METAL CARBONYLS

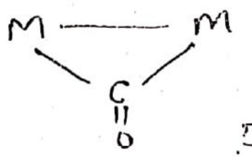
⇒ Transition metal complexes with CO are called metal carbonyls.

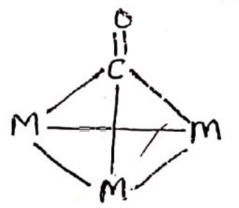
(A.) Neutral Binary metal complexes of carbonyls :-
$[M_y(CO)_x]$
eg:- $[Fe_2(CO)_9]$

→ The oxidation state of metal in a neutral Binary metal carbonyl is zero.

→ The no. of CO groups attached to a metal atom depends on the electronic configuration of the metal atom.

→ $M \leftarrow CO$ = called terminal CO

→ 
= Doubly bridged CO
This bond always occur when CO behaves as bridging ligand.

→ 
→ Triply bridged CO gp.

→ EAN & 18 e^- rule is obeyed in 99% cases. except $[V(CO)_6]$, $Co_6(CO)_{16}$ etc.

→ All metal carbonyls are diamagnetic solid/liq. except $[V(CO)_6]$, $Co_6(CO)_{16}$ etc.

→ These are covalent compound, almost insoluble in water but soluble in organic solvent.

÷ In $[V(CO)_6]^-$, ~~$[Co_6(CO)_{16}]$ etc~~ $[Fe(CO)_4]^{-2}$, $[Mo(CO)_4]^{-4}$
↳ max. −ve oxidation state.

÷→ $M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} CO$ ⟶ σ-donor
π-acceptor.

CLASSIFICATION

- Mononuclear $[M(CO)_x]$
  eg: $[V(CO)_6]$, $[Cr(CO)_6]$
- Polynuclear $[M_x(CO)_y]$
  eg: $[Mn_2(CO)_{10}]$
  $[Fe_2(CO)_9]$
  $[Co_2(CO)_8]$

÷ In d-block the carbonyls compounds are listed as ÷

Sc	Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$
Y	Zr	Nb	$Mo(CO)_6$	$Tc_2(CO)_{10}$
La	Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$
Ac				

Sc, Y, La, Ac ↓ Do not form metal carbonyl

Ti, Zr, Hf and Nb, Ta ↓ Do not form metal carbonyl

			IB	IIB
$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$	Cu	Zn
$Fe_2(CO)_9$	$Co_4(CO)_{12}$	$Pd(CO)_4$	Ag	Cd
$Fe_3(CO)_{12}$	$Co_6(CO)_{16}$	$Pt(CO)_4$	Au	Hg
$Ru_3(CO)_{12}$	$Rh_4(CO)_{12}$			
$Os(CO)_5$	$Rh_6(CO)_{16}$			
$Os_2(CO)_9$	$Ir_4(CO)_{12}$			
$Os_3(CO)_{12}$				

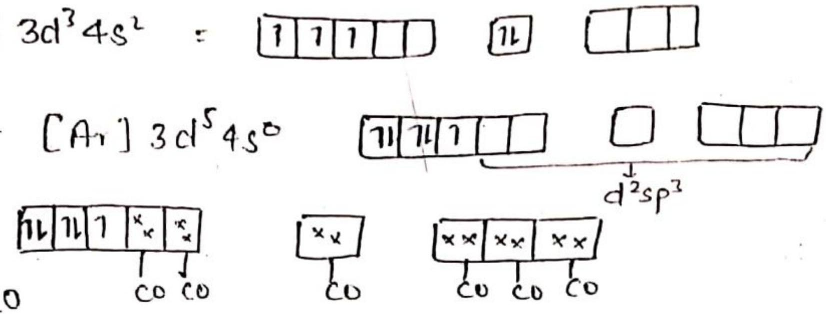
Cu, Ag, Au, Zn, Cd, Hg ↓ do not form metal carbonyl.

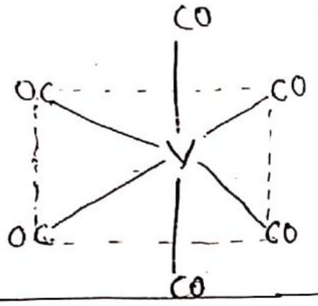
1) Mononuclear Metal carbonyls :-

① $V(CO)_6$:-

$_{23}V$ = [Ar] $3d^3 4s^2$ =

due to effect of CO In $[V(CO)_6]$, V = [Ar] $3d^5 4s^0$





EAN = At. No of M − e^- lost + e^- gain

* d^2sp^3
* Paramagnetic
* EAN − 35
* Total e^- in outer shell = 5+12 = 17 e^- (do not obey 18 e^- Rule)

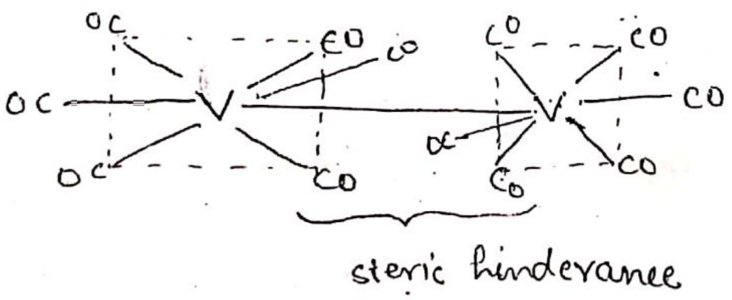
* Mononuclear $V(CO)_6$ is least stable.

→ Thus to attain 36 (EAN), it undergoes reaction with Na.

$$[V(CO)_6] \xrightarrow[e^-]{Na} Na^+[V(CO)_6]^-$$

↓ In which V is in −ve oxidation state

→ It doesnot undergo dimerisation to attain E.A.N., because 7- co-ordination leads to steric hinderence.



2) $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$

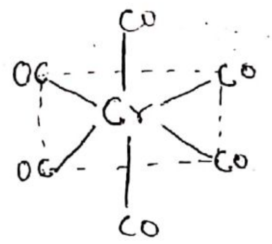
$_{24}Cr$ = $3d^5, 4s^1$ = [1|1|1|1|1] [1] [| |]

6 e⁻

Cr = [1L|1L|1L| |] [ ] [| |]

d^2sp^3 = oct

$Cr(CO)_6$ = [1L|1L|1L|xx|xx] [xx] [xx|xx|xx]



→ Octahedral.
→ d^2sp^3
→ Diamagnetic
→ EAN = 36
→ $18e^-$ is followed.

Transitions Metals :-

Outer electronic configuration = $(n-1) d^{1-10} ns^{1-2}$

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac									

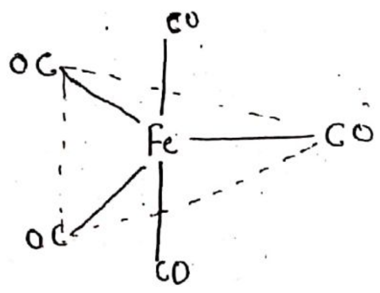
→ $Fe(CO)_5$:

$_{26}Fe^x$ = $3d^6$ $4s^2$ $4p^0$

[1L|1|1|1|1] [1L] [| |]

In $Fe(CO)_5$ = [1L|1L|1L|1L|xx] [xx] [xx|xx|xx]

dsp^3



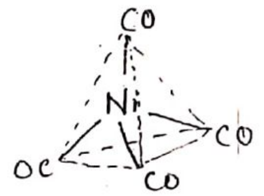
→ $Fe(CO)_5$
→ TBP
→ dsp^3)
→ Diamagnetic
→ EAN = 26+10 = 36 e^-

for dsp^3 → d_{z^2} participate in hybridisation gives → T.B.
→ $d_{x^2-y^2}$ " " " " → square pyramidal

÷ $Ni(CO)_4$:-

$_{28}Ni$ = [Ar] $3d^8$ $4s^2$ = [↑↓|↑↓|↑↓|↑|↑] [↑↓] [| |]

In $[Ni(CO)_4]$ = [↑↓|↑↓|↑↓|↑↓|↑↓] [××] [××|××|××]



* Tetrahedral
* sp^3
* Diamagnetic
* EAN = 28+8 = 36 = 18 e^- rule followed.

Note: Mond's process :-

$Ni + 4CO \longrightarrow Ni(CO)_4 \xrightarrow{\Delta} Ni$ (Pure)
(Impure)

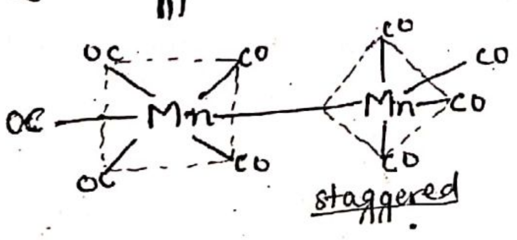
÷ Poly nuclear Metal Cluster :-

① $Mn_2(CO)_{10}$ (Dimangnese Decarbonyl) :
or $Tc(CO)_{10}$ or $Re_2(CO)_{10}$

$Mn(CO)_5 \xrightarrow{+e^-} [Mn(CO)_5]^-$
7+10 = 17 e^-
$\xrightarrow{\cdot H}$ $[HMn(CO)_5]^*$
$\xrightarrow{\cdot CH_3}$ $[CH_3Mn(CO)_5]$
$\xrightarrow{\cdot Br}$ $[BrMn(CO)_5]$
} all obey 18 e^- & EAN

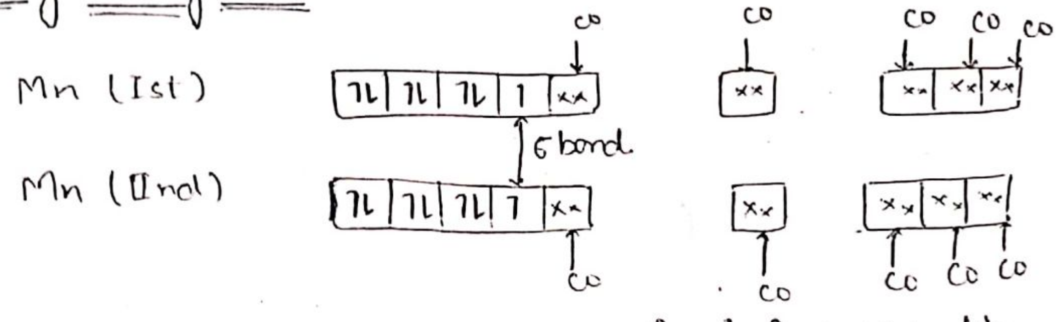
↓ $Mn(CO)_5$

$Mn_2(CO)_{10}$
$[(CO)_5Mn - Mn(CO)_5]$



* Each Mn → 5 terminal CO gp.
* No Bridging ligand
* One Mn-Mn bond.
* e^- count = 10+7+1 = 18 e^-

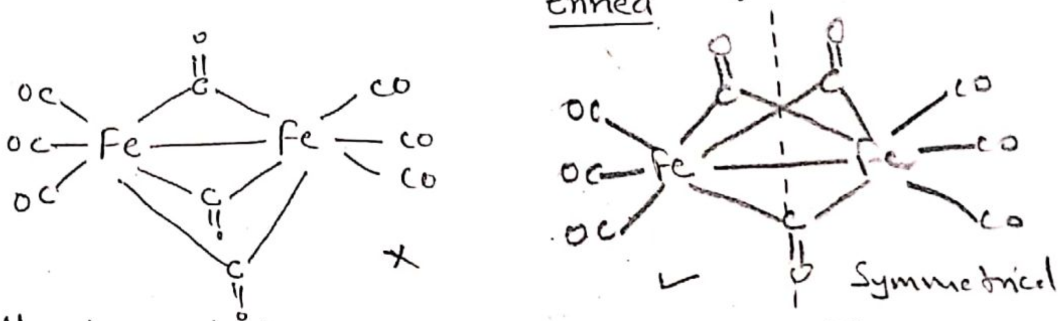
Bonding Diagram :-



d^2sp^3 hybridisation

Fe$_2$(CO)$_9$:- (Diiron Nona carbonyl)

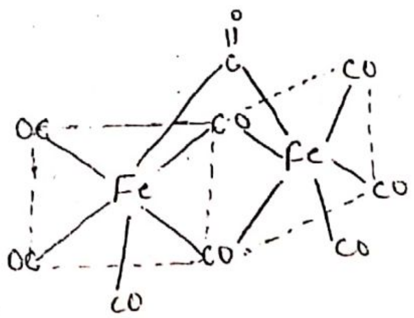
ennea



* Both iron linked with 3-terminal CO.

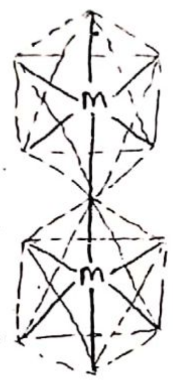
* Both iron linked with 3-doubly bridging CO.

* On Fe - Fe bond

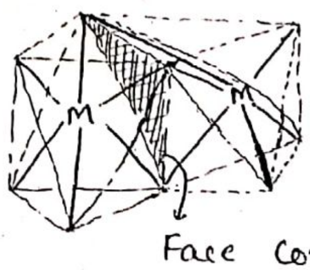


→ sharing of two octahedr may be

modes :- (i)



(iii).



Face Common

[Fe$_2$(CO)$_9$]

(ii)