Chapter 8

ORGANOMETALLIC CHEMISTRY

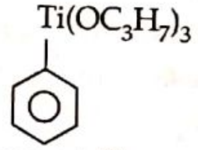
CONTENTS

- Definition, nomenclature and classification of organometallic compounds.
- Preparation, properties, bonding and applications of alkyls and aryls of Li, Al, Hg, Sn and Ti.
- A brief account of metal–ethylenic complexes and homogeneous hydrogenation.
- Mononuclear carbonyls and nature of bonding in metal carbonyls.

There are certain compounds which contain a direct bond between a metal atom and one or more carbon atoms. These are called **organometallic compounds.** It may be noted that all the compounds containing carbon and a metal atom are not organometallic. We use this term for compounds which contain at least one M—C bond. For example, an alkoxide such as $(C_3H_7O)_4Ti$ is not considered to be an organometallic compound because the organic group is bonded to Ti atom by oxygen and there is no Ti—C bond. On the other hand, the compound $C_6H_5\ Ti(OC_3H_7)_3$ is an organometallic compound because it contains a Ti—C bond $(C_6H_5—Ti)$ in the compound.

$Ti—(OC_3H_7)_4$

Not organometallic
(No Ti—C bond)



Organometallic
(Ti—C bond)

Organometallic chemistry is a rapidly growing field of chemistry. It is an important branch of chemistry which bridges the fields of organic and inorganic chemistry together. Progress in this field has resulted in the formation of new reagents and catalysts which are finding important uses in synthetic chemistry. The discovery of Grignard reagents (organomagnesium halides) in 1900 gave versatile intermediates for a variety of organic preparations. The synthesis of ferrocene $(C_5H_5)_2Fe$ in 1951 and its structural determination has given significant contribution to our understanding of chemical bonding.

DEFINITION OF ORGANOMETALLIC COMPOUNDS

Organometallic compounds are those compounds which contain one or more metal carbon bonds. The common examples of organometallic compounds are $Pb(C_2H_5)_4$ (tetraethyl lead), $(C_5H_5)_2Fe$ (ferrocene), $(C_2H_5)_2\ Zn$ (diethyl zinc), $Sn(C_2H_5)_4$ (tetraethyl tin), $K[PtCl_3\ (C_2H_4)]$ (Zeise salt), $Os(C_5H_5)_2$ (osmocene), etc.

It may be noted that metal cyanides (M–CN) and metal carbides (*e.g.* CaC_2, Al_4C_3, *etc.*) contain M–C bonds, but they are not considered as organometallic compounds because their properties are closely related to those of many other compounds usually considered in inorganic chemistry. In contrast the complexes formed by the ligand CO, known as ***metal carbonyls*** are considered to be organometallics because their properties resemble with these compounds.

TYPES OF ORGANOMETALLIC COMPOUNDS

The organometallic compounds may be classified into the following types on the basis of nature of metal and the nature of bonding between metal and carbon.

1. Ionic compounds of electropositive metals

These organometallic compounds are formed by the most electropositive metals of group I A and II A. In these compounds, the hydrocarbon is present as a carbon which has negative charge and the positively charged alkali or alkaline earth metal. The formation of these compounds is generally favoured when the hydrocarbon anion may be stabilized *i.e.*, the negative charge may be delocalised over several carbon atoms in an aromatic or unsaturated ring of carbon atoms. The common example is $K^+C_5H_5^-$ in which the negative charge is stabilised due to its delocalisation over the five carbon atoms of the cyclopentadienyl ring. Some other examples are : $Na^+ C_6H_5^-$, $Na^+C_4H_9$, $Mg^{2+}[(C_5H_5)^-]_2$, $(C_6H_5)_3 C^-Na^+$, *etc.*

These organometallic compounds show behaviour of typical ionic compounds and are insoluble in hydrocarbon non-polar solvents. They occur in crystalline form when pure and their structures depend upon the manner of packing in the crystal. For example, in $Mn(C_5H_5)_2$, each Mn^{2+} ion is present midway between two parallel $C_5H_5^-$ ions.

These compounds are unstable in air and are readily hydrolysed in water to liberate the hydrocarbon with the formation of hydroxide. The reactivity of these compounds depends upon the stability of the anion. The compounds containing unstable anions are generally highly reactive and unstable and are therefore, difficult to isolate.

2. Covalent organometallic compounds

These compounds have organic part bonded to the metal atom by a normal two electron sigma covalent bond. These compounds are very common and are generally formed by Zn, Cd, Hg and representative metals of group III, IV and V. In most of these compounds, the bonding is predominantly covalent and their properties resemble those of typical organic compounds.

These are insoluble in water but are soluble in organic solvents. The polarity of metal carbon bonds in these compounds depends upon the difference in electronegativity between metal atom and carbon but also on the orbitals which are available, the stearic requirements and polarizability of electron clouds.

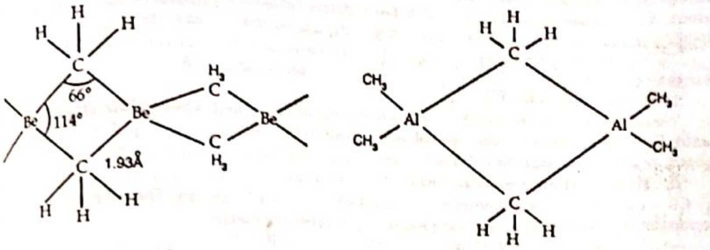
The common examples are $Pb(C_2H_5)_2$, $(C_6H_5)_2 Zn$, $(CH_3)_2Cd$, $(CH_3)_2Hg$, $Si(CH_3)_4$, $Al(CH_3)$, $(CH_3)_3 SnCl$, $(CH_3)SnCl_3$.

3. Electron deficient organometallic compounds

These are the compounds which cannot be explained on the basis of formation of traditional two electrons two centre bonds with carbon and metal atom. These include the alkyls of lithium, beryllium, magnesium and aluminium which have bridging alkyl groups. For example, dimeric trialkyl aluminium (Al_2R_6), polymeric dimethyl beryllium $(BeMe_2)_n$ or diethyl magnesium ($MgEt_2$). All these metals have strongly polarizing cation (*i.e.*, they have very high charge to mass ratio) and pulls the electron density away from the anion. Therefore, the charge separation in these compounds decreases and a polar covalent bond results.

$$M^+ CH_3^- \text{ changes to } M^{\delta+} - CH_3^{\delta-}$$

Such polar molecules will have tendency to associate strongly and lead to the formation of polymeric structures. For example, trialkyl aluminium exists as dimeric in which the alkyl group is present as bridge. The structures of polymeric dimethyl beryllium $(BeMe_2)_n$ and dimeric Al_2Me_6 is shown in Fig. 1.



(*a*) Polymeric $[Be(Me)_2]_n$.

(*b*) Dimeric Al_2Me_6.

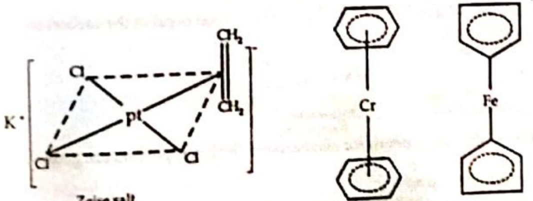
Fig. 1. Structure of (*a*) polymeric $(BeMe_2)_n$ and (*b*) Al_2Me_6.

In these compounds, the alkyl bridges are present in which the carbon atom of the bridging alkyl group is equidistant from both the metal atoms.

4. Transition metal organometallic compounds

These organometallic compounds include transition metals bonded to unsaturated organic compounds in which the transition metal forms bonds to more than one carbon atoms of the same organic compound. The interaction occurs between the π-orbitals of the organic ligands with the suitable *d* or *p* orbitals of the metal atom.

For example, the common examples of ligands forming such type of organometallic compounds are (*i*) alkene (2-electron donors) (*ii*) butadiene (4 electron donors) (*iii*) cyclo pentadiene (5 electron donors) and (*iv*) benzene ring (6 electron donors). The common examples of such type of organometallic compounds are dibenzene chromium, $(C_6H_6)_2 Cr$, ferrocene $(C_5H_5)_2Fe$, Zeise salt $[PtCl_3(C_2H_4)]^-$, *etc.* For example, structures of dibenzene chromium $(C_6H_6)_2 Cr$ and ferrocene $(C_5H_5)_2 Fe$ are shown in Fig. 2. Their structures are known as ***sandwich structures*** in which metal atom lies in between two rings.



Zeise salt

Fig. 2. Structures of (a) $(C_6H_6)_2$ Cr and (b) $(C_5H_5)_2$ Fe.

The ability of transition metals to form such a large variety of complexes is due to the symmetry properties of the *d*-orbitals present in the valence shells of the transition metals.

CLASSIFICATION OF LIGANDS

We have learnt that ***an atom, ion or molecule which is capable of donating a pair of electrons to the metal atom*** is called a ligand. Representative metals form organometallic compounds with only a simple type of ligands such as alkyl or aryl groups. However, transition metals form organometallic compounds with a wide range of organic groups. The important difference between transition metals and representative metals is the ability of the transition metal atom to form bonds with more than one carbon atoms of the organic ligand. There are certain ligands which may attach to a central metal atom using several of its atoms simultaneously. For example, in the case of ethylene group, its two carbon atoms are both within the same bonding distance. Similarly in ferrocene, the five carbon atoms of C_5H_5 ligand are within bonding distance of ions. *The number of atoms of the ligand which are within bonding distance of the metal atom* is called its **hapticity**. It is written by using the symbol η (eta).

Therefore, the ligands may be classified on the basis of number of carbon atoms involved in bonding to the metal atom *i.e.* hapticity. The hapticity ranges from 1–8.

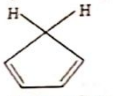
1. One carbon bonded ligands

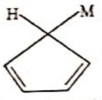
These are the molecules in which the carbon atom of the ligand is bonded directly to the metal atom. Such ligands are also called **monohapto ligands** (one electron donors), η^1. For example, $-CH_3$ group attaches by a single M – C bond. These ligands may be further sub-divided as :

(*i*) **Hydrocarbon ligands.** These include alkyl ($-CH_3$), aryl ($-C_6H_5$), alkenyl ($-CR=CR_2$), σ-cyclo pentadienyl ($-C_5H_5$), alkynyl ($-C\equiv CR$) groups. These ligands may form compounds with both transition metals and representative metals.

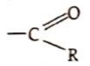
$-CH_3$,	$-C_6H_5$	$-CR=CR_2$	$-C_5H_5$	$-C\equiv CR$
Alkyl	Aryl	alkenyl	cyclopentadienyl	alkynl

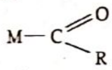
For example, cyclopentadiene, C_5H_5 combines with alkali metals to form $(\sigma\text{-}C_5H_5)M$ compound as shown below :


Cyclopentadiene


(One carbon bonded cyclopentadienyl compound).

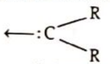
(*ii*) **Acyl ligands.** These include acyl group which involves direct bonding of the acyl group ($-COR$) to a metal atom as shown below :

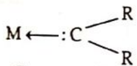

Acyl group


Organometallic compound

These compounds are formed by transition metals only.

(*iii*) **Carbene ligands.** These involve the direct metal carbon bond of the carbon atom of carbene (alkylidene) to a metal atom.

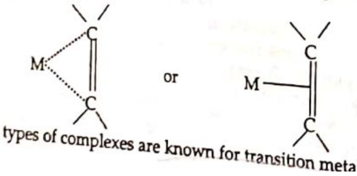

Carbene ligand


Organometallic compound

where R may be $-OR$, $-NR_2$, phenyl or alkyl groups. Such compounds are generally known for transition metals.

2. Two carbon bonded ligands

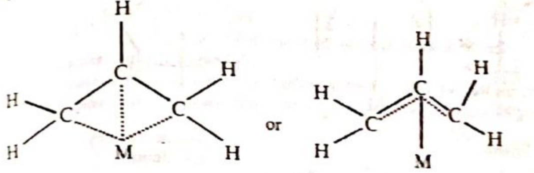
These are the molecules in which two carbon atoms of the ligands are bonded to the metal atom. These are called **dihapto (η^2) ligands** (*or two electron donors*). These include alkenes or alkynes in which both the carbon atoms at each end of the multiple bond are involved in forming the metal-carbon bonds. The bonding in these ligands is indicated either by two dotted lines to the participating carbon atom or a single solid line from the centre of the participating carbon atoms of the ligand to the metal atom.



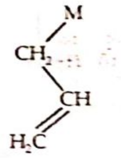
These types of complexes are known for transition metals only.

3. Three carbon bonded ligands.

These are the molecules in which three carbon atoms of the ligands are bonded to the metal atom. These are called **trihapto ligands** (η^3). These include allyl group (C_3H_5) known as π-allyl ligands as shown below. These may be distinguished from σ-allyl complexes in which the allyl group is bonded through one carbon atom only (monohapto).

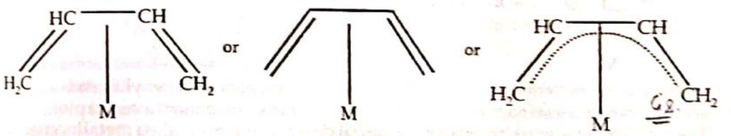


π-Allyl complex ($3e^-$ donor)

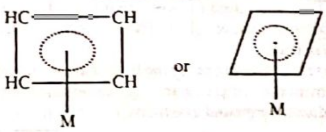

σ-Allyl complex ($1e^-$ donor)

4. Four carbon bonded ligands

These ligands have four carbon atoms which may be bonded to the metal atom. Therefore, these are called **tetrahapto** (*4 electron donors*) or η^4 ligands. These include acyclic ligands such as 1,3-butadiene and cyclic ligands such as cyclobutadiene.

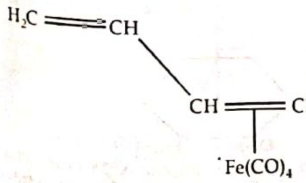


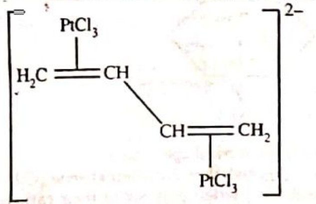
1, 3-Butadiene ligand ($4e^-$ donor)



Cyclobutadiene ligand ($4e^-$ donor)

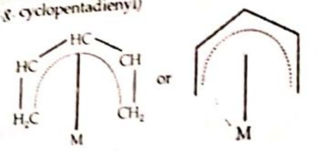
It may be noted that cyclobutadiene always behaves as four carbon bonded ligand but 1,3-butadiene may behave as monoalkene ligand or two independent monoalkene ligands as shown below.


Mono alkene complex

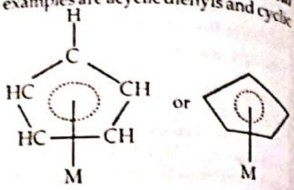

Two independent mono alkene ligands

5. Five carbon bonded ligands

These ligands are molecules in which five carbon atoms of the ligands are bonded to the metal atom. These are called **pentahapto** (η^5) **ligands**. The common examples are acyclic dienyls and cyclic dienyls (*e.g.* cyclopentadienyl)



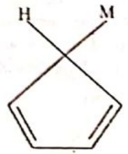
Acyclic dienyl ligand
($5e^-$ donor)
Pentadienyl



Cyclopentadienyl
($5e^-$ donor)

The five carbon bonded cyclopentadienyl is also called π-cyclopentadienyl ligand to distinguish it from one carbon bonded cyclopentadienyl (σ – cyclopentadienyl) as shown below :

π-cyclopentadienyl
5 electron donor (pentahapto)

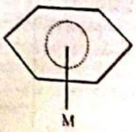


σ-cyclopentadienyl ligand
1 electron donor (monohapto)

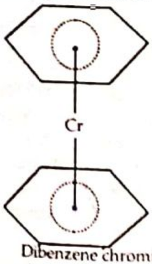
The π-cyclopentadienyl ligands form a special class of complexes called **metallocenes,** in which the metal atom is sandwiched between two planar cyclopentadienyl ligands. For example, ferrocene, $(\pi\text{–}C_5H_5)_2$ Fe in which iron is sandwiched between two $\pi\text{–}C_5H_5$ ligands (Fig. 2). Other examples are nickelocene, $Ni(C_5H_5)_2$, cobaltocene, $Co(C_5H_5)_2$, chromocene, $Cr(C_5H_5)_2$.

6. Six carbon bonded ligands

The molecules in which six carbon atoms of the ligand are bonded to the metal atom. The common example is benzene. The common example of an organometallic compound is dibenzene chromium, $(C_6H_6)_2Cr$. This is also a *sandwich compound* in which Cr atom is present in between two benzene rings.

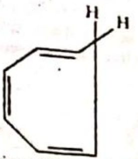


Benzene as hexahapto ligand



Dibenzene chromium $(C_6H_6)_2Cr$

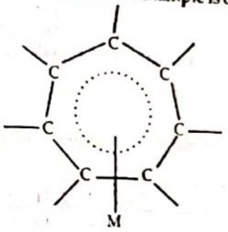
It may be noted that cycloheptatriene (C_7H_8) and cyclooctatetracene (C_8H_8) can act as hexa hepto ligands (η^6) when only six of their carbon atoms in the ring are involved in bonding. For example, cycloheptatriene (C_7H_8) acting as six electron donor through its three double bonds is shown ahead :



Cycloheptatriene acting as six electron donor

7. Seven carbon bonded ligands

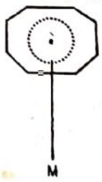
These are molecules in which seven carbon atoms act as electron donors by participating all the even carbon atoms in bond formation. The common example is cycloheptatrienyl ($-C_7H_7$) as shown elow :



Cycloheptatrienyl
($7e^-$ donor)

8. Eight carbon bonded ligands

These are molecules in which eight carbon atoms are involved in bond formation. These are also alled *octahapto ligands*. The common example is cyclo-octatetraene (C_8H_8). The common example of the complex is $U(C_8H_8)_2$.

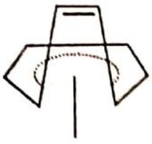


Cyclo-octatetraene (C_8H_8)

Dicyclooctatetraeneuranium

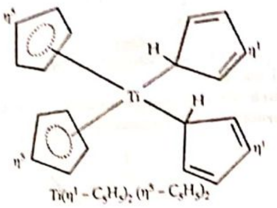
Cyclotetraene can also act as four electron donor or six electron donor as shown below :

$Fe(CO)_3$
Cyclooctatetraene
acting as 4e donor



$Mo(CO)_3$
Cyclooctatetraene
acting as 6e donor

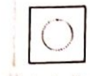
It may be noted that certain ligands may bond through different number of carbon atoms in different compounds. For example, the ligand cyclo-pentadienyl, C_5H_5 can form bond through one carbon atom (monohapto) and through five carbon atoms (pentahapto) in the same complex. For example.



$Ti(\eta^1-C_5H_5)_2(\eta^5-C_5H_5)_2$

Sun Up

Classification of ligands according to the number of electrons donoted to metal atom

Type	Hapticity	Symbol	Examples
1-electron donors	monohapto	η^1	$-CH_3, -CH_2R$ alkyl $-C_6H_5$ aryl
2–electron donors	dihapto	η^2	$CH_2=CH_2$, $HC\equiv CH$ Alkenes, alkynes
3–electron donors	trihapto	η^3	$CH_2\cdots CH\cdots CH_2$ π-allyl
4–electron donors	tetrahapto	η^4	 dienes, cyclobutadienyl
5–electron donors	pentahapto	η^5	 acylic dienyl cyclopentadienyl
6–electron donors	hexahapto	η^6	 arenes
7-electron donors	heptahapto	η^7	 cycloheptatrienyl
8-electron donors	octahepto	η^8	 cyclo octatetraenyl

PRACTICE Problems

1. Give one example each of 3 electron donor and 4 electron donor ligand.
   - **Ans.** π-allyl (3 electron donor), 1, 3-butadiene
2. In ferrocene, each cyclo-pentadienyl ring behaves as .... electrons donor. Complete the statement.
   - **Ans.** Five
3. Show the structure of a complex in which cyclo-heptatriene acts as six electron donor.

EFFECTIVE ATOMIC NUMBER

Sidgwick in 1927 extended the Lewis theory of electron pair bond formation to explain the bonding in coordination compounds. He suggested the term coordinate bond in which the metal atom/ion accepts electron pairs from ligands (donors). He suggested that *metal ion accepts electron pairs from the ligands until it achieves the next noble gas configuration*. This is called **effective atomic number rule**. *The total number of electrons possessed by the central metal ion and the electrons gained by it from ligands* is called the **effective atomic number** (EAN). Thus, according to effective atomic number rule, the effective atomic number in a complex should be equal to 36 (electrons in Kr), 54 (electrons in Xe) and 86 (electrons in radon).

To illustrate this, consider the complex ion, **hexaammine cabalt (III) ion,** $[Co(NH_3)_6]^{3+}$. The atomic number of Co is 27 and therefore, the number of electrons in Co^{3+} ion is 24. Each of the six ammonia molecules donates a pair of electrons so that total of 12 electrons are donated by six NH_3 molecules. Thus,

No. of electrons in Co^{3+} = 24
Electrons from six NH_3 molecules 2×6 = 12
Total number of electrons in the compound (EAN) = $24 + 12 = 36$

Thus, the effective atomic number is same as the atomic number of krypton (36). Similarly, EAN rule is obeyed for the following coordination compounds :

(i) **Hexacyanoferrate (II) ion,** $[Fe(CN)_6]^{4-}$

Atomic number of Fe = 26
No. of electrons in Fe^{2+} = 24
Electrons from 6 CN^- ions = 12
EAN of $[Fe(CN)_6]^{4-}$ = 36 (EAN rule is obeyed)

(*ii*) **Chloropentaammine platinum ion, $[Pt(NH_3)_5Cl]^{3+}$**

Atomic number of Pt = 78
No. of electrons in Pt^{4+} = 74
Electron from $5NH_3$ and one Cl^- = 12
EAN of $[Pt(NH_3)_5Cl]^{3+}$ = 86 (EAN rule is obeyed)

(*iii*) **Tetracyanocuprate (I) ion, $[Cu(CN)_4]^{3-}$**

Atomic number of Cu = 29
No. of electrons in Cu^+ = 28
Electrons from 4 CN^- = 8
EAN of $[Cu(CN)_4]^{3-}$ = 36 (EAN rule is obeyed)

Some other examples of complexes obeying the EAN rule are given in Table 1.

Table 1. Complexes obeying effective atomic number rule.

Complex	Central metal ion	At. No.	No. of electrons in metal ion	Electrons gained from ligands	EAN
$[Fe(CN)_6]^{4-}$	Fe^{2+}	26	24	12	36 (Kr)
$[Fe(CO)_5]$	Fe	26	26	10	36 (Kr)
$[Cr(CO)_6]$	Cr	24	24	12	36 (Kr)
$[Ni(CO)_4]$	Ni	28	28	8	36 (Kr)
$[Pt(NH_3)_6]^{4+}$	Pt^{4+}	78	74	12	86 (Rn)
$[PtCl_6]^{2-}$	Pt^{4+}	78	74	12	86 (Rn)
$[Pd(NH_3)_6]^{4+}$	Pd^{4+}	46	42	12	54 (Xe)

However, there are many exceptions to the EAN rule. Many stable complexes are known in which the EAN rule is not obeyed. These are given in Table 2.

Table 2. Complexes not obeying effective atomic number rule.

Complex	Metal ion	At. No.	No. of electrons in metal ions	No. of electrons from ligands	EAN
$[Ni(CN)_4]^{2-}$	Ni^{2+}	28	28–2 = 26	8	34
$[Ni(NH_3)_6]^{2+}$	Ni^{2+}	28	28–2 = 26	12	38
$[Pt(NH_3)_4]^{2+}$	Pt^{2+}	78	78–2 = 76	8	84
$[Fe(CN)_6]^{3-}$	Fe^{3+}	26	26–3 = 23	12	35
$[Cr(NH_3)_6]^{3+}$	Cr^{3+}	24	24–3 = 21	12	33
$[Ag(NH_3)_2]^+$	Ag^+	47	47–1 = 46	4	50
$[PdCl_4]^{2-}$	Pd^{2+}	46	46–2 = 44	8	52

If we look at Table 2 it is clear that there are many well known stable coordination compounds which do not obey EAN rule. This reduces the importance of application of EAN rule to coordination compounds. However, it has been observed that this rule can be extended successfully to bonding in organometallic compounds and particularly to metal carbonyls.

EAN rule for Organometallic compounds and metal carbonyls.

(*i*) **Tetracarbonyl nickel (0), $Ni(CO)_4$**

Atomic number of Ni = 28
Ni(0) in $Ni(CO)_4$ = 28
Four CO groups give two electrons each (4 × 2) = 8
EAN of $[Ni(CO)_4]$ = 36

Thus, the complex $[Ni(CO)_4]$ obeys EAN rule.

36 Kr
54 Xe
86 Rn

(*ii*) **Hexacarbonylchromium (0), $Cr(CO)_6$**

Atomic number of Cr = 24
Cr(0) = 24
Six CO groups (6 × 2) = 12
EAN = 36

Thus, EAN rule is obeyed.

(*iii*) **Pentacarbonyliron (0), $Fe(CO)_5$**

Atomic number of Fe = 26
Fe(0) = 26
Five CO groups (5 × 2) = 10
EAN = 36

Thus, EAN rule is obeyed.

(*iv*) **Pentacarbonylmanganate (–I) ion, $[Mn(CO)_5]^-$**

Atomic number of Mn = 25
Mn(–1) = 26
Five CO groups (5 × 2) = 10
EAN = 36

36
54
86

Thus, $[Mn(CO)_5]^-$ obeys EAN rule.

(*v*) **Hexacarbonyl molybdenum (0), $Mo(CO)_6$**

Atomic number of Mo = 42
Mo(0) = 42
Six CO groups (6 × 2) = 12
EAN = 54

Thus, $Mo(CO)_6$ obeys EAN rule.

It has been observed that about 99% of the metal carbonyls obey EAN rule. Some examples are given in Table 3.

Table 3. Metal carbonyls obeying EAN rule.

Complex	Metal ion	Electrons in Metal ion	Electrons donated from ligands	EAN
$Cr(CO)_6$	Cr	24	12	36
$Fe(CO)_5$	Fe	26	10	36
$Ni(CO)_4$	Ni	28	8	36
$Mo(CO)_6$	Mo	42	12	54
$Ru(CO)_5$	Ru	44	10	54
$Os(CO)_6$	Os	76	10	86
$W(CO)_6$	W	74	12	86

EAN rule can explain the stability of metal carbonyls but it cannot be the *sole criteria to form stable carbonyls.* Metals with odd number of electrons cannot obey EAN rule because total number of electrons will be odd no matter how many carbonyls are added. For example, hexacarbonyl vanadium $V(CO)_6$ is a stable complex though it does not obey EAN rule as :

Atomic No. of V = 23
V(0) = 23
6 CO groups (6 × 2) = 12
EAN = 35

Therefore, the complex $V(CO)_6$ does not obey EAN rule.

Similarly, other metal atoms with odd number of electrons such as Mn(25), Co(27) and Cu(29) cannot satisfy EAN rule in their neutral monocarbonyl complexes (these are not known). In order to satisfy EAN rule, there are some options for the metal ions. These are :

(*i*) They may form carbonylate anion such as $[M(CO)_n]^-$ by gaining an electron from a reducing agent or they may form cationic species, $[M(CO)_n]^+$ by losing an electron. For example, the anions $[V(CO)_6]^-$, $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$ obey EAN rule. For example,

$[V(CO)_6]^-$
Atomic number of V = 23
V(–1) = 24
Six CO groups (6 × 2) = 12
EAN = 36

Thus, $V(CO)_6^-$ obeys EAN rule.

(*ii*) They may form single covalent bond with an atom or group having a single unpaired electron *e.g.* hydrogen ($H^\bullet$) or chlorine ($Cl^\bullet$) $[H\,M(CO)_n]$ or $[M(CO)_nCl]$. For example,

$Mn(CO)_5Cl$
Mn(0) = 25
5 CO groups (5 × 2) = 10
$Cl^\bullet$ = 1
EAN = 36

∴ EAN for $Mn(CO)_5Cl$ = 36 electrons.

Similarly, $H\,CO(CO)_4$
Co(0) = 27
4 CO groups (4 × 2) = 8
H = 1
EAN = 36

Some examples of cationic and anionic metal carbonyls obeying EAN rule are summed up below.

Table 4. Anionic and cationic metal carbonyls obeying EAN rule.

Complex	Metal ion	Electrons in metal ion	Electrons donated by ligands	EAN
$V(CO_6)^-$	V^-	24	12	36
$Mn(CO)_5$	Mn^-	26	10	36
$Mn(CO)_6^+$	Mn^+	24	12	36
$Fe(CO)_4^{2-}$	Fe^{2-}	28	8	36
$Co(CO)_4^-$	Co^-	28	8	36

(*iii*) If no other species is available with which the metal carbonyl containing odd number of electrons can interact, it can dimerize resulting pairing of electrons. This will lead to the formation of metal – metal bond. While counting the EAN, the electron pair shared between two metal atoms forming metal – metal bond is counted on both the metals.

For example, manganese forms a stable dinuclear carbonyl, $Mn_2(CO)_{10}$ having metal - metal bond, $(CO)_5Mn - Mn(CO)_5$. Let us calculate EAN for this complex.

$Mn_2(CO)_{10}$
2 Mn (2 × 25) = 50
10 CO groups (10 × 2) = 20
One Mn—Mn bond = 2
EAN for $Mn_2(CO)_{10}$ = 72/2 = 36 e
∴ EAN per Mn atom = 36 e^-(Kr)

Similarly, cobalt forms $Co_2(CO)_8$ which also obeys EAN rule as shown below :

$Co_2(CO)_8$
2Co (2 × 27)
8 CO groups = 54
One Co—Co bond = 16
EAN for $Co_2(CO)_8$ = 2
EAN per Co atom = 36 e^-(Kr) = 72

Beside dinuclear carbonyls, the carbonyls containing odd number of electrons can also form trinuclear, tetranuclear or polynuclear metal carbonyls. The EAN rule can also be used to predict the structures of new compounds. For example, consider the metal carbonyls $Fe_2(CO)_9$ and $Fe_3(CO)_2$:

$Fe_2(CO)_9$. In this case, the atomic number of Fe = 26
2 Fe atoms (2 × 26) = 52
9 CO groups (9 × 2) = 18
EAN = 70 or EAN per Fe atom = 35

This means that for the metal carbonyl $Fe_2(CO)_9$ to obey EAN requirement of 36 e^- on each metal atom, it would require one Fe – Fe bond in $Fe_2(CO)_9$.

Similarly, in $Fe_3(CO)_{12}$,
3 Fe (3 × 26) = 78
12 CO groups (12 × 2) = 24
= 102 or EAN per atom = 34

Therefore, the EAN requirement of 36 e^- on each metal atom would require that each Fe should form two Fe – Fe bonds in $Fe_3(CO)_{12}$. The experimental structural studies have shown that in $Fe_2(CO)_9$, each Fe atom form on Fe – Fe bond while in $Fe_3(CO)_{12}$, each Fe atom forms two Fe – Fe bonds. The structures of these complexes are discussed later.

EAN rule for other organometallic compounds

EAN rule can also be applied to other organometallic compounds. We have already studied that some ligands commonly encountered in organometallic compounds provide more than two electrons. The different number of electrons donated to a metal atom by some typical ligands found in organometallic compounds are listed in Table 5.

Table. 5. Number of electrons donated by different ligands.

Ligand	Number of electronsdonated
$\dot{H}$, $\dot{Cl}$, $\dot{C}H_3$, σ allyl ($\dot{C}H_2CH = CH_2$)	1
H^-, alkyl (e.g. CH_3^-, $C_2H_5^-$), aryl (*e.g.* $C_6H_5^-$, $C_6H_5CH_2^-$), σ-allyl $(CH_2–CH = CH_2)^-$, alkene	2
Diene, (π-allyl)	3
Butadiene, cyclobutadiene, alkynes	4
π-cyclopentadienyl (C_5H_5)	5
Benzene	6
Cycloheptatrienyl (C_7H_7)	7
Cyclooctatetraene (C_8H_8)	8

It may be noted that certain ligands can behave as different number of electron donors in different complexes. For example, alkynes behave both as 4-electron donors and 2-electron donors. A cyclopentadienyl radical (C_5H_5) behaves as a five electron donor whereas a cyclopentadienide ion

($C_5H_5^-$) behaves as a six electron donor. Similarly, a π-bonded allyl (C_3H_5) group behaves as a three electron donor whereas σ-allyl ($-CH_2-CH=CH_2$) acts as one electron donor.

Let us illustrate the calculation of EAN for some complexes.

(*a*) **Alkyl groups as 1 electron donors**

$CH_3Re(CO)_5$

Re = 75
5(CO) = 10
CH_3 = 1
EAN = 86

(*b*) **Olefins and alkynes acting as 2 e donors**

$[Mn(CO)_5C_2H_4]^+$

Mn^+ = 24
5(CO) = 10
C_2H_4 = 2
EAN = 36

(*c*) **Diene and alkynes acting as 4 e donors**

$Fe(CO)_3(C_4H_6)$

Fe = 26
3(CO) = 6
C_4H_6 = 4
EAN = 36

$Co_2(CO)_6(RC\equiv CR)$

2 Co = 54
6(CO) = 12
$RC\equiv CR$ = 4
Co – Co = 2
EAN = 72
EAN per Co = 36

(*d*) **π-allyls acting as 3e donors**

$Mn(\pi-C_3H_5)(CO)_4$

Mn = 25
$\pi-C_3H_5$ = 3
4(CO) = 8
EAN = 36

$Co(\pi-C_3H_5)(CO)_3$

Co = 27
$\pi-C_3H_5$ = 3
3(CO) = 6
EAN = 36

(*e*) **π-cyclo pentadienes as 5e donors**

$Co(\pi-C_5H_5)(CO)_2$

Co = 27
$\pi-C_5H_5$ = 5
2(CO) = 4
EAN = 36

$Fe(\pi C_5H_5)_2$

Fe = 26
$2(\pi-C_5H_5)$ = 10
EAN = 36

$(\pi-C_5H_5)Co(C_4H_4)$

Co = 27
$(\pi-C_5H_5)$ = 5
C_4H_4 = 4
EAN = 36

$(\pi-C_5H_5)Mo(CO)_2\,\pi-C_3H_5$

Mo = 42
$\pi-C_5H_5$ = 5
$\pi-C_3H_5$ = 3
2(CO) = 4
EAN = 54

(*f*) Benzene acting as 6 e^- donors

$Cr(C_6H_6)_2$

Cr = 24
$2(C_6H_6)$ = 12
EAN = 36

$Cr(CO)_3(C_6H_6)$

Cr = 24
C_6H_6 = 6
3(CO) = 6
EAN = 36

Thus, it has been observed that most of the organometallic compounds obey EAN rule. There are some exceptions also in which EAN rule is not obeyed. For example,

$Co(\pi-C_5H_5)_2$

Co = 27
$2(\pi-C_5H_5)$ = 10
EAN = 37

$Cr(C_6H_6)(CO)_4$

Cr = 24
C_6H_6 = 6
4(CO) = 8
EAN = 38

$Fe(\pi-C_5H_5)(CO)_3$

Fe = 26
$\pi\,C_5H_5$ = 5
3(CO) = 6
EAN = 37

$Co(\pi-C_5H_5)(CH_3)_2$

Co = 27
$\pi-C_5H_5$ = 5
$2(CH_3)$ = 2
EAN = 34

$Mo(CO)_3(\pi-C_5H_5)$

Mo = 42
$\pi-C_5H_5$ = 5
3(CO) = 6
EAN = 53

$Ni(\pi-C_5H_5)_2$

Ni = 28
$2(\pi-C_5H_5)$ = 10
EAN = 38

PRACTICE Problems

4. In which of the following organometallic compound EAN rule is not obeyed ?
   (*i*) $Cr(C_6H_6)(CO)_3$ (*ii*) $Ni(\pi-C_5H_5)_2$
   (*iii*) $Fe(\pi-C_5H_5)(CO)_3$ (*iv*) $Fe(CO)_3(C_4H_6)$
   - **Ans.** (*ii*), (*iii*)
5. In which of the following complexes EAN rule is obeyed ?
   (*i*) $[Mn(CO)_5(C_2H_4)]^+$ (*ii*) $Mo(CO)_6$
   (*iii*) $[Cu(NH_3)_4]^{2+}$ (*iv*) $HCo(CO)_4$
   - **Ans.** (*i*), (*ii*), (*iv*)

NOMENCLATURE OF ORGANOMETALLIC COMPOUNDS

We have already studied the IUPAC rules for naming the coordination complexes. These are given in Appendix. All the main rules are applied to organometallic compounds also but some are modified due to complex nature of ligands. The simple alkyl or aryl organometallic compounds of metals are named by writing the name of the metal after the name of organic group. For example,

CH_3Li	Methyl lithium
$(C_2H_5)_2Zn$	Diethyl zinc
C_2H_5MgBr	Ethyl magnesium bromide
C_6H_5MgCl	Phenyl magnesium chloride

The general rules are followed in naming simple compounds containing organometallic ligands such as CO, ethylene, (two electron donors). CO is named as carbonyl and C_2H_4 is named as ethylene. The alkyl and aryl ligands are generally considered as anions for calculating the oxidation state of the central metal ion, although they may or may not behave as anions. Some examples are :

$K[PtCl_3(C_2H_4)]$	Potassium trichloro (ethylene) platinate (II) (ethylene is a neutral ligand)
$K_3[Fe(CN)_5CO]$	Potassium carbonylpentacyanoferrate (II)
$K[B(CH_3)_4]$	Potassium tetramethylborate (III) (Methyl radical is taken as anion)
$K[SbCl_5(C_6H_5)]$	Potassium pentachloro (phenyl) antimonate (V) (Phenyl radical is taken as anion)
$Fe(C_5H_5)_2$	Bis (cyclopentadienyl) iron (II)

Bis is used because the ligand is complex and contains the prefix penta in its name. The common and popular name of this compound is **ferrocene.**

Nomenclature of carbonyls

The compounds containing CO as ligands are called *metal carbonyls.* In case, the metal has zero oxidation state, it may not be mentioned.

For example,

$Ni(CO)_4$	Tetracarbonyl nickel
$Mn_2(CO)_{10}$	Decacarbonyl dimanganese
$Fe_2(CO)_9$	Nonacarbonyldiiron
$Co_2(CO)_8$	Octacarbonyldicobalt
$Co_4(CO)_{12}$	Dodecacarbonyltetracobalt
$[V(CO)_6]^-$	Hexacarbonylvanadate (–I)
$[Co(CO)_4]^-$	Tetracarbonylcobaltate (–I)
$[Mn(CO)_5(C_2H_4)]^+$	Pentacarbonyl(ethylene) manganese (I)

Oxidation state is mentioned because it is not zero.

(*ii*) If the ligands act as bridges between two metal atoms, the Greek letter *mu* (μ) is written before their names. The prefix μ is repeated before the name of each kind of bridging ligand. For example,

$[(CO)_3Co(CO)_2Co(CO)_3]$	Di-μ-carbonyl bis (tricarbonylcobalt)
$[(CO)_3Fe(CO)_3Fe(CO)_3]$	Tri-μ-carbonyl bis (tricarbonyliron)
$[(CO)_4Os(CO)Os(CO)_4]$	μ-carbonyl bis (tetracarbonylosmium)

(*iii*) When the metal carbonyls contain metal-metal bonds, these may be classified as *symmetrical* or *unsymmetrical*. The symmetrical metal carbonyls are named by the use of multiple prefixes (bis, tris etc). In case of unsymmetrical metal carbonyls, one central metal atom and its ligands are treated as a ligand on the other central metal atom. For example,

$[(CO)_4Co-Co(CO)_4]$ (symmetrical)	Bis (tetracarbonylcobalt)
$[(CO)_5Mn-Mn(CO)_5]$ (symmetrical)	Bis (pentacarbonylmanganese)
$[(CO)_4Co-Re(CO)_5]$ (unsymmetrical)	Pentacarbonyl (tetracarbonylcobaltio) -rhenium
$C_2H_5Hg-Ta(CO)_6$ (unsymmetrical)	Hexacarbonyl (ethyl mercurio) tantalum
$[(Ph_3PAu)_2-Fe(CO)_4]$	Tetracarbonyl [bis (triphenylphosphinoaurio)] iron

Naming σ and π bonded ligands

To distinguish between one carbon bonded ligand and multiple carbon bonded ligands, the notation σ and π are used. For example, cyclopentadiene (C_5H_5) is referred as $\sigma-C_5H_5$ (*e.g.* LiC_5H_5) when it behaves as one carbon bonded ligand. However, when it behaves as five carbon bonded ligand it is referred as $\pi-C_5H_5$ (*e.g.* $\pi(C_5H_5)_2Fe$). Similarly, alkyl group is referred as σ-allyl or π-allyl depending upon whether it behaves as one electron donor or three electron donor.

In the case of unsaturated molecules or groups, the prefix η (may be read as eta or hapto, derived from Greek letter haptein meaning to fasten) is used. For example, a one carbon bonded ligand is specified by monohapto (or η^1), two carbon bonded ligand as dihapto (or η^2), three carbon bonded ligand as trihapto (or η^3), a four carbon bonded ligand as tetrahapto (or η^4) and so on. According to latest IUPAC convention, the η notation is recommended.

For example,

$K[PtCl_3(C_2H_4)]$	Potassium trichloro (η^2-ethylene) platinate (II)
$Fe(C_5H_5)_2$	Bis (η^5-cyclopentadienyl) iron
$Cr(C_6H_6)_2$	Bis (η^6-benzene) chromium
$Co(CO)_3(\pi-C_3H_5)$	(η^3-allyl) tricarbonyl cobalt
$(C_6H_6)Cr(CO)_3$	(η^6-benzene) tricarbonyl chromium
$ReH(\pi-C_5H_5)_2$	Bis (η^5-cyclopentadienyl) hydrido rhenium
$Fe_2(CO)_4(C_5H_5)_2$	Bis (η^5-cyclopentadienyl) tetracarbonyldi iron
$(Me_3Si)W(CO)_3(\pi-C_5H_5)$	Tricarbonyl (η^5-cyclopentadienyl) trimethylsilyl tungsten
$Fe(CO)_2(\sigma-C_5H_5)(\pi-C_5H_5)$	Dicarbonyl (η^1-cyclopentadienyl) (η^5-cyclopentadienyl) iron
$Fe(CO)_3(C_4H_6)$	(η^4-butadiene) tricarbonyl iron
$Mn(CO)_5(-CH_2-CH=CH_2)$	(η^3-allyl) tricarbonyl iron
$(\sigma-C_3H_5)(\pi-C_5H_5)Mo(CO)_3$	(η^1-allyl) tricarbonyl (η^5-cyclopentadienyl) molybdneum.
$(\sigma-C_5H_5)_2Ti(\pi-C_5H_5)_2$	Bis(η^1-cyclopentadienyl) bis (η^5-cyclopentadienyl) titanium

BONDING IN ORGANOMETALLIC COMPOUNDS

The properties of organometallic compounds depend upon the nature and stability of the metal-carbon bonds present in them. The bonding in organometallic compounds may be classified as

1. *Ionic bonding*
2. *σ-covalent bonding*
3. *Multiple covalent bonding.*

1. Ionic bonding

This type of bonding is generally observed in organometallic compounds of the most electropositive metals like sodium, potassium, rubidium, cesium, *etc.* Slightly electropositive metals like magnesium also form ionic compounds. In these compounds, the hydrocarbon is present as a carbon carrying negative charge which is strongly attracted by the positively charged metal ion by electrostatic forces of attraction. In some cases, the negative charge is delocalised over the ring of different number of