

THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

Fourth Edition

ROBERT H. CRABTREE

Yale University, New Haven, Connecticut

 **WILEY-
INTERSCIENCE**

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
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Library of Congress Cataloging-in-Publication Data is available.

ISBN 0-471-66256-9

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

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PREFACE

I would like to thank the many colleagues who kindly pointed out corrections, or contributed in some other way to this edition—Jack Faller, Ged Parkin, Robin Tanke, Joshua Telser, Fabiola Barrios-Landeros, Carole Velleca, Li Zeng, Guoan Du, Ipe Mavunkal, Xingwei Li, Marcetta Darenbourg, Greg Peters, Karen Goldberg, Odile Eisenstein, Eric Clot and Bruno Chaudret. I also thank UC Berkeley for hospitality while I was revising the book.

ROBERT H. CRABTREE

*New Haven, Connecticut
January 2005*

LIST OF ABBREVIATIONS

[]	Encloses complex molecules or ions
□	Vacant site or labile ligand
1°, 2°, ...	Primary, secondary, ...
A	Associative substitution (Section 4.4)
acac	Acetylacetonone
AO	Atomic orbital
at.	Pressure in atmospheres
bipy	2,2'-Bipyridyl
Bu	Butyl
cata	Catalyst
CIDNP	Chemically induced dynamic nuclear polarization (Section 6.3)
CN	Coordination number
cod	1,5-Cyclooctadiene
coe	Cyclooctene
cot	Cyclooctatetraene
Cp, Cp*	C ₅ H ₅ , C ₅ Me ₅
Cy	Cyclohexyl
δ ⁺	Partial positive charge
δ	Chemical shift (NMR)
Δ	Crystal field splitting (Section 1.4)
D	Dissociative substitution mechanism (Section 4.3)
<i>d</i> _σ , <i>d</i> _π	σ-Acceptor and π-donor metal orbitals (see Section 1.4)
diars	Me ₂ AsCH ₂ CH ₂ AsMe ₂
dpe or dppe	Ph ₂ PCH ₂ CH ₂ PPh ₂

dmf	Dimethylformamide
dmg	Dimethyl glyoximate
dmpe	Me ₂ PCH ₂ CH ₂ PMe ₂
DMSO	Dimethyl sulfoxide
<i>dⁿ</i>	Electron configuration (Section 1.4)
η	Shows hapticity in π -bonding ligands (Section 2.1)
E, E ⁺	Generalized electrophile such as H ⁺
e	Electron, as in 18e rule
e.e.	Enantiomeric excess (Section 9.2)
en	H ₂ NCH ₂ CH ₂ NH ₂
eq	Equivalent
Et	Ethyl
EPR	Electron paramagnetic resonance
eu	Entropy units
Fp	(C ₅ H ₅)(CO) ₂ Fe
fac	Facial (stereochemistry)
Hal	Halogen
HBpz ₃	Tris(pyrazolyl)borate
HOMO	Highest occupied molecular orbital
<i>I</i>	Nuclear spin
I	Intermediate substitution mechanism
IPR	Isotopic perturbation of resonance (Section 10.8)
IR	Infrared
κ	Shows hapticity in σ -bonding ligands (Section 2.1)
L	Generalized ligand, in particular a 2e ligand (L model for ligand binding is discussed in Section 2.1)
L _{<i>n</i>} M	Generalized metal fragment with <i>n</i> ligands
lin	linear
LUMO	Lowest unoccupied molecular orbital
μ	Descriptor for bridging (Section 1.1)
<i>m</i> -	Meta
Me	Methyl
mer	Meridional (stereochemistry)
<i>m_r</i>	Reduced mass
MO	Molecular orbital
ν	Frequency
nbd	Norbornadiene
NMR	Nuclear magnetic resonance (Sections 10.2–10.8)
NOE	Nuclear Overhauser effect (Section 10.7)
Np	Neopentyl
Nu, Nu ⁻	Generalized nucleophile, such as H ⁻
<i>o</i> -	Ortho
OAc	Acetate
oct	Octahedral (Table 2.5)
ofcot	Octafluorocyclooctadiene

OS	Oxidation state (Section 2.4)
<i>p</i> -	Para
Ph	Phenyl
py	Pyridine
RF	Radio frequency
SET	Single electron transfer (Section 8.6)
solv	Solvent
sq. py.	Square pyramidal (Table 2.5)
T_1	Spin-lattice relaxation time
tbe	<i>t</i> -BuCH=CH ₂
thf	Tetrahydrofuran
triphos	MeC(CH ₂ PPh ₂) ₃
TBP or trig. bipy	Trigonal bipyramidal (Table 2.5)
TMEDA	Me ₂ NCH ₂ CH ₂ NMe ₂
TMS	Trimethylsilyl
Ts	<i>p</i> -tolyl SO ₂
VB	Valence bond
X	Generalized 1e anionic ligand (Section 2.1) (X ₂ model for ligand binding is discussed on p. 126)

1

INTRODUCTION

Organometallic compounds, with their metal–carbon bonds (e.g., WMe_6), lie at the interface between classical organic and inorganic chemistry in dealing with the interaction between inorganic metal species and organic molecules. In the related metal–organic compound area, in contrast, the organic fragment is bound only by metal–heteroatom bonds [e.g., $Ti(OMe)_4$].

The organometallic field has provided a series of important conceptual insights, surprising structures, and useful catalysts both for industrial processes and for organic synthesis. Many catalysts are capable of very high levels of asymmetric induction in preferentially forming one enantiomer of a chiral product. The field is beginning to make links with biochemistry with the discovery of enzymes that carry out organometallic catalysis (e.g., acetyl CoA synthase). Ideas drawn from organometallic chemistry have helped interpret the chemistry of metal and metal oxide surfaces, both key actors in heterogeneous catalysis. The field is also creating links with the chemistry of materials because organometallic and metal–organic compounds are increasingly preferred as the precursors for depositing materials on various substrates via thermal decomposition of the metal compound. Nanoscience and nanotechnology are also benefiting with the use of such compounds as the most common precursors for nanoparticles. These small particles of a metal or alloy, with properties quite unlike the bulk material, are finding more and more useful applications in electronic, magnetic, or optical devices or in sensors.

Public concern for the environment has led to the rise of *green chemistry*, with the object of minimizing both energy use and chemical waste in industry

and commerce. One strategy is *atom economy* in which reactions are chosen that minimize the formation of by-products or unreacted starting materials. For example, rhodium or iridium-based catalysts directly convert MeOH and CO to MeCOOH with no significant by-products. Organometallic catalysis is likely to be a key contributor when climate change become severe enough to force government action to mandate the use of renewable fuels.

The presence of *d* electrons in their valence shell distinguishes the organometallic chemistry of the elements of groups 3–12 of the periodic table, the transition elements, from that of groups 1–2 and 12–18, the main-group elements. Group 12, and to some extent also group 3, often show greater resemblance to the main-group elements.

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

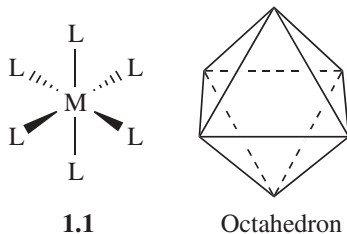
In this chapter we review some fundamental ideas of coordination chemistry, which also apply to organometallic complexes.

1.1 WERNER COMPLEXES

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

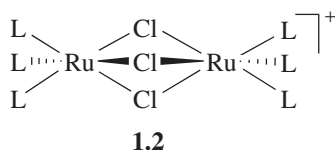
Stereochemistry

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



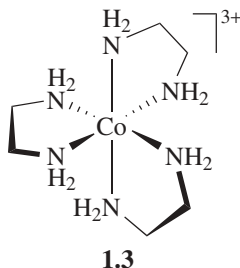
The assembly of metal and ligands that we call a *complex* may have a net ionic charge, in which case it is a complex ion (e.g., $[\text{PtCl}_4]^{2-}$). Together with the counterions, we have a complex salt (e.g., $\text{K}_2[\text{PtCl}_4]$). In some cases both the cation and the anion may be complex, as in the picturesquely named *Magnus' green salt* $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$. Square brackets are used to enclose the individual complex molecules or ions where necessary to avoid ambiguity.

Those ligands that have a donor atom with more than one lone pair can donate one lone pair to each of two or more metal ions. This gives rise to polynuclear complexes, such as the orange crystalline compound **1.2** ($\text{L} = \text{PR}_3$). The bridging group is represented in formulas by using the Greek letter μ (pronounced “mu”) as in $[\text{Ru}_2(\mu\text{-Cl})_3(\text{PR}_3)_6]^+$. Note how **1.2** can be considered as two octahedral fragments sharing the face that contains the three chloride bridges.

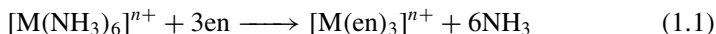


Chelate Effect

Other ligands can have more than one donor atom, each with its lone pair; an example is ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, often abbreviated “en”). Such ligands most commonly donate both lone pairs to the same metal to give a ring compound, known as a *chelate*, from the Greek word for “claw” (**1.3**). Chelate ligands may be bidentate, such as ethylenediamine, or polydentate, such as **1.4** and **1.5**.

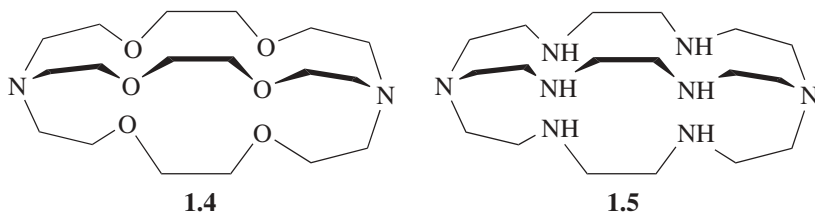


The early Russian investigator Chugaev first drew attention to the fact that chelating ligands are much less easily displaced from a complex than are monodentate ligands of the same type. The reason is illustrated in Eq. 1.1:



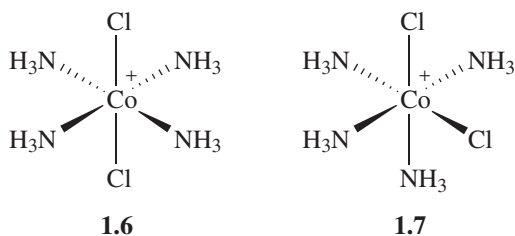
Formation of the tris chelate releases six NH_3 molecules so that the total number of particles increases from four to seven. This creates entropy and so favors the chelate form. Each chelate ring usually leads to an additional factor of about 10^5 in the equilibrium constant for reactions such as Eq.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

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

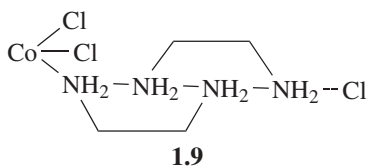
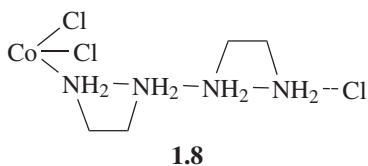


Werner Complexes

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

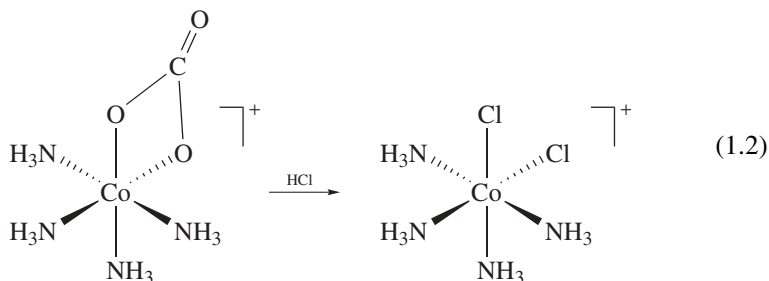


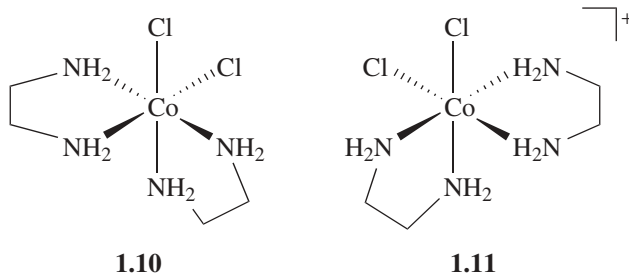
opposing all the major figures in the field, who held that the ligands were bound to one another in chains, and that only the ends of the chains were bound to the metal as in **1.8** and **1.9**. Jørgensen, who led the traditionalists against the



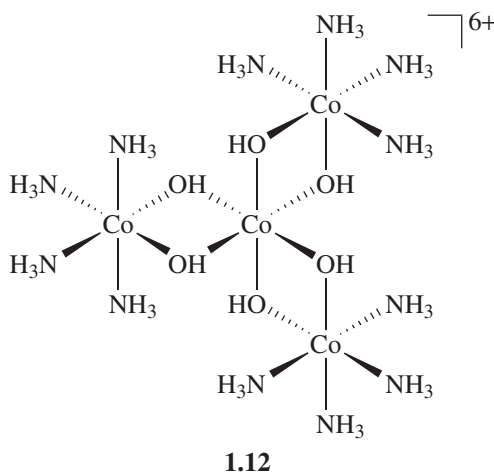
Werner insurgency, was not willing to accept that a trivalent metal, Co^{3+} , could form bonds to six groups; in the chain theory, there were never more than three bonds to Co. Each time Werner came up with what he believed to be proof for his theory, Jørgensen would find a way of interpreting the chain theory to fit the new facts. For example, coordination theory predicts that there should be two isomers of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (**1.6** and **1.7**). Up to that time, only a green one had ever been found. We now call this the *trans isomer* (**1.6**) because the two Cl ligands occupy opposite vertices of the octahedron. According to Werner's theory, there should also have been a second isomer, **1.7** (cis), in which the Cl ligands occupy adjacent vertices. Changing the anionic ligand, Werner was able to obtain both green and purple isomers of the nitrite complex $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$. Jørgensen quite reasonably (but wrongly) countered this finding by arguing that the nitrite ligands in the two isomers were simply bound in a different way (*linkage isomers*), via N in one case ($\text{Co}-\text{NO}_2$) and O ($\text{Co}-\text{ONO}$) in the other. Werner then showed that there were two isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, one green and one purple, in a case where no linkage isomerism was possible. Jørgensen brushed this observation aside by invoking the two chain isomers **1.8** and **1.9** in which the topology of the chains differ.

In 1907, Werner finally succeeded in making the elusive purple isomer of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ by an ingenious route (Eq. 1.2) via the carbonate $[\text{Co}(\text{NH}_3)_4(\text{O}_2\text{CO})]$ in which two oxygens of the chelating dianion are necessarily cis. Treatment with HCl at 0°C liberates CO_2 and gives the cis dichloride. Jørgensen, receiving a sample of this purple cis complex by mail, conceded defeat.





Finally, Werner resolved optical isomers of some of his compounds of the general type $[\text{Co}(\text{en})_2\text{X}_2]^{2+}$ (**1.10** and **1.11**). Only an octahedral array can account for the optical isomerism of these complexes. Even this point was challenged on the grounds that only organic compounds can be optically active, and so the optical activity must reside in the organic ligands. Werner responded by resolving a complex (**1.12**) containing only inorganic elements. This species has the extraordinarily high specific rotation of $36,000^\circ$ and required 1000 recrystallizations to resolve. Werner won the chemistry Nobel Prize for this work in 1913.



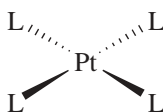
1.2 THE TRANS EFFECT

We now move from complexes of tripositive cobalt, often termed “Co(III) compounds,” where the III refers to the +3 oxidation state (Section 2.4) of the central metal, to the case of Pt(II). In the 1920s, Chernaev discovered that certain ligands, L^{\ddagger} , facilitate the departure of a second ligand, L , trans to the first, and their replacement or *substitution*, by an external ligand. Ligands, L^{\ddagger} , that are more effective at this labilization are said to have a higher *trans effect*. We consider in detail how this happens on page 109, for the moment we need only note that

the effect is most clearly marked in substitution in Pt(II), and that the highest trans effect ligands form either unusually strong σ bonds, such as $L^1 = H^-$, Me^- , or $SnCl_3^-$, or unusually strong π bonds, such as $L^1 = CO$, C_2H_4 , and thiourea $[(NH_2)_2CS]$, a ligand often represented as "tu"].

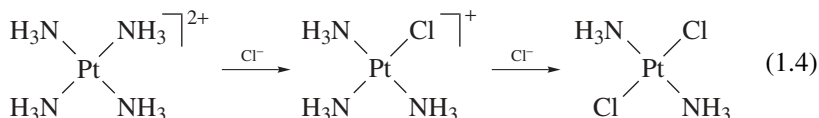
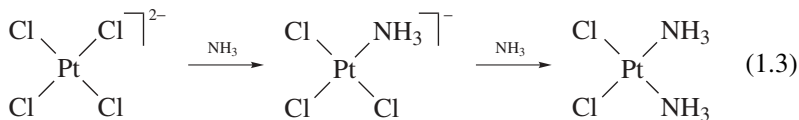
The same ligands also weaken the trans $M-L$ bonds, as shown by a lengthening of the $M-L$ distances found by X-ray crystallography or by some spectroscopic measure, such as M,L coupling constant in the nuclear magnetic resonance (NMR) spectroscopy (Section 10.4), or the $\nu(M-L)$ stretching frequency in the IR (infrared) spectrum (Section 10.9). A change in the ground-state thermodynamic properties, such as these, is usually termed the *trans influence* to distinguish it from the 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 substitution.

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).



1.13

An important application of the trans effect is the synthesis of specific isomers of coordination compounds. Equations 1.3 and 1.4 show how the cis and trans isomers of $Pt(NH_3)_2Cl_2$ can be prepared selectively by taking advantage of the trans effect order $Cl > NH_3$, so $L^1 = Cl$. This example is also of practical interest because the cis isomer is an important antitumor drug, but the trans isomer is ineffective. In each case the first step of the substitution can give only one isomer. In Eq. 1.3, the cis isomer is formed in the second step because the Cl trans to Cl is more labile than the Cl trans to the lower trans effect ligand, ammonia. On the other hand, in Eq. 1.4, the first Cl to substitute labilizes the ammonia trans to itself to give the trans dichloride as final product.



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



1.3 SOFT VERSUS HARD LIGANDS

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

The halide series ends with I^- , termed *soft* because it is large, easy to polarize, and forms predominantly covalent bonds. It binds best to a soft cation, Hg^{2+} , which is also large and easy to polarize. In this context, high polarizability means that electrons from each partner readily engage in covalent bonding. The $\text{Hg}^{2+}/\text{I}^-$ soft–soft combination is therefore a very good one—by far the best in the table—and dominated by covalent bonding.³

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

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+}	1.2	0.05	−0.03	—
Hg^{2+} (soft)	1.03	6.74	8.94	12.87

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

- High-trans-effect ligands labilize the ligand located opposite to themselves.
- Hard ligands have first-row donors and no multiple bonds (e.g., NH_3).
- Soft ligands have second- or later-row donors and/or multiple bonds (e.g., PH_3 or CO).

1.4 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 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—they act as negative charges. For Cl^- as a ligand, we just think of the net negative charge on the ion; for NH_3 , we think of the lone pair on nitrogen acting as a local concentration of negative charge. If we imagine the metal ion isolated in space, then the d orbitals are *degenerate* (have the same energy). As the ligands L approach the metal from the six octahedral directions $\pm x$, $\pm y$, 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.

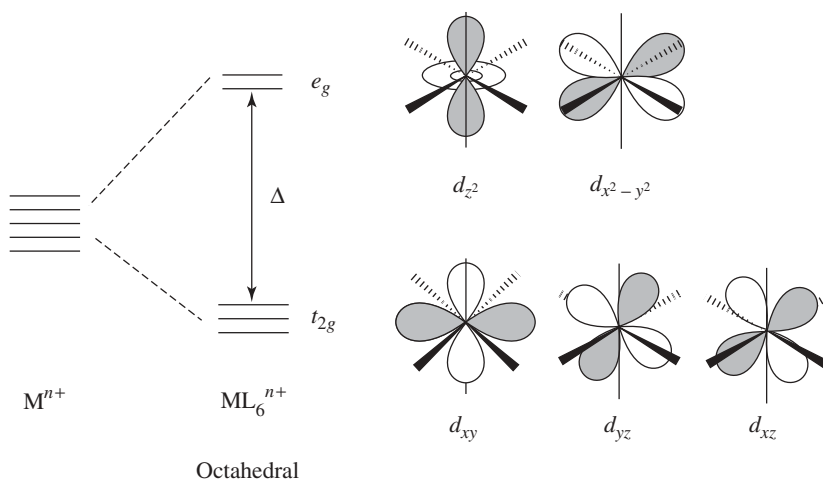


FIGURE 1.1 Effect on the d orbitals of bringing up six ligands along the $\pm x$, $\pm y$, and $\pm z$ directions. In this figure, shading represents the symmetry (not the occupation) of the d orbitals; shaded parts have the same sign of ψ .

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 $10Dq$) 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 $[\text{Ar}]4s^23d^7$ in the free atom, with nine valence electrons. Once the atom forms a complex, however, the d orbitals become more stable as a result of metal–ligand bonding, and the electron configuration becomes $[\text{Ar}]4s^03d^9$ for the case of a Co(0) complex, or $[\text{Ar}]3s^04d^6$ 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 $t_{2g}^6e_g^0$), if the ligand field splitting is small enough, then the electrons may occasionally rearrange to give the *high-spin* form $t_{2g}^4e_g^2$. 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

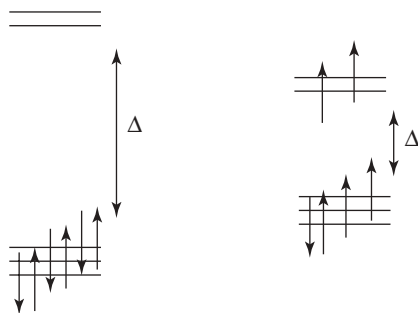


FIGURE 1.2 In a d^6 metal ion, both low- and high-spin complexes are possible depending on the value of Δ . A high Δ leads to the low-spin form.

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 do respond to the external field by lining up together when we measure the magnetic moment.

Although the great majority of organometallic complexes are diamagnetic, because Δ is usually large in these complexes, we should not lose sight of the possibility that any given complex or reaction intermediate may be paramagnetic. This will always be the case for molecules such as d^5 $\text{V}(\text{CO})_6$, 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 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 $\text{Fe}(\text{dpe})_2\text{Cl}_2$, 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., $\text{Co}(\text{II})$], which are more reactive than their d^6 analogs. For example, they undergo ligand dissociation much more readily. The reason

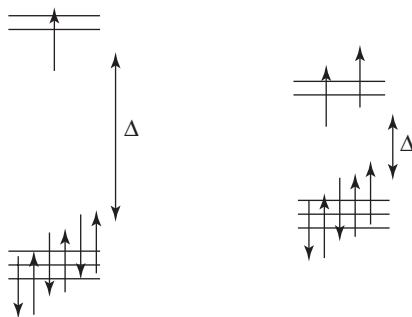


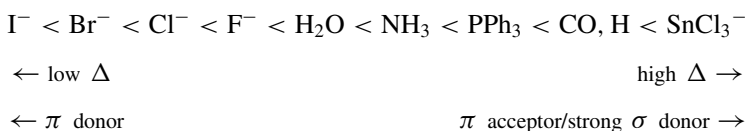
FIGURE 1.3 A d^7 octahedral ion is paramagnetic even in the low-spin form.

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.



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

Odd Versus Even d^n Configurations

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

This is why third-row metals tend to be used when isolation of stable compounds is the aim. When catalysis is the goal (Chapter 9), the intermediates involved have to be reactive and therefore relatively less stable, and first- or second-row metals are sometimes preferred.

Isoconfigurational Ions

Transition metals tend to be treated as a group rather than as individual elements. One reason is that d^n ions of the same configuration (e.g., $n = 6$) show important similarities independent of the identity of the element. This means that d^6 Co(III) is closer in properties to d^6 Fe(II) than to d^7 Co(II). The variable valency of the transition metals leads to many cases of isoconfigurational ions.

1.5 THE LIGAND FIELD

The crystal field picture gives a useful qualitative understanding, but, once having established what to expect, we turn to the more sophisticated *ligand field* model, really a conventional molecular orbital, or MO, 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 σ -donor ligands in an octahedron around the metal. Six of the metal orbitals, the s , the three p , and the two d_σ , which we will call the dsp_σ set, find symmetry matches in the six ligand lone-pair orbitals. In combining the six metal orbitals with the six ligand orbitals, we make a bonding set of six (the M–L σ bonds) that are stabilized, and an antibonding set of six (the M–L σ^* levels) that are destabilized when the six L groups approach to bonding distance. The remaining three d orbitals, the d_π set, do not overlap with the ligand orbitals, and remain nonbonding. In a d^6 ion, we have 6e (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_π set are filled, and the M–L σ^* levels remain unfilled. Note that we can identify the familiar crystal field splitting pattern in the d_π and two of the M–L σ^* levels. The Δ splitting will increase as the strength of the M–L σ bonds 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 σ bonds. We can now see that a d_σ orbital of the crystal field picture is an M–L σ -antibonding orbital.

The L lone pairs start out in free L as pure ligand electrons but become bonding electron pairs shared between L and M when the M–L σ bonds are formed; these are the 6 lowest orbitals in Fig. 1.5 and are always completely filled (12 electrons). Each M–L σ -bonding MO is formed by the combination of the ligand lone pair, $\text{L}(\sigma)$, with $\text{M}(d_\sigma)$ and has both metal and ligand character, but $\text{L}(\sigma)$ predominates. Any MO will more closely resemble the parent atomic orbital that lies closest in energy to it, and $\text{L}(\sigma)$ almost always lies below $\text{M}(d_\sigma)$ and therefore closer to the M–L σ -bonding orbitals. This means that electrons