1

INTRODUCTION

Organometallic chemistry fills in a gap and makes a conceptual link between organic and inorganic chemistry in its focus on the binding of organic fragments to metals via one or more M–C bonds. The metals can come from the main group, in the s and p blocks of the periodic table, as in the Grignard reagent, CH_3MgBr, or from the transition elements of the d and f blocks, as in the ethylene complex salt, $K[(C_2H_4)PtCl_3]$. Main-group organometallics, such as n-BuLi and $PhB(OH)_2$, have proved so useful for organic synthesis that they are extensively covered in organic chemistry courses and textbooks. Here, we look instead at the transition metals where the intervention of metal d and f orbitals opens reaction pathways not otherwise accessible. While main-group organometallic reagents are typically stoichiometric – used in a simple mole ratio with the reactant – many transition metal organometallics are now most often seen as catalysts, where the metal-to-reactant ratio is typically 1 : 100 but can be 1 : 10^6 or even beyond. The higher the ratio, the greater the practicality of an organometallic catalyst, even if expensive.

1.1 WHY STUDY ORGANOMETALLIC CHEMISTRY?

The expanding range of applications of transition metal catalysis in organic chemistry helped explain the rise of d block organometallics from the late twentieth century. As late as 1975, the great majority of organic syntheses had no recourse to transition metals at any stage; in contrast, they now almost always appear, often as catalysts. Catalysis is also a central principle of the twenty-first century field of green or sustainable chemistry[1] because it helps avoid the waste formation in chemical processes, for example, of Mg salts from Grignard reactions, and its high selectivity minimizes the need for product separations.

The Organometallic Chemistry of the Transition Metals, Seventh Edition. Robert H. Crabtree.

In 2012, the noted organic chemist and Associate Editor of the *Journal of Organic Chemistry*, Carsten Bolm[2], published a ringing endorsement of organometallic methods as applied to organic synthesis:

> In 1989, OMCOS-VI [the 6th International Conference on Organometallic Chemistry Directed Toward Organic Synthesis] took place in Florence and … left me with the impression that all important transformations could – now or in the future – be performed with the aid of adequately fine-tuned metal catalysts. Today, it is safe to say that those early findings were key discoveries for a conceptual revolution that occurred in organic chemistry in recent years. Metal catalysts can be found everywhere, and many synthetic advances are directly linked to … developments in catalytic chemistry.

Organometallics have a much longer history in industrial chemistry. In the 1880s, Ludwig Mond refined crude nickel in a stream of hot CO to volatilize the Ni as $Ni(CO)_4$; subsequent stronger heating then deposited pure Ni. From the 1930s, the $Co_2(CO)_8$ catalyzed hydroformylation of 1- or 2-butene with H_2 and CO was applied to *n*-pentanal and *n*-pentanol manufacture. From the 1970s right up to today, a variety of homochiral pharmaceuticals have been produced by asymmetric catalysis, in which racemic reagents are transformed into single pure product enantiomers. Other examples include alkene polymerization to give polyethylene and polypropylene, hydrocyanation of butadiene for nylon manufacture, acetic acid synthesis from MeOH and CO, and hydrosilylation to produce silicone materials.

We are beginning to see applications elsewhere. From 2001, Cu catalyzed “click” chemistry has allowed coupling molecular units even within living cells or in advanced materials[3]. Some of the organic light-emitting diodes (OLEDs) in cell phone displays rely on organometallics. Samsung has produced OLED screens since 2008 that use a cyclometallated Ir complex as the red emitter. They are also useful in solid-state light-emitting electrochemical cells (LECs)[4]. Photoredox catalysis (Section 14.9) is a rising field in organic synthesis in which a favored photosensitizer is an organometallic iridium complex resembling the OLED emitters.

Surprisingly, organometallics have a multibillion year history in biology. Although most metalloenzymes employ classical coordination chemistry, the metal ions being surrounded by N- or O-donor ligands, a small but growing class of organometallic metalloenzymes is emerging. Ligands such as CO and CN^- appear in hydrogenases and even a carbide in nitrogenase, both being enzymes that are believed to have evolved very early in the Earth’s history. Biomedical applications are beginning to be seen: organometallic pharmaceuticals[5] such as the antimalarial, ferroquine, and the antitumoral, ferrocifen, are also emerging, together with a variety of diagnostic imaging agents such as cardiolite[6].

Another practical problem[7], alternative energy research, is driven by climate change concerns[8]. Solar and wind energy being intermittent, the resulting electrical energy needs to be converted into a storable fuel. This is most plausibly done by splitting water into O_2 and either H_2 or $2(H^+ + e^-)$ that can reduce CO_2 to a fuel such as MeOH. This strategy, termed artificial photosynthesis, needs catalysts some of which are organometallic[9, 10].

1.2 COORDINATION CHEMISTRY

Along with M–C bonds, organometallic compounds often also contain N- or O-donor coligands typical of coordination chemistry. Mixed ligand sets being so common, the distinction between coordination and organometallic chemistry is increasingly blurred. More importantly, organometallics are governed by many of the principles of coordination chemistry, so we look at these next[11].

The fundamentals of metal–ligand bonding were first established for coordination compounds by the founder of the field, Alfred Werner (1866–1919) who was even able to identify the octahedral geometry of CoL_6 complexes without the aid of modern spectroscopy or crystallography[12].

Central to our modern understanding both of transition metal coordination and organometallic compounds are d orbitals. Main-group compounds either have a filled d level that is too stable (e.g. Sn) or an empty d level that is too unstable (e.g. C) to participate significantly in bonding. Partial filling of the d orbitals in the d block metals gives them their characteristic properties. Some early transition metal ions with no d electrons (e.g. group 4 Ti^{4+}) and some late metals with a filled and stable set of 10e (e.g. group 12 Zn^{2+}) more closely resemble main-group elements. The terms "early" and "late" here refer to the left-hand (e.g. Ti, V, Ta, etc.) versus the right-hand side (e.g. Cu, Pd, Ir, etc.) d block 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 can thus also be seen as a subfield of coordination chemistry in which the complex contains an M–C bond. Even in the absence of M–C bonds, compounds with M–Q bonds where the atom Q has an electronegativity similar to C (e.g. $M–SiR_3$, M–H, etc.) also have organometallic properties and are treated here. Organometallic M–L bonds tend to be more covalent than M–N or M–O bonds of coordination compounds because the electronegativity difference between M and C is lower than for M and N or O. Typical C-donor ligands that usually bind to metal ions in their more reduced, low-valent forms are CO, alkenes, and arenes, as in zerovalent $Mo(CO)_6$, $Pt(C_2H_4)_3$, and $(C_6H_6)Cr(CO)_3$. Higher valent states are beginning to play a more important role, however, particularly with alkyl and aryl ligands, as in hexavalent WMe_6 and pentavalent $O{=}Ir(mesityl)_3$ (Chap. 15).

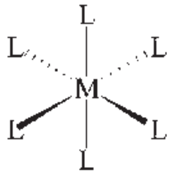
1.3 WERNER COMPLEXES

Werner complexes consist of a central metal, M, surrounded by ligands, L, that contain electronegative donor atoms, typically O, N, or halide. The ligand lone pairs bind to the metal to form such complexes as $[Co(NH_3)_6]^{3+}$, the M–L bond having a marked polar covalent character. The $M–NH_3$ bond itself consists of the 2e of the lone pair of free NH_3 but now shared with the metal in a polar covalency.

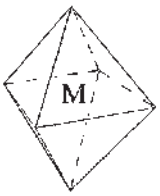
Stereochemistry

The most common type of complex, octahedral ML_6, adopts a geometry (**1.1**) based on the Pythagorean octahedron. By occupying its six vertices, the ligands can form

M–L bonds, while maximizing the L$\cdots$L nonbonding distances. The solid and dashed wedges in structure **1.1** indicate bonds that point toward or away from us, respectively.



1.1

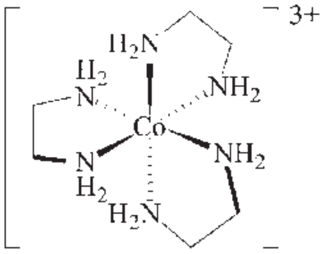


Octahedron

The complex may have a net ionic charge to make a complex ion (e.g. $[PtCl_4]^{2-}$); together with the counterions, we then have a complex salt (e.g. $K_2[PtCl_4]$). In some cases, both cation and anion may be complex, as in the picturesquely named *Magnus' green salt* $[Pt(NH_3)_4][PtCl_4]$, where the square brackets enclose the individual ions.

Ligands with more than one lone pair can donate each pair to different metals to form bridges in polynuclear complexes, such as **1.2** (L = PR_3). The bridging group is represented by the Greek letter μ (mu) as in $[Ru_2(\mu\text{-}Cl)_3(PR_3)_6]^+$. Dinuclear **1.2** consists of two octahedra sharing a face containing three chloride bridges.

1.2

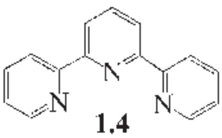


1.3

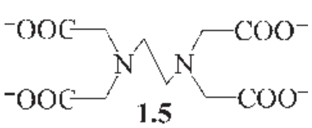
Chelate Effect

Ligands with more than one donor atom, such as ethylenediamine ($NH_2CH_2CH_2NH_2$, or "en"), can donate both lone pairs to a single metal to form a *chelate* ring (**1.3**). The most favorable ring size is five, but six is also common. Chelating ligands are much less easily displaced from a complex than are comparable monodentate ligands. For example, the reactants in Eq. (1.1) release six NH_3 molecules, increasing the total number of particles from four to seven; this creates entropy and so favors the chelate. Each chelate ring usually stabilizes the complex by about 10^5 in the equilibrium constant for the reaction. Such equilibrium constants are called *formation constants*; the higher the value, the more stable the complex.

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



1.4

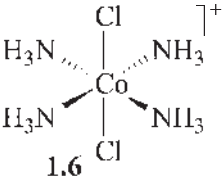


1.5

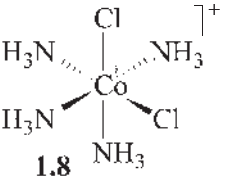
Chelate ligands can also be polydentate, as in tridentate **1.4** and hexadentate **1.5**. As a tridentate planar ligand, **1.4** is termed a *pincer*[13, 14]. Ethylenediaminetetraacetic acid (EDTA, **1.5**) can take up all six sites of an octahedron and thus completely wrap up most metal ions. Reactivity in metal complexes usually requires open sites or at least labile sites at the metal. The food preservative EDTA acts by binding free metal ions, blocking all the sites so that they can no longer catalyze aerial oxidation of the foodstuff.

Werner's Coordination Theory

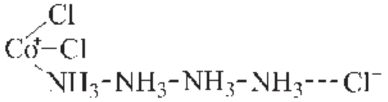
Alfred Werner developed the modern picture of coordination complexes in the years following 1893, when, as a young scientist, he proposed that the cobalt ammines (ammonia complexes) have an octahedral structure as in **1.6**, where the abbreviated square brackets stand in for the full set in structures **1.2** and **1.3**.



1.6

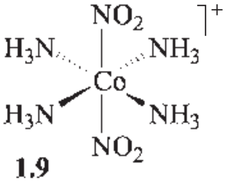


1.8

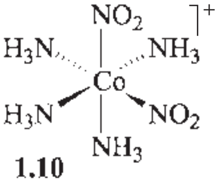


1.7

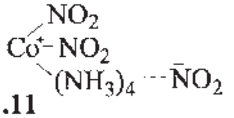
In doing so, he rejected the then-standard view that the ligands were bound in chains with the metal at one end (e.g. **1.7**). The third chloride ion was thought to be weakly attached to the chain and so easily dissociating in water. Naturally, Werner was opposed by supporters of the standard model who were only willing to slightly adjust their model to take account of his new data. Jørgensen, who led the traditionalists against the Werner insurgency, would not accept that a trivalent metal, Co^{3+}, could form more than the three bonds needed in the chain theory. At first, as each new "proof" came from Werner, Jørgensen was able to point to problems in the proof or reinterpret the chain theory to fit the new facts. For example, coordination theory calls for two isomers of $[Co(NH_3)_4Cl_2]^+$ (**1.6** and **1.8**). Up to then, only a green one was known, Werner's trans isomer (**1.6**), so called because the two Cl ligands occupy opposite vertices of the octahedron. According to Werner, a second isomer, **1.8** (cis), having adjacent Cl ligands should exist. Not only was it then unknown but initial attempts to make it failed. Changing the chloride to nitrite, Werner was indeed able to obtain both green cis and purple trans isomers of $[Co(NH_3)_4(NO_2)_2]^+$ (**1.9** and **1.10**). Jørgensen quite reasonably – but wrongly – countered this by saying that the nitrite ligands in the two isomers were simply bound differently (*linkage* *isomers*), via N (Co–NO_2) or O (Co–ONO) (**1.11** and **1.12**). Undismayed, Werner then produced the green and purple isomers, **1.13** and **1.14**, of $[Co(en)_2Cl_2]^+$, in a case where no linkage isomerism was possible. Somewhat less plausibly, Jørgensen brushed this observation aside by invoking different chain arrangements as in **1.15** and **1.16**.



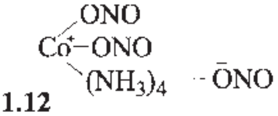
1.9



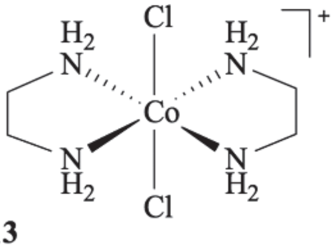
1.10



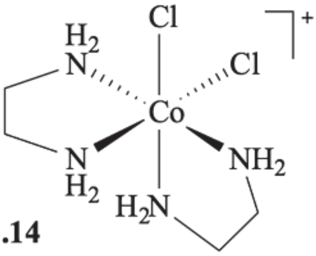
1.11



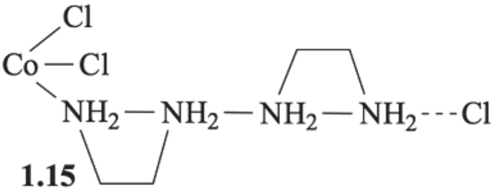
1.12



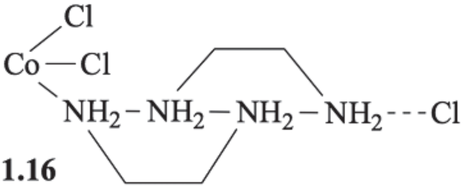
1.13



1.14

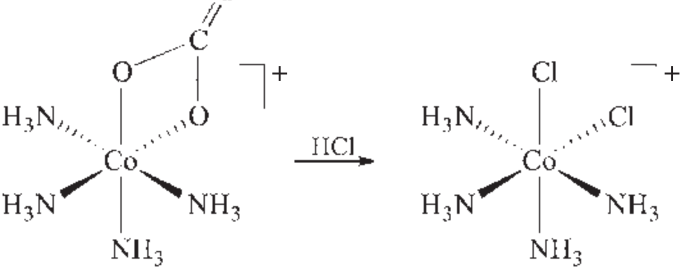


1.15



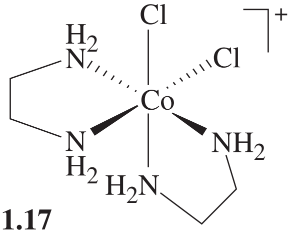
1.16

In 1907, Werner finally made the elusive purple isomer of $[Co(NH_3)_4Cl_2]^+$ by an ingenious route (Eq. (1.2)) via the necessarily cis carbonate $[Co(NH_3)_4(O_2CO)]$. Treatment with HCl in the solid state at 0 °C liberated CO_2 and gave the elusive cis dichloride. Jørgensen, receiving a sample of this purple complex by mail, finally conceded defeat.

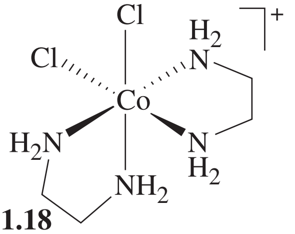


(1.2)

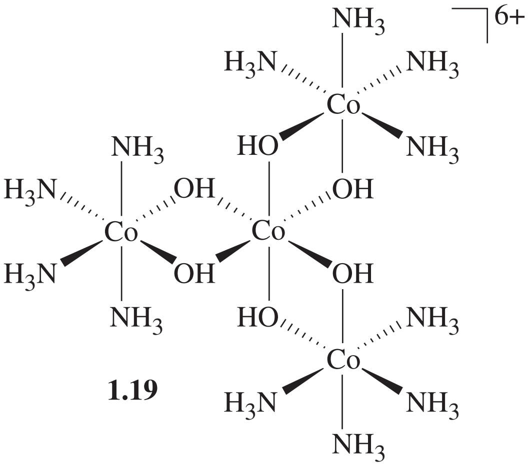
On resolving optical isomers of the halides $[Co(en)_2X_2]^+$ (**1.17** and **1.18**), Werner argued that the isomerism could only arise from the octahedral array, not otherwise. Even this point was challenged by traditionalists on the grounds that only organic compounds could be optically active, and so this activity must come from the organic ligands in some undefined way. Werner responded by resolving a complex (**1.19**) containing only inorganic elements. This has the extraordinarily high specific rotation of $3.6 \times 10^4°$ and required 1000 recrystallizations to resolve.



1.17



1.18



1.19

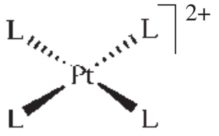
Several important conclusions follow. Scientific ideas are only provisional, so some of our current ones are likely to be wrong – we just do not know which ones. The literature must thus be read critically with an eye for possible flaws in the results, inferences, or arguments. Nugent has reviewed a series of ideas, once generally held, that subsequently fell from grace[15]. Another cogent lesson from Werner is that we must take objections seriously and test alternative theories with critical experiments, not merely ones that aim to confirm our prior ideas.

1.4 THE TRANS EFFECT

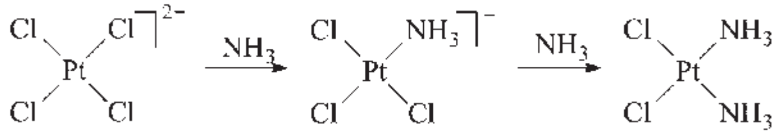
Ligands, L^t, that are more effective at labilizing any ligand trans to themselves have a higher trans effect. We see the reason in Sections 4.3 and 4.4, but for the moment only note that the effect is very marked for Pt(II), and that the highest trans effect ligands either (i) form strong σ bonds, such as $L^t = H^-$ or Me^-, or (ii) are strong π acceptors, such as $L^t = CO$, C_2H_4, or (iii) have polarizable period 3 or higher p block elements as the donor as in S-bound thiourea, $\{(NH_2)_2CS$ or "tu"$\}$.

High trans effect L^t ligands also lengthen and weaken trans M–L bonds, as shown in X-ray crystallography by an increase in the M–L distance or in nuclear magnetic resonance (NMR) spectroscopy by a decrease in the M,L coupling (Section 10.4), or in the infrared (IR) spectrum (Section 10.8) by a decrease in the ν(M–L) stretching frequency. When L^t changes the ground-state thermodynamic properties of a complex in one of these ways, we use the term *trans influence* to distinguish the situation from the trans effect proper in which L^t accelerates the rate of substitution, a kinetic effect.

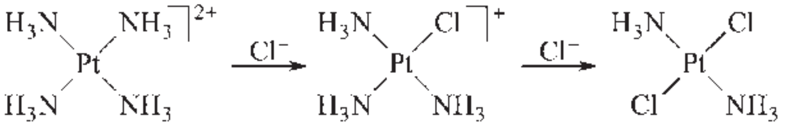
To illustrate this, we now move to Pt(II), where the II refers to the +2 oxidation state (Section 2.4). Pt(II) is four-coordinate and adopts a square planar geometry as in **1.20.** These complexes can react with incoming ligands, L^i, to replace an existing ligand L in a *substitution* reaction. Where a choice exists between two possible product geometries, as in Eqs. (1.3) and (1.4), the outcome is governed by the trans effect. For example, in the second step of Eq. (1.3), the NH_3 does not replace the Cl trans to NH_3 but only the Cl trans to Cl. This means that Cl has a higher trans effect ligand than NH_3: the Cl effectively weakens the M–NH_3 bond. The same holds in Eq. (1.4), where the NH_3 trans to Cl, not the one trans to NH_3, is displaced. This lets us synthesize specific isomers by choosing the right route. This example is also of practical interest because the cis isomer is a very important antitumor drug (Section 16.6), but the trans isomer is toxic.



1.20



(1.3)



(1.4)

A typical trans effect series for Pt(II) is given here, but the order can change somewhat for different metals, coligands, and oxidation states.

$$OH^- < NH_3 < Cl^- < Br^- < CN^- \approx CO \approx C_2H_4 \approx CH_3^- < I^- < PR_3 < H^- < CF_3^-$$

← Low trans effect High trans effect →

1.5 SOFT VERSUS HARD LIGANDS

Ligands and metals may be *hard* or *soft* depending on their propensity for ionic (hard) or covalent (soft) bonding[16]. The favored, well-matched combinations involve a hard ligand and a hard metal or a soft ligand with a soft metal; hard–soft combinations are disfavored because of the mismatch of bonding preferences.

Table 1.1 shows formation constants for different metal ion–halide combinations[15], where large positive numbers reflect strong binding. The hardest halide is F^- 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 therefore leads to strong bonding and HF is thus a weak acid (pK_a +3). However, alternative explanations of the experimental data have been proposed[17]. Table 1.2 gives some general characteristics of soft and hard metals and ligands.

Iodide is the softest halide because it is large, easy to polarize, and forms predominantly covalent M–L 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 are readily shared in covalent bonding. The Hg^{2+}/I^- soft–soft combination is therefore a very good one – by far the best in Table 1.1 – and dominated by covalent bonding. A mismatched pairing, as in HI, results in a strong acid (pK_a −9.5), so these combinations can have value in enhancing reactivity.

TABLE 1.1 Hard and soft acids and bases: some formation constants.[a]

Metal ion (acid)	Ligand (base)			
	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+}	0.05	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 heavy halide ions.

TABLE 1.2 Characteristics of hard and soft metals and ligands.

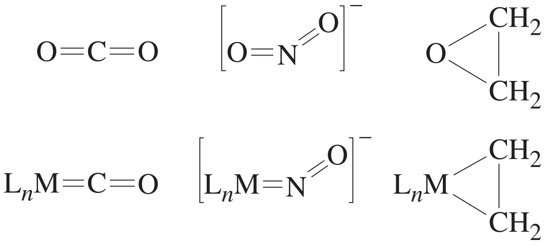
Hard M or L	Soft M or L
Favors ionic or polar covalent bonding	Favors covalent or polar covalent bonding
Donor atom has high electronegativity	Donor atom has low electronegativity
Ligand is saturated	Ligand is unsaturated[a]
High-oxidation-state metal	Low-oxidation-state metal
Less polarizable	More polarizable

[a] Meaning that the donor atom takes part in multiple bonds (e.g. MeCN, CO, or C_2H_4 but not N-bound $PhNH_2$).

Soft bases either have lone pairs on atoms of the second or later row of the periodic table (e.g. Cl^-, Br^-, PPh_3) or have a donor atom involved in intraligand multiple bonding (e.g. $C{\equiv}N^-$, C_2H_4, benzene). Soft acids can 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)]. Organometallic chemistry has traditionally been dominated by soft–soft interactions, as in metal CO, alkene, and arene complexes, while traditional coordination chemistry involves harder metals (oxidation state ≥ 2) and ligands (N or O donors or F^-). In this, as in so many other respects, these organometallic/coordination distinctions are now becoming much more blurred.

Proton/Oxide Analogies

The ultimate hard "metal" is the proton, so if a ligand protonates easily it is likely to form strong complexes with hard metals (e.g. H–F, H–OAc, [H–pyridine]$^+$). As a powerful π donor, an oxygen atom is an analog of a soft metal, so soft ligands, L, often form stable oxides, L=O. The examples given also illustrate how the L=O structure even mirrors the structural preferences of M–L with strongly back donating metals, e.g. CO (linear, end-on), NO^- (bent, end-on) and ethylene (side-on).



1.6 THE CRYSTAL FIELD

The *crystal field theory* (CFT) shows how the d orbitals of a transition metal are affected by the ligands and helps us decipher the resulting spectra, structures, and magnetic properties. In CFT, the ligands are modeled as simple negative charges, hence crystal *field*. For Cl^-, this is the negative charge on the ion and for NH_3, it is the N lone pair, a local concentration of negative charge. In an isolated metal ion, the five d orbitals are *degenerate* (have the same energy). As the six ligands approach from the octahedral directions $\pm x$, $\pm y$, and $\pm z$, the d orbitals take the form shown in Fig. 1.1. The d orbitals that point along the axes toward the incoming L groups ($d_{(x^2-y^2)}$ and d_{z^2}) are destabilized by the negative charge of the ligands and move to a higher energy. The three that point away from L (d_{xy}, d_{yz}, and d_{xz}) are less destabilized, leading to an energy gap with the other set.

The most strongly destabilized pair of orbitals are labeled e_g, from their symmetry, or, because they point along the M–L σ bonds, more simply as d_σ. At lower energy are the set of three more stable orbitals with the label t_{2g}, or simply d_π. They point

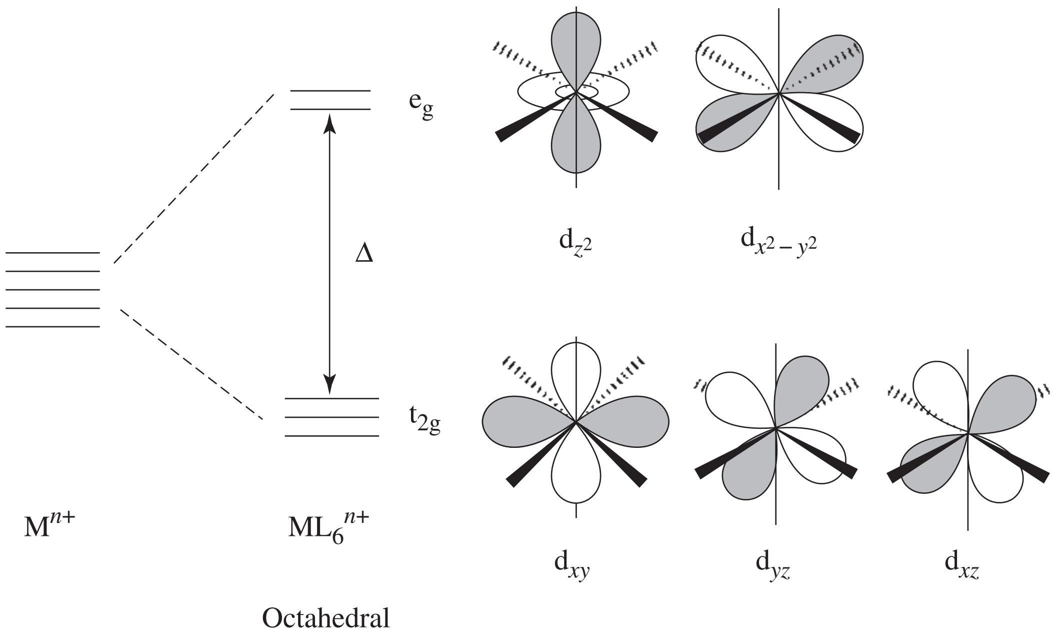


FIGURE 1.1 Effect on the d orbitals of bringing up six ligands along the ±*x*, ±*y*, and ±*z* directions. Shading represents the symmetry of the d orbitals, the shaded parts having the same sign of ψ. For convenience, energies are shown relative to the average d-orbital energy. The energy levels are shown stacked in pairs or threes for clarity; in reality, both levels of the e_g and all three of the t_{2g} set have the same energy.

between the ligand directions but can still form π bonds with suitable π bonding ligands. The energy gap between the d_σ and d_π set, the *crystal field splitting* Δ (or sometimes 10Dq), depends on the effective negative charge of the ligands. A higher Δ also implies that we have stronger M–L bonds.

High Spin Versus Low Spin

In group 9 cobalt, the nine valence electrons have the configuration $[Ar]4s^2 3d^7$, but only in the free atom. Formation of M^{n+} or ML_n stabilizes the 3d orbitals over the 4s, and the configuration becomes $[Ar]4s^0 3d^9$ for a Co(0) complex, or $[Ar]4s^0 3d^6$ for Co(III) complex; these configurations are usually written as d^9 or d^6. The 4s orbital is now less stable than 3d because, pointing as it does in all directions, the 4s suffers CFT repulsion from all the ligands in any Co complex, while the 3d orbitals only interact with a subset of the ligands in the case of the d_σ set or, even less destabilizing, point between the ligands in the case of the d_π set.

This crystal field picture explains why Werner's d^6 Co^{3+} has such a strong octahedral preference. Its six d electrons just fill the three low-lying d_π orbitals of the octahedral crystal field diagram and leave the higher energy d_σ orbitals empty. The six electrons are CFT-stabilized because they point away from the ligand negative charges. Stabilizing the electrons in a molecule is equivalent to stabilizing the molecule itself. Because of its favorable M–L bonding properties, octahedral d^6

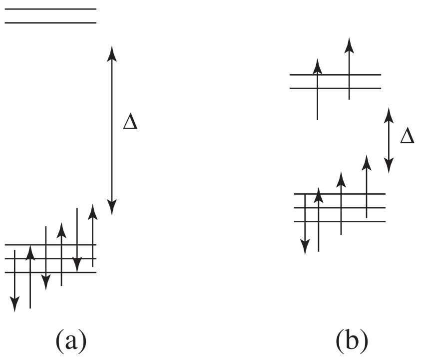


FIGURE 1.2 In an octahedral d^6 metal ion, both low- and high-spin complexes are possible depending on the value of Δ. A high Δ leads to the low-spin form (a). All unpaired electrons in high spin (b) have the same spin to conform with Hund's rule.

is by far the commonest type of metal complex in all of organometallic chemistry, as commonly seen in Mo(0), Re(I), Fe(II), Ir(III), and Pt(IV) complexes. In spite of the high tendency to spin pair the electrons in the d^6 configuration (to give the common *low-spin* (l.s.) form $t_{2g}{}^6e_g{}^0$), if Δ is small enough, the electrons may rearrange to give the rare *high-spin* (h.s.) form $t_{2g}{}^4e_g{}^2$. In h.s., all the unpaired spins are aligned (Fig. 1.2), as called for in the free ion by Hund's rule. Two spin-paired (↑↓) electrons in the same orbital suffer increased electron–electron repulsion than if each occupied separate orbitals (↑)(↑). The h.s. form thus benefits from having fewer electrons paired up in this way. Unless Δ is very small, however, the energy gained by dropping from the e_g to the t_{2g} level to go from h.s. to l.s. is sufficient to overcome the e^-–e^- repulsion from spin pairing, resulting in an l.s. state.

The spin state is found from the magnetic moment, determined by comparing the apparent weight of a sample of the complex in the presence and absence of a magnetic field gradient. In l.s. d^6, the complex is *diamagnetic* and very weakly repelled by the field, as is found for most organic compounds, also spin paired. On the other hand, the h.s. form is *paramagnetic*, in which case it is attracted into the field because of the magnetic field of the unpaired electrons. The complex does not itself form a permanent magnet, as can 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. However, they do respond to the external field by aligning against the applied field when we put them in a magnetic field to measure the magnetic moment.

The majority of organometallic complexes are diamagnetic from having high-field ligands, even d^n configurations and high Δ, but interest in paramagnetic organometallics (Chap. 15) is on the rise. Mononuclear complexes with an uneven number of electrons, such as d^5 $V(CO)_6$, cannot avoid paramagnetism even in the l.s. case. For even d^n configurations, h.s. is more often seen for the first-row metals, where Δ tends to be smaller than in the later rows. Different spin states have different structures and reactivities and, unlike resonance forms, may have a separate existence. For example, if the l.s. and h.s. isomers have almost exactly the same energy – a rare situation – each state can now coexist in a temperature-dependent equilibrium, as in $Fe(dpe)_2Cl_2$.

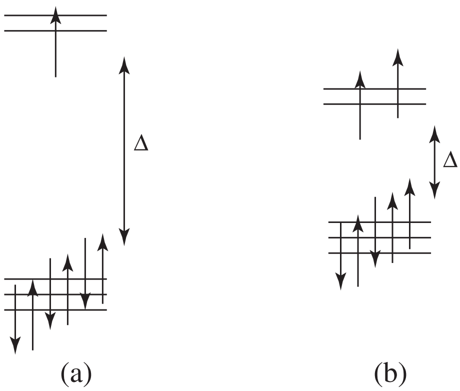


FIGURE 1.3 An octahedral d^7 ion is paramagnetic in both the low-spin (a) and high-spin (b) forms.

Inert Versus Labile Coordination

In octahedral d^7, one electron has to go into the higher energy, less stable e_g level to give the l.s. $t_{2g}{}^6e_g{}^1$ configuration and make the complex paramagnetic (Fig. 1.3). The *crystal field stabilization energy* (CFSE) of such a system is therefore less than for low spin d^6, 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 such as Co(II) that are orders of magnitude more reactive in ligand dissociation than their d^6 analogs because the e_g or d_σ levels are M–L σ-antibonding (Section 1.7) and so electron occupation weakens the M–L bonds. Werner studied d^6 Co(III) precisely because the ligands tend to stay put. This is why Co(III) and other l.s., octahedral d^6 ions are considered *coordinatively inert*. A half-filled t_{2g} level is also specially stable, so octahedral d^3 is also considered coordination inert, as in Cr(III). On the other hand, in the absence of contrary information, Co(II), Cr(II), and all other non-d^6 l.s. and non-d^3 ions are considered *coordinatively labile*. Second- and third-row transition metals form much more inert complexes than the first-row metals because of their higher Δ and CFSE. To take an extreme case, octahedral Ir(IV), although d^5, is very inert.

Jahn–Teller Distortion

The lability of coordination-labile ions such as d^7 l.s. is accompanied by a geometrical distortion even in the ground-state structure. This Jahn–Teller (J–T) distortion occurs whenever the individual orbitals in a set of orbitals of the same energy – degenerate orbitals – are unequally occupied. For a pair of degenerate e_g orbitals, this requires occupation by one or three electrons. This is the case for l.s. d^7 where only one of the e_g orbitals is half filled (Fig. 1.4). In that case, a pair of ligands that lie along one axis – 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 $d_{(x^2-y^2)}$ or d_{z^2} orbital is half-occupied. On crystal field ideas, the electron in the half-filled d_{z^2} orbital repels the ligands that lie on the z axis, making these M–L bonds longer; if the $d_{(x^2-y^2)}$ orbital is half-occupied, the bonds in the xy plane are longer. This distortion

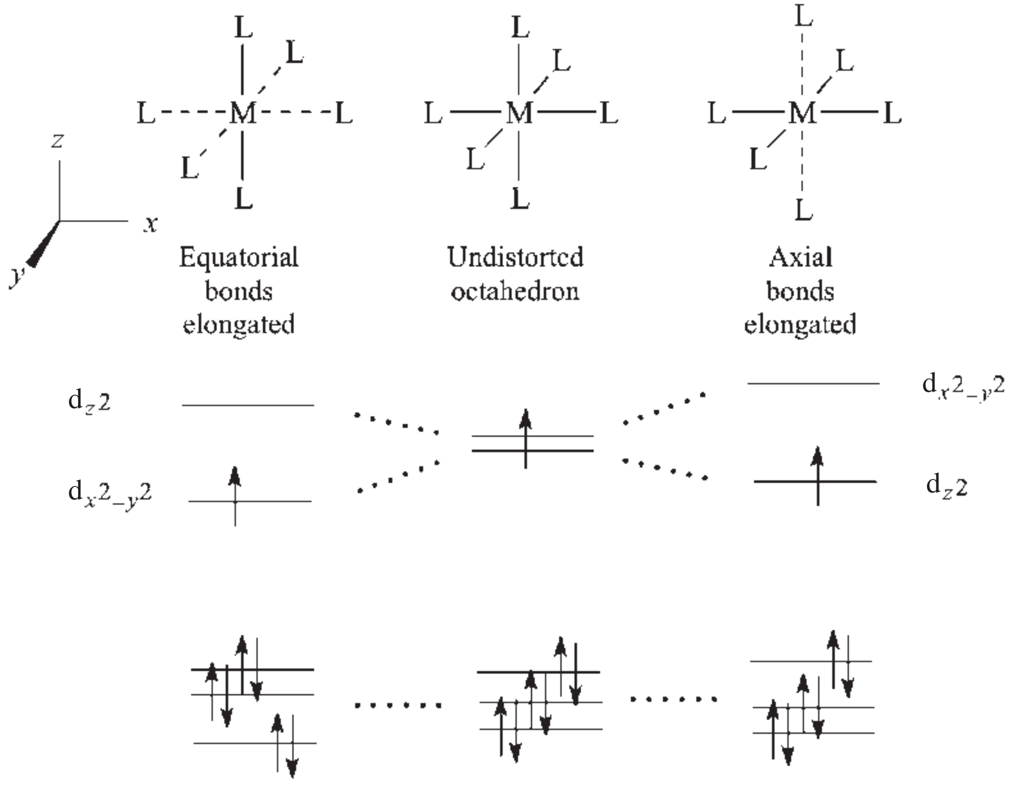


FIGURE 1.4 Jahn–Teller distortions for octahedral d^7 low-spin ions occur for uneven occupation of the d_σ orbitals. This leads to a distortion in which either the xy ML_4 ligand set (left) or the z ML_2 ligand set (right) shows an M–L elongation because of electron–electron repulsions. Minor splitting also occurs in the d_π set. These types of diagrams do not show absolute energies – instead, the "center of gravity" of the orbital pattern is artificially kept the same for clarity.

promotes ligand dissociation because two or four of the M–L distances are already elongated and weakened relative to the d^6 l.s. comparison case. A J–T distortion also occurs if the t_{2g} set of three orbitals are unevenly occupied with 1, 2, 4, or 5 electrons in t_{2g}, as in d^6 h.s. (Fig. 1.2b), but the distortion is now smaller because these t_{2g} orbitals do not point directly at the ligands (Table 1.3). The J–T distortion splits the d orbitals to give a net electron stabilization relative to the pure octahedron.

TABLE 1.3 Jahn–Teller distortions versus d^n configuration (octahedral case).

d^n configuration	1	2	3	4	4	5	5	6	6	7	7	8	9	10
Spin				hs	ls	hs	ls	hs	ls	hs	ls			
J–T effect	w	w	0	s	w	0	w	w	0	w	s	0	s	0

hs, high spin; ls, low spin; w, weak distortion; s, strong distortion; 0, no distortion.

This is seen in Fig. 1.4, where the seventh electron is stabilized whichever of the two distortions, axial or equatorial, is favored.

Low- Versus High-Field Ligands

Light absorption at an energy that corresponds to the d_π–d_σ splitting, Δ, leads to temporary promotion of a d_π electron to the d_σ level, typically giving d block ions their bright colors. The UV-visible spectrum of the complex can then give a direct measure of Δ and therefore of the crystal field strength of the ligands. *High-field* ligands such as CO and C_2H_4 lead to a large Δ. *Low-field* ligands, such as F− or H_2O can give such a low Δ that even the d^6 configuration can become h.s. and thus paramagnetic (Fig. 1.2b).

The *spectrochemical series* ranks ligands in order of increasing Δ. The range extends from weak-field π-donor ligands such as halide and H_2O with low Δ, to strong-field π-acceptor ligands such as CO that give high Δ (Section 1.10). These π effects are not the whole story[18], however, because H, although not a π-bonding ligand, is nevertheless a very strong-field ligand from its very strong M–H σ bonds.

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

← Low Δ High Δ →

← π donor π acceptor/strong σ donor →

Hydrides and carbonyls – metal complexes of H and CO – with their strong metal–ligand bonds and high Δ, are most often diamagnetic. High-field ligands resemble high-trans-effect ligands in forming strong σ and/or π bonds, but the precise order differs a little in the two series and between complexes.

Magnetism and Nuclearity

Although an odd d^n configuration, such as in d^7 $[Re(CO)_3(PCy_3)_2]$, leads to paramagnetism in a mononuclear complex, in a dinuclear complex, however, the odd electron on each metal can now pair up in forming the M–M bond, as in the diamagnetic d^7–d^7 dimer, $[(OC)_5Re–Re(CO)_5]$. Mononuclear complexes with an even d^n configuration can be diamagnetic or paramagnetic depending on whether they are l.s. or h.s. The practical difficulties of working with paramagnetic complexes, such as the complexity of analyzing their NMR spectra – if indeed any NMR spectrum is detectable at all (Section 10.2) – has slowed research in the area. The rise in importance of first-row metal complexes resulting from the rising concern for sustainability is reversing this trend because paramagnetic complexes are more common in the first row from their smaller Δ.

Other Geometries

After octahedral, the next most common geometries are two types of four-coordination: tetrahedral and square planar, as well as five-coordinate square pyramidal. Tetrahedral is seen for d^0, d^5 (h.s.), and d^{10}, where we have symmetrical occupation of all the d orbitals, each having zero, one, or two electrons as in d^0 Ti(IV), d^5 h.s. Mn(II), and d^{10} Pt(0). Since crystal field effects require *un*symmetrical d orbital occupation, such effects no longer apply and a tetrahedral geometry is often adopted on purely steric grounds. The orbital pattern for tetrahedral – three up, two down (Fig. 1.5, top) – is the opposite of that for octahedral geometry and Δ_{tet} is smaller than Δ_{oct}, all else being equal, because we now only have four ligands rather than six to split the d orbitals. Tetrahedral geometry is also typical for d^4 (low spin), as in Re(III), where only the low-lying pair of d orbitals is occupied.

The important square planar geometry, formally derived from an octahedron by removing a pair of trans ligands along the ±z axis, has a more complex splitting pattern (Fig. 1.5, right). This derives from the octahedral pattern by pushing the

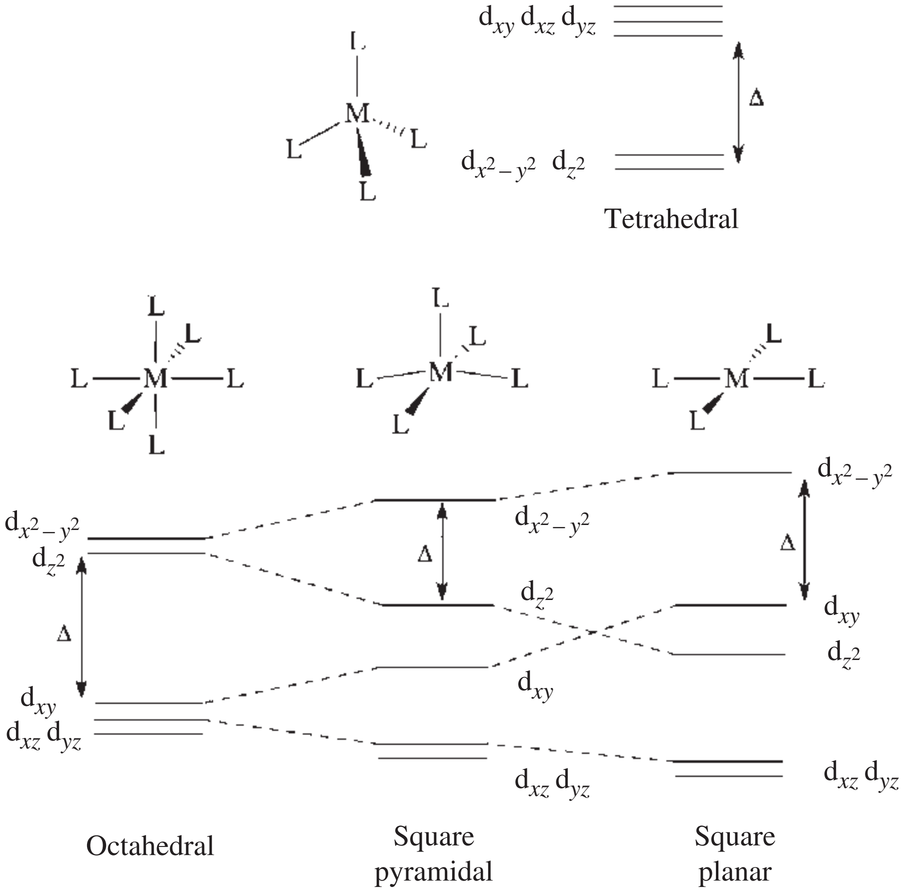


FIGURE 1.5 Crystal field splitting patterns for the most common four- and five-coordinate geometries: tetrahedral, square pyramidal, and square planar. For the square pyramidal and square planar arrangements, the z axis is conventionally taken to be perpendicular to the L_4 plane. Octahedral geometry is expected for d^6, while square planar and square pyramidal are preferred in d^8; the ΔHOMO–LUMO splittings shown apply to those d^n configurations.

distortion of Fig. 1.4 (right) to the limit. The biggest splitting, Δ in Fig. 1.5, separates the two highest energy orbitals. The square planar geometry is most often seen for d^8 (l.s.), as in Pd(II), where only the highest energy orbital remains unoccupied. It is also common for paramagnetic d^9, as in Cu(II). In square pyramidal geometry, only one axial L is removed from the octahedral parent structure. Figure 1.5 shows idealized crystal field pictures that treat the ligands as point charges – real compounds can have different ordering of the orbitals depending on the type of ligands, any distortions, etc. as shown by full calculations[19]. Even so, the orbital, always having the highest energy in square planar ML_4, typically remains empty.

Holding the geometry and ligand set fixed, different metal ions can show 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:

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

← Low Δ High Δ →

← Low valent, first row High valent, third row →

Second- and particularly third-row metals tend to have a higher Δ than first-row metals; thus, they have stronger M–L bonds, and give more thermally stable complexes that are also more likely to be diamagnetic. Higher oxidation states of a given metal also tend to produce higher Δ, enhancing these trends; but for a fair comparison, we would need to keep the same M and L_n in different oxidation states. This is rarely the case because low-oxidation-state metals are usually found with strong-field ligands that tend to give a high Δ (see the spectrochemical series earlier) and high-oxidation-state metals are usually most accessible with weak-field ligands that tend to give a low Δ. The oxidation state trend is therefore partially counteracted by the change in ligand preferences.

Isoconfigurational Ions

Ions of the same d^n configuration 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, and this idea helps us predict new complexes from the existence of isoconfigurational analogs. Numerous analogies of this type have been established for the d^6 pair Ir(III) and Ru(II), for example.

1.7 THE LIGAND FIELD

The crystal field picture is qualitative, but for a more complete picture, we turn to the more sophisticated *ligand field theory* (LFT), really a conventional molecular orbital

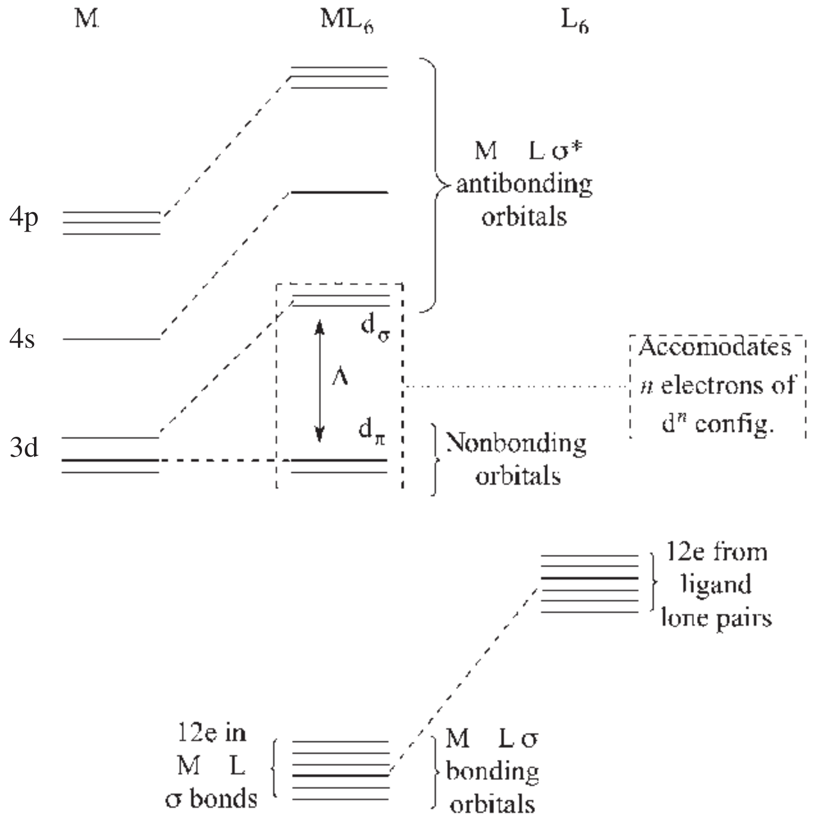


FIGURE 1.6 Molecular orbital, or ligand field picture, of M–L bonding in an octahedral ML_6 complex. The box contains the d orbitals that are filled with *n* electrons to give the d^n electron configuration.

(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 metal ion as well as the six lone-pair orbitals of a set of pure σ-donor ligands in an octahedral array. 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. Combining the six metal orbitals with the six ligand orbitals gives rise to a bonding set of six MOs (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, somewhat resembling lone pairs in p block compounds. In the d^6 ion $[Co(NH_3)_6]^{3+}$ we have 6e from Co^{3+} and 12e from the six :NH_3 ligands, giving 18e in all. This means that all the bonding and nonbonding levels up to and including the d_π set are filled, and all the antibonding M–L σ* levels remain unfilled – the most favorable situation for high stability. In Fig. 1.6 we can identify the familiar crystal field d orbital splitting pattern in the d_π set and two of the M–L σ* levels. The Δ splitting increases as the strength of the M–L σ bonds increases, so bond strength is analogous to the effective ligand charge in the crystal field model. In LFT, the d_σ orbital of CFT becomes an M–L σ-antibonding orbital with key consequences such as J–T distortion.

The L lone pairs in the free ligand become bonding pairs shared between L and M when the M–L σ bonds are formed; these are the six lowest orbitals in Fig. 1.6 and are always completely filled with 12e. 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 M and L character, but L(σ) predominates. Any MO more closely resembles the parent atomic orbital that lies closest to it in energy, and L(σ) almost always lies below M(d_σ) and therefore closer to the M–L σ-bonding orbitals. Electrons that were purely L lone pairs in free L now gain some metal character in ML_6; 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 together with the extent of electron pair transfer to M. An orbital that moves to higher energy moves higher in the MO diagram and tends to occupy a larger volume of space; any electrons it contains become less stable and more available for chemical bonding or removal by electron loss in any oxidation.

Ligands are generally *nucleophilic* because they have high-lying lone-pair electrons available, while a metal ion is *electrophilic* because it has low-lying empty d orbitals available. A nucleophilic ligand, a lone-pair donor, can thus attack an electrophilic metal, a lone-pair acceptor, to give a metal complex. Metal ions can accept multiple lone pairs so that the complex formed is not just ML but ML_n ($n = 2$–9).

Figures 1.3, 1.5, and 1.6 are idealized and only apply to ML_n complexes where all the ligands are identical and monodentate. In any other case – the vast majority therefore – the orbitals will depart somewhat from the ideal (Section 15.1).

Inverted Ligand Field

Very occasionally, the lone-pair energy of a strongly basic ligand lies *above* the metal d set. If so, the ligand field is thought to invert with an X^- ligand formally transferring 2e to M^+ to give X^+ and M^-. As a result, the OS of the metal is reduced by two units and the metal–ligand bond is now seen as $M^- \rightarrow X^+$. One such complex that has led to friendly disagreement in the literature is square planar $[Cu(CF_3)_4]^-$, which would be Cu(III) as conventionally counted, but some think it should be considered as having a T-shaped $\{Cu^I(CF_3)_3\}^{2-}$ group bound to a CF_3^+ with resonance making all the bonds equivalent[20].

1.8 TWO-ELECTRON THREE-CENTER BONDING

Standard covalent bonds, as in H–H, have 2e shared between two atomic centers and are thus termed 2e,2-center (2e,2c) bonds. We later meet many metal–ligand bonds that retain the 2e but instead spread them over three centers (2e,3c bonds). The simplest 2e,3c bond occurs in H_3^+, an abundant ion in interstellar space. Gas-phase H_3^+ only has 2e. So there is no possible ambiguity about the electron count. The molecular orbital diagram for triangular H_3^+ shows three orbitals, only the symmetrical Ψ_1 being bonding, but since we only have 2e, these can both be assigned to Ψ_1 (Fig. 1.7). With 2e spread over the three H- - -H bonds, we have a ⅓ bond order for each one making them longer (0.90 Å) and weaker than in H–H (0.74 Å). In later sections, we see how 2e,3c bonding contributes to the stability of numerous metal–ligand bonds such as M–(H_2) and M–(C_2H_4).

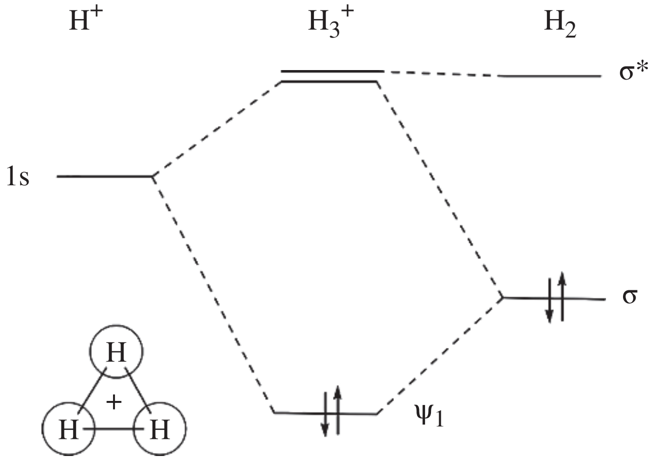


FIGURE 1.7 The two-electron three-center (2e-3c) bond type illustrated for the simplest case in which an H^+ interacts with H_2 to give the triangular $[H_3]^+$ ion. Ψ_1 is fully bonding and occupied by the two available electrons for an H–H bond order of ⅓. The two antibonding orbitals are vacant.

1.9 FOUR-ELECTRON THREE-CENTER BONDING

The ligand field model is currently being challenged by a different three-center bonding picture, the sd^n model[21] This considers the *n*p orbitals as being ineffective in M–L bonding owing to poor overlap and mismatched energies and proposes that only the *n*s and five ($n - 1$)d orbitals contribute, *n* being 4, 5, and 6 for the first-, second-, and third-row d block metals. For example, photoelectron spectroscopy shows experimentally that Me_2TiCl_2 has sd^3 hybridization, not the familiar sp^3 hybridization, of, say, Me_2CCl_2. If so, one might expect d^6 metal complexes to prefer a 12 valence electron count, not 18e, since 12e would entirely fill the sd^5 set if we restrict ourselves to 2e,3c bonds. This would, however, wrongly lead us to expect to find $Mo(CO)_3$ rather than the observed $Mo(CO)_6$. To account for the additional bonding power of $Mo(CO)_3$, hypervalency is invoked, a model that calls for 4e to be delocalized over three centers (4e,3c bond).

Hypervalency[22], the ability of an element to exceed the valence electron count normally appropriate for the number of orbitals that are available, is best established in the main-group elements[23] such as sulfur, where an octet of eight valence electrons is appropriate for its single s and three p orbitals. In hypervalent SF_6, however, 6 electrons come from S and 1 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, now exploded, that empty d orbitals, such as 3d orbitals for S, allow the atom to house the excess electrons. In an important structural difference from the 2e,3c case which involved a ring arrangement of the three bonded atoms, the 4e,3c cases tend to be linear, leading to a different molecular orbital pattern (Fig. 1.8).

Hypervalent bonding is most simply illustrated for linear $[F–H–F]^-$ anion, where H formally has four valence electrons, exceeding its normal maximum of 2e. In $[FHF]^-$, the zero electron H^+ formally receives 2e from each of the lone pairs

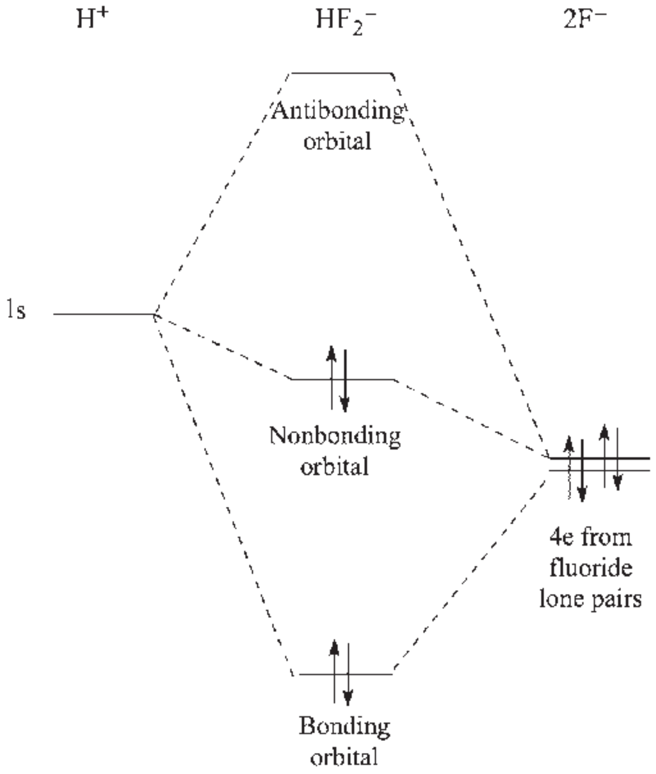


FIGURE 1.8 The four-electron three-center (4e-3c) hypervalent bonding model for $[FHF]^-$ anion in which the fluoride ions are considered ligands for the central H^+. The bonding and nonbonding orbitals are occupied and the antibonding orbital left vacant.

of the two F^- anions coordinated to it, thus resembling an ML_2 complex. The bonding pattern, shown in Fig. 1.8, allows the 4e from the two F^- to occupy two lower lying orbitals, each having a predominant F character – Ψ_1 bonding, Ψ_2 nonbonding – while leaving the highest energy Ψ_3 antibonding orbital empty. In effect, the 2e in Ψ_1 is spread over the two H–F bonds and the remaining 2e in the nonbonding Ψ_2 orbital are predominantly located on F. Not only is the conventional 2e limit for H essentially maintained but also the extra 2e are located on a highly electronegative atom, F. Notably, hypervalent compounds are much more common with electronegative ligands, so we have PF_5 but not PH_5.

The 4e–3c bonding in HF_2^- implies that each H- - -F bond is half-order, resulting in somewhat longer bonds (1.15 Å) than in the corresponding 2e,2c species, H–F (0.92 Å). $[FHF]^-$ anion, normally considered as a strong hydrogen-bonded adduct of HF and F^-, is here seen as hypervalent. Moving to the heavier p block elements, hypervalency is much more common: octahedral SF_6, for example, is hypervalent[22].

Hypervalency is most effective if the terminal atoms are electronegative since they must tolerate a significant partial negative charge. In d block complexes, the ligands are indeed often more electronegative than the metal, especially for O and N donors.

For CO, the carbon is unusually electronegative for that element because it has both an sp lone pair and a flanking O. In Mo(CO)$_6$, the bonding is explained in terms of three pairs of trans L–M–L hypervalent 4e–3c bonds, formed from sd^2 hybrids. This leaves three d orbitals that are set aside for back bonding to CO as the d_π set, as in LFT.

The fate of the sd^n model depends on whether it finds favor in the scientific community, and we do not use it extensively here. Textbooks can give the impression that everything is settled and agreed upon, but that agreement is achieved only after much argument, leading to an evolution of the community's understanding. Ideas that come to dominate often start out as a minority view. The sd^n model may therefore fade, flower, or evolve in future. The bonding model for hypervalency is uncontroversial in the main group, the only question being how far it can be applied to the d block.

1.10 BACK BONDING

Ligands such as NH$_3$ are good σ donors but insignificant π acceptors. CO, in contrast, is a good π acceptor (Chap. 4) but so poor a σ donor that free CO does not protonate. Such π-*acid* (i.e. π acceptor) ligands are of very great importance in organometallic chemistry as very high field ligands that form strong M–L bonds. All have empty orbitals of the right symmetry to overlap with a filled d_π orbital of the metal: for CO, this acceptor is the empty CO π*. Figure 1.9 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 only antibonding with respect to C and O and can still be bonding with respect to M and C. A second CO π*, oriented out of the image plane, can accept back bonding from a second d_π orbital that is similarly oriented. Back bonding takes its name because the M → L π electron donation is in the opposite direction from the L → M σ electron donation.

The ligand field diagram of Fig. 1.6 has to be modified for π acceptor ligands such as CO because we now need to include the CO π* levels (Fig. 1.10). The M d_π set now interacts strongly with the empty CO π* levels to form M–C π bonds. For d^6

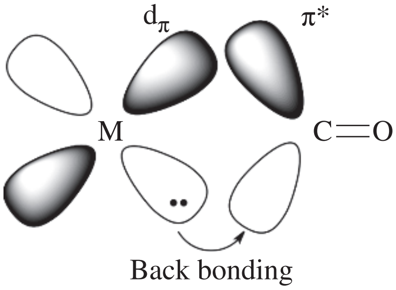


FIGURE 1.9 Overlap between a filled metal d_π orbital and an empty CO π* orbital to give the π component of the M–CO bond. The shading refers to the orbital symmetry. The M–CO σ bond is formed by the donation of a lone pair on C into an empty d_σ orbital on the metal (not shown).

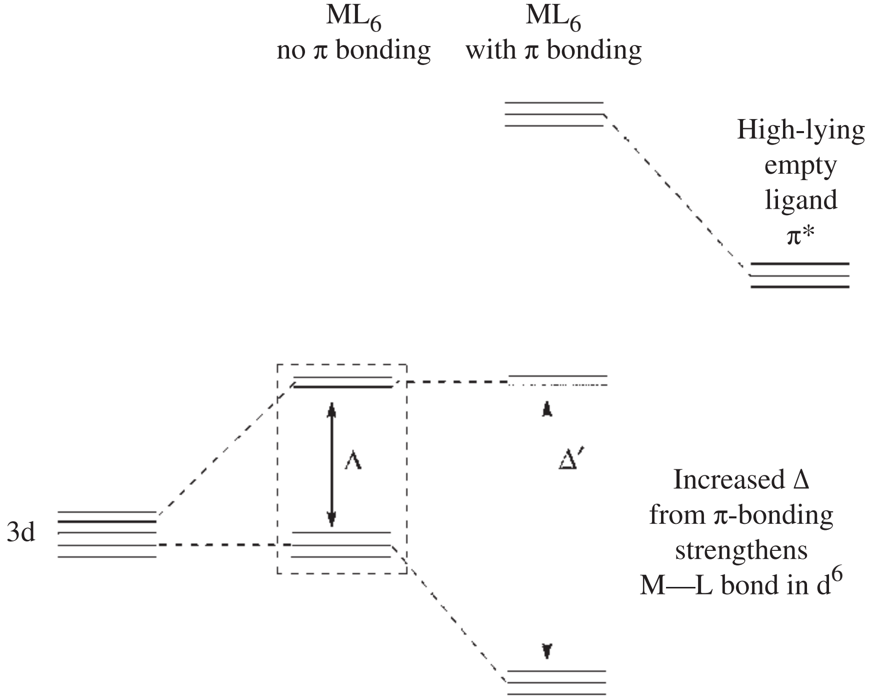


FIGURE 1.10 Effect of "turning on" the π interaction between a π-acceptor ligand such as CO and the metal. The unoccupied, and relatively unstable, π* orbitals of the ligand are shown on the right. Their effect is to stabilize the filled d_π orbitals of a d^6 complex, and increase both Δ and the metal–ligand bond strength.

complexes such as $W(CO)_6$, where the M d_π set is filled, the M d_π electrons now spend some of their time on the ligands by back bonding.

Back bonding can occur for a wide variety of M–L bonds as long as L contains a suitable empty orbital. In one type, where the donor atom participates in one or more multiple bonds, the empty orbital is a ligand π*, as is the case for CO or C_2H_4. As we see in detail in Sections 3.4 and 4.1, another type of ligand has suitable empty σ* orbitals, as in the case for PF_3 or H_2. Back bonding can only be effective in d^2 or higher configuration metals; a d^0 ion such as Ti^{4+} cannot back bond and very seldom forms stable complexes with strong π acceptor ligands such as CO.

Being antibonding, 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. 1.10. This has two important consequences: (i) The ligand field splitting parameter Δ rises, explaining why π-bonding ligands have such a strong ligand field and make such strong M–L bonds; and (ii) back bonding allows electron density on a low-oxidation-state metal to make its way back to the π-acid ligands. This applies when low-valent or zero-valent metals form CO complexes. Such metals have a high electron density in the free state and are thus reluctant to accept further electrons from pure σ donors; this is why $W(NH_3)_6$ is not known, alternatively seen as a mismatched soft–hard pair. By back bonding, the metal can get rid of some of this excess electron density and delocalize it over the π-acid ligands. In $W(CO)_6$, back bonding is so effective that the compound is air stable and relatively unreactive, unusual for W(0); the CO groups have so stabilized the metal electrons that they have no tendency to be abstracted by an oxidant such as air. In $W(PMe_3)_6$, in contrast, back bonding is weak and the complex is reactive and air unstable.

Their structures show that π back donation is a big contributor to the M=C bond in metal carbonyls, making the M=C bond much shorter than an M–C single bond. For example, in $CpMo(CO)_3Me$, M–CH_3 is 2.38 Å, but M=CO is 1.99 Å. A true M–CO single bond would be shorter than 2.38 Å by about 0.07 Å, to allow for the higher *s* character of sp CO versus sp^3 CH_3, leaving the substantial shortening of 0.32 Å that can be ascribed to back bonding.

IR spectroscopy identifies the CO π* orbital as the acceptor in back bonding. A CO bound only by its carbon lone pair – nonbonding with respect to CO – would have a ν(CO) frequency close to that in free CO. BH_3, a predominant σ acceptor, shows a slight shift of ν(CO) to *higher* energy in H_3B–CO: free CO, 2143 cm^{-1}; H_3B–CO, 2178 cm^{-1} so the shift is +35 cm^{-1}. Metal carbonyls, in contrast, usually show ν(CO) coordination shifts of hundreds of wavenumbers to *lower* energy, consistent with the weakening of the C–O bond as the CO π* is partially filled by back donation; for $Cr(CO)_6$, ν(CO) is 2000 cm^{-1}, so the shift is −143 cm^{-1}. Not only is there a coordination shift but the shift is also larger in cases where we would expect stronger back donation (Section 2.7) and ν(CO) is considered a good comparison indicator of basicity variations in different ML_n groups in $L_nM(CO)$. In Section 4.2, we see how the ν(CO) of $LNi(CO)_3$ helps us rank different ligands L in terms of their comparative donor power to M; better donor L ligands make the Ni back donate more strongly into the CO groups, thus lowering ν(CO).

Formation of the M–CO bond weakens the C≡O bond of free CO. This can still lead to a stable complex as long as the energy gained from the new M–C bond exceeds the loss in C≡O. Bond weakening within the ligand on binding is very common in M–L complexes where back bonding is significant. Not surprisingly, this effect also alters the reactivity pattern of the ligand (Section 4.1).

$[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$ are *isoelectronic* because V(−I), Cr(0), and Mn(I), all being d^6, have the same number of electrons similarly distributed. Isoelectronic ligands include CO, N_2 and NO^+, and CN^-, for example. Similarities and differences among isoelectronic metals or ligands can reveal trends[23] and suggest synthetic targets.

Frontier Orbitals

A similar picture holds for a whole series of soft, π-acceptor 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 molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of L, respectively. With a suitable choice of M and L, the HOMO of L is an electron pair donor to the d_σ LUMO of the metal, while the ligand LUMO is the acceptor for back donation from the metal HOMO, a filled metal d_π orbital. The HOMO and LUMO of each fragment, the so-called *frontier orbitals*, often dominate the bonding between the fragments. Strong interactions between orbitals require not only good overlap but also that the energy separation between them be small. The HOMO of each fragment, M and L, is usually closer in energy to the LUMO of the partner fragment than to any other vacant orbital of the partner. Strong bonding is thus expected if the HOMO–LUMO gap of both partners is small. Indeed, a small HOMO–LUMO gap for any molecule gives it high reactivity. A small HOMO–LUMO gap also makes a ligand soft because it becomes a good π acceptor, and for d^6, makes the metal soft because it becomes a good π donor.

π-Donor Ligands

Ligands such as OR^- and F^- 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 an octahedral 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. 1.11, and leads to a weaker M–L bond than in the π-acceptor case, as in high spin d^6 $[CoF_6]^{3-}$. Lone pairs on electronegative atoms such as F^- and RO^- are much more stable than the $M(d_\pi)$ level, and this is why they are lower in Fig. 1.11 than are the π* orbitals in Fig. 1.10. Having more diffuse lone pairs, larger donor atoms pose fewer such problems and Cl^- and R_2P^- are much better tolerated by d^6 metals.

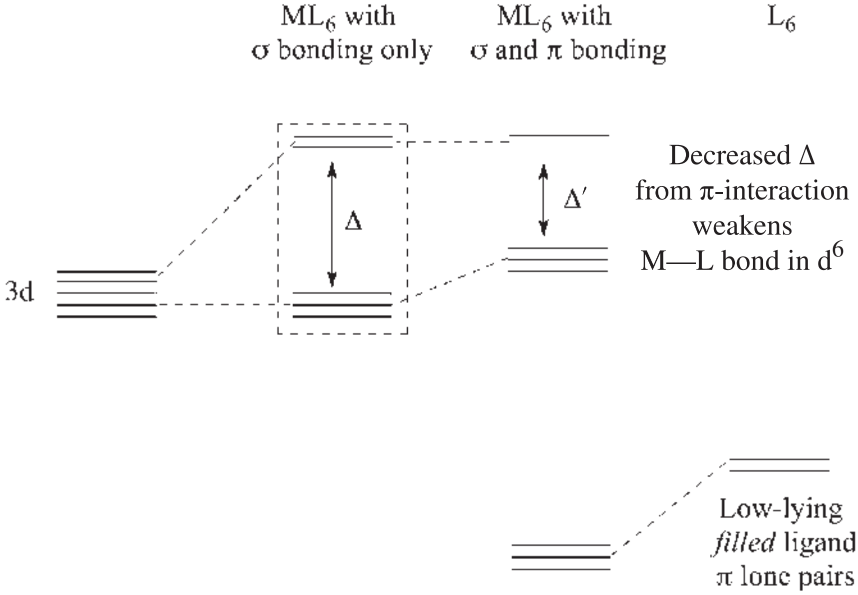


FIGURE 1.11 Effect of "turning on" the π interaction between a π-donor ligand such as F^- and the metal. The occupied, and relatively stable, lone-pair (π) orbitals of the ligand are shown on the right. Their effect is to destabilize the filled d_π orbitals of the d^6 complex and so decrease Δ. This is effectively a repulsion between two lone pairs, one on the metal and the other on the ligand, and thus weakens the M–L bond. In d^0, in contrast, not only is this repulsion no longer present but the π donation from the ligand lone pairs into the empty metal d_π orbitals stabilizes these electrons and strengthens M–L bonding.

In sharp contrast, if the metal has empty d_π orbitals, as in the d^0 ion Ti^{4+}, π donation from the π-donor ligand to the metal d_π orbitals now leads to stronger metal–ligand bonding; d^0 metals therefore form particularly strong bonds with such ligands, as in $W(OMe)_6$ or $[TiF_6]^{2-}$, both also examples of favorable hard metal–hard ligand combinations.

1.11 TRENDS IN d ORBITAL ENERGIES

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, thus providing an extra positive charge that stabilizes all the orbitals but the extra electron added goes into an existing level if we keep in the same row. The earlier metals are more electropositive because it is easier to remove electrons from their less-stable orbitals. The orbitals are more stabilized in the order $d \sim s > p$ because the s orbital, having a maximum electron density at the nucleus, is more stabilized by the added protons than are the p orbitals, with a planar node at the nucleus. The d orbitals are also stabilized because of their lower principal quantum number as is the case for 3d versus 4s and 4p in the valence shell of Fe. One special property of the transition metals is that all three types of orbital are in the valence shell with similar energies so all contribute significantly to the bonding, only omitting the 4p if the sd^n model is adopted. Metal carbonyls, for example, are most stable for groups 4–8 because CO requires back bonding to bind strongly; and in the later groups, the needed d_π orbitals become too stable to be effective.

There is a sharp difference between d^0 and d^2 as in Ti(IV) versus Ti(II): d^0 Ti(IV) cannot back bond at all, while d^2 Ti(II) is a very strong back bonder because early in the transition series, where d^2 states are most common, the d orbitals are relatively unstable for the reasons mentioned. 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 low ν(CO) IR frequency, indicating very strong back bonding (Chap. 4).

Finally, as we go down a given group in the d block from the first to the second row, the outer valence electrons become more *shielded* from the nucleus by the extra shell of electrons added. They are therefore more easily lost, making the heavier d block element more basic and more easily able to attain high oxidation states. 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 thus a smaller change on going from the second to the third row than from the first to the second. Compare, for example, the powerfully oxidizing Cr(VI) in Na_2CrO_4 and Mn(VII) in $KMnO_4$, with their stable second- and third-row analogs, Na_2MoO_4, Na_2WO_4, and $KReO_4$; the very weakly oxidizing character of the latter indicates an increased stability for the higher oxidation state. For the same reason, the increase in covalent radii is larger on going from the first to the second row than from the second to the third. This anomaly in atomic radius for the third row is termed the *lanthanide contraction* and results from the 14 extra protons in the nucleus from the intervening f elements not being adequately shielded by the added f electrons.

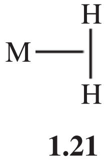
Another trend to look for in what follows is the preference of the first-row d block to undergo ±1e oxidation state changes (e.g. Co(I,II,III)) versus the tendency to undergo ±2e oxidation state changes in the second and third row (e.g. Ir(I,III,V)). The greater preference for even d^n configurations in the second and third row is one factor: for example, Ir(I), (III), and (V) are spin paired d^8, d^6, and d^4. This probably arises from the larger orbitals in the second and third row reducing the e – e repulsion penalty of having 2e in the same orbital, taken together with the greater ligand field splittings which make low spin and the even d^n states relatively more stable, the HOMO tending to be more stable and the LUMO to be less stable in the heavier metals.

Mononuclear ionic complexes with excessively high positive or negative net ionic charges are not normally seen. The majority of isolable compounds are neutral, net charges of ±1 are not uncommon, but higher net ionic charges are increasingly rare.

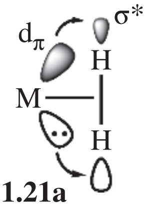
1.12 TYPES OF LIGAND

Most ligands are Lewis bases and thus typically neutral or anionic, rarely cationic[24]. Anionic ligands, often represented as X, or X^- in the ionic model, form polar covalent M–X bonds. In addition to the σ bond, there can also be a π interaction which may be favorable or unfavorable, as discussed in Section 1.10.

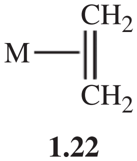
Among neutral ligands, often denoted L, we find lone-pair (l.p.) donors such as :CO or :NH_3 that bind end-on as in M–C≡O. In contrast, π donors such as C_2H_4 or C_6H_6, and σ donors such as H_2 bind side-on, as in **1.21** and **1.22**. The π donors bind via donation of a ligand π-bonding electron pair, and σ donors bind via donation of a ligand σ-bonding electron pair to the metal. Structure **1.21** is a clear example of 2e,3c bonding. In this case, the 2e from the H–H′ bond are donated to M so as to link all three centers, M, H, and H′. The very weakly basic H–H σ bond would form only a very weak M–(H_2) bond if acting alone. There is also some back bonding (Section 1.10) from the filled M d_π orbitals into the empty H–H σ^* orbital (see **1.21a**, where only two of the M d_π lobes are shown). If back bonding becomes very strong, a dihydride can form by OA as in Eq. (1.5). The strength of M–L binding tends to decrease as we move from lone pair to π bond to σ bond donor ligands, other factors being equal, because basic character tends to fall as l.p. > π bond > σ bond. We defer a detailed discussion of M–L bonding to Chaps 4–6.



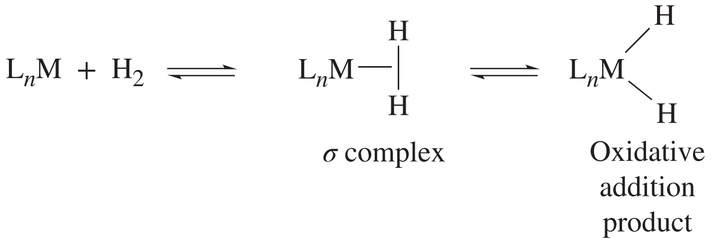
1.21



1.21a



1.22



(1.5)

Zero-Electron Ligands

Not all ligands are bases – we can also have *e* pair acceptors, such as BF_3, where the direction of the donation is metal-to-ligand. Since they donate zero electrons to the metal, they are often designated Z ligands. These form the most recently recognized class, about which there is still some controversy[25, 26].

Ambidentate Ligands

The $\{(NH_3)_5Os^{II}\}^{2+}$ fragment in Eq. (1.8) is a very strong π donor because Os(II) is soft and NH_3 is not a π acceptor; the π-basic Os thus prefers to bind to the π-acceptor aromatic C=C bond of aniline, not to the nitrogen. Oxidation to Os^{III} causes a sharp falloff in π-donor power because the extra positive charge stabilizes the d orbitals, and the Os(III) complex slowly rearranges to the more stable N-bound form. This illustrates how the electronic character of a metal can be altered by changing the ligand set and oxidation state; soft Os(II) prefers the soft C=C bond and hard Os(III) prefers the hard $ArNH_2$ group.

Fig. 1.12 shows the typical ligands found for different oxidation states of Re, an element with a very wide range of accessible states. Low OS complexes are stabilized by multiple π-acceptor CO ligands, intermediate OSs by less π-acceptor phosphines,

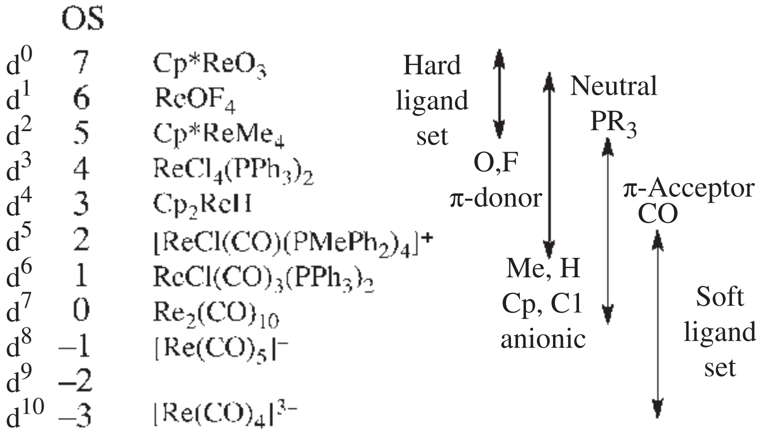


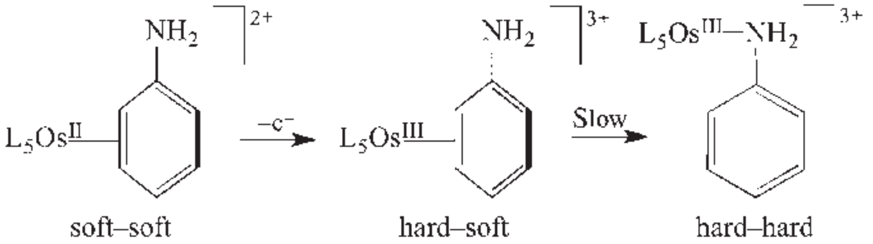
FIGURE 1.12 Some Re complexes showing typical variation of ligand type with oxidation state (OS): hard ligands with high OS and soft ligands with low OS.

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.

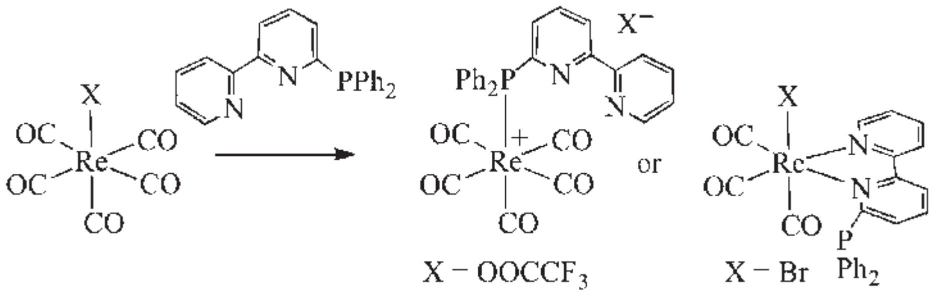
Some ligands have alternative binding sites, as we can see in Eq. (1.6–1.9)[27].

(1.6)

(1.7)



(1.8)

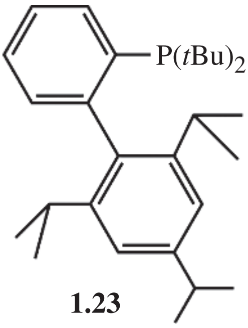


(1.9)

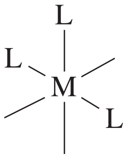
Actor and Spectator Ligands

Spectator ligands remain unchanged during chemical transformations but still play an important role by tuning the properties of the metal to vary its key characteristics. For example, in the extensive chemistry of $[CpFe(CO)_2X]$ and $[CpFe(CO)_2L]^+$ (Cp = cyclopentadienyl; X = anion; L = neutral ligand), the $\{CpFe(CO)_2\}$ fragment usually remains intact. The spectators impart solubility, stabilize Fe(II), and influence the electronic and steric properties of the complex. It is an art to pick suitable spectator ligand sets to elicit desired properties. What seem small changes in a ligand can entirely change the chemistry. For example, PPh_3 is an exceptionally useful ligand, while the apparently similar NPh_3, $BiPh_3$, and $P(C_6F_5)_3$ are of very little use. The hard N donor, NPh_3, is unlike softer PPh_3; the Bi–Ph bond in $BiPh_3$ is too easily cleaved; and the electron-withdrawing C_6F_5 substituents of $P(C_6F_5)_3$ completely deactivate the P lone pair. In contrast, actor ligands react in some useful way, for example, by association, dissociation, or rearrangement.

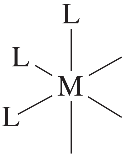
Steric size sets the maximum number of ligands, n, that can fit around a given metal in a d block ML_n complex. Typical n values depend on the size of the ligand: H, 9; CO, 7; PMe_3, 6; PPh_3, 4; $P(C_6H_{11})_3$, 2 and then only in a trans arrangement; a few ligands are so big that $n = 1$, e.g. X-Phos (**1.23**). If a big spectator ligand can occupy no more than n sites when the metal has m sites available, then $m - n$ sites are kept open for smaller actor ligands. Multidentate spectator ligands can have the n donor atoms arranged in specific patterns and geometries, making the $m - n$ available sites take up a predictable geometry. A small sample of such ligands is shown in Fig. 1.12. The tridentate ligands can bind to an octahedron either in a *mer* (meridonal) manner **1.24m** or *fac* (facial) **1.24f**, or in some cases, in both ways. Ligands that normally bind in terdentate *mer* manner are termed pincers. Not only do these benefit from the chelate effect but they also allow us to control the binding at three sites of an octahedron, leaving three *mer* sites accessible to reagents.



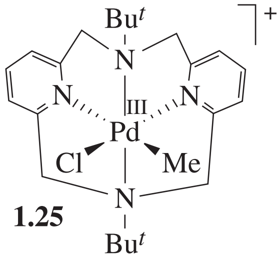
1.23



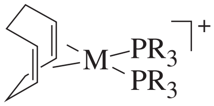
1.24m
mer



1.24f
fac



1.25



1.26

Tetradentate ligands such as **1.25** can also prove useful, in this case by stabilizing the unusual Pd(III) oxidation state[28]. The choice of ligand is an art because subtle stereoelectronic effects, still not fully understood, can play an important role. The two PPP pincer ligands in Fig. 1.13 impart substantially different properties to their complexes in spite of their apparent similarity, probably because of the greater flexibility of the three-carbon linker.

Actor ligands may allow isolation of a stable, storable material as a precursor to a reactive species only formed subsequently after the departure of the actor, the reactive species either being too reactive to isolate or not otherwise easily accessible. A classic example is chelating 1,5-cyclooctadiene (cod) that binds to Rh(I) or Ir(I) in the $[(cod)M(PR_3)_2]^+$ hydrogenation catalysts (**1.26** M = Rh, Ir). Under H_2, the cod is hydrogenated to free cyclooctane, liberating $\{M(PR_3)_2\}^+$ as the active catalyst. Until

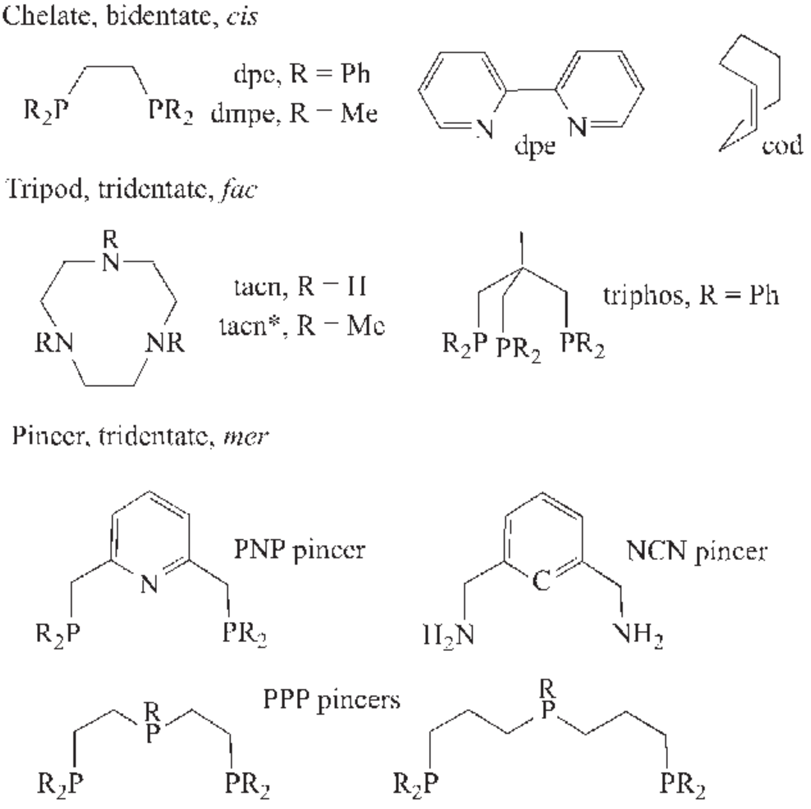


FIGURE 1.13 A selection of common ligands with different binding preferences.

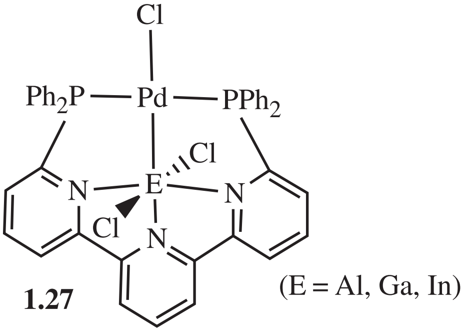
recently, Cp* was regarded as a reliable spectator, but occasional contrary examples are now being found. For example, the Cp* in a Cp*IrL_2Cl complex is lost under relatively mild conditions to give a catalyst capable of hydrogenating C=O bonds[29].

Multifunctional Ligands

This rising class of more sophisticated ligands are increasingly being seen. Beyond the simple metal-binding function, numerous additional functionalities can also be incorporated[30]. Some ligands reversibly bind protons, altering their donor properties, others have hydrogen bonding functionality for molecular recognition. Sometimes, a complex can be oxidized or reduced[31], but the resulting radical is ligand-centered so that the metal oxidation state is unchanged.

Main-group Ligands

Complexes between transition metals and the heavier main-group elements beyond P, Si, and the halides, although long known, as in $[Pt(SnCl_3)_5]^{3-}$, have recently attracted increased attention, as in **1.27**[32]. Hydrosilylation catalysis (Section 9.6), the addition of H–SiR_3 across alkene C=C bonds, also involves M–SiR_3 intermediates.



1.27

- High trans effect ligands such as H or CO labilize ligands that are located trans to themselves.
- In CFT (Section 1.6), 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 1.7) 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. 1.10 and 1.11).
- Ligands can bind via lone pairs, π bonding e⁻ pairs or σ bonding e⁻ pairs (Section 1.12).
- Octahedral d^3 and d^6 are coordination inert and slow to dissociate a ligand.

REFERENCES

1. Sheldon, R.A. (2017). *Green Chem.* 19: 18.
2. Bolm, C. (2012). *Org. Lett.* 14: 2926.
3. Lahann, J. (2009). *Click Chemistry for Biotechnology and Materials Science*. New York: Wiley.
4. Lan, Y., Li, G., Wang, Z. et al. (2017). *Dyes Pigm.* 144: 158.
5. Marloye, M., Berger, G., Gelbcke, M., and Dufrasne, F. (2016). *Future Med. Chem.* 8: 2263.
6. Jaouen, G. and Salmain, M. (2015). *Bioorganometallic Chemistry: Application in Drug Discovery, Biocatalysis, and Imaging*. Weinheim: Wiley-VCH.
7. Whitesides, G.M. and Deutch, J. (2011). *Nature* 469: 21.
8. Marcott, S.A., Shakun, J.D., Clark, P.U., and Mix, A.C. (2013). *Science* 339: 1198.
9. Helm, M.L., Stewart, M.P., Bullock, R.M. et al. (2011). *Science* 333: 863.
10. Michaelos, T., Shopov, D.Y., Sinha, S.B. et al. (2017). *Acc. Chem. Res.* 50: 952.
11. Lawrance, G.A. (2009). *Introduction to Coordination Chemistry*. New York: Wiley.
12. Constable, E.C. and Housecroft, C.E. (2013). *Chem. Soc. Rev.* 42: 1429.

13. Peris, E. and Crabtree, R.H. (2018). *Chem. Soc. Rev.* 47: 1959.
14. van Koten, G. (2017). *J. Organomet. Chem.* 845: 4.
15. Nugent, W.A. (2012). *Angew. Chem. Int. Ed.* 51: 2.
16. Liang, L.C. (2006). *Coord. Chem. Rev.* 250: 1152.
17. Gerber, W.J., van Wyk, P.-H., van Niekerk, D.M.E., and Koch, K.R. (2015). *Phys. Chem. Chem. Phys.* 17: 5712.
18. Bolvin, H. (2010). *Eur. J. Inorg. Chem.* 2010: 2221.
19. Boergel, J., Campbell, M.G., and Ritter, T. (2016). *J. Chem. Educ.* 93: 118.
20. Hoffmann, R., Alvarez, S., Mealli, C. et al. (2016). *Chem. Rev.* 116: 8173.
21. Weinhold, F. and Landis, C.R. (2005). *Valency and Bonding*. Cambridge University Press.
22. Crabtree, R.H. (2017). *Chem. Soc. Rev.* 46: 1720.
23. Green, M.L.H. and Parkin, G. (2016). *Dalton Trans.* 45: 18784.
24. Solans-Monfort, X., Coperet, C., and Eisenstein, O. (2012). *Organometallics* 31: 6812.
25. Green, M.L.H. and Parkin, G. (2014). *J. Chem. Educ.* 91: 807.
26. Parkin, G. (2006). *Organometallics* 25: 4744.
27. West, N.M., Labinger, J.A., and Bercaw, J.E. (2011). *Organometallics* 30: 2690.
28. Khusnutdinova, J.R., Rath, N.P., and Mirica, L.M. (2010). *J. Am. Chem. Soc.* 132: 7303.
29. Campos, J., Hintermair, U., Brewster, T.P. et al. (2014). *ACS Catal.* 4: 973.
30. Crabtree, R.H. (2011). *New J. Chem.* 35: 18.
31. Luca, O.R. and Crabtree, R.H. (2013). *Chem. Soc. Rev.* 42: 1440.
32. Takaya, J. and Iwasawa, N. (2017). *J. Am. Chem. Soc.* 139: 6074.

PROBLEMS

1.1. How many isomers would you expect for a complex with an *empirical* formula corresponding to $Pt(NH_3)_2Cl_2$?

1.2. What d^n configurations should be assigned to the following and what magnetic properties – dia- or paramagnetic – are to be expected from the hexaqua complexes of Zn(II), Cu(II), Cr(II), Cr(III), Mn(II), and Co(II)?

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

1.4. How would you design a synthesis of the complex *trans*-$[PtCl_2(NH_3)(tu)]$, (trans means that the Cl ligands are mutually trans), given that the trans effect order is $tu > Cl > NH_3$ [$tu = (H_2N)_2CS$, a ligand that binds via S]?

1.5. Predict the relative rates of reaction of NMe_3, PMe_3, and CO with each of the two complexes $MeTiCl_3$ and $(CO)_5W(thf)$.

1.6. Without using crystallography, how could you distinguish between a square planar and a tetrahedral geometry in a nickel(II) complex such as $K_2[NiCl_4]$?

1.7. 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?

1.8. The stability of metal carbonyl complexes falls off markedly as we go to the right of group 10 in the periodic table. For example, Cu complexes only bind CO weakly or not at all. Why is this? Which oxidation state, of the ones commonly available to copper, would you expect to bind CO most strongly?

1.9. Low-oxidation-state complexes are often air sensitive (i.e. they react with the O_2 in the air) but are rarely water sensitive. Why do you think this is so?

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

1.11. Why does the ligand in **1.25** bind as a clamshell with the Me and Cl sites mutually cis, and not in a coplanar arrangement with Me and Cl mutually trans?

1.12. Work out the Jahn–Teller effects expected for octahedral ions of all possible d^n configurations and spin states to check that the information in Table 1.3 is correct.