1

INTRODUCTION

1.1 WHY STUDY ORGANOMETALLIC CHEMISTRY?

Organometallic chemistry grew out of an exchange between inorganic and organic chemistry. By associating a metal center and an organic fragment into a single molecule, the properties of both components proved to be profoundly modified. The first examples were found for the main-group elements from the *s* and *p* blocks of the periodic table (groups 1–2 and 13–18). In particular, organolithium, -magnesium, -zinc, and -aluminum compounds have had a revolutionary impact in organic chemistry by providing stabilized but still highly reactive carbanions able to act as nucleophiles or strong bases. These reagents were incorporated into the standard toolbox of organic chemistry during the twentieth century and are covered in organic chemistry courses.

A later development, transition metal organometallic chemistry, has had a different type of impact on organic chemistry. Main-group organometallics are normally stoichiometric reagents, but transition metal organometallics are typically catalysts. This has several advantages. These catalysts not only enhance selectivity for known reactions, but they also open up entirely novel synthetic pathways that can be applied to complex molecule synthesis. Catalysts are only needed in small quantity—often at a 1 mol% level relative to the reactants, but sometimes even at 1 part per million. They avoid the waste formation associated with main-group reagents and thus contribute to green chemistry.

The Organometallic Chemistry of the Transition Metals, *Fifth Edition,* by Robert H. Crabtree

An industrial application of transition metal organometallic chemistry appeared as early as the 1880s, when Ludwig Mond showed how nickel can be purified by using CO to pick up nickel in the form of gaseous $Ni(CO)_4$ that can easily be separated from solid impurities and later be thermally decomposed to give pure nickel. An early catalytic application, the use of $Co_2(CO)_8$ in hydroformylation catalysis, appeared in the 1930s, a period when much research was empirical and mechanistic understanding was limited. More recently, a whole series of industrial processes has been developed based on transition metal organometallic catalysts. Leading examples include polymerization of alkenes to give polyethylene and polypropylene, hydrocyanation of butadiene for nylon manufacture, acetic acid manufacture from MeOH and CO, and hydrosilylation for silicone materials. An important aspect of such reactions is atom economy. Direct conversion of MeOH and CO to MeCOOH, for example, leads to incorporation of all the reactant atoms into products and thus occurs with a theoretical atom economy of 100%.

Inorganic chemistry has been influenced by organometallic chemistry in several ways. Materials synthesis (e.g., of thin films or nanoparticles) often starts from organometallic precursors. Soon to be commercialized for cell phone display panels are light-emitting diodes containing luminescent organometallic compounds.

Bioinorganic chemistry has traditionally been concerned with coordination chemistry—considered as the chemistry of metal ions surrounded by N- or O-donor ligands such as imidazole or acetate—because metalloenzymes typically bind metals via such N or O donors. Recent work has shown the existence of a growing class of metalloenzymes having organometallic ligand environments—considered as the chemistry of metal ions having C-donor ligands such as CO or the methyl group. Medicinally useful organometallics are also emerging either as drugs or imaging agents.

Alternative energy research will also benefit from organometallic catalysts, particularly with climate change forcing a redoubled emphasis on this vital area.

1.2 COORDINATION CHEMISTRY

Even in organometallic compounds, N- or O-donor coligands are very often present. Indeed, the distinction between coordination and organometallic chemistry is becoming blurred with the increasing level of cross fertilization that we now see.

The fundamentals of metal–ligand bonding were first established for coordination compounds. Some key points of coordination chemistry are therefore established in this chapter using the work of the founder of the field, Alfred Werner.

Central to our understanding both of coordination and organometallic compounds are *d* electrons. Main-group compounds either have no *d* electrons (e.g., Li) or a filled *d* level that is too stable to participate significantly in bonding (e.g., Si). Transition metals (groups 3–12) often have partially filled *d* orbitais, a situation that imparts their characteristic properties. Some metal ions have no *d* electrons (e.g., Ti^{4+}) or a filled set of 10 (e.g., Zn^{2+}) and these more closely resemble main-group elements.

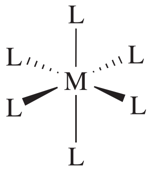
Transition metal ions can bind *ligands* (L) to give a coordination compound, or *complex* ML_n, as in the familiar aqua ions $[M(OH_2)_6]^{2+}$ (M=V, Cr, Mn, Fe, Co, or Ni). Organometallic chemistry is a subfield of coordination chemistry in which the complex contains an M—C or M—H bond [e.g., $Mo(CO)_6$]. Organometallic species tend to be more covalent, and the metal is often more reduced, than in other coordination compounds. Typical ligands that usually bind to metals in their lower oxidation states are CO, alkenes, and arenes, for example, $Mo(CO)_6$, $(C_6H_6)Cr(CO)_3$, or $Pt(C_2H_4)_3$.

1.3 WERNER COMPLEXES

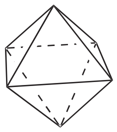
Complexes in which the metal binds to noncarbon ligands have been known longest and are often called *classical* or *Werner complexes* such as $[Co(NH_3)_6]^{3+}$. The simplest metal–ligand bond is perhaps $L_nM—NH_3$, where an ammonia binds to a metal fragment. This fragment will usually also have other ligands, represented here by L_n. The bond consists of the lone pair of electrons present in free NH_3 that is donated to the metal to form the complex. The metal is a polyvalent Lewis acid capable of accepting the lone pairs of several ligands L, which act as Lewis bases.

Stereochemistry

The most common type of complex is ML_6, which adopts an octahedral coordination geometry (**1.1**) based on one of the Pythagorean regular solids. The ligands occupy the six vertices of the octahedron, which allows them to minimize their M—L bonding distances, while maximizing their L . . . L nonbonding distances. For the coordination chemist, it is unfortunate that Pythagoras decided to name his solids after the number of faces (*octa* = eight) rather than the number of vertices. After ML_6, ML_4, and ML_5 are the next most common types. The solid and dashed wedges in **1.1** indicate bonds located in front of and behind the plane of the paper, respectively.



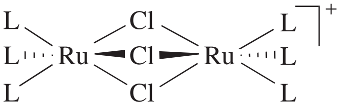
1.1



Octahedron

The assembly of metal and ligands that we call a *complex* may have a net ionic charge, in which case it is a complex ion (e.g., $[PtCl_4]^{2-}$). Together with the counterions, we have a complex salt (e.g., $K_2[PtCl_4]$). In some cases both the cation and the anion may be complex, as in the picturesquely named *Magnus' green salt* $[Pt(NH_3)_4][PtCl_4]$. Square brackets enclose the individual complex molecules or ions where necessary to avoid ambiguity.

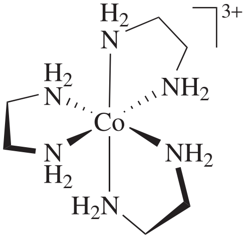
Those ligands that have a donor atom with more than one lone pair can donate one lone pair to each of two or more metal ions. This gives rise to polynuclear complexes, such as the orange crystalline compound **1.2** (L = PR_3). The bridging group is represented by the Greek letter μ (pronounced "mu") as in $[Ru_2(\mu\text{-}Cl)_3(PR_3)_6]^+$. Thus, **1.2** can be considered as two octahedral fragments sharing the face that contains the three chloride bridges.



1.2

Chelate Effect

Ligands with more than one donor atom, such as ethylenediamine ($NH_2CH_2CH_2NH_2$, often abbreviated "en") can donate both lone pairs to the same metal to give a ring compound, known as a *chelate*, from the Greek word for "claw" (**1.3**). Chelate ligands may be bidentate, such as ethylenediamine, or polydentate, such as **1.4** and **1.5**. The most favorable chelate ring size is 5 or 6 atoms.



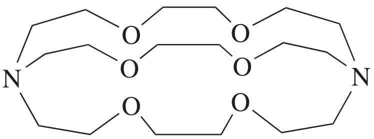
1.3

The early Russian investigator Chugaev first drew attention to the fact that chelating ligands are much less easily displaced from a complex than are monodentate ligands of the same type. The reason is illustrated in Eq. 1.1:

$$[M(NH_3)_6]^{n+} + 3en \rightarrow [M(en)_3]^{n+} + 6NH_3 \tag{1.1}$$

Formation of the tris chelate releases six NH_3 molecules so that the total number of particles increases from four to seven. This creates entropy and so favors the chelate form. Each chelate ring usually leads to an additional factor of about 10^5 in the equilibrium constant for reactions such as Eq. 1.1. Equilibrium constants for complex formation are usually called *formation constants*; the higher the value, the more stable the complex.

Chelation not only makes the complex more stable but also forces the donor atoms to take up adjacent or cis sites in the resulting complex. Polydentate chelating ligands with three or more donor atoms also exist. Macrocyclic ligands, such as **1.4** and **1.5** confer an additional increment in the formation constant (the macrocyclic effect); they tend to be given rather lugubrious trivial names, such as *cryptates* (**1.4**) and *sepulchrates* (**1.5**).[1]



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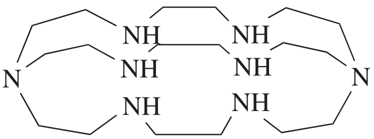
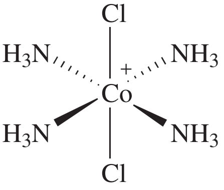


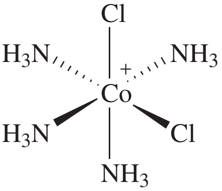
1.5

Werner Complexes

Alfred Werner developed the modern picture of coordination complexes in the 20 years that followed 1893, when, as a young scientist, he proposed that in the well-known cobalt ammines (ammonia complexes) the metal ion is surrounded by six ligands in an octahedral array as in **1.6** and **1.7**:

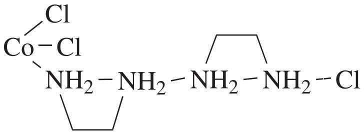


1.6



1.7

In doing so, he was opposing all the major figures in the field, who held that the ligands were bound to one another in chains, and that only the ends of the chains were bound to the metal as in **1.8** and **1.9**. Jørgensen, who led the traditionalists against the Werner insurgency, was not willing to accept that a trivalent metal, Co^{3+}, could form bonds to six groups; in the chain theory, there were never more than three bonds to Co. Each time Werner came up with what he believed to be proof for his theory, Jørgensen would find a way of interpreting the chain theory to fit the new facts. For example, coordination theory predicts that there should be two isomers of $[Co(NH_3)_4Cl_2]^+$ (**1.6** and **1.7**). Up to that time, only a green one had ever been found. We now call this the *trans isomer* (**1.6**) because the two Cl ligands occupy opposite vertices of the octahedron. According to Werner's theory, there should also have been a second isomer, **1.7** (cis), in which the Cl ligands occupy adjacent vertices. Changing the anionic ligand, Werner was able to obtain both green cis and purple trans isomers of the nitrite complex $[Co(NH_3)_4(NO_2)_2]^+$. Jørgensen quite reasonably (but wrongly) countered this finding by arguing that the nitrite ligands in the two isomers were simply bound in a different way (*linkage isomers*), via N in one case (Co—NO_2) and O (Co—ONO) in the other. Werner then showed that there were two isomers of $[Co(en)_2Cl_2]^+$, one green and one purple, in a case where no linkage isomerism was possible. Jørgensen brushed this observation aside by invoking the two chain isomers **1.8** and **1.9** in which the topology of the chains differ.



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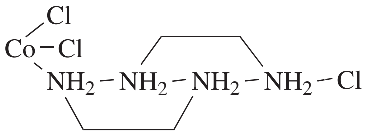
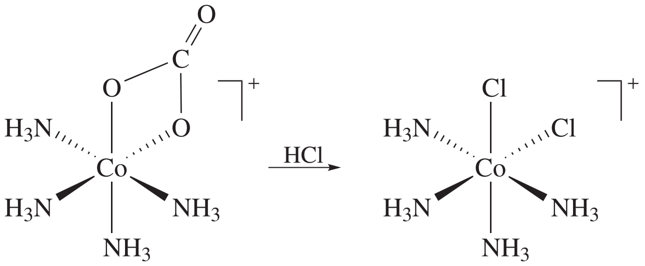


1.9

In 1907, Werner finally succeeded in making the elusive purple isomer of $[Co(NH_3)_4Cl_2]^+$ by an ingenious route (Eq. 1.2) via the carbonate $[Co(NH_3)_4(O_2CO)]$ in which two oxygens of the chelating dianion are necessarily cis. Treatment with HCl at 0 °C liberates CO_2 and gives the cis dichloride. Jørgensen, receiving a sample of this purple cis complex by mail, conceded defeat.



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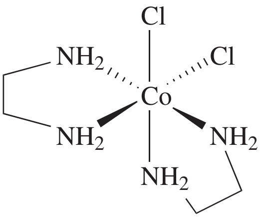
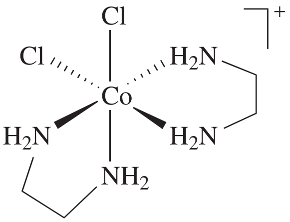
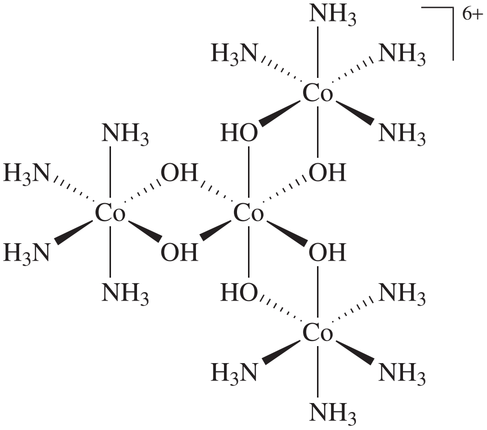




1.10 **1.11**

Finally, Werner resolved optical isomers of the general type $[Co(en)_2X_2]^{2+}$ (**1.10** and **1.11**). Only an octahedral array can account for the optical isomerism of these complexes. Even this point was challenged by critics on the grounds that only organic compounds can be optically active, and so the optical activity must reside in the organic ligands. Werner responded by resolving a complex (**1.12**) containing only inorganic elements. This species has the extraordinarily high specific rotation of 36,000 ° and required 1000 recrystallizations to resolve. Werner won the chemistry Nobel Prize for this work in 1913.



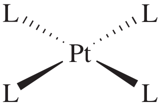
1.12

1.4 THE TRANS EFFECT

We now move from complexes of tripositive cobalt, often termed "Co(III) compounds," where the III refers to the +3 oxidation state (Section 2.4) of the central metal, to the case of Pt(II). In the 1920s, Chernaev discovered that certain ligands, L^t, facilitate the departure of a second ligand, L, trans to the first, and their replacement or *substitution*, by an external ligand. Ligands, L^t, that are more effective at this labilization are said to have a higher *trans effect*. We consider in detail how this happens in Sections 4.3–4.4; for the moment we need only note that the effect is most clearly marked in substitution in Pt(II), and that the highest trans effect ligands form either unusually strong σ bonds, such as $L^t = H^-$, Me^-, or $SnCl_3^-$, or unusually strong π bonds, such as $L^t = CO$, C_2H_4, and thiourea, $[(NH_2)_2CS$, a ligand often represented as "tu"].

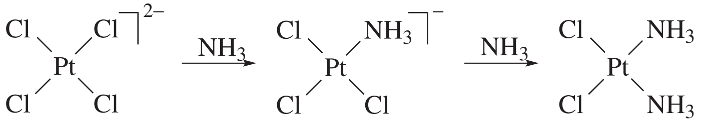
The same ligands also weaken the trans M—L bonds, as shown by a lengthening of the M—L distances found by X-ray crystallography or by some spectroscopic measure, such as M,L coupling in nuclear magnetic resonance (NMR) spectroscopy (Section 10.4), or the ν(M—L) stretching frequency in the IR (infrared) spectrum (Section 10.9). A change in the ground-state thermodynamic properties, such as these, is usually termed the *trans influence* to distinguish it from the true trans effect for the substitution reaction, which refers to differences in *rates* of substitution and is therefore a result of a decrease in the energy difference between the ground state and transition state for the substitution as the trans effect of L^t increases.

Pt(II) adopts a coordination geometry different from that of Co(III). The ligands in these Pt complexes lie at the corners of a square with the metal at the center. This is called the *square planar geometry* (**1.13**).



1.13

An important application of the trans effect is the synthesis of specific isomers of coordination compounds. Equations 1.3 and 1.4 show how the cis and trans isomers of $Pt(NH_3)_2Cl_2$ can be prepared selectively by taking advantage of the trans effect order $Cl > NH_3$, where $L^t = Cl$. This example is also of practical interest because the cis isomer is an important antitumor drug, but the trans isomer is ineffective. In each case the first step of the substitution can give only one isomer. In Eq. 1.3, the cis isomer is formed in the second step because the Cl trans to Cl is more labile than the Cl trans to the lower trans effect ligand, ammonia. On the other hand, in Eq. 1.4, the first Cl to substitute labilizes the ammonia trans to itself to give the trans dichloride as final product.



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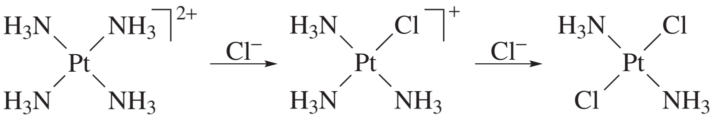


(1.4)

A trans effect series for a typical Pt(II) system is given below. The order can change somewhat for different metals and oxidation states.

$$OH^- < NH_3 < Cl^- < Br^- < CN^-, CO, C_2H_4, CH_3^- < I^- < PR_3 < H^-$$

← low trans effect high trans effect →

1.5 SOFT VERSUS HARD LIGANDS

The nature and number of ligands are key in altering the electronic and steric environment of the metal and thus the reactivity of the complex. A chelate ligand can reliably introduce a specific arrangement of specific donor atoms;

TABLE 1.1 Hard and Soft Acids and Bases: Some Formation Constants[a]

	Ligand (Base)			
Metal Ion (Acid)	F^- (Hard)	Cl^-	Br^-	I^- (Soft)
H^+ (hard)	3	−7	−9	−9.5
Zn^{2+}	0.7	−0.2	−0.6	−1.3
Cu^{2+}	1.2	0.05	−0.03	—
Hg^{2+} (soft)	1.03	6.74	8.94	12.87

[a] The values are the negative logarithms of the equilibrium constant for $[M.aq]^{n+} + X^- \leftrightharpoons [MX.aq]^{(n-1)+}$ and show how H^+ and Zn^{2+} are hard acids, forming stronger complexes with F^- than with Cl^-, Br^-, or I^-. Cu^{2+} is a borderline case, and Hg^{2+} is a very soft acid, forming much stronger complexes with the more polarizable halide ions.

$H_2NCH_2CH_2NH_2$, for example, introduces two cis nitrogens. Ligands are said to be *hard* or *soft* depending on their propensity for ionic or covalent bonding, respectively. Likewise metals can be hard or soft. The favored, well-matched combinations are a hard ligand with a hard metal and a soft ligand with a soft metal; hard–soft combinations are disfavored.

Table 1.1 shows formation constants for different metal ion (acid)–halide ligand (base) combinations,[2] where large positive numbers mean strong binding. The series of halide ions starts with F^-, hard because it is small, difficult to polarize, and forms predominantly ionic bonds. It binds best to a hard cation, H^+, also small and difficult to polarize. This hard–hard combination is therefore a good one and HF is a weak acid.

The halide series ends with I^-, soft because it is large, easy to polarize, and forms predominantly covalent bonds. It binds best to a soft cation, Hg^{2+}, also large and easy to polarize. In this context, high polarizability means that electrons from each partner readily engage in covalent bonding. The Hg^{2+}/I^- soft–soft combination is therefore a very good one—by far the best in the table—and dominated by covalent bonding.

Soft bases have lone pairs on atoms of the second or later row of the periodic table (e.g., Cl^-, Br^-, PPh_3) or have double or triple bonds (e.g., CN^-, C_2H_4, benzene). Soft acids can also come from the second or later row of the periodic table (e.g., Hg^{2+}) or contain atoms that are relatively electropositive (e.g., BH_3) or are metals in a low (≤2) oxidation state [e.g., Ni(0), Re(I), Pt(II), Ti(II)]. An important part of organometallic chemistry is dominated by soft–soft interactions (e.g., metal carbonyl, alkene, and arene chemistry).

1.6 THE CRYSTAL FIELD

An important advance in understanding the spectra, structure, and magnetism of transition metal complexes is provided by the *crystal field theory* (CFT). The idea is to find out how the *d* orbitals of the transition metal are affected

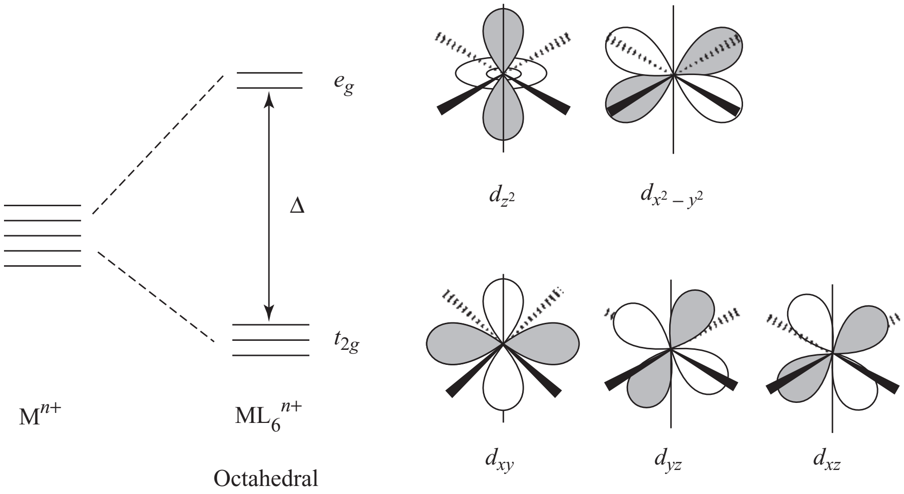


FIGURE 1.1 Effect on the *d* orbitals of bringing up six ligands along the ±*x*, ±*y*, and ±*z* directions. In this figure, shading represents the symmetry (not the occupation) of the *d* orbitals; shaded parts have the same sign of ψ. For convenience, energies are shown negative to the average *d*-orbital energy.

by the presence of the ligands. To do this, we make the simplest possible assumption about the ligands—that they act as negative charges. For Cl^- as a ligand, we just think of the net negative charge on the ion; for NH_3, we think of the lone pair on nitrogen acting as a local concentration of negative charge. If we imagine the metal ion isolated in space, then the *d* orbitals are *degenerate* (have the same energy). As the ligands L approach the metal from the six octahedral directions ±*x*, ±*y*, and ±*z*, the *d* orbitals take the form shown in Fig. 1.1. Those *d* orbitals that point toward the L groups ($d_{x^2-y^2}$ and d_{z^2}) are destabilized by the negative charge of the ligands and move to higher energy. Those that point away from L (d_{xy}, d_{yz}, and d_{xz}) are less destabilized.

The pair of orbitals that are most strongly destabilized are often identified by their symmetry label, e_g, or simply as d_σ, because they point along the M—L σ-bonding directions. The three more stable orbitals have the label t_{2g}, or simply d_π; these point away from the ligand directions but can form π bonds with the ligands. The magnitude of the energy difference between the d_σ and d_π set, usually called the *crystal field splitting*, and labeled Δ (or sometimes 10*Dq*) depends on the value of the effective negative charge and therefore on the nature of the ligands. Higher Δ leads to stronger M—L bonds.

High Spin versus Low Spin

Cobalt, in group 9 of the periodic table, has the electron configuration $[Ar]4s^23d^7$ in the free atom, with nine valence electrons. Once the atom forms a complex, however, the *d* orbitals become more stable than the *s* as a result of metal–ligand bonding, and the electron configuration becomes [Ar]$4s^0 3d^9$ for the case of a Co(0) complex, or [Ar]$3s^0 4d^6$ for Co(III), usually shortened to d^9 and d^6, respectively. This crystal field picture explains why Co^{3+}, the metal ion Werner studied, has such a strong preference for the octahedral geometry. With its d^6 configuration, six electrons just fill the three low-lying d_π orbitals of the octahedral crystal field diagram and leave the d_σ empty. This is a particularly stable arrangement, and other d^6 metals, Mo(0), Re(I), Fe(II), Ir(III), and Pt(IV) also show a very strong preference for the octahedral geometry. Indeed, low spin d^6 is by far the commonest type of metal complex in organometallic chemistry. In spite of the high tendency to spin-pair the electrons in the d^6 configuration (to give the *low-spin* form $t_{2g^6} e_{g^0}$), if the ligand field splitting is small enough, then the electrons may occasionally rearrange to give the *high-spin* form $t_{2g^4} e_{g^2}$. In the high-spin form all the unpaired spins are aligned, as prescribed for the free ion by Hund's rule. This is shown in Fig. 1.2. The factor that favors the high-spin form is the fact that fewer electrons are paired up in the same orbitals and so the electron–electron repulsions are reduced. On the other hand, if Δ becomes large enough, then the energy gained by dropping from the e_g to the t_{2g} level will be sufficient to drive the electrons into pairing up. The spin state of the complex can usually be determined by measuring the magnetic moment. This is done by weighing a sample of the complex in a magnetic field gradient. In the low-spin form of a d^6 ion, the molecule is *diamagnetic*, that is, it is very weakly repelled by the field. This behavior is exactly the same as that found for the vast majority of organic compounds, which are also spin paired. On the other hand, the high-spin form is *paramagnetic*, in which case it is attracted into the field because there are unpaired electrons. The complex does not itself form a permanent magnet as does a piece of iron or nickel (this is *ferromagnetism*) because the spins are not aligned in the crystal in the absence of an external field, but they do respond to the external field by lining up together when we measure the magnetic moment.

Although the great majority of organometallic complexes are diamagnetic, because Δ is usually large in these complexes, we should not lose sight of the

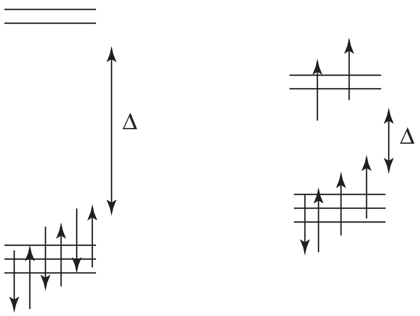


FIGURE 1.2 In a d^6 metal ion, both low- and high-spin complexes are possible depending on the value of Δ. A high Δ leads to the low-spin form (*left*).

possibility that any given complex or reaction intermediate may be paramagnetic. This will always be the case for molecules such as d^5 $V(CO)_6$, which have an uneven number of electrons. For molecules with an even number of electrons, a high-spin configuration is more likely for the first row metals, where Δ tends to be smaller than in the later rows. Sometimes the low- and high-spin isomers have almost exactly the same energy. Each state can now be populated, and the relative populations of the two states vary with temperature; this happens for $Fe(dpe)_2Cl_2$, for example.

Inert versus Labile Coordination

In an octahedral d^7 ion we are obliged to place one electron in the higher energy (less stable) d_σ level to give the low-spin configuration $t_{2g^6}e_{g^1}$, to make the complex paramagnetic (Fig. 1.3). The net stabilization, the *crystal field stabilization energy* (CFSE) of such a system will also be less than for d^6 (low spin), where we can put all the electrons into the more stable t_{2g} level. This is reflected in the chemistry of octahedral d^7 ions [e.g., Co(II)], which are more reactive than their d^6 analogs. For example, they undergo ligand dissociation much more readily. The reason is that the d_σ levels are M—L σ-antibonding in character (Section 1.5). Werner studied Co(III) because the ligands tend to stay put. This is why Co(III) and other low-spin d^6 ions are often referred to as *coordinatively inert*; d^3 ions such as Cr(III) are also coordination inert because the t_{2g} level is now exactly half-filled, another favorable situation. On the other hand, Co(II) and other non-d^6 and -d^3 ions are considered *coordinatively labile*. The second- and third-row transition metals form much more inert complexes because of their higher Δ and CFSE.

Jahn–Teller Distortion

Closely linked to the lability of d^7 low spin and other coordination labile ions is an associated geometrical change. This Jahn–Teller distortion occurs when-

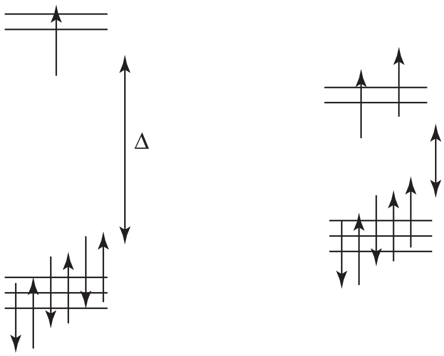


FIGURE 1.3 A d^7 octahedral ion is paramagnetic in both the low-spin (*left*) and high-spin (*right*) forms.

ever a set of orbitals of the same energy, or degenerate orbitals, are unequally occupied. For a pair of degenerate orbitals, this would occur for occupation either by 1e or 3e (e for electron). Such is the case for d^7 low spin where only one of the e_g orbitals is half filled (Fig. 1.4). A pair of trans ligands along one axis—we can call this the z axis—either shows an elongation or a contraction of the M–L distances relative to those in the xy plane, depending on whether the d_{z^2} or $d_{x^2-y^2}$ orbital is half-occupied. On crystal field ideas, the electron in the half-filled d_{z^2} orbital repels the ligand lone pairs that lie on the z axis,

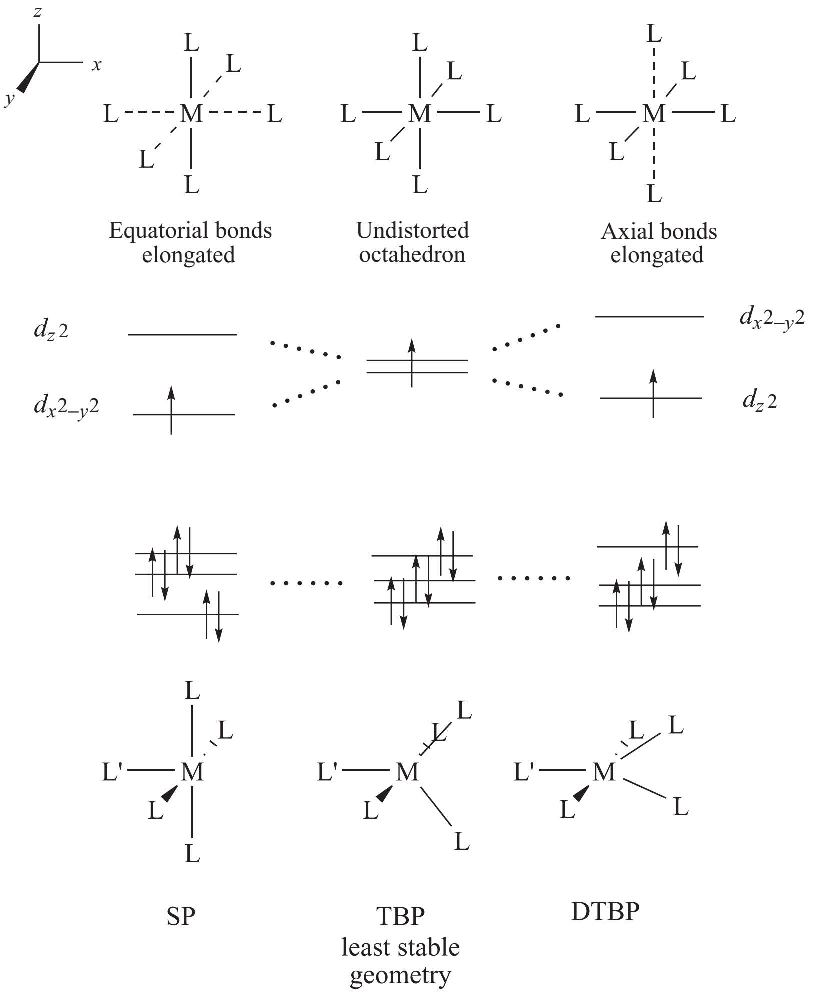


FIGURE 1.4 Jahn–Teller distortions in the d^7 low-spin case. Uneven occupation of the d_σ orbitals leads to a distortion in which either the xy ML_4 ligand set (left) or the z ML_2 ligand set (right) shows an M–L elongation because of electron–electron repulsions. Minor splitting also occurs in the d_π set.

making these M—L bonds longer. Alternatively, if the $d_{x^2-y^2}$ orbital is half occupied, the M—L bonds in the xy plane are longer. This distortion helps ligand dissociation because two or more of the M—L distances are already elongated and weakened relative to the d^6 low-spin comparison case. A Jahn–Teller distortion also occurs if the t_{2g} set of three orbitals are unevenly occupied, as in d^6 high spin (Fig. 1.2 right), but the distortion effects are now smaller because these orbitals do not point directly at the ligands.

Low- versus High-Field Ligands

The colors of transition metal ions often arise from the absorption of light that corresponds to the d_π–d_σ energy gap, Δ. The spectrum of the complex can then give a direct measure of this gap and therefore of the crystal field strength of the ligands. So-called *high-field ligands* such as CO and C_2H_4 give rise to a large value of Δ. *Low-field ligands*, such as H_2O or NH_3, can give such a low Δ that the spin pairing is lost and even the d^6 configuration can become paramagnetic (Fig. 1.2, right side).

The *spectrochemical series* of ligands, which lists the common ligands in order of increasing Δ, allows us to see the general trend that π-donor ligands such as halide or H_2O tend to be weak-field and π-acceptor ligands such as CO tend to be strong-field ligands as discussed in Section 1.6. These π effects are not the whole story, however, because H, which has no π-donor or acceptor properties at all, is nevertheless a very strong-field ligand, because of the very strong M—H σ bonds.

$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < PPh_3 < CO, H < SnCl_3^-$$

$\leftarrow$ low Δ high Δ $\rightarrow$

$\leftarrow$ π donor/weak σ donor π acceptor/strong σ donor $\rightarrow$

Hydrides and carbonyls therefore have very strong M—L bonds (L = H, CO) and have a very strong tendency to give diamagnetic complexes. High-field ligands, such as high-trans-effect ligands, tend to form strong σ and/or π bonds, but the precise order is significantly different in the two series.

Odd versus Even d^n Configurations

If a molecule has an odd number of electrons, not all of them can be paired up. An odd d^n configuration, such as d^7 (e.g., $[Re(CO)_3(PCy_3)_2]$), therefore guarantees paramagnetism if we are dealing with a mononuclear complex—one containing only a single metal atom. In dinuclear complexes, the odd electrons on each metal may pair up, however, as in the diamagnetic d^7–d^7 dimer, $[(OC)_5Re–Re(CO)_5]$. Complexes with an even d^n configuration can be

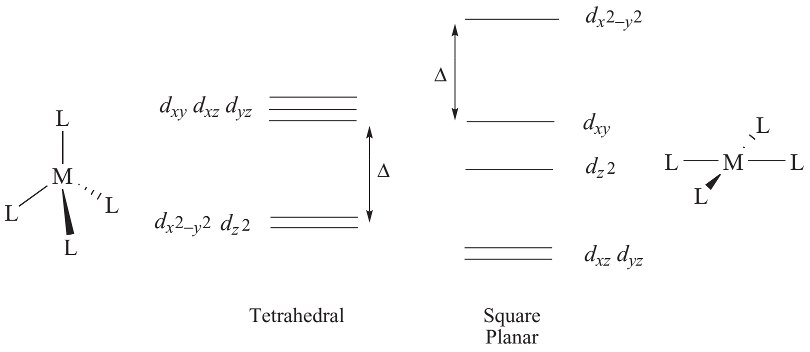


FIGURE 1.5 Crystal field splitting patterns for the common 4-coordinate geometries: tetrahedral and square planar. For the square planar arrangement, the z axis is conventionally taken to be perpendicular to the square plane.

diamagnetic or paramagnetic depending on whether they are high or low spin, but low-spin diamagnetic complexes are much more common in organometallic chemistry because the most commonly encountered ligands are high field.

Other Geometries

After the octahedral case, two types of four coordination are the next most common—tetrahedral and square planar. Tetrahedral is seen for d^0, d^5 (h.s.) and d^{10} cases [e.g., Ti(IV), Mn(II), and Pt(0)] where symmetrical occupation of all the d orbitals occurs, each with zero, one, or two electrons. In such cases, ligand field effects no longer apply and a tetrahedral geometry is adopted from steric considerations. The orbital pattern—three up, two down (Fig. 1.5 left)—is the opposite of that for octahedral geometry and the splitting is smaller. Tetrahedral is also seen for d^4 (low spin) [e.g., Re(III)] where occupation only of the low-lying orbitals can occur.

The important square planar geometry has a more complex splitting pattern (Fig. 1.5 right) that is derived from an octahedron by completely removing the pair of ligands along the z axis. This is equivalent to pushing the distortion shown in Fig. 1.4 (right) to an extreme. The largest splitting, labeled Δ in Fig. 1.5, separates the two highest energy orbitals. The square planar geometry is therefore most often seen for d^8 (low spin), where the highest energy orbital remains unoccupied [e.g., Pd(II)]. It is also common for paramagnetic d^9 [e.g., Cu(II)].

For a given geometry and ligand set, metal ions can have very different values of Δ. For example, first-row metals and metals in a low oxidation state tend to have low Δ, while second- and third-row metals and metals in a high oxidation state tend to have high Δ. The trend is illustrated by the *spectrochemical series* of metal ions in order of increasing Δ:

$$\mathrm{Mn^{2+} < V^{2+} < Co^{2+} < Fe^{2+} < Ni^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+}} \\ \mathrm{< Rh^{3+} < Ru^{3+} < Rd^{4+} < Ir^{3+} < Pt^{4+}}$$

← low Δ high Δ →

← low valent, first row high valent, third row →

High Δ means strong M—L bonding, so third-row metals tend to form stronger M—L bonds and more thermally stable complexes and are also more likely to give diamagnetic complexes. Comparison of the same metal and ligand set in different oxidation states is complicated by the fact that low oxidation states are usually accessible only with strong-field ligands that tend to give a high Δ (see the spectrochemical series of ligands above).

Isoconfigurational Ions

The d^n ions of the same configuration (e.g., $n = 6$) show important similarities independent of the identity of the element. This means that d^6 Co(III) is closer in many properties to d^6 Fe(II) than to d^7 Co(II). The variable valency of the transition metals leads to many cases of isoconfigurational ions.

1.7 THE LIGAND FIELD

The crystal field picture gives a useful qualitative understanding, but, for a more complete picture, we turn to the more sophisticated *ligand field theory* (LFT), really a conventional molecular orbital, or MO, picture. In this model (Fig. 1.6), we consider the *s*, the three *p*, and the five *d* orbitals of the valence shell of the isolated ion as well as the six lone-pair orbitals of a set of pure σ-donor ligands in an octahedron around the metal. Six of the metal orbitals, the *s*, the three *p*, and the two d_σ, the dsp_σ set, find symmetry matches in the six ligand lone-pair orbitals. In combining the six metal orbitals with the six ligand orbitals, we make a bonding set of six (the M—L σ bonds) that are stabilized, and an antibonding set of six (the M—L σ^* levels) that are destabilized. The remaining three *d* orbitals, the d_π set, do not overlap with the ligand orbitals and remain nonbonding. In a d^6 ion, we have 6e from $\mathrm{Co^{3+}}$ and 12e from the ligands, giving 18e in all. This means that all the levels up to and including the d_π set are filled, and the M—L σ^* levels remain unfilled. Note that we can identify the familiar crystal field splitting pattern in the d_π and two of the M—L σ^* levels. The Δ splitting will increase as the strength of the M—L σ bonds increases. The bond strength is the analogue of the effective charge in the crystal field model. In the ligand field picture, high-field ligands are ones that form strong σ bonds. We can now see that the d_σ orbital of the crystal field picture becomes an M—L σ-antibonding orbital in the ligand field model.

The L lone pairs start out in free L as pure ligand electrons but become bonding electron pairs shared between L and M when the M—L σ bonds are

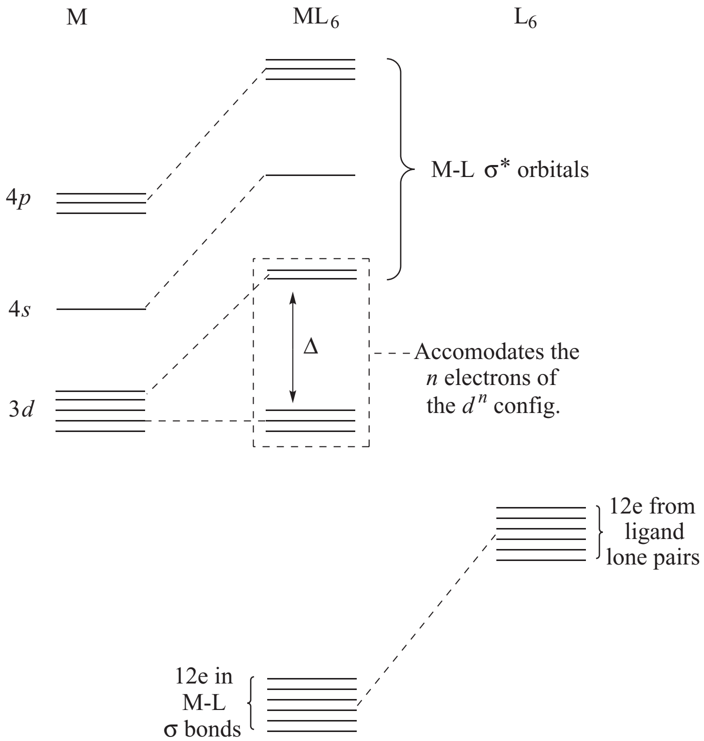


FIGURE 1.6 Molecular orbital, or ligand field picture, of metal–ligand bonding in an octahedral ML$_6$ complex. The box contains the d orbitals that are filled with n electrons to give the d^n electron configuration.

formed; these are the 6 lowest orbitals in Fig. 1.6 and are always completely filled (12 e). Each M—L σ-bonding MO is formed by the combination of the ligand lone pair, L(σ), with M(d_σ) and has both metal and ligand character, but L(σ) predominates. Any MO will more closely resemble the parent atomic orbital that lies closest in energy to it, and L(σ) almost always lies below M(d_σ) and therefore closer to the M—L σ-bonding orbitals. This means that electrons that were purely L lone pairs in the free ligand gain some metal character in the complex; in other words, the L(σ) lone pairs are partially transferred to the metal. As L becomes more basic, the energy of the L(σ) orbital increases, and the extent of electron transfer will increase. An orbital that is higher in energy will appear higher in the MO diagram and will tend to occupy a larger volume of space, and any electrons in it will tend to be less stable and more available for chemical bonding or removal by ionization.

Ligands are generally *nucleophilic* because they have available (high-lying) electron lone pairs. The metal ion is *electrophilic* because it has available (low-lying) empty d orbitals. The nucleophilic ligands, which are lone-pair donors, attack the electrophilic metal, an acceptor for lone pairs, to give the metal complex. Metal ions can accept multiple lone pairs so that the complex formed is not just ML but ML_n (n = 2–9).

Figure 1.6 also shows why the very common d^6 ML_6 complex class has 18 valence electrons: 12 come from the L lone pairs and 6 from the metal's d^6 configuration.

The sd^n Model[3]

The still-dominant ligand field model is currently being challenged by another picture, the sd^n model. For example, in the first-row metals, this model considers the 4*p* orbital as being ineffective in M—L bonding owing to poor overlap and mismatched energies and proposes that, only the 4*s* and five 3*d* orbitals contribute. If so, one might expect d^6 metal complexes to prefer to have 12 valence electrons, not 18e, since 12e would entirely fill the sd^5 set. This would, however, lead to $Mo(CO)_3$ being the stable form rather than the observed $Mo(CO)_6$. To account for the additional bonding power, hypervalency is invoked.

Hypervalency, the ability of an element to exceed the valence electron count normally appropriate for the orbitals that are available, is best established in the main-group elements such as S, where an octet of 8 valence electrons is appropriate for its single *s* and three *p* orbitals. In hypervalent SF_6, for example, six electrons come from S and one each from the six F atoms for a total of 12 valence electrons, greatly exceeding the expected octet. The modern theory of hypervalency avoids the earlier idea that empty *d* orbitals (3*d* orbitals for S) allow the atom to house the excess electrons.

Hypervalent bonding is most simply illustrated for $[FHF]^-$ anion, where H has 4 valence electrons, exceeding its nominal maximum of 2e. In $[FHF]^-$, zero electron H^+ receives 2e from the lone pairs of each of two F^- anions coordinated to it. The bonding pattern, shown in Fig. 1.7, allows the 4e to occupy two lower-lying orbitals each having large F character, one bonding, one nonbonding, while leaving the highest lying orbital empty. The resulting 4 electron–3 center (4e–3c) bonding leads to half-order bonding between H and each F, resulting in somewhat longer bonds than in nonhypervalent species such as HF. HF_2^- anion is normally considered as a hydrogen-bonded adduct between HF and F^-, but here we see that H bonding is a type of hypervalency as well as being related to metal complexes. SF_6 is then considered as being built up of three trans F–S–F units each bonded via 4e–3c bonds.

Hypervalent bonding is enhanced by the presence of a ligand, here F, that is more electronegative than the central atom, here H, and thus capable of stabilizing the bonding and nonbonding orbitals of Fig. 1.7. This results in the accumulation of negative charge on the terminal F atoms that are best able to accommodate it. In coordination complexes, the ligands are indeed always much more electronegative than the metal. To return to $Mo(CO)_6$, the bonding is explained in terms of three pairs of trans L–M–L hypervalent 4e–3c bonds,

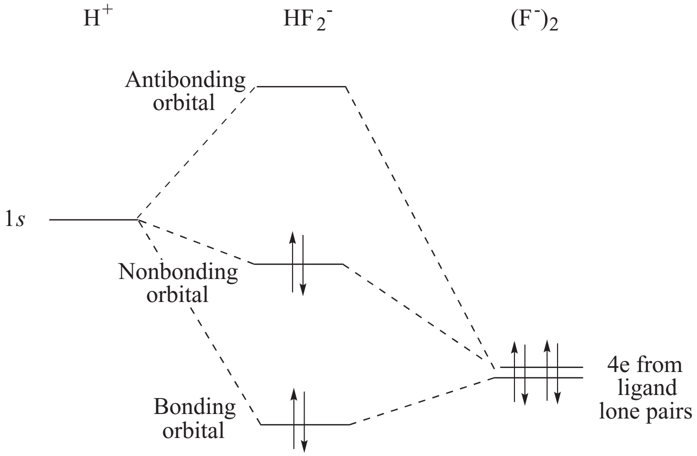


FIGURE 1.7 The 4e–3c hypervalent bonding model for $[FHF]^-$ anion. The bonding and nonbonding orbitals are occupied and the antibonding orbital left vacant. The fluoride ions are considered ligands for the central H^+.

formed from sd^2 hybrids. This leaves three d orbitals that are set aside for back bonding as the d_π set, as in ligand field theory. The fate of this new approach depends on whether it finds favor in the scientific community, and we will not use it extensively in what follows.

Textbooks inevitably give the impression of a field as a settled and agreed-upon body of science, but that agreement is only achieved after much argument, leading to an evolution of the community's understanding. Ideas that come to dominate a field often start out as a minority point of view. The sd^n model is a potential example of such an idea—it may either fade or flower from this point forward.

1.8 BACK BONDING

Ligands such as NH_3 are good σ donors but are not significant π acceptors. CO, in contrast, is an example of a good π acceptor. Such *π-acid* ligands are of very great importance in organometallic chemistry. They tend to be very high field ligands and form strong M–L bonds. All have empty orbitals of the right symmetry to overlap with a filled d_π orbital of the metal. In the case of CO, this orbital is the CO π^*. Figure 1.8 shows how overlap takes place to form the M–C π bond. It may seem paradoxical that an antibonding orbital such as the π^*(CO) can form a bond, but this orbital is antibonding only with respect to C and O and can still be bonding with respect to M and C.

We can make the ligand field diagram of Fig. 1.6 appropriate for the case of $W(CO)_6$ by including the π^* levels of CO (Fig. 1.9). The d_π set of levels still

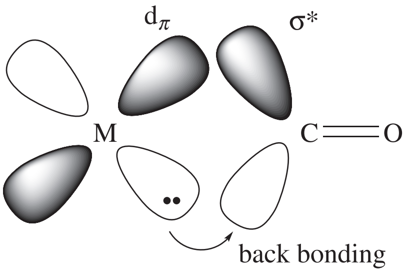


FIGURE 1.8 Overlap between a filled metal d_π orbital and an empty CO π^* orbital to give the π component of the M—CO bond. The shading refers to symmetry of the orbitals. The M—CO σ bond is formed by the donation of a lone pair on C into an empty d_σ orbital on the metal (not shown).

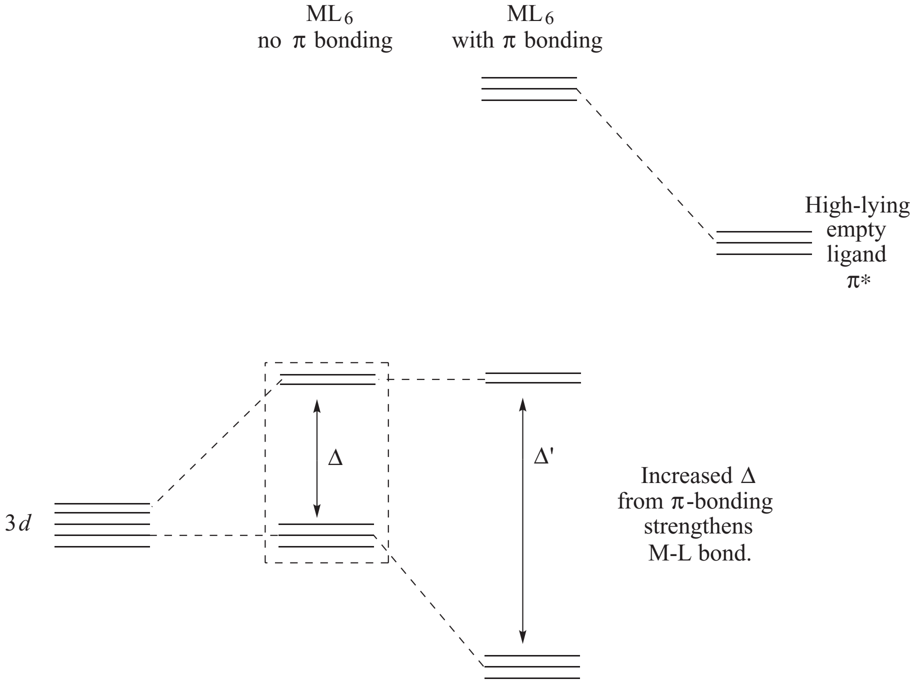


FIGURE 1.9 Effect of "turning on" the π interaction between a π-acceptor ligand and the metal. The unoccupied, and relatively unstable, π^* orbitals of the ligand are shown on the right. Their effect is to stabilize the filled d_π orbitals of the complex and so increase Δ. In $W(CO)_6$, the lowest three orbitals are filled.

find no match with the six CO(σ) orbitals, which are lone pairs on C. They do interact strongly with the empty CO π^* levels. Since the Md_π set is filled in this d^6 complex, the d_π electrons that were metal centered now spend some of their time on the ligands: This means that the metal has donated some electron density to the ligands. This *back bonding* is a key feature of M—L bonds where L is unsaturated (i.e., has multiple bonds). Note that this can only happen in d^1 or higher configurations; a d^0 ion such as Ti^{4+} cannot back bond and very seldom forms stable complexes with strong Ti bonding ligands like CO.

As antibonding orbitals, the CO π^* levels are high in energy, but they are able to stabilize the d_π set by back bonding as shown in Fig. 1.9. This has two important consequences: (1) The ligand field splitting parameter Δ rises, explaining why π-bonding ligands have such a strong ligand field and make such strong bonds; and (2) back bonding allows electron density on the metal to make its way back to the ligands. This, in turn, allows low-valent or zero-valent metals to form CO complexes. Such metals are in a reduced state and already have a high electron density. (They are said to be very *basic*). They cannot accept further electrons from pure σ donors; this is why $W(NH_3)_6$ is not a stable compound. By back bonding, the metal can get rid of some of this excess electron density. In $W(CO)_6$ back bonding is so effective that the compound is air stable and relatively unreactive; the CO groups have so stabilized the metal electrons that they have no tendency to be abstracted by air as an oxidant. In $W(PMe_3)_6$, in contrast, back bonding is inefficient and the compound exists but is very air sensitive and reactive.

Spectroscopic and theoretical studies show that for CO this π back donation is usually comparable to or greater in size than the CO-to-metal electron donation in the σ bond. One of the most direct arguments is structural. The M=C bond in metal carbonyls is usually substantially shorter than an M—C single bond. This is easiest to test when both types of bond are present in the same complex, such as $CpMo(CO)_3Me$, where M—C is 2.38 Å, and M=CO is 1.99 Å. We have to consider that a putative M—CO single bond would be shorter than 2.38 Å by about 0.07 Å, to allow for the higher *s* character (and therefore shorter bond length) of the *sp* hybrid on CO compared to the sp^3 hybrid of the methyl group. The remaining shortening of 0.32 Å is still substantial.

To confirm that it really is the π^* orbital of CO that is involved in the back bonding, we turn to IR spectroscopy. If CO were bound to the metal only by its carbon lone pair, nonbonding with respect to CO, then the $\nu(CO)$ frequency in the complex would differ very little from that in free CO. The compound BH_3, which is as pure as a σ acceptor as will bind to CO, shows a slight shift of $\nu(CO)$ to higher energy: free CO, 2149 cm^{-1}; $H_3B—CO$, 2178 cm^{-1}. Metal complexes, in contrast, show $\nu(CO)$ coordination shifts of hundreds of wavenumbers to lower energy, consistent with the weakening of the C—O bond as the π^* orbital is filled [e.g., $Cr(CO)_6$, $\nu(CO) = 2000\,cm^{-1}$]. Not only is there a coordination shift, but the shift is larger in cases where we would expect stronger back donation and vice versa. A net positive charge raises $\nu(CO)$, and a net negative charge lowers it [e.g., $V(CO)_6^-$, 1860 cm^{-1}; $Mn(CO)_6^+$, 2090 cm^{-1}]. The effect of replacing three π-acceptor COs by the three pure σ-donor nitrogens of the tren ligand ($H_2NCH_2CH_2NHCH_2CH_2NH_2$) is almost as great as changing the net ionic charge by one unit [e.g., Cr(tren)(CO)$_3$, 1880 cm^{-1}]. This makes ν(CO) a good indicator of how electron rich a metal is and it often correlates well with other ways of estimating nucleophilic character, such as the ease of removing an electron.[4]

Series of compounds such as $V(CO)_6^-$, Cr(CO)$_6$, and $Mn(CO)_6^+$ are *isoelectronic complexes* because they have the same number of electrons distributed in very similar structures. Isoelectronic ligands are CO and NO$^+$ or CO and CN$^-$, for example. Strictly speaking, CO and CS are not isoelectronic, but as the difference between O and S lies in the number of core levels, while the valence shell is the same, the term *isoelectronic* is often extended to cover such pairs. A comparison of isoelectronic complexes or ligands can be useful in making analogies and pointing out contrasts.[5]

Formation of the M—CO bond weakens the C—O bond relative to free CO. This will still lead to a stable complex as long as the energy gained from the M—C bond exceeds the loss in C—O. Bond weakening in L on binding is a very common feature in many M—L systems.

Frontier Orbitals

The picture for CO holds with slight modifications for a whole series of π acceptor (or soft) ligands, such as alkenes, alkynes, arenes, carbenes, carbynes, NO, N$_2$, and PF$_3$. Each has a filled orbital that acts as a σ donor and an empty orbital that acts as a π acceptor. These orbitals are almost always the highest occupied (*HOMO*) and lowest unoccupied molecular orbitals (*LUMO*) of L, respectively. The HOMO of L is a donor to the LUMO of the metal, which is normally d_σ. The LUMO of the ligand accepts back donation from a filled d_π orbital of the metal. The HOMO and LUMO of each fragment, the so-called *frontier orbitals*, nearly always dominate the bonding. This is because strong interactions between orbitals require not only that the overlap between the orbitals be large but also that the energy separation between them be small. The HOMO of each fragment, M and L, is usually closest in energy `to the LUMO of the partner fragment than to any other vacant orbital of the partner. Strong bonding is expected if the HOMO–LUMO gap of both partners is small. A small HOMO–LUMO gap usually makes a ligand soft because it is a good π acceptor, and for d^6, makes the metal soft because it is a good π donor.

π-Donor Ligands

Ligands such as OR$^-$, F$^-$, and Cl$^-$ are π donors as a result of the lone pairs that are left after one lone pair has formed the M—L σ bond. Instead of stabilizing the d_π electrons of a d^6 ion as does a π acceptor, these d_π electrons are now destabilized by what is effectively a repulsion between two filled orbitals. This lowers Δ, as shown in Fig. 1.10, and leads to a weaker M—L bond (e.g., high spin CoF_6^{3-}) than in the π-acceptor case. Lone pairs on electronegative atoms such as Cl and O are much more stable than the M(d_π) level, and this is why

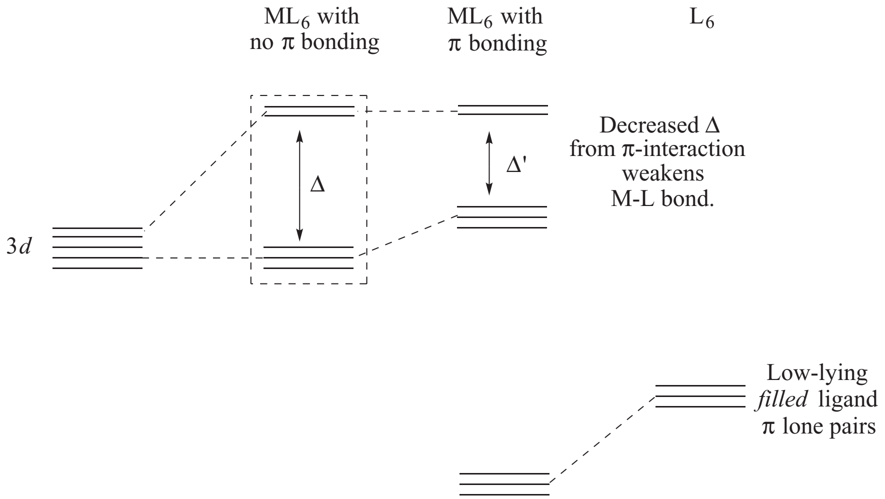


FIGURE 1.10 Effect of "turning on" the π interaction between a π-donor ligand and the metal. The occupied, and relatively stable, lone-pair (π) orbitals of the ligand are shown on the right. Their effect is to destabilize the filled d_π orbitals of the complex and so decrease Δ. This is effectively a repulsion between two lone pairs, one on the metal and the other on the ligand.

they are lower in Fig. 1.10 than are the π^* orbitals in Fig. 1.9. If the metal has empty d_π orbitals, as in the d^0 ion Ti^{4+}, π donation from the ligand to the metal d_π orbitals now leads to stronger metal–ligand bonding; d^0 metals therefore form particularly strong bonds with π-donor ligands [e.g., $W(OMe)_6$, $[TiF_6]^{2-}$].

1.9 ELECTRONEUTRALITY

In 1948 Pauling proposed the powerful *electroneutrality principle*. This says that the atoms in molecules arrange themselves so that their net charges fall within rather narrow limits, from about +1 to −1 overall. In fact, the range for any given element is likely to be narrower than this, and tends toward a preferred charge, which differs according to the electronegativity of the element concerned. The nonmetals, such as C, N, or O, tend to be closer to −1, and the metals, such as Li, Mg, and Fe, tend to be closer to +1. This implies that as far as electroneutrality arguments go, an element will bond best to other elements that have complementary preferred charges. In this way, each can satisfy the other. An electropositive element prefers an electronegative one, as in the compounds NaCl and TiO_2, and elements with an intermediate electronegativity tend to prefer each other, as in HgS and Au metal. An isolated Co^{3+} ion is not a electroneutral species, as it has an excessively high positive charge. In its compounds it will therefore seek good electron donors as ligands, such as O^{2-} in Co_2O_3, or NH_3, in the ammine (NH_3) complexes. On the other hand, an isolated W(0) atom is too electron rich for its electronegativity, so it will prefer net electron-attracting ligands such as CO that can remove electron density by π back donation.

Trends with Oxidation State

The *d* orbitals of transition metals are available for back donation only in electron-rich complexes. Co(III), for example, has a filled d_π level, but Co(III) does not bind CO because the d_π orbital is too low in energy and therefore not sufficiently basic thanks to the high positive change in Co^{3+}.

Periodic Trends

The orbital energies fall as we go from left to right in the transition series. For each step to the right, a proton is added to the nucleus. This extra positive charge stabilizes all the orbitals. The earlier metals are more electropositive because it is easier to remove electrons from their less stable orbitals. The sensitivity of the orbitals to this change is $d \sim s > p$ because the *s* orbital, having a maximum electron density at the nucleus, is more stabilized by the extra protons that we add for each step to the right in the periodic table, than are the *p* orbitals, which have a planar node at the nucleus. The *d* orbitals are stabilized because of their lower principal quantum number (e.g., 3*d* versus 4*s* and 4*p* for Fe). The special property of the transition metals is that all three types of orbital are in the valence shell and have similar energies so they can all contribute significantly to the bonding. Metal carbonyls, for example, are most stable for groups 4–10 because CO requires *d*-orbital back bonding to bind effectively.

There is a large difference between a d^0 state and a d^2 state, both common in the early transition metals [e.g., d^0 Ti(IV) and a d^2 Ti(II)]. The d^0 oxidation state cannot back bond because it lacks *d* electrons, while a d^2 state often has an exceptionally high back-bonding power because early in the transition series the *d* orbitals are relatively unstable for the reasons mentioned above. The d^0 Ti(IV) species $(C_5H_5)_2TiCl_2$ therefore does not react with CO at all, while the corresponding d^2 Ti(II) fragment, $(C_5H_5)_2Ti$, forms a very stable monocarbonyl, $(C_5H_5)_2Ti(CO)$, with a very low ν(CO) IR frequency, indicating very strong back bonding.

Finally, as we go down a group from the first-row transition element to the second row, the outer valence electrons become more and more *shielded* from the nucleus by the extra shell of electrons added. They are therefore more easily lost, and the heavier element will be the more basic and high oxidation states will be more stable. This trend also extends to the third row, but as the *f* electrons that were added to build up the lanthanide elements are not as effective as *s, p*, or even *d* electrons in shielding the valence electrons from the nucleus, there is a smaller change on going from the second- to the third-row elements than was the case for moving from the first row to the second. Compare, for example, Cr(VI) in Na_2CrO_4 and Mn(VII) in $KMnO_4$, both being powerful oxidizing agents, with their stable analogs in the second and third rows, Na_2MoO_4, Na_2WO_4, and $KReO_4$, which are only very weakly oxidizing. Similarly, the increase in covalent radii is larger on going from the first to the second row than it is on going from the second to the third. This is termed the *lanthanide contraction*.

Ionic compounds with excessively high positive or negative net ionic charges are not normally formed. The great majority of isolable compounds are neutral, net charges of ±1 are not uncommon, but net ionic charges of ±2 or greater are increasingly rare.

1.10 TYPES OF LIGAND

Ligands are Lewis bases and thus typically neutral or anionic, rarely cationic. Anionic ligands, often represented as X, form polar covalent M—X bonds with the metal atom. Two common models, covalent or ionic, exaggerate the polar or covalent character of M—X bonds. The first treats the bond as a pure covalent M—X link, but the second regards it as an ionic $M^+ \leftarrow :X^-$ bond where an X^- lone pair is the donor function to the metal. In addition to the σ bond, there can also be a π interaction. For a metal with basic d_π electrons, this π interaction can be favorable if the X ligand has a π-acceptor function, such as the π^* orbital of cyanide (Figs. 1.8 and 1.9), or unfavorable if the ligand is a π donor, as in the case of fluoride lone pairs (Fig. 1.10).

Among neutral ligands, often denoted L, we find lone-pair donors such as :CO or $:NH_3$, π donors such as C_2H_4, and σ donors[6] such as H_2. The first group—the only type known by Werner—bind via a lone pair. In contrast, π donors bind via donation of a ligand π-bonding electron pair, and σ donors bind via donation of a ligand σ-bonding electron pair to the metal. As poor donors, σ- and π-bonding electrons would form very weak M—L bonds if acting on their own. Both σ and π donors therefore normally require back bonding to produce a stable M—L bond. For the π donor, ethylene, Fig. 1.11*a* shows how L to M donation from the C=C π orbital to M d_σ, marked "1," is accompanied by back donation from M d_π into the C=C π^* orbital, marked "2." For the σ donor, H_2, Fig. 1.11*b* shows how L to M donation from the H—H σ orbital to M d_σ, marked "3," is accompanied by back donation from M d_π into the H—H σ^* orbital, marked "4." Back bonding requires a d^2 or higher electron configuration and relatively basic M d_π electrons, usually found in low oxidation states.

Both σ and π donors bind side-on such that there are two short bonding distances to the ligand. This type of binding is represented as η^2-C_2H_4 or η^2-H_2, where the letter η (pronounced eeta) denotes the *hapticity* of the ligand or the number of ligand atoms directly bound to the metal.

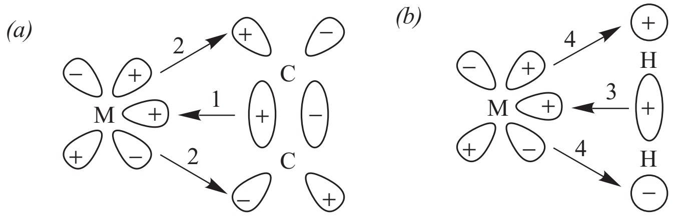


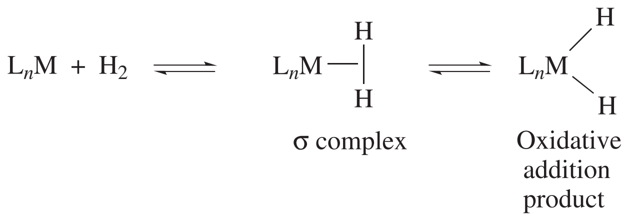
FIGURE 1.11 (a) Bonding of a π-bond donor, ethylene, to a metal. The arrow labeled "1" represents electron donation from the filled C=C π bond to the empty d_σ orbital on the metal; "2" represents the back donation from the filled $M(d_\pi)$ orbital to the empty C=C π^*. (b) Bonding of a σ-bond donor, hydrogen, to a metal. The label "3" represents electron donation from the filled H—H σ bond to the empty d_σ orbital on the metal, and "4" represents the back donation from the filled $M(d_\pi)$ orbital to the empty H—H σ^*. Only one of the four lobes of the d_σ orbital is shown.

TABLE 1.2 Types of Ligand[a]

Ligand	Strong π Acceptor	Weak π Bonding	Strong π Donor
Lone-pair donor	CO PF_3 CR_2^{+b}	$CH_3^-H^{-c}$, PPh_3 NH_3	CR_2^- OR^- F^-
π-Bonding electron pair donor	C_2F_4 O_2	C_2H_4 $RCHO^d$	
σ-Bonding electron pair donor	Oxidative addition[e]	R_3Si—H, H_2 R_3C—H	

[a] Ligands are listed in approximate order of π-donor/acceptor power, with acceptors to the left.
[b] CH_2^+ and CH_2^- refer to Fischer and Schrock carbenes of Chapter 11.
[c] Ligands like this are considered here as anions rather than radicals.
[d] Can also bind as a lone-pair donor (Eq. 1.6).
[e] Oxidative addition occurs when σ-bond donors bind very strongly (Eq. 1.5).

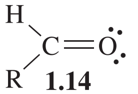
For σ donors such as H_2,[7] forming the M—L σ bond partially depletes the H—H σ bond because electrons that were fully engaged in keeping the two H atoms together in free H_2 are now also delocalized over the metal (hence the name *two-electron, three-center bond* for this interaction). Back bonding into the H—H σ^* causes additional weakening or even breaking of the H—H σ bond because the σ^* is antibonding with respect to H—H. Free H_2 has an H—H distance of 0.74 Å, but the H—H distances in H_2 complexes go all the way from 0.82 to 1.5 Å. Eventually the H—H bond breaks and a dihydride is formed (Eq. 1.5). This is the *oxidative addition reaction* (see Chapter 6). Formation of a σ complex can be thought of as an incomplete oxidative addition. Table 1.2 classifies common ligands by the nature of the M—L σ and π bonds. Both σ and π bonds bind side-on to metals when they act as ligands. Alkane C—H bonds behave similarly.[8]



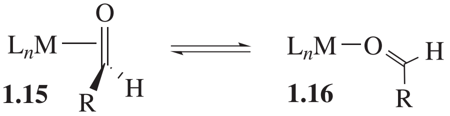
(1.5)

Ambidentate Ligands

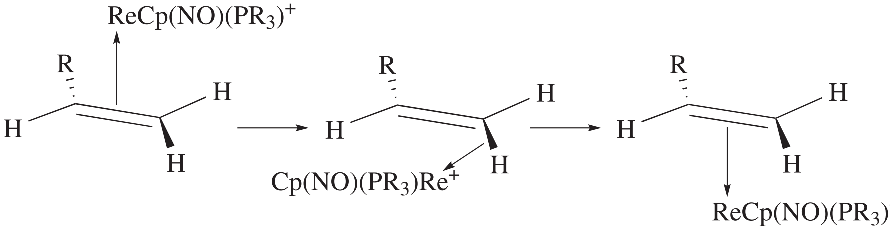
Some ligands have several alternate types of electron pair available for bonding. For example, aldehydes (**1.14**) have the C=O π bond and lone pairs on the oxygen. When they act as π-bond donors, aldehydes bind side-on (**1.15**) like ethylene, when they act as lone-pair donors, they bind end-on (**1.16**). Equilibria such as Eq. 1.6 [R = aryl; $L_nM = CpRe(NO)PPh_3^+$] are possible, as Gladysz has shown.[9a] The more sterically demanding π-bound form (**1.15**) is favored for unhindered metal complexes; **1.15** also involves back donation and so is also favored by more electron-donor metal fragments and more electron-acceptor R groups. Alkenes have both a C=C π bond and C–H σ bonds. Peng and Gladysz[9b] have also shown how metals can move from one face of a C=C bond to the other without decoordination, presumably via intermediate σ binding to the C–H bond (Eq. 1.7).



1.14

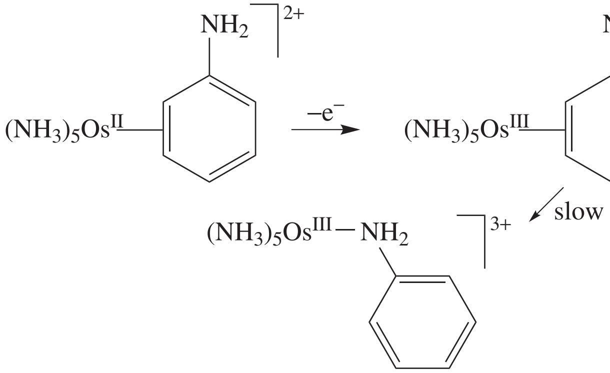


(1.6)



(1.7)

The $\{(NH_3)_5Os^{II}\}^{2+}$ fragment in Eq. 1.8 is a very strong π donor because NH_3 is strongly σ donor but not a π-acceptor ligand, so it prefers to bind to a π acceptor an aromatic C=C bond of aniline. Oxidation to Os^{III} causes a sharp falloff in π-donor power because the extra positive charge stabilizes the *d* orbitals, and the complex rearranges to the *N*-bound aniline form.[10] This illustrates how the electronic character of a metal can be altered by changing the ligand set and oxidation state; soft Os(II) binds to the soft C=C bond and hard Os(III) binds to the hard NH_2 group.



(1.8)

Figure 1.12 shows the typical ligands found for different oxidation states (OSs) of Re, an element with a very wide range of accessible OSs. Low OS complexes are stabilized by multiple π-acceptor CO ligands, intermediate OSs by less π-acceptor phosphines, high OS by σ-donor anionic ligands such as Me, and very high OS by O or F, ligands that are both σ donor and π donor.

Spectator versus Actor Ligands

Spectator ligands remain unchanged during chemical transformations. Actor ligands dissociate or undergo some chemical conversion. For example, there is a very extensive chemistry of $[CpFe(CO)_2X]$ and $[CpFe(CO)_2L]^+$ (Cp = cyclopentadienyl; X = anion; L = neutral ligand) where the $\{CpFe(CO)_2\}$

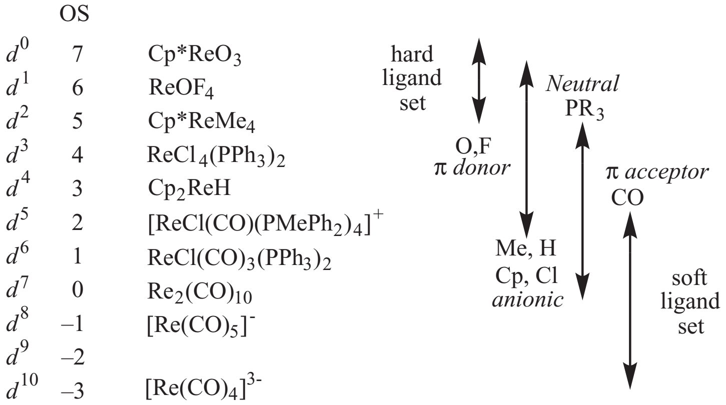
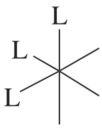


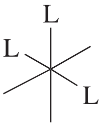
FIGURE 1.12 Some Re complexes showing typical variation of ligand type with oxidation state (OS): hard ligands with high OS and soft ligands with low OS.

fragment remains intact. The role of these ligands is to impart solubility in organic solvents, prevent loss of the metal, and influence the electronic and steric properties of the complex so as to favor any desired goal. An important part of the art of organometallic chemistry is to pick suitable spectator ligand sets to elicit desired properties. Apparently small changes in ligand can entirely change the chemistry. For example, PPh_3 is an exceptionally useful ligand with tens of thousands of complexes, while apparently similar compounds NPh_3, $BiPh_3$, and $P(C_6F_5)_3$ appear to be of very little use as ligands. A hard N donor such as NPh_3 is very different from a P donor such as PPh_3. The strongly electron-withdrawing C_6F_5 substituents in $P(C_6F_5)_3$ completely deactivate the lone pair for coordinate bonding. The strong effect of the steric factor is shown by the difference between PMe_3 and $P(C_6H_{11})_3$; up to five or even six of the smaller PMe_3 ligands are easily able to bind to a typical metal to give stable complexes, while only two or at most three of the bulky $P(C_6H_{11})_3$ ligands can normally bind to a single metal at the same time.

One role of spectator ligands is to occupy certain sites, say of an octahedron, to leave a specific set of sites available for the actor ligands so the desired chemistry can occur. These spectator ligands are commonly polydentate with the donor atoms arranged in specific patterns. A small sample of such ligands is shown in Fig. 1.13. The tridentate ligands can bind to an octahedron either in a *mer* (meridonal) fashion **1.18** (pincer ligands) or *fac* (facial) **1.17**, or in some cases, in both ways. The choice of ligand is still something of an art because subtle stereoelectronic effects, still not fully understood, can play an important role. Ligands **1.19** and **1.20** (Fig. 1.13) impart substantially different properties to their complexes in spite of their apparent similarity, probably as a result of the greater flexibility of the three-carbon linker in **1.20**.



1.17
fac

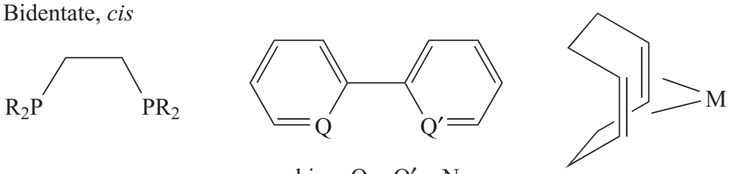


1.18
mer

Organometallic versus Coordination Compounds

This distinction was originally simple—the presence of M—C bonds made a compound organometallic—but the rise of catalysis began to raise problems. Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, one of the most important compounds in the development of organometallic chemistry (see Chapter 9), lacks M—C bonds and only involves them in some of the intermediates in the catalytic cycle. Likewise, CH activation is one of the most active areas in the field, but many of the catalysts used are coordination compounds that operate via organometallic intermediates (e.g., $[ReH_7(PPh_3)_2]$ or $K_2[PtCl_4]$). In an increasing number of cases, such as the metal oxo mechanism for CH activation

Bidentate, *cis*

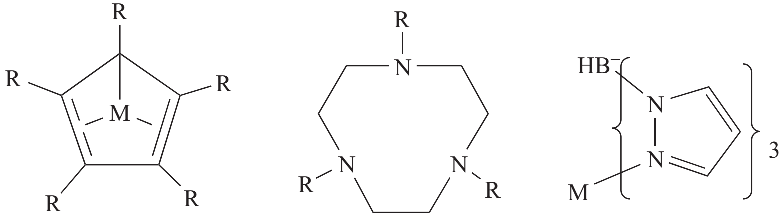


dpe, R = Ph
dmpe, R = Me

bipy, Q = Q′ = N
phpy, Q = C; Q′ = N
biph, Q = Q′ = C

cod

Tridentate, *fac*

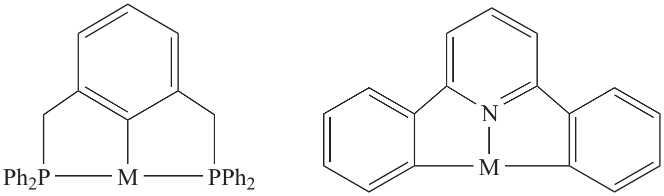


Cp, R = H
Cp*, R = Me

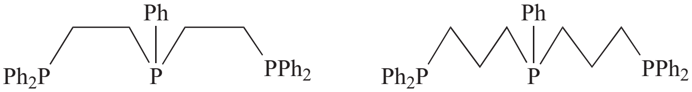
tacn, R = H
tacn*, R = Me

Tp

Tridentate, *mer*



Tridentate, *fac* and *mer*



1.19 **1.20**

FIGURE 1.13 A selection of common ligands with different binding preferences. The metal is shown where the binding mode might otherwise be unclear. Cp and Cp* can formally be considered as facial tridentate ligands (see Chapter 5).

(Sections 12.4 and 14.7), no M—C bonds are ever present, even in reaction intermediates. The organometallic coordination chemistry distinction is therefore losing its relevance and this edition therefore reflects that change, particularly in Chapters 14–16.

- High trans effect ligands such as H or CO labilize ligands that are trans to themselves. In CFT (Section 1.4), the *d*-orbital splitting, Δ, and e^- occupation determine the properties of the complex.
- Hard ligands such as NH_3 have first-row donor atoms and no multiple bonds; soft ligands such as PR_3 or CO have second-row donors or multiple bonds.
- Ligands donate electrons from their HOMO and accept them into their LUMO (p. 22). LFT (Section 1.5) identifies the d_σ orbitals as M—L antibonding.
- M—L π bonding strongly affects Δ and thus the strength of M—L bonding (Figs. 1.7 and 1.8).
- Ligands can bind via lone pairs, π bonding e^- pairs or σ bonding e^- pairs (Table 1.2).
- Octahedral d^3 and d^6 are coordination inert and slow to react.

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PROBLEMS

1. How many isomers would you expect for a complex with the empirical formula $Pt(NH_3)_2Cl_2$?

2. What d^n configurations should be assigned to the following and what magnetic properties—dia- or paramagnetic—are to be expected from their hexaqua complexes: Cu(I), Cu(II), Cr(II), Cr(III), Mn(II), and Zn(II).

3. Why is $R_2PCH_2CH_2PR_2$ so much better as a chelating ligand than $R_2PCH_2PR_2$? Why is H_2O a lower-field ligand for Co^{3+} than NH_3?

4. How would you design a synthesis of the complex *trans*-$[PtCl_2(NH_3)(tu)]$, (the trans descriptor refers to the fact a pair of identical ligands, Cl in this case, is mutually trans), given that the trans effect order is $tu > Cl > NH_3$ $[tu = (H_2N)_2CS]$?

5. Consider the two complexes $MeTiCl_3$ and $(CO)_5W(thf)$. Predict the order of reactivity in each case toward the following sets of ligands: NMe_3, PMe_3, CO.

6. How could you distinguish between a square planar and a tetrahedral structure in a nickel(II) complex of which you have a pure sample, without using crystallography?

7. You have a set of different ligands of the PR_3 type and a large supply of $(CO)_5W(thf)$ with which to make a series of complexes $(CO)_5W(PR_3)$. How could you estimate the relative ordering of the electron-donor power of the different PR_3 ligands?

8. The stability of metal carbonyl complexes falls off markedly as we go to the right of group 10 in the periodic table. For example, copper forms only a few weakly bound complexes with CO. Why is this? What oxidation state, of the ones commonly available to copper, would you think form the strongest CO complexes?

9. Low-oxidation-state complexes are often air sensitive (i.e., they react with the oxygen in the air) but are rarely water sensitive. Why do you think this is so?

10. $MnCp_2$ is high spin, while $MnCp^*_2$ ($Cp^* = \eta^5$-C_5Me_5) is low spin. How many unpaired electrons does each metal have, and which ligand has the stronger ligand field?

11. Make up a problem on the subject matter of this chapter and provide an answer. This is a good thing for you to do for subsequent chapters as well. It gives you an idea of topics and issues on which to base questions and will therefore guide you in studying for tests.