ORGANOMETALLIC COMPOUNDS

by

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VOLUME TWO

The Transition Elements

by

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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 phenylchromium 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.

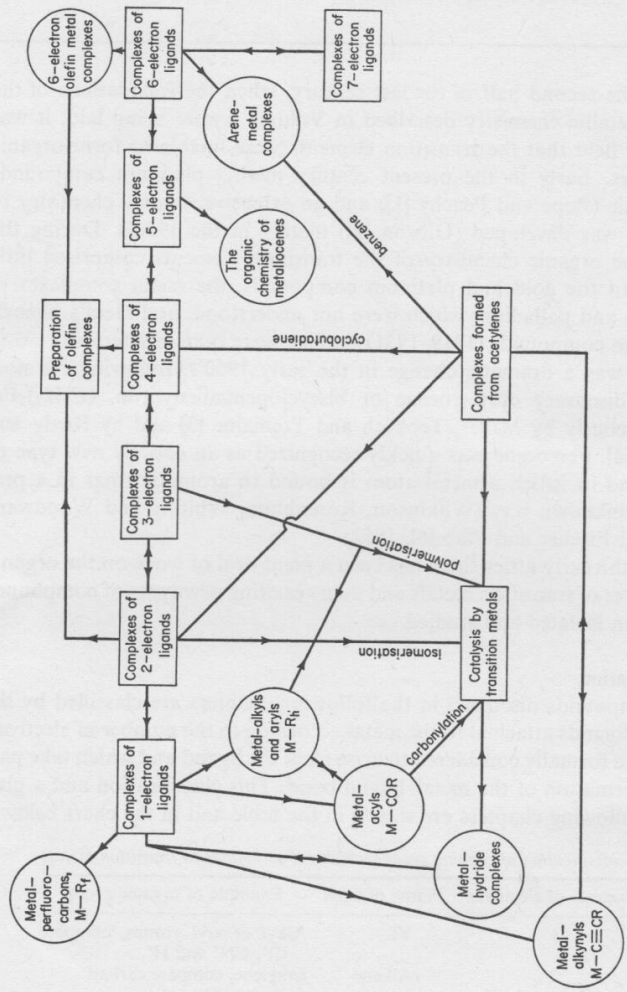
Classification

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

The basis of the above classification is the 18-electron rule and it is appropriate to discuss this rule here.



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.

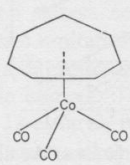
In order to test the application of the 18-electron rule to a compound it is necessary to count the number of electrons which are formally in the valence shell of the metal atom. This is most easily achieved in the following manner:

(*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.

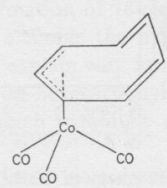
(*b*) Sum the number of electrons which the ligands formally contribute to the metal, according to the classification of ligands given above. Add this sum to the metal electrons from (*a*).

To exemplify this procedure we consider first the complex cation $[\pi\text{-}C_5H_5Fe(CO)_2C_2H_4]^+$ which does not require further structural evidence before the electrons can be counted. The electrons come from $Fe^+ = 7$; $\pi\text{-}C_5H_5 = 5$; $(CO)_2 = 4$; $C_2H_4 = 2$; the total is therefore 18 electrons. Another example is $\pi\text{-}C_5H_5(Me)_2Re(C_5H_5Me)$; in this case the structure of the ReC_5H_5Me group must be known before we can unambiguously count electrons. The electrons arise from $Re = 7$; $\pi\text{-}C_5H_5 = 5$; $Me_2 = 2$; and, since X-ray diffraction shows that the methylcyclopentadiene ligand has all four diene carbons bonded to the metal, $C_5H_5Me = 4$; again the total = 18 electrons. Contrast this complex with the cyclopentadiene complex $\pi\text{-}C_5H_5Re(CO)_2C_5H_6$ in which the cyclopentadiene group is only bonded to the metal by one carbon–carbon double bond (see p. 23).

Finally, consider the complex $C_7H_7Co(CO)_3$ 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:



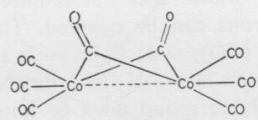
I.1



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. $(CO)_5Mn—Mn(CO)_5$, 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 $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ 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 4*s*, 4*p* and 3*d* 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:

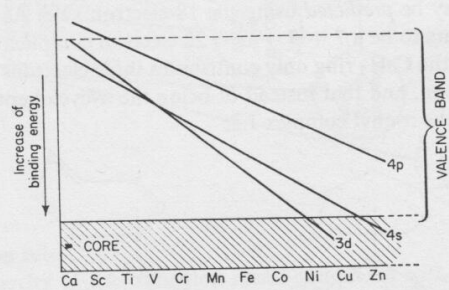


Fig. 1. The change in energy of the 3*d*, 4*s* and 4*p* orbitals of the first transition series (after Phillips and Williams [7])

(*a*) For scandium and titanium the 3*d* 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 3*d* orbitals decrease in energy more rapidly than the 4*s* and 4*p* 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 3*d* orbitals and the 4*s*, 4*p* 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 3*d*, 4*s* and 4*p* 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 3*d* orbitals as valence or core orbitals since in both cases there remain the valence 4*s* and 4*p* orbitals which, when filled, would give tetrahedral nickel complexes, e.g. $Ni(CO)_4$.

(*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 3*d* 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 $[Cr(CO)_9]^{6+}$. Steric limitations may also explain why vanadium forms the monomeric, paramagnetic and 17-electron hexacarbonyl, $V(CO)_6$, rather than the dimeric complex $[V(CO)_6]_2$ 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 3*d* orbitals go into the metal core and the energy separation between the 4*s* and 4*p* orbitals becomes greater. As the difference of energy of the 4*s* and 4*p* orbitals increases, the 4*s* orbital becomes more important in bonding whilst the 4*p* orbitals become less significant. The stepwise removal of two of the three 4*p* 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 n*s*, n*p* and (n − 1)*d* orbitals may also be significant. For example there is an increase in the separation between the n*s* and n*p* 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.

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