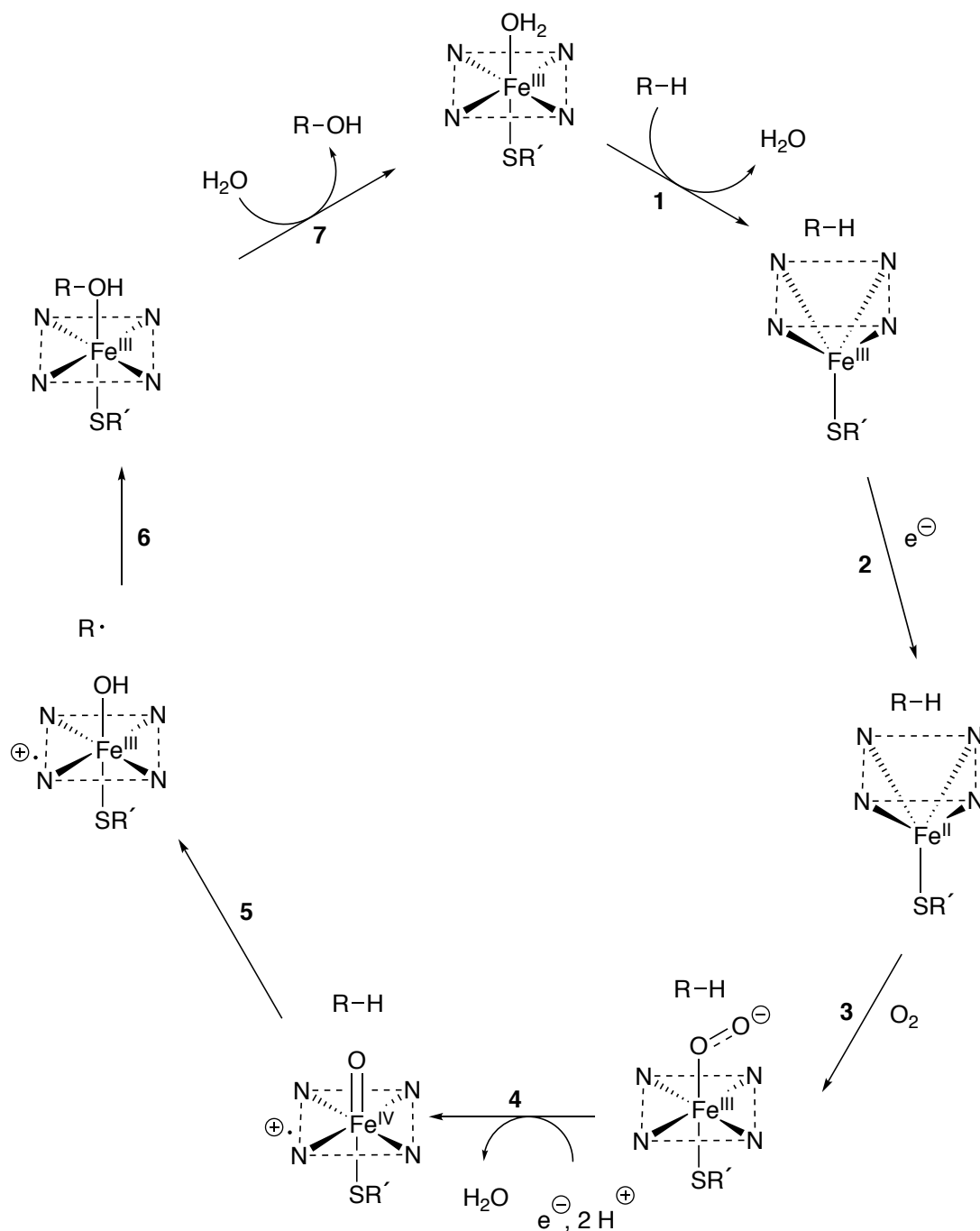


Figure 18.5. The generally accepted mechanism of C-H oxidation by cytochrome P-450.

A hallmark of many enzyme-catalyzed reactions is their stereospecificity, and the enzymes of the P-450 family are no exception. When the substrate carbon atom being hydroxylated is a chiral center, retention of stereochemistry is observed with P-450. This might strike you as inconsistent with a mechanism involving an alkyl radical (steps **5** and **6**): since alkyl radicals undergo rapid inversion at the radical carbon, one might expect stereochemical scrambling at that carbon. The fact that such scrambling does not occur is attributed to the extremely rapid nature of these steps, enforced by the proximity of the radical and Fe due to the shape of the enzyme's active site. The alkyl radical is hydroxylated almost as soon as it is formed, faster than inversion can occur. These steps are sometimes referred to as a "rebound" mechanism: an H atom is abstracted from the organic substrate, but a hydroxyl group "rebounds" right back on.

The P-450 enzymes are of great significance in medicine, as they are involved in the metabolism of most drugs. Many drugs are not terribly polar molecules, so they are lipophilic, being more soluble in fat than in water. Oxidation by P-450 transforms them into more polar (hydrophilic) species, which can then be excreted in the urine. Some drugs, however, bind to P-450 enzymes in a fashion that inhibits their activity, and this phenomenon is responsible for some negative drug interactions: if a substantial fraction of the body's P-450 is inhibited by one drug, another drug might then be metabolized more slowly, and thus can build up to toxic levels. Such interactions are not limited to prescription drugs: patients taking certain drugs are warned to avoid the consumption of grapefruit juice, as it contains furanocoumarin compounds that can irreversibly inhibit P-450 enzymes, potentially leading to drug toxicity.

Another medically relevant feature of P-450 enzymes is their ability to catalyze some oxygenation reactions other than hydroxylation. Some organic substrates containing C-C multiple bonds undergo epoxidation catalyzed by P-450, rather than hydroxylation, as shown in Figure 18.6 on the following page. This addition of a polar, reactive functional group to a hydrophobic system can make the substrate more readily excreted, similar to hydroxylation. Unfortunately, however, it can also make that substrate significantly more toxic. For example, benzene is well known as a hazardous solvent due to its ability to cause

leukemia and aplastic anemia, and for that reason large-scale industrial use of benzene has declined, and researchers using benzene as a solvent treat it with extreme caution. However, benzene itself does not damage DNA. Instead, cytochrome P-450 2E1 catalyzes the epoxidation of benzene to benzene oxide, a fused-ring epoxide in equilibrium with the seven-membered monocyclic compound oxepin, as shown in Figure 18.7 below.

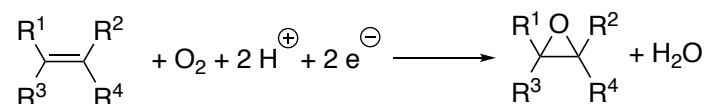


Figure 18.6. Epoxidation catalyzed by cytochrome P-450.

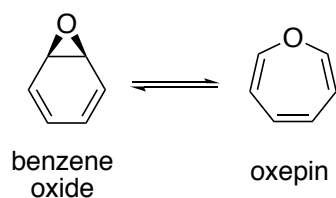


Figure 18.7. Benzene oxide in equilibrium with oxepin.

Epoxides are, in general, very powerful alkylating agents due to their ring strain, and benzene oxide, with its fused ring system, is even more strained and an even more potent alkylator. It is this compound that is responsible for much of the DNA damage that makes benzene a carcinogen. Interestingly, toluene is much less hazardous than benzene: while chronic exposure to toluene can cause neurological harm, it is not a potent carcinogen like benzene, because its methyl group is readily oxidized to benzoic acid (which is essentially nontoxic) before its aromatic ring system can be epoxidized (recall that benzylic C-H bonds are weak compared to most sp^3 C-H bonds), as shown in Figure 18.8 below.

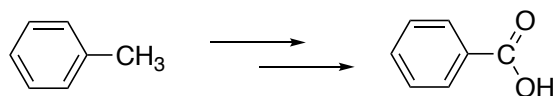


Figure 18.8. Benzylic oxidation of toluene to benzoic acid.

18.4. Corrins and Coenzyme B₁₂

We have seen that porphyrins, and their doubly deprotonated forms porphyrinates, are important macrocyclic ligands in biological coordination chemistry. Another important macrocycle is the corrin, which can be thought of as a less oxidized (and non-aromatic) analog of the porphyrin system, with one fewer carbon atom. Corrin can be deprotonated once (at its NH group) to yield a monoanionic ligand whose negative charge is highly delocalized over a conjugated π system, though this system is not aromatic. Cobalamins, also known as coenzyme B₁₂ or vitamin B₁₂, are cobalt complexes of a highly substituted corrin anion. The structures of a general corrin and of cobalamins is shown in Figure 18.9 below.

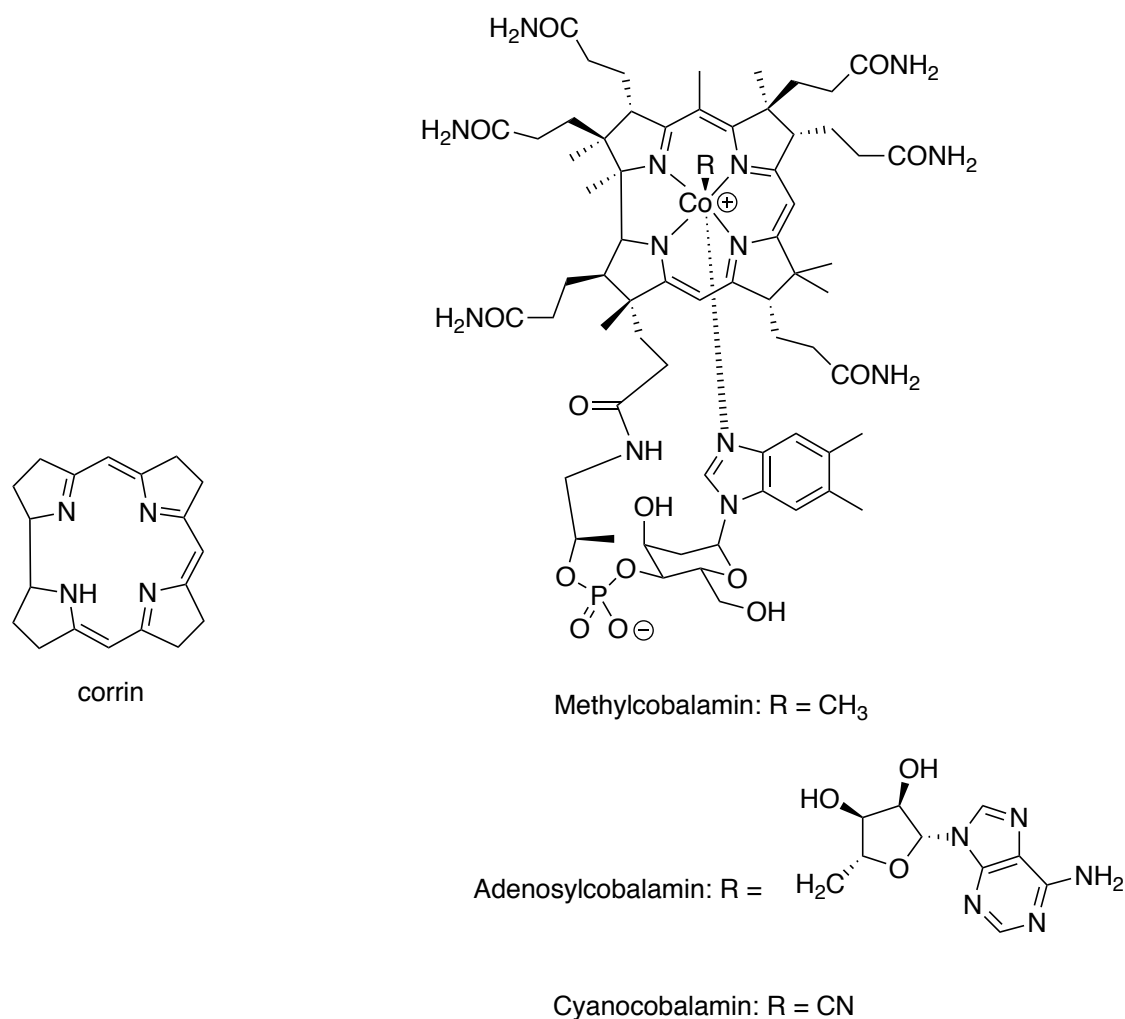


Figure 18.9. Structures of corrin and cobalamins.

The endogenous forms of cobalamin are methylcobalamin (MeCbl) and adenosylcobalamin (AdoCbl), each of which is present in certain enzymes as a cofactor. They are notable for being rare examples of truly *organometallic* biological compounds: while many enzymes are transition metal complexes, few have metal-carbon bonds. Cyanocobalamin (CNCbl) is not formed in living systems, but when B₁₂ was first isolated, the alkyl (methyl or adenosyl) ligands were replaced by cyanide as an artifact of the purification process. Because “vitamin B₁₂” was named when it was (mistakenly) thought that a CN⁻ ligand was present in the biological compound, vitamin supplements labeled as vitamin B₁₂ today are actually CNCbl. CNCbl is readily converted to MeCbl or AdoCbl in the body, and the amounts of CN⁻ released do not pose any threat of cyanide poisoning, given the low levels of B₁₂ that one needs.

The chemistry of B₁₂ and its roles in enzyme active sites are complicated, and one reason for this complexity is the ability of the Co center in B₁₂ to have a variety of oxidation states. The cobalamins drawn in Figure 18.9 are Co(III) species, but the Co is sometimes reduced to Co(II), leading to species labeled B_{12r} (“r” for “reduced”), or even to Co(I), leading to species labeled B_{12s} (“s” for “super-reduced”). This latter oxidation state is especially striking, given that stable Co(I) complexes are significantly less common than those with the more frequently seen Co(II) and Co(III) oxidation states, and that small-molecule Co(I) complexes such as CpCo(CO)₂ are often air-sensitive.

AdoCbl is present in a variety of enzymes known as mutases, which catalyze reactions in which functional groups migrate between carbon atoms on a chain. One example of such a reaction is shown in Figure 18.10 on the following page, catalyzed by the AdoCbl-containing enzyme methylmalonyl-CoA mutase, where CoA is an abbreviation for a larger group called coenzyme A.

The mechanism for this reaction, shown in Figure 18.11 on the following page, is believed to involve the homolytic cleavage of the Co(III)–adenosyl bond to yield a Co(II) species and an adenosyl radical. The adenosyl radical then abstracts an H atom from the substrate, leading to a radical that undergoes rearrangement and then re-abstracts the H atom, regenerating

the adenosyl radical, which can then return to Co. A sketch of this is shown below, with the adenosyl group abbreviated as R.

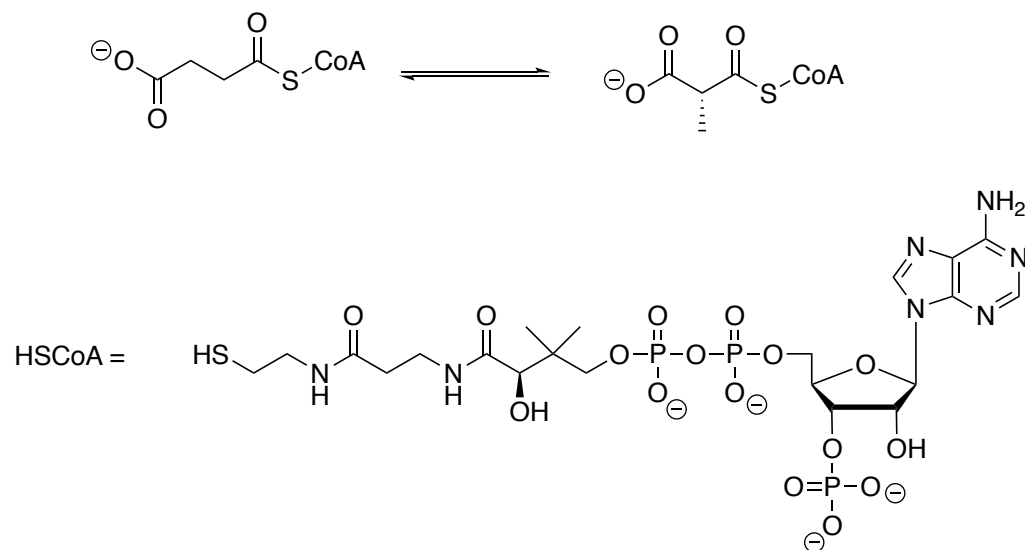


Figure 18.10. The reaction catalyzed by methylmalonyl-CoA mutase.

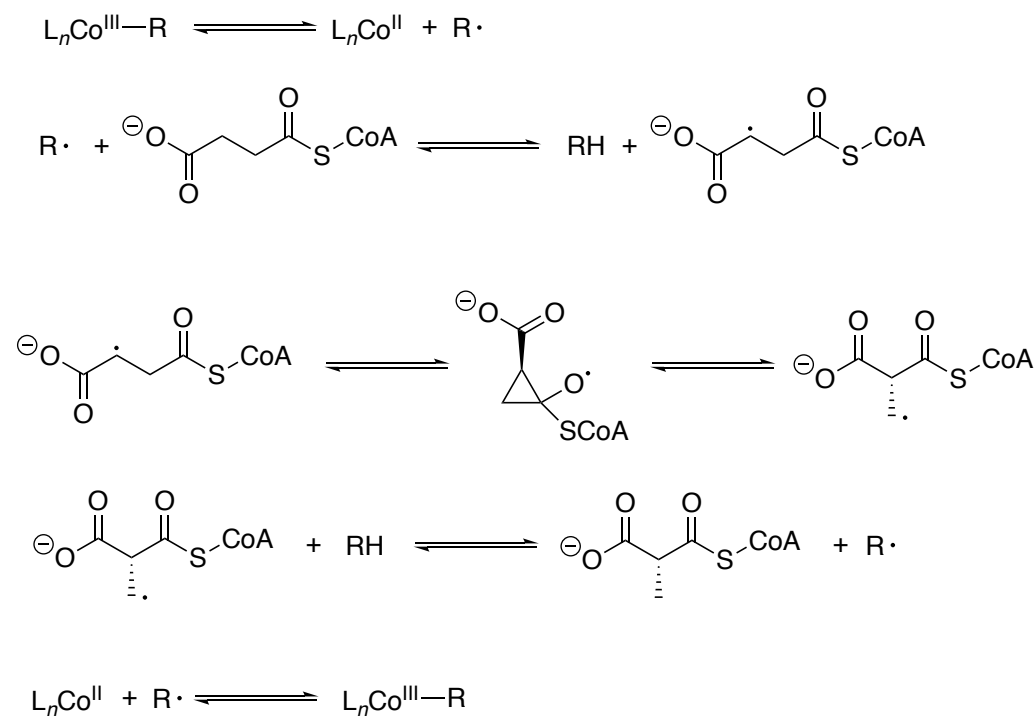


Figure 18.11. The mechanism of reactions catalyzed by methylmalonyl-CoA mutase.

In contrast to AdoCbl, which undergoes homolytic Co–C bond cleavage, MeCbl undergoes heterolytic Co–C cleavage. It is actually a methylating agent (CH_3^+ donor) in the enzymatic synthesis of methionine from homocysteine, with a Co(I) ($\text{B}_{12\text{s}}$) leaving group. The $\text{B}_{12\text{s}}$ produced is then taken back to Co(III) by transfer of CH_3^+ from protonated methyltetrahydrofolate. One might expect reactions involving highly reduced Co(I) complexes as leaving groups to be confined to anaerobic chemistry performed in gloveboxes or on Schlenk lines, but they can nonetheless occur in aqueous, aerobic life.

18.5. Nitric Oxide

Nitric oxide (NO) is a simple, diatomic molecule, and also a rather unusual species in that it is a stable radical with one unpaired electron (which resides in one of two degenerate N–O π -antibonding MOs). While it dimerizes in condensed phases (liquid and solid), NO gas exists almost entirely as the monomer. This colorless gas is stable in the absence of oxygen, but reacts rapidly with atmospheric oxygen to form amber-brown nitrogen dioxide (NO_2), one of the main components of smog: $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$. In oxygenated water, NO instead forms nitrous acid (HNO_2) according to $4 \text{NO} + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{HNO}_2$.

NO has long been known as a ligand for transition metals, and it is in some ways analogous to CO. The principal difference between CO and NO as ligands is the ability of NO to bind to a metal in either a linear (M–N–O angle $\approx 180^\circ$) or a bent (M–N–O $< 180^\circ$) fashion. The linear fashion is perhaps easier to envision in orbital terms. If we consider NO to be neutral, it donates 2e to the metal in a σ fashion *via* its roughly nonbonding σ “lone pair.” At the same time, a π interaction occurs in which 1e comes from a singly occupied π -antibonding MO, and another from a metal d AO with suitable symmetry. Thus, linear neutral NO can be considered a 3e ligand. Alternatively, we may consider linear NO ligands to be bound NO^+ , isoelectronic to CO, donating only 2e (in a σ sense), with the π -antibonding MOs empty on the ligand, accepting electron density through backbonding just like in the case of CO. As in the case of CO, in linear NO complexes there is substantial M–N double bond character. A sketch of the orbital interactions involved in the coordination of linear NO is shown in Figure 18.12 on the following page.

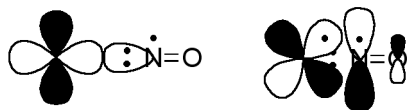


Figure 18.12. Orbital interactions in the coordination of linear NO.

The situation is different for bent NO. If we consider the ligand as neutral NO, the singly occupied π -antibonding MO can donate 1e into a metal d AO that also contains 1e. The resulting bond is σ between the metal and N, even though it is N–O π antibonding. In valence bond terms, one might consider the N atom of bent NO to be sp^2 -hybridized, whereas it is sp -hybridized in linear NO. Thus, bent neutral NO is considered a 1e ligand. Alternatively, we may consider bent NO ligands to be bound NO^- , isoelectronic to O_2 , donating 2e (in a σ sense), from a π -antibonding ligand MO. A sketch of the orbital interaction involved in the coordination of bent NO is shown in Figure 18.13 below.

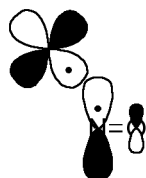


Figure 18.13. The key orbital interaction involved in the coordination of bent NO.

In a given complex, the energy difference between linear and bent NO is sometimes small; in such cases, molecules with the linear geometry can be in equilibrium with those in the bent geometry, as in the example shown in Figure 18.14 below.

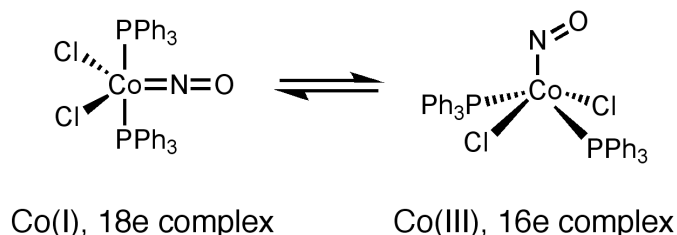


Figure 18.14. An example of an equilibrium between linear and bent NO ligands.

Note that when a bent NO ligand becomes linear, this corresponds to a decrease of 2e in the electron count at the metal (from 18e with linear NO to 16e with bent NO, in this case). Concomitantly, the metal's formal oxidation state increases by 2, since linear NO is counted as NO⁺ and bent NO as NO⁻. The linear → bent geometrical change can be thought of as a transfer of electron density from the metal to NO, and for this reason NO, with its variable geometry, is often described as a redox-active or “non-innocent” ligand.

NO became highly significant to biologists and biochemists, as well as coordination chemists, in the 1980s. Biologists had known that there existed an “endothelium-derived relaxing factor” (EDRF), a molecule produced by the endothelium (the cells lining blood and lymph vessels) that induced muscle relaxation and vasodilation (the widening of blood vessels). The discovery that NO was the EDRF¹²¹ was a breakthrough in biochemistry, and the 1998 Nobel Prize in Physiology or Medicine was awarded to Robert Furchgott of SUNY Downstate Medical Center (1916-2009), Louis Ignarro of the UCLA School of Medicine (b. 1941), and Ferid Murad of George Washington University (1936-2023) for their work in identifying NO as the EDRF.

The vasodilatory effect of NO is due to its ability as a ligand. The heme enzyme soluble guanylate cyclase (sGC) catalyzes the conversion of guanosine triphosphate (GTP) to cyclic guanosine monophosphate (cGMP). Without NO, sGC does not function to catalyze this reaction, but coordination of NO to the heme Fe of sGC activates it toward catalysis. The cGMP thus produced activates enzymes that lower Ca²⁺ levels; since proteins involved in muscle contraction require Ca²⁺ to function, the lowering of Ca²⁺ levels induces muscle relaxation.

There exists an interesting feedback loop involving the synthesis of NO. Endogenous NO is produced from the amino acid L-arginine in a reaction catalyzed by the heme-containing enzymes nitric oxide synthase (NOS), shown in Figure 18.15 on the following page.

¹²¹ Some sources do not state that NO is *the* singular EDRF. Instead, they hold that there exist multiple EDRFs, including both NO and other molecules that release NO in the body, such as nitrosothiols (general formula RSNO).

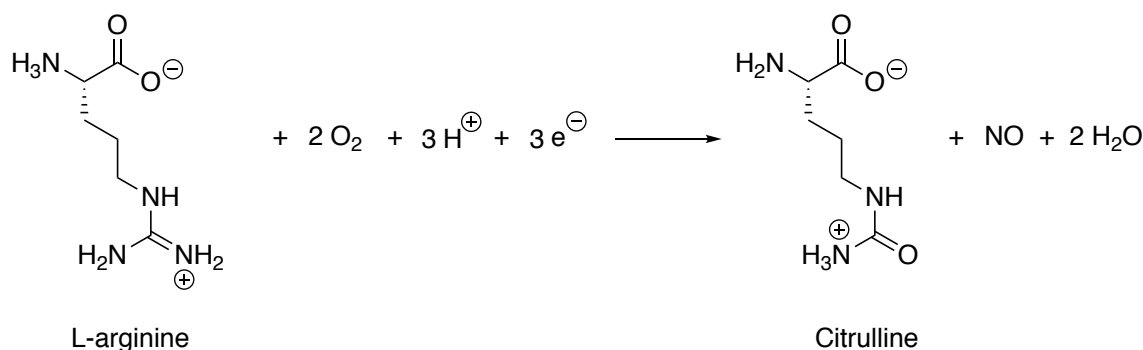


Figure 18.15. Production of NO from L-arginine.

NOS enzymes are themselves inhibited by NO, by binding of NO to the heme Fe centers. As high concentrations of NO are toxic (see below), this helps prevent too much NO from being produced in a cell signaling context. Additionally, endothelial NOS (eNOS) can bind calmodulin, a protein that itself binds Ca^{2+} . The binding of calmodulin and Ca^{2+} activates eNOS toward catalysis. Thus, under high Ca^{2+} concentration (required for muscle contraction), eNOS is activated and produces NO, leading to muscle relaxation. At low Ca^{2+} concentration, eNOS will not be active, and NO will no longer be produced as a signaling molecule to lower Ca^{2+} levels further.

Several drugs that act as vasodilators function by increasing NO concentrations. Nitroglycerin and amyl nitrite release NO upon reaction with physiological thiols, while sodium nitroprusside, a rare example of a transition metal-containing pharmaceutical, slowly releases NO on its own. Given the toxicity of CN^- (by its binding to, and inactivation of, the heme enzyme cytochrome c oxidase in the mitochondrial electron transport chain), one might wonder why $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ is a safe drug. The answer is that the $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ complex anion does not release CN^- quickly, as it is Fe(II) with strong-field ligands, and thus low-spin d^6 , and the ligand field activation energy for dissociative substitution on low-spin d^6 complexes is large. (The enzyme rhodanase converts small amounts of CN^- to SCN^- , which is less toxic and readily excreted.) The erectile dysfunction drug sildenafil (trade name Viagra) is also a vasodilator, but does not act by releasing NO directly: rather, it prolongs vasodilation by inhibiting the enzyme that degrades cGMP, the messenger molecule whose

production is activated by NO. The structures of these drugs are shown in Figure 18.16 below.

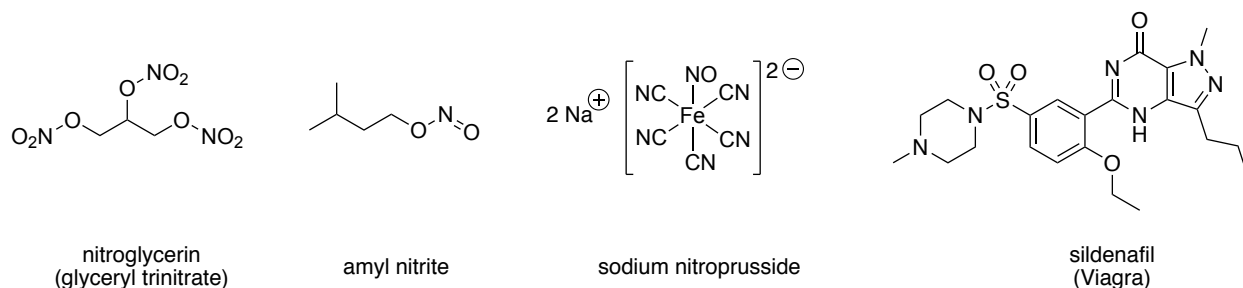


Figure 18.16. Some vasodilatory drugs.

In addition to muscle relaxation and vasodilation, NO is involved in immune response. High NO concentrations are cytotoxic, and macrophages (a type of white blood cell) have been shown to produce NO at (local) high concentration in order to kill tumor cells. Some of the toxicity of NO may be due to its reaction with the radical anion superoxide (O_2^-), one of the common reactive oxygen species that can arise in biological systems, to form the peroxynitrite anion, ONOO^- , a “linear” isomer of the familiar, trigonal planar nitrate anion, as shown in Figure 18.17 below.

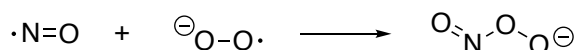


Figure 18.17. Formation of peroxynitrite from NO and superoxide.

While peroxynitrite is itself a closed-shell species, it can exert toxic effects by reacting with CO_2 to form the nitrosoperoxycarbonate anion (ONOOOCO_2^-), which undergoes O–O homolytic bond cleavage to yield two radicals, NO_2 and the carbonate radical anion CO_3^- (not to be confused with regular carbonate, CO_3^{2-}), both of which are harmful oxidants. Additionally, peroxynitrite can be protonated to yield peroxynitrous acid (ONOOH), a weak acid with $\text{p}K_a \approx 6.8$, which can undergo O–O homolysis to form NO_2 and the famously toxic hydroxyl radical ($\text{OH}\cdot$). These reactions are shown in Figure 18.18 on the following page.

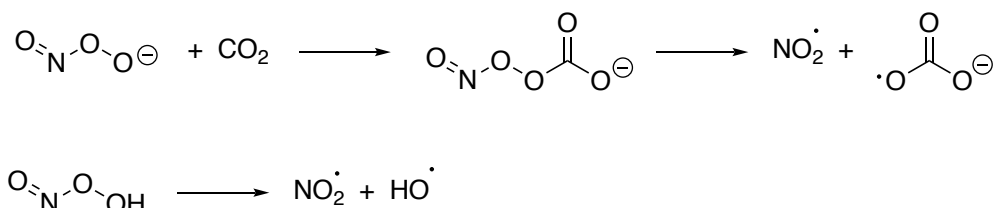


Figure 18.18. Reactions of peroxynitrite that yield toxic radical species.

18.6. Soft-Acid Metals and Toxicity

In Sections 5.9-5.11, we discussed Pearson's hard and soft acid-base (HSAB) theory for trends in Lewis acid-base reactivity, and in Section 11.11, we applied this theory to the nucleophilicity of different ligands in associative ligand substitution on Pt(II) complexes. We saw that, while nucleophilicity in organic substitution reactions often tracks fairly well with Brønsted basicity, this is not so in Pt chemistry, as softer bases prefer to bind to the soft acid Pt^{2+} , while harder bases prefer to bind to the hard acid H^+ . An additional, and very important, application of HSAB theory is to toxicology, medicinal chemistry, and environmental chemistry, concerning the relative toxicities of metal ions.

Compounds of metals are often pollutants, with toxic effects on humans and other life forms. Many metal ions with high oxidation states are toxic due to their ability to oxidize the organic molecules of life (compounds of Cr^{6+} , or "hexavalent chromium," compounds are notorious in this regard), but among those with fairly low metal oxidation states, soft acid metal compounds are generally the most toxic. For instance, Pb compounds can cause neurological problems in children, and anemia generally, Hg compounds are potent neurotoxins, Cd compounds cause the weakening of bones and are teratogens (reproductive toxins), Ti_2SO_4 was once widely used as a rat poison, and arsenic should be familiar to any reader of murder mysteries (in Renaissance France, As_4O_6 was known as *poudre de succession*, or "inheritance powder"). There are exceptions to this trend: for instance, Ag^+ and Au^+ are very soft acids, but their salts are not very toxic. Nevertheless, the trend does suggest that it is worth being especially cautious when handling soft-acid metal compounds in the laboratory.

While there are many mechanisms by which a given chemical may be toxic to life, the most common way in which soft-acid metals are poisonous is their coordination to sulfur-containing groups on proteins. Recall that the amino acid cysteine has the side chain $-\text{CH}_2\text{SH}$, and methionine has the side chain $-\text{CH}_2\text{CH}_2\text{SCH}_3$. The sulfur atoms of these amino acids are both soft bases, and will coordinate strongly to soft metal ions such as Hg^{2+} . (In fact, the older term “mercaptan” for thiols is a contraction of the Latin phrase *mercurium captans*, “capturing mercury.”) When cysteine or methionine side chains are accessible on the outsides of proteins, metal ions bind to them, which alters the proteins’ shapes and functions, almost invariably for the worse. Two cysteine side chains can be attached to each other to form the so-called cystine residue $-\text{CH}_2\text{S}-\text{SCH}_2-$, with a fairly weak S–S disulfide bond; this bond is very important to the structure of many proteins, and it can easily be broken by a soft-acid (thiophilic) metal. As an example of enzymatic disruption, the anemia caused by lead poisoning is caused by the binding of lead to cysteine residues in enzymes that synthesize heme, the prosthetic group in hemoglobin. This prevents the enzymes from functioning correctly, and a heme deficiency (anemia) results.

The HSAB principle has been exploited in medicine. During World War I, Winford Lee Lewis (1878-1943), a professor of chemistry at Northwestern University, left his academic position to develop chemical weapons for the US military. He developed the soft-acid arsenic poison dichloro(*trans*-2-chloroethenyl)arsine, a powerful vesicant (blistering agent) popularly dubbed “Lewisite.” As it happened, World War I ended before Lewisite could be used on the battlefield, and it has fortunately never actually been used in combat. However, fear that it would be used by the Nazis in World War II spurred the development, at Oxford University, of an antidote to Lewisite poisoning, the soft sulfur base 2,3-dimercaptopropanol or dimercaprol, sometimes known as “British anti-Lewisite,” or BAL. The structures of Lewisite and dimercaprol are shown in Figure 18.19 on the following page.

While Lewisite was never used on the battlefield, its antidote dimercaprol has been used as an effective antidote to many non-military cases of heavy metal poisoning. In particular, it allowed sufferers of Wilson’s disease, a genetic disorder in which the body accumulates copper, to live normal lives (although it has been replaced for this purpose by later

medications with milder side effects). Lewis, the chemical-weapons designer, ended up making a significantly net *positive* contribution to human well-being, though perhaps not to his credit.

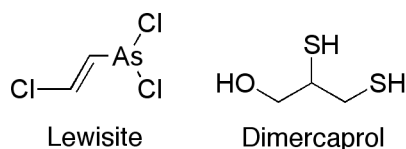


Figure 18.18. The structures of Lewisite and dimercaprol.

The toxicity of arsenic may also help explain an interesting feature of classical mythology. In general, the ancient Greeks and Romans portrayed their deities as, essentially, like human beings in perfect physical health. A notable *exception* to this is the god of fire and metalworking, known as Hephaestus (Ἥφαιστος) to the Greeks and Vulcan (Vulcanus or Volcanus) to the Romans. Unlike his Olympian peers, Hephaestus was consistently portrayed as walking with a limp. While a sure knowledge of why he was so portrayed must remain lost to the mists of antiquity, some chemists, physicians, and archaeologists have speculated that Hephaestus' limp may have its roots in an early example of an occupational illness.

Humans realized early on that pure copper metal was too soft for many uses in tools and weapons, but that alloys of copper with other metals are harder and stronger. Traditionally, the term “bronze” has been used to refer to alloys of copper with tin, while alloys of copper with zinc are called “brass.” However, since copper was alloyed with a wide variety of other elements in antiquity, archaeologists now often use the term “bronze” more generally, to describe any alloy whose main component is copper. The nature of the alloys can be specified in more detail as “tin bronze,” “zinc bronze,” “arsenic bronze,” *etc.*

As it happens, mines yielding tin are fairly rare in the area around the Mediterranean,¹²² copper was commonly alloyed with arsenic to yield objects of arsenic bronze. Once present

¹²² Tin was primarily acquired and sold by the Phoenicians, a seafaring people living in the coastal areas of what is now Lebanon and Syria (and whose alphabet was adapted into our

in an alloy, the arsenic will not leach out readily: arsenic poisoning would be the least of the concerns of a warrior wounded by an arsenic bronze sword or spear. The preparation of these alloys, however, entailed considerable risk for blacksmiths. At the temperatures used to cast metal objects in a forge, arsenic will react with O_2 in the air to form the oxide As_4O_6 , which, at forge temperatures, will be sufficiently volatile to be harmful to human health. In particular, chronic arsenic exposure by inhalation can cause peripheral neuropathy, in some cases leading to a limp. As Hephaestus was the patron god of blacksmiths, his limp may reflect a common malady among his worshippers.

18.7. Platinum-Based Anticancer Drugs

One of the biggest “inorganic” success stories in medicine is the use of cisplatin, *cis*- $Pt(NH_3)_2Cl_2$, as an anticancer drug. It is effective as a chemotherapeutic agent against many cancers, and especially against testicular cancer; the use of cisplatin increased the testicular cancer cure rate from about 10% to over 85%. Since the discovery of cisplatin, several other Pt-based anticancer drugs have been developed, some of whose structures are shown in Figure 18.19 on the following page.¹²³

The synthesis and structure of cisplatin were known by the end of the 1800s; recall that Pt(II) coordination chemistry was thoroughly studied early on in the history of transition metal chemistry. Knowledge of its medicinal use came later, and it is a good example of serendipity in science. In 1965, the biophysicist Barnett Rosenberg (1926-2009) of Michigan State University was studying the effects of electric fields on the cell division of the bacterium *Escherichia coli*, and he found that the electric field apparently had a cytostatic effect: it stopped the *E. coli* from dividing. Further research, however, indicated that the cytostatic effect was due to chemicals produced during the experiments, rather than due to the electric

own, by way of Greek and Etruscan intermediaries). Some Phoenicians may have sailed west through the Strait of Gibraltar to reach what is now northwestern France and southern England, where tin-bearing mines are plentiful.

¹²³ Note that all of these drugs are Pt(II) complexes *except* satraplatin, which is a Pt(IV) species. It is generally believed that satraplatin is actually a prodrug: it is reduced in the body to a Pt(II) species which has the cytostatic effect.

field directly. Rosenberg used Pt electrodes in his experiments, since elemental Pt was widely held to be chemically inert. It is true that, under many conditions, elemental Pt is oxidized less readily than most transition metals. In Rosenberg's experiments, however, passage of an electric current *via* the Pt electrode into the buffer solution used, which contained NH_4Cl , resulted in the oxidation of Pt atoms at the electrode surface to form soluble Pt compounds, including cisplatin. Later tests using independently prepared cisplatin showed that it inhibited the division of both bacteria and animal tumor cells, and cisplatin received FDA approval in 1978 for the treatment of testicular and ovarian cancers.

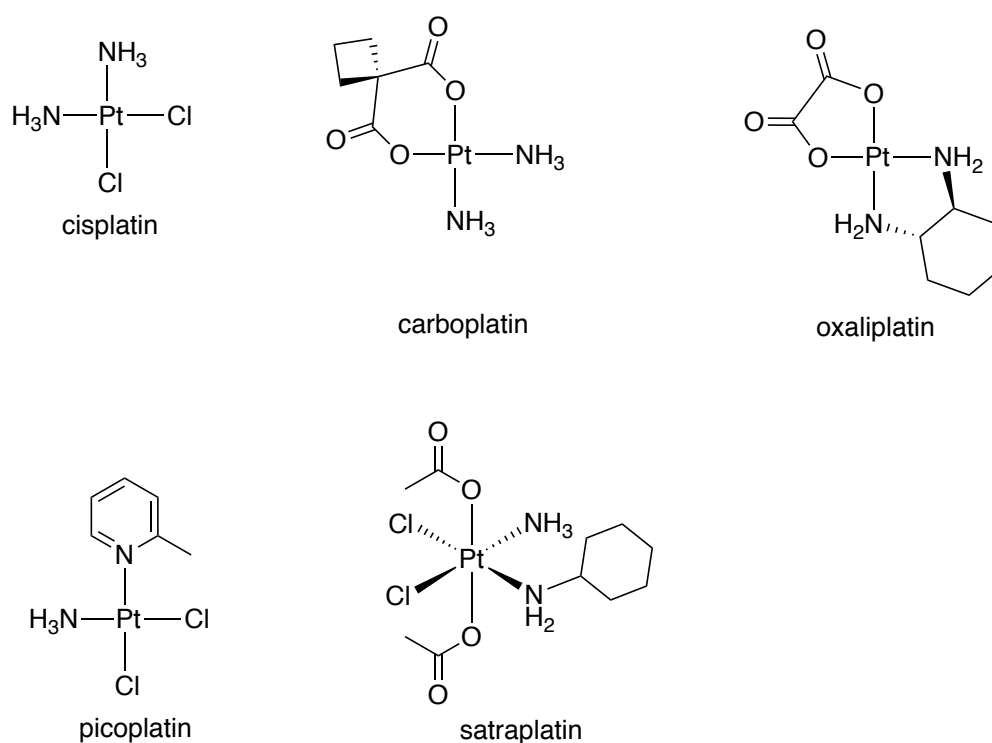
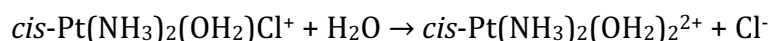
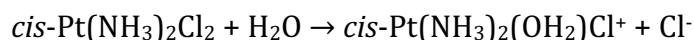


Figure 18.19. Structures of some platinum-containing anticancer drugs.

Cisplatin exerts its cytostatic effect by damaging DNA enough that replication is arrested. Cisplatin is relatively water-sensitive, and when dissolved in water will form the monocationic aqua complex $\text{cis-Pt}(\text{NH}_3)_2(\text{OH}_2)\text{Cl}^+$ and the dicationic diaqua complex $\text{cis-Pt}(\text{NH}_3)_2(\text{OH}_2)_2^{2+}$ according to the following ligand substitution reactions:



The water ligands of $cis\text{-Pt}(\text{NH}_3)_2(\text{OH}_2)\text{Cl}^+$ and $cis\text{-Pt}(\text{NH}_3)_2(\text{OH}_2)_2^{2+}$ are themselves readily displaced by other N-donor ligands, in particular the N-7 position of guanine, one of the DNA bases. A second guanine N-7 may then displace the other water ligand or the Cl^- , thus cross-linking two portions of DNA. Guanine, with N-7 labeled, is shown in Figure 18.20 below.

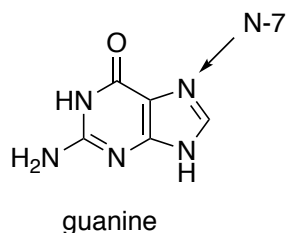


Figure 18.20. Guanine and position 7.

This cross-linking sometimes connects two strands of DNA with a Pt bridge, but the Pt more often links two guanines in the same strand of DNA, inducing a bend or “kink” in the structure. In 1996, the group of Stephen Lippard (b. 1940) at MIT solved the X-ray crystal structure of a cisplatin-bound DNA strand with such an intrastrand kink. This DNA damage can then prevent replication and induce apoptosis (programmed cell death). The aquation of cisplatin to form more reactive cationic complexes is undesirable if it occurs outside of cells. Some of the side effects of cisplatin may be due to the reaction of $cis\text{-Pt}(\text{NH}_3)_2(\text{OH}_2)\text{Cl}^+$ or $cis\text{-Pt}(\text{NH}_3)_2(\text{OH}_2)_2^{2+}$ with cysteine thiol groups of proteins: recall that Pt(II) compounds are fairly soft acids. This aquation is minimized in medical settings by the intravenous administration of cisplatin in a saline (NaCl) solution: the Cl^- in the saline inhibits aquation by Le Chatelier’s principle. This aquation is also minimized in blood, as the Cl^- concentration in blood is significantly higher than that in cells.

The mechanism of action of cisplatin is (perhaps surprisingly) fairly similar to that of a class of organic anticancer drugs called alkylating agents. Anticancer alkylating agents generally contain two good leaving groups that can be displaced (in an $\text{S}_{\text{N}}2$ reaction) by N-7 of guanine, as well as a nucleophilic atom in the molecule that enhances alkylation by the anchimeric effect. They are thus able to cross-link two guanines by an organic group, as opposed to Pt.

The investigation of alkylating agents in cancer therapy actually goes back to the use of chemical weapons in World War I. One frequently used such weapon was bis(2-chloroethyl)thioether, commonly known as “mustard gas” (actually a liquid, dispersed as an aerosol), a powerful vesicant. It was found that soldiers who had been injured by mustard gas exposure, but who survived, tended to display low white blood cell counts, which spurred efforts to use it and related compounds to treat white blood cell cancers such as lymphoma and leukemia. The related nitrogen-containing alkylating agent mustine was the first cancer chemotherapy drug to be used in humans, and the more complex cyclophosphamide is widely used today. The structures of these sulfur- and nitrogen-containing “mustard” agents are shown in Figure 18.21 below.

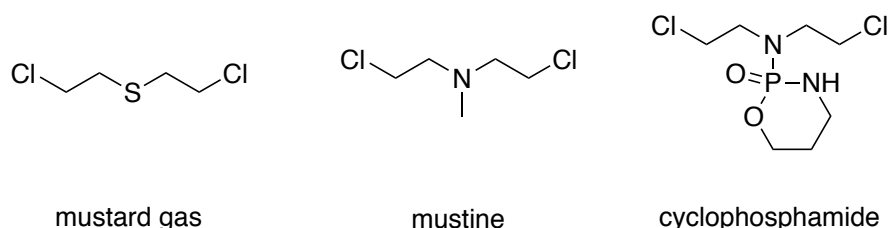


Figure 18.21. Structures of mustard-type alkylating agents.

Because of the similarity of the mechanisms of action of alkylating agents and cisplatin (cross-linking guanine bases), cisplatin and other Pt anticancer drugs are often called “non-classical alkylating agents,” although they of course have no alkyl groups to add to DNA.