→ Organometallic - Compounds:

The compounds which contain carbon-metal bond is known as "organo-metallic compounds".

* M ———— C
* "Carbon" must be organic-molecule.
* "Metal" may be transition, main-group etc.

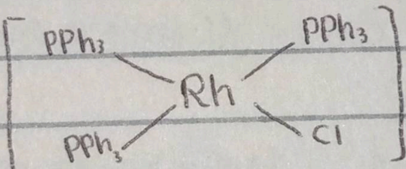
→ Examples:

1) R-Mg-X (Grignard-reagent).
2) Wilklinson - Catalyst ($Rh(PPh_3)_3Cl$).

Question: where is "C-M" bond in wilklinson-catalyst?

Answer: The wilklinson-catalyst is mostly used in the "Hydrogenation-Reactions".

→ Structural-Formula:



Wilklinson-catalyst.

During the catalytical-cycle (Hydrogenation Rxn) the carbon-metal direct bond are formed in any one step. Therefore this is called "organometallic".

→ Non-organo-metallic Compounds:

Compounds that are not-organometallic.

→ Examples:

1) NaCN (cynides)
2) CaC_2 (Carbides)

These compounds are not organometallic.

B/c → These are in-organic compounds.

→ There properties are different from organo-metallic compounds.

→ "Some compounds which are in-organic but show same behaviours / properties like organo-metallic compounds are also called "organo-metallic compounds".

→ **Examples:**

1) $Ni(CO)_4$.

→ **Applications:**

1) **As a reagent:**
   a) R-Mg-X (Grignard-reagent)
   b) R-Li
   c) n-BuLi
   d) R_2CuLi (Gilmen-reagent).

2) **As a Catalyst:**
   a) $[Rh(PPh_3)_3Cl]$ (Wilkinson-catalyst)
   b) $CO_2(CO)_8$ → Used in Hydroformolation Rxn.

3) **As a drug:**
   a) Cp_2TiCl_2
      → used as a anti-cancer drug.
   b) Cis-platin.
      → anti-cancer-drug.

4) **As a additives:**
   a) TEL (Tetraethyl lead).
      → Used as anti-knocking agent in the fuel.

→ Classifications of organo-metallic Compounds:

→ On the basis of metal used in omc.

1) Main-Group OMC:

→ The metal in the organo-metallic compound is from main group.

Examples:

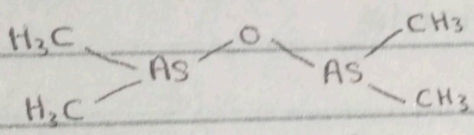
a) R-Mg-X

b) R-Li

c) $Na^{+}C_5H_5^{-}$

d) $Al(Et)_3$ ∴ Et: Ethyle group.

e) Cacodyl-oxide.



→ (This is the first-organometallic compound.

2) Transition-metal-OMC:

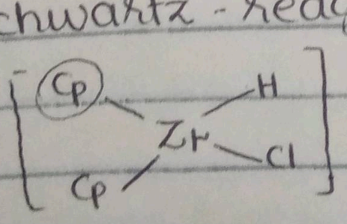
→ The metal in the organometallic-compds is transition metal.

Examples:

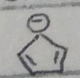
a) $[Rh(PPh_3)_3Cl]$ Wilklinson-catalyst.

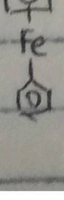
b) R_2CuLi Gilmen-reagent.

c) Schwartz-reagent.

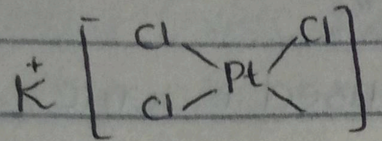


∴ Cp: Cyclo-pentadienyl anion.



d)  Ferrocine.

e) Zeise's salt → is the first Transition-metal organometallic - Cmpd.



f) Collman's reagent.

$[Fe(CO_4)]^{-2}$

g) Vaska's complex

$[Ir(PPh_3)_2(CO)Cl]$.

3) Lanthenide / Actinide OMC:

→ The metal in the organo-metallic compounds is Lanthenide / Actinide.

Examples:

Ligands:

1) Hepticity (η):

It is the no. of donor atoms that are directly connected to metal-center.

→ This no. atoms of a particular ligand is known as "Hepticity".

→ It is represented by eta 'η'.

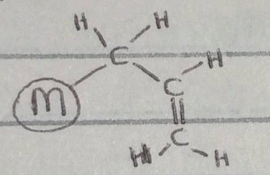
→ It is a property of ligand.

→ Generally representation of Heptaicity of ligand:

- $M(\eta^x L)$. ∴ x = is the no. donor atoms that are directly attached to metal.

Example:

a):



→ one donor atom directly attached to ligand.

→ Group is allyl.

So; → $M(\eta^1$-allyl$)$.

→ Hepticity of different Ligands:

1) Mono-hapto-Ligand (η^1):

→ Ligand attached to C.M atom by one donor atom.

Examples:

a) M – R (alkyl-group).

b) $M-\overset{O}{\overset{\|}{C}}-R$ (Carbonyl-group).

c) $M=C\langle^{R}_{R'}$ (Carbine).

2) Di-hapto-Ligand (η^2):

→ two donor atoms.

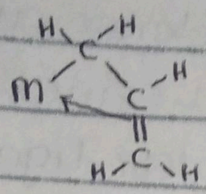
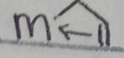
Examples: a) $M-\overset{CH_2}{\underset{CH_2}{\|}}$ (alkene).

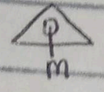
b) M–|| (akene with other group).

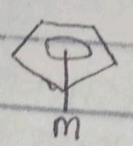
3) Tri-hapto Ligand : (η^3).

→ Three-donor atoms.

Examples:

a):  

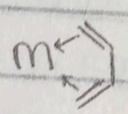
b):  → $M(\eta^3 - C_3H_3)$.

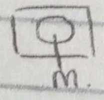
c): 

4) Tetra-hapto Ligands: (η^4)

→ four donor atoms.

Examples:

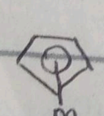
a): 

b): 

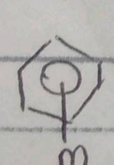
5) Penta & Hexa hapto Ligand:

→ five and six donor atoms.

Examples:

a): 

→ $M(\eta^5 - Cp)$

b): 

$M(\eta^6 - C_6H_6)$.

→ **Formal-Charge:**

A method of counting ~~charge~~ electrons in a covelantly bonded molecules or ion; counts bonding electrons as though they were equally shared between the two atoms.

Formula used to find the formal-charge:

→ $C = M + L$

∴ C = Charge on complex.

∴ M = Oxidation state.

∴ L = Charge on Ligand.

How to find?

→ **Electron Contribution of a Ligand?**

Two methods are used:

1) **Ionic-Method:**

In ionic method first the bond b/w metal and Ligand are hetrocyclically cleave then find the contribution of electrons b/w Ligand and metal.

Example:

if

$(M) \colon CH_2 - CH_3$

→ hetrocyclically cleave.

So, $\overset{+}{M} \; \overset{\ominus}{C}H_2 - CH_3$

Here the electron contribution is 2 and the formal charge is -1.

2) Neutral-Method:

In this method the bond b/w Ligand and metal are homolytically cleave.

Example:

* $M - CH_2 - CH_3$ (homolytically cleave.)

So, $\dot{M}$ $\dot{C}H_2 - CH_3$

The electron contribution is 1.

→ **Ligands and their electron-contribution:**

1) All-alkyl having hepticity (η^1):

e.g: $M - CH_2 - CH_3$

☺ **Point-to-be noted:**

If The Ligand, connected to the metal are negatively charged

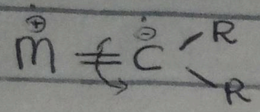
a) In ionic method the electronic contribution is two.

b) In neutral method the E.C is one.

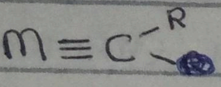
* $\overset{\oplus}{M}$ $\overset{\ominus}{C}H_2 - CH_3$

Electron-contribution:

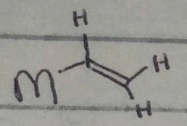
Ionic-method	Neutral method
2	1

2) 

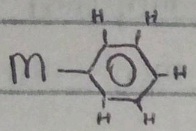
~~ionic method~~	~~Neutral method~~
2	4

3) 

N.m	I.m
3	6

4) 

N.I.m	I.m
12	2

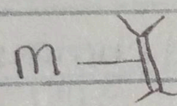
5) 

N.I.m	I.m
1	2

☺ **If the Ligand is Neutral:**

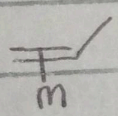
→ No. coordinate bond = no. electron contribution.

Example:

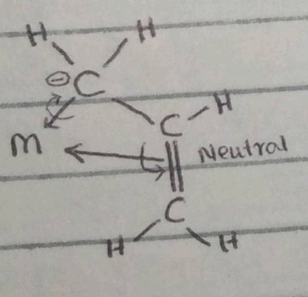
6) 

N.m	I.m
2	2

(Same)

7) 

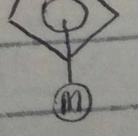
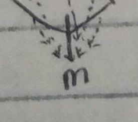
N.m	I.m
2	2

8) 

→ Two Ligands

a) Negative b) Neutral.

I.Method	N.method
4	3

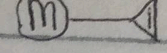
9)  rep: 

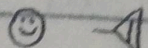
I.m	N.m
6	5

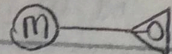
→ Fluxonial-Ligands:

Those Ligands which can show more Than one hepticity, are know as "fluxonial-Ligands".

Example:

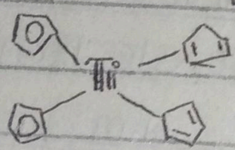
a)  hepticity = 1 $m(\eta^1\text{-}C_3H_3)$

 Cycloprioponium anion.

b)  hepticity = 3 $m(\eta^3\text{-}C_3H_3)$.

→ How to find formal-Charge of metal:

Formula = ($C = m + L$)

1) 

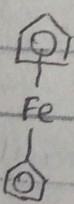
$C = m + L$

L = Ligand charges = -4

$C = 0$

so $0 = m - 4$

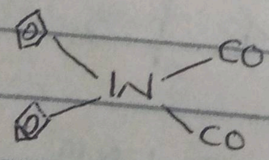
$\boxed{m = +4}$

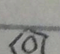
2) 

$C = m + L$

$0 = m - 2$

$\boxed{m = +2}$

3) 

 $= -1$

∴ $CO = 0$

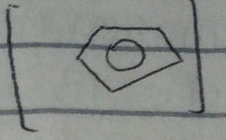
∴

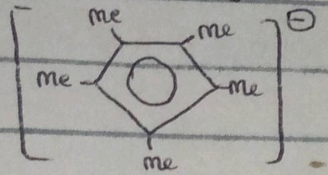
$C = m + L$

$0 = m - 2$

$\boxed{m = +2}$

→ Cp and Cp*:

* Cp: Cyclopentadianion-anion. 
* Cp*: The all five hydrogens of a Cp remove and five metals attached.



→ Cp* is a better Ligand than the Cp b/c in Cp* the five metal atoms attached and increase electron density and increase The coordinating power of a Ligand with metal.

→ 18-e rule:

☺ History:

→ Effective atomic number: "When E.A.N equal to The Noble gas configuratio → Molecule become stable."

* Octet-rule: Proposed by lewis.

"Some molecules found in nature which exist as a stable molecule and the common feature in all the stable molecule is that That 8-electrons is ~~the~~ present in Their valence-shell.

→ Lewis says That every atom want to keep 8-ēs in their ~~Octet~~ valence shell and called Octet.

É.A.No = Electrons of metal + electrons donated by Ligands.

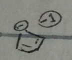
→ **Later;**

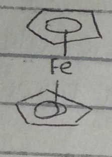
→ "Sidwick modified the Octet rule for coordination compounds and proposed new rule, called "18-electron rule".

18ē-rule: Valence ēs of metal + ēs donated by Ligands ± charge.

Configuration = $ns^2 (n-1)d^{10} np^6$.

Example:

① 

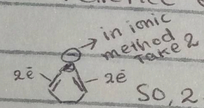


① Ionic-method —— Neutral-method.

→ 6+6+6 = 18ē

* From ionic method. Show that it follow 18ē-rule.

Valence electrons of $Fe = 3d^6 4s^2$



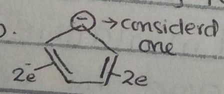
$Fe^{+2} = 3d^6$

So, 2+2+2 = 6ē × 2 = 12ē.

Total = 18ē.

2) **Neutral-method:** (No matter with oxidation state).

× valence ēs of Fe = 8ē

× Cp. 

= 5ē × 2 = 10

So 8+10 = 18

→ Show that, molecule follow 18e-rule.

2) $Fe(CO)_5$.

∴ Co = neutral. & no charge on fe.

a) Ionic-method

* Fe ($3d^6 4s^2$) → 8ē

* Co (The è contribution) → 2ē

5CO → 2×5 = 10è

Total = 18è

So, $Fe(CO)_5$ follow 18-ē rule.

b) Neutral-method:

* Fe 8ē

$(CO)_5$ 10ē → $Fe(CO)_5$ follow 18ē-rule.

Total = 18ē.

d^8-configuration metal → Square planner complex follow the "16-ē rule".

→ Some examples which follow 18ē rule or not:

1) $Fe(CO)_4^{-2}$ →(Solved by Neutral method)

Fe → 8e

$(CO)_4$ → 2×4 = 8ē

-2 charge will add so = 8+8+2

Total = 18e

So, $[Fe(CO)_4]^{-2}$ follow 18e-rule.

2) $[V(CO)_6]^-$

V → 5e

$(CO)_6$ → 12ē

-1 add

5+12+1 = 18è.

3) $Rh(PPh_3)_3Cl$

$Rh \rightarrow 9\bar{e}$

$PPh_3 \rightarrow$ neutral Ligand and Contribute $2\bar{e}$.

$(PPh_3)_3 \rightarrow 6\bar{e}$

$Cl^- \rightarrow$ -1 add , So, $9+6+1$

Total = $16\bar{e}$

→ Not follow $18\bar{e}$ rule.

4) $Cp\,Mo(CO)_3$.

$Mo \rightarrow 6\bar{e}$.

$Cp \rightarrow 5\bar{e}$

$(CO)_3 \rightarrow 2\times3$

Total = $17\bar{e}$

→ Not follow $18\bar{e}$ rule.

5) Cp_2Co

$Co \rightarrow 9\bar{e}s$

$Cp \rightarrow 5\bar{e}$

$(Cp)_2 \rightarrow 10\bar{e}$

Total = $19\bar{e}$

→ Not follow $18\bar{e}$ rule.