

THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

Fourth Edition

ROBERT H. CRABTREE

Yale University, New Haven, Connecticut

 **WILEY-
INTERSCIENCE**

A JOHN WILEY & SONS, INC., PUBLICATION

**THE ORGANOMETALLIC
CHEMISTRY OF THE
TRANSITION METALS**

THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

Fourth Edition

ROBERT H. CRABTREE

Yale University, New Haven, Connecticut

 **WILEY-
INTERSCIENCE**

A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2005 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

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

CONTENTS

Preface	ix
List of Abbreviations	xi
1 Introduction	1
1.1 Werner Complexes, 2	
1.2 The Trans Effect, 6	
1.3 Soft Versus Hard Ligands, 8	
1.4 The Crystal Field, 9	
1.5 The Ligand Field, 14	
1.6 Back Bonding, 15	
1.7 Electroneutrality, 19	
1.8 Types of Ligand, 21	
2 General Properties of Organometallic Complexes	29
2.1 The 18-Electron Rule, 30	
2.2 Limitations of the 18-Electron Rule, 35	
2.3 Electron Counting in Reactions, 37	
2.4 Oxidation State, 39	
2.5 Coordination Number and Geometry, 41	
2.6 Effects of Complexation, 45	
2.7 Differences between Metals, 47	
2.8 Outer-Sphere Coordination, 49	

3	Metal Alkyls, Aryls, and Hydrides and Related σ-Bonded Ligands	53
3.1	Transition Metal Alkyls and Aryls, 53	
3.2	Related σ -Bonded Ligands, 68	
3.3	Metal Hydride Complexes, 72	
3.4	σ Complexes, 75	
3.5	Bond Strengths for Classical σ -Bonding Ligands, 79	
4	Carbonyls, Phosphine Complexes, and Ligand Substitution Reactions	87
4.1	Metal Complexes of CO, RNC, CS, and NO, 87	
4.2	Phosphines and Related Ligands, 99	
4.3	Dissociative Substitution, 104	
4.4	Associative Mechanism, 109	
4.5	Redox Effects, the I Mechanism, and Rearrangements in Substitution, 112	
4.6	Photochemical Substitution, 115	
4.7	Steric and Solvent Effects in Substitution, 118	
5	Complexes of π-Bound Ligands	125
5.1	Alkene and Alkyne Complexes, 125	
5.2	Allyl Complexes, 131	
5.3	Diene Complexes, 136	
5.4	Cyclopentadienyl Complexes, 140	
5.5	Arenes and Other Alicyclic Ligands, 148	
5.6	Metalacycles and Isoelectronic and Isolobal Replacement, 152	
5.7	Stability of Polyene and Polyenyl Complexes, 154	
6	Oxidative Addition and Reductive Elimination	159
6.1	Concerted Additions, 162	
6.2	S_N2 Reactions, 165	
6.3	Radical Mechanisms, 166	
6.4	Ionic Mechanisms, 169	
6.5	Reductive Elimination, 170	
6.6	σ -Bond Metathesis, 176	
6.7	Oxidative Coupling and Reductive Cleavage, 177	
7	Insertion and Elimination	183
7.1	Reactions Involving CO, 185	
7.2	Insertions Involving Alkenes, 191	
7.3	Other Insertions, 197	
7.4	α , β , γ , and δ Elimination, 199	

8	Nucleophilic and Electrophilic Addition and Abstraction	207
8.1	Nucleophilic Addition to CO, 210	
8.2	Nucleophilic Addition to Polyene and Polyenyl Ligands, 213	
8.3	Nucleophilic Abstraction in Hydrides, Alkyls, and Acyls, 221	
8.4	Electrophilic Addition, 222	
8.5	Electrophilic Abstraction of Alkyl Groups, 226	
8.6	Single-Electron Transfer Pathways, 228	
8.7	Reactions of Organic Free Radicals with Metal Complexes, 229	
9	Homogeneous Catalysis	235
9.1	Alkene Isomerization, 239	
9.2	Alkene Hydrogenation, 241	
9.3	Alkene Hydroformylation, 254	
9.4	Hydrocyanation of Butadiene, 257	
9.5	Alkene Hydrosilation and Hydroboration, 261	
9.6	Coupling Reactions, 263	
9.7	Surface and Supported Organometallic Catalysis, 266	
10	Physical Methods in Organometallic Chemistry	275
10.1	Isolation, 275	
10.2	^1H NMR Spectroscopy, 276	
10.3	^{13}C NMR Spectroscopy, 281	
10.4	^{31}P NMR Spectroscopy, 282	
10.5	Dynamic NMR, 284	
10.6	Spin Saturation Transfer, 288	
10.7	T_1 and the Nuclear Overhauser Effect, 290	
10.8	Isotopic Perturbation of Resonance, 294	
10.9	IR Spectroscopy, 297	
10.10	Crystallography, 300	
10.11	Other Methods, 302	
11	Metal–Ligand Multiple Bonds	309
11.1	Carbenes, 309	
11.2	Carbynes, 325	
11.3	Bridging Carbenes and Carbynes, 327	
11.4	<i>N</i> -Heterocyclic Carbenes, 330	
11.5	Multiple Bonds to Heteroatoms, 334	
12	Applications of Organometallic Chemistry	343
12.1	Alkene Metathesis, 343	
12.2	Dimerization, Oligomerization, and Polymerization of Alkenes, 350	

12.3	Activation of CO and CO ₂ , 360	
12.4	CH Activation, 364	
12.5	Organometallic Materials and Polymers, 371	
13	Clusters and the Metal–Metal Bond	379
13.1	Structures, 380	
13.2	The Isolobal Analogy, 393	
13.3	Synthesis, 397	
13.4	Reactions, 399	
13.5	Giant Clusters and Nanoparticles, 407	
13.6	Giant Molecules, 411	
14	Applications to Organic Synthesis	417
14.1	Metal Alkyls Aryls, and Hydrides, 418	
14.2	Reduction, Oxidation, and Control of Stereochemistry, 429	
14.3	Protection and Deprotection, 435	
14.4	Reductive Elimination and Coupling Reactions, 438	
14.5	Insertion Reactions, 443	
14.6	Nucleophilic Attack on a Ligand, 447	
14.7	Heterocycles, 454	
14.8	More Complex Molecules, 455	
15	Paramagnetic, High-Oxidation-State, and High-Coordination-Number Complexes	463
15.1	Magnetism and Spin States, 464	
15.2	Polyalkyls, 471	
15.3	Polyhydrides, 476	
15.4	Cyclopentadienyl Complexes, 479	
15.5	<i>f</i> -Block Complexes, 481	
16	Bioorganometallic Chemistry	491
16.1	Introduction, 492	
16.2	Coenzyme B ₁₂ , 497	
16.3	Nitrogen Fixation, 503	
16.4	Nickel Enzymes, 509	
16.5	Biomedical Applications, 517	
	Useful Texts on Allied Topics	521
	Major Reaction Types	523
	Solutions to Problems	525
	Index	539

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 $Pt(C_2H_4)_3$.

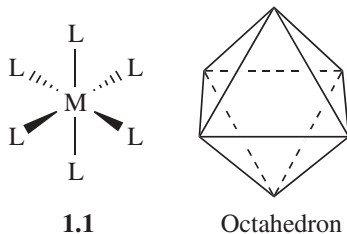
In this chapter we review some fundamental ideas of coordination chemistry, which also apply to organometallic complexes.

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.

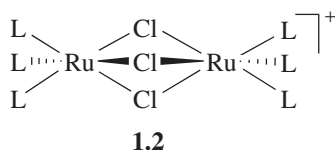
Stereochemistry

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.



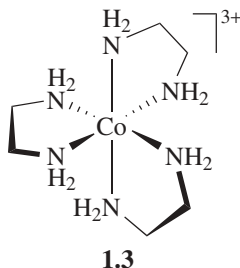
The assembly of metal and ligands that we call a *complex* may have a net ionic charge, in which case it is a complex ion (e.g., $[\text{PtCl}_4]^{2-}$). Together with the counterions, we have a complex salt (e.g., $\text{K}_2[\text{PtCl}_4]$). In some cases both the cation and the anion may be complex, 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.

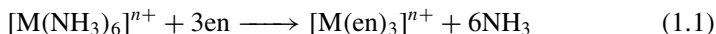


Chelate Effect

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**.

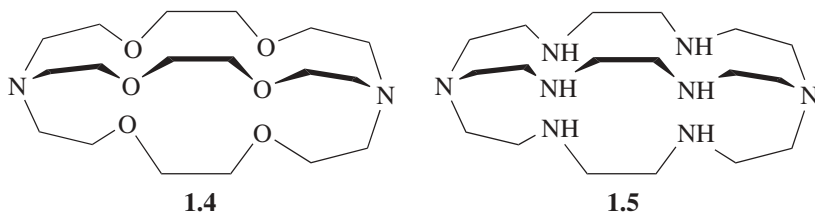


The early Russian investigator Chugaev first drew attention to the fact that chelating ligands are much less easily displaced from a complex than are monodentate ligands of the same type. The reason is illustrated in Eq. 1.1:



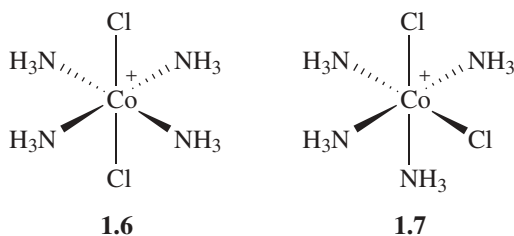
Formation of the tris chelate releases six NH_3 molecules so that the total number of particles increases from four to seven. This creates entropy and so favors the chelate form. Each chelate ring usually leads to an additional factor of about 10^5 in the equilibrium constant for reactions such as Eq. 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

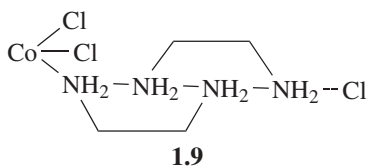
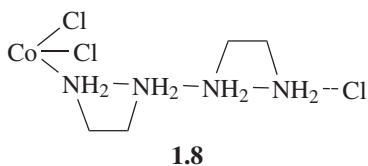


Werner Complexes

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

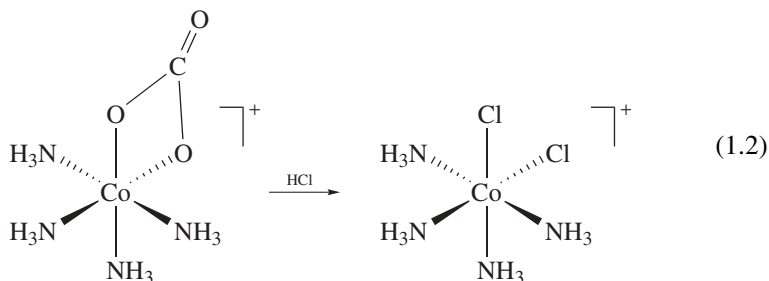


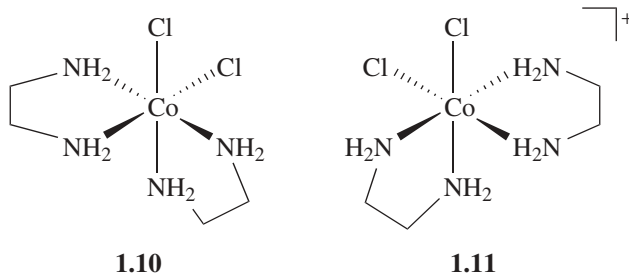
opposing all the major figures in the field, who held that the ligands were bound to one another in chains, and that only the ends of the chains were bound to the metal as in **1.8** and **1.9**. Jørgensen, who led the traditionalists against the



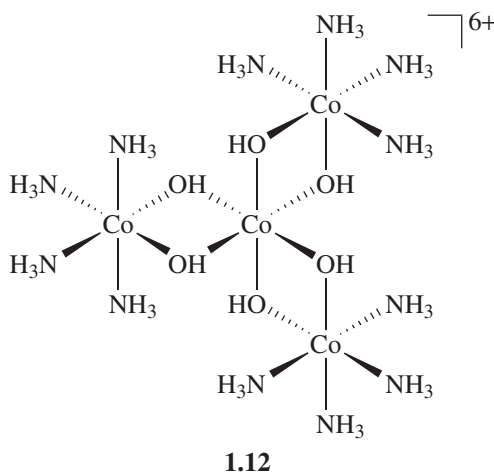
Werner insurgency, was not willing to accept that a trivalent metal, Co^{3+} , could form bonds to six groups; in the chain theory, there were never more than three bonds to Co. Each time Werner came up with what he believed to be proof for his theory, Jørgensen would find a way of interpreting the chain 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.



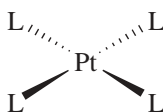
1.2 THE TRANS EFFECT

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".

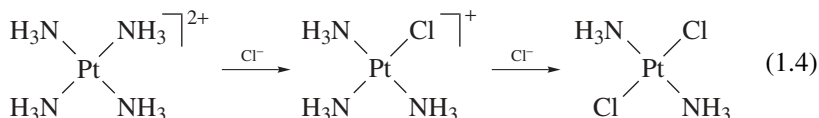
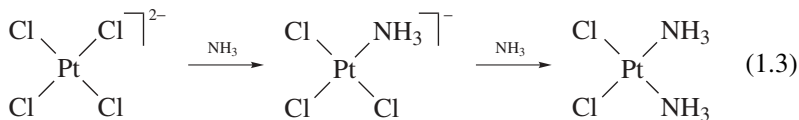
The same ligands also weaken the trans $M-L$ bonds, as shown by a lengthening of the $M-L$ distances found by X-ray crystallography or by some spectroscopic measure, such as M,L coupling constant in the nuclear magnetic resonance (NMR) spectroscopy (Section 10.4), or the $\nu(M-L)$ stretching frequency 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.

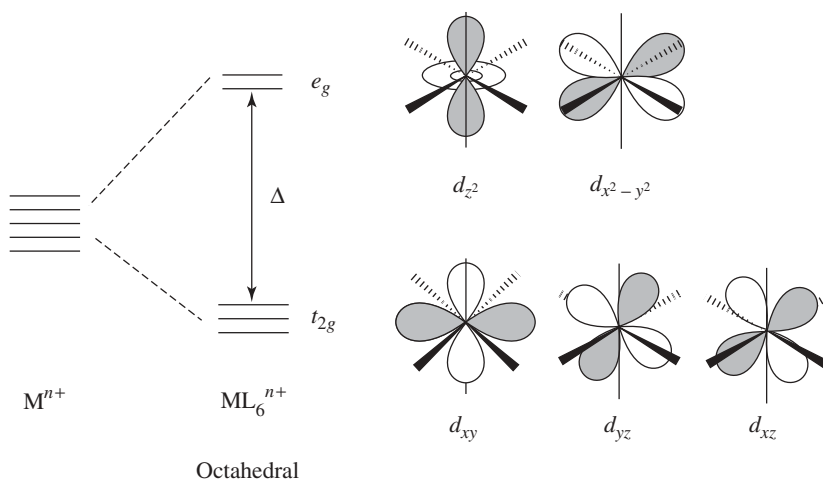


FIGURE 1.1 Effect on the d orbitals of bringing up six ligands along the $\pm x$, $\pm y$, and $\pm z$ directions. In this figure, shading represents the symmetry (not the occupation) of the d orbitals; shaded parts have the same sign of ψ .

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

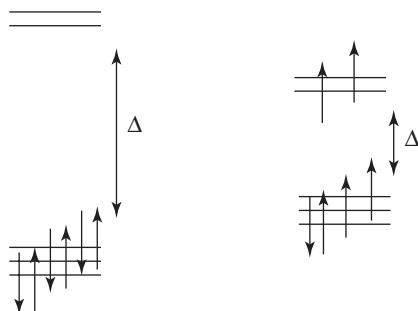


FIGURE 1.2 In a d^6 metal ion, both low- and high-spin complexes are possible depending on the value of Δ . A high Δ leads to the low-spin form.

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

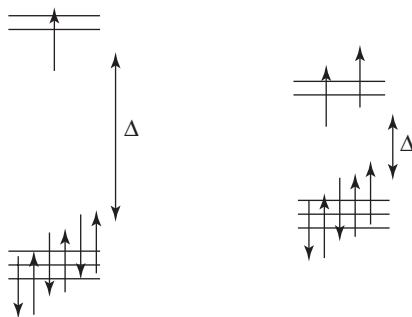


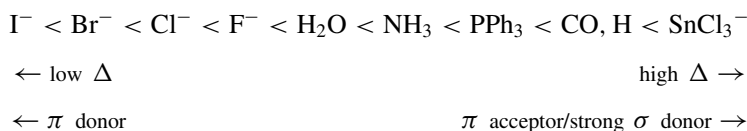
FIGURE 1.3 A d^7 octahedral ion is paramagnetic even in the low-spin form.

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.

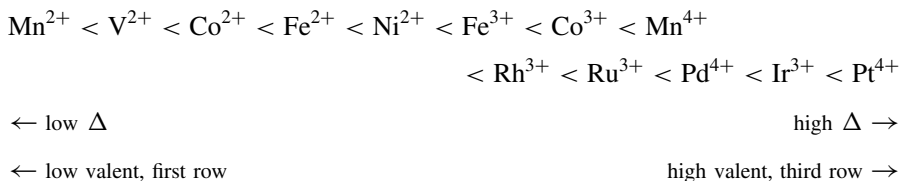
Odd Versus Even d^n Configurations

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.

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 .



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).

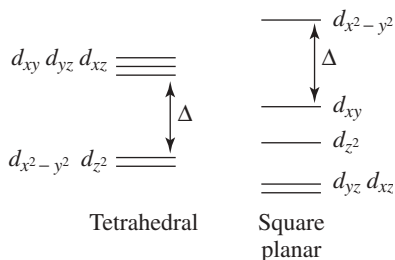


FIGURE 1.4 Crystal field splitting patterns for the common 4-coordinate geometries: tetrahedral and square planar. For the square planar arrangement, the z axis is conventionally taken to be perpendicular to the square plane.

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

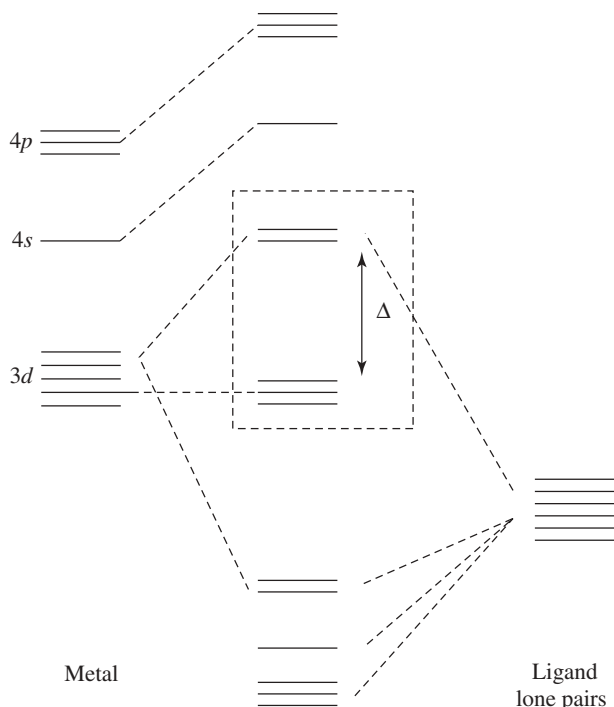


FIGURE 1.5 Molecular orbital, or ligand field picture, of metal ligand bonding in an octahedral ML_6 complex. The box contains the d orbitals.

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 MO diagram and will tend to occupy a larger volume of space, and any electrons in it will tend to be less stable and more available for chemical bonding or removal by ionization.

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

1.6 BACK BONDING

Ligands such as NH_3 are good σ donors but are not significant π acceptors. CO, in contrast, is an example of a good π acceptor. Such π -acid ligands are of very great importance in organometallic chemistry. They tend to be very high

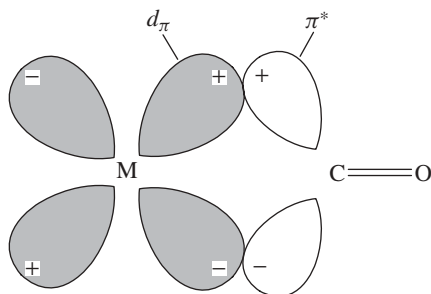


FIGURE 1.6 Overlap between a filled metal d_{π} orbital and an empty CO π^* orbital to give the π component of the M–CO bond. The shading refers to occupancy of the orbitals and the + and – signs, to the symmetry. The M–CO σ bond is formed by the donation of a lone pair on C into an empty d_{σ} orbital on the metal (not shown).

field ligands and form strong M–L bonds. All have empty orbitals of the right symmetry to overlap with a filled d_{π} orbital of the metal. In the case of CO, this orbital is the CO π^* . Figure 1.6 shows how overlap takes place to form the M–C π bond. It may seem paradoxical that an antibonding orbital such as the $\pi^*(\text{CO})$ can form a bond, but this orbital is antibonding only with respect to C and O and can still be bonding with respect to M and C.

We can make the ligand field diagram of Fig. 1.5 appropriate for the case of $\text{W}(\text{CO})_6$ by including the π^* levels of CO (Fig. 1.7). The d_{π} set of levels still find no match with the six CO(σ) orbitals, which are lone pairs on C. They do interact strongly with the empty CO π^* levels. Since the Md_{π} set are filled in this d^6 complex, the d_{π} electrons that were metal centered now spend some of their time on the ligands: This means that the metal has donated some electron density to the ligands. This *back bonding* is a key feature of M–L bonds where L is unsaturated (i.e., has multiple bonds). Note that this can only happen in d^2 or higher configurations; a d^0 ion such as Ti^{4+} cannot back bond and seldom forms stable carbonyl complexes.

As antibonding orbitals, the CO π^* levels are high in energy, but they are able to stabilize the d_{π} set as shown in Fig. 1.7. This has two important consequences: (1) The ligand field splitting parameter Δ rises, explaining why π -bonding ligands have such a strong ligand field; and (2) back bonding allows electron density on the metal as it 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 *basic* or *electron rich*.) They cannot accept further electrons from pure σ donors; this is why $\text{W}(\text{NH}_3)_6$ is not a stable compound. By back bonding, the metal can get rid of some of this excess electron density. In $\text{W}(\text{CO})_6$ 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 air as an oxidant. In $\text{W}(\text{PMe}_3)_6$, in contrast, back bonding is inefficient and the compound exists but is very air sensitive and reactive.

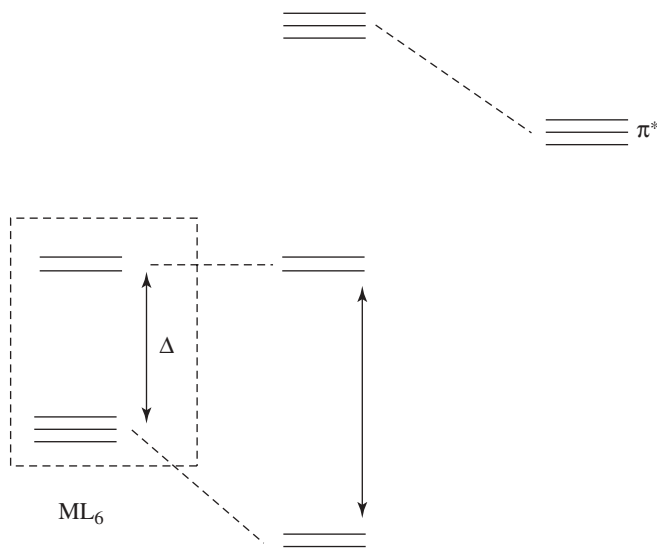


FIGURE 1.7 Effect of “turning on” the π interaction between a π -acceptor ligand and the metal. The unoccupied, and relatively unstable π^* orbitals of the ligand are shown on the right. Their effect is to stabilize the filled d_{π} orbitals of the complex and so increase Δ . In $W(CO)_6$, the lowest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

Spectroscopic and theoretical studies show that for CO this π back donation is usually comparable to or greater than the CO-to-metal electron donation in the σ bond. One of the most direct arguments is structural. The $M=C$ bond in metal carbonyls is usually substantially shorter than an $M-C$ single bond. This is easiest to test when both types of bond are present in the same complex, such as $CpMo(CO)_3Me$, where $M-C$ is 2.38 Å, and $M=CO$ is 1.99 Å. We have to 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.

To confirm that it really is the π^* orbital of CO that is involved in the back bonding, we turn to IR spectroscopy. If CO were bound to the metal by its carbon lone pair, nonbonding with respect to CO, then the $\nu(CO)$ frequency in the complex would differ very little from that in free CO. The compound BH_3 , which is as pure as a σ acceptor as will bind to CO, shows a slight shift of $\nu(CO)$ to higher energy: free CO, 2149 cm^{-1} ; H_3B-CO , 2178 cm^{-1} . Metal complexes, in contrast, show $\nu(CO)$ coordination shifts of hundreds of wavenumbers to lower energy, consistent with the weakening of the C–O bond that would be expected if the π^* orbital were being filled [e.g., $Cr(CO)_6$, $\nu(CO) = 2000\text{ cm}^{-1}$]. 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} ;

$\text{Mn}(\text{CO})_6^+$, 2090 cm^{-1}]. The effect of replacing three π -acceptor COs by the three pure σ -donor nitrogens of the tren ligand ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$) is almost as great as changing the net ionic charge by one unit [e.g., $\text{Cr}(\text{tren})(\text{CO})_3$, 1880 cm^{-1}]. This makes $\nu(\text{CO})$ a good indicator of how electron rich a metal is, and it often correlates well with other ways of estimating nucleophilic character, such as the ease of removing an electron.⁴

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

The dipole moments of a variety of coordination compounds show that the bond moments of the M–L bonds of most σ -donor ligands are about 4 D, with the donor atom positive. In contrast, metal carbonyls show an M–C bond moment that is essentially zero because the M→L back donation and L→M direct donation, together with CO polarization (Section 2.6), cancel out. Formation of the M–CO bond weakens the C–O bond relative to free CO. This will still lead to a stable complex as long as the energy gained from the M–C bond exceeds the loss in C–O. Bond weakening in L on binding is a very common feature in many M–L systems.

Frontier Orbitals

The picture for CO holds with slight modifications for a whole series of π acceptor (or soft) ligands, such as alkenes, alkynes, arenes, carbenes, carbynes, NO, N_2 , and PF_3 . Each has a filled orbital that acts as a σ donor and an empty orbital that acts as a π acceptor. These orbitals are almost always the highest occupied (*HOMO*) and lowest unoccupied molecular orbitals (*LUMO*) of L, respectively. The HOMO of L is a donor to the LUMO of the metal, which is normally d_σ . The LUMO of the ligand accepts back donation from a filled d_π orbital of the metal. The HOMO and LUMO of each fragment, the so-called *frontier orbitals*, nearly always dominate the bonding. This is because strong interactions between orbitals require not only that the overlap between the orbitals be large but also that the energy separation be small. The HOMO of each fragment, M and L, is usually closest in energy to the LUMO of the partner fragment than to any other vacant orbital of the partner. Strong bonding is expected if the HOMO–LUMO gap of both partners is small. A small HOMO–LUMO gap usually makes a ligand soft because it is a good π acceptor, and a d^6 metal soft because it is a good π donor.

π -Donor Ligands

Ligands such as OR^- , F^- , and Cl^- are π donors as a result of the lone pairs that are left after one lone pair has formed the M–L σ bond. Instead of stabilizing the

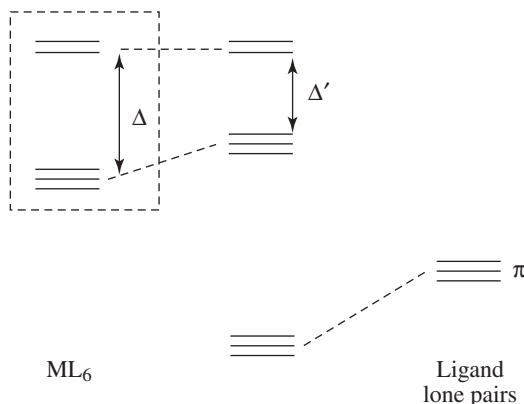


FIGURE 1.8 Effect of “turning on” the π interaction between a π -donor ligand and the metal. The occupied, and relatively stable, lone-pair (π) orbitals of the ligand are shown on the right. Their effect is to destabilize the filled d_{π} orbitals of the complex and so decrease Δ . This is effectively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

d_{π} electrons of a d^6 ion as does a π acceptor, these electrons are now destabilized by what is effectively a repulsion between two filled orbitals. This lowers Δ , as shown in Fig. 1.8, and leads to a weaker M–L bond than in the π -acceptor case (e.g., CoF_6^{3-}). 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 π^* orbitals in Fig. 1.7. If the metal has empty d_{π} orbitals, as in the d^0 ion Ti^{4+} , π donation from the ligand to the metal d_{π} orbitals now leads to stronger metal–ligand bonding; d^0 metals therefore form particularly strong bonds with π -donor ligands [e.g., $\text{W}(\text{OMe})_6$, $[\text{TiF}_6]^{2-}$].

- Coordination inert cases include d^6 octahedral low spin and d^3 octahedral.
- In the commonest geometry, octahedral, d orbitals split into a 3-below-2 pattern.
- The splitting varies as: 3rd row > 2nd row > 1st row metal and high-field > low-field ligand.
- Ligands with back bonding (and also hydride) are soft and high field.

1.7 ELECTRONEUTRALITY

In 1948 Pauling proposed the powerful *electroneutrality principle*. This says that the atoms in molecules arrange themselves so that their net charges fall within rather narrow limits, from about +1 to –1 overall. In fact, the range for any

given element is likely to be narrower than this, and tends toward a preferred charge, which differs according to the electronegativity of the element concerned. The nonmetals, such as C, N, or O, tend to be closer to -1 , and the metals, such as Li, Mg, and Fe, tend to be closer to $+1$. This implies that as far as electroneutrality arguments go, an element will bond best to other elements that have complementary preferred charges. In this way, each can satisfy the other. An electropositive element prefers an electronegative one, as in the compounds NaCl and TiO₂, and elements with an intermediate electronegativity tend to prefer each other, as in HgS and Au metal. An isolated Co³⁺ ion is not a electroneutral species, as it has an excessively high positive charge. In its compounds it will therefore seek good electron donors as ligands, such as O²⁻ in Co₂O₃, or NH₃, in the ammine (NH₃) complexes. On the other hand, an isolated W(0) atom is too electron rich for its electronegativity, so it will prefer net electron-attracting ligands such as CO that can remove electron density.

Trends with Oxidation State

There is a deeper reason why the d orbitals of transition metals are available for back donation only in electron-rich complexes. Co(III), for example, has a filled d_{π} level, but Co(III) does not bind CO because the d_{π} orbital is too low in energy and therefore not sufficiently basic. The reason is that the s , p , and d orbitals respond differently to a change in the charge on the metal. If the metal is in a high oxidation state, like Co(III), then there are electron “holes” in the valence shell compared with the neutral atom. This means that the valence shell of the ion is positive with respect to the situation in the atom. Since d orbitals tend to have their maximum electron density far away from the nucleus (because they have two planar nodes or planes of zero electron density that pass through the nucleus), p orbitals reach their maximum somewhat closer to the nucleus (one planar node), and s orbitals reach their maximum at the nucleus (no planar nodes), the orbitals will be less sensitive to the $3+$ change in the net charge that took place on going from Co(0) to Co(III), in the order $d > p > s$. In other words, the d orbitals will be much more strongly stabilized than the others on going from the atom to the ion. This is why the atomic electron configuration for the transition metals involves s -orbital occupation (e.g., Co, d^7s^2), but the configuration of the ion is d^6 , not d^4s^2 . On the other hand, the more electron rich (i.e., the more reduced, or low oxidation state) the metal complex, the less positive will be the charge on the metal. This will destabilize the d orbitals and make them more available for back donation.

Periodic Trends

We also alter the orbital energies as we go from left to right in the transition series. For each step to the right, a proton is added to the nucleus. This extra positive charge stabilizes all the orbitals. The earlier metals are more electropositive because it is easier to remove electrons from their less stable energy levels. The

sensitivity of the orbitals to this change is different from what we saw above. This time the order is $d \sim s > p$ because the s orbital, having a maximum electron density at the nucleus, is more stabilized by the extra protons that we add for each step to the right in the periodic table, than are the p orbitals, which have a planar node at the nucleus. The d orbitals are stabilized because of their lower principal quantum number (e.g., $3d$ versus $4s$ and $4p$ for Fe). The special property of the transition metals is that all three types of orbital are in the valence shell and have similar energies so they are neither too stable nor too unstable to contribute significantly to the bonding. Metal carbonyls, for example, are most stable for groups 4–10 because CO requires d -orbital participation to bind effectively.

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

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

Ionic compounds with excessively high positive or negative net ionic charges are not normally formed. The great majority of compounds are neutral, net charges of ± 1 are not uncommon, but net ionic charges of ± 2 or greater are increasingly rare unless there is some special reason to expect them, such as the presence of several metals to share the ionic charge.

1.8 TYPES OF LIGAND

Most ligands form the M–L σ bond by using a lone pair, that is, a pair of electrons that are nonbonding in the free ligand. For ligands such as PR_3 or pyridine, these 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, π and σ , of which C_2H_4 and H_2 are typical examples.

π Complexes

Ethylene has no lone pairs, yet it binds strongly to low-valent metals. In this case the HOMO is the $C=C$ π bond, and it is these electrons that form the $M-L$ σ bond, as shown in Fig. 1.9a, hence the term π -complex. The arrow marked “1” represents the π -bonding electron pair of ethylene being donated to the metal. There is also a back-bonding component (marked “2”) where the π^* orbital of ethylene plays the role of acceptor. Since the $C=C$ π bond lies both above and below the molecular plane, the metal has to bind out of the C_2H_4 plane, where the electrons are. This type of binding is represented as $(\eta^2-C_2H_4)$ (pronounced “eta-two ethylene”) where η represents the *hapticity* of the ligand, defined as the number of atoms in the ligand bonded to the metal.

σ Complexes

Molecular hydrogen has neither a lone pair nor a π 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 $H-H$ σ 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 σ^* orbital. The metal binds side-on to H_2 to maximize $\sigma-d_\sigma$ overlap. Related σ complexes⁶ 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 $>$ π -bonding pairs $>$ σ -bonding pairs, because being part of a bond stabilizes electrons. The usual order of binding ability is therefore as follows: lone-pair donor $>$ π donor $>$ σ donor.

M–L Bonding

For lone-pair donors the $M-L$ π 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

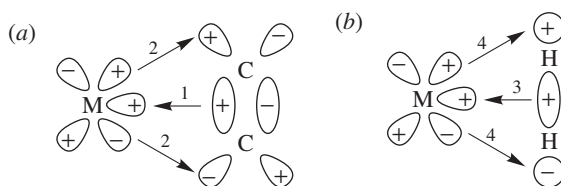
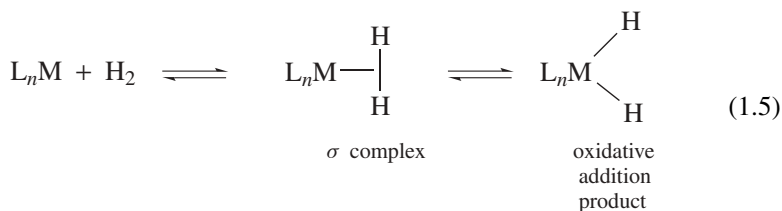


FIGURE 1.9 (a) Bonding of a π -bond donor, ethylene, to a metal. The arrow labeled “1” represents electron donation from the filled $C=C$ π bond to the empty d_σ orbital on the metal; “2” represents the back donation from the filled $M(d_\pi)$ orbital to the empty $C=C$ π^* . (b) Bonding of a σ -bond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

the case for $M-F^-$ ($M = d^6$ metal, Fig. 1.8). For σ and π donors, the $M-L$ π bond is nearly always attractive because if it were not, L would not bind strongly enough to form an isolable complex. In the π -bond case, an $M(d_\pi)$ electron pair is donated to an empty antibonding orbital of the ligand, usually a π^* for π -bond donors and a σ^* for σ -bond donors (Fig. 1.9b). In the case of a π ligand such as ethylene, this back bonding weakens the $C=C$ π bond but does not break it because C_2H_4 is still held together by strong $C-C$ and $C-H$ σ 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. PF_3 is unusual because it is a strong π acceptor even though it has no multiple bonds; in Section 4.2 we see that PF σ^* orbital plays the role of ligand LUMO.

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



Ambidentate Ligands

Some ligands have several alternate types of electron pair available for bonding. For example, aldehydes (**1.14**) have the $C=O$ π bond and lone pairs on the oxygen. When they act as π -bond donors, aldehydes bind side-on (**1.15**) like ethylene, when they act as lone-pair donors, they bind end-on (**1.16**). Equilibria such as Eq. 1.6 [$R = \text{aryl}$; $L_nM = \text{CpRe}(\text{NO})\text{PPh}_3^+$] are possible, as Gladysz has shown.^{8a} The more sterically demanding π -bound form (**1.15**) is favored for unhindered metal complexes; **1.15** also involves back donation and so is also favored by more electron-donor metal fragments and more electron-acceptor R groups. Alkenes have both a $C=C$ π bond and $C-H$ σ bonds. Gladysz^{8b} has

