



# TRANSITION-METAL ORGANOMETALLIC CHEMISTRY

## An Introduction

R. Bruce King

*Department of Chemistry  
University of Georgia  
Athens, Georgia*



ACADEMIC PRESS

New York and London 1969

COPYRIGHT © 1969, BY ACADEMIC PRESS, INC.

ALL RIGHTS RESERVED

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,  
BY PHOTOSTAT, MICROFILM, RETRIEVAL SYSTEM, OR ANY  
OTHER MEANS, WITHOUT WRITTEN PERMISSION FROM  
THE PUBLISHERS.

ACADEMIC PRESS, INC.

111 Fifth Avenue, New York, New York 10003

*United Kingdom Edition published by*

ACADEMIC PRESS, INC. (LONDON) LTD.

Berkeley Square House, London W1X 6BA

LIBRARY OF CONGRESS CATALOG CARD NUMBER : 72-84240

PRINTED IN THE UNITED STATES OF AMERICA

**Transition-Metal  
Organometallic Chemistry**  
**An Introduction**

## PREFACE

Since the discovery of ferrocene in 1951, transition-metal organometallic chemistry has developed into a major discipline. Many compounds with unusual structures, reactions, and physical properties have been discovered. Such compounds are of interest both in various areas of basic chemistry and in certain applications, notably catalysis and metal deposition.

The growing body of information in this discipline, as well as its increasing relevance to most areas of chemistry, makes some knowledge of this field necessary for many practicing chemists in other areas. This book presents the basic facts and principles of transition-metal organometallic chemistry in a manner suitable to introduce this field to graduate students, advanced undergraduates, and practicing research workers. Although the entire field is not covered exhaustively, extensive references are given for the reader wishing more detailed information on various subjects discussed in the book.

The first chapter is the longest one since it summarizes the most important principles in the field. The later chapters are more descriptive in nature, summarizing specific organometallic chemistry of the various transition metals according to their positions in the Periodic Table. This type of organization not only permits emphasis of general principles such as might be desirable for a course, but also makes this book suitable for an introduction to the organometallic chemistry of a specific metal which may be of particular interest to the reader.

The material for this book is based on a short course sponsored by the American Chemical Society which I presented in Atlanta, Georgia, Bethlehem, Pennsylvania, and Boston, Massachusetts at various times during 1967 and 1968. It should be useful as a text for a portion of a graduate level course in organometallic chemistry. It is directed to a reader at the level of a beginning graduate student with a good background in all areas of undergraduate chemistry but no prior specific background in transition-metal organometallic chemistry. However, many active research workers in one area of this field may also find this work a useful review for other areas of the discipline.

I would like to acknowledge helpful discussions with Professor E. C. Ashby of the Georgia Institute of Technology with whom I gave the short course mentioned above. I would also like to acknowledge the cooperation of my wife and family during the various phases of preparing this book.

*Athens, Georgia*  
*July, 1969*

R. BRUCE KING

# Contents

<i>Preface</i>	...	v
----------------	-----	---

## Chapter I.      **General Principles of Transition-Metal Organometallic Chemistry**

Introduction	1
Historical Development of Transition-Metal Organometallic Chemistry	3
Some Aspects of the Bonding in Coordination Compounds	4
Metal Carbonyls	9
Metal Cyclopentadienyls	14
Metal Complexes of Other $C_n H_n$ Ring Systems and Their Derivatives	20
Preparation of $\pi$ -Complexes of Benzene and Related Aromatic Compounds	22
Metal-Olefin Complexes	25
Metal-Alkyne (Acetylene) Complexes	29
Metal $\pi$ -Allyl Derivatives	31
Other Delocalized Carbon Ligands	34
Compounds with Transition-Metal-Carbon $\sigma$ -Bonds	35
Summary of Chapter I and Further Plan of This Volume	39
References	40
Supplementary Reading	42
Questions	42

## Chapter II.      **Organometallic Derivatives of the Early Transition Metals**

Introduction	44
Organometallic Chemistry of the Lanthanides (Including Scandium and Yttrium)	44
Organometallic Chemistry of the Actinides	45
Organometallic Chemistry of Titanium- $\pi$ -Cyclopentadienyl Derivatives	46
Other Organometallic Derivatives of Titanium	50
Organometallic Chemistry of Zirconium and Hafnium	51
Organometallic Chemistry of Vanadium	53
Organometallic Chemistry of Niobium and Tantalum	59
References	60
Supplementary Reading	62
Questions	62

### Chapter III. Organometallic Derivatives of Chromium, Molybdenum, and Tungsten

Introduction ... ..	63
The Metal Hexacarbonyls ... ..	63
Reactions of the Metal Hexacarbonyls ... ..	64
Metal Carbonyl Halide Derivatives ... ..	65
Metal Carbonyl Anions ... ..	67
Metal Carbonyl Derivatives of Olefins, Alkynes, and Aromatic Compounds (Arenes) ... ..	68
Substituted Octahedral Metal Carbonyls ... ..	73
Cyclopentadienylmetal Carbonyl Derivatives ... ..	75
Cyclopentadienylmetal Nitrosyl Derivatives ... ..	81
Biscyclopentadienyl Derivatives of Chromium, Molybdenum, and Tungsten ... ..	83
Other Chromium, Molybdenum, and Tungsten Derivatives with Two $\pi$ -Bonded Rings ... ..	85
Miscellaneous Organochromium Compounds ... ..	88
References ... ..	89
Supplementary Reading ... ..	91
Questions ... ..	91

### Chapter IV. Organometallic Derivatives of Manganese, Technetium, and Rhenium

Introduction ... ..	93
The Dimetal Decacarbonyls ... ..	94
Other Metal Carbonyl Derivatives ... ..	95
$\pi$ -Cyclopentadienyl Derivatives ... ..	100
Miscellaneous Organometallic Derivatives ... ..	106
References ... ..	109
Questions ... ..	110

### Chapter V. Organometallic Derivatives of Iron, Ruthenium, and Osmium

Introduction ... ..	111
Metallocenes ... ..	112
Iron Carbonyls ... ..	118
Iron Carbonyl Anions ... ..	119
Iron Carbonyl Halide Derivatives ... ..	120
Iron Carbonyl Sulfur Derivatives ... ..	122
Iron Carbonyl Nitrosyl Derivatives ... ..	123
Olefin Derivatives of Iron Carbonyls ... ..	124
Cyclobutadienetetracarbonyliron and Its Derivatives ... ..	129
$\pi$ -Allyliron Carbonyl Derivatives ... ..	131
Reactions of Iron Carbonyls with Allenes and Cumulenes; Other Delocalized Systems ... ..	131
Reactions of Acetylenes with Iron Carbonyls ... ..	133
Fluorocarbon Derivatives of Iron Carbonyls ... ..	134
Ruthenium and Osmium Carbonyl Derivatives ... ..	136
Cyclopentadienylmetal Carbonyl Derivatives ... ..	138
Benzene, Cyclohexadienyl, and Cyclohexadiene Derivatives ... ..	143

References	...	...	...	...	...	...	144
Supplementary Reading			...	...	...	...	147
Questions	...	...	...	...	...	...	147

## Chapter VI. Organometallic Derivatives of Cobalt, Rhodium, and Iridium

Introduction	...	...	...	...	...	...	148
Cobalt Carbonyls	...	...	...	...	...	...	148
Other Cobalt Carbonyl Derivatives	...	...	...	...	...	...	150
Rhodium and Iridium Carbonyls	...	...	...	...	...	...	153
$\pi$ -Cyclopentadienyl Derivatives	...	...	...	...	...	...	155
Olefin Complexes (Rhodium)	...	...	...	...	...	...	159
Allyl Derivatives (Rhodium)	...	...	...	...	...	...	160
Cobalt Alkyls	...	...	...	...	...	...	161
References	...	...	...	...	...	...	163
Supplementary Reading	...	...	...	...	...	...	165
Questions	...	...	...	...	...	...	165

## Chapter VII. Organometallic Derivatives of Nickel, Palladium, and Platinum

Introduction	...	...	...	...	...	...	166
Organometallic Chemistry of Nickel	...	...	...	...	...	...	166
$\pi$ -Allyl Derivatives of Nickel, Palladium, and Platinum	...	...	...	...	...	...	172
Alkyl Derivatives of Nickel, Palladium, and Platinum	...	...	...	...	...	...	173
Olefin Complexes of Palladium and Platinum	...	...	...	...	...	...	174
References	...	...	...	...	...	...	176
Supplementary Reading	...	...	...	...	...	...	177

## Chapter VIII. Organometallic Derivatives of Copper, Silver, and Gold

Text	...	...	...	...	...	...	...	178
References	...	...	...	...	...	...	...	180

<b>Supplementary Readings</b> ...	...	...	...	...	181
-----------------------------------	-----	-----	-----	-----	-----

*Author Index* ... .. 183

*Subject Index* ... .. 193



## CHAPTER I

# General Principles of Transition-Metal Organometallic Chemistry

### Introduction

Transition metals are defined as elements which possess incompletely filled  $d$  orbitals in the ground state. They thus include the metals shown in the portion of the periodic table depicted in Table I-1. All of these metals form organometallic derivatives. However, with one exception, presently known organometallic derivatives of the lanthanides and actinides are limited to highly ionic derivatives of the cyclopentadienide and substituted cyclopentadienide anions.

The availability of low-lying, filled metal  $d$  orbitals for participation in the bonding makes transition-metal organometallic derivatives very different both in type and properties from nontransition-metal organometallic derivatives. The nontransition-metal organometallic compounds normally have "conventional" organic groups, such as methyl, ethyl, and phenyl, bonded to the metal atom by  $\sigma$ -bonds similar in type to the carbon-carbon and carbon-hydrogen bonds commonly encountered in organic chemistry. The only significant deviations from this pattern in nontransition-metal organometallic chemistry occur in the highly ionic bonds found in alkyls and aryls of the alkali metals and other very electropositive elements, and in the electron-deficient alkyl bridge bonds found in aluminum alkyls and related compounds. By contrast, transition-metal organometallic compounds contain a much greater variety of organic groups, often with much more complicated (and sometimes ill-understood) bonding schemes frequently involving the  $d$  electrons of the transition metals. Many of the most common organic groups in transition-metal organometallic chemistry, including the ubiquitous carbonyl and  $\pi$ -cyclopentadienyl groups, are not encountered at all in nontransition-metal organometallic chemistry. The first chapter in this book on transition-metal organometallic chemistry will discuss, in a qualitative and somewhat oversimplified manner, the bonding to transition metals of some of the most

TABLE I-I  
THE TRANSITION METALS

Group	III	IV	V	VI	VII	VIII	VIII	VIII	IB
Electrons needed to attain rare-gas configuration	15	14	13	12	11	10	9	8	7
3 <i>d</i> Transition series	Sc Scandium Z = 21	Ti Titanium Z = 22	V Vanadium Z = 23	Cr Chromium Z = 24	Mn Manganese Z = 25	Fe Iron Z = 26	Co Cobalt Z = 27	Ni Nickel Z = 28	Cu Copper Z = 29
4 <i>d</i> Transition series	Y Yttrium Z = 39	Zr Zirconium Z = 40	Nb Niobium Z = 41	Mo Molybdenum Z = 42	Tc Technetium Z = 43	Ru Ruthenium Z = 44	Rh Rhodium Z = 45	Pd Palladium Z = 46	Ag Silver Z = 47
5 <i>d</i> Transition series	Lanthanides La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu	Hf Hafnium Z = 72	Ta Tantalum Z = 73	W Tungsten Z = 74	Re Rhenium Z = 75	Os Osmium Z = 76	Ir Iridium Z = 77	Pt Platinum Z = 78	Au Gold Z = 79

important organic groups forming metal-carbon bonds. However, in order to give the reader an approximate indication of the development of transition-metal organometallic chemistry, a brief historical survey of some of the key developments in this area will first be presented.

### Historical Development of Transition-Metal Organometallic Chemistry

The development of transition-metal organometallic chemistry dates back to 1827 when Zeise [1] reported the first transition-metal organometallic compound, the ethylene-platinum complex  $\text{K}[\text{PtCl}_3\text{C}_2\text{H}_4]$ . Subsequent developments in this area of organometallic chemistry arose not in orderly steps from this original discovery but, instead, from several other initially unrelated discoveries. These include the discovery of nickel tetracarbonyl in 1890 by Mond, Langer, and Quincke [2] which led to the area of metal carbonyl chemistry developed further largely by Hieber and his co-workers from about 1920 to the present. Another initially unrelated discovery was that of the polyphenylchromium compounds by Hein in 1919 [3]. These compounds represented one of the great enigmas in inorganic chemistry for several decades until Fischer and Hafner [4] discovered dibenzenechromium in 1955. Subsequently the bonding in dibenzenechromium was shown to be similar to that in the polyphenylchromium compounds of Hein. Meanwhile, another key event in transition-metal organometallic chemistry had occurred: the discovery of ferrocene (biscyclopentadienyliron) in 1951 by two different groups of workers (Kealy and Pauson [5] in the United States and Miller, Tebboth, and Tremaine [6] in Great Britain). The discovery of ferrocene led to the development of metal cyclopentadienyl chemistry largely in two different laboratories: that of Wilkinson at Harvard University (United States) and that of E. O. Fischer in Munich, Germany. Since the middle 1950's the synthesis and study of unusual transition-metal organometallic derivatives has continued at a fast and furious rate in many laboratories throughout all developed nations of the world. Many of these studies have been of an intensive nature, concentrating on a specific transition-metal organometallic system, often for achieving a specific scientific or practical objective. However, a few laboratories, including particularly that of E. O. Fischer, have been actively pursuing extensive research programs in transition-metal organometallic chemistry involving almost all available transition metals and organic groups capable of forming metal-carbon bonds of one type or another.

Transition-metal organometallic compounds have been found to have certain applications of practical or potentially practical interest. Some types have catalytic applications, such as certain organotitanium systems acting as

components of Ziegler–Natta polymerization catalysts, certain organorhodium systems serving as catalysts for the preparation of unusual olefins (e.g., 1,4-hexadiene), and organopalladium compounds acting as intermediates in the palladium-catalyzed oxidation of olefins. Two metal carbonyls manufactured in tonnage quantities are iron pentacarbonyl, from which special iron powders are prepared by thermal decomposition, and methylcyclopentadienylmanganese tricarbonyl, for use as an additive to improve the combustion of certain liquid fuels. Further applications of metal carbonyls as vehicles for the transport and deposition of metals are exemplified by the role of nickel tetracarbonyl in the Mond process for nickel refining and by the use of the thermal decomposition of molybdenum hexacarbonyl as a means of depositing metallic molybdenum.

At the present time, many transition-metal organometallic compounds, including most of the metal carbonyls, metal cyclopentadienyls, and cyclopentadienyl metal carbonyls are commercially available at prices ranging from one to two dollars per pound for some products produced in tonnage quantities, such as iron pentacarbonyl and methylcyclopentadienylmanganese tricarbonyl, to hundreds of dollars per gram for difficultly preparable compounds and derivatives of rare metals, such as ditechneum decacarbonyl. This makes much significant research in transition-metal organometallic chemistry possible with equipment hardly more complicated and unusual than that customarily used for much research in more traditional areas of organic chemistry. The main difference is that many laboratory operations which would be done in air in conventional organic chemistry must often be done under an inert atmosphere (almost always nitrogen) in transition-metal organometallic chemistry.

### **Some Aspects of the Bonding in Coordination Compounds**

Transition-metal organometallic compounds may be regarded as special types of coordination compounds. In understanding the various types of transition-metal organometallic compounds, it is first useful to consider some of the aspects of bonding in coordination compounds. The ligands commonly found in transition-metal organometallic compounds, such as carbonyls, cyclopentadienyls, and olefins, are strong-field ligands (such as cyanide in potassium ferrocyanide, etc.). Such strong-field ligands can cause electrons in the free transition-metal ion to pair, generally resulting in complexes with a minimum of unpaired electrons. A recently reported [7] formal scheme for organizing coordination compounds is particularly appropriate for derivatives with strong-field ligands, such as transition-metal organometallic compounds. The following discussion will use the formalism of this recently reported scheme where appropriate.

Two concepts crucial to the understanding of coordination compounds are electronic configuration and coordination number. Both of these concepts, although inherently simple, may acquire certain complexities when applied to certain types of transition-metal organometallic compounds. In complexes with strong-field ligands, such as transition-metal organometallic derivatives, attainment of a favorable electronic configuration, generally the eighteen- (outer-) electron configuration of the next rare gas, takes precedence over attainment of a favorable coordination number, such as 4 or 6. This contrasts with the case of transition-metal complexes of weak-field ligands, where attainment of a favorable coordination number (generally 4 or 6) takes precedence over attainment of a favorable electronic configuration.

Consideration of the electronic configuration of a transition-metal organometallic derivative is clearest if both the metal atom and the ligands are regarded as neutral species [7]. Ligands encountered in transition-metal organometallic chemistry can donate from zero to eight electrons to the metal atom. Examples of ligands donating various numbers of electrons to the central metal atom are listed in Table I-2.

TABLE I-2  
EXAMPLES OF LIGANDS DONATING VARIOUS NUMBERS OF ELECTRONS

Number of electrons donated to metal	Examples of ligands donating this number of electrons
0	BH <sub>3</sub> , O (oxide)
1	Halides, Alkyl and Aryl Groups, R <sub>3</sub> Sn, H, SCN, NO <sub>2</sub> , NO <sub>3</sub>
2	C <sub>2</sub> H <sub>4</sub> , CO, R <sub>3</sub> N, R <sub>3</sub> P, R <sub>3</sub> As, RCN, RNC, R <sub>2</sub> O, R <sub>2</sub> S
3	$\pi$ -C <sub>3</sub> H <sub>5</sub> (allyl), NO, RN <sub>2</sub>
4	$\pi$ -C <sub>4</sub> H <sub>4</sub> (cyclobutadiene), $\pi$ -C <sub>4</sub> H <sub>6</sub> (butadiene)
5	$\pi$ -C <sub>5</sub> H <sub>5</sub> (cyclopentadienyl), $\pi$ -C <sub>9</sub> H <sub>7</sub> (indenyl)
6	$\pi$ -C <sub>6</sub> H <sub>6</sub> (benzene), $\pi$ -C <sub>7</sub> H <sub>8</sub> (cycloheptatriene)
7	$\pi$ -C <sub>7</sub> H <sub>7</sub> (cycloheptatrienyl)
8	$\pi$ -C <sub>8</sub> H <sub>8</sub> (cyclooctatetraene)—very rare

In calculating the electronic configuration of a metal atom in a complex, the total number of electrons donated by all of the (neutral) ligands is added to the number of electrons of the neutral metal atom. In most transition-metal organometallic derivatives, the metal atom will be found to attain the electronic configuration of the next rare (inert) gas (krypton, xenon, or radon). Examples of such complexes with the electronic configuration of the next rare gas and illustrations of the method of calculation of the electronic configuration

are given in Table I-3. A few examples of complexes with electronic configurations other than that of the next rare gas are given in Table I-4. In Tables I-3 and I-4, only the electrons in the outer, incomplete shells of the metal atoms are considered, which makes eighteen (outer) electrons the configuration of the next inert gas, whether krypton, xenon, or radon.

The second concept of importance is that of coordination number. In complexes containing exclusively monodentate ligands, the coordination number is the number of ligands bonded to the metal atom. In the cases of

TABLE I-3  
EXAMPLES OF ELECTRONIC CONFIGURATION CALCULATIONS

<hr/>		
(A)	$\text{Ni}(\text{CO})_4$	
	Neutral nickel atom	10
	Four carbonyl groups	$4 \times 2 = 8$
		<hr/>
	Electronic configuration	18
(B)	$\text{Mn}_2(\text{CO})_{10}$	
	Neutral manganese atom	7
	Five carbonyl groups (per manganese atom)	$5 \times 2 = 10$
	Manganese-manganese covalent bond	1
		<hr/>
	Electronic configuration	18
(C)	$\text{C}_5\text{H}_5(\text{CO})_4$	
	Neutral vanadium atom	5
	Four carbonyl groups	$4 \times 2 = 8$
	$\pi$ -Cyclopentadienyl ring	5
		<hr/>
	Electronic configuration	18
(D)	$\text{C}_7\text{H}_7\text{W}(\text{CO})_2\text{I}$	
	Neutral tungsten atom	6
	Two carbonyl groups	$2 \times 2 = 4$
	Iodine atom	1
	$\pi$ -Cycloheptatrienyl ring	7
		<hr/>
	Electronic configuration	18
(E)	$\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{NO}$	
	Neutral iron atom	8
	Two carbonyl groups	$2 \times 2 = 4$
	Nitrosyl group	3
	$\pi$ -Allyl ligand	3
		<hr/>
	Electronic configuration	18
<hr/>		

TABLE I-4

FURTHER EXAMPLES OF ELECTRONIC CONFIGURATION CALCULATIONS

(F) $\text{V}(\text{CO})_6$		
Neutral vanadium atom		5
Six carbonyl groups	$6 \times 2 =$	12
		—
Electronic configuration		17
(G) $(\text{C}_5\text{H}_5)_2\text{Ni}$		
Neutral nickel atom		10
Two $\pi$ -cyclopentadienyl ligands	$2 \times 5 =$	10
		—
Electronic configuration		20
(H) $(\text{R}_3\text{P})_2\text{IrCOCl}$		
Neutral iridium atom		9
One carbonyl group		2
Two $\text{R}_3\text{P}$ ligands	$2 \times 2 =$	4
Chlorine atom		1
		—
Electronic configuration		16

polydentate ligands, it is necessary to count the “arms” of the ligands rather than the number of individual ligands. Delocalized ligands including cyclic  $\text{C}_n\text{H}_n$  systems, such as  $\pi$ -cyclopentadienyl, can generally be considered as bonded to the metal atom by donation of two or three electron pairs. Such delocalized ligands may be considered as formally bidentate or tridentate

TABLE I-5

EXAMPLES OF TRANSITION METAL ORGANOMETALLIC DERIVATIVES WITH DIFFERENT COORDINATION NUMBERS

Coordination number	Examples
3	$\text{C}_{12}\text{H}_{18}\text{Ni}$ (three nickel-olefin bonds)
4	$\text{Ni}(\text{CO})_4$ , $\text{C}_5\text{H}_5\text{NiNO}$ , $\text{Co}(\text{CO})_3\text{NO}$ , $\text{Co}(\text{CO})_4^-$ , $\text{Fe}(\text{CO})_3\text{NO}^-$
5	$\text{Fe}(\text{CO})_5$ , $\text{R}_3\text{SnCo}(\text{CO})_4$ , $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ , $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$
6	$\text{Cr}(\text{CO})_6$ , $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ , $\text{RMn}(\text{CO})_5$ , $(\text{C}_5\text{H}_5)_2\text{Fe}$ , $(\text{C}_6\text{H}_6)_2\text{Cr}$ , $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , $(\text{C}_6\text{H}_5)_3\text{PV}(\text{CO})_4\text{NO}$ , $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$
7	$\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ , $\text{RHgTa}(\text{CO})_6$ , $[\text{Mo}(\text{CO})_4\text{X}_3]^-$ , $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})\text{C}_6\text{H}_6]^+$
8	$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{I}_3$ , $\text{Mo}(\text{CN})_8^{4-}$
9	$\text{ReH}_9^-$ , $[\text{C}_5\text{H}_5\text{FeCO}]_4$

ligands, respectively. Table I-5 gives examples of transition-metal organometallic derivatives with different coordination numbers (from 3 to 9) of the central metal atom.

When considering transition-metal organometallic compounds, it is convenient to classify the carbon ligands according to the number of their carbon atoms bonded to one (or sometimes two or more) metal atoms. Examples of this classification of carbon ligands are given in Table I-6. Ligands bonding

TABLE I-6  
CLASSIFICATION OF CARBON LIGANDS BASED ON NUMBER OF CARBON ATOMS BONDED TO METAL ATOM(S)

Number of carbon atoms	Number of metal atoms	Ligands
1	1	CO, CH <sub>3</sub> , CF <sub>3</sub> , C <sub>6</sub> H <sub>5</sub> , CNR
2	1	Ethylene
3	1	$\pi$ -Allyl
4	1	$\pi$ -Butadiene, $\pi$ -cyclobutadiene, trimethylenemethane
5	1	$\pi$ -Cyclopentadienyl, $\pi$ -indenyl, $\pi$ -cyclohexadienyl
6	1	$\pi$ -Benzene, $\pi$ -cycloheptatriene
7	1	$\pi$ -Cycloheptatrienyl
8	1	$\pi$ -C <sub>8</sub> H <sub>8</sub> in (C <sub>8</sub> H <sub>8</sub> ) <sub>3</sub> Ti <sub>2</sub>
1	2	Bridging CO [e.g., Co <sub>2</sub> (CO) <sub>8</sub> ]
2	2	Bridging acetylene [e.g., R <sub>2</sub> C <sub>2</sub> Co <sub>2</sub> (CO) <sub>6</sub> ]
3	2	
4	2	Butatriene [e.g., C <sub>4</sub> H <sub>4</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ]
5	2	
6	2	Bisallylene [e.g., C <sub>6</sub> H <sub>8</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ]
1	3	Three-way bridging CO [e.g., (C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Ni <sub>3</sub> (CO) <sub>2</sub> ]

to a single metal atom by means of one carbon atom include carbon monoxide, various isocyanides, and various alkyl, fluoroalkyl, aryl, fluoroaryl, and acyl groups. Ethylene and substituted olefins may bond to a single transition-metal atom by means of two carbon atoms. The  $\pi$ -allyl group is a V-shaped array of three carbon atoms which can bond to a single metal atom. The related triangular array of three carbon atoms (the  $\pi$ -cyclopropenyl ligand) is also, in principle, capable of bonding to a single metal atom. Ligands where four carbon atoms can bond to a single metal atom include cases where the four carbon atoms form a rectangle (cyclobutadiene), chain (butadiene), or Y (trimethylenemethane). Ligands in which five to eight carbon atoms can bond to a single metal atom include, particularly, the regular C<sub>n</sub>H<sub>n</sub> polygons. Such important ligands as  $\pi$ -cyclopentadienyl and benzene fall into this category.



Carbon ligands are also encountered in transition-metal organometallic chemistry where one or more carbon atoms bond simultaneously to two or more metal atoms. Thus the single carbon atom in a carbonyl group can bond simultaneously to two or three metal atoms forming metal derivatives with bridging carbonyl groups. Similarly, in compounds of the type  $R_2C_2Co_2(CO)_6$ , the two carbon atoms of an acetylene derivative can bond simultaneously to two metal atoms. Extreme examples of a single carbon atom bonding to many metal atoms occur in the carbonyl carbides  $Fe_5(CO)_{15}C$  and  $Ru_6(CO)_{17}C$ , where the single carbon atom bonds simultaneously to five iron atoms [8] and six ruthenium atoms [9], respectively. In both of these cases, the single carbon atom is located in the center of a polyhedron of the metal atoms.

A characteristic feature of transition-metal atoms with coordination numbers less than nine is the availability of electron pairs in  $d$  orbitals not involved in the bonds formed by electron donation from the ligands to the metal atom. These filled metal  $d$  orbitals can overlap with the empty antibonding orbitals in many of the ligands commonly encountered in transition-metal organometallic chemistry. This additional bond strengthens the metal–ligand linkage. However, since this additional bonding places additional electrons in ligand antibonding orbitals, it weakens certain bonds in the ligand. This additional bonding gives transition-metal organometallic chemistry many of its distinctive features, and is known colloquially as “back bonding” or, more precisely, as “retroductive  $\pi$ -bonding.”

Nontransition metals do not have filled  $d$  orbitals of appropriate energies and, therefore, cannot participate in retroductive  $\pi$ -bonding. The phenomenon of retroductive  $\pi$ -bonding accounts for the unique ability of transition metals with available filled  $d$  orbitals to form stable complexes with the extremely weak Lewis base carbon monoxide. The retroductive  $\pi$ -bonding of this type is important in metal carbonyls, olefin complexes, and derivatives of certain tricovalent phosphorus compounds, notably  $PF_3$ . Analogous retroductive  $\delta$ -bonding occurs in  $\pi$ -cyclopentadienyl derivatives and similar compounds; this will be discussed briefly when the  $\pi$ - $C_5H_5$  ligand is treated.

## Metal Carbonyls

### BONDING

One of the most commonly encountered ligands in transition-metal organometallic chemistry is carbon monoxide which forms complexes with these metals known as the metal carbonyls. Figure I-1 depicts the salient features of the bond between transition metals and carbon monoxide. The carbon monoxide has lone electron pairs on both the carbon and oxygen atoms. The  $sp$  orbital of the carbon atom containing its lone electron pair can overlap with