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

High Spin Versus Low Spin

Cobalt, which is in group 9 of the periodic table, has the electron configuration $[Ar]4s^2 3d^7$ in the free atom, with nine valence electrons. Once the atom forms a complex, however, the d orbitals become more stable as a result of metal–ligand bonding, and the electron configuration becomes $[Ar]4s^0 3d^9$ for the case of a Co(0) complex, or $[Ar]3s^0 4d^6$ for Co(III), usually shortened to d^9 and d^6, respectively. This picture explains why Co^{3+}, the metal ion Werner studied, has such a strong preference for the octahedral geometry. With its d^6 configuration, six electrons just fill the three low-lying d_π orbitals of the crystal field diagram and leave the d_σ empty. This is a particularly stable arrangement, and other d^6 metals, Mo(0), Re(I), Fe(II), Ir(III), and Pt(IV) also show a very strong preference for the octahedral geometry. Indeed, low spin d^6 is by far the commonest type of metal complex in organometallic chemistry. In spite of the high tendency to spin-pair the electrons in the d^6 configuration (to give the *low-spin* form $t_{2g}^6 e_g^0$), if the ligand field splitting is small enough, then the electrons may occasionally rearrange to give the *high-spin* form $t_{2g}^4 e_g^2$. In the high-spin form all the unpaired spins are aligned, as prescribed for the free ion by Hund's rule. This is shown in Fig. 1.2. The factor that favors the high-spin form is the fact that fewer electrons are paired up in the same orbitals and so the electron–electron repulsions are reduced. On the other hand, if Δ becomes large enough, then the energy gained by dropping from the e_g to the t_{2g} level will be
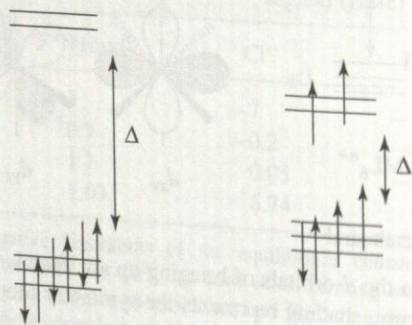

FIGURE 1.2 In a d^6 metal ion, both low- and high-spin complexes are possible depending on the value of Δ. A high Δ leads to the low-spin form.

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 weighing a sample of the complex in a magnetic field gradient. In the low-spin form of a d^6 ion, the molecule is *diamagnetic*, that is, it is very weakly repelled by the field. This behavior is exactly the same as that found for the vast majority of organic compounds, which are also spin-paired. On the other hand, the high-spin form is *paramagnetic*, in which case it is attracted into the field because there are unpaired electrons. The complex does not itself form a permanent magnet as does a piece of iron or nickel (this property is called *ferromagnetism*) because the spins are not aligned in the crystal in the absence of an external field, but they respond to the external field by lining up together when we measure the magnetic moment.

Although the great majority of organometallic complexes are diamagnetic, because Δ is usually large in these complexes, we should not lose sight of the possibility that any given complex or reaction intermediate may be paramagnetic. This will always be the case for molecules such as d^5 $V(CO)_6$, which have an uneven number of electrons. For molecules with an even number of electrons, a high-spin configuration is more likely for the first row metals, where Δ tends to be smaller than in the later rows. Sometimes the low- and high-spin isomers have almost exactly the same energy. Each state can now be populated, and the relative populations of the two states vary with temperature; this happens for $Fe(dpe)_2Cl_2$, for example.

Inert Versus Labile Coordination

In an octahedral d^7 ion we are obliged to place one electron in the higher-energy (less stable) d_σ level to give the configuration $t_{2g}^6 e_g^1$, to make the complex paramagnetic (Fig. 1.3). The net stabilization, the *crystal field stabilization energy* (CFSE) of such a system will also be less than for d^6 (low spin), where we can put all the electrons into the more stable t_{2g} level. This is reflected in the chemistry of octahedral d^7 ions [e.g., Co(II)], which are more reactive than their d^6 analogs. For example, they undergo ligand dissociation much more readily. The reason

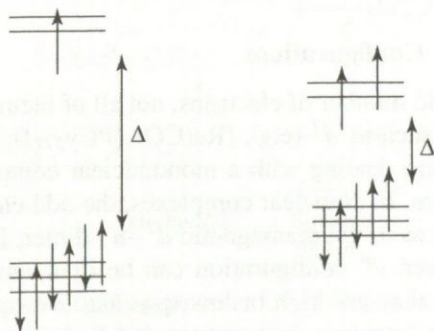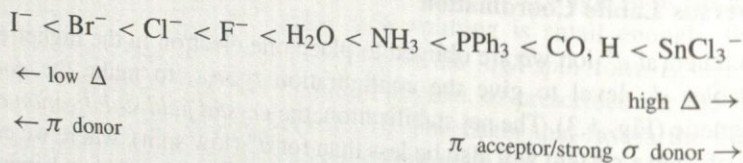**FIGURE 1.3**   A d^7 octahedral ion is paramagnetic even in the low-spin form.

is that the d_σ levels are M−L σ-antibonding in character (Section 1.5). Werner studied Co(III) because the ligands tend to stay put. This is why Co(III) and other low-spin d^6 ions are often referred to as *coordinatively inert*; d^3 ions such as Cr(III) are also coordination inert because the t_{2g} level is now exactly half-filled, another favorable situation. On the other hand, Co(II) and other non-d^6 and -d^3 ions can be *coordinatively labile*. The second- and third-row transition metals form much more inert complexes because of their higher Δ and CFSE.

Low- Versus High-Field Ligands

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

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

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

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

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

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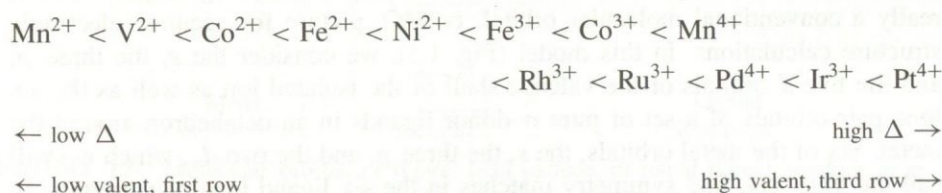
Odd Versus Even d^n Configurations

If a molecule has an odd number of electrons, not all of them can be paired up. An odd d^n configuration, such as d^7 (e.g., [Re(CO)$_3$(PCy$_3$)$_2$]), therefore, guarantees paramagnetism if we are dealing with a mononuclear complex—one containing only a single metal atom. In dinuclear complexes, the odd electrons on each metal may pair up, however, as in the diamagnetic d^7−d^7 dimer, [(OC)$_5$Re−Re(CO)$_5$]. Complexes with an even d^n configuration can be diamagnetic or paramagnetic depending on whether they are high or low spin, but low-spin diamagnetic complexes are much more common in organometallic chemistry because the most commonly encountered ligands are high field.

Other Geometries

In 4 coordination, two geometries are common, tetrahedral and square planar, for which the 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 $\frac{2}{3}$ 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 diamagnetic d^8 ions such as Au(III), Ni(II), Pd(II) or Pt(II), and Rh(I) or Ir(I); it is also common for paramagnetic d^9, such as Cu(II).

For a given geometry and ligand set, metal ions tend to have 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.

$$Mn^{2+} < V^{2+} < Co^{2+} < Fe^{2+} < Ni^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+}$$

$$< Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$$

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

$\leftarrow$ low valent, first row   high valent, third row $\rightarrow$

Third-row metals therefore tend to form stronger M−L bonds and more thermally stable complexes and are also more likely to give diamagnetic complexes. Comparison of the same metal and ligand set in different oxidation states is complicated by the fact that low oxidation states are usually accessible only with strong-field ligands that tend to give a high Δ (see the spectrochemical series of ligands on page 12).

$d_{xy}\, d_{yz}\, d_{xz}$ ═══

Δ

$d_{x^2-y^2}\, d_{z^2}$ ═══

Tetrahedral

$d_{x^2-y^2}$ ───

Δ

d_{xy} ───

d_{z^2} ───
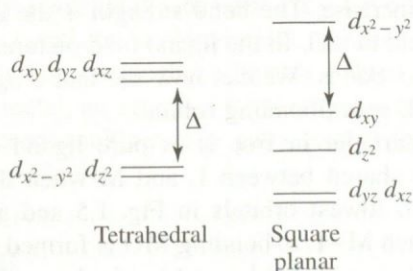
$d_{yz}\, d_{xz}$ ═══

Square planar

FIGURE 1.4 Crystal field splitting patterns for the common 4-coordinate geometries: tetrahedral and square planar. For the square planar arrangement, the z axis is conventionally taken to be perpendicular to the square plane.

THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

Fourth Edition

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