

## Review of Basic Principles:

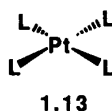
The following was adapted from *The Organometallic Chemistry of the Transition Metals*, 2<sup>nd</sup> Edition by Robert H. Crabtree. If you have not previously studied the chemistry of transition metals in undergrad, this is an excellent text to bring you up to speed.

## THE TRANS EFFECT

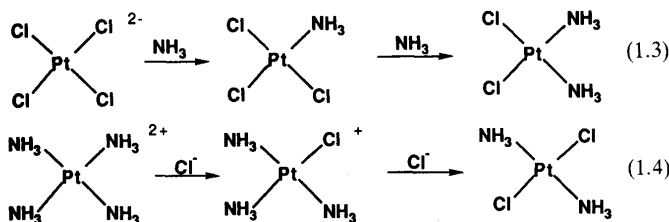
In the 1920s, Chernaev discovered that certain ligands facilitate the departure of a second ligand trans to the first, and their replacement or *substitution*, by an external ligand. Ligands that are more effective at this labilization are said to have a higher *trans effect*. The effect is most marked in substitution in Pt(II), and that the highest trans-effect ligands either form unusually strong  $\sigma$  bonds, such as  $\text{H}^-$ ,  $\text{Me}^-$ , or  $\text{SnCl}_3^-$ , or unusually strong  $\pi$  bonds, such as  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ , and thiourea  $(\text{NH}_2)_2\text{CS}$ , 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 constant in the NMR, or the  $\nu(\text{M-L})$  stretching frequency in the IR (infrared) spectrum. A change in the ground-state thermodynamic properties, such as these, is usually termed the *trans influence* to distinguish it from the parallel effect on the properties of the transition state for the substitution reaction, which is the trans effect proper, and refers to differences in *rates* of substitution and is therefore a result of a change in the energy difference between the ground state and transition state for the reaction.

Note that 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).



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  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  can be prepared selectively by taking advantage of the trans-effect order  $\text{Cl} > \text{NH}_3$ . 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.

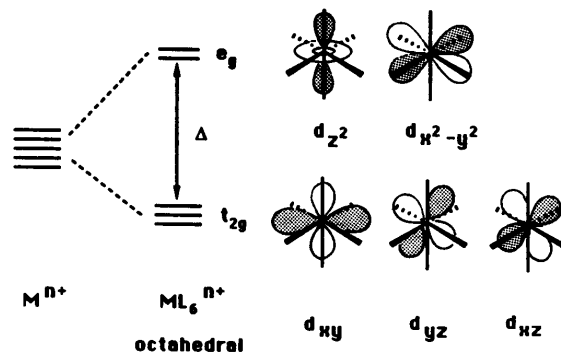


## THE CRYSTAL FIELD

An important advance in understanding the spectra, structure, and magnetism of transition metal complexes is provided by the *crystal field* model. The idea is to try to find out how the  $d$  orbitals of the transition metal are affected 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  $\text{Cl}^-$  as a ligand, we just think of the net negative charge on the ion; for  $\text{NH}_3$ , 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  $\pm x$ ,  $\pm y$ , and  $\pm z$ , 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.

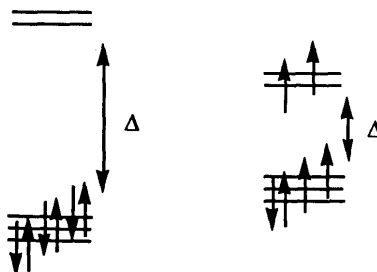
The pair of orbitals that are most strongly destabilized are often identified by their symmetry label,  $e_g$ , or simply as  $d_\sigma$ , because they point along the M-L  $\sigma$ -bonding directions. The three more stable orbitals have the label  $t_{2g}$ , or simply  $d_\pi$ ; these point away from the ligand directions but can form  $\pi$  bonds with the ligands. The magnitude of the

energy difference between the  $d_\sigma$  and  $d_\pi$  set, usually called the *crystal field splitting*, and labeled  $\Delta$  (or sometimes  $10Dq$ ) depends on the value of the effective negative charge and therefore on the nature of the ligands.



**FIGURE 1.1** The effect on the  $d$  orbitals of bringing up six ligands along the  $\pm x$ ,  $\pm y$ , and  $\pm z$  directions. In this figure, shading represents the symmetry (not the occupation) of the  $d$  orbitals; shaded parts have the same sign of  $\psi$ .

This picture explains why  $\text{Co}^{3+}$ , the metal ion Werner studied, has such a strong preference for the octahedral geometry. As a Group 9 element, Co has 9 electrons. The  $3+$  ion, of course, has  $(9 - 3)$  or 6 electrons, and is therefore said to have a  $d^6$  configuration. Six electrons just fill the three low-lying  $d_\pi$  orbitals of the crystal field diagram, and leave the  $d_\sigma$  empty. This is a particularly stable arrangement, and other  $d^6$  metals,  $\text{Mo}(\text{O})$ ,  $\text{Re}(\text{I})$ ,  $\text{Fe}(\text{II})$ ,  $\text{Ir}(\text{III})$ , and  $\text{Pt}(\text{IV})$  also show a very strong preference for the octahedral geometry. 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 rearrange to give the *high-spin* form  $t_{2g}^4 e_g^2$ . In the high-spin form all the 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  $\Delta$  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 of the complex. This is done by placing 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. The complex does not itself form a permanent magnet as will a piece of iron or nickel (this property is called *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.



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

Although the great majority of organometallic complexes are diamagnetic, because  $\Delta$  is usually large in these complexes, we should not lose sight of the possibility that any given complex may be paramagnetic. This will always be the case for molecules like  $\text{V}(\text{CO})_6$ , 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  $\Delta$  tends to be smaller than in the later rows. Sometimes the low- and high-spin forms 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  $\text{Fe}(\text{S}_2\text{CNET}_2)_3$ , for example.

In an octahedral  $d^7$  ion we are obliged to place one electron in the higher-energy (less stable)  $d_\sigma$  level to give the configuration  $t_{2g}^6 e_g^1$ , and this will normally make the complex paramagnetic (Fig. 1.3). The net stabilization, often termed 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  $d^7$  ions [e.g.,  $\text{Co}(\text{II})$ ],

which, as long as they remain octahedral, are more reactive than their  $d^6$  analogs. For example, they undergo ligand dissociation much more readily. The reason is that the  $d_{\sigma}$  levels are really M-L  $\sigma$ -antibonding in character, as we see later. Werner was able to study his chemistry with Co(III) because the ligands tend to stay put. This is why Co(III) and other  $d^6$  ions are often referred to as *coordinatively inert*;  $d^3$  ions like 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 can be *coordinatively labile*.

The colors of transition metal ions often arise from the absorption of light that corresponds to the  $d_{\pi}$ - $d_{\sigma}$  energy gap,  $\Delta$ . 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  $\Delta$ . Low-field ligands, such as  $H_2O$  or  $NH_3$ , can give such a low  $\Delta$ , that the spin pairing is lost and even *the  $d^6$  configuration can become paramagnetic* (Fig. 1.2, right hand side). This rarely occurs for organometallic ligands, since they tend to induce a large  $\Delta$  splitting, and are therefore high-field ligands.

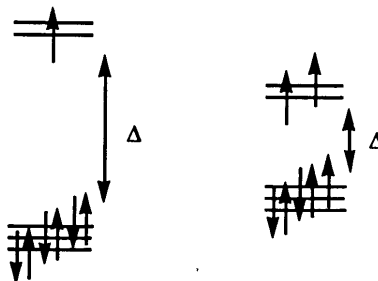


FIGURE 1.3 A  $d^7$  ion is paramagnetic even in the low-spin form.

Other important crystal field splitting patterns are shown in Fig. 1.4. For the same ligand set, the tetrahedral splitting parameter is smaller than that for the octahedral geometry by a factor of  $2/3$  because we now have only four ligands, not six, and so the chance of having a high-spin species is greater. The ordering of the levels is also reversed; three increase and only two decrease in energy. This is because the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals now point toward, and the  $d_{x^2-y^2}$ , and  $d_{z^2}$  orbitals away from, the ligands. The  $d^{10}$  ions [e.g., Zn(II), Pt(0), Cu(I)] are often tetrahedral. The square planar splitting pattern is also shown. This geometry tends to be adopted by  $d^8$  ions such as Au(III), Ni, Pd or Pt(II), and Rh or Ir(I), in which case the complex is diamagnetic; it is also common for paramagnetic  $d^9$ , such as Cu(II).

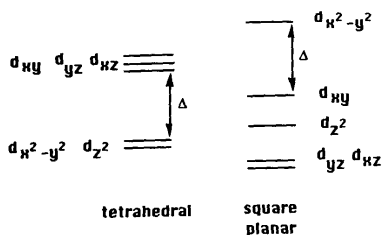
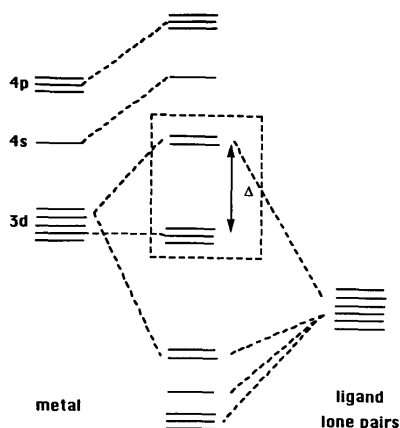


FIGURE 1.4 Crystal field splitting patterns for the common coordination geometries: tetrahedral and square planar. For the square planar arrangement, the  $z$  axis is conventionally taken to be perpendicular to the square plane.

## THE LIGAND FIELD

The crystal field picture gives a useful understanding, which is widely used for *"back of the envelope"* (qualitative) discussions. Once having established an idea of what to expect, we may need to turn to the more sophisticated *ligand field* model, which is really a conventional molecular orbital or m.o. picture for accurate electronic structure calculations. In this model (Fig. 1.5), 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  $\sigma$ -donor ligands in an octahedron around the metal. Six of the metal orbitals, the  $s$ , the three  $p$ , and the two  $d_{\sigma}$ , which we will call the  $d_{sp_{\sigma}}$  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  $\sigma$  bonds) that are stabilized, and an antibonding set of six (the M-L  $\sigma^*$  levels) that are destabilized when the six L groups approach bonding distance. The remaining three  $d$  orbitals, the  $d_{\pi}$  set, do not find a match among the ligand orbitals, and remain nonbonding. In a  $d^6$  ion, we have 6e (six electrons) from  $Co^{3+}$  and 12e from the ligands, giving 18e in all. This means that all the levels up to and including the  $d_{\pi}$  set are filled, and the M-L  $\sigma^*$  levels remain unfilled. Note that we can identify the familiar crystal field splitting pattern in the  $d$ , and two of the M-L  $\sigma^*$  levels. The  $\Delta$  splitting will increase as the strength of the M-L  $\sigma$  bonds increase. The bond strength is the analog of the effective charge in the crystal field model. In the ligand field picture, high-field ligands are ones that form strong  $\sigma$  bonds. We can now see that a  $d_{\sigma}$  orbital is better described in the crystal field picture as an M-L  $\sigma$  antibonding orbital.



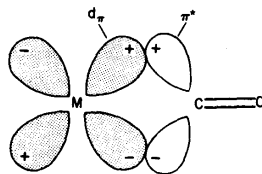
**FIGURE 1.5** The molecular orbital, or ligand field picture of metal ligand bonding in an  $ML_n$  complex.

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  $\sigma$  bonds are formed; these are the six lowest orbitals in Fig. 1.5 and are always completely filled (12 electrons). Each M-L  $\sigma$ -bonding m.o. is formed by the combination of the ligand lone pair,  $L(\sigma)$ , with  $M(d_\sigma)$  and has both metal and ligand character, but  $L(\sigma)$  predominates. Any m.o. will more closely resemble the parent atomic orbital that lies closest in energy to it, and  $L(\sigma)$  almost always lies below  $M(d_\sigma)$  and therefore closer to the M-L  $\sigma$ -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  $L(\sigma)$  lone pairs are partially transferred to the metal. As L becomes more basic, the energy of the  $L(\sigma)$  orbital increases, and the extent of electron transfer will increase. An orbital that is higher in energy will appear higher in the m.o. 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 interactions.

Using the language of organic chemistry, 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, tend to attack the electrophilic metal, which is an acceptor for lone pairs, to give the metal complex. One special feature of metal ions is their ability to accept multiple lone pairs so that the complex formed is not just ML but  $ML_n$  ( $n = 2-9$ ).

## BACK BONDING

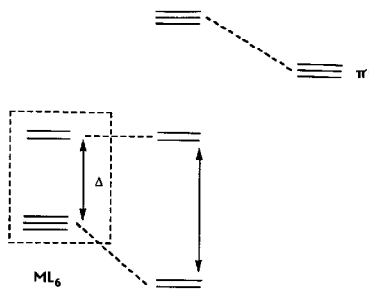
Ligands like  $NH_3$  are good  $\sigma$  donors but are not significant  $\pi$  acceptors. CO, in contrast, is an example of a good  $\pi$  acceptor, sometimes also called a  *$\pi$ -acid ligand*. Such ligands are of very great importance in organometallic chemistry. They tend to be very high-field ligands and form strong M-L bonds. All have empty orbitals of the right symmetry to overlap with a filled  $d_\pi$  orbital of the metal. In the case of CO, this orbital is the  $CO \pi^*$ . Figure 1.6 shows how overlap takes place to form the M-C  $\pi$  bond. It may seem paradoxical that an antibonding orbital like the  $\pi^*(CO)$  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.



**FIGURE 1.6** The overlap between a filled metal  $d_\pi$  orbital and an empty  $CO \pi^*$  orbital to give the  $\pi$  component of the M—CO bond. The shading refers to occupancy of the orbitals and the + and - signs, to the symmetry. The M—CO sigma bond is formed by the donation of a lone pair on C into an empty  $d_\sigma$  orbital on the metal (not shown).

We can make the ligand field diagram of Fig. 1.5 appropriate for the case of  $W(CO)_6$  by including the  $\pi^*$  levels of CO (Fig. 1.7). The  $d_\pi$  set of levels still find no match with the six  $CO(\sigma)$  orbitals, which are lone pairs on C. They do interact strongly with the empty  $CO \pi^*$  levels. Since the  $Md_\pi$  set are filled in this  $d^6$  complex, the result is that  $d_\pi$  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 is called *back bonding* and is a key feature of M-L bonds where L is an unsaturated molecule (i.e., has double bonds). Note that this can only happen in  $d^2$  or higher configurations; a  $d^0$  ion like  $Ti^{4+}$  cannot back bond and does not form stable carbonyl complexes.

As antibonding orbitals, the CO  $-\pi^*$  levels are high in energy, but they are able to stabilize the  $d_{\pi}$  set as shown in Fig. 1.7. This has two important consequences: (1) the ligand field splitting parameter  $\Delta$  rises, explaining why  $\pi$ -bonding ligands have such a strong ligand field; and (2) back bonding allows electron density on the metal makes its way back to the ligands. This, in turn, allows low-valent or zero-valent metals to form complexes. Such metals are in a reduced state, and already have a high electron density. (They are said to be very *electron-rich*.) They cannot accept further electrons from pure  $\sigma$  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 electrons that they have no tendency to be abstracted by an oxidizing agent. In  $W(PMe_3)_6$ , in contrast, back bonding is inefficient and the compound is very air-sensitive and reactive.



**FIGURE 1.7** The effect of “turning on” the  $\pi$  interaction between a  $\pi$ -acceptor ligand and the metal. The unoccupied, and relatively unstable  $\pi^*$  orbitals of the ligand are shown on the right. Their effect is to stabilize the filled  $d_{\pi}$  orbitals of the complex and so increase  $\Delta$ . In  $W(CO)_6$ , the lowest three orbitals are filled.

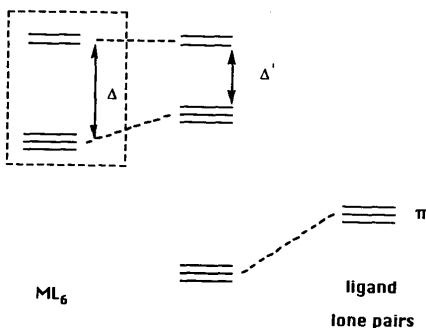
Spectroscopic and theoretical studies show that for CO this  $\pi$  back donation is usually comparable to or greater than the CO-to-metal electron donation that constitutes the  $\sigma$  bond. One of the most direct arguments is structural. The M=C bond in metal carbonyls is usually substantially shorter 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 remember 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.

We now need to confirm that it really is the  $\pi^*$  orbital of CO that is involved in the back bonding. To do this we turn to IR (infrared) spectroscopy. If CO were bound to the metal by its carbon lone pair, which is nonbonding with respect to CO, then the  $\nu(CO)$  frequency in the complex would be very little different from that in free CO. The compound  $BH_3$ , which is as pure a  $\sigma$  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 that would be expected if the  $\pi^*$  orbital were being 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  $\sigma$ -acceptor COs by the three pure  $\sigma$ -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  $\nu(CO)$  a good indicator of how electron-rich a metal is, and it often correlates well with other ways of estimating electron-rich character, such as the ease of removing an electron.<sup>4</sup>

**Frontier Orbitals** The picture we have sketched out for CO holds with slight modifications for a whole series of  $\pi$  acceptor (or soft) ligands, such as alkenes, alkynes, arenes, carbenes, carbynes, NO,  $N_2$ , and  $PF_3$ . Each of these ligands has a filled orbital that acts as a  $\sigma$  donor and an empty orbital that acts as a  $\pi$  acceptor. These orbitals are almost always the highest filled (*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  $d_{\sigma}$ . The *lumo* of the ligand accepts back donation from a filled  $d_{\pi}$  orbital of the metal. The *homo* and *lumo* of each fragment are the so-called *frontier orbitals*, and it is nearly always the case that these 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 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  $\pi$  acceptor.

**$\pi$ -Donor Ligands** Ligands such as  $OR^-$ ,  $F^-$ , and  $Cl^-$  are  $\pi$  donors as a result of the lone pairs that are left after one

lone pair has formed the M-L  $\sigma$  bond. Instead of stabilizing the  $d_{\pi}$  electrons of a  $d^6$  ion as does a  $\pi$  acceptor, these electrons are now destabilized by what is effectively a repulsion between two filled orbitals. This lowers  $\Delta$ , as shown in Fig. 1.8 and leads to a weaker M-L bond than in the  $\pi$ -acceptor case. Lone pairs on electronegative atoms such as Cl and O are much more stable than the  $M(d_{\pi})$  level, and this is why they are lower in Fig. 1.8 than are the  $\pi^*$  orbitals in Fig. 1.7. If the metal has empty  $d_{\pi}$  orbitals, as in the  $d^0$  ion  $Ti^{4+}$ ,  $\pi$  donation from the ligand to the metal  $d_{\pi}$  orbitals now leads to stronger metal-ligand bonding;  $d^0$  metals therefore form particularly strong bonds with  $\pi$  donor ligands.

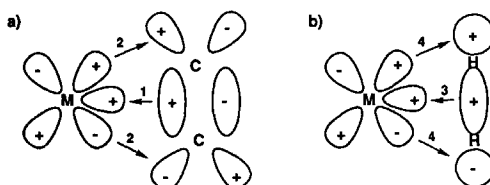


**FIGURE 1.8** The effect of “turning on” the  $\pi$  interaction between a  $\pi$ -donor ligand and the metal. The occupied, and relatively stable, lone pair ( $\pi$ ) orbitals of the ligand are shown on the right. Their effect is to destabilize the filled  $d_{\pi}$  orbitals of the complex and so decrease  $\Delta$ . This is effectively a repulsion between two lone pairs, one on the metal and the other on the ligand.

## TYPES OF LIGAND

Most ligands form the M-L  $\sigma$  bond by using a lone pair, that is, a pair of electrons that are nonbonding in the free ligand. For ligands that have the lone pairs are often the homo and the most basic electrons in the molecule. Classical Werner coordination complexes always involve lone pair donor ligands. There are two other types of ligand found in organometallic compounds of which  $C_2H_4$  and  $H_2$  are typical examples. Ethylene is an example of a molecule that has no lone pairs, yet it binds strongly to low-valent metals. In this case the homo is the C=C  $\pi$  bond, and it is these electrons that form the M-L  $\sigma$  bond, as shown in Fig. 1.9a. The arrow marked “1” represents the  $\pi$ -bonding electron pair of ethylene being donated to the metal. There is also a back-bonding component (marked “2”) where the  $\pi^*$  orbital of ethylene plays the role of acceptor. Since the C=C  $\pi$  bond lies both above and below the molecular plane, the metal has to bind out of the plane, where the electrons are. This type of binding is sometimes represented as  $(\eta^2-C_2H_4)$  (pronounced “eta-two ethylene”) where  $\eta$  represents the *hapticity* of the ligand, defined as the number of atoms in the ligand bonded to the metal.

Molecular hydrogen has neither a lone pair nor a  $\pi$  bond, yet it also binds as an intact molecule to metals in such complexes as  $[W(\eta^2-H_2)(CO)_3L_2]$ . The only available electron pair is the H-H  $\sigma$  bond, and this becomes the donor (“3” in Fig. 1.9b). Back donation in this case (“4” in Fig. 1.9b) is accepted by the  $H_2 \sigma^*$  orbital. The metal binds side-on to  $H_2$  to maximize  $\sigma-d_{\sigma}$  overlap. Related  $\sigma$ -bond complexes are formed with C-H, Si-H, B-H, and M-H bonds. In general, the basicity of electron pairs decreases in the following order: lone pairs >  $\pi$ -bonding pairs >  $\sigma$ -bonding pairs, because being part of a bond stabilizes electrons. The usual order of binding ability is therefore as follows: lone pair donor >  $\pi$ -bond donor >  $\sigma$ -bond donor.



**FIGURE 1.9** (a) The bonding of a  $\pi$ -bond donor, ethylene, to a metal. The arrow labeled “1” represents electron donation from the filled C=C  $\pi$  bond to the empty  $d_{\pi}$  orbital on the metal; “2” represents the back donation from the filled  $M(d_{\pi})$  orbital to the empty C=C  $\pi^*$ . (b) The bonding of a  $\sigma$ -bond donor, hydrogen, to a metal. The label “3” represents electron donation from the filled H—H  $\sigma$  bond to the empty  $d_{\sigma}$  orbital on the metal, and “4” represents the back donation from the filled  $M(d_{\sigma})$  orbital to the empty H—H  $\sigma^*$ . Only one of the four lobes of the  $d_{\sigma}$  orbital is shown.

For lone pair donors the M-L  $\pi$  bond can have 2e and be attractive, as we saw for M-CO (M =  $d^6$  metal, Figs. 1.6 and 1.7) or 4e and be repulsive, as is the case for M-F<sup>-</sup> (M =  $d^6$  metal, Fig. 1.8). For the more weakly binding  $\sigma$ - and  $\pi$ -bond donors, the M-L  $\pi$  bond is nearly always attractive because if it were not, L would not bind strongly enough to form an isolable complex. In the  $\pi$  bond, a M( $d_{\pi}$ ) electron pair is donated to an empty antibonding orbital of the ligand, usually a  $\pi^*$  for  $\pi$ -bond donors and a  $\sigma^*$  for  $\sigma$ -bond donors (Fig. 1.9). In the case of a  $\pi$ -bond donor like ethylene, this back bonding weakens the C=C  $\pi$  bond but does not break it because C<sub>2</sub>H<sub>4</sub> is still held together by strong C-C and C-H  $\sigma$  bonds that are not involved in M-L bond formation. The C=C distance of 1.32 Å in free ethylene is lengthened only to 1.35-1.5 Å in the complex.

For  $\sigma$ -bond donors such as H<sub>2</sub>, forming the M-L  $\sigma$  bond partially depletes the H-H  $\sigma$  bond because electrons that were fully engaged in keeping the two H atoms together in free H, are now also delocalized over the metal (hence the name *two-electron, three-center bond* for this type of interaction). Back bonding into the H-H  $\sigma^*$  causes additional weakening of the H-H  $\sigma$  bond because the  $\sigma^*$  is antibonding with respect to H-H. Free H, has an H-H distance of 0.74 Å, but the H-H distances in H<sub>2</sub> 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 called the oxidative addition reaction. Formation of a  $\sigma$ -bond complex can be thought of as an incomplete oxidative addition. Table 1.2 classifies common ligands by the nature of the M-L  $\sigma$  and  $\pi$  bonds. Both  $\sigma$  and  $\pi$  bonds bind side-on to metals when they act as ligands.

TABLE 1.2 Types of Ligands<sup>a</sup>

$\sigma$ \ $\pi$	Strong $\pi$ Acceptor	Weak $\pi$ -Bonding	Strong $\pi$ Donor
Lone pair donor	CO PF <sub>3</sub> CR <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> H <sup>-c</sup> NH <sub>3</sub>	CR <sub>2</sub> OR <sup>-</sup> F <sup>-</sup>
$\pi$ -Bonding electron pair donor	C <sub>2</sub> F <sub>4</sub> O <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> RCHO <sup>d</sup>	
$\sigma$ -Bonding electron pair donor	Oxidative addition <sup>e</sup>	R <sub>3</sub> Si-H, H <sub>2</sub> R <sub>3</sub> C-H <sup>f</sup>	

<sup>a</sup>Ligands are listed in approximate order of  $\pi$ -donor/acceptor power, with acceptors to the left.

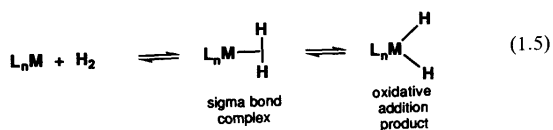
<sup>b</sup>CH<sub>2</sub> and CH<sub>3</sub> refer to Fischer and Schrock carbenes of Chapter 11.

<sup>c</sup>Ligands like this are considered here as anions rather than radicals.

<sup>d</sup>Can also bind as a lone pair donor (Eq. 1.5).

<sup>e</sup>Oxidative addition occurs when  $\sigma$ -bond donors bind very strongly (see text).

<sup>f</sup>A stable complex is formed only when the C-H bond is part of a ligand such as PPh<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>.



## THE 18-ELECTRON RULE

The 18e rule is a way to help us decide whether a given d-block transition metal organometallic complex is likely to be stable. Not all the organic formulas we can write down correspond to stable species. For example, CH<sub>5</sub> requires a 5-valent carbon, and is therefore not stable. Stable compounds, such as CH<sub>4</sub>, have the noble gas octet, and so carbon can be thought of as following an 8e rule. This corresponds to carbon using its s and three p orbitals to form four filled bonding orbitals, and four unfilled antibonding orbitals. On the covalent model, we can consider that of the eight electrons required to fill the bonding orbitals, four come from carbon and one each comes from the four H substituents. We can therefore think of each H atom as being a 1e ligand to carbon.

We sometimes find it useful to assign a formal oxidation state to carbon in an organic molecule. For this we impose an ionic model on the compound by artificially dissecting it into ions. In doing this, each electron pair in any bond is assigned to the most electronegative of the two atoms or groups that constitute the bond. For methane, this dissection gives C<sup>4-</sup> + 4H<sup>+</sup>, with carbon as the more electronegative element. This makes methane an 8e compound with an oxidation state of -4, which is usually written C(-IV). Note that the net electron count remains the same, whether we adopt the covalent (4e {C atom} + 4 x 1e {4 H atoms} = 8e), or ionic models (8e {C<sup>4-</sup> ion} + 4 x 0e {4 H<sup>+</sup> ions} = 8e).

The 18e rule, which applies to many low-valent transition metal complexes, follows a similar line of reasoning. The metal now has one s, and three p orbitals, as before, but now also five d orbitals. We will need 18e to fill all nine orbitals: some will come from the metal, the rest from the ligands. Only a limited number of combinations of metal and

ligand will give an 18e count. Figure 1.5 shows that 18e will fill the m.o. diagram of the complex  $ML_6$  up to the  $d_{\pi}$  level, and leave the  $d_{\sigma}$  orbitals empty. The resulting configuration is analogous to the closed shell present in the Group 18 elements and is therefore called *the noble gas configuration*. Each atomic orbital (a.o.) on the metal that remains nonbonding will clearly give rise to one molecular orbital (m.o.) in the complex; each a.o. that interacts with a ligand orbital will give rise to one bonding m.o., which will be filled in the complex, and one antibonding m.o., which will normally be empty. Our nine metal orbitals will therefore give rise to nine low lying orbitals in the complex and to fill these we will need 18 electrons.

A glance at Table 2.1 will show how the first-row carbonyls mostly follow the 18e rule. Each metal contributes the same number of electrons as its group number, and each CO contributes 2e for its lone pair;  $\pi$ -back bonding makes no difference to the electron count for the metal. In the free atom, it had one atomic orbital (a.o.) for each pair of  $d_{\pi}$  electrons it uses for back bonding; in the complex it still has one filled molecular orbital (m.o.), now delocalized over metal and ligands.

**TABLE 2.1 The First-Row Carbonyls**

$V(CO)_6$	17e; 18e $V(CO)_6^-$ also stable
$Cr(CO)_6$	Octahedral
$(CO)_5Mn-Mn(CO)_5$	The M—M bond contributes 1e to each metal; all the CO groups are terminal
$Fe(CO)_5$	Trigonal bipyramidal
$(CO)_3Co(\mu-CO)_2Co(CO)_3$	A $\mu$ -CO contributes 1e to each metal, and there is also an M—M bond
$Ni(CO)_4$	Tetrahedral

In cases where we start with an odd number of electrons on the metal, we can never reach an even number, 18, by adding 2e ligands like CO. In each case the system resolves this problem in a different way. In  $V(CO)_6$ , the complex is 17e, but is easily reduced to the 18e anion  $V(CO)_6^-$ . Unlike  $V(CO)_6$ , the  $Mn(CO)_5$  fragment, also 17e, does dimerize, probably because, as a 5-coordinate species, there is more space available to make the M-M bond. This completes the noble gas configuration for each metal because the unpaired electron in each fragment is shared with the other in forming the bond, much as the 7e methyl radical dimerizes to give the 8e compound, ethane. In the 17e fragment  $Co(CO)_4$ , dimerization also takes place via a metal-metal bond, but a pair of COs also move into bridging positions. This makes no difference in the electron count, because the bridging CO is a 1e ligand to each metal, so an M-M bond is still required to attain 18e. The even-electron metals are able to achieve 18e without M-M bond formation, and in each case they do so by binding the appropriate number of COs, the odd electron metals need to form M-M bonds.

Unfortunately, there are two conventions for counting electrons: the ionic and covalent models, both of which have roughly equal numbers of supporters. Both methods lead to *exactly the same net result*; they differ only in the way that the electrons are considered as "coming from" the metal or from the ligands. **(NOTE I PREFER THE IONIC MODEL AND WILL USE IT EXCLUSIVELY IN THIS CLASS, IF YOU WANT TO USE THE COVALENT MODEL, YOU ARE ON YOUR OWN).**

Let us take  $HMn(CO)_5$  as an example. We can adopt the covalent model and argue that the H $\cdot$  atom, a 1e ligand, is coordinated to a 17e  $Mn(CO)_5$  fragment. On the other hand, on the ionic model, one can consider the complex as being derived from an anionic 2e  $H^-$  ligand, coordinated to a cationic 16e  $Mn(CO)_5^+$  fragment. The reason is that H is more electronegative than Mn and so is formally assigned the bonding electron pair when we dissect the complex. Fortunately, no one has yet suggested counting the molecule as arising from a 0e  $H^+$  ligand and an 18e  $Mn(CO)_5^-$  anion; ironically, protonation of the anion is the most common preparative method for this hydride.

In Table 2.2 we see some of the common ligands and their electron counts on the two models. The symbol L is commonly used to signify a neutral ligand, which can be a (one pair donor, such as CO or  $NH_3$ , a  $\pi$ -bond donor, such as  $C_2H_4$ , or a  $\sigma$ -bond donor such as  $H_2$ , which are all 2e ligands on both models. The symbol X refers to ligands such as H, Cl, or Me, which are 1e X ligands on the covalent model and 2e  $X^-$  ligands on the ionic model. In the covalent model we regard them as 1e  $X\cdot$  radicals bonding to the neutral metal atom; in the ionic model, we regard them as 2e  $X^-$  anions bonding to the  $M^+$  cation.



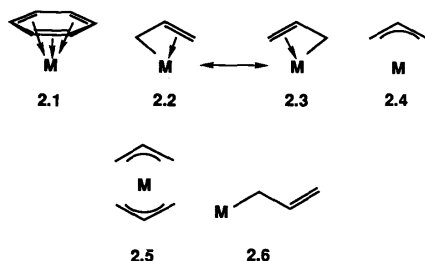
**TABLE 2.2 Common Ligands and Their Electron Counts**

Ligand	Type	Covalent Model	Ionic Model
Me, Cl, Ph, Cl, $\eta^1$ -allyl, NO (bent) <sup>a</sup>	X	1e	2e
Lone pair donors: CO, NH <sub>3</sub>	L	2e	2e
$\pi$ -Bond donors: C <sub>2</sub> H <sub>4</sub>	L	2e	2e
$\sigma$ -Bond donors: (H <sub>2</sub> )	L	2e	2e
$\eta^3$ -Allyl, $\eta^3$ -acetate	LX	3e	4e
NO (linear) <sup>a</sup>	LX	3e	2e
$\eta^1$ -Butadiene	L <sub>2</sub> <sup>b</sup>	4e	4e
$\eta^5$ -Cp	L <sub>2</sub> X	5e	6e
$\eta^6$ -Benzene	L <sub>3</sub>	6e	6e

<sup>a</sup>Linear NO is considered as NO<sup>+</sup> on the ionic model; see Section 4.1.

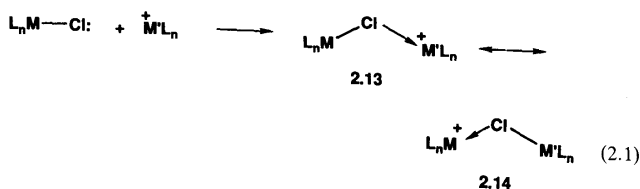
<sup>b</sup>The alternative LX<sub>2</sub> structure sometimes adopted gives the same electron count.

Green has developed a useful extension of this nomenclature by which more complicated ligands can be classified. For example, benzene (2.1) can be considered as a combination of three C=C ligands, and therefore as L<sub>3</sub>. The allyl group can be considered as a combination of an alkyl and a C=C group. The two canonical forms 2.2 and 2.3 show how we can consider allyl groups in which all three carbons are bound to the metal as LX ligands. This can also be represented in the delocalized form as 2.4. In such a case, the *hapticity* of the ligand, the number of ligand atoms bound to the metal, is 3 and so 2.5, referred to as bis- $\eta^3$ -allyl nickel in the older literature, is now known as bis- $\eta^3$ -allyl nickel, or [Ni( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>]. Occasionally the letter "h" is used instead of  $\eta$ , and sometimes  $\eta$  is used without a superscript as a synonym for the older form,  $\pi$ ; such things tend to be frowned on. The electron count of the  $\eta^3$  form of the allyl group is 3e on the covalent model and 4e on the ionic model, as suggested by the LX label. The advantage of the LX label is that those who follow the covalent model will translate LX as meaning a 3e ligand, and the devotees of the ionic model will translate LX as meaning a 4e ligand.



The allyl group can also bind in another way (2.6). Since only one carbon is now bound to the metal, this is the  $\eta^1$ -allyl, or  $\sigma$ -allyl form. In this bonding mode, the allyl behaves as an X-type ligand, like a methyl group, and is therefore a 1e ligand on the covalent model and a 2e ligand on the ionic model. Some examples of electron counting are shown in Fig. 2.1. Note the dissection into atoms and radicals in the covalent model and into ions in the ionic model.

Bridging ligands are very common in organometallic chemistry and are prefixed by the symbol  $\mu$ . Bridging CO ligands are usually counted as shown in Table 2.1. Next we will look at bridging halide. This carries a lone pair, which is donated to the second metal in forming the bridge. An L<sub>n</sub>MCl group is effectively acting as a ligand to the second metal. If ML<sub>n</sub> = M'L<sub>n</sub> then the two bonds to Cl are indistinguishable by resonance between 2.13 and 2.14. For electron counting purposes, we can consider that the chlorine atom is a 1e donor to M and a 2e donor to M' via its lone pair (or, on the ionic model, that Cl<sup>-</sup> is a 2e donor to each metal via two lone pairs, as an X-ligand to one metal, and an L-ligand to the other). The same usually holds true for other X-type ligands, such as halide, -SR, -OR, or -PR<sub>2</sub>. As shown in 2.13 and 2.14, we often write M-X to signify the covalent bond, but L→M for the coordinate bond, as an indication that both electrons are regarded as "coming from" the ligand L.



Ionic Model			Covalent Model	
$C_3H_5^-$	6e	 <b>Fe</b>	$C_3H_5^\bullet$	5e
$C_3H_5^-$	6e		$C_3H_5^\bullet$	5e
$Fe^{2+}$	$\frac{6e}{18e}$		Fe	$\frac{8e}{18e}$
<b>2.7</b>				
$Mo^{4+}$	2e	 <b>MoH<sub>4</sub>(PR<sub>3</sub>)<sub>4</sub></b>	Mo	6e
$4 \times H^-$	8e		$4 \times H^\bullet$	4e
$4 \times PR_3$	$\frac{8e}{18e}$		$4 \times PR_3$	$\frac{8e}{18e}$
<b>2.8</b>				
$Ni^{2+}$	8e	 <b>Ni</b>	Ni	10e
$2 \times C_3H_5^-$	$\frac{8e}{16e}$		$2 \times C_3H_5^\bullet$	$\frac{6e}{16e}$
<b>2.9</b>				
$Mo$	6e	 <b>Mo</b>	Mo	6e
$2 \times C_6H_6$	$\frac{12e}{18e}$		$2 \times C_6H_6$	$\frac{12e}{18e}$
<b>2.10</b>				
$2 \times Cl^-$	4e	 <b>Ti</b>	$2 \times Cl^-$	2e
$Ti^{4+}$	0e		Ti	4e
$2 \times C_5H_5^-$	$\frac{12e}{16e}$		$2 \times C_5H_5^\bullet$	$\frac{10e}{16e}$
<b>2.11</b>				
$Co^{3+}$	6e	 <b>Co</b>	Co	9e
$2 \times C_5H_5^-$	$\frac{12e}{18e}$		$2 \times C_5H_5^\bullet$	10e
			Positive charge <sup>a</sup>	$\frac{-1e}{18e}$
<b>2.12</b>				

<sup>a</sup>To account for the positive ionic charge on the complex as a whole; for anions, the net charge is added to the total.

**FIGURE 2.1** Electron counting on the covalent and ionic models.

## LIMITATIONS OF THE 18-ELECTRON RULE

For the 18e rule to be useful, we need to be able to predict when it will be obeyed and when it will not. The rule works best for hydrides and carbonyls, because these are sterically small, high-field ligands. Because they are small, as many will generally bind as are required to achieve 18e. With high-field ligands,  $\Delta$  for the complex will be large. This will mean that the  $d_{\sigma}^*$  orbitals that would be filled if the metal had more than 18e are high in energy and therefore poor acceptors. On the other hand, the  $d_{\pi}$  orbitals, which would have to give up electrons if the molecule had less than 18e are low-in energy because of  $\pi$  bonding by CO (or, in the case of H, because of the very strong  $\sigma$  bond and the absence of repulsive  $\pi$  interactions with lone pairs). The  $d_{\pi}$  level is therefore a good acceptor, and to be stable, a complex must have this level filled (otherwise the electrophilic metal will gain electrons by binding more CO, or the solvent or some functional group in the ligands until the 18e configuration is attained).

Conversely, the rule works least well for high-valent metals with weak-field ligands. In the hexaaqua ions  $[M(H_2O)_6]^{2+}$  ( $M = V, Cr, Mn, Fe, Co, Ni$ ), the structure is the same whatever the electron count of the metal and so must be dictated by the fact that six  $H_2O$ 's fit well around a metal ion.  $H_2O$  has two lone pairs, one of which it uses to form a  $\sigma$  bond. This leaves one remaining on the ligand, which acts as a  $\pi$  donor to the metal and so lowers  $\Delta$ ;  $H_2O$  is therefore a weak field ligand. If  $\Delta$  is small, then the tendency to adopt the 18e configuration is also small because it is easy to add electrons to the low-lying  $d_{\sigma}^*$ , or to remove them from the high-lying  $d_{\pi}$ .

An important class of complexes follow a 16e, rather than an 18e, rule because one of the nine orbitals is very high-lying and is usually empty. This can happen for the  $d^8$  metals of Groups 8-11 (Table 2.3). Group 8 shows the least, and Group 11 the highest tendency to become 16e. When these metals are 16e, they normally adopt the square planar geometry, which makes the  $d_{x^2-y^2}$  orbital very high in energy because it experiences crystal field repulsion from all four ligands. To go to an 18e species, the metal has to rehybridize to give a trigonal bipyramidal geometry, so as to direct the empty orbital toward the incoming fifth ligand and, by avoiding crystal field repulsions, lower its energy. Some examples of 16e complexes of this sort are  $RhClL_3$ ,  $IrCl(CO)L_2$ ,  $PdCl_2L_2$  and  $[PtCl_4]^{2-}$ ,  $[AuMe_4]^-$  ( $L = 3^{\circ}$  phosphine).

**TABLE 2.3 The  $d^n$  Metals that Can Adopt a 16e Configuration**

Group			
8	9	10	11
Fe(0) <sup>a</sup>	Co(I) <sup>b</sup>	Ni(II)	Cu(III) <sup>c</sup>
Ru(0) <sup>a</sup>	Rh(I) <sup>b</sup>	Pd(II)	—
Os(0) <sup>a</sup>	Ir(I) <sup>b</sup>	Pt(II)	Au(III)

<sup>a</sup>These metals prefer 18e to 16e.<sup>b</sup>The 16e configuration is more often seen, but 18e complexes are common.<sup>c</sup>A rare oxidation state.

The smaller metal clusters, such as Os<sub>3</sub>(CO)<sub>12</sub>, often obey the 18e rule for each metal, but for clusters of six metals or more, there are deviations, for which special cluster counting rules have been devised. The rule is not useful for Main Group elements, such as ZnMe<sub>2</sub>, 14e; MeHg(bipy)<sup>+</sup>, 16e; [I(py)<sub>2</sub>]<sup>+</sup>, 20e; [SbF<sub>6</sub>]<sup>-</sup>, 22e; and IF<sub>7</sub>, 24e, where no particular electron count is favored. The lanthanides and actinides have seven *f* orbitals to fill before they even start on the *d* orbitals, and so they are essentially never able to bind a sufficient number of ligands to raise the electron count to the  $s^2p^6d^{10}f^{14}$  or 32e configuration of the appropriate noble gas; some examples are U(cot)<sub>2</sub>, 22e, and Cp<sub>2</sub>LuMe, 28e. This means that the stoichiometry of an *f* block complex tends to be decided by steric saturation of the space around the metal. Paramagnetic complexes (e.g., V(CO)<sub>6</sub>, 17e; Cp<sub>2</sub>Fe<sup>+</sup>, 17e; Cp<sub>2</sub>Ni, 20e) generally do not obey the 18e rule, but many of these have reactions in which they attain an 18e configuration, for example, the 19e CpFe(η<sup>6</sup>-arene) is a powerful 1e donor.

## OXIDATION STATE

The oxidation state of a metal in a complex is simply the charge that the metal would have on the ionic model. In practice, all we have to do for a neutral complex is to count the number of X ligands. For example, Cp<sub>2</sub>Fe has two L<sub>2</sub>X ligands and so can be represented as MX<sub>2</sub>L<sub>4</sub>; this means that the oxidation state (O.S.) is 2+, so Cp<sub>2</sub>Fe is said to be Fe(II). For a complex ion, we need also to take account of the net charge as shown for [MX<sub>a</sub>L<sub>b</sub>]<sup>c+</sup> in Eq. 2.7. For example, Cp<sub>2</sub>Fe<sup>+</sup> is Fe(III), and [W(CO)<sub>5</sub>]<sup>2-</sup> is W(-II). Once we have the oxidation state, we can immediately obtain the corresponding  $d^n$  configuration. This is simply the number of *d* electrons that would be present in the free metal ion, which corresponds to the oxidation state we have assigned. For Cp<sub>2</sub>Fe<sup>+</sup> the O.S. is Fe(III), which corresponds to the Fe<sup>3+</sup> ion. The iron atom, which is in Group 8, has 8e, and so the ion has 8 - 3 = 5e. Cp<sub>2</sub>Fe<sup>+</sup> is therefore said to be a  $d^5$  complex. Equation 2.8 gives the value of *n* in a general form. The significance of the  $d^n$  configuration is that it tells us how to fill up the crystal field diagrams. For example, the odd number for Cp<sub>2</sub>Fe<sup>+</sup> implies paramagnetism because in a mononuclear complex we cannot pair 5 electrons whatever the *d*-orbital splitting.

$$\text{O.S.} = c + a \quad (2.7)$$

$$n = N - (c + a) = N - c - a \quad (2.8)$$

Many organometallic compounds have low or intermediate formal oxidation states. High oxidation states are still rather rare. The reason is that back donation is severely reduced in higher oxidation states because (1) there are fewer (or no) nonbonding *d* electrons available and (2) the increased partial positive charge present on the metal in the high-oxidation-state complex strongly stabilizes the *d* levels so that any electrons they contain become less available. Those high-valent species that do exist, generally come from the third-row metals. The extra shielding provided by the *f* electrons added in building up the lanthanides makes the outer electrons of the third-row metals less tightly bound and therefore more available. There are many situations in which it is useful to refer to the oxidation state and  $d^n$  configuration, but they are a useful classification only and do not allow us to deduce the real partial charge present on the metal. It is therefore important not to read too much into oxidation states and  $d^n$  configurations.

## COORDINATION NUMBER AND GEOMETRY

The coordination number (C.N.) of a complex is easily defined in cases in which the ligands are all monodentate; it is simply the number of ligands present [e.g., [PtCl<sub>4</sub>]<sup>2-</sup>, C.N. = 4, W(CO)<sub>6</sub>, C.N. = 6]. A useful generalization is that the coordination number cannot exceed 9 for the transition metals. This is because the metal only has 9 valence orbitals, and each ligand will need its own orbital. In most cases the C.N. will be less than 9, and some of the 9 orbitals will either be lone pairs on the metal or engaged in back bonding.

Each coordination number has one or more coordination geometries associated with it. Table 2.5 lists some

examples. In order to reach the maximum coordination number of 9, we need relatively small ligands (e.g.,  $[\text{ReH}_9]^{2-}$ ). Coordination numbers lower than 4 tend to be found with bulky ligands, which cannot bind in greater number without prohibitive steric interference between the ligands [e.g.,  $\text{Pt}(\text{PCy}_3)_2$ ]. Certain geometries are favored by particular  $d^n$  configurations, for example,  $d^6$  strongly favors octahedral,  $d^8$  prefers square planar, trigonal bipyramidal, or square pyramidal, and  $d^4$  and  $d^{10}$  prefer tetrahedral. In each case, the preferred geometry leads to a favorable occupation pattern of the orbitals in the appropriate crystal field diagram. For example, eight electrons just fill the four most stable orbitals in the square planar splitting pattern and four electrons just fill the two most stable orbitals of the tetrahedral splitting pattern of Fig. 1.4.

Unfortunately, the definition of coordination number and geometry is less clear-cut for organometallic species, such as  $\text{Cp}_2\text{Fe}$ . Is this molecule 2-coordinate (there are two ligands), 6-coordinate (there are six electron pairs involved in metal-ligand bonding), or 10-coordinate (the 10 C atoms are all within bonding distance of the metal)? Most often, it is the second definition that is used, which is equivalent to adding up the number of L's and X's from all the ligands.

Equations 2.9-2.12 summarize the different counting rules as applied to our generalized transition metal complex  $[\text{MX}_a\text{L}_b]^{c+}$  where N is the Group number, and  $n$  is the  $d^n$  configuration.

$$\text{Coordination number: } \text{C.N.} = a + b \leq 9 \quad (2.9)$$

$$\text{Electron count: } N + a + 2b - c = 18 \quad (2.10)$$

$$\text{Oxidation state: } \text{O.S.} = a + c \leq N \quad (2.11)$$

$$d^n \text{ configuration: } n = N - \text{O.S.} = N - a - c \quad (2.12)$$

TABLE 2.5 Some Common Coordination Numbers and Geometries

2 linear		$(\text{Me}_3\text{SiCH}_2)_2\text{Mn}$
3 trigonal		$\text{Al}(\text{mesityl})_3$
T-shaped		$\text{Rh}(\text{PPh}_3)_3$
4 square planar		$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$
tetrahedral		$\text{Ni}(\text{CO})_4$
5 trigonal bipyramidal		$\text{Fe}(\text{CO})_5$
square pyramidal		$\text{Co}(\text{CNPh})_5^{2+}$
6 octahedral		$\text{Mo}(\text{CO})_6$
7 capped octahedron		$\text{ReH}(\text{PR}_3)_3(\text{MeCN})_3^+$
pentagonal bipyramid		$\text{IrH}_5(\text{PPh}_3)_2$