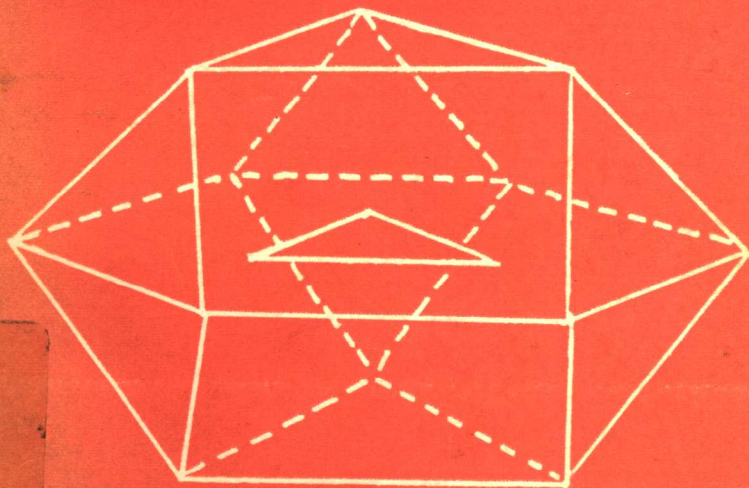


THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

Robert H. Crabtree



A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

World Publishing Corporation

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Robert H. Crabtree
Yale University
New Haven, Connecticut

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PREFACE

This book is intended for senior undergraduate and graduate courses in organometallic chemistry. It is based on a course given at Yale University for a number of years by the author. It should also prove useful to research workers in allied fields who want to become better acquainted with the subject.

The chapters are relatively self-contained and some (e.g., Chapter 10 or 16) may be omitted if desired. There are frequent cross-references and references to the literature, which should prove useful to graduate students and organometallic chemists in general. Problems and solutions are included.

I thank Rich Uriarte (General Electric) for encouraging me to write this book, my former student Charles Parnell (du Pont) for technical help, and my colleague Jack Faller for helpful suggestions. I also thank my teachers Malcolm Green and Joseph Chatt, who helped me think more deeply about the subject, and Hugh Felkin, who sensitized me to the organic implications of organometallic chemistry. I thank Ms. Lisa Crocker for helpful suggestions. Yale University gave me a semester leave to write this book; part of it was also written during the tenure of an Albright and Wilson Visiting Professorship at Warwick University and an Esso Visiting Lectureship at the University of Toronto.

ROBERT H. CRABTREE

*Bethany, Connecticut
September 1987*

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
a.o.	Atomic orbital
bipy	2,2'-Bipyridyl
Bu	Butyl
cata	Catalyst
CIDNP	Chemically induced dynamic nuclear polarization (Section 6.3)
C.N.	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)
d_{σ}, d_{π}	σ -Acceptor and π -donor metal orbitals (see Section 1.4)
dpe	$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$
dmf	Dimethylformamide
dmg	Dimethyl glyoximate
dmpe	$\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$
dmso	Dimethyl sulfoxide
η	Descriptor for hapticity (Section 2.1)
E, E^+	Generalized electrophile
e.e.	Enantiomeric excess
en	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
eq	Equivalent
Et	Ethyl
Fp	$(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}$
fac	Facial (stereochemistry)
HBpz ₃	Tris(pyrazolyl)borate
homo	Highest occupied molecular orbital
I	Nuclear spin or intermediate substitution mechanism
IPR	Isotopic perturbation of resonance (Section 10.8)
L	Generalized ligand, in particular a 2e ligand (L model for ligand binding is discussed on pp. 90–91)
L_nM	Generalized metal fragment with n ligands
lumo	Lowest unoccupied molecular orbital
μ	Descriptor for bridging (Section 1.1)
m -	Meta
Me	Methyl
mer	Meridional (stereochemistry)
m_r	Reduced mass
m.o.	Molecular orbital
ν	Frequency
nbd	Norbornadiene
NOE	Nuclear Overhauser effect (Section 10.7)
Np	Neopentyl
Nu, Nu^-	Generalized nucleophile

o-	Ortho
OAc	Acetate
oct	Octahedral (Table 2.5)
ofcot	Octafluorocyclooctadiene
O.S.	Oxidation state (Section 2.4)
p-	Para
Ph	Phenyl
py	Pyridine
r.f.	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	$t\text{-BuCH=CH}_2$
thf	Tetrahydrofuran
triphos	$\text{MeC}(\text{CH}_2\text{PPh}_2)_3$
TBP or trig. bipy	Trigonal bipyramidal (Table 2.5)
TMEDA	$\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$
TMS	Trimethylsilyl
v.b.	Valence bond
X	Generalized 1e anionic ligand (Section 2.1) (X_2 model for ligand binding is discussed on pp. 90–91)

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1

INTRODUCTION

Transition metal organometallic chemistry is an important part of the modern renaissance of inorganic chemistry that began in the 1950s and 1960s. It has always had strong links with organic chemistry and is beginning to make them with biochemistry. It is a young and vigorous field: much of the work described in this book has been carried out in the last 15 years.

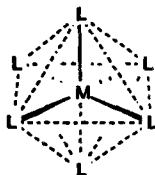
Transition metal ions are Lewis acids. This means that they can bind the lone pairs of *ligands* L , which are simply Lewis bases, to give a coordination compound, or *complex* ML_n , as in the familiar aqua ions $[M(OH_2)_6]^{2+}$ ($M = V, Cr, Mn, Fe, Co, \text{ or } Ni$).

Organometallic complexes contain an $M-C$ bond. Such species tend to be more covalent, and the metal is often more reduced, than in classical coordination compounds such as the aqua ions. Ligands which 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 $Pt(C_2H_4)_2$.

In the first few sections of this chapter we will review some fundamental ideas of coordination chemistry, which also apply to organometallic complexes.

1.1 Werner Complexes

The geometry most commonly adopted for coordination compounds¹ (or Werner complexes) is the octahedron (1.1), one of the Pythagorean regular

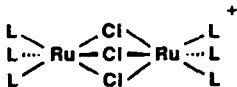


1.1

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.

The assembly of metal and ligands that we call a complex may have a net charge, in which case we call it a complex ion (e.g., $[PtCl_4]^{2-}$). Together with the counter ions, 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's Green Salt $[Pt(NH_3)_4][PtCl_4]$. Square brackets are used where necessary to enclose the individual complex molecules or ions.

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

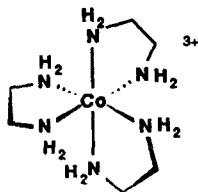


1.2

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 as 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. Structure 1.3 is a typical example of such a complex.

The early Russian investigator Chugaev first noted that chelating ligands are much less easily displaced from a complex than are monodentate ligands of the same type. The main reason is illustrated in Eq. (1.1).

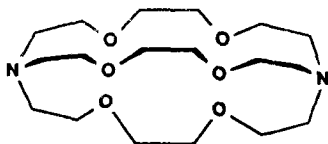




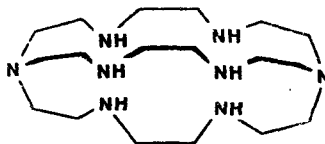
1.3

The number of particles increases from 4 to 7 on making the chelate complex. This creates entropy, and so favors the chelate form. Each chelate ring leads to an additional factor of about 10^5 in the equilibrium constant for reactions like Eq. (1.1). Equilibrium constants for complex formation are usually called formation constants; the higher the value the more stable the complex.

Not only does chelation make the complex more stable, but it also has stereochemical consequences. 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

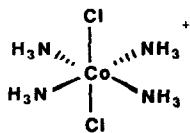


1.4

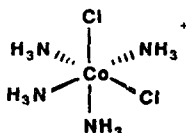


1.5

Alfred Werner developed the modern picture of coordination complexes in the 20 years that followed 1896 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**.

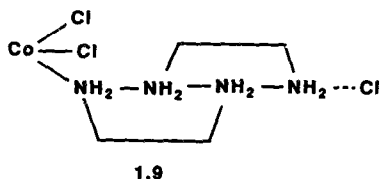
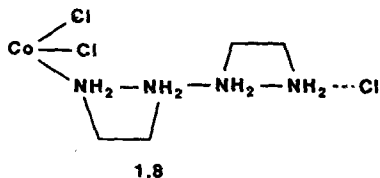


1.6



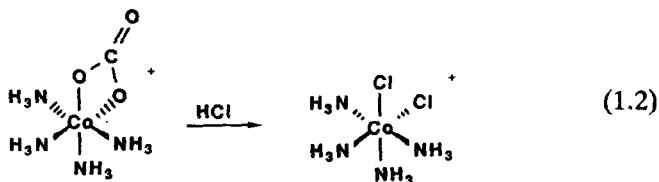
1.7

In doing so, he was opposing the views of 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.

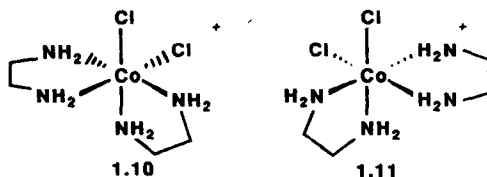


Jørgensen, who led the traditionalists against the Werner insurgency, was not willing to accept that a trivalent metal, Co^{3+} , could form bonds to six groups; in the chain theory, there were never more than three bonds to Co. Each time Werner came up with what he believed to be proof for his theory, 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); the chain theory predicts that there should be only one isomer. Up to that time, only a green isomer had ever been found. We now call this the trans isomer (1.6), because the two Cl ligands occupy opposite vertices of the octahedron. Using Werner's theory, there should also have been a second isomer, 1.7 (now called cis), in which the Cl ligands occupy adjacent vertices. On the other hand, 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 argument by saying that these were not cis and trans isomers but that the nitrite ligands in the two isomers were simply bound in a different way, 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. Jørgensen brushed this aside by invoking the two chain isomers 1.8 and 1.9.

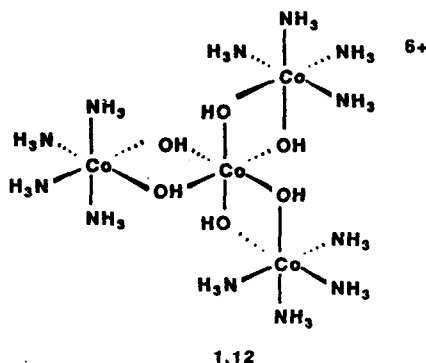
In 1907 Werner finally succeeded in making the elusive purple cis isomer of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (1.7) by a clever route (Eq. 1.2) involving the corresponding carbonate $[\text{Co}(\text{NH}_3)_4(\text{O}_2\text{CO})]$, in which two oxygens of the chelating dianion are both bound to the metal and are therefore necessarily cis.



Treatment with HCl at 0°C liberates CO₂ and gives the cis dichloride. Jørgensen, receiving a sample of this purple cis complex by mail, conceded defeat. Later, Werner resolved optical isomers of some of his compounds of the general type [Co(en)₂XY]ⁿ⁺ (1.10 and 1.11). Only an octahedral ligand 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, hence 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°, and required 1000 recrystallizations to resolve. Werner won the Nobel Prize in chemistry for this work in 1915.



1.2 The Trans Effect

In the 1920s Chernaev discovered that certain ligands facilitate the replacement or *substitution* of a second ligand trans to the first by an external ligand. Ligands that are more effective at this labilization are said to have a higher *trans effect*. We discuss in detail how this happens in Section 4.4, for the moment we need only note that the effect is most marked in substitution on Pt(II), and that the highest trans effect ligands either form unusually strong σ -bonds, such as H⁻, Me⁻, or SnCl₃⁻, or unusually strong