Introduction to Organometallic Chemistry

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Organometallic chemistry is a branch of coordination chemistry and deals with compounds which have **at least one metal-carbon** bond. Since metals are more electropositive than carbon it is considered that the metal-carbon bond is slightly polarised; localizing a small negative charge on carbon and a small positive charge on the metal (*i.e.*, $M^{\delta+}-C^{\delta-}$). Organic ligands which are coordinated to transition metals can be classified according to (i) **hapticity** of the ligand and (ii) the number of metal atoms directly bonded to a ligand (*i.e.*, bridging ligands).

What is hapticity (η^n)?

The hapticity of a ligand refers to the number of **adjacent** atoms in the ligand (preferably in a delocalised system) directly bonded to the metal centre. There are mainly three types of ligands.

1. *Monohapto* **ligands (η^1)** - The ligand is attached through only one of its carbon atoms to a single metal centre. Some examples are given in Fig. 1.

2. *Polyhapto* **ligands (η^n)** - The ligand is attached through two or more of its carbon atoms to one metal centre. Common suffixes are: η^2 = *dihapto*, η^3 = *trihapto*, η^4 = *tetrahapto*, η^5 = *pentahapto*, η^6 = *hexahapto*, η^7 = *heptahapto*, *etc*. Some examples are given in Fig. 2.

Polyhapto ligands can be **acyclic** or **cyclic**; most of them are **conjugated olefins**; some are **aromatic**.
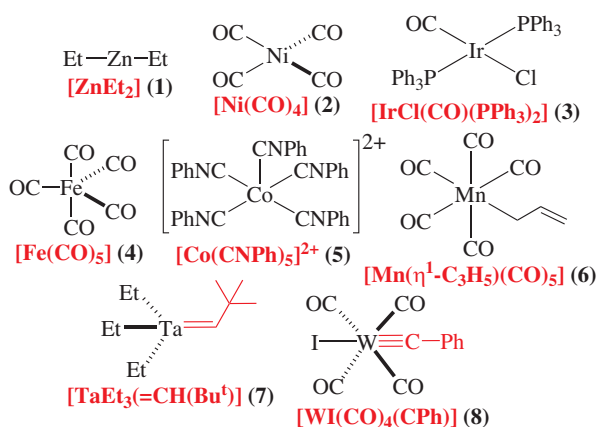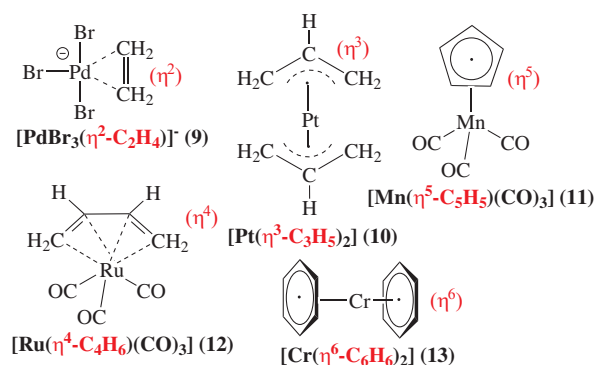

Figure 1. Complexes with η^1-ligands

Figure 2. Complexes with *polyhapto* ligands

3. Bridging (or μ-bonded) ligands - The ligand functions as a bridge, linking two or more metal atoms together. μ_n indicates a ligand bridging n metal atoms (see Fig. 3).
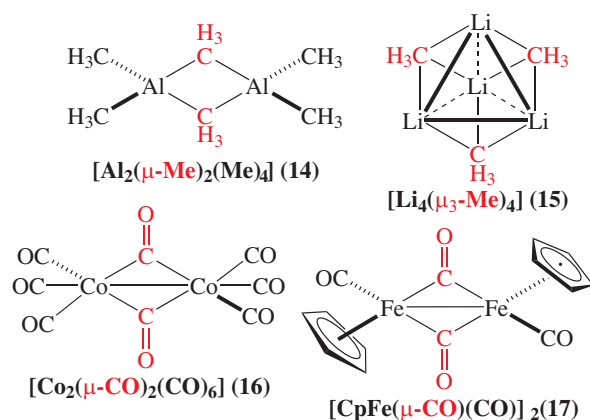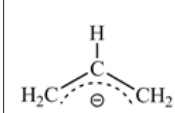

Figure 3. Complexes with bridging ligands

Anionic ligands containing heteroatoms (*e.g.*, -OR, -OAc, -SR, -NR$_2$, -PR$_2$, *etc*) can also act as bridging ligands.

Hapticities of some of the organic ligands are given in Table 1.

Table 1. Hapticities of organic ligands

Name of the group/molecule	Formula	Possible η^n
Methyl	Me-	η^1
Ethyl	Et-	η^1
iso-Propyl	Me$_2$CH- (Pr^i-)	η^1
tert-Butyl	Me$_3$C- (Bu^t-)	η^1
Cyclopentadienyl	C$_5$H$_5^-$ or Cp$^-$	η^1, η^3, η^5
Phenyl	C$_6$H$_5^-$ or Ph$^-$	η^1
Benzene	C$_6$H$_6$	η^2, η^4, η^6
Acetyl	Me(C=O)-	η^1
2-Propenyl or Allyl	CH$_2$=CHCH$_2$- (structure)	η^1 (σ-allyl) η^3 (π-allyl)
Cyclopropenyl	(C$_3$H$_3$)$^-$	η^1, η^3
1,3-Butadiene	C$_4$H$_6$	η^2, η^4
Cyclobutadiene	C$_4$H$_4$	η^2, η^4
Ethenyl/vinyl	CH$_2$=CH-	η^1
Ethene	CH$_2$=CH$_2$	η^2
Ethynyl	CH$\equiv$C-	η^1
Ethyne	CH$\equiv$CH	η^2
Cycloheptatriene	C$_7$H$_8$	η^2, η^4, η^6
Tropylium	(C$_7$H$_7$)$^+$	η^7
Cyclooctatetraene	C$_8$H$_8$	η^2, η^4, η^6, η^8

Note that cyclooctatetraene (C$_8$H$_8$) can act as a η^2, η^4, η^6 or η^8 ligand. It can bridge two metals in the η^4 coordination mode.

Carbene (=CHBu^t) and **carbyne** ($\equiv$CPh) ligands in complexes (**7**) and (**8**) are *monohapto* ligands and they donate **two** and **three** electrons to the metal centre, respectively.

Isoelectronic ligands

Isoelectronic ligands have the same number of electrons, *e.g.*, CO, NO$^+$, CN$^-$, HC$\equiv$CH *etc.* have a total number 14 electrons.

Metal centres

Generally, most electropositive main group elements form (M^+R^- type) ionic compounds, *e.g.*, cyclopentadienyl sodium, NaCp or Na(η^5–C_5H_5). Less electropositive metals such as lithium and magnesium form organometallic compounds with covalent M–C bonds, *e.g.*, $[LiMe]_4$ and MeMgBr. Organic ligands form M–C bonds with most of the transition metals.

Group number of a metal centre

The Group number (Table 2) is equal to the sum of *s*- and *d*-electrons in the zerovalent metal atom. The number of *d*-electrons (d^n) in each metal centre (M) with the formal oxidation states 0, +1 and +2 (*i.e.*, M^0, M^+ and M^{2+}) are given in the Table 2. Similarly, one can calculate d^n for M^{m+}.

Table 2. *d*-Electron configuration ($3d^n$) of 3d elements as a function of the formal oxidation number

Element (Group number)	n of $3d^n$ of M^0	n of $3d^n$ of M^+	n of $3d^n$ of M^{2+}
Sc (3)	3	2	1
Ti (4)	4	3	2
V (5)	5	4	3
Cr (6)	6	5	4
Mn (7)	7	6	5
Fe (8)	8	7	6
Co (9)	9	8	7
Ni (10)	10	9	8
Cu (11)	-	10	9

Electronegativity of transition metals

The electronegativity of an element increases from left to right of the Periodic Table. Early transition metals are electropositive and they readily lose their valence electrons. Thus, they are found in the highest possible oxidation state. Late transition metals are more electronegative and they tend to keep their valence electrons. They can form relatively stable complexes with low oxidation states. The electron-loving metals are more basic and prefer to form bonds with soft ligands (*e.g.*, CO, PR_3).

Oxidation number

Oxidation number (or state) of a metal in a coordination compound can be defined as the charge left on the metal when all the ligands are removed from the metal. For example, when L is a **neutral** ligand and X is a **monoanionic** ligand, the formal oxidation number (O.N.) of M in coordination compounds such as $[MX_3L_3]$, $[MX_2L_3]X$, $[MXL_3]X_2$ and $[ML_3]X_3$ is +3. This number relates to the total charge of the negative ions, X. Note that most of the organometallic complexes contain organic ligands and have covalent bonds. Thus, the oxidation numbers of organometallic complexes are less important. For example, the charge on Fe in ferrocene is +0.2. However, the oxidation numbers are determined using the ionic model.

σ-Donors and π-acceptors

Donation of a lone pair of electrons in a ligand to a vacant orbital of a metal centre results in a σ-bond. Such ligands are known as σ donors.

$$M \xleftarrow{\sigma} \mathbf{:}L \qquad L = NH_3, Cl^-, H_2O$$

Donation of filled dπ-electrons in the metal centre to a suitable orbital of a ligand is called "back donation", which results in a π-bond. Such ligands are known as π acceptors/π-acids.

$$M \underset{\pi}{\overset{\sigma}{\rightleftarrows}} L \qquad L = CO, CNR \text{ and } PR_3$$

Hard metals and soft metals

Early transition metals in higher oxidation states are positively charged and are classified as **hard metals**. They are more likely to form strong bonds with electron rich σ donors. These hard metals are **electrophilic**, *i.e.*, they are electron loving.
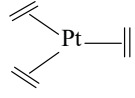
Late transition metals in lower or zero oxidation states are electron rich (or more π-basic) and are classified as **soft metals**. They are more likely to form strong bonds with electron withdrawing ligands or π **acceptors**. These π-basic metal centres are **nucleophilic**.

Coordination number and geometry

Coordination number (C.N.) can be defined as the number of monodentate ligands (or **electron pairs**)

coordinated (or **donated**) to a metal centre. Possible geometries for different coordination numbers are shown in Table 3.

Table 3. Geometry of metal complexes

C.N.	Geometry	Example
2	Linear	[ZnEt$_2$] (**1**)
3	Trigonal planar	
4	Tetrahedral	Complex (**2**)
	Square planar	Complex (**3**)
5	Trigonal bipyramidal	Complex (**4**)
	Square pyramidal	Complex (**5**)
6	Octahedral	Complex (**6**)

Some geometries are favoured by certain d-electron configurations. For example, d^6 favours the octahedral geometry; d^8 favours the square-planar geometry; d^4 and d^{10} prefer the tetrahedral geometry.

LX classification

If we consider two-electron donor ligands such as CO, PMe$_3$ as L type monodentate ligands, then, we can consider 1,3-butadiene with two double bonds as a L$_2$ type bidentate ligand; similarly, benzene with three double bonds as a L$_3$ type tridentate ligand. Thus, one can assume coordination number of M in [M(L)(L$_2$)(L$_3$)] as 6.

If we represent monoanionic ligands (*e.g.*, hydride, halides, hydroxide *etc.*) by X, we can consider η^3-allyl ligand as a LX type ligand. Similarly, we can consider η^5 cyclopentadienyl ligand as a L$_2$X type ligand.

According to the **covalent model**, X donates 1e; LX donates 3e; L$_2$X donates 5e. According to the **ionic model**, X donates 2e; LX donates 4e; L$_2$X donates 6e (Table 4).

Valence electron count

The 18-electron rule says that a metal centre would form a stable complex if the VEC of the metal is 18. Such complexes are coordinatively saturated. Complexes with incompletely filled valence shell (*i.e.*, VEC<18e) are coordinatively unsaturated. Such complexes would prefer to take up a suitable ligand(s) in order to fulfil the 18e rule. There are two methods to calculate the VEC of a complex, (i) **covalent** model and (ii) **ionic** model.

Neutral ligands provide the same number of electrons irrespective of the type of the model. Monodentate ligands such as CO, NH$_3$, NR$_3$, PR$_3$, SMe$_2$, OR$_2$, provide two electrons. Bidentate ligands such as H$_2$NCH$_2$CH$_2$NH$_2$ and Ph$_2$PCH$_2$CH$_2$PPh$_2$ provide four electrons. The following π-donors provide number of electrons as same as their hapticity; η^2-CH$_2$=CH$_2$ (2e), η^2 cyclobutadiene (2e), η^6-C$_6$H$_6$ (6e), and η^4-CH$_2$=CHCH=CH$_2$ (4e). According to the covalent model the η^3-allyl ligand contributes 3e to the metal centre but according to the ionic model it provides 4e.

According to covalent model, bridging ligands donate three electrons (one σ-bond and one coordinate bond) to both metal centres. An anionic ligand provides **one electron more** on the ionic model than on the covalent model as shown in Table 4.

Table 4. Electron contribution by anionic ligands to both covalent and ionic models

Anionic ligand	Covalent Model	Ionic Model
H$^-$, X$^-$, R$^-$, Ar$^-$, -SR, -OR, -NR$_2$, C$_3$H$_5$$^-$ (η^1-allyl)	1e	2e
η^3-Allyl/(C$_3$H$_5$)$^-$	3e	4e
η^3-Cyclopropenyl (C$_3$H$_3$)$^-$	3e	4e
η^5-Cyclopentadienyl (C$_5$H$_5$)$^-$	5e	6e
η^7-Cycloheptatrienyl (C$_7$H$_7$)$^-$	7e	8e

Let us determine the VEC of [Mn(η^3-C$_3$H$_5$)(CO)$_4$] (**18**) using both models.

Complex	Covalent model	Ionic model
(**18**)	4 CO = 8e 1 C$_3$H$_5$$^{\cdot}$ = 3e 1 Mn^0 (d^7) = 7e 18e	4 CO = 8e 1 C$_3$H$_5$$^-$ = 4e 1 Mn$^+$ (d^6) = 6e 18e

Exceptions to the 18-electron rule

There are exceptions to the 18e-rule. There are stable complexes with VEC less than 18e (VEC < 18e). For

example, square-planar complexes with d^8 metal centres {*e.g.* Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II)} contain only 16 electrons. Stable complexes with VEC <18e can also be prepared using bulky ligands. These sterically demanding ligands protect the metal centre from being attacked by other molecules/ions. For example, the complex $[Cr(CH_2SiMe_3)_3]$ (VEC of Cr = 9e) is an isolable crystalline solid, but $[CrMe_3]$ is unknown. Stable metallocenes containing more than 18 valence electrons, *e.g.*, $[CoCp_2]$ (19e) and $[NiCp_2]$ (20e) are also known.

Nomenclature

General rules used in naming of coordination compounds are applied here. The degree of back bonding to the unsaturated molecule (or to the π system) may vary depending on the π acceptability and the substituents present on the ligands.

The oxidation state of the metal (or the formal charge on the metal centre) in organometallic complexes cannot be well defined, thus, the oxidation state of the metal is **not** included in the name.

In general, organic ligands bound by a single carbon atom to metals are named by the customary substituent group (radical) names. Ligands of alkylidene complexes with metal carbon double bonds (M=C) and alkylidyne complexes with metal carbon triple bonds (M≡C) are also given substituent group (radical) names.

Prefixes should be disregarded when alphabetising ligands. Some examples are given below.

a) $[ReO_3(Et)]$ = Ethyltrioxorhenium

b) $[Ni(\eta^3-C_3H_5)_2]$ = Di(η^3-allyl)nickel

c) $[Ti(\eta^5-C_5H_5)_2(\eta^2-CH_2=CH_2)]$ =
Bis(η^5-cyclopentadienyl)(η^2-ethene)titanium

d) $[Cr(\eta^6-C_6H_6)_2]$ = Di(η^6-benzene)chromium

e) $[W(O_2)(CO)_2(\eta^6-C_6H_6)]$ =
(η^6-benzene)dicarbonyl(dioxygen)tungsten

Names of complex anions end with ***ate***.

a) $[ReMe_8]^{2-}$ = Octamethylrhen**ate**

b) $[Co(CO)_4]^-$ = Tetracarbonylcobalt**ate**

c) $[W(\eta^5-C_5H_5)(N_2)(CO)]^-$ = Carbonyl(η^5-cyclopentadienyl)(dinitrogen)tungst**ate**

Problems

1. (i) What is the C.N. of the metal centre in each of the following complexes?

   (ii) Determine the **O.N.** of the metal centre using the **ionic** model.

      (a) *cis*-$[PtCl_2(\eta^2-CH_2=CH_2)(CO)]$

      (b) $[PtCl_2(H)(C≡CPh)(PEt_3)_2]$

      (c) $[W(CPh)I(CO)_4]$ (**8**)

      (d) $[W(\eta^3-C_3H_5)(\eta^5-C_5H_5)(CO)_2]$

      (e) $[Mn(\eta^6-C_6H_6)(CO)_3]^+$

2. Determine the **VEC** of metal centres in the complexes (**a**)-(**e**) given in question 1.

3. Draw the structures of the following complexes/ions.

   a) $[Co(CO)_4]^-$

   b) $[PtCl_2(cycloocta-1,5-diene)]$

   c) $[Mn_2(CO)_{10}]$

   d) $[Rh_2(\mu-Cl)_2(\eta^2-CH_2=CH_2)_4]$

   e) $[W(\eta^3-C_3H_5)(\eta^5-C_5H_5)(CO)_2]$

   f) $[Mn(\eta^6-C_6H_6)(CO)_3]^+$

   g) $[PtCl_2(H)(C≡CPh)(PEt_3)_2]$

   h) $[W(\eta^5-Cp)(\eta^2-H_2)(CO)_3]BF_4$

4. Give the **IUPAC** names of the metal complexes (**a**)-(**e**) given in question 1.

5. Draw the structure of (η^3-allyl)carbonyl(η^3-cyclopropenyl)(η^1-ethynyl)iridium.