

ORGANOMETALLIC COMPOUNDS

by

G. E. COATES M.A., D.Sc., F.R.I.C.

Professor of Chemistry in the University of Durham

M. L. H. GREEN Ph.D., M.A.

Fellow and Tutor in Inorganic Chemistry, Balliol College, Oxford

K. WADE B.Sc., Ph.D.

Lecturer in Chemistry in the University of Durham

VOLUME TWO

The Transition Elements

by

M. L. H. GREEN

CHAPMAN AND HALL

11 NEW FETTER LANE · LONDON EC4P 4EE

*First published 1956
by Methuen & Co Ltd
Second edition published 1960
Third edition published in two volumes
Volume 1 published 1967, Volume 2 published 1968
Reprinted 1972
Published by Chapman and Hall Ltd
Third edition, Volume 2 © 1968 M. L. H. Green
Printed in Great Britain by
Butler & Tanner Ltd, Frome and London*

SBN 416 19230 0

All rights reserved. No part of this book may be reprinted, or reproduced or utilized in any form or by any electronic, mechanical or other means, now known or hereafter invented, including photocopying and recording, or in any information storage and retrieval system, without permission in writing from the Publisher.

Distribution in the U.S.A. by
HARPER & ROW PUBLISHERS, INC.
BARNES & NOBLE IMPORT DIVISION

Contents

<i>Preface to the Third Edition, Volume Two</i>	Page v
INTRODUCTION TO VOLUME TWO	1
Classification	1
The 18-electron rule	2
(i) The basis of the 18-electron rule p. 4, (ii) Exceptions to the 18-electron rule p. 5	
 1. TWO-ELECTRON LIGANDS	 7
A. Classification	7
B. The preparation of olefin-transition metal complexes	7
(a) Displacement of solvent ligands p. 9, (b) Preparations from metal carbonyls p. 9, (c) Less common preparative routes p. 11, <i>Reductive olefination method</i> p. 12	
C. A molecular orbital description of the bonding in organo-metallic complexes	13
(a) General comments p. 13, (b) Symmetry considerations p. 13, (c) Energies of the molecular orbitals p. 14	
D. A description of the bonding of 2-electron ligands to transition metals	14
E. General comments of 2-electron ligands	19
(a) Infrared studies p. 20, (b) Effect of olefin substituents p. 21, (c) The rotation of ethylene about the ligand-metal bond p. 22, (d) Chemical properties p. 23	
F. Particular complexes of metals with 2-electron ligands	25
(a) Copper, silver and gold p. 25, <i>Complexes with benzene</i> p. 28, (b) Nickel, palladium and platinum p. 30, <i>Trans effects</i> p. 32, (c) Rhodium, iridium, ruthenium, osmium and rhenium p. 33, (d) Miscellaneous p. 34	
 2. THREE-ELECTRON LIGANDS	 39
A. Preparation of π-enyl complexes	39
(a) From allyl Grignard reagents p. 39, (b) From allyl halides and allyl alcohols p. 39, (c) From olefins p. 40, (d) From allenes p. 43	
B. The structure of π-enyl complexes	43

C. The π-allyl metal bond	45
D. Dynamic equilibria in allyl complexes	46
E. The chemistry of particular π-enyl complexes	48
(a) Pure π -allyl metal complexes p. 50, (b) π -Enyl complexes of nickel, palladium and platinum p. 51, (i) <i>Cyclobutenyl complexes</i> p. 55, (ii) <i>Cyclopentenyl complexes</i> p. 56, (iii) <i>Cyclopropenyl complexes</i> p. 56, (c) π -Enyl cobalt and rhodium complexes p. 56, (d) Iron π -enyl complexes p. 57, (e) Miscellaneous p. 60	
3. FOUR-ELECTRON LIGANDS	65
A. Some differences between unconjugated and conjugated olefin ligands	66
B. The bonding of 4-electron ligands to transition metals	68
(a) Cyclobutadiene complexes p. 68, (b) Butadiene complexes p. 70	
C. Particular studies	74
(a) Cyclobutadiene complexes p. 74, (i) <i>Preparation</i> p. 74, (ii) <i>Properties</i> p. 78, (b) Cyclopentadiene complexes p. 80, (c) Non-cyclic diene-metal complexes p. 81, (d) Miscellaneous 4-electron ligands p. 86	
4. FIVE-ELECTRON LIGANDS	90
A. Cyclopentadienyl metal complexes	90
(a) Classification and nomenclature p. 90	
B. π-Cyclopentadienyl transition metal complexes	90
(a) Preparation p. 90, (i) <i>Reaction of alkali metal cyclopentadienides with metal complexes</i> p. 90, (ii) <i>Reaction between cyclopentadiene and metal complexes</i> p. 93, (iii) <i>Reaction between fulvenes and metal carbonyls</i> p. 94, (b) Bis- π -cyclopentadienyl transition metal complexes p. 95, (i) <i>Crystal structure</i> p. 95, (ii) <i>Molecular structure</i> p. 97, (iii) <i>Electronic structure</i> p. 97, (iv) <i>The stability of bis-π-cyclopentadienyl complexes</i> p. 104, (v) <i>The solubility properties of the cations $[(\pi\text{-C}_5\text{H}_5)_2\text{M}]^+$</i> p. 106, (vi) <i>Some chemical reactions of bis-π-cyclopentadienyl complexes</i> p. 106, (c) π -Cyclopentadienyl complexes of uranium, thorium and actinide metals p. 108	
C. Cyclopentadienide transition metal complexes	110
(a) Manganocene p. 110, (b) Ionic character in the bis- π -cyclopentadienyls p. 110, (c) Rare earth cyclopentadienides p. 111	

CONTENTS

ix

D. The bonding in mono-π-cyclopentadienyl transition metal complexes	112
(a) The bonding in metal-tricarbonyl groups p. 113	
E. π-Cyclopentadienyl carbonyl complexes	115
(a) Vanadium, niobium and tantalum complexes p. 117,	
(b) Complexes of chromium, molybdenum and tungsten	
p. 117, (c) Some π -cyclopentadienyl iron carbonyl chemistry	
p. 119, (d) Cobalt and rhodium complexes p. 122, (e) Com-	
plexes of nickel, and platinum p. 124, (f) Ligand substitution	
reactions of π -cyclopentadienyl manganese tricarbonyl p. 125	
F. π-Cyclopentadienyl nitrosyl complexes	126
G. Brief notes on binuclear π-cyclopentadienyl complexes con-	
taining bridging ligands	127
H. π-Cyclopentadienyl hydride complexes	128
I. π-Cyclopentadienyl halides and oxides	131
(a) π -Cyclopentadienyl titanium halide chemistry and related	
topics p. 131, (b) Vanadium, niobium and tantalum complexes	
p. 134, (c) Chromium, molybdenum and tungsten complexes	
p. 135	
J. Other 5-electron ligands	136
(a) π -Cyclohexadienyl complexes p. 136, (b) π -Cyclohepta-	
dienyl complexes p. 138, (c) Pentadienyl complexes p. 138	
K. The organic chemistry of π-cyclopentadienyl transition metal	
complexes	139
(a) Electronic effects in ferrocene p. 140, (b) The participation	
of the iron atom in the chemistry of ferrocenes p. 141, (i)	
<i>Some mechanisms of electrophilic and radical substitution</i>	
<i>reactions</i> p. 141, (ii) <i>The interaction of the iron atom with ring</i>	
<i>substituents</i> p. 142: <i>α-Carbonium ion stabilization</i> p. 142;	
<i>Weak hydrogen bonding by the iron atom</i> p. 144, (e) Trends	
in the chemistry of ferrocene, ruthenocene and osmocene	
p. 145	
L. Some particular reactions	145
(a) Acylation p. 145, (b) Alkylation reactions p. 147, (c) Aryla-	
tion reactions p. 149, (d) Halogenation p. 149, (e) Hydroxyl	
compounds p. 150, (f) Metallation studies p. 151, (g) Nitra-	
tion and sulphonation p. 152, (h) Amine derivatives p. 152,	

(i) Carboxylic acid derivatives p. 153, (j) Carboxaldehyde derivatives p. 153

5. SIX-ELECTRON LIGANDS	165
A. Arene transition metal complexes	165
(a) Preparation p. 165, (i) <i>Fischer's reducing Friedel-Crafts method</i> p. 165, (ii) <i>Cyclic polymerization of disubstituted acetylenes</i> p. 169, (iii) <i>From aryl Grignard reagents</i> p. 169, (iv) <i>From metal carbonyls</i> p. 169, (v) <i>From substituted metal carbonyls</i> p. 171, (b) <i>Structural studies</i> p. 171, (c) <i>The bonding in bis-π-arene complexes</i> p. 173, (d) <i>The stability of bis-π-arene complexes</i> p. 176, (e) <i>Some chemistry of bis-π-arene complexes</i> p. 178, (f) <i>The stereochemistry of some arene metal carbonyls</i> p. 180, (g) <i>Some reactions of arene metal carbonyls</i> p. 180, (h) <i>Polynuclear complexes of the Group IV and Group V metals</i> p. 182	
B. Olefin 6-electron ligands	183
C. Transition metal complexes containing π -bonded heterocyclic ligands	185
6. SEVEN-ELECTRON LIGANDS, MIXED SANDWICH COMPLEXES, RELATED AZULENE DERIVATIVES AND CYCLO-OCTATETRAENE COMPLEXES	190
A. 7-Electron ligands	190
(a) <i>Preparation of π-cycloheptatrienyl complexes</i> p. 190, (b) <i>Structure</i> p. 191, (c) <i>The chemistry of π-cycloheptatrienyl complexes</i> p. 192, <i>Ring contraction and expansion reactions</i> p. 194	
B. Mixed sandwich complexes	195
C. Metal complexes formed from azulenes	196
D. Cyclo-octatetraene complexes	197
7. ONE-ELECTRON LIGANDS	203
I.1. <i>Hydrocarbon alkyl and aryl complexes</i>	203
A. General preparative methods	204
(a) <i>From Grignard reagents and organoalkali metal derivatives</i> p. 205, (b) <i>From complex metal anions and organic halides</i> p. 205, (c) <i>From metal hydrides</i> p. 207, (d) <i>Miscellaneous</i> p. 208	

CONTENTS

xi

B. General chemical properties	208
(a) Stability p. 208, (b) Cleavage reactions of the metal-carbon bond p. 208, (c) Insertion reactions p. 209	
C. The nature of interactions between transition metals and σ-bonded organic substituents	209
(a) Transition metal- α -interactions p. 209, <i>Metal carbene complexes</i> p. 209, (b) Transition metal- β -interactions p. 211, (c) The possible nature of the β -effect p. 215	
D. The bonding of 1-electron ligands to transition metals	217
(a) Metal-carbon single bonds p. 218, (b) Metal-carbon multiple bonds p. 218, (i) <i>Metal aryls</i> p. 218, (ii) <i>Metal 'carbenes'</i> p. 219	
E. The stability of metal-σ-organo complexes	220
(a) Introduction p. 220, (b) The thermodynamic stability of metal- σ -organo complexes p. 220, (c) The kinetic stability of metal- σ -organo complexes p. 222, <i>The kinetic stability of organic complexes of square-planar nickel, palladium and platinum</i> p. 222	
F. Tertiary phosphine transition metal-alkyl and -aryl complexes and related compounds	224
(a) Nickel, palladium and platinum p. 224, (i) <i>Nickel</i> p. 224, (ii) <i>Palladium</i> p. 226, (iii) <i>Platinum</i> p. 228, (b) Cobalt, rhodium and iridium p. 230, (c) Iron and ruthenium p. 232, (d) Miscellaneous p. 233	
G. π-Cyclopentadienyl carbonyl complexes	233
(a) π -Cyclopentadienyl iron dicarbonyl derivatives p. 233, (b) π -Cyclopentadienyltricarbonyl complexes of chromium, molybdenum and tungsten p. 235, Cobalt, rhodium and nickel p. 236	
H. Carbonyl alkyl, aryl and acyl complexes	236
(a) Manganese and rhenium p. 236, (b) Cobalt p. 236, (c) Platinum p. 237, (d) Miscellaneous p. 237	
I. Bis-π-cyclopentadienyl alkyl and aryl complexes	237
J. σ-Bonded organic derivatives of particular metals	238
(a) Pure alkyl and aryl complexes and alkyl halides of titanium, vanadium, niobium, tantalum and manganese p. 238, (i) <i>Titanium complexes</i> p. 238, (ii) <i>Vanadium, niobium and tantalum</i> p. 240, (iii) <i>Manganese</i> p. 240, (b) Alkyl and aryl complexes of chromium p. 240, (i) <i>Neutral alkyl and aryl chromium</i>	

<i>complexes</i> p. 242, (ii) <i>Anionic alkyl and aryl chromium complexes</i> p. 244, (iii) <i>Penta-aquo chromium(III) alkyls</i> p. 245, (c) <i>Cobalt(III) complexes with σ-bonded ligands</i> p. 247, <i>Vitamin B₁₂ chemistry</i> p. 248, (d) <i>Alkyl complexes of platinum (IV)</i> p. 250, <i>Trimethylplatinum (IV) complexes</i> p. 250, <i>Cyclopropane complexes of platinum</i> p. 253, (e) <i>Alkyls and aryls of copper, silver and gold</i> p. 253, (i) <i>Copper</i> p. 253, (ii) <i>Silver</i> p. 254, (iii) <i>Gold</i> p. 255	
I.2 <i>Transition metal-acyl complexes</i>	257
A. <i>The carbonylation of pentacarbonylmanganese alkyls and aryls</i>	258
B. <i>Related carbonylation reactions</i>	260
C. <i>The metal-acyl bond</i>	261
I.3. <i>σ-Cyclopentadienyl complexes</i>	261
II. <i>Transition metal fluorocarbon complexes</i>	263
A. <i>Preparation</i>	263
(a) <i>From perfluoroacyl halides</i> p. 263, (b) <i>From perfluoroalkyl halides</i> p. 264, (c) <i>From perfluoro-olefins and related compounds</i> p. 264, (d) <i>From perfluoro Grignard reagents and lithium compounds</i> p. 267	
B. <i>The properties of perfluoro-alkyl and -aryl transition metal complexes</i>	267
C. <i>The metal-perfluorocarbon bond</i>	269
III. <i>Transition metal acetylides and alkynyls</i>	271
A. <i>Complex acetylides</i>	271
B. <i>'Pure' metal acetylides and alkynyls</i>	274
C. <i>Alkynyl-transition metal tertiary phosphines and related complexes</i>	276
(a) <i>Nickel, palladium and platinum</i> p. 276, (b) <i>Copper, silver and gold</i> p. 277, (c) <i>Miscellaneous</i> p. 280	
8. <i>ORGANOMETALLIC COMPLEXES FORMED FROM ACETYLENES</i>	288
A. <i>Monoacetylene, mononuclear complexes: acetylenes as 2-electron ligands</i>	288
B. <i>Monoacetylene, binuclear complexes: acetylenes as 4-electron ligands</i>	292
C. <i>Monoacetylene, trinuclear complexes</i>	294
D. <i>Monoacetylene, tetranuclear complexes</i>	295

CONTENTS	xiii
E. Bis-acetylene, mononuclear complexes	296
(a) Cyclopentadienone and quinone metal complexes p. 296,	
(i) <i>Preparation</i> p. 296, (ii) <i>Properties of cyclopentadienone metal complexes</i> p. 297, (b) Quinone complexes p. 299, (c) Ferra-	
cyclopentadiene complexes p. 302	
F. Bis-acetylene, trinuclear complexes	305
G. Tris-acetylene, mononuclear complexes	306
H. Tris-acetylene, binuclear complexes	307
I. Miscellaneous	309
 9. THE ROLE OF ORGANOTRANSITION METAL COMPLEXES IN SOME CATALYTIC REACTIONS	 312
A. Some chemistry of transition metal hydride complexes	312
(a) Preparation p. 313, (b) The nature of the metal-hydrogen bond p. 315, (c) Properties p. 316, (d) Bridging hydrogen systems, p. 316	
B. Some catalytic reactions which involve hydrogen transfer: isomerization reactions	317
C. Homogeneous hydrogenation of olefins and acetylenes	321
(a) Catalysis by cobalt cyanide solutions p. 323	
D. Some dimerization, oligomerization and polymerization reactions of olefins and acetylenes	325
(a) Dimerization reactions p. 325, (b) Trimerization reactions p. 327, (i) <i>The trimerization of acetylenes</i> p. 327, (ii) <i>The tri-</i> <i>merization of butadiene and related reactions catalysed by some</i> <i>π-allyl metal complexes</i> p. 327, (iii) <i>Other nickel catalysts</i> p. 330, (c) Some comments on polymerization of olefins by Ziegler catalysts p. 331, (d) Some mechanisms of olefin poly- merization by Ziegler catalysts p. 333	
E. Hydroformylation and related carbonylation reactions	334
F. Some general comments on the relationship between hetero- geneous and homogeneous transition metal catalysts	337
G. Miscellaneous	339
(a) The oxidation of ethylene to acetaldehyde p. 339, (b) Some reactions catalysed by copper and its derivatives p. 340, (c) Nitrogen fixation p. 341	
<i>Index to Volume Two</i>	
<i>Author</i>	349
<i>Subject</i>	368
<i>Crystal Structures</i>	375

Introduction to Volume Two

During the second half of the last century, when the foundations of the organometallic chemistry described in Volume I were being laid, it was generally held that the transition elements were unable to form organic derivatives. Early in the present century methyl platinum compounds were made (Pope and Peachy [1]) and an extensive organic chemistry of gold(III) was developed (Gibson [2]) mainly in the 1930's. During the 1940's the organic chemistry of the transition elements comprised little more than the gold and platinum compounds, the olefin complexes of platinum and palladium which were not understood, and Hein's phenyl-chromium compounds (1919-1931) - which were quite mysterious.

There was a dramatic change in the early 1950's, following the now famous discovery of ferrocene or biscyclopentadienyliron, $(C_5H_5)_2Fe$, simultaneously by Miller, Tebboth and Tremaine [3] and by Kealy and Pauson [4]. Ferrocene was quickly recognized as an entirely new type of compound in which a metal atom is bound to aromatic rings in a previously unknown way (Wilkinson, Rosenblum, Whiting and Woodward [5], 1952; Fischer and Pfab [6], 1952).

Since the early fifties there has been a great deal of work on the organic derivatives of transition metals and many exciting new types of compounds have been isolated and studied.

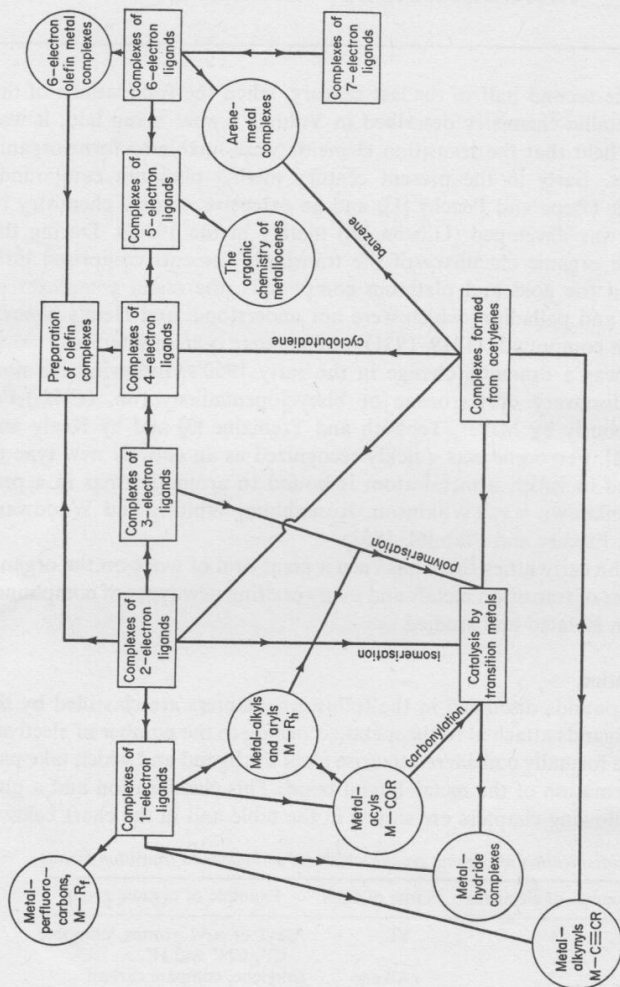
Classification

The compounds discussed in the following chapters are classified by the organic ligands attached to the metal according to the number of electrons which are formally considered to arise from the ligand and which take part in the formation of the metal-ligand bond. This classification and a plan of the following chapters are shown in the table and in the chart below.

A classification of organic groups which act as ligands to transition metals

Number of electrons	Name of class	Example of organic group
1	Yl	Alkyl or aryl groups, compare Cl^{\bullet} , CN^{\bullet} and H^{\bullet} .
2	Alkene	Ethylene, compare carbon monoxide
3	Enyl	π -Allyl, compare nitric oxide
4	Diene	Cyclobutadiene, butadiene
5	Dienyl	π -Cyclopentadienyl
6	Triene	Benzene, cycloheptatriene
7	Trienyl	π -Cycloheptatrienyl

Plan of chapters and major topics in this book: the chapter titles are in the square boxes.



The 18-electron rule

The large majority of the transition metal complexes with metal-carbon organic, -carbonyl or -hydride ligands isolable at room temperature can be regarded as having 18 electrons in their valence shell. This is the

empirical basis of the rule 'a valence shell containing 18 electrons gives stable complexes'. It is argued in Chapter 7 that the greater stability associated with the 18-electron valence shell may arise both from thermodynamic and kinetic factors.

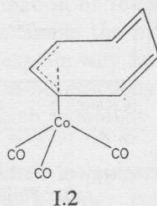
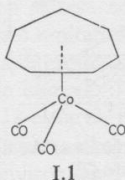
In order to test the application of the 18-electron rule to a compound it is necessary to count the number of electrons which are formally in the valence shell of the metal atom. This is most easily achieved in the following manner:

(a) Take the number of electrons in the valence shell of the uncomplexed metal atom and add or subtract electrons according to the total charge on the metal complex. Thus iron in a unipositive cation has $8 - 1 = 7$ electrons, in a neutral compound has 8 electrons and in a uninegative anion has 9 electrons.

(b) Sum the number of electrons which the ligands formally contribute to the metal, according to the classification of ligands given above. Add this sum to the metal electrons from (a).

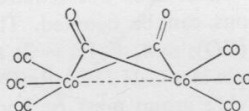
To exemplify this procedure we consider first the complex cation $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_2\text{H}_4]^+$ which does not require further structural evidence before the electrons can be counted. The electrons come from $\text{Fe}^+ = 7$; $\pi\text{-C}_5\text{H}_5 = 5$; $(\text{CO})_2 = 4$; $\text{C}_2\text{H}_4 = 2$; the total is therefore 18 electrons. Another example is $\pi\text{-C}_5\text{H}_5(\text{Me})_2\text{Re}(\text{C}_5\text{H}_5\text{Me})$; in this case the structure of the $\text{ReC}_5\text{H}_5\text{Me}$ group must be known before we can unambiguously count electrons. The electrons arise from $\text{Re} = 7$; $\pi\text{-C}_5\text{H}_5 = 5$; $\text{Me}_2 = 2$; and, since X-ray diffraction shows that the methylcyclopentadiene ligand has all four diene carbons bonded to the metal, $\text{C}_5\text{H}_5\text{Me} = 4$; again the total = 18 electrons. Contrast this complex with the cyclopentadiene complex $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{C}_5\text{H}_6$ in which the cyclopentadiene group is only bonded to the metal by one carbon-carbon double bond (see p. 23).

Finally, consider the complex $\text{C}_7\text{H}_7\text{Co}(\text{CO})_3$ whose structure is unknown but may be *predicted* using the 18-electron rule. At first sight the complex appears to be a $7 + 9 + 6 = 22$ electron complex. It is therefore proposed that the C_7H_7 ring only contributes three electrons to the cobalt, rather than seven, and that instead of being the π -cycloheptatrienyl complex, I.1, it is the π -enyl complex I.2:



A problem in the counting of electrons may arise with complexes containing metal-metal bonds. In complexes for which X-ray diffraction clearly shows there to be metal-metal bonding, e.g. $(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_5$, the bond is represented by an *unbroken* line. In these complexes each metal atom acts as a one-electron ligand to the other.

Those complexes which contain bridging ligands between two metal atoms are *assumed* to contain a metal-metal bond when this is required by the 18-electron rule and if it is suggested by experiment, for example by magnetic data. Both dicobalt octacarbonyl, I.3, and the binuclear complex $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ have two bridging carbonyl groups and they are diamagnetic. It is therefore normally assumed that spin-pairing between the metal atoms occurs via a metal-metal bond, otherwise the metal atoms would have an odd, 17-electron environment. However, spin-pairing may possibly occur by mechanisms other than direct metal-metal interaction; for example via a bridging ligand. A metal-metal interaction which is *postulated* solely on the basis of magnetic data or the 18-electron rule is therefore represented by a *dotted* line in this book (see I.3).



I.3

(i) *The basis of the 18-electron rule*

The change in energy of the 4s, 4p and 3d orbitals with increasing atomic number across the first long series of the transition elements is given in Figure 1. This figure shows several points of interest:

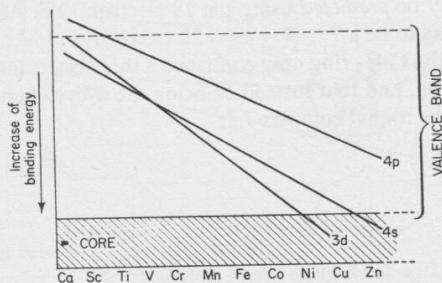


Fig. 1. The change in energy of the 3d, 4s and 4p orbitals of the first transition series (after Phillips and Williams [7])

(a) For scandium and titanium the $3d$ orbitals are rather high in energy and are unlikely to be very important in metal-ligand bonding.

(b) Across the series V, Cr, Mn, Fe, Co the $3d$ orbitals decrease in energy more rapidly than the $4s$ and $4p$ orbitals, yet all three types of orbitals are fairly close in energy and are of suitable energy to be important in metal-ligand bonding.

(c) Across the series Ni, Cu, Zn the d orbitals continue to decrease in energy and at Cu and Zn they are best regarded as core electrons, that is they are no longer 'valence electrons' and cannot be expected to make significant contributions to the metal-ligand bonding.

It should also be noted that for all the transition metals the effect of a positive charge on the metal is to lower the energy of all the orbitals. More important, however, is the increase in the separation between the $3d$ orbitals and the $4s$, $4p$ orbitals. From these observations we may, in a very qualitative manner, understand the occurrence and limitations of the 18-electron rule, as follows.

When the energies of the $3d$, $4s$ and $4p$ orbitals are fairly close together and are suitable for metal-ligand bonding, i.e. when the orbitals are in the valence band, then the maximum bonding occurs when they are all filled, and this is of course the case when the metal atom has an 18-electron environment. It follows from (b) that the low (and negative) oxidation states of the metals V, Cr, Fe and Co would be expected to obey an 18-electron rule. In the case of Ni then, it makes little difference whether we regard the $3d$ orbitals as valence or core orbitals since in both cases there remain the valence $4s$ and $4p$ orbitals which, when filled, would give tetrahedral nickel complexes, e.g. $\text{Ni}(\text{CO})_4$.

(ii) *Exceptions to the 18-electron rule*

It follows from (a) and (c) above, that the 18-electron rule would be expected to break down for transition metals in low oxidation states at both ends of the transition series, either because the $3d$ orbitals are too high (Ti) or too low (Cu) in energy. This is indeed the case and there are no known 18-electron complexes of Ti and few of Cu.

It can be seen also that the 18-electron rule will tend to break down when the first-row transition metals are in a high oxidation state. There may also be steric limitations to the formation of 18-electron complexes in high oxidation states – consider for example the hypothetical cation $[\text{Cr}(\text{CO})_9]^{6+}$. Steric limitations may also explain why vanadium forms the monomeric, paramagnetic and 17-electron hexacarbonyl, $\text{V}(\text{CO})_6$, rather than the dimeric complex $[\text{V}(\text{CO})_6]_2$ which would be diamagnetic and would obey the 18-electron rule.

It is observed that nickel frequently forms complexes in which it has a 16-electron environment, e.g. in square-planar complexes such as

$(PR'_3)_2NiR_2$. Also, copper sometimes and gold frequently form 14-electron complexes, of the type PR_3MR . These observations can be understood in terms of Figure 1 as follows.

Across the series Co, Ni, Cu and Zn the $3d$ orbitals go into the metal core and the energy separation between the $4s$ and $4p$ orbitals becomes greater. As the difference of energy of the $4s$ and $4p$ orbitals increases, the $4s$ orbital becomes more important in bonding whilst the $4p$ orbitals become less significant. The stepwise removal of two of the three $4p$ orbitals may account for the occurrence of stable complexes of Co, Ni and Cu in which the metals have 18-, 16- and 14-electron environments respectively.

It should be noted that all the above arguments apply also to the second and third d -block transition series and that differences between the *relative* energies of the ns , np and $(n-1)d$ orbitals may also be significant. For example there is an increase in the separation between the ns and np orbitals in the series Cu, Ag and Au. This may account for the apparently greater stability of the 14-electron gold complexes PR_3AuR compared to that of the copper analogues.

Finally, it is emphasized that the 18-electron rule is unsophisticated and provides no detailed insight into the chemistry of organometallic complexes.

REFERENCES

- [1] W. J. Pope and S. J. Peachy, *Proc. Chem. Soc.*, 1907, **23**, 86; and idem, *J. Chem. Soc.*, 1909, 571.
- [2] See Chapter 7, refs [171–175] and [177–179].
- [3] S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 1952, 632.
- [4] T. J. Kealy and P. L. Pauson, *Nature*, 1951, **168**, 1039.
- [5] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Amer. Chem. Soc.*, 1952, **74**, 2125.
- [6] E. O. Fischer and W. Pfab, *Z. Naturforsch.*, **7b**, 377.
- [7] C. S. G. Phillips and R. J. P. Williams, *Inorganic Chemistry*, Vol. 2, p. 218, Oxford University Press, 1966.