Unit – II :

Organometallic Compounds of transition metals :→

Introduction: → OMC are those in ⊆ there is a metal - carbon bond, in the case of transition metals, this group of compounds includes not only metal carbonyls, Olefin complexes, cyclopentadienyl, and other π- complexes.

→ Transition metal ions can bind ligands (L) to give a Coordination Compound, or complex $[ML_n]$

for ex:- $[M(H_2O)_6]^{2+}$ (M = V, Cr, Mn, Fe, Co, Ni)

Ligands usually bind to metals in their lower oxidation states are CO, alkenes, and arenes for example $Mo(CO)_6$ or $Pt(C_2H_4)_3$. or $(C_6H_6)Cr(CO)_3$., $Zn(CH_3)_2$, $Zn(C_2H_5)_2$, $Mg(CH_3)_2$, ~~Sn(t~~

Nature of bonding : →

→ Many accessible oxidation states

→ Preference for σ-donars/π-acceptor combinations (CO)

M-H and M-C σ bonds: →

M-H Hydride

M-C Alkyl

Vinyl (alkenyl)

M-C≡C- Acetylide (alkynyl)

Aryl

Common ligands for transition metals →

π-ligands, CO, phosphines

CO

PR_3

σ-donar character :-

phosphines > alkenes, CO

π-acceptor character

CO > alkenes > phosphines

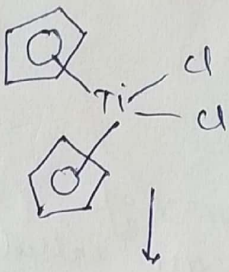
→ CO is one of the best π - acceptors (π-acids)

→ Isocyanides are stronger donors, weaker acceptors

→ PMe_3 very weak π-acceptor, good σ-donor

→ C_2H_4 weak π - acceptor

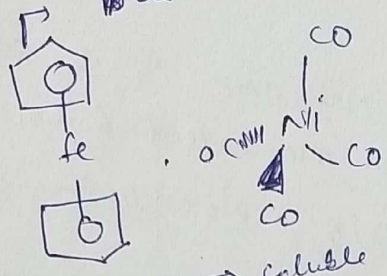
~~(19)~~ Transition Metal OMC ⟹ bis (cyclopentadienyl) iron (II)



(Cp_2TiCl_2)

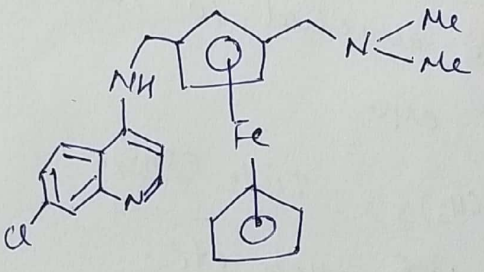
↓

The first OMC found for antitumor activity

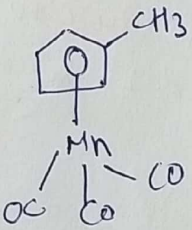


Ferrocene → soluble in liquid fuels, air stable, non toxic, thermally stable.

$Rh(PPh_3)_3Cl$ etc.



Ferroquine → used as antimalarial drug.



MMT (methyl cyclopenta dienyl manganese tricarbonyl)

⇒ σ-Bonded OMC →

$W(CH_3)_6$, $CH_3-Mn(CO)_5$, $[Ta(\eta^5-C_5H_5)_2(CH_3)_3]$, $Ta(CH_3)_5$

⇒ π- Bonded OMC → In the OMC of the transition metals unsaturated organic compounds/groups such as ethylene, acetylene, cyclopentadienyl, benzene etc. there is interaction b/t the atomic orbitals (AOs) of the metal atom and the π- molecular orbitals (MOs) of the organic ligand. For example, in ferrocene, $[Fe(\eta^5-C_5H_5)_2]$, the atomic orbitals of iron atom interact with π-MOs of

cyclopentadienyl rings forming the MOs of the Ferrocene molecule.

⇒ σ- Bonded OMC in transition metals ⇒

(A) The σ- bonded transition metal hydrocarbyls can be classified on the basis of nature of groups attached to the central metal atom as follows: ⟶

(a) Homoleptic OMC ⟶ The OMC in ⊆ same organic groups are attached to the metal atom are called homoleptic OMC.

Examples: ⟶ $Al(CH_3)_6$, $Ti(CH_3)_4$, $W(CH_3)_5$ etc.

(b) Heteroleptic OMC ⟶ The OMC in ⊆ more than one types of groups are attached to the central metal atom are called heteroleptic OMC

Ex) ⟶ $PdCl_2(CH_3)_3$, $TiCl_2(CH_3)_2$, $(OC)_5Mn-CH_3$, ~~$Zr(CH_3)_2$~~

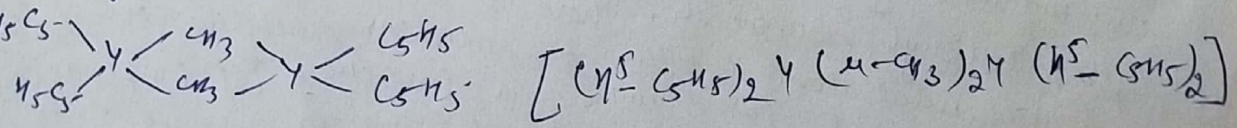
$Zr(CH_3)_2(\eta^5-C_5H_5)_2$ etc.

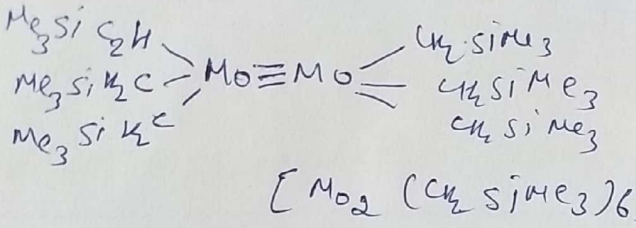
[B] The σ- bonded transition metal hydrocarbyls can also be classified on the basis of number of metal atoms per molecule as follows ⟶

(a) Mononuclear OMC ⇒ The OMC ⊆ have only one metal atom per molecule are called mono- nuclear OMC.

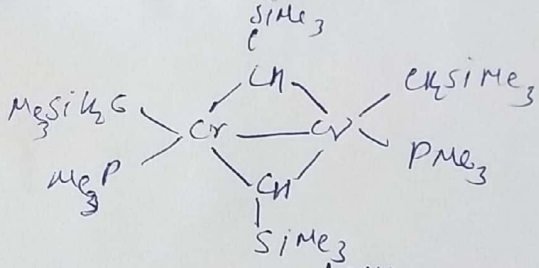
ex) ⟶ $Pa(CH_3)_5$, $W(CH_3)_6$, $Ti(CH_3)_4$ etc.

(b) Polynuclear OMC ⇒ The OMC ⊆ have more than one metal atom per molecule are called polynuclear OMC. These are formed through bridging alkyl (aryl) groups and / or metal- metal interaction

ex) ⟶ 



$[Mo_2(CH_2SiMe_3)_6]$



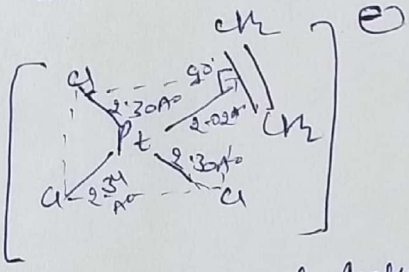
⇒ ## Transition Metal π- complexes ⇒ the molecules that have multiple bonds such as C=C, C≡C, M=O, M≡M etc. can form complexes & Transition metals & are called π- complexes.

prep^n :-

$$K_2[PtCl_4] + C_2H_5OH \xrightarrow[\text{Refluxed}]{C_2H_5OH} K[PtCl_3(C_2H_4)]\cdot H_2O + KCl.$$

Zeise's salt

Structure; → The methods neutron diffraction technique we can find the str. of Zeise's salt.



The main structural features of the anion of Zeise's salt are ; →

(1) Pt^{+2} ion is present at the centre of a square - plane

(2) ~~three~~ Three corners of the square - plane are occupied by Cl⊖ ions

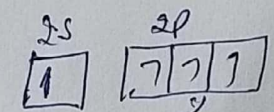
(3) C_2H_4 occupies the 4th coordination site of the square - planes complexes & the C=C bond ⊥ to the $PtCl_3$ plane. Pt ligand plane and the centre of the C=C bond lies on the square - plane ~~correct~~ comes.

Nature of bonding ; →

$CH_2=CH_2$ (ethylene)

↓ sp2 hybridised

VSEC of C atoms in C_2H_4 molecule



↓ sp2 hybridised