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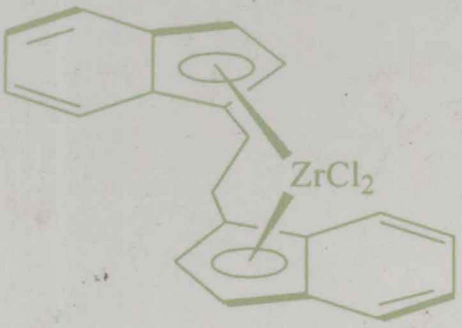
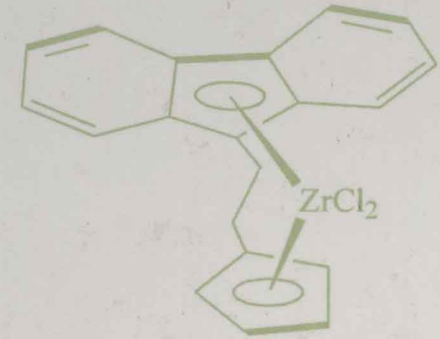
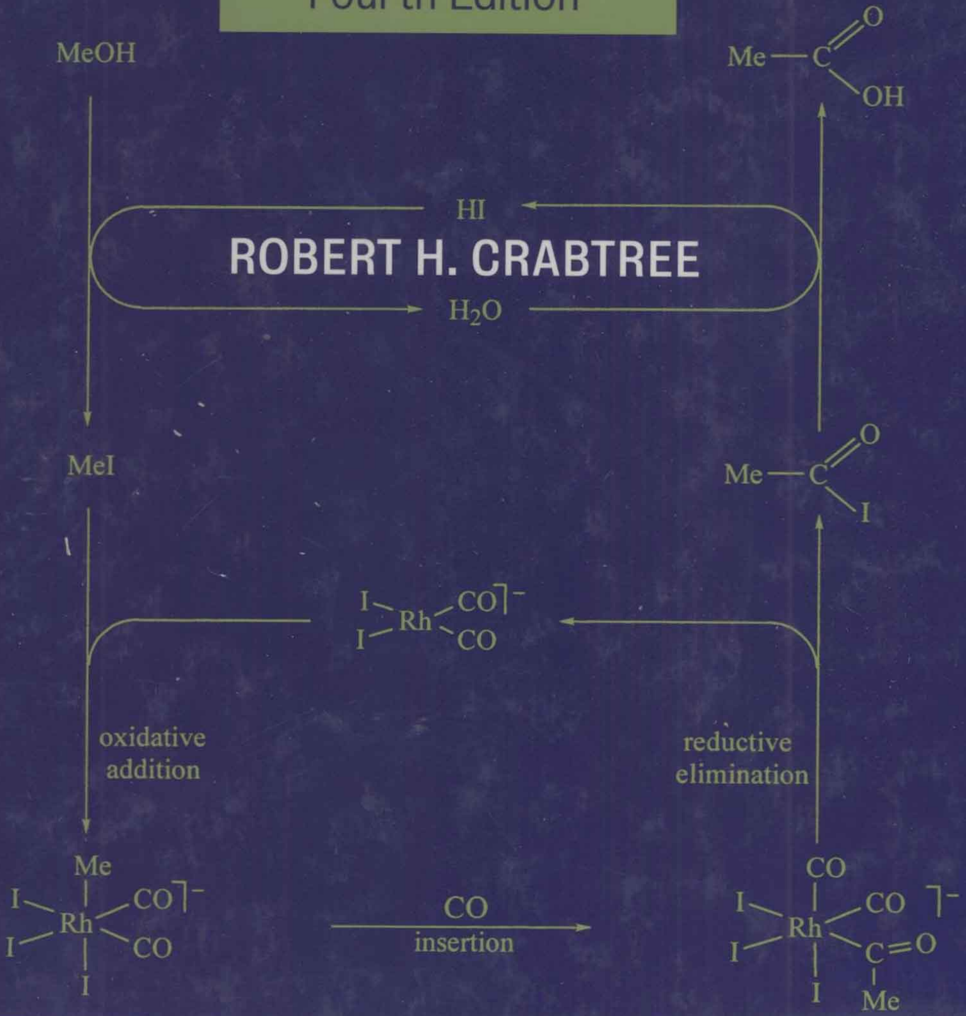




THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

Fourth Edition

ROBERT H. CRABTREE


MeOH
$Me-C(=O)OH$
HI
H_2O
MeI
$Me-C(=O)I$
$[RhI_2(CO)_2]^-$
oxidative addition
reductive elimination
$[RhI_3(Me)(CO)_2]^-$
CO insertion
$[RhI_3(CO)_2(COMe)]^-$

THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

Fourth Edition

ROBERT H. CRABTREE
Yale University, New Haven, Connecticut

WILEY-
INTERSCIENCE

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PREFACE

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ROBERT H. CRABTREE

New Haven, Connecticut
January 2005

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LIST OF ABBREVIATIONS

[]	Encloses complex molecules or ions
□	Vacant site or labile ligand
1°, 2°, ...	Primary, secondary, ...
A	Associative substitution (Section 4.4)
acac	Acetylacetone
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_5H_5, C_5Me_5
Cy	Cyclohexyl
∂^+	Partial positive charge
δ	Chemical shift (NMR)
Δ	Crystal field splitting (Section 1.4)
D	Dissociative substitution mechanism (Section 4.3)
d_σ, d_π	σ-Acceptor and π-donor metal orbitals (see Section 1.4)
diars	$Me_2AsCH_2CH_2AsMe_2$
dpe or dppe	$Ph_2PCH_2CH_2PPh_2$

dmf	Dimethylformamide
dmg	Dimethyl glyoximate
dmpe	$Me_2PCH_2CH_2PMe_2$
DMSO	Dimethyl sulfoxide
d^n	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	$H_2NCH_2CH_2NH_2$
eq	Equivalent
Et	Ethyl
EPR	Electron paramagnetic resonance
eu	Entropy units
Fp	$(C_5H_5)(CO)_2Fe$
fac	Facial (stereochemistry)
Hal	Halogen
$HBpz_3$	Tris(pyrazolyl)borate
HOMO	Highest occupied molecular orbital
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_nM	Generalized metal fragment with n ligands
lin	linear
LUMO	Lowest unoccupied molecular orbital
μ	Descriptor for bridging (Section 1.1)
m-	Meta
Me	Methyl
mer	Meridional (stereochemistry)
m_r	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^-
o-	Ortho
OAc	Acetate
oct	Octahedral (Table 2.5)
ofcot	Octafluorocyclooctadiene

OS	Oxidation state (Section 2.4)
p-	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	t-BuCH=CH_2
thf	Tetrahydrofuran
triphos	$MeC(CH_2PPh_2)_3$
TBP or trig. bipy	Trigonal bipyramidal (Table 2.5)
TMEDA	$Me_2NCH_2CH_2NMe_2$
TMS	Trimethylsilyl
Ts	*p*-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)

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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

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The Organometallic Chemistry of the Transition Metals, Fourth Edition, by Robert H. Crabtree
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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 $Pt(C_2H_4)_3$.

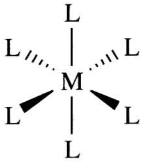
In this chapter we review some fundamental ideas of coordination chemistry, which also apply to organometallic complexes.

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.



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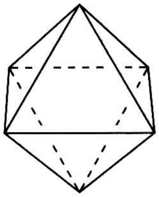
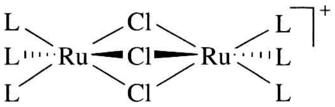


Octahedron

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., $[PtCl_4]^{2-}$). Together with the counterions, we have a complex salt (e.g., $K_2[PtCl_4]$). In some cases both the cation and the anion may be complex, as in the picturesquely named *Magnus' green salt* $[Pt(NH_3)_4][PtCl_4]$. Square brackets are used to enclose the individual complex molecules or ions where necessary to avoid ambiguity.

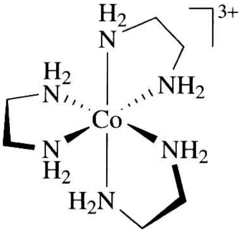
Those ligands that have a donor atom with more than one lone pair can donate one lone pair to each of two or more metal ions. This gives rise to polynuclear complexes, such as the orange crystalline compound **1.2** ($L = PR_3$). The bridging group is represented in formulas by using the Greek letter μ (pronounced "mu") as in $[Ru_2(\mu\text{-}Cl)_3(PR_3)_6]^+$. Note how **1.2** can be considered as two octahedral fragments sharing the face that contains the three chloride bridges.



1.2

Chelate Effect

Other ligands can have more than one donor atom, each with its lone pair; an example is ethylenediamine ($NH_2CH_2CH_2NH_2$, 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**.



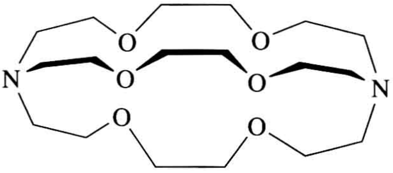
1.3

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:

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

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]



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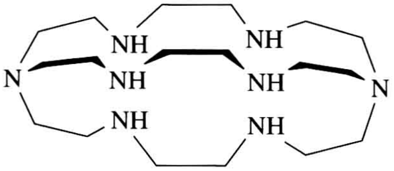
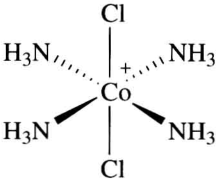


1.5

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



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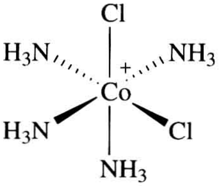
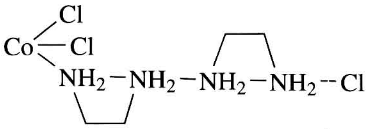


1.7

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



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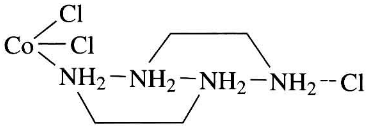
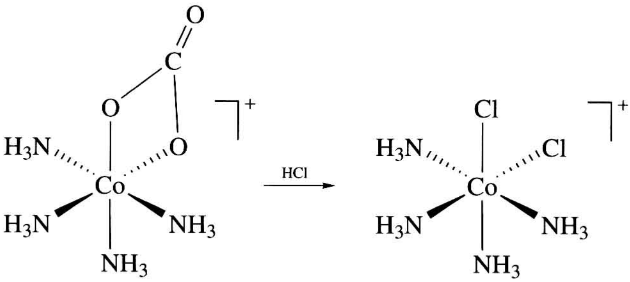


1.9

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 $[Co(NH_3)_4Cl_2]^+$ (**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 $[Co(NH_3)_4(NO_2)_2]^+$. 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 ($Co{-}NO_2$) and O ($Co{-}ONO$) in the other. Werner then showed that there were two isomers of $[Co(en)_2Cl_2]^+$, 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 $[Co(NH_3)_4Cl_2]^+$ by an ingenious route (Eq. 1.2) via the carbonate $[Co(NH_3)_4(O_2CO)]$ 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. Jorgensen, receiving a sample of this purple cis complex by mail, conceded defeat.



(1.2)

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