Bhawana Saklani / Quantum girl

Genesis Tutorials

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Organometallic

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OMC

* Unit - I →

18 valence electron rule -

* VSE * Ligand contribution * Hapto Number. * oxidation state * Formal charge * 18 e^- VS 16 e^- * TVE * Bonds per metal atom * M-M bonds.

* TVE = VSE of free metal + contribution by the ligand ± charge.

3	4	5	6	7	8	9			
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Ni	Mo	Tc	Ru	Rh	Pd		

* 18 valence e^- rule

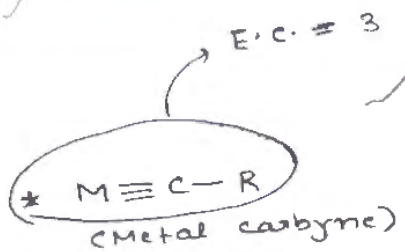
* The requirement for 18 e^-, comes from the need to fill one s orbital, 3P orbital & 5d orbitals with two e^-s in each.

* 18 e^- rule is applicable for transition element only, it is not applicable for main groups, Lanthanoides & Actinides.

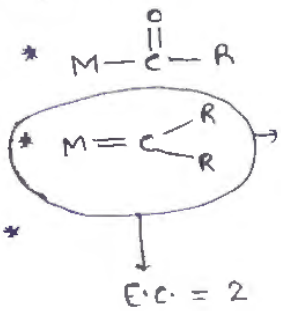
(follows octet rule instead of 18 e^-)

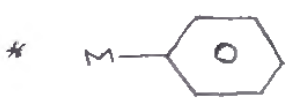
Hapto number → (η) →

① Monohapto ligand (η^1) →

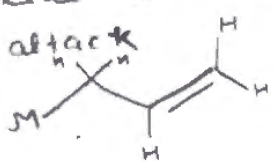


e.g. * M—R



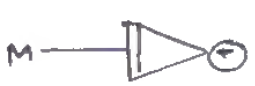


Means metal is directly attack kitne carbon

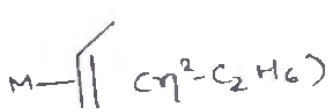


η^1-C_3H_5

(II) → Dihapto → (η^2)

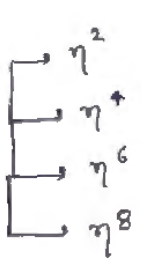


(η^2-C_2H_4)



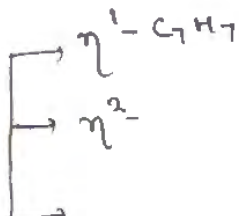
Imp →

Best fluoxinol ligand



can show different kind of hepaticity.

*



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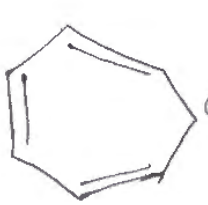
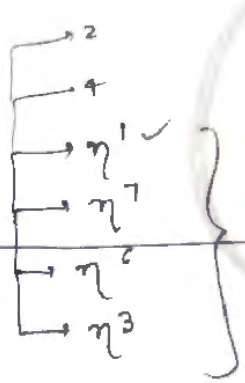




	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	Sc (21)	Ti (22)	V (23)	Cr (24)	Mn (25)	Fe (26)	Co (27)	Ni (28)	Cu (29)	Zn (30)
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

e.g:→ (i) $[\overset{I}{Rh}(PPh_3)_3Cl]$ → Wilkinson's catalyst. (Ro, Pc)

(ii) $[\overset{II}{Pt}Cl_3(\eta^2-C_2H_4)]^-$ → Zeise's salt. (Ptarchlan $\eta^2-C_2H_4$ zeiss vaska h)

(iii) $[\overset{I}{Ir}(CO)(Cl)(PPh_3)_2]$ → vaska's complex

CO
Rh
Ir

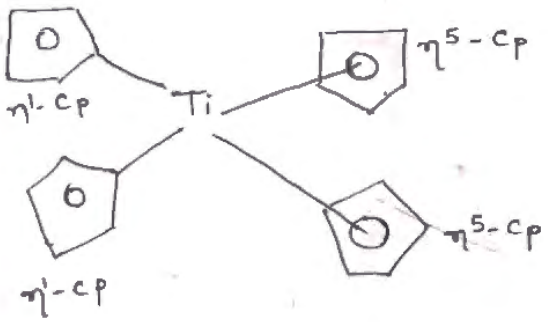
Ir CO Cl peran vaska

(iv) $[Ti(CP)_4]$

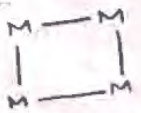
(v) $[Co(CO)_3]^-$ → 16

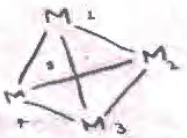
(vi) $[Rh(CO)_2I_2]^-K^+$

(vii) $[PtCl_3(C_2H_4)]^-$

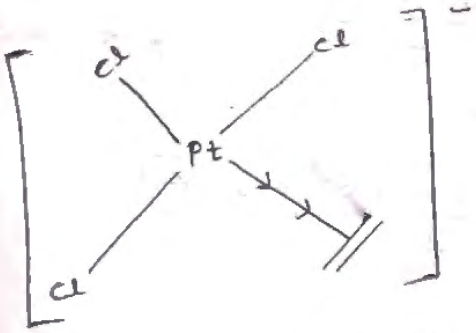


- M-M = 3, M = 3 } Triangle ⇒ 

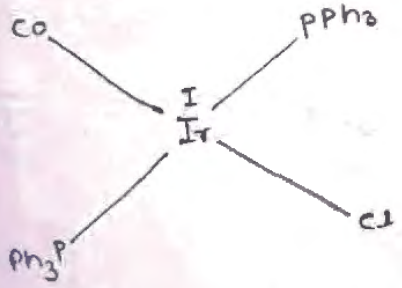
- M-M = 4, M = 4 

- M-M = 6, M = 4 

- B/M = 3



- All Pt-Cl, bond length, not equal.



$Ir_4(CO)_{12}$

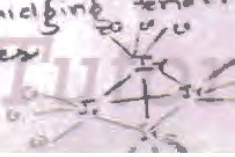
M-M = $\frac{18\times4 - (36+24)}{2}$

= $\frac{72-60}{2Rh} = \frac{12}{2} = 6$

B/M = $18 - \frac{TVE}{n}$

$18 - \frac{60}{4}$ 18 − 15 = 3

on moving down, bridging tendency decreases



* Total metal-metal bonds

$$\frac{18n - TVE}{2}$$

* Bonds per metal atom

$$18 - \frac{TVE}{n}$$

---

* Total metal-metal bonds

$$\frac{16n - TVE}{2}$$

* Bonds per metal atom

$$16 - \frac{TVE}{n}$$

---

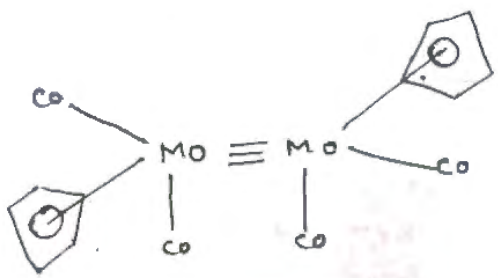
16 e^- rule:→

Out of 9 orbitals, energy of one orbitals becomes higher, thats why remains vacant.

* Co-ordination NO = 4
* Square planar. (⇒ (C.N. can be increased, ∵ two axial positions vacant.
  - dsp^2
  - $d^n \longrightarrow d^8$
  - Metals involved
    - $Ni^{II}, Pd^{II}, Pt^{II} \longrightarrow d^8$ (28, 10)
    - $Co^{I}, Rh^{I}, Ir^{I} \longrightarrow d^8$ (9)
    - Ti, Zr - don't follow d^8 (22, 4)

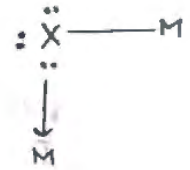
e.g. Most probably catalyst.

$[Cp^5$



Halide → Terminal = 1 e^- donar

Halide → Bridge = 3 e^- donar



$[\overset{0}{Ir}_4(CO)_{12}]$ As Ir is zero, so follows 18 e^- rule.

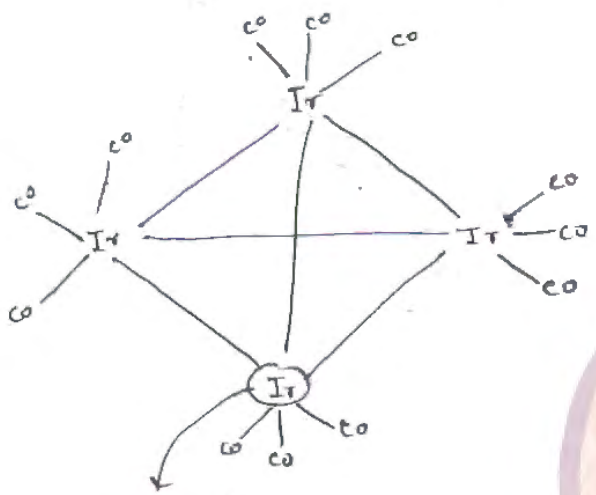
$$\frac{18 - TVE}{2} = \frac{18 - (36 + 24)}{2} = \frac{72 - 60}{2} = \frac{12}{2} = 6$$

(36, 24 — 8)

(Ir)

$$B/M = 18 - \frac{TVE}{n} = 18 - \frac{60}{4} = 3$$

(15)



$Ir = 9$

$B/M = 3$

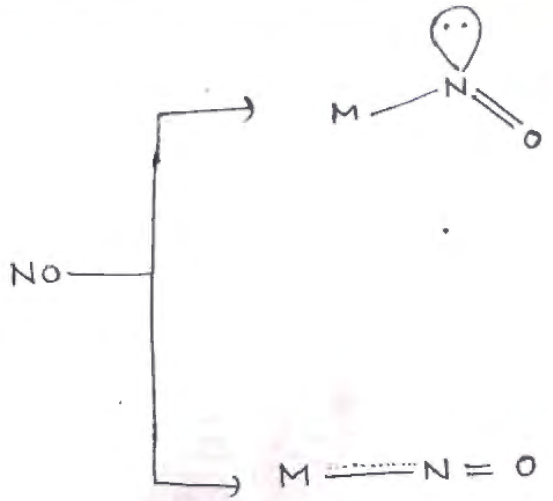
$3 \times CO = 6$

18

Co

Rh

Ir



→ formal charge = −1 = 1e⁻ donar

→ formal charge +1 = 3e⁻ donor

(5) → $(\eta^5\text{-}Cp)_2\,Fe$

(a) $(\eta^5\text{-}Cp)$ — Fe

B → NO → 5+8+1 = 14

L → NO → 5+8+3 = 16

(b) $(\eta^5\text{-}Cp)_2\,Co\,Cl$

B → NO = 5+9+1+1 = 16

L → NO = 18
3

Fe Co Ni Cu Zn
26 27 28 29 30

(c) → $(\eta^5\text{-}Cp)\,Ni$

B → 5+1+10 = 16

L → 18

$\eta^5\text{-}Cp\;Ni(NO)^{Bent}$

$x + (-1) - 1 = 0$

$x - 2 = 0$

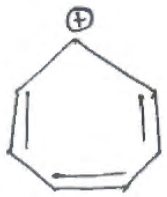
$x = 2$

(d) $(\eta^5\text{-}Cp)_2\,Co$

B → 5+10

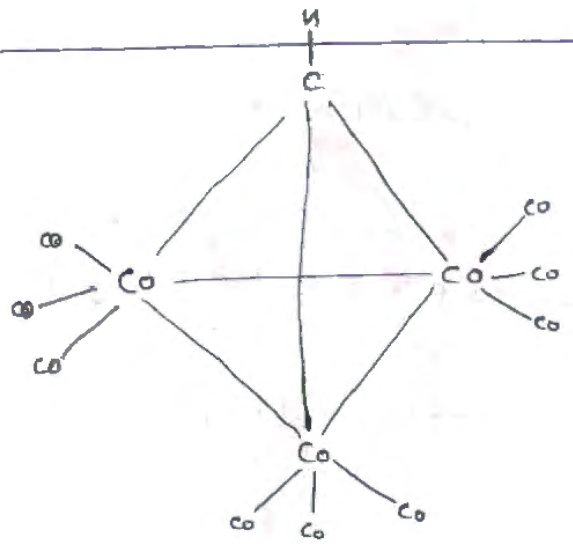
L →

(8) →



	contribution
CH_4	0
CH_3	1

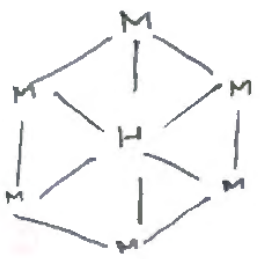
(7)



Co = 9
3TCO = 6
B/M = 2
μ-CH = 1
18

Extended formula = $[Co_3(\mu_3\text{-}CH)(CO)_9]$

$(\mu_6\text{-}H)$



(12) → $[(\eta^x - C_6H_6)\ Ru\ (\eta^y - C_6H_6)]$

↓

8 + 6

Limitations of 18 e⁻ rule : →

→ * $M \leq 4$ → Borderline e.g. $Fe_4CP_4(CO)_4$

→ * $M > 4$ → XXX

↓

$[\eta^5\text{-}Cp \quad T\text{-}Co \quad \mu\text{-}CO]$

↳ * Not applicable on lanthanoids & Actinoids.

* Ligand → Total M-M bonds ⟶ B/M → skeleton

if M-M = 3, M = 3 } Triangle

if M-M = 4/6, M = 4 } Tetrahedron

if M-M = 4, M = 2 } M≡M

Ligand Distribution

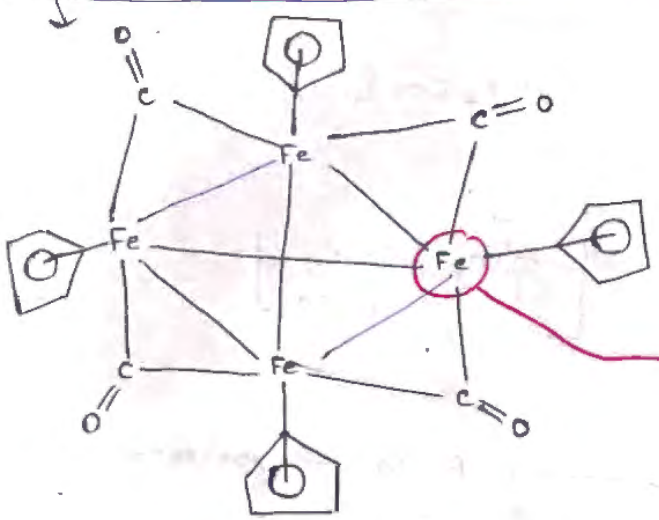
- even
- odd
  - ↓
  - Bridging
  - ↓
  - $Fe_2(CO)_9$

$[Fe_4 Cp_4 (CO)_4]$

M-M bond = $\frac{18\times4 - (8\times4 + 5\times4 + 2\times4)}{2}$

$= \frac{72-60}{2} = \frac{12}{2} = 6$

B/M = 3



Fe = 8

η^5-C_p = 5

B/M = 3

$2\mu_2$ CO $1\times2 = 2$

18

3d - Fe
4d Ru
5d Os

extended structure

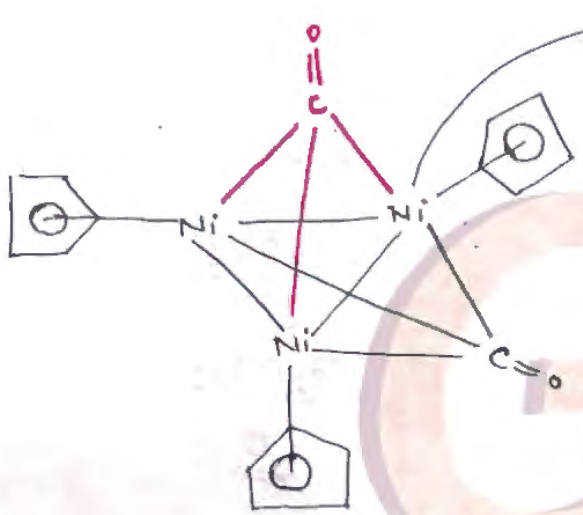
$[Fe_4 (\eta^5\text{-}C_5H_5)_4 (\mu\text{-}CO)_4]$

$[Ni_3 CP_3 (CO)_2]$

M-M bond = $\frac{18\times3 - \ell}{2}$

Ni - Ni = 3

Ni
Pd
Pt



$_{28}Ni$ = 10

η^5-Cp = 5

B/M = 2

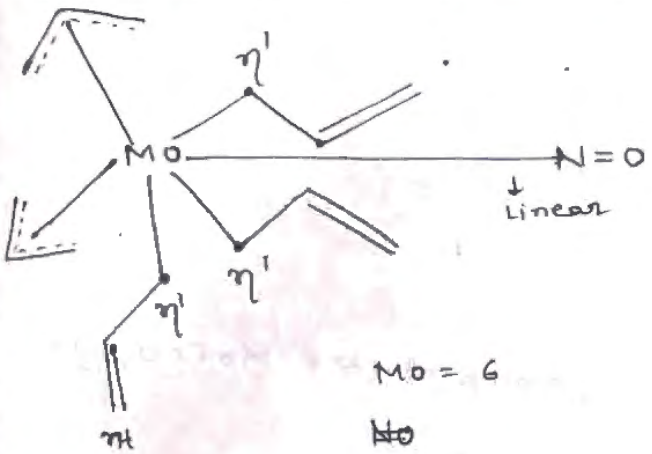
$2\mu_3$-CO = $\frac{2}{3}\times2 = \frac{4}{3}$

$1\frac{1}{3}$

$18\frac{1}{3}$

$[Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3]$

* (14) → $[Mo(\eta^1\text{-allyl})_3(\eta^3\text{-allyl})_2NO]$



Cr
Mo
W

Mo = 6

~~No~~

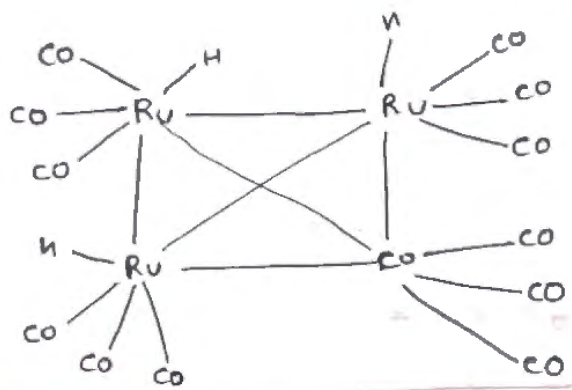
3 η^1 allyl = 3

2 η^3 allyl = 6

linear NO = 3

18

(10) →



(24) → (b) $[R\,Co(CO)_4] \Rightarrow x + (-1) + (4 \times 0) = 0$

R, CO

$x = +1$

(c) $Na^+[Co_4(CO)_{12}]^-$

$-\frac{1}{4}$

(d) $Na[Co(CO)_4]$

$Na^+[Co(CO)_4]^-$

$3d^7$

Fe Co Ni Cu Zn

$_{26}$ $_{27}$

(27) →

$x + (+1) + (5 \times -1) = -2$

~~$x + 1 + x + -5 = -2$~~

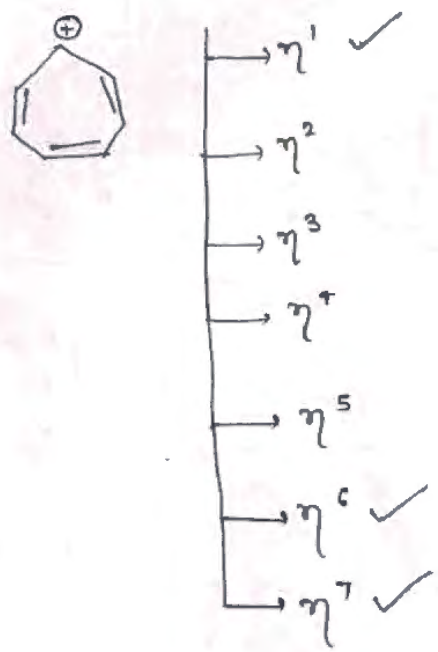
$x + 1 - 5 = -2.$

$x - 4 = -2$

$x = -2 + 4$

$x = 2$

(19) →



[Cycloheptatriene, $Mo(CO_3)$]

Mo = 6

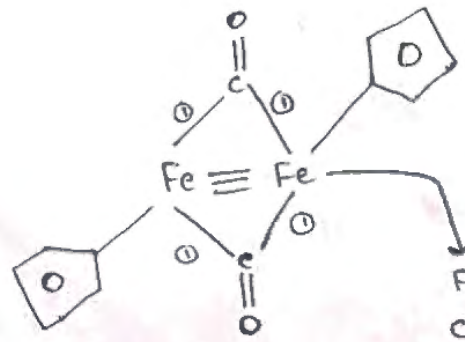
Co = 6

12

(30) →

$M - M = \frac{18 \times 2 - (10 + 16 + 4)}{2}$

$= \frac{36 - (30)}{2} = (3)$



Fe = 8

Cp = 5

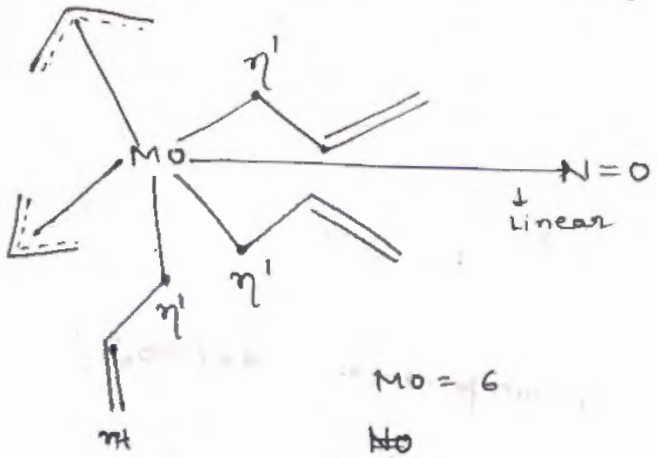
B/M = 3

$2\mu_2\text{-}CO = 2$

18

*

(14) → $[Mo(\eta^1\text{-allyl})_3(\eta^3\text{-allyl})_2NO]$



Cr
Mo
W

Mo = 6

~~No~~

3 η^1 allyl = 3

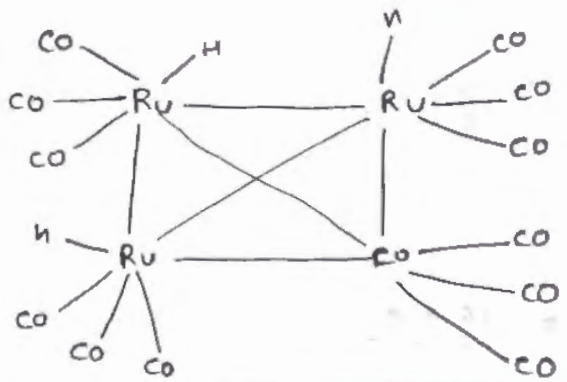
2 η^3 allyl = 6

linear NO = 3

18

---

(10) →



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(24) → (b) $[R\,Co(CO)_4] \Rightarrow x + (-1) + (4 \times 0) = 0$

R, CO

$x = +1$

(c) $Na^+[Co_4(CO)_{12}]^-$

$-1/4$

(d) $Na[Co(CO)_4]$

$Na^+[Co(CO)_4]^-$

3d⁷

Fe Co Ni Cu Zn

26 27

(27) →

$x + (+1) + (5 \times -1) = -2$

~~$x + + \quad x + -5 = -2$~~

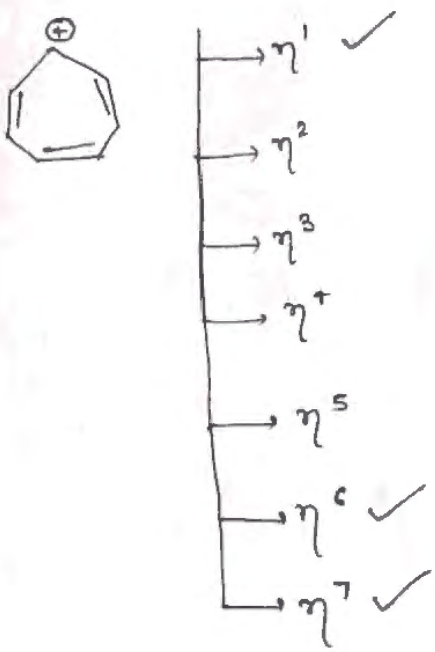
$x + 1 - 5 = -2$

$x - 4 = -2$

$x = -2 + 4$

$x = 2$

(19) →



[Cycloheptatriene, $Mo(CO_3)$]

Mo = 6

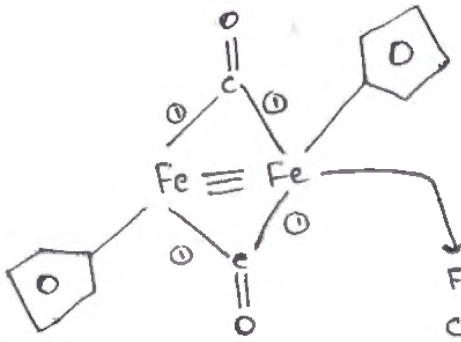
CO = 6

12

(30) →

$M - M = \dfrac{18 \times 2 - (10 + 16 + 4)}{2}$

$= \dfrac{36 - (30)}{2} = (3)$



Fe = 8

Cp = 5

B/M = 3

$2\mu_2 - CO = 2$

18

(a) $[(C_5H_5)W(CO)_3]^-Na^+$ ①, $[(C_5H_5)W(CO)_3H]$ ⑨

$5+6+6+1 = 18$ ✓ ; 18

(32) →

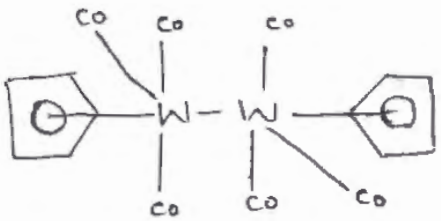
(a) → $[(C_5H_5)W(CO)_3]_2$ [

$$M-M = \frac{18n - TVE}{2}$$

$$= \frac{36-(10+12+12)}{2}$$

$$= \frac{36-34}{2}$$

$$= 1$$



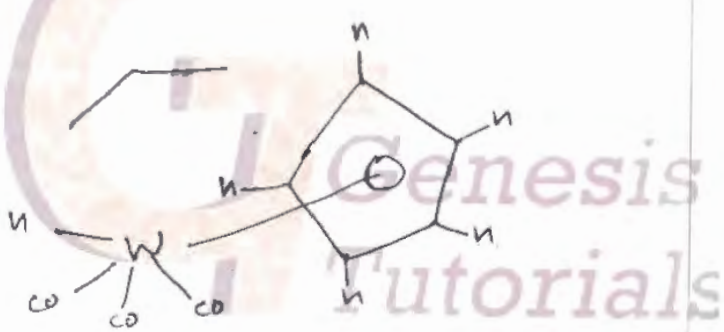
$W(CO)_6 \xrightarrow[(Cp^-Na^+)]{C_5H_5Na} M \xrightarrow{CH_3COOH} N$

M: $[W(CO)_3(Cp)]^-Na^+$ (18)

N: $[W(CO)_3(Cp)H]$ (18)

N: ↓ (5:1) ^{1}HNMR

$N \xrightarrow[-H_2]{\Delta} O \xrightarrow{Br_2} P$



$$[W(CP)(CO)_3H]_2 \xrightarrow[-H_2]{\Delta} [W(CO)_3(CP)]_2$$

O

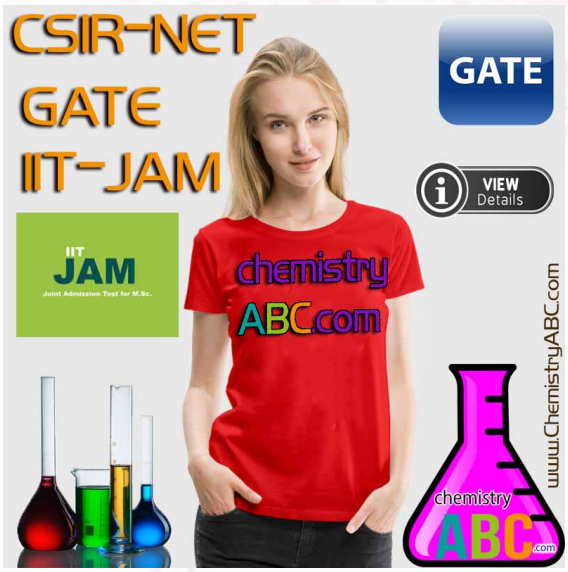
↓ yha M-M bond break kiya hai

$$2[W(CO)_3CP]^-$$

↓ $Br-Br$

$$2[W(CO)_3CP\,Br]$$

(P)

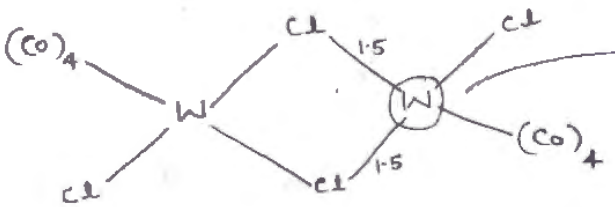


(36) → $[Ti(CP)_4]$

- η^5-CP
- η^5-CP
- η^1-CP
- η^1-CP

(38) → $[W(\mu_2\text{-}Cl)\,Cl\,(CO)_4]_2$

$$M\text{-}M = \frac{18n - TVE}{2} = \frac{36 - (12+6+2+16)}{2} = \frac{36-36}{2} = 0$$



W = 6

$2\mu_2\text{-}Cl = 1.5 \times 2 = 3$

$4\,T\,CO = 8$

$1\,T\,Cl = 1$

18

Mn Fe Co Ni Cu Zn
25 26 27 28 29 30

---

(1) →

(a) $Na_2Fe(CO)_n = 2Na^+[Fe(CO)_n]^{(b)}$

$+2+8+2n = 18$

$10+2n = 18$

$2n = 8$

$n = 4$

$MnBr(CO)_n$

$7+1+2n = 18$

$8+2n = 18$

$2n = 10$

$n = 5$

Ionic →

$x + (0 \times n) = -2$

$x = -2$

$Fe^{-2} = 10\,e^-$

(c) $W(\eta^6\text{-}C_6H_6)(CO)_n$

$6+6+2n = 18$

$12+2n = 18$

$2n = 6$

$n = \frac{6}{2} = 3$

Ionic

$x + 0 + 0 = 0$

$W^0 = 6$

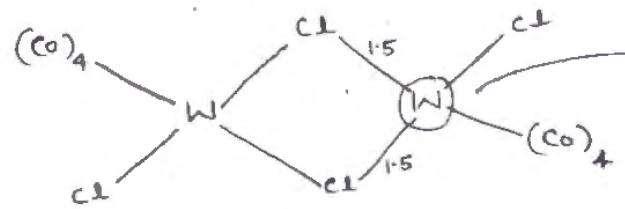
$\eta^6\text{-}C_6H_6 = 6$

$2n = 6$

$n = 3$

(38) → $[W(\mu_2\text{-}Cl)\,Cl\,(CO)_4]_2$

$$M\text{-}M = \frac{18n - TVE}{2} = \frac{36 - (12+6+2+16)}{2} = \frac{36-36}{2} = 0$$



W = 6

$2\mu_2\text{-}Cl = 1.5 \times 2 = 3$

$4 T CO = 8$

$1 T Cl = 1$

18

Mn 25 Fe 26 Co 27 Ni 28 Cu 29 Zn 30

---

(1) →

(a) $Na_2 Fe(CO)_n = 2Na^+[Fe(CO)_n](b)$.

$12 + 8 + 2n = 18$

$10 + 2n = 18$

$2n = 8$

$n = 4$

Ionic →

$x + (0 \times n) = -2$

$x = -2$

$Fe^{-} = 10\ e^-$

$MnBr(CO)n$

$7 + 1 + 2n = 18$

$8 + 2n = 18$

$2n = 10$

$n = 5$

(c) $W(\eta^6\text{-}C_6H_6)(CO)_n$

$6 + 6 + 2n = 18$

$12 + 2n = 18$

$2n = 6$

$n = \frac{6}{2} = 3$

Ionic

$x + 0 + 0 = 0$

$W^0 = 6$

$\eta^6\text{-}C_6H_6 = 6$

$2n = 6$

$n = 3$

(d) → $Rh(\eta^5-C_5H_5)(CO)_n$

$9+5+2n=18$

$2n=4 \Rightarrow n=2$

(e) $Cr(\eta^3-C_5H_5)(CO)_n(CH_3)$

$6+3+2n+1$

$2n+10=18$

$2n=8$

$n=4$

Ionic

$x+(-1)+(2n\times0)+(-1)=0$

$x-1-1=0$

$x-2=0$

$x=2$

$Cr^{++} \rightarrow 6-2=4$

$CH_3^- \rightarrow 1+1=2$

$\eta^3-C_p^- \rightarrow 3+1=4$

10

(b) $Mn\,Br\,(CO)_n$

Ionic →

We need O.S. of Mn

Let it be x

$x+(-1)+(2n\times0)=0$

$x-1=0$

$x=1$

$Mn^+ = 7-1=6$

$Br^- = 1+1=2$

$(CO)_n = 10$

$(CO)_5 = 10$

$n=5$

(f) → $Ir\,Br_2(CO)_n(PPh_3)_2(CH_3)$

$9 + (-2) + 2n + 2\times2 + 1$

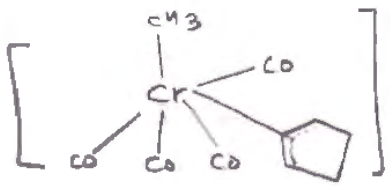
$9 - 2 + 2n + 4 + 1$

$2n + 12 = 18$

$2n = 6$

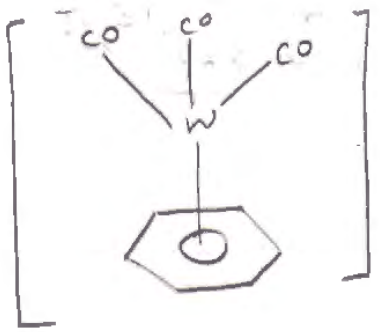
$n = 3$

(e) →



$(\eta^3\text{-cp})$

(c)



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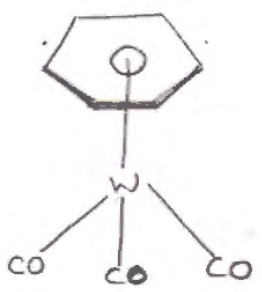


η^6

(2) → (a) $[Pt(NH_3)_4]^{2+}$

e⁻ count =

$10 + 8 - 2 = 16\ e^-$

formal charge $x + (4 \times 0) = +2$

$x = +2$

$Pt^{+2} = 10 - 2 = 8$

d^8

$[Pt\,Cl_2(NH_3)_2]$

Covalent

$10 + 2 + 4$

$= 16$

Ionic

$x + (-1 \times 2) + 2 \times 0 = 0$

$x - 2 = 0$

$x = 2$

$Pt^{++} = 10 - 2 = 8 = d^8$

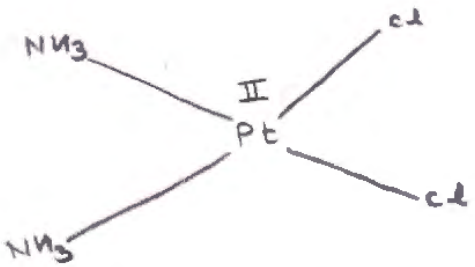
$2Cl^- \longrightarrow 1 + 1 = 2 \times 2 = 4$

$2NH_3 \rightarrow 2 \times 2 = 4$

16

$\Rightarrow$ C.No = 4.

$\Rightarrow$ d^8



(c) $[PtCl_4]^{2-}$

Ionic

$x + (-1 \times 4) = -2$

$x - 4 = -2$

$x = -2 + 4$

$x = 2$

$Pt^{++} = 10 - 2 = 8 \rightarrow d^8$

$4Cl^- = 4 \times 2 = 8$

16

covalent

$10 + 4 + 2 = 16$

(d) $(\eta^5\text{-}\ C_5H_5)_2\ Ni$

5^- Cp^- = 6

10 Ni^{++} = 8

5 Cp^- = 6

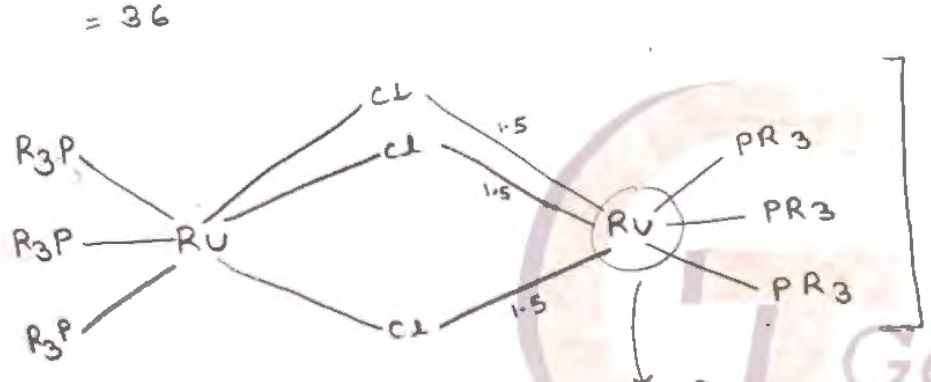
20

(e) $[(R_3P)_3Ru(\mu\text{-}Cl)_3\ Ru(PR_3)_3]^+$

$3 \times 2 + 8 + 3 \times 3 + 8 + 3 \times 2 - 1 =$

$6 + 8 + 9 + 8 + 6 - 1$

$= 36$



Ru = 8

$PR_3 = 3 \times 2$

$3\mu_2\text{-}Cl = 4.5 - 0.5 = 4$

18

Ionic

$2x + (6 \times 0) + (-1 \times 3) = 1$

(PR_3, Cl)

$2x + 0 - 3 = 1$

$2x = 1 + 3$

$2x = 4$

$x = 2$

Ru

$Ru^{++} = 8 - 2 = 6e^-$

$3 : PR_3 = 3 \times 2 = 6e^-$

$3\ \mu_2\text{-}Cl^- = 3 - 1 = 4$ so $50\% = 2$

so $3 \times 2 = 6$

18

(f) → $[Re\ Hg]^{2-}$ $3d^5\ 4s^2$

covalent

$7 + 9 + 2$

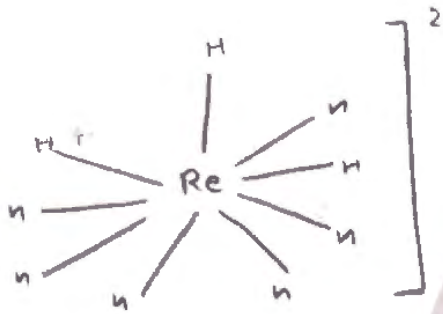
$= 18$

$x - 9 = -2$

$x = -2 + 9 = 7$

$H \rightarrow H^- = 1 + 1 = 2 \times 9 = 18$

d^0



(g) → Cp Ir Me_4

$5 + 9 + 4 = 18$

Ionic

$x - 1 - 1 \times 4$

$x - 1 - 4$

$x - 5$ $\quad x = +5$

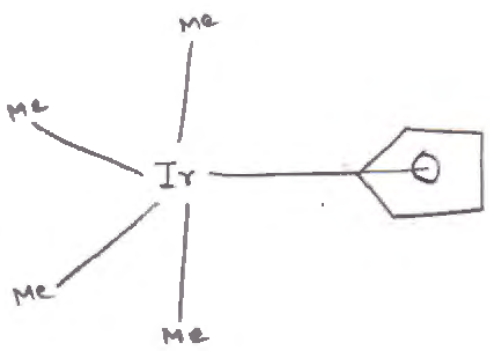
d^4

Ir^{+5} $\quad 9 - 5 = 4$

Cp^{-1} $\quad 5 + 1 = 6$

$4Me$ $\quad 1 + 1 = 2 \times 4 = 8$

18



(h) Ta Me_5 $\quad 2s^2 3p^3 4s^2$

covalent: →

$5 + 5$

$= 10$

Ionic method: →

$x + (-1 \times 5) = 0$

$x - 5 = 0$

$x = 5$

$Ta^{5+} = 5 - 5 = 0 = d^0$

$5\,Me^- = 1 + 1 = 2 \times 5 = 10$

(j) → $[Mc\,Re(O)_3]$

(I) $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$

$x + (-1 \times 2) + (-1 \times 2) = 0$

$x - 2 - 2 = 0$

$x = 4$

$Ti^{4+} \longrightarrow 4 - 4 = 0 = d^0$

$2\,Cp^- \longrightarrow 5+1 = 6e^- = 12e^-$

$2\,Cl^- \longrightarrow 1+1 \times 2 = 4e^-$

$16e^-$

③ → water will donate 1 pair

$[Ir\,H_2(PPh_3)_2(OH_2)_2]^+$

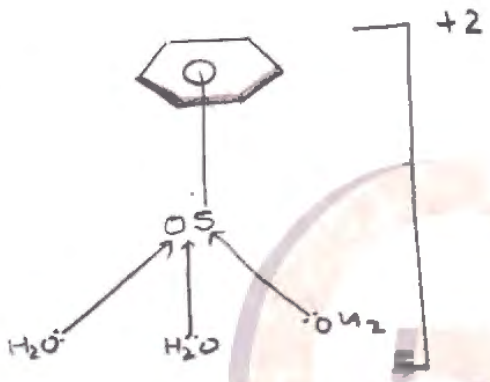
$9 + 2 + 2 \times 2 - 1 + 4$

$= 18$

$[Os(\eta^6\text{-}C_6H_6)(OH_2)_3]^{2+}$

$8 + 6 + 6 - 2 = 18$

Bengene
↓
6π e⁻ donor
3π bond donor



④ → (i) → $[Cp\ Co\ (CO)]_2\ (\mu\text{-}CO)$

$$2x + (-1) \times 2 + 2 \times 0 + (0) = 0$$

(-1 ↓ Cp; 2×0 ↓ T-CO; (0) ↓ μ-CO)

$$2x - 2 + 0 + 0 = 0$$

$$2x = 2$$

$$\boxed{x = 1}$$

$Co^{+} \longrightarrow 9 - 1 = 8e^{-} \rightarrow d^8$

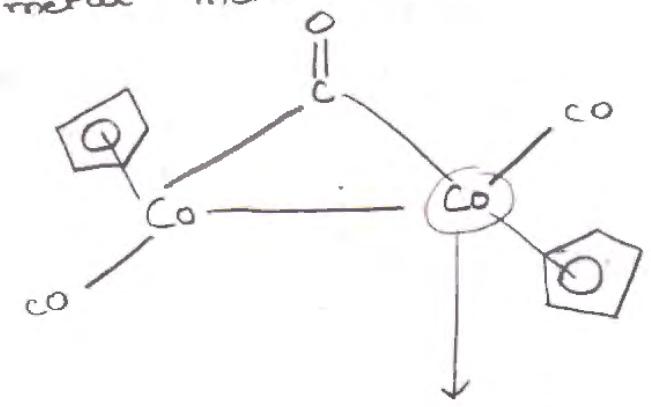
$Cp^{-} \longrightarrow 5 + 1 = 6e^{-}$

$CO \longrightarrow 2 = 2e^{-}$

$\mu\text{-}CO \rightarrow 1 = 1$

$17\ e^{-}$

Total metal metal bond =



$Co = 9$

$\eta^5 - Cp = 5$

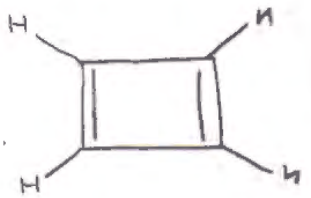
$1\ \mu_2 - Co = 1$

$B/M = 1$

$T\ CO = 2$

18

(ii) → (cyclo C_4H_4) $PdCl_2$



$x + (-2) + (-1 \times 2) = 0$

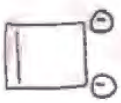
$x - 2 - 2 = 0$

$x - 4 = 0$

$x = +4$

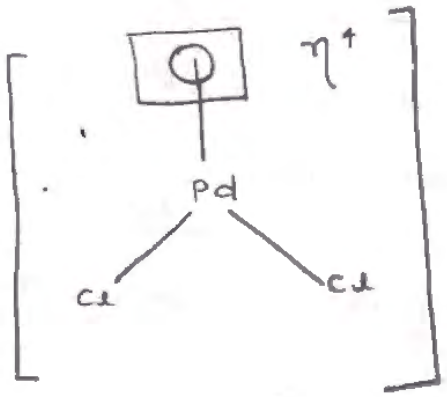
Anti-aromatic

$Pd^{+4} \rightarrow 10 - 4 = 6\ e^-$

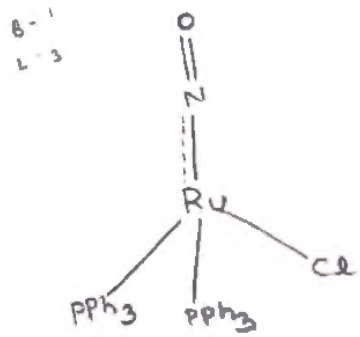
 $\rightarrow 4 + 2 = 6e^-$

$2Cl^- \rightarrow 2 \times 2 = 4e^-$

$16e^-$



(v) → $Ru(PPh_3)_2Cl(NO)$ (linear NO)



$x + (2 \times 0) + (-1) + (+1) = 0$

(PPh_3)

$x - 1 + 1 = 0$

$x = 0$

$2PPh_3 = 2 \times 2 \rightarrow 4$

$Ru^0 = 8 \longrightarrow d^8 = 8$

$Cl^- = 1 + 1 = 2$

$NO^+ = 3 - 1 = 2$

16

(4) → (i) → $[Cp\ Co\ (CO)]_2\ (\mu\text{-}CO)$

$$2x + (-1)\times 2 + 2\times 0 + (0) = 0$$

-1 → Cp; 2×0 → T-CO; (0) → μ-CO

$$2x - 2 + 0 + 0 = 0$$

$$2x = 2$$

$$\boxed{x = 1}$$

$Co^{+} \longrightarrow 9 - 1 = 8e^{-} \rightarrow d^{8}$

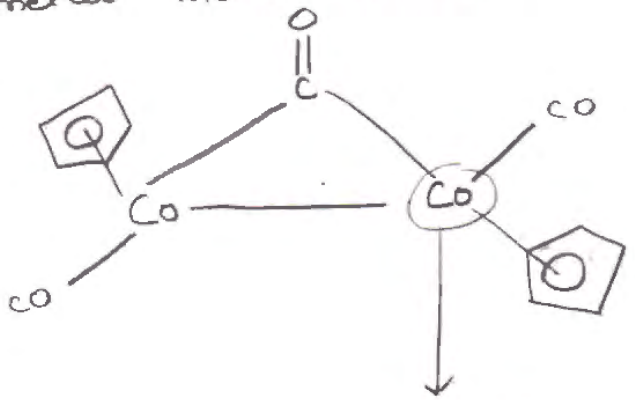
$Cp^{-} \longrightarrow 5 + 1 = 6e^{-}$

$CO \longrightarrow 2 = 2e^{-}$

$\mu\text{-}CO \rightarrow 1 = 1$

$17\ e^{-}$

Total metal metal bond =



$Co = 9$

$\eta^5 - Cp = 5$

$1\ \mu_2 - CO = 1$

$B/M = 1$

$T\ CO = 2$

18

(iv) → $[Cp\ Mo\ (CO)_3]^-$

$Y + (-1) + 3\times 0 = -1$

$Y - 1 = -1$

$Y = -1 + 1$

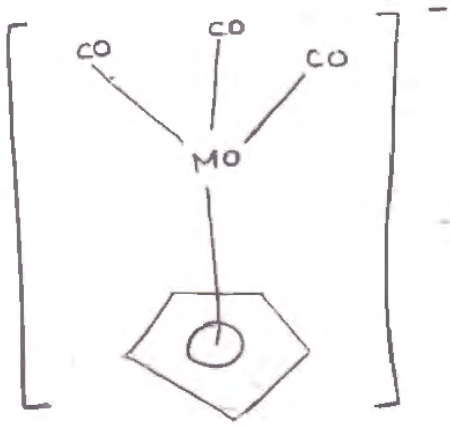
$Y = 0$

$Mo^0 = 6e^- \rightarrow d^6$

$Cp^- = 6e^-$

$3CO = 6e^-$

18



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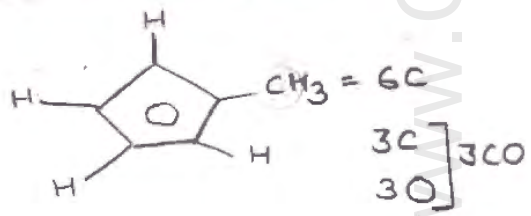
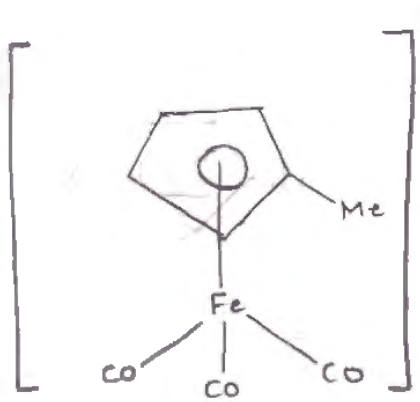
(5) → $Fe\ C_9\ H_7\ O_3\ Cl$



Fe

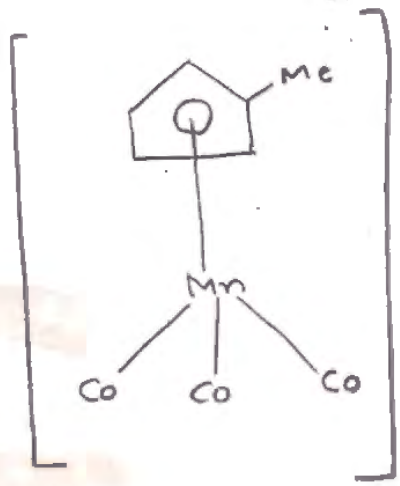


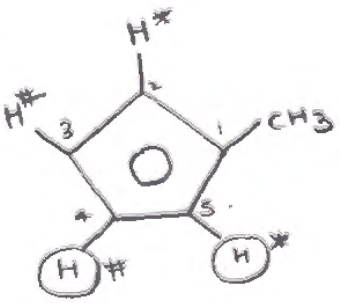
$Cl^{\ominus}$

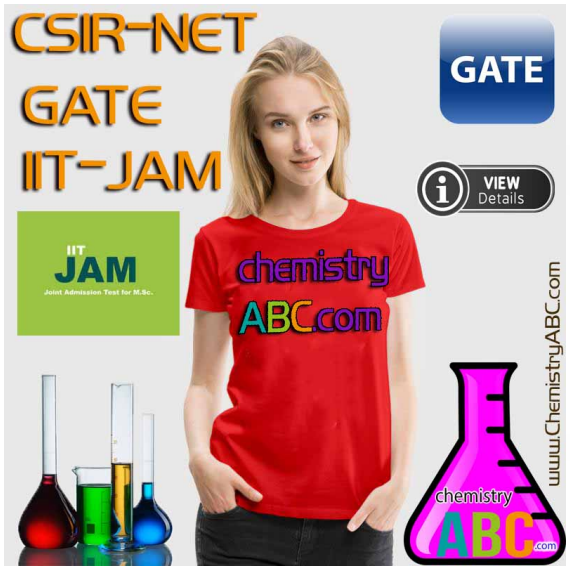
$Ag^{\oplus}$

$AgCl$

PPt







(c) → $\frac{18 - TVE}{2}$

$= \frac{2 \times 18 - 4 + 9 + 3 \times 2 + 9 + 4}{2}$

$= \frac{36 - 4 + 9 + 6 + 9 + 4}{2}$

$= \frac{36 - 32}{2} = \frac{4}{2} = 2$

B/M = $\frac{18 - TVE}{2} = \frac{18 - 32}{2}$

$= 2$

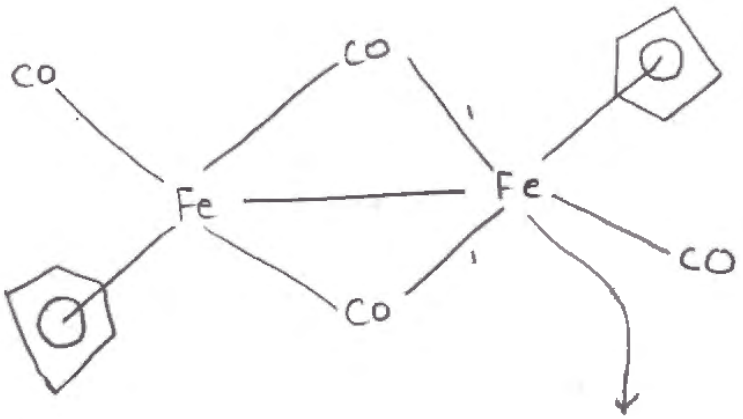
(b) → $(\eta^5 - C_5H_5)(CO)Fe(\mu\text{-}CO)_2Fe(CO)(\eta^5\text{-}C_5H_5)$

$= \frac{18 - TVE}{2}$

$= \frac{2 \times 18 - (5 + 2 + 8 + 4 + 8 + 2 + 5)}{2}$

$= \frac{36 - 34}{2} = \frac{2}{2} = 1$

$$B/M = 18 - \frac{34}{2} = 18 - 17 = 1$$



Fe = 8

1 T CO = 2

2 μ CO = 2

CP = 5

B/M = 1 −

18

---

(7) →

(a) $[CpW(CO)_x]_2$

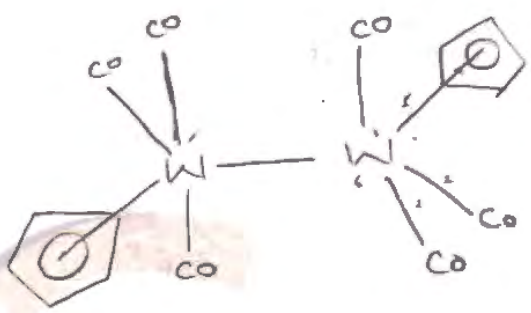
$5 + 6 + 1 + x = 18$

$12 + x = 18$

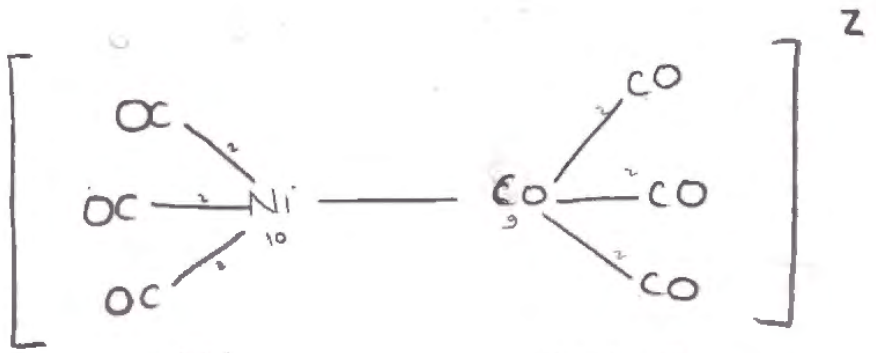
$12 + x = 18$

$x = 6$

$\Rightarrow x = 3$



(b) → $\left[(CO)_3 Ni - Co(CO)_3\right]^z$



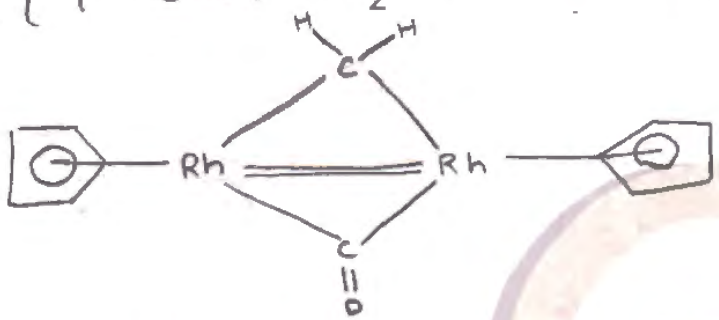
10+6+1 | 9+1+6

17 | =16

-1 | -2

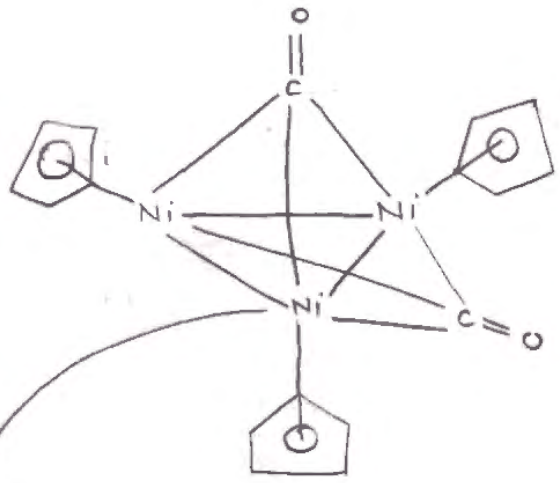
$\Rightarrow \quad z = -3$

Prob → $\left[\{\eta^5-C_5H_5)Rh\}_2 \ (\mu-CH_2)\ (\mu-CO)\right]$



M-M bond → (2)

7- (d) → $[(CP)_3Ni_3(\mu_3-CO)_2]^Z$



Ni = 10

Cp = 5

B/M = 2

μ_3-CO = $2/3 \times 2 = \frac{4}{3} = 1\frac{1}{3}$

$18\frac{1}{3}$

⇒ Z = +1

(e) → $[Cp\ M\ (CO)_3]_2$

$5 + x + 6 + 1$

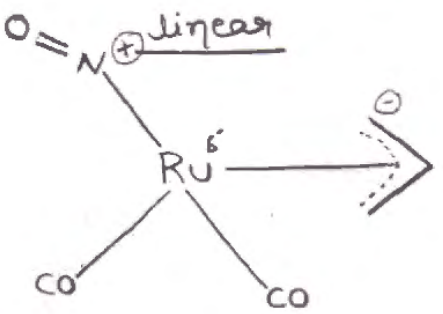
$12 + x$

⇒ $x = 6$

⇒ Cr metal

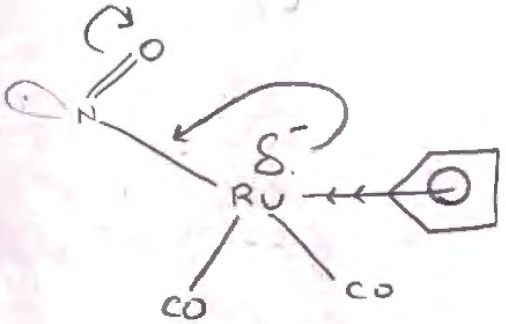
B.O. $\propto \frac{1}{B.l.}$

(8) (a) (η^3- allyl)



C_3

(b)



slow back donation
slow back bonding
→ shorter bond length

(a)

(b)

(b)- More e⁻ rich.

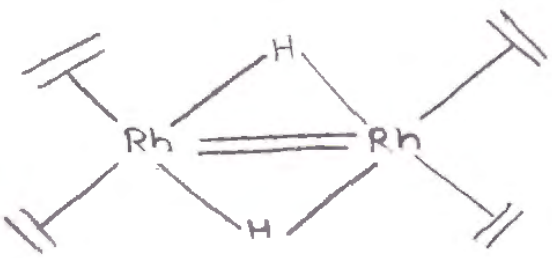
(9) (a) $\left[(\eta^2\text{- ethylene})_2\ Rh\ (\mu\text{-}H)\right]_2$

$$\frac{16 \times n - TVE}{2}$$

$$\frac{16 \times 2 - (4 + 9 + 1) \times 2}{2}$$

$$\frac{32 - 28}{2} = \frac{4}{2} = 2$$

$$B/M = 16 - \frac{TVE}{n} = 16 - \frac{28}{2} = 2$$



Rh = 9

$\eta^2 - C_2H_4 = 4$

B/M = 2

$2\mu - H = 1$

16

Let O.S = +z

$2z + (4 \times 0) + (-1 \times 2) = 0$

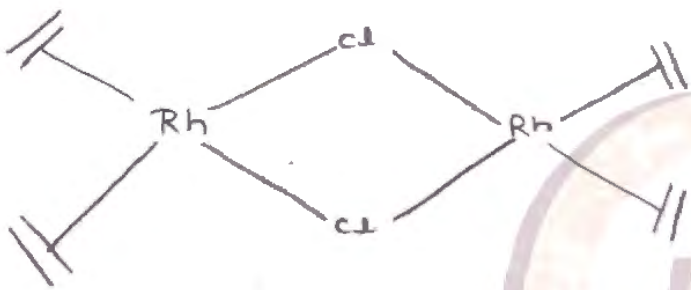
$2z + 0 - 2 = 0$

$2z - 2 = 0$

$2z = 2$

$\Rightarrow z = 1$

(b) → $[(\eta^2\text{- ethylene})_2\ Rh\ (\mu\text{-Cl})]_2$



$2x + 4 \times 0 + (-1 \times 2) = 0$

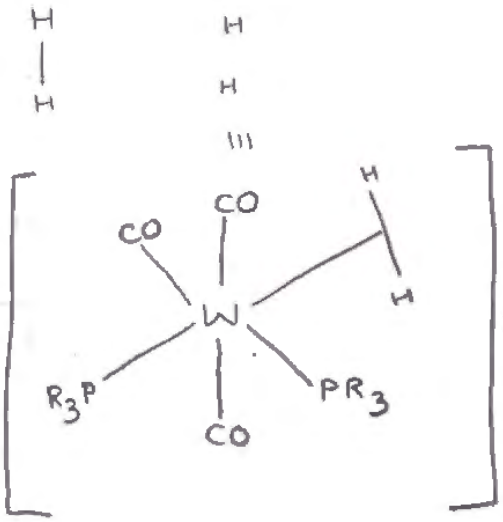
$2x - 2 = 0$

$2x = 2$

$\Rightarrow x = 1$

(10) → $W(\eta^2-H_2)(CO)_3(PR_3)_2 \rightleftharpoons WCH)_2CCO)_3(PR_3)_2$

H_2 vs. $(H)_2$



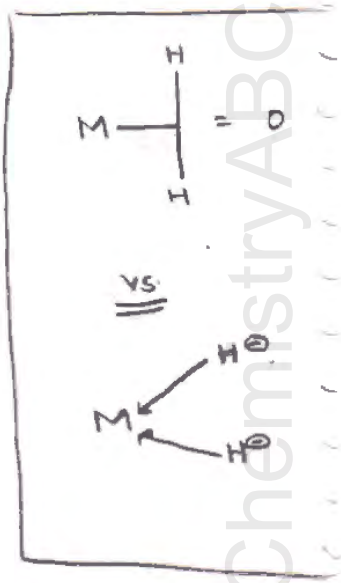
$W^0 = 6 \longrightarrow d^6$

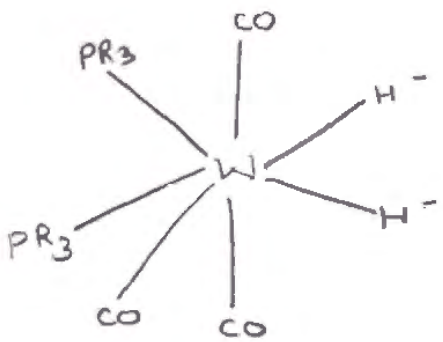
$3CO = 6$

$2PR_3 = 4$

$\eta^2-H_2 = 2$

18





$W^{++} = 4 \longrightarrow d^4$

$2H^- = 4$

$3CO = 6$

$2PR_3 = 4$

18

Ru = 8

(11) $[Ru_3(CO)_{10}(PPh_3)_2]$

M-M bond

$$\frac{x \times 18 - TVE}{2} = \frac{18 \times 3 - 8 \times 3 + 2 \times 10 + 4}{2}$$

54 - 24 + 20 + 4 = 54 - 48 = 6

$$\frac{54 - 24 + 20 + 4}{2} = \frac{54 - 48}{2} = \frac{6}{2} = 3$$

B/M = $18 - \frac{TVE}{n}$

$= 18 - \frac{48}{3}$

$18 - 16 = 2$

(12) → A = Ni, Pd, Pt

B = Co, Rh, Ir

C = Mn, Tc, Re

(a) →

(5)

(3)

(13) → $Cr(CO)_n(NO)_m$

$6 + 2n + 3m$

$n = 0$, $m = 4$ **n=0 m=4** ✓

$6 + 3\times4$

$= 18$

$n = 3$, $m = 2$ **n=3 m=2** ✓

$6 + 6 + 6 = 18$

(14) →

(a) $[\eta^5 - CpOs(CO)_x]_2$

$5 + 1 + 8 + 2x$

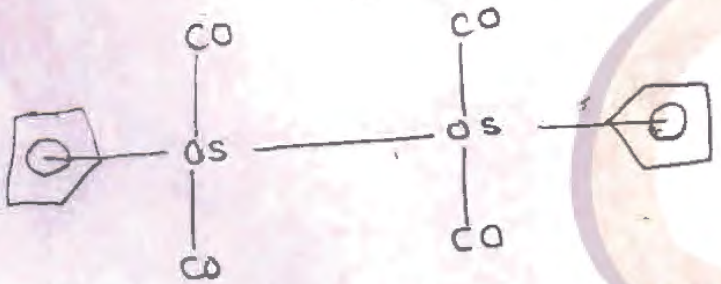
$14 + 2x$

$x = 2$

M-M- bond

$$\frac{18 - TVE}{2}, \quad \frac{2\times18 - (5 + 1 + 8 + 4)\times2}{2}$$

$$\frac{36 - 36}{2} = \frac{2}{2} = 1$$



* $[Fe(NO)_4]$

$8 + 3 \text{ linear}^{2-} + 1 \text{ Bent}^{2+}$

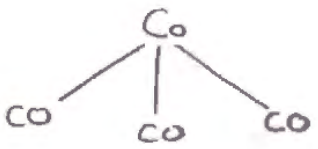
$8 + 9 + 1 = (18)$

(b) $[Co(CO)_3]^x$

$9 + 6 + x = 0$

$15 + x = 0$

$\Rightarrow x = 3$



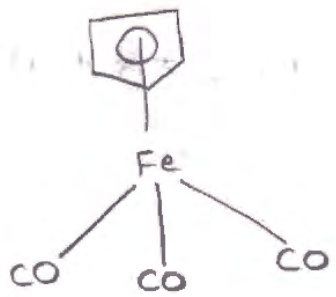
B - 1
L 3

(c) → $[\eta^5 - Cp\ Fe(CO)_3]^x$

$5 + 8 + 6 + x$

$19 + x$

$x = +1$

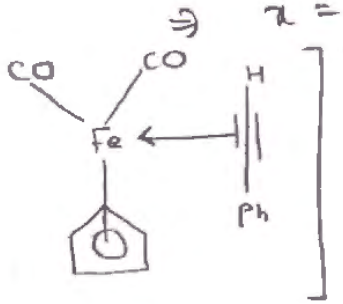


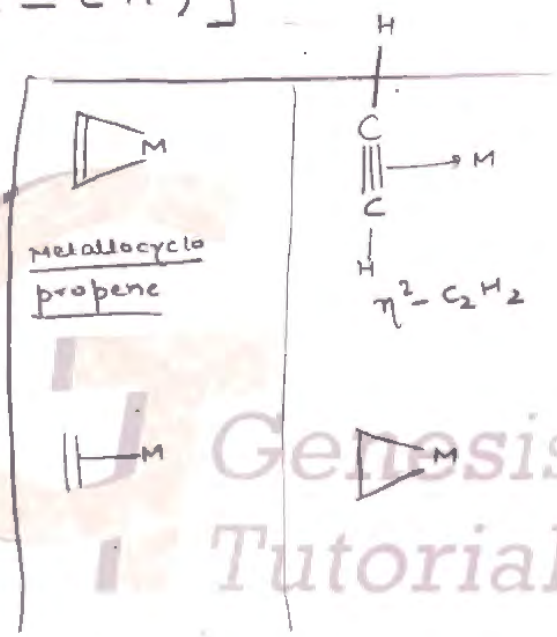
(f) → $[\eta^5 - Cp(CO)_2\ Fe(PhC \equiv CH)]^x$

$5 + 4 + 8 + 2$

19

$\Rightarrow x = +1$

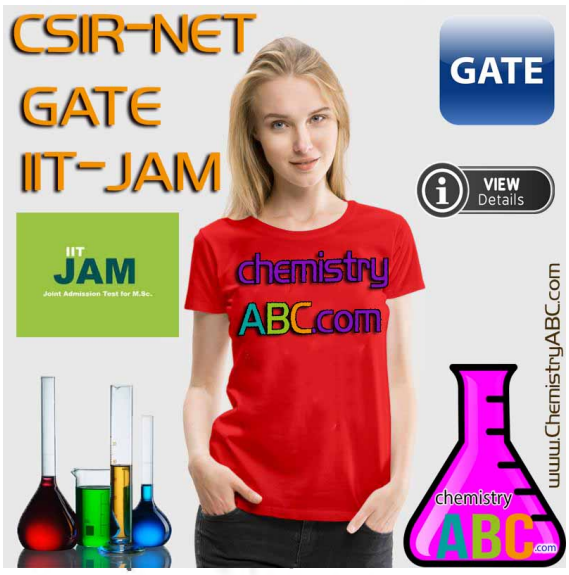




(15) →

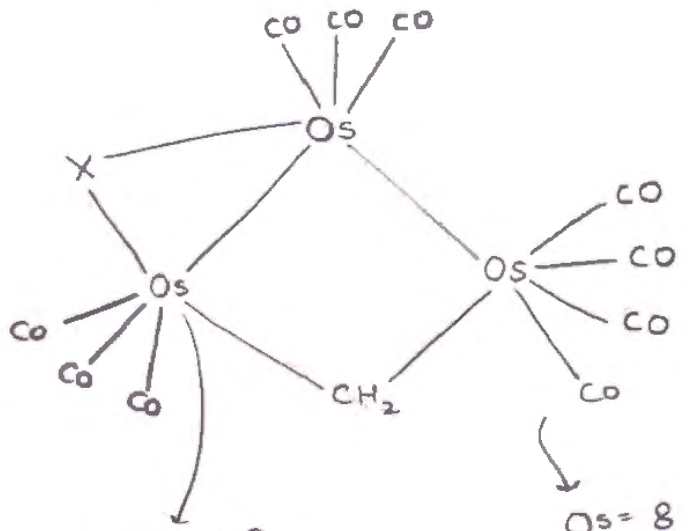
(a) → $(\mu\text{-}H)_2 [\eta^5\text{-} Cp(NO) WH]_2$

(NO is linear)



(c) → $\mu\text{-}CO\text{-}\mu\text{-}CH_2 [\eta^5\text{-} Cp\ Rh]_2$

(d) → $[\mu\text{-X-}\mu\text{-}CH_2Os_3(CO)_{10}]^-$



Os = 8
3CO = 6
μ-X = 1.5
μ-CH_2 = 1
B/M = 1
17.5

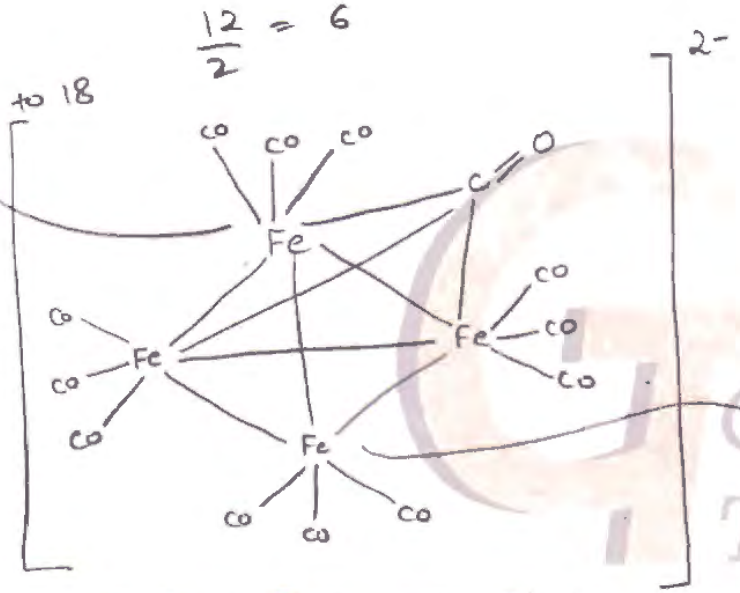
Os = 8
3CO = 6
B/M = 1
μ-CH_2 = 1
16

(e) → $(\mu_3\text{-CO})\text{-}[Fe_4(CO)_{12}]^{2-}$

$$M\text{-}M = \frac{72-(2+32+24+2)}{2} = \frac{12}{2} = 6$$

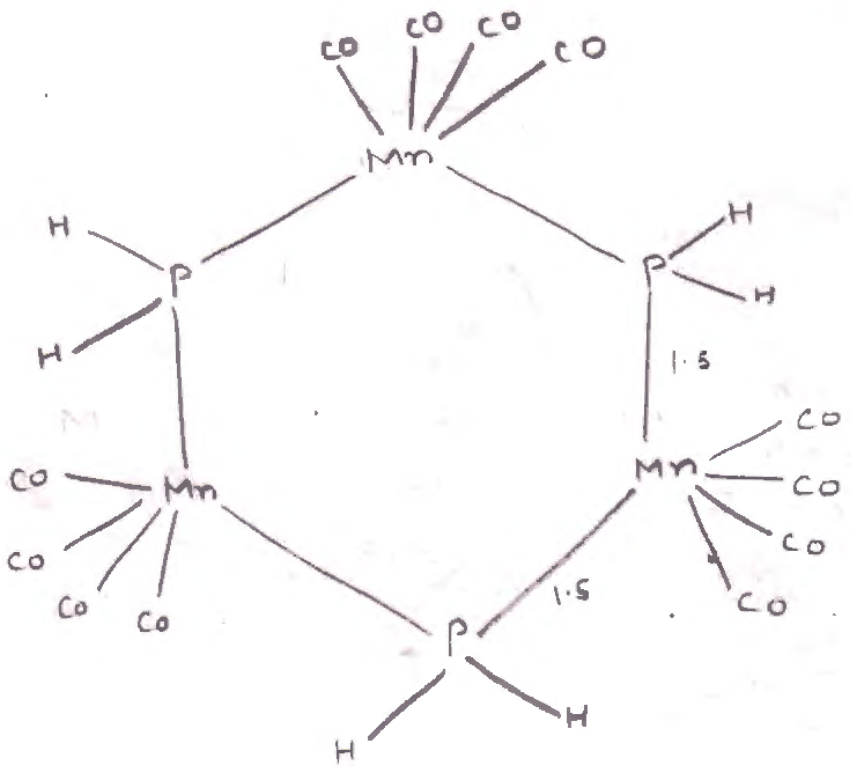
8+6+3+ 2/3 - 17 2/3 , 1/3 required to 18

2/3 + 1/3 = 3/3



8+6+3 = 17

(16) → $[Mn(\mu\text{-}PH_2)(CO)_4]_3$



Mn = 7

4 CO = 8

3 μ-PH_2 = 3

18

Unit - II^nd →

Metal clusters :→

* M-M bonds
* formation of Δ or larger cyclic structure.
  ↳ triangular

classification (Metal- carbonyl)

I — On the basis of ligands

- **Homoleptic**
  * M + CO only
  e.g. $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Ru_3(CO)_{12}$
- **Heteroleptic**
  consisting M + CO + other ligand.
  e.g. $Mo(CO)_3$, $\zeta = 12$, so, $Mo(CO_3)$

Other ligands may be π acceptor series
$-PR_3$, PX_3, PY, NR_3, alkene, diene

II — On the basis of Nuclearity

M + CO + other ligands

On the basis of Nuclearity-

e.g. of Heteroleptic →

(i) $[Cr(CO)_3(PCy_3)_3]$
$6 + 6 = 12$

(ii) $[Ni(CO)_3(NR_3)_x]$
$x = 1$

(iii) $[Fe(CO)_2(\eta^2\text{-}C_2H_4)(PF_3)_2]$
$8 + 4 + 2 +$

Nuclearity

I st

Ye polynuclear ki II category

LNCC M=4

M ≤ 4 → Borderline → May follow or not.

18 e⁻

e.g. $[Fe_3(CO)_{12}]$,

$Ir_4(CO)_{12}$,

$Fe_2(CO)_9$, $Mn_2(CO)_{10}$

$[Co_2(CO)_8]$

Wade-Mingos Rule (Kaise exists)

HNCC

M > 4 Not follow 18e⁻

M ≥ 6

Do n't follow 18 e⁻ rule.

Pentanuclear nhi bnta

e.g. $[Co_6(CO)_{16}]$

-"

For existance

Wade Mingo

Icosahedron formation

M-M = 12 B/M = 4

Homo nuclear

→ Mononuclear

e.g. $[Fe(CO)_5]$

$[V(CO)_6]$

$[M(CO)_6]$, M = Cr, Mo, W

→ Polynuclear

Heteronuclear

$[Mn\,Re(CO)_{10}]$ = $[(CO)_5-M-Re-(CO)_5]$

ek M-Re bond ho skta h

Bridged

$Fe_2(CO)_9$

$[Co_2(CO)_8]$ ✓ solid

• carboranes

Non-bridged

$[Co_2(CO)_8]$ ✓ solution

Mono nuclear

Poly nuclear

Heteronuclear

$[(CO)_5Mn-Re(CO)_5]$

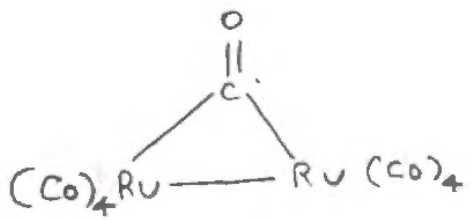
Bridged

- $[Fe_2(CO)_9]$ (3b)
- $[Ru_2(CO)_9]$ (2b)
- $[Os_2(CO)_9]$
- Bridging k liye penle to odd (CO).
- Jitna chota size utna acha Bridging ki tendency.

$\bar{\nu} \propto B.O.$

Non-bridging

- ~~$Co_4(CO)_{12}$~~
- $[Ir_4(CO)_{12}]$



Metal clusters :→

(A) Metal carbonyl complexes - are those in which carbonyl ligands attach with metal-centre.

(B) Metal carbonyl ∧ nitrosyl complexes

(C) Metal Halide & Metal oxide complexes.

Bonding & Spectrum of carbonyl complexes:→

IR → Identification - carbonyls → organic spectra (organic spectra) attached to functional group

IR → $M-C\equiv O$

Stretching frequency of CO with attachment of M.

we study in it →
- Back-Bonding / Synergism / synergic bonding
- $\bar{\nu}_{CO}$
- π-acceptor series

- Series

Coordination {
- * Spectrochemical series
- * Irving-williams series
- * Trans-directing series

Inorganic series {
- * π-acceptor series
- * Electrochemical Series

Bonding →

* Metal
  - → consists filled d orbitals → HOMO
  - → Vacant d- orbital → LUMO

:C≡O
- → HUMO → $\frac{1b}{\sigma}$ nb / σ 2px
  - Non bonding but slightly antibonding
  - IUPAC
- → LUMO → π_3/π_4 - Antibonding

Jab Lewis acid ko donate

Al ← 1b C≡O

$\overset{\oplus}{CO}$ — $\overset{\ominus}{AlCl_3}$

ν_{CO}

Maximum BO- 3.5

Metal- back donate

σ- donor HUMO, → Back- donation → π- acceptor.

MOT
- → N_2, C_2, B_2 ....
- → CO, NO

CO is isoelectronic with $\overset{+}{N}O$.

$C\overset{+}{N}O$ means, linear nature of nitrosyl).

CO
6 8 = (14)

- If TVE ≤ 14, ⇒ B^2A^2 B^2A^2 → B | B B | B A | A A | A

K.K σ_1 σ_2 π_1 π_2 σ_3 σ_4 π_3 π_4

- If TVE > 14 ⇒

BA BA B | B B | | A A | A

$\sigma 1s$ $\sigma^* 1s$ $\sigma^* 2s$ $\sigma^* 2s$

$\sigma 2p_x$ | $\pi 2p_y$ $\pi 2p_z$ | | $\pi^* 2p_y$ $\pi^* 2p_z$ | $\sigma^* 2p_x$

π-mode k anden, baki sab σ

k.k complet σ_1 σ_2 σ_3 π_1 = π_2 π_3 = π_4 | σ_4

CO ≤ 14

B^2 A^2 B^2A^2 | B^2 B^2 | B^2 A^2 | A A |

σ_1 σ_2 σ_3

HUMO of CO

C_2 →

B^2A^2 B^2A^2 B^2 B^2 B

HUMO

$\pi 2p_y = \pi_1$

$\pi 2p_z = \pi_2$

LUMO → σ_3

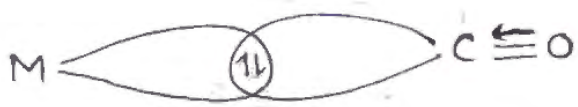
- NO^- ka HUMO → π_3^1

  π_4^1

CO = σ donor = π acceptor

- Step- I →
  - Formation of σ bond (M ← L)

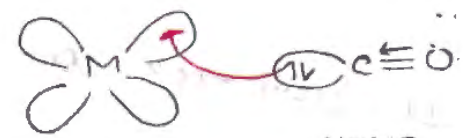
    (Ligand to metal)



M ← CO

M ← L

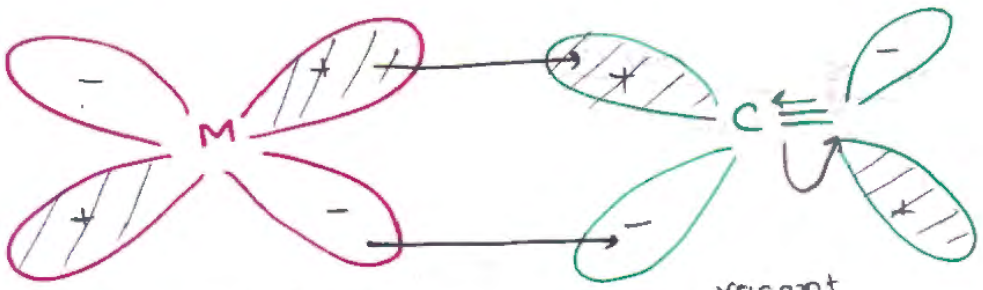
σ-bond



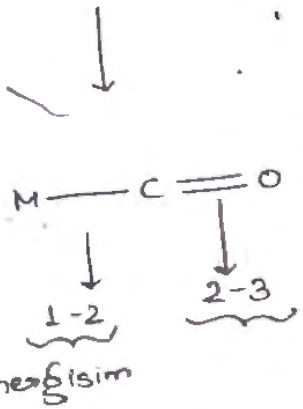
vacant d orbital

* Bond order is unaffected in this case.

Step - IInd - formation of π- bond → (M ⟶ L ≡ back donation)



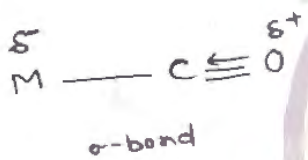
LUMO = π_3/π_4



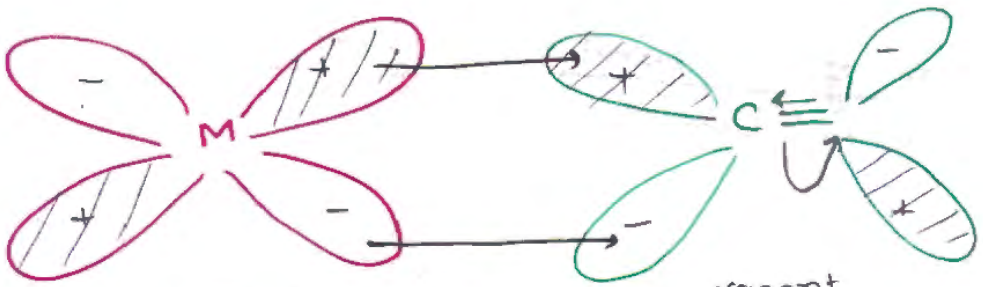
• Synergisim → ek strong, dusra week.

B.O. of CO ↓, $\bar{\nu}_{CO}$ ↓

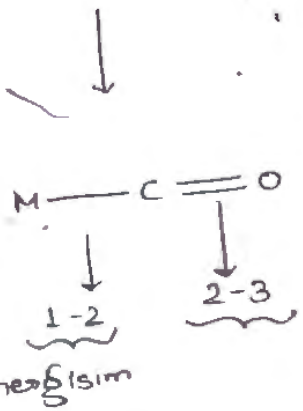
B.O $\propto \frac{1}{B.L.}$



Step - IInd - formation of π- bond → (M ⟶ L ≡ back donation)



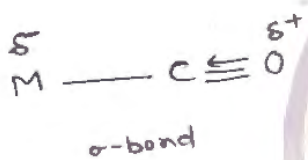
LUMO = π_3/π_4



• Synergisim → ek strong, dusra week.

B.O. of CO ↓, $\bar{\nu}_{CO}$ ↓

B.O ∝ $\frac{1}{B.L.}$



Spectrum - IR → M—CO

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad cm^{-1}$$

or stayard

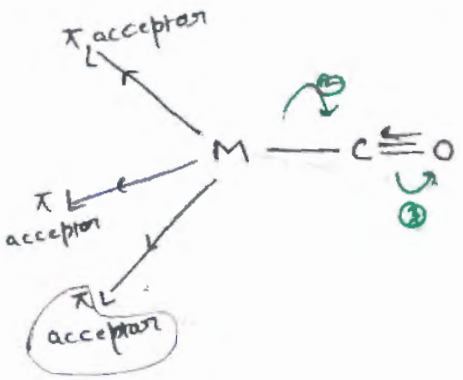
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad Hz$$

$$\bar{\nu} \propto k \propto \frac{1}{\mu}$$

K = force constant, μ = reduced mass

= " " b/w M & C.

f.c. ↑ = B.O. ↑ = ↑ $\bar{\nu}_{CO}$



π acceptor ↑ (1) — edensity on Metal ↓ (2)

bond shift order ↓ees (3) → $\bar{\nu}_{CO}$ increases decreases (4)

due to π acceptor

π acceptor ↑ — 2 decreases ⇒ 3 decreases

π acceptor ∝ $\bar{\nu}_{CO}$

Stayard ligand ka h

① No ⇐ M — C ≡ O, $\bar{\nu}_{CO}$ ↑

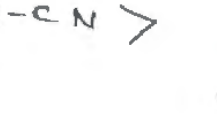
② $PCl_3 \leftarrow M^{\delta-} — C \equiv O$; ν_{CO} ↓

π acceptor ∝ $\bar{\nu}_{CO}$

→ shared π^e bond

π- acceptor series →

$NO^+ > CO > PF_3 > M-NC > PCl_3 > PCOR_3 >$

$PPh_3 > PR_3 > M-CN > NR_3 >$ 

σ donor

σ donor

>

Electronegativity order

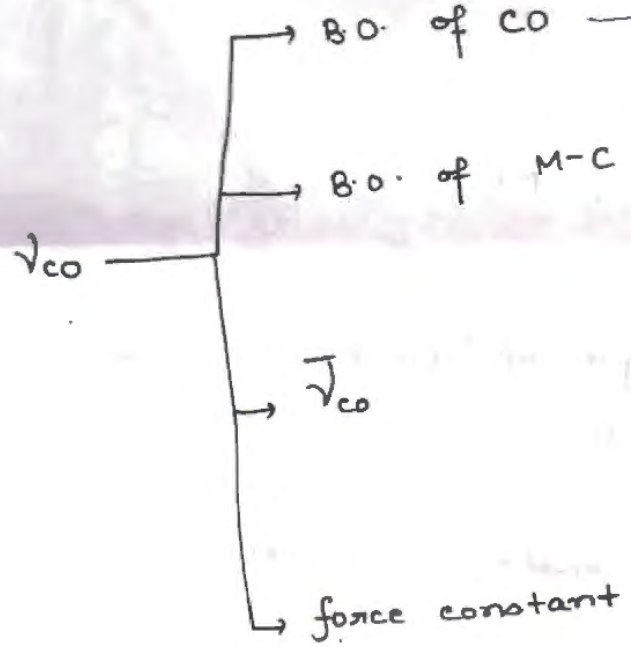
$F > O > N > Cl > C$

Negativity order

$F^{\ominus} < O^{\ominus} < N^{\ominus} < Cl < C^{\ominus}$

Q- $\bar{\nu}_{CO}$

- → on basis of π acceptor series.
- → on basis of σ donor ligand.
- → on basis of charge
  - → +ve → e⁻ density of metal ↓
  - → -ve → e⁻ density ↑
- → on basis of no of CO ligands
- → on basis of electronegativity of metal



If B.O. of CO ↓ then M-C bond increases.

e.g.

Q-1 → $[M(CO)_3(PF_3)_3]$ Given metal of 4d, find M?

(I)

M = Mo (4d)

$[M(CO)_3(COR)_3]$ $[M(CO)_3(CNR_3)_3]$

II III

(IV) $[M(CO)_3(CN)_3]$

$\bar{\nu}_{CO} \propto$ B.O. of CO

(i) Order of $\bar{\nu}_{CO}$?

✓ I > II > IV > III

PF_3 $P(OR)_3$ $C(CN)_3$ NR_3

(ii) order of Bond length of CO ?

I < II < IV < III

(iii) order of force constant of M–C

✓ I < II < IV < III

(iii') Order of Bond length of M–C ?

✓ I > II > IV > III

✓ B.O of M–C I < II < IV < III

(iv) Bond order of CO

✓ I > II > IV > III

(v) Order of Bond length of ligand.

$\pi_{acceptor} \propto \frac{1}{e^-\text{ density on metal centre}} \propto \frac{1}{\text{Tendency on back donation}} \propto$ Bond order of CO

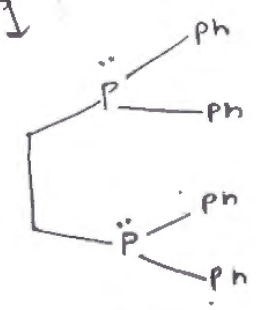
$\propto \frac{1}{\text{Bond order of M–C}} \propto \bar{\nu}_{CO}$

σ - donor - ligand

~~Py — dppe , NR3 , PR3~~

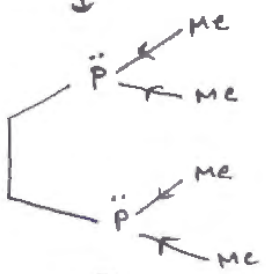
Py dppe dmpe NR_3 $:P(Me)_3$

dppe →



(I)

dmpe →



(II)

yha lone pair h, lekin benzene k sath conjugation

⇒ II walla better donor, donor to I^{st} walla bhi h.

dppe gives 4e

$[M(CO)_2(dppe)]^{--}$ ⇒ M can be Fe, Ru, Os

(I)

$[M(CO)_2(dmpe)]^{--}$

II

∴ $\bar{\nu}_{CO}$ I > II (on basis of e^- density on metal centre)

Gate 15

- $[W(CO)_6] \xrightarrow[-PPh_3]{-CO} [W(CO)_5(PPh_3)]$ ⊗

Product

(a) B.L. of M-C increases & B.L. of C-O ↑es

(b) B.L. of MC ↓ & B.L of CO ↑es

(c) B.L. of MC ↓ & " " " ↓

(d) " " ↑ & ↓es

B.O

B.O. CO CO↓, M-C↑

CO↑, M-C↓

Q→ On the basis of charge

$[V(CO)_6]^-$ (I) d^6 $[Cr(CO)_6]^0$ II d^6 $[Mn(CO)_6]^+$ III d^6

$[Fe(CO)_6]^{+2}$ 12+8 (IV) d^6 $[Ni(CO)_6]^{+4}$ d^6 (V) ~~electronegativity~~ σ

order of e^- density

I

ν_{CO} I < II < III < IV < V

1750 1860 2000 2100 2200

Q- $[Co(CO)_4]^-$ (Co^{-I}, d^{10}), is oelectronic with.

(a) $[Ni(CO)_6]^{++++}$

(b) $[Fe(CO)_5]$

✓(c) $[Ni(CO)_4]$ d^{10}

(d) $[Cr(CO)_6]$

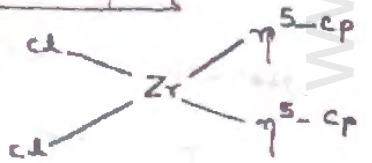
Structure of metal carbonyl

→ M-M bonds & bonds per metal atom. → 16 e⁻ rule

$n = \frac{18n - TVE}{2}$; $18 - \frac{TVE}{n}$

$M\text{-}M = \frac{16n - TVE}{2}$; $16 - \frac{TVE}{n}$

Co^+	Ni^0	Zr
Rh^+	Pd^0	Ti
Ir^+	Pt	



→ Skeleton

M-M	M	
3	4	△
4	4	◇
6	4	
12	6	Icosahedron

⟷ Bridging & Terminal carbonyls

→ Extended formula

→ Colour

→ Point group

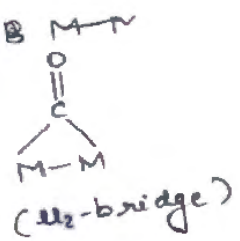
Bonding with CO

Nature of CO

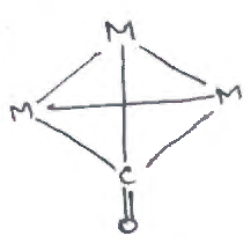
(i) CO^+ (free) (with lewis acid) $H_3B \leftarrow CO$ — $\bar{\nu}_{CO}$ (in cm^{-1}) — 2183 — 2143 — Difference 40 cm^{-1}

(ii) CO (free) — 2020 - 1850 — 2120 - 1830

(iii) M-CO (Terminal) — 1860 - 1750 — 1850 - 1750

(iv) 

(μ_2-bridge)

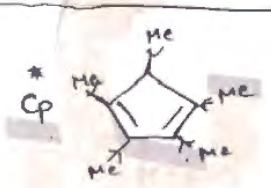
(v) 

(μ_3-bridge) — 1750 - 1600 — 1750 - 1620

1730 - 1600

Group - III rd

Group III	IV	V	VI	VII
Sc *	Ti	V	Cr	Mn
Y *	$[Ti(CO)_6]^{--}$ (18e⁻) Carbonylate; $[Ti(Cp)_4]$ (16e⁻)	$[V(CO)_6]$ 17e⁻ (Paramagnetic)	$Cr(CO)_6$	$[Mn_2(CO)_{10}]$
La *	Zr	Nb	Mo	Tc
Hf *	$[Zr\ Cp^*_2\ Cl_2] \rightarrow 16e^-$	$[NbX_{12}]^{++}$	$[Mo(CO)_6]$	$[Tc_2(CO)_{10}]$
		Ta	W	Re
		$[TaX_{12}]^{++}$	$[W(CO)_6]$	$[Re_2(CO)_{10}]$



Cp = C_5H_5

Cp^* = C_5

$[M^{\delta-}(Cp)_4] \gg [M^{\delta-}_{II}(Cp^*)_T]$

I

So $\nu_{CO_I} > \nu_{CO_{II}}$

Cp^* ye wall Cp ache σ donate.

GER / LEO

↓

Gain e⁻ Reduction

* $[V(CO)_6] \xrightarrow{\text{Dimeri}}$ not possible

By ESR, we distinguish paramagnetic character

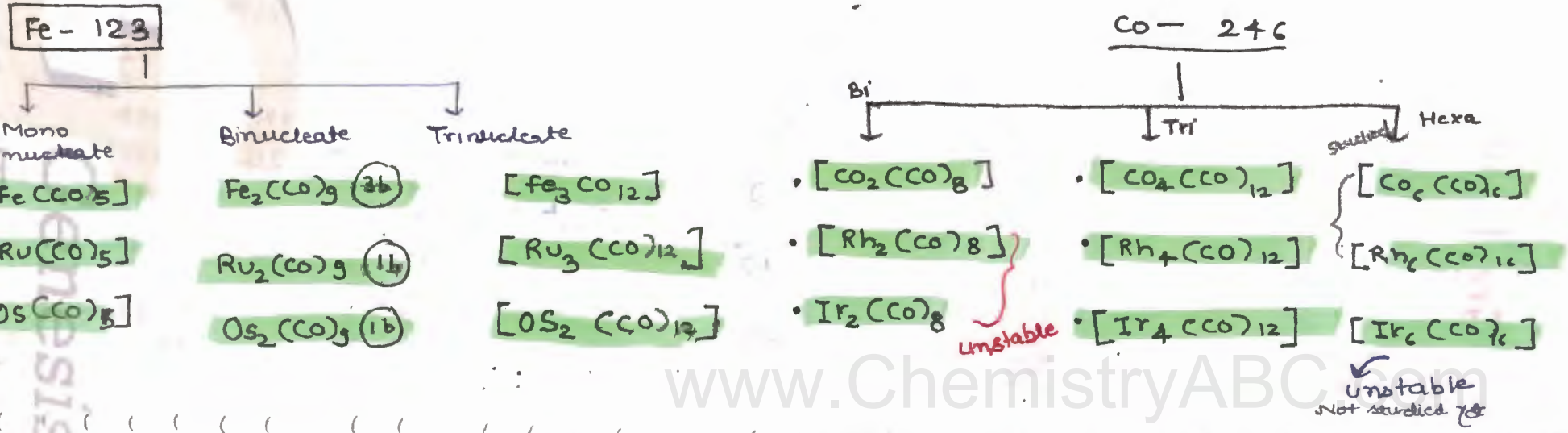
26 | 27 | 28

VIII | IX

$_{26}Fe$ | Co | *

Ru | Rh

Os | Ir



26 | 27 | 28

VIII

$_{26}Fe$

Ru

Os

IX

Co

Rh

Ir

Fe - 123

Mononucleate	Binucleate	Trinucleate
$[Fe(CO)_5]$	$Fe_2(CO)_9$ (3b)	$[Fe_3CO_{12}]$
$[Ru(CO)_5]$	$Ru_2(CO)_9$ (1b)	$[Ru_3(CO)_{12}]$
$[Os(CO)_5]$	$Os_2(CO)_9$ (1b)	$[Os_2(CO)_{12}]$

Co — 2+c

Bi	Tri	Hexa
• $[Co_2(CO)_8]$	• $[Co_4(CO)_{12}]$	$[Co_6(CO)_{16}]$
• $[Rh_2(CO)_8]$ unstable	• $[Rh_4(CO)_{12}]$	$[Rh_6(CO)_{16}]$
• $Ir_2(CO)_8$	• $[Ir_4(CO)_{12}]$	$[Ir_6(CO)_{16}]$ unstable (Not studied yet)

studied

X

$_{28}Ni$

- $[Ni(CO)_4]$ - Imp — tetrahedral

- $[Pd(CO)_4]$
- $[Pt(CO)_4]$

} unstable

XI

~~Cu~~

~~Ag~~

~~Au~~

XII

~~Zn~~

~~Cd~~

~~Hg~~

Structure :→

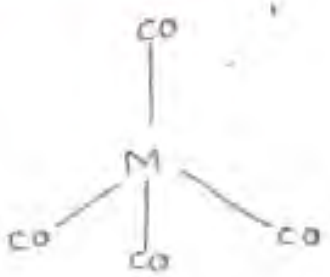
* Metal-Metal bond ③
* B/M atom.
* μ-CO
* Bands (IR data)
* Extended formula
* Point group.
* Colours

MNCC

① Mononuclear :→

84	85	86
$[M(CO)_4]$	$[M(CO)_5]$	$[M(CO)_6]$
M = Ni, Pd, Pt (unstable)	M = Fe, Ru, Os	M = Cr, Mo, W
Td	TBP	Octahedral

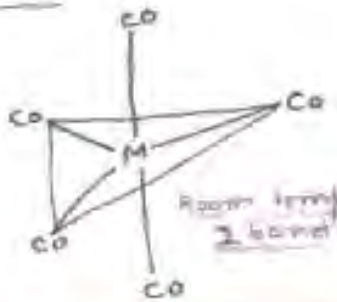
(84) → $M[CO)_4$



M = Ni

(85) $M(CO)_5$

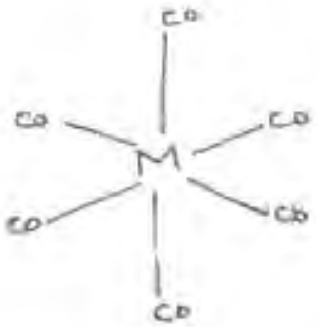
$C_3 + 2C_2 + 3\sigma v + 1ch + E = D_{3h}$



Room temperature
2 bond

T ↑↑
1 bond

(86)



84 - Td - Td

85 - TBP - D_{3h}

86 → Octahedral - O_h

for carbonyl

DNCC

(2)- DINUCLEAR

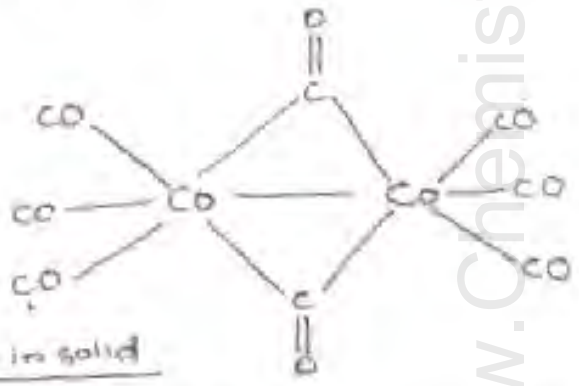
28, 29, 210

- $[M_2(CO)_8]$ → M = Co, Rh_2, Ir (unstable)
- $[M_2(CO)_9]$ → add one alternate bridge; M = Fe, Ru, Os; 3 bridge
- $[M_2(CO)_{10}]$ → M = Mn, Tc, Re

* $[Co_2(CO)_8]$

M-M bonds $= \frac{36 - 18(6) - 2}{2} = 1$

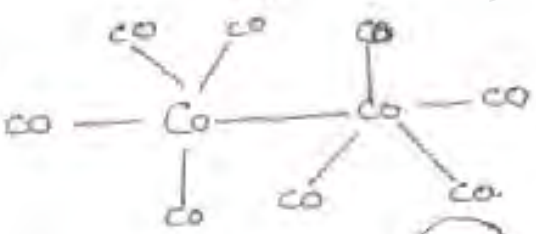
E/N atom $= 18 - \frac{34}{2} - 1$



(1) Exists in solid

solvent

Bridging ligand = 0



D_{3h}

(2) Exists in solution (Hexane)

(I) M-M = 1

E/M = 1

Bridging = 2

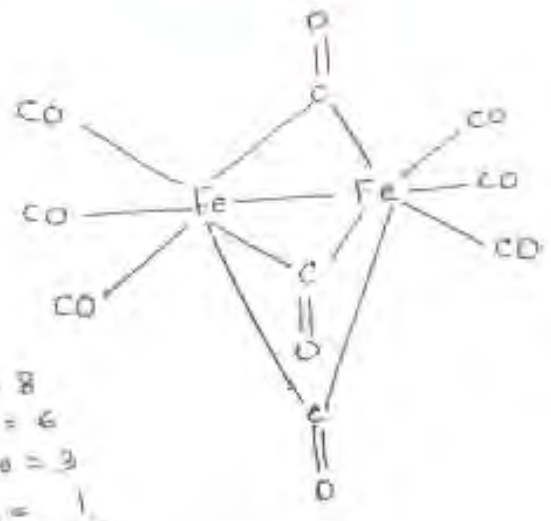
Extended formula

$[Co_2(\mu_2\text{-}CO)_2(CO)_6]$

Point group- C_{2v} D_3

of solid

(B) → $[M_2(CO)_9]$



Fe = 8
T-CO = 6
B-CO = 3
B/M = 1
18

Point group = D_{3h}

μ_2-CO = 3

M-M = 1

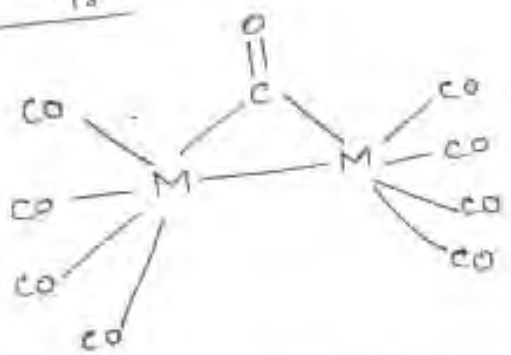
B/M = 1

B-Ligand = 3

Extending Formula

= $[Fe_2(\mu_2\text{-}CO)_3(CO)_6]$

Colour = Solid plates



M = OS, RU

M-M = 1

B/M = 1

Bridging = 1

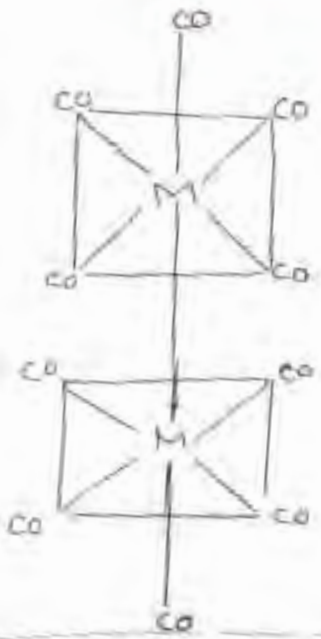
Extended formula →

$[Ru_2(CO)_8(\mu_2\text{-}CO)]$

or

$[Ru_2(CO)_8(\mu\text{-}CO)]$

① $M_2(CO)_{10}$



M = Mn, Tc, Re

M – M = 1

B – M = 1

μ – CO = 0

Point group = D_{4d}

colour = Yellow

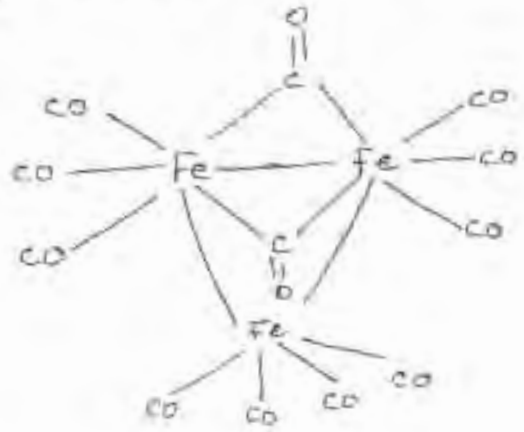
(Transition is almost forbidden)

② →

Trinuclear → $[M_3(CO)_{12}]$ M = Fe, Ru, OS

(Low) – C_{2v} (Low)

$Fe_3(CO)_{12}$



M –

M – M = 3

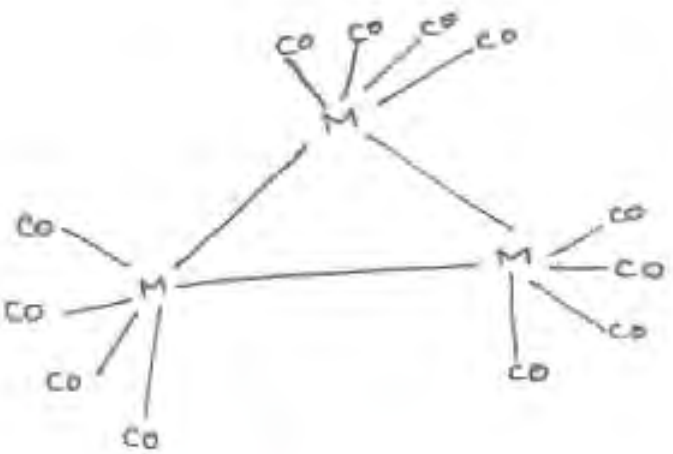
B/M = 2

Bridging ligand = 2

= $[Fe_3(\mu_2\text{-}CO)_2(CO)_{10}]$

↑ extended formula

$Ru_3(CO)_{12}$ & $Os_3(CO)_{12}$



Same group T_3 th

$Ru_3(CO)_{12}$ - orange

$Os_3(CO)_{12}$ - yellow

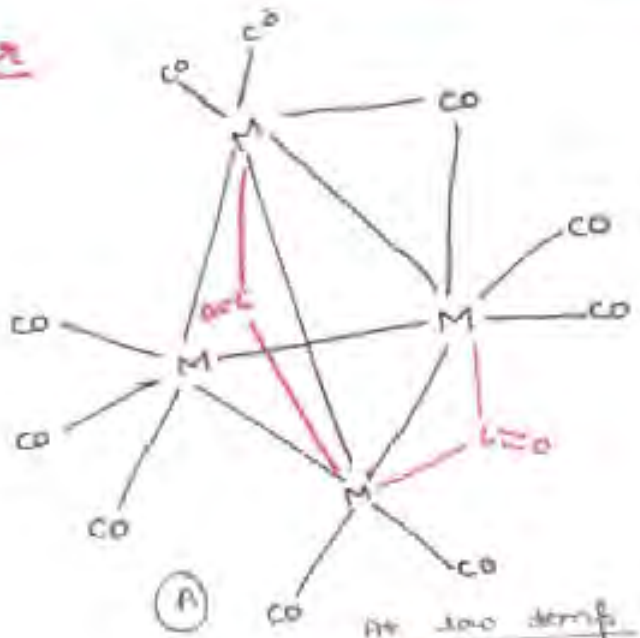
---

(4)- Tetranuclear

* $Co_4(CO)_{12}$

* $Rh_4(CO)_{12}$

* $Ir_4(CO)_{12}$



(A) At 100 temp

In above

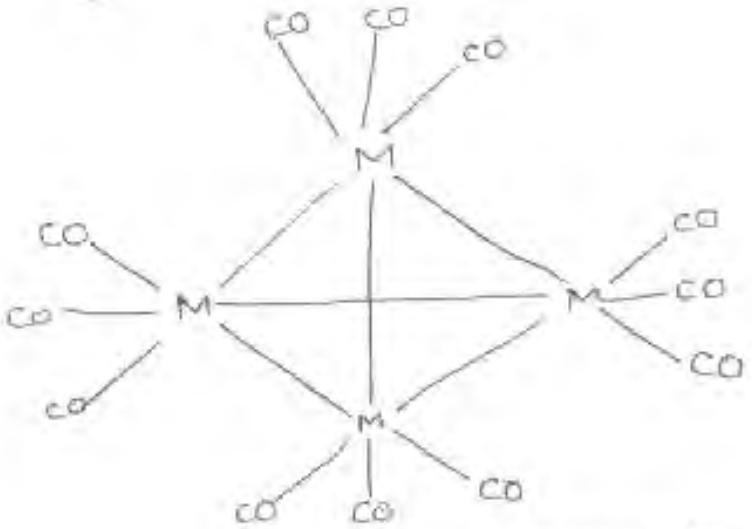
M = Co, Rh

Same

T ↑

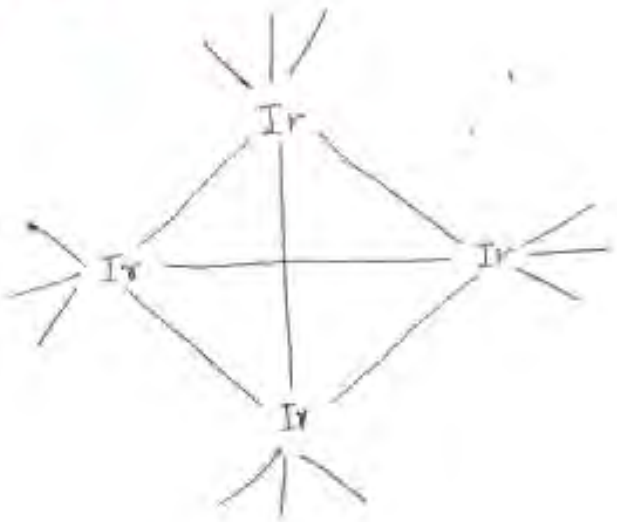
(B)

Same for Rh)-Co



At high temperature A will be as above

$Ir_4(CO)_{12}$ =



$Co_4(CO)_{12}$ →
$Rh_4(CO)_{12}$ →

M - M = 6
B/M = 3
M - CO = 3

Extended formula = $[M_4(M_2-CO)_3(CO)_3]$

Colour: for Rh = Red

Point group = C_{3v}

Str

(6) Hexanuclear –

M – M = 12
B / M = 4
} fix

MNCC - Mononuclear carbonyl complex.

DNCC

TNCC

TrNCC

$[Co_6(CO)_{16}]$
$[Rh_6(CO)_{16}]$
} M = Co, Rh

$[Ir_6(CO)_{16}]$ → trimilla

[

M = Co, Rh
M – 9
B/M = 4
27 – CO = 4
2 μ_3 – CO = $\frac{2}{3} \times 2 = \frac{4}{3} = 1\frac{1}{3}$

$18\frac{1}{3}$

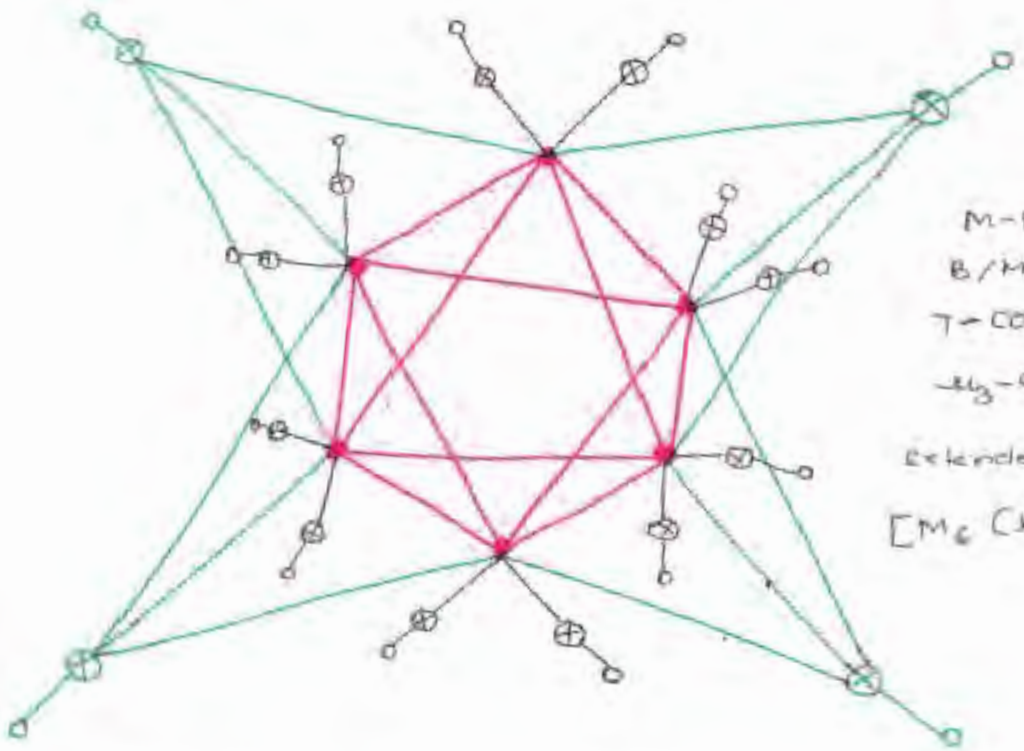
Huheey - 588

@ 13 & 14, Assignment:

• M

⊕—c — t-co

⊕—c — co



M-M = 12

B/M = 4

T-CO = 12

μ_3-CO = 4

Extended formula

$[M_6(\mu_3\text{-}CO)_4(CO)_{12}]$

Bridging always on square gon.

M-M =

e.g. → $[H_2Ru_6(CO)_{18}]$, In the following structure

(i) Ru = 8, coordinated

Structure

Ru = 8

3CO = 6

B/M = 4

$\frac{1}{3}\mu_3$-M = $\frac{1}{3}$

$18\frac{1}{3}$

* **Encapsulation →** (Cluster ref)

$H_6 - H$

(a) $H_2 OSc(CO)_{18}$

(b) $HOSc(CO)_{18}$

(c) $H_2 FC(CO)_{18}$

Among these, which metal carbonyl is encapsulated

26- August-

MOF →

1 (1) → By the reaction of freshly cut / finely divided metal with CO. in presence of easily e⁻ donating metals i.e. a strong reducing agent.

2 (2) → from transition metal oxide.
~~By the reductive carbonylation of~~

\+ (3) → from photochemical or thermal reactions of metal carbonyl (LNMC).

2 (4) → By the reaction of metal halide with CO in presence of easily e⁻ donating i.e. strong reducing agents.
By the reductive carbonylation i.e. By the reaction of metal halides with CO.

(1) → By the reaction of freshly cut / finely divided metal with CO-

(i) • $Ni + 4CO \xrightarrow[1atm]{25^\circ C} [Ni(CO)_4]$ → colourless toxic liquid

(ii) • $[Ni(CO)_4] \xrightarrow{50^\circ C} Ni + 4CO$ → Mond's process

Ni → Pure

(iii) • $Fe + 5CO \xrightarrow[200\ atm]{200^\circ C}$ Formation of $[Fe(CO)_5]$

(iv) $Co + 8CO \longrightarrow [Co_2(CO)_8]$

(2) →

(i) $VCl_3 + Na + 6CO \xrightarrow{160^\circ C}$ (T, should be b/w 150-175) diglyme 200 atm

$[V(CO)_6]^-$ + $[Na(diglyme)_2]^+$ + 3NaCl

Net 4 marks

$[V(CO)_6]$

↓

Air sensitive Green black paramagnetic

diglyme

Diethyl Glycol Dimethyl ether

$VCl_3 + 4Na + 6CO \xrightarrow[200\ atm]{Diglyme} [Na(diglyme)_2]^+ [V(CO)_6]^-$ + 3NaCl

↓ $H_2PO_4^-$

$[V(CO)_6]$

$$[Co(CO)_4] \xrightarrow{H^+} [HCo(CO)_4]$$

(i) $VCl_3 + Na + CO \xrightarrow[200\,atm]{Diglyme} [Na_4(diglyme)_2]^+ [V(CO)_6]^-$

(ii) $CrCl_3 + Al + 6CO \xrightarrow{165^\circ C} [Cr(CO)_6] + AlCl_3$

$Cr(CO)_6$: 18 e⁻ complex; $AlCl_3$: Lewis acid

(iii) $CrCl_3 + CO + Na \xrightarrow[Pn-H]{140^\circ C} [Cr(CO)_6] + NaCl$

(iii) $MoCl_5 + CO + Na \xrightarrow[155^\circ C]{} [Mo(CO)_6] + 5NaCl$

Don't learn particular temp. - should be b/w 150-170 °C.

(iv)

$$Mn(OAc)_2 + Na + CO \xrightarrow{diglyme} [Mn_2(CO)_{10}] + NaOAc$$

(3) → From transition metal oxide:→

(i) $2CoO + 10CO \xrightarrow[1900\,atm]{80^\circ C} Co_2(CO)_8 + 2CO_2\uparrow$

→ CO acts as reducing agent itself & convert itself into CO_2.

(ii) $Re_2O_7 + 11CO \xrightarrow[350\,atm]{250^\circ C} [Re_2(CO)_{10}] + 7CO_2\uparrow$

(iii) $Re_2S_7 + CO \longrightarrow [Re_2(CO)_{10}] + 7S{=}C{=}O$

CO acts as reducing agent = oxidation

(4) from photochemical or thermal reactions of metal carbonyls –

(i) $[Fe(CO)_5] \xrightarrow{h\nu} [Fe_2(CO)_9] + CO \xrightarrow{h\nu} [Fe_3(CO)_{12}]$

Photons mild system

~~R–CH₂–OH~~
like mild oxidising agent

$R-CH_2-OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$

1 — $KMnO_4$ & MnO_2 — direct 2 & 3

Δ (heat) lab direct milega

(means more than room temperature)

(ii) $Co_2(CO)_8$ (I) $\xrightarrow{h\nu} [Co_4(CO)_{12}]$ (II) $\xrightarrow{h\nu} [Co_6(CO)_{16}]$ (X)

Δ (✓)

second iske n manega

$[V(CO)_6] \xrightarrow[\text{or } \Delta]{h\nu} \times$

$[Cr(CO)_6] \xrightarrow[\Delta \text{ or } L]{h\nu} \times$

(iii) $Mn_2(CO)_{10} + Re_2(CO)_{10} \longrightarrow 2\,[(CO)_5Re-Mn(CO)_5]$

SADI

Imp Reactions of Metal carbonyl

— carbene formation

1. Substitution Rxn
2. Addition "
3. Disproportion
4. Interchange
   - I_d
   - I_a

① - Substitution Reactions

(I) → Dissociative

II → Photochemical ④
& Thermal subst

III → Associative substitution

Acetonitrile → CH_3-CN (3 CO replace)

THF →  (1 CO replace)

DCM → CH_2Cl_2

NBD → 

COD → 2 CO
COT → 4 CO 

Dissociative substitution

* Given by 18 e^- complexes.
* Like S_N1, so rate depends on conc. of complex

Rate = K [complex]

* Rate will be slow.

---

* Formation of solvated intermediate.

Solvent → THF, ()

MeCN

• MeCN always replaces three CO ligands.

* Labile ligands (easily dissociation)

• DCM (Dichloromethane)

• NBD (Norbornadiene)

Photochemical & Thermal substitution

* Change in hapto number / Hapticity, (fluxional ligands)

allyl, cp, COT,

such as Cp, Cp^*

CHT (cycloheptatriene) (Tropylium carbocation)

Isme nitrosyl bhi aayega, 3 e^- donation bhi change karega

⇒ Jab η not mentioned, then we took η - max

Associative substitution

* Given by 16 e^-, 17 e^-, complexes
* Rate will be dependent on

Rate = K [complex] [$\bar{\text{L}}$]

• Rate will be fast

* [illegible] unfavourable [illegible]

* formation of unfavourable 20 e^- activated complex.

* 18 e^- species also give this type of reaction when ligand is fluxional (like NO)

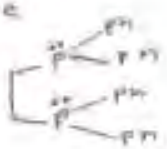
Labile ligands

= CNBD

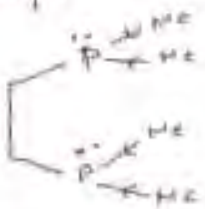
COD (cyclooctadiene)

* COT

* dppe



* dmpe



Dissociative substitution → (28)

$$L_nM-CO \underset{+CO\ K_{-1}}{\overset{-CO\ K_1}{\rightleftharpoons}} L_nM \xrightarrow[K_2]{+Y} L_nM-Y$$

Slow (RDS)

$$Rate = k[complex]$$

⇒ Like SN_1.

In this mechanism an intermediate of reduced C.No or more commonly solvated intermediate is formed, this intermediate then combine with incoming ligand.

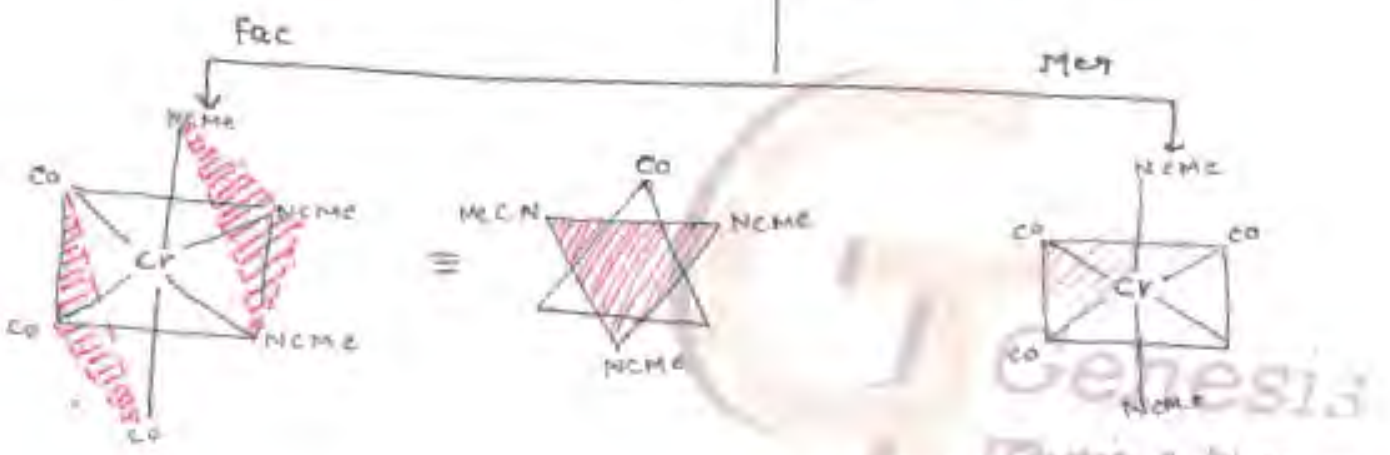
Dissociative Substitution :→

Fac
Mer

(i) $[Cr(CO)_6] \xrightarrow{3MeCN} [Cr(CO)_3(NCMe)_3] = Ma_3b_3$

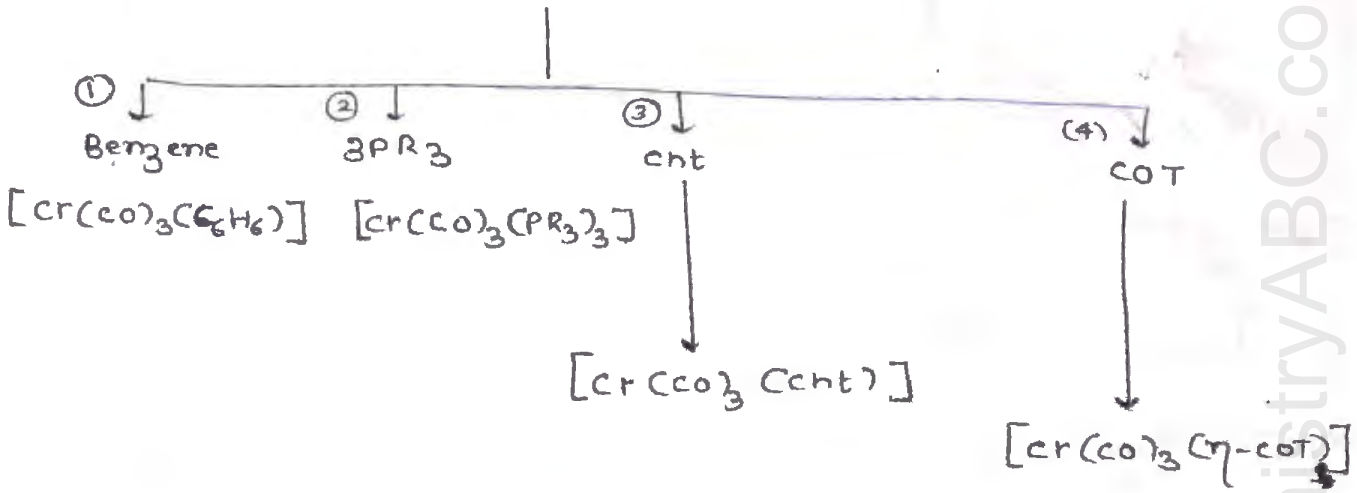
18 e⁻

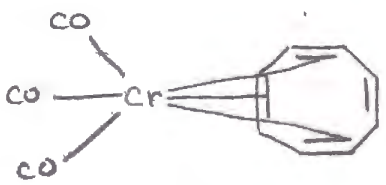
but | Solvated intermediate
stable intermediate

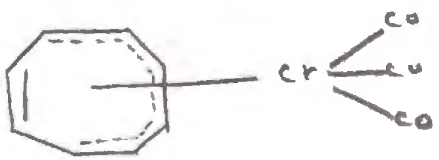


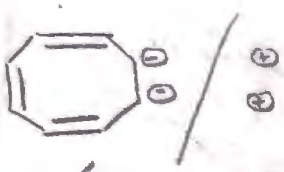
Not

Now, solvated intermediate can be replaced by

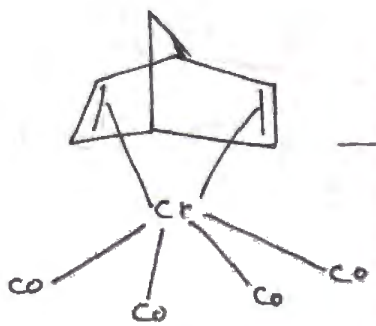


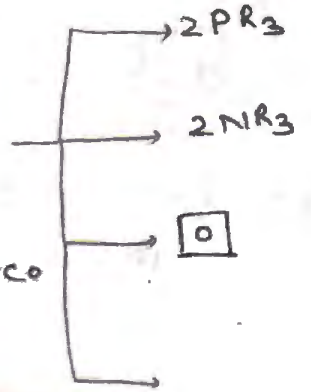






(ii)- $Cr(CO)_6$ —NBD (4e⁻ donor)→ (so replace two CO)





Hepaticity 4 wale replace

(iii) $Fe(CO)_5$ (18e⁻) —THF→ $[Fe(CO)_4 \cdot THF]$ (–CO)

$[Fe(CO)_4 \cdot THF] \rightarrow [(CO)_4-Fe-\parallel]$

$\xrightarrow{PCl_3} [(CO)_4-Fe-PCl_3]$

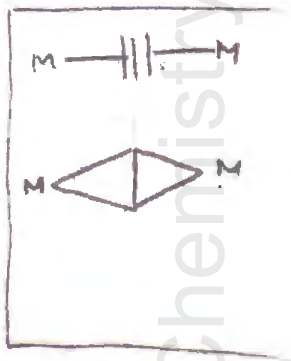
$\rightarrow [(CO)_4Fe-\parallel]$

$\rightarrow (CO)_4Fe-$ 

2 e⁻ donor s replace.

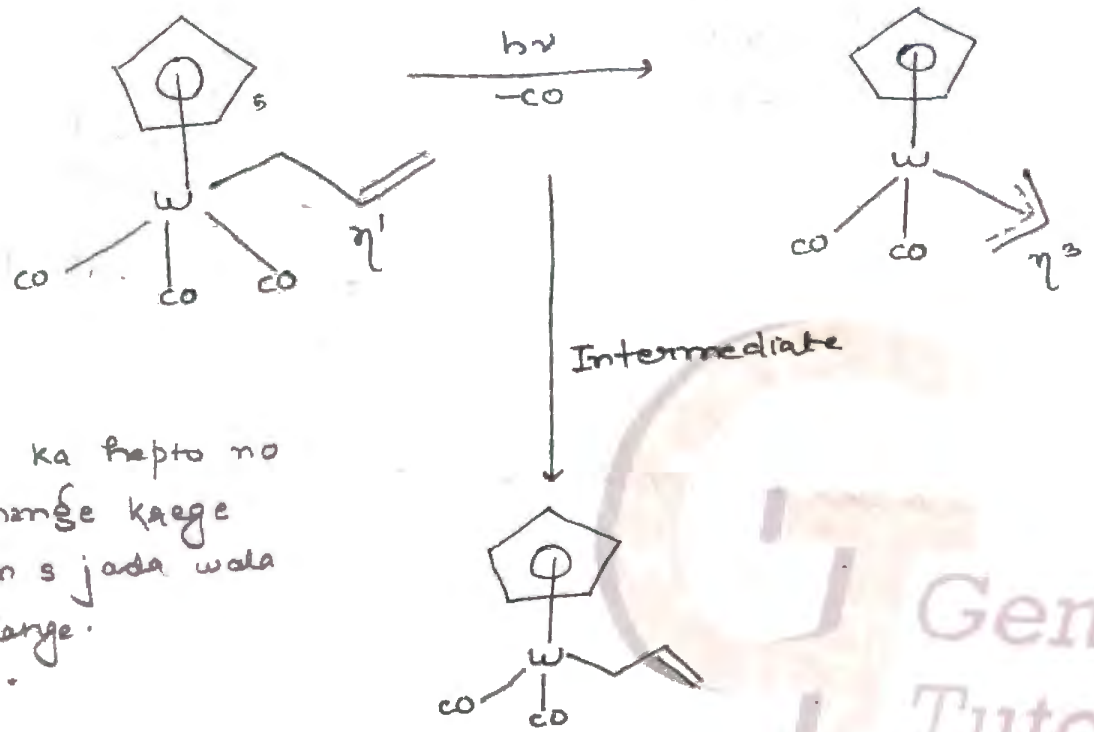
(i) $[M(CO)_6] \xrightarrow{THF} [M(CO)_5 \cdot THF]$

$[M(CO)_5 \cdot THF] \xrightarrow{+PPh_3,\ +CO} [M(CO)_5(PPh_3)] + THF$ (18e⁻)



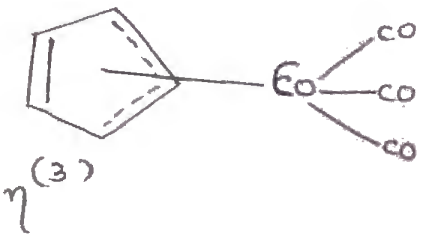
-weakly coordinated ligand ie.. more labile ligands such as acetonitrile (CH_3-CN) {it replaces atleast 3 CO ligands)

(II) → Photochemical & thermal Substitution –

(i) 

cp ka hapto no nhi change kaega kam s jada wala change.

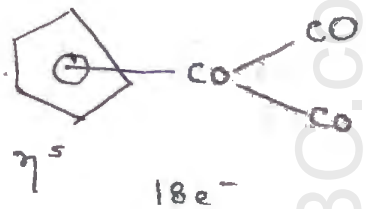
(ii)



$\eta^{(3)}$

18e⁻

$\xrightarrow[-CO]{h\nu}$



η^5 18e⁻

(iii)

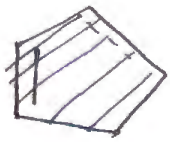
$\xrightarrow{h\nu}$

η^1- allyl

$[(CO)_4Mn \longrightarrow]$

18 e⁻

(7)



(III) → Associative Substitution →

In this mechanism the incoming ligand first adds to the metal complex to form an intermediate in the next step, the dissociation of one of the original ligands occurs rapidly.

$LnM-CO \xrightarrow[\text{Slow}]{Y:} LnM(CO)Y$

rds

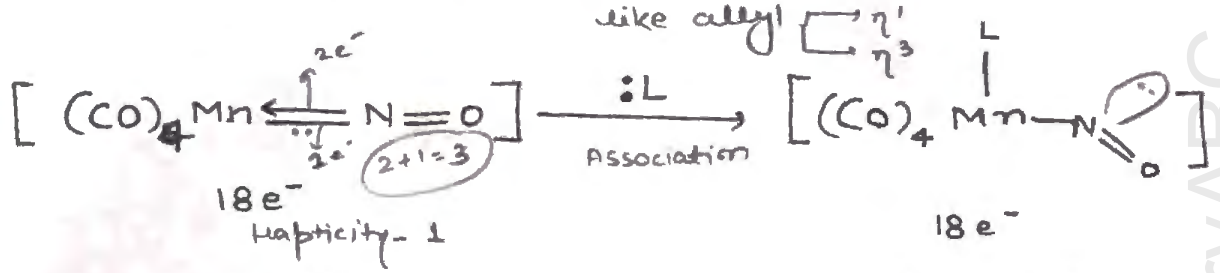
(i) Association

(ii) Dissociation

$LnM(CO)Y \xrightarrow[-CO]{\text{Fast}} [LnM-Y]$

$\text{Rate} = k[LnM-CO][Y]$

- 16 e⁻ complex, 17 e⁻ complex bnayega
- 18e⁻ " bhi bnayega, but usko liye fluoxinal hona chahiye, ligand like NO → B, L; like allyl → η¹, η³

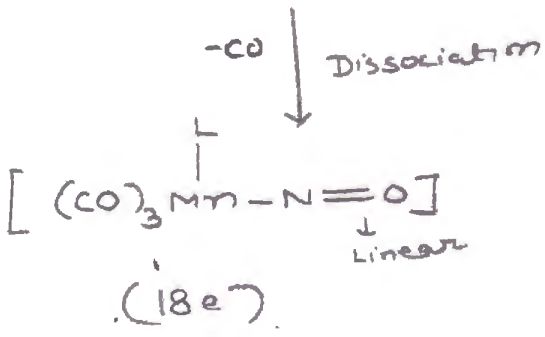


18e⁻
Hapticity - 1

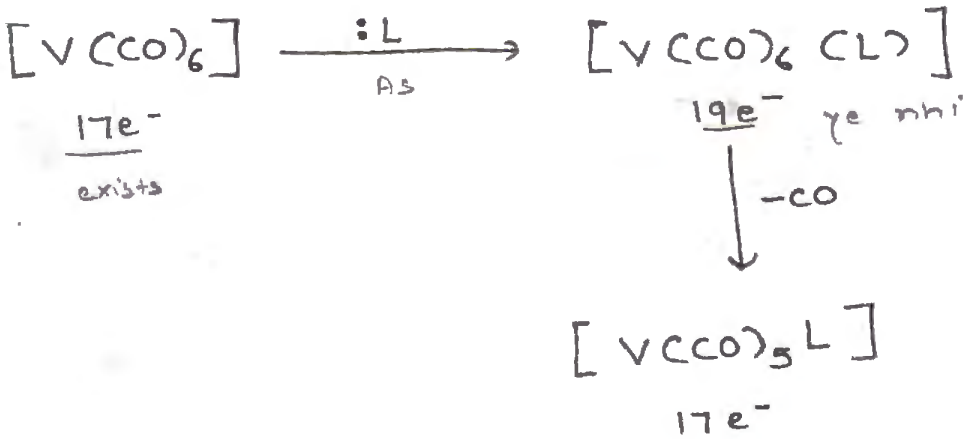
Linear NO

18 e⁻

Bent NO



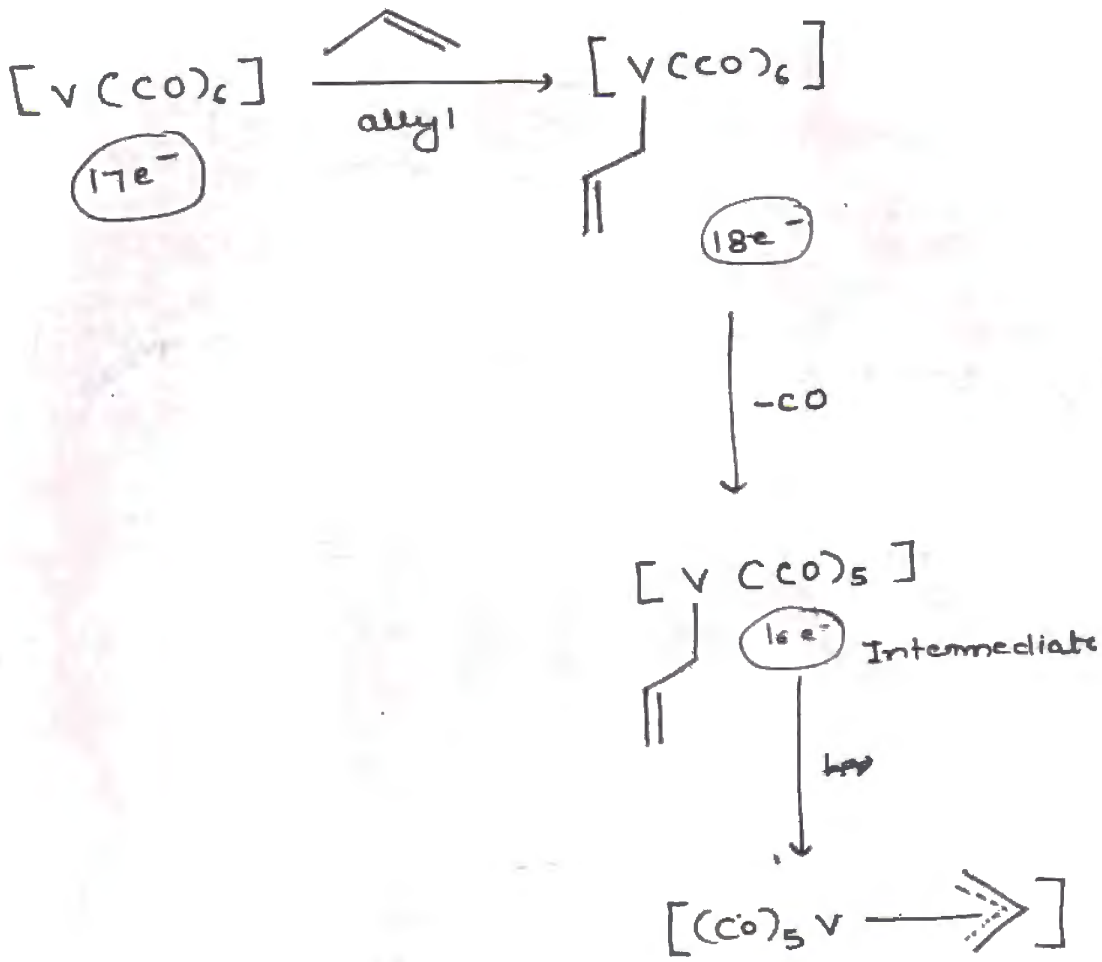
(18e⁻)

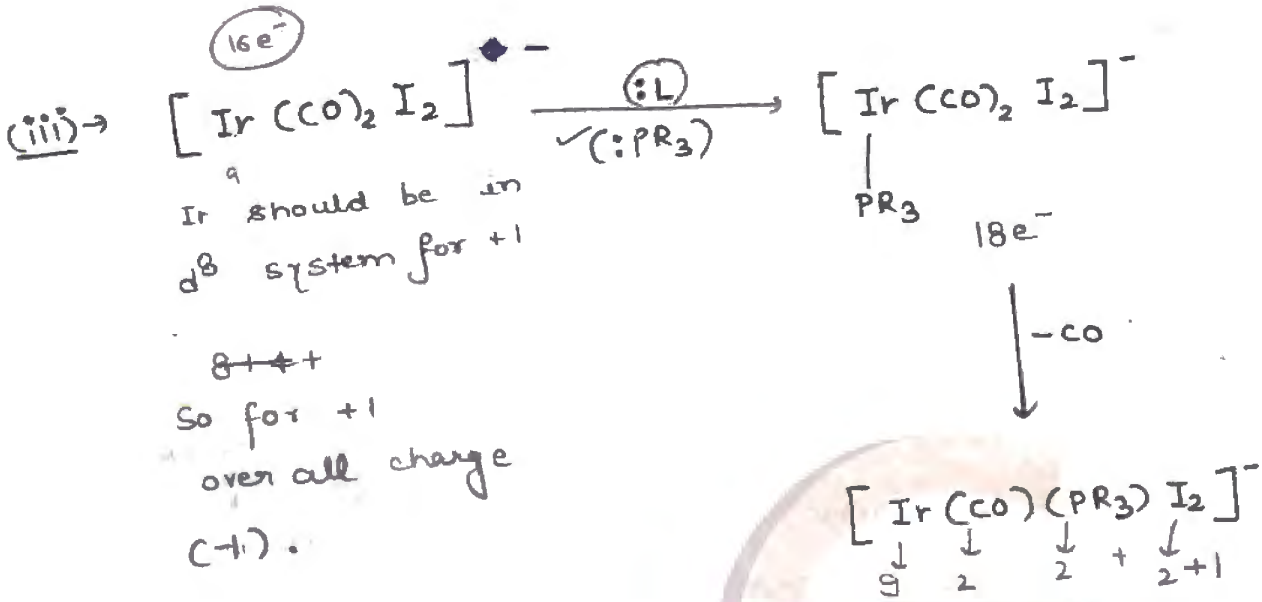


17e⁻
exists

17e⁻

* $[V(CO)_6]$ reacts 10^{10} times faster as compared to $[Cr(CO)_6]$
17 (6 + 12)



(iii) → 

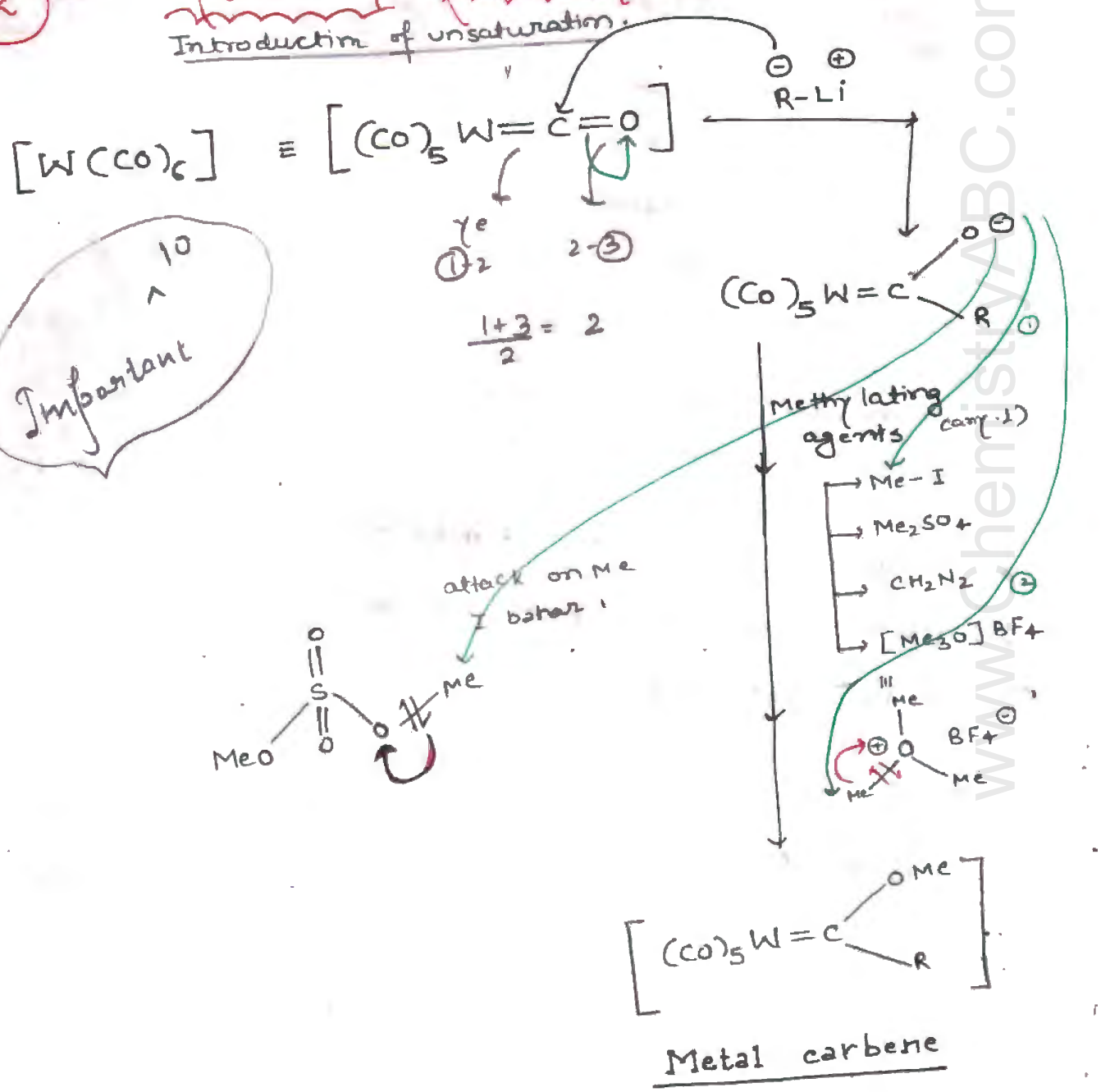
Ir should be in d^8 system for +1

~~8+4+~~

So for +1 over all charge (-1).

2 → Addition Reactions :→ (Nucleophillic addition)

Introduction of unsaturation.



Important

10

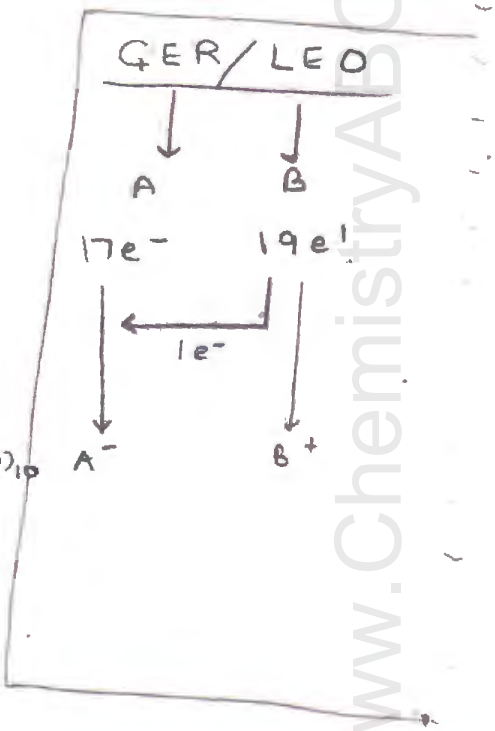
Carbene

- Fischer carbene
  - Metal carbonyl starting material
  - consisting of Heteroatom
  - ~~F & E~~

③- Disproportion Reactions

- e^- wo lega jiske bad 18s kam
- one species is oxidised & other is reduced.

e.g. : cannizaro reaction.



* e^- transfer takes from 19 e^- species to 17 e^- species
* Metal carbonyl ⇒ M-M bonds → $Mn_2(CO)_{10}$
* Ligand ⇒ Non-π acceptor liganals.
  ⇒ Py, dppe, NH_3

(i) $[Mn_2(CO)_{10}] + NH_3 \longrightarrow [Mn(CO)_5] + [Mn(CO)_5]$

equal divide kr lo — 17e⁻ — 17e⁻

$\downarrow 3NH_3$

~~$Mn(CO)_2(NH_3)_3$~~

ek ko 19 banana h & dusra 17e⁻

$[Mn(CO)_3(NH_3)_3]$ — 19e⁻

Self e⁻

Gain / Loose

$[Mn(CO)_3(NH_3)_3]^+$ — 18e⁻ — (A)

$[Mn(CO)_5]$

Loose / Gain

$[Mn(CO)_5]^-$ — 18e⁻ — (B)

(42)

(i) → $[Mn_2(CO)_{10}]$ (dppe) ⟶ $[Mn(CO)_5] + [Mn(CO)_5]$

dppe: 4e⁻ donor; $[Mn(CO)_5]$: 17e⁻

$[Mn(dppe)(CO)_4]$ + $[Mn(CO)_5]$

7 + 4 + 8 = 19e⁻ ; 17e⁻

Minimum no of CO

X $Mn_2(CO)_2(dppe)_2$

7 + 4 + 8

$[Mn(dppe)(CO)_4]^+$ + $[Mn(CO)_5]^-$

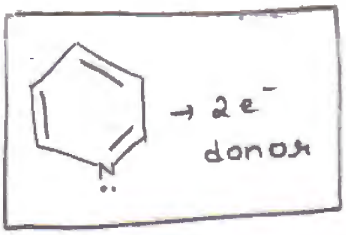
18e⁻ ; 18e⁻

(ii) →

3 $[Mn_2(CO)_{10}]$ + 12 Py $\xrightarrow{120^\circ C}$ $[Mn(CO)_5] + [Mn(CO)_3]$

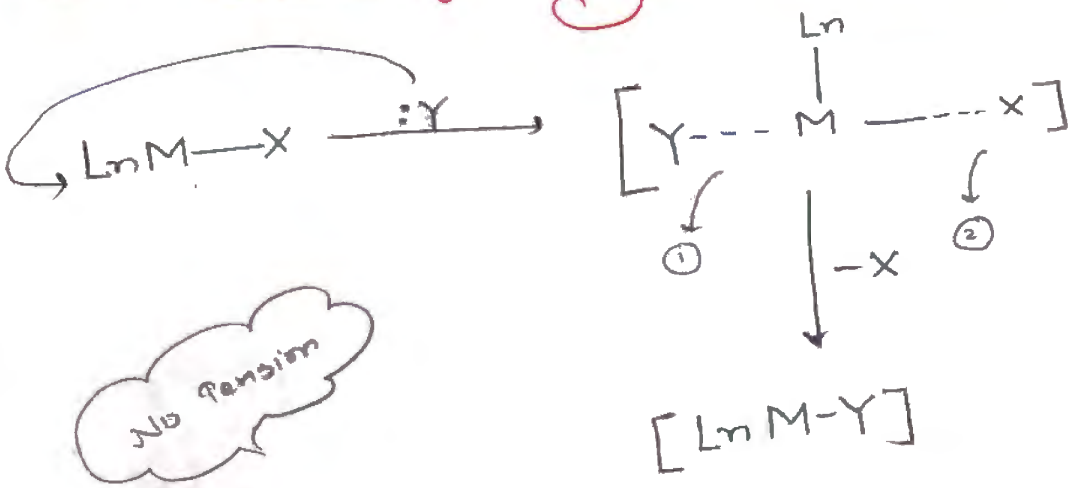
$[Mn(CO)_5]$ —(−CO, +Py)→ $2[Mn(Py)_6]^+ + 4[Mn(CO)_5]^-$

+10 CO



→ 2e⁻ donor

④ → Interchange Mechanism :→



I_d

(Thoda sa evidence)

- Interchange dissociation

I_a

✗ No evidence

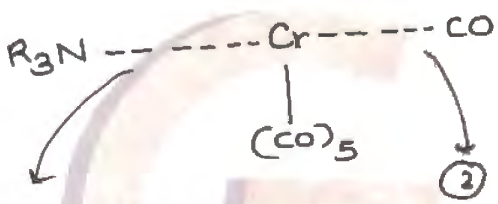
↓

Interchange association

I_d :→

$[Cr(CO)_6] \xrightarrow{:NR_3}$ ~~(CO)~~

$[R_3NCr(CO)_5] \xleftarrow{-CO}$



①

1 bna ya 2 leave

(Penle 2 leave)

thats why it is dissociative.

Q. which mechanism is involved?

Solut $Ni(CO)_4 \xrightarrow[(L = PR_3, NR_3 \ldots)]{:L} [Ni(CO)_3L]$

(a) dissociation

(b) Associatim

(c) Ia

✓ (d) Id

---

③ Metal carbonylate anions:→ $[M_xCO)_y]^{2-}$

① By the reduction of metal carbonyl with strong reducing agent

② By disproportionation

③ By the reaction of metal carbonyl with strong bases

① → Met By Reduction of metal carbonyl with strong reducing agent–

(i) $[Fe(CO)_5] + Na \xrightarrow[-CO]{} [Fe(CO)_4]^{--} \; 2Na^+$

8 + 8 = 16

(ii) - $[Cr(CO)_6] + Na \longrightarrow [Cr(CO)_5]^{2-}\ 2Na^+$

$[Cr(CO)_6]$ (18e⁻)

$[Cr(CO)_5]^{2-}$ (18e⁻) $\xrightarrow[-CO]{Na}$ $[Cr(CO)_4]^{4-}$

8+4+6

(iii) → $[V(CO)_6] \xrightarrow{Na} [V(CO)_6]^-$

$[V(CO)_6]$ 17e⁻ ; $[V(CO)_6]^-$ 18e⁻

$[V(CO)_6]^-$ + E^+ → $[MeV(CO)_6]$

δ^+ δ^- Me-X

$[V(CO)_6]^-$ + H^+ → $[HV(CO)_6]$

Metal hydride complexes

(iv) → $Fe_2(CO)_9 \xrightarrow{Mg}$

$[Fe(CO)_4]^{2-} \cdot Mg^{++} + [Fe(CO)_4]^{2-} \cdot Mg^{++} + CO$

(v) $Fe_3(CO)_{12} \xrightarrow{Mg} 3[Fe(CO)_4]^{2-}\ Mg^{++}$

(vi) → $Co_6(CO)_{16} \xrightarrow{Na} 6[Co(CO)_2]^{5-} + 4CO$

(vii) $Co_2(CO)_8 \xrightarrow{Na} [Co(CO)_4]^- + [Co(CO)_4]^-$

$$[Rh_4(CO)_{12}] \xrightarrow{Na} 4[Rh(CO)_3]^{---} \; 3Na^+$$

2- Disproportionation →

$$3[Mn_2(CO)_{10}] + 12\,PY \longrightarrow Mn(CO)_5 + Mn(CO)_5$$

$-5CO$ ↓ $+6PY$

$$[Mn(PY)_6] + [Mn(CO)_5]$$

$19e^-$ $\qquad$ $17e^-$

$-e^-$ transfer

$$2[Mn(PY)_6]^+ + 4[Mn(CO)_5]^-$$

$18e^-$ $\qquad$ $18e^-$

$$\longrightarrow 2[Mn(PY)_6]^+ + 4[Mn(CO)_5]^-$$

$18e^-$ $\qquad$ $18e^-$

3- Reduction of metalcarbonyl with strong base:→

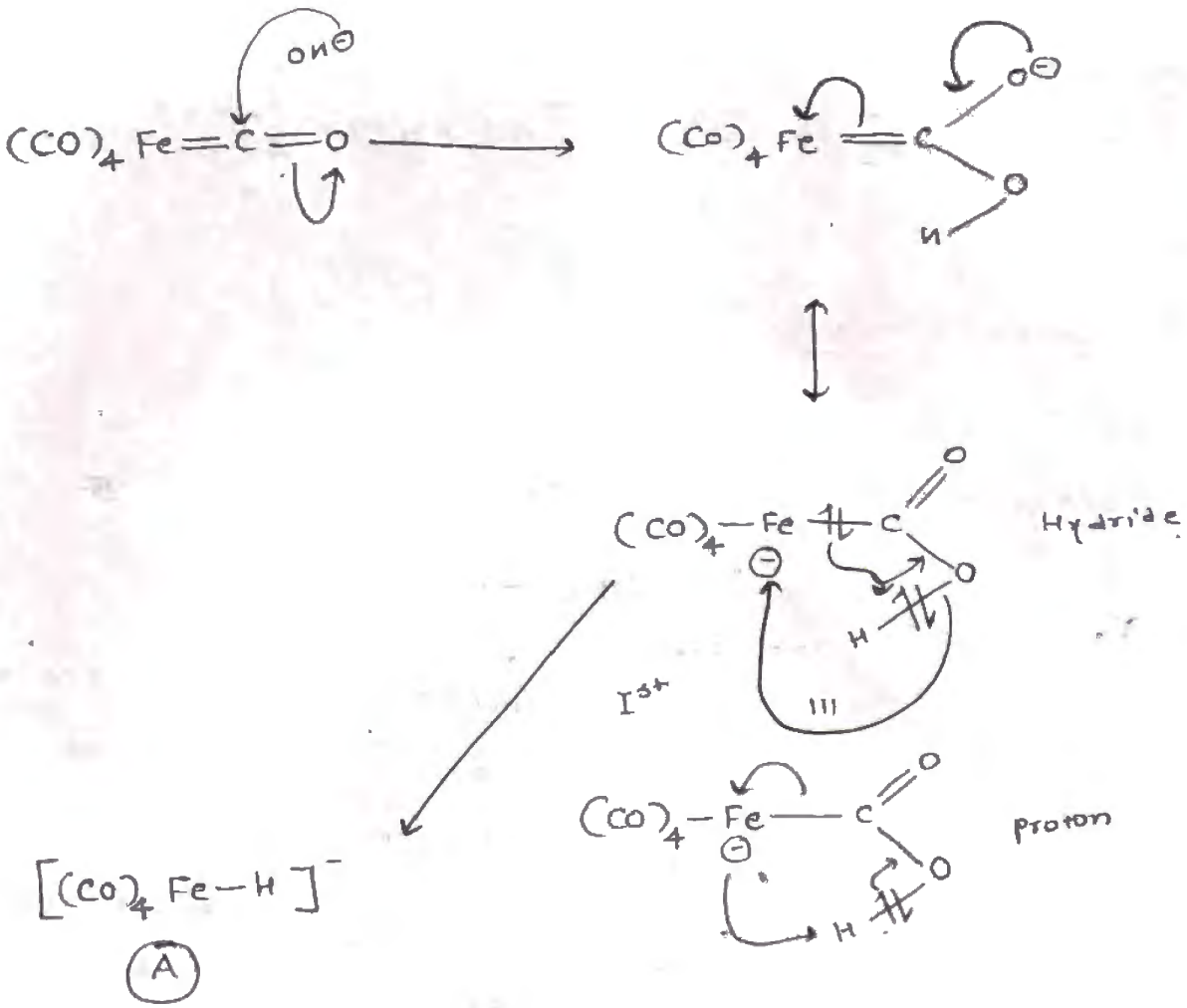
Net 4-Marks

$$[Fe(CO)_5] \xrightarrow{OH^-} A \xrightarrow[KH]{NaH} B$$

$Na^+NH_2^-$

$A \xrightarrow{MnO_2} C$

NET



Same mechanism, if we took $SH^{\ominus}$, instead of $OH^{\ominus}$.

$OH^{\ominus}$ or $SH^{\ominus}$ or Hydride donor reagent

* $NaBH_4$
* $LiAlH_4$
* $LiBH_4$

$[(CO)_4Fe-H]^-$ $\xrightarrow{Na^{\oplus}H^{\ominus}}$ $[Fe(CO)_4]^{--}$ + $2Na^+$

Metal hydride complex ∵ H directly attached.

(A)

(B)

MnO_2 (Specific for allylic, benzylic, propargylic

$[Fe_2(CO)_9]$

$Fe_3(CO)_{12}$

(C)

Properties of metal carbonylate→

Anions:→

$[Fe(CO)_4]^{--}$

$[Ru(CO)_4]^{--}$

$[Os(CO)_4]^{--}$

Nucleophility decrease ↓

① $[M_x(CO)_Y]^{--}$

② [ ]$^{--}$

③ [ ]$^{---}$

② > ① > ③

Order of Basicity

Donating ↓ → Basicity ↓

$[Mn(CO)_5]^-$ —$H^{\oplus}$→ $[H-Mn(CO)_4]$

Basic nature

Metal Hydride complex

Q- when will metal Hydride formation takes place?

① H^{+} ← M

ii) $H^{\ominus}$ → M

- Nucleophillic nature of metal carbonylate ions.

Q- which one will have more acidity?

(i) $[H-Mn(CO)_4]$

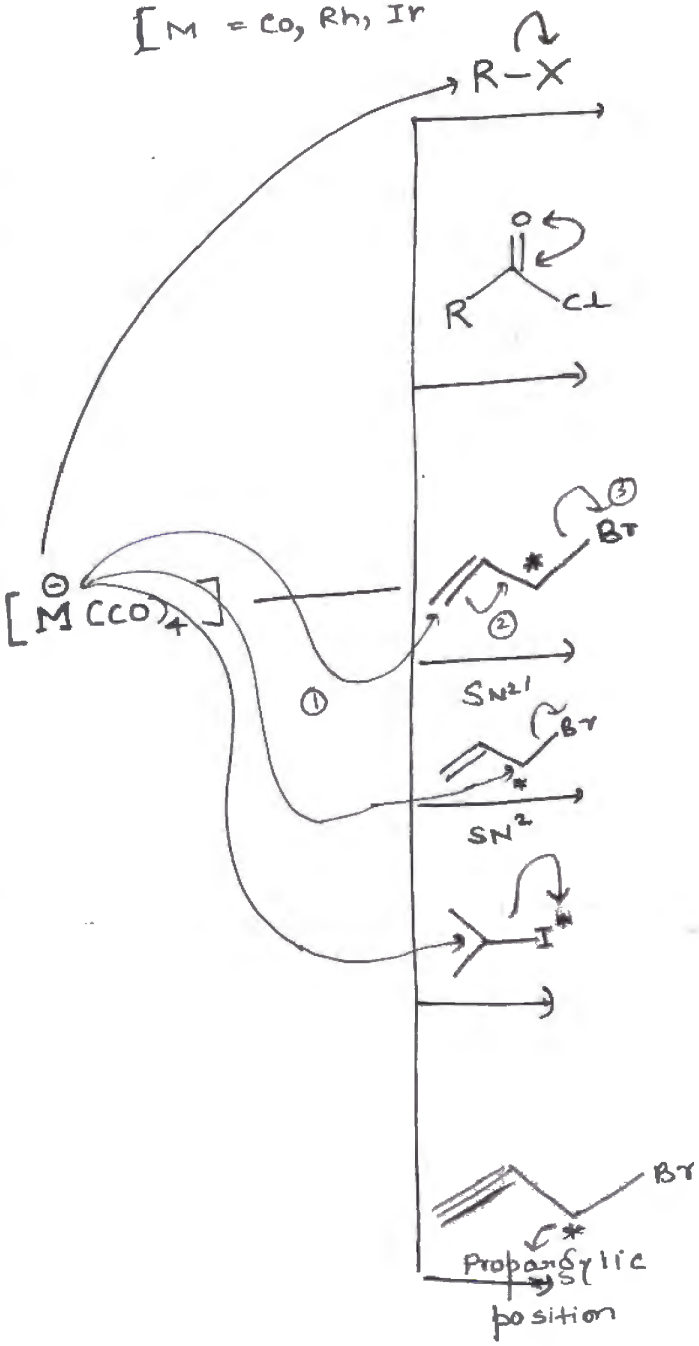
(ii) $[H_2-Fe(CO)_4]$ → ∵ more Hydrogen

(i) $[M(CO)_3]^{---}$

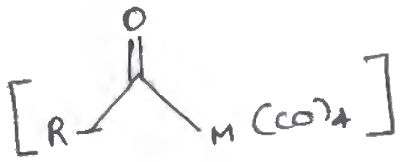
↓

G+3 → 9

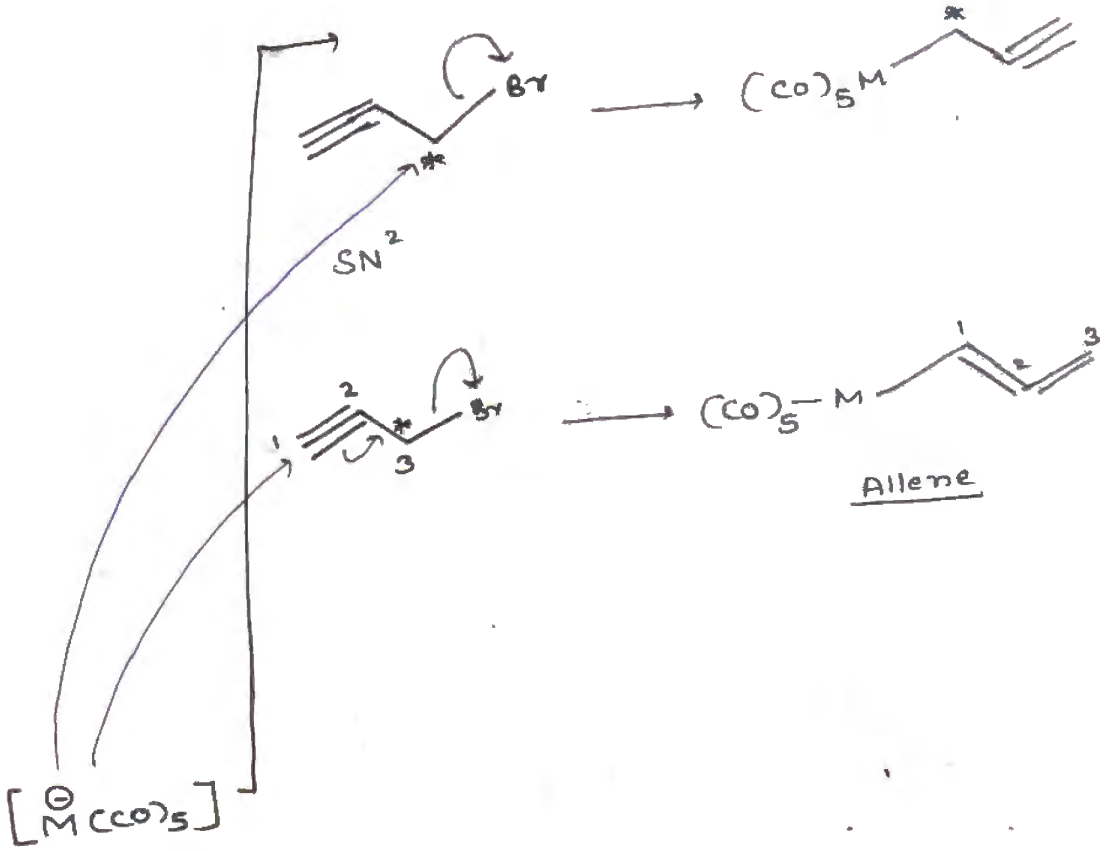
[M = Co, Rh, Ir



$[R-M(CO)_4]$



SN^2' → Bond shifting



Collmann's Reagent →

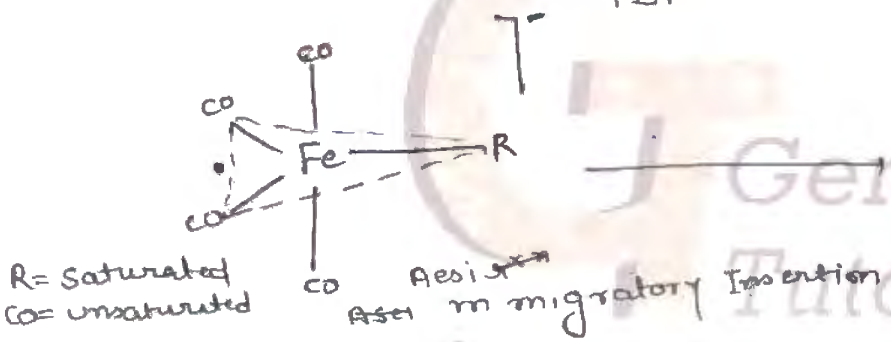
$[Fe(CO)_4]^{--}\ 2Na^+$

$= Na_2[Fe(CO)_4]$

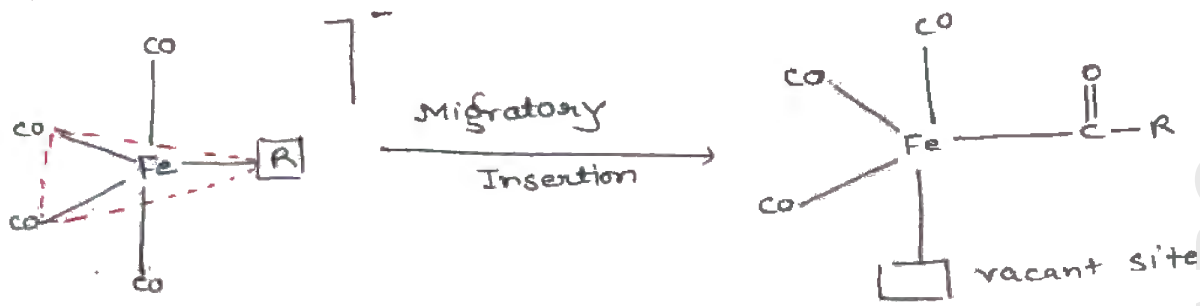
$2Na^+[\overline{Fe(CO)_4}] \xrightarrow{R-X} [R-Fe(CO)_4]^- \equiv$

(85)

TBP



* We carried Migratory Insertion to generate vacant site.

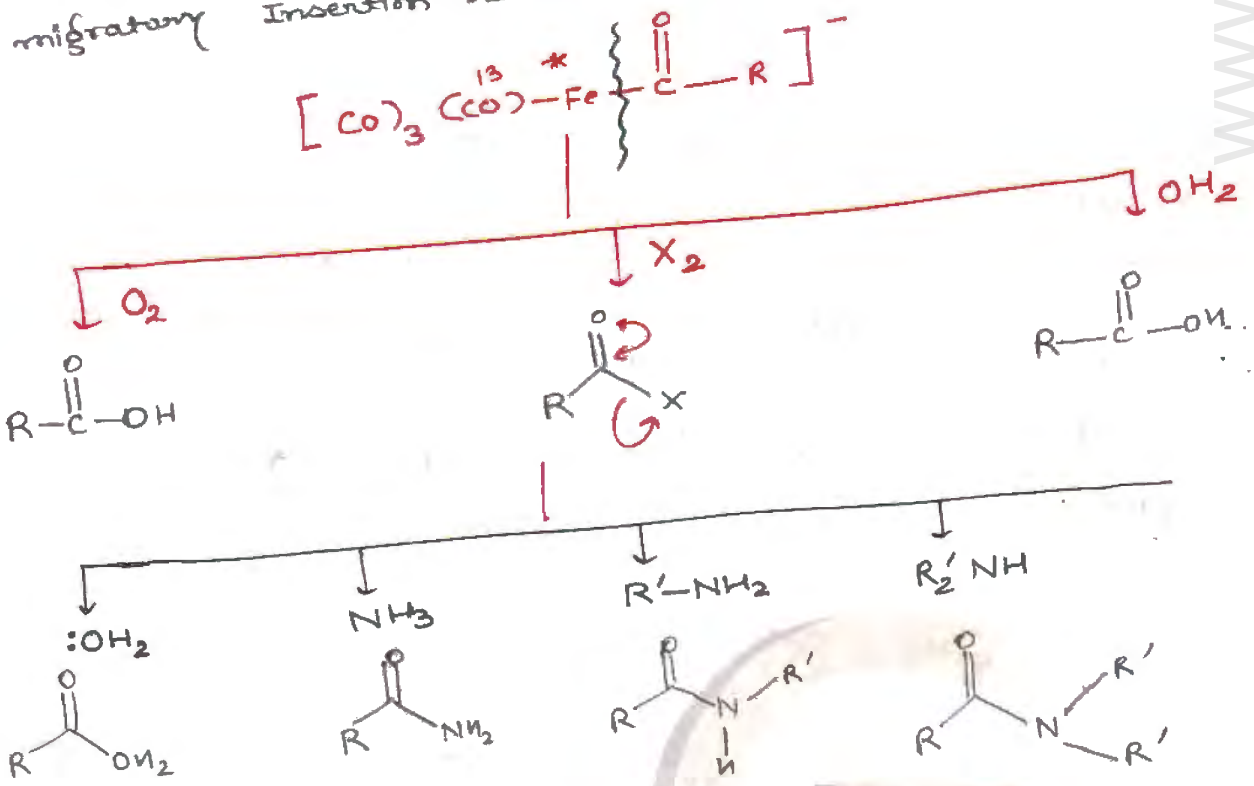


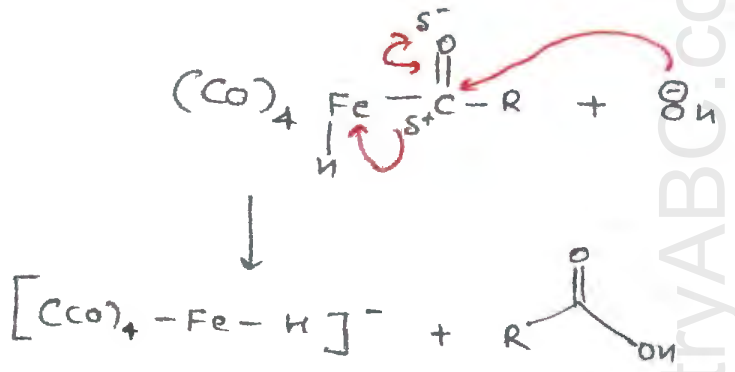
COR - 1 deta h

$: C^{13} \equiv O$

$[Fe(CO)_3(^{13}CO)COR]^*$

- Jab ek saturated & ek unsaturated ligand to migratory Insertion reactions.





Metal Carbonyl Hydrides

MOP →

① - By the acidification of metal carbonylate ions

② - By the reaction of metal carbonyl complexes with Hydride donor reagents, such as $LiAlH_4$, $NaBH_4$,

③ - By the direct addition of molecular H_2 with carbonyl complexes.

④ → from vaska's complex.

Imp

(1) → By the acidification of metal carbonylate anions :→

In presence of

* $[Mn(CO)_5]^-$ ⟶ $[H-Mn(CO)_5]$

$H_2O/H^+ \equiv H_3O^+ \equiv H^+ \equiv$ Any acid ≡ Alcohol (MeOH)

• $[Fe(CO)_4]^{--}$ ⟶ $[H_2Fe(CO)_4]$

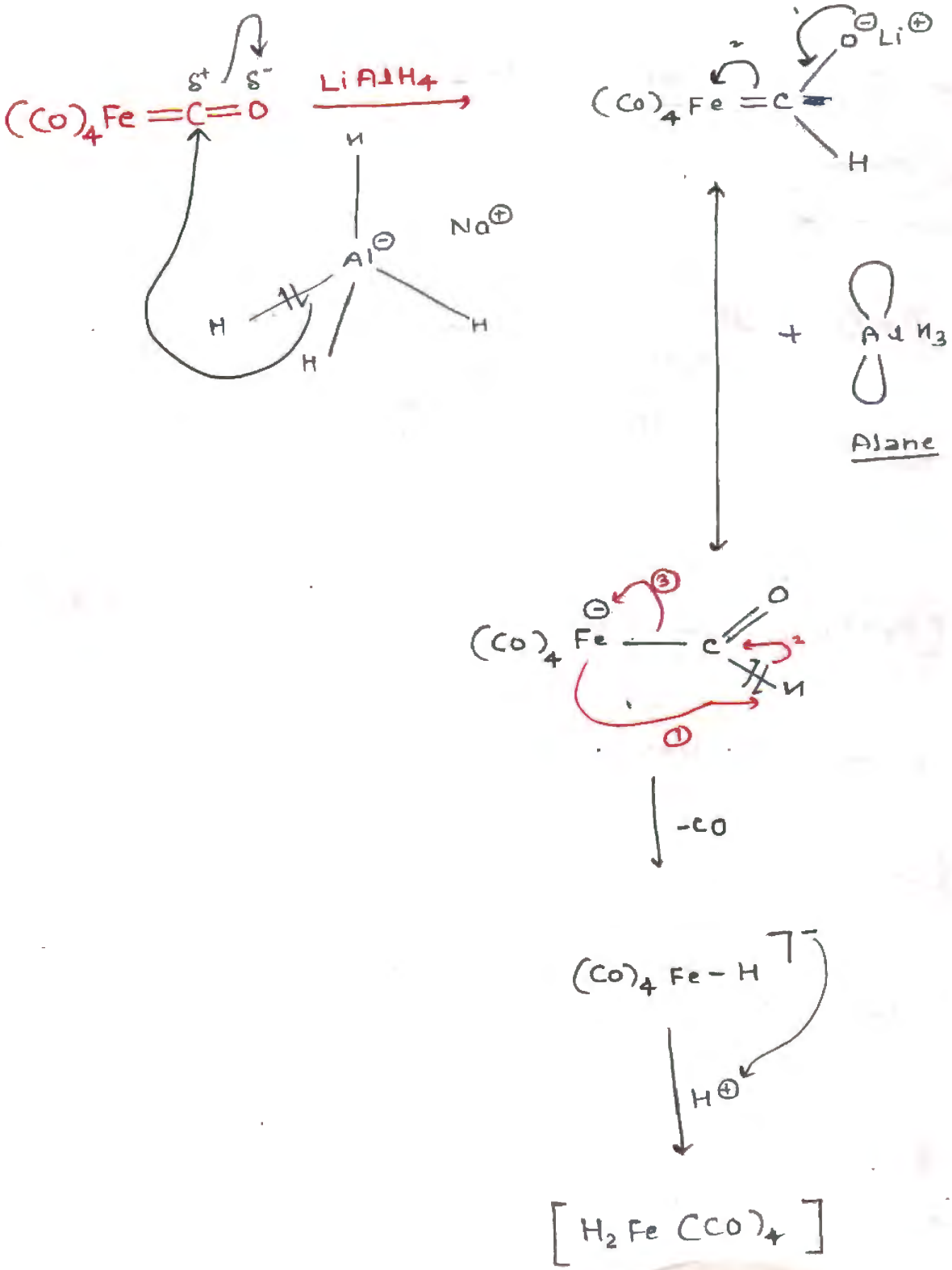
*, • Acts as basic.

• $[Co(CO)_4]^-$ ⟶ $[H-Co(CO)_4]$

• $[Cr(CO)_5]^{--}$ ⟶ $[H_2-Cr(CO)_5]$

(2) → By the

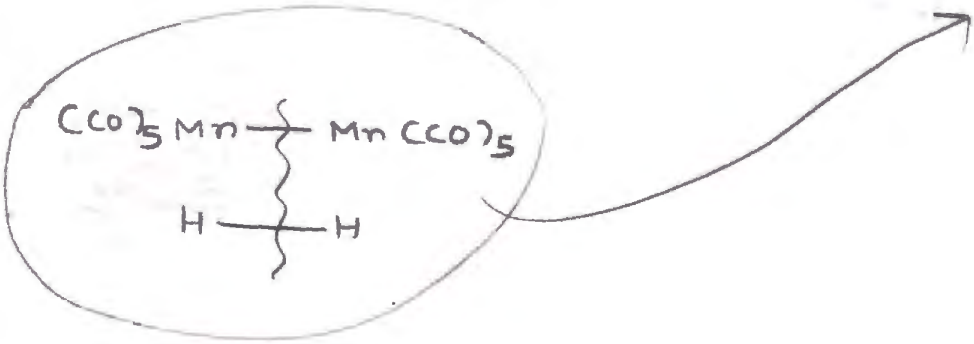
CO)



(3)- By

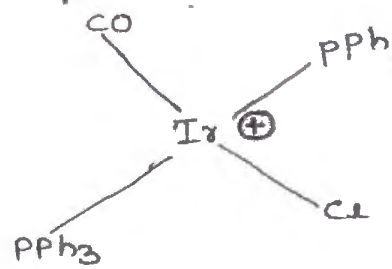
- At least consisting one metal-metal bond

$$Mn_2(CO)_{10} + H_2 \longrightarrow 2[H\,Mn(CO)_5]$$



(4)- from vaska's complex

$$[Ir(CO)(Cl)(PPh_3)_2] \equiv$$



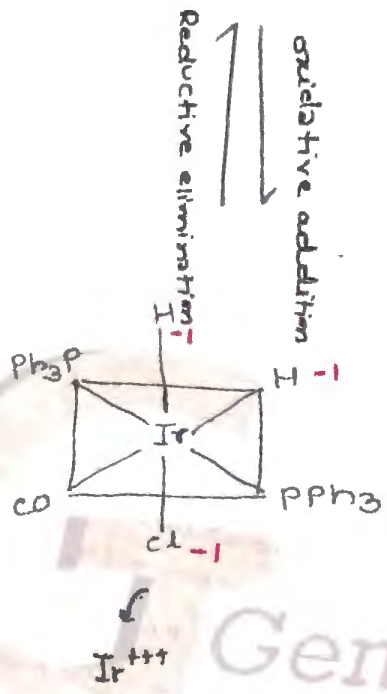
$+ H_2$

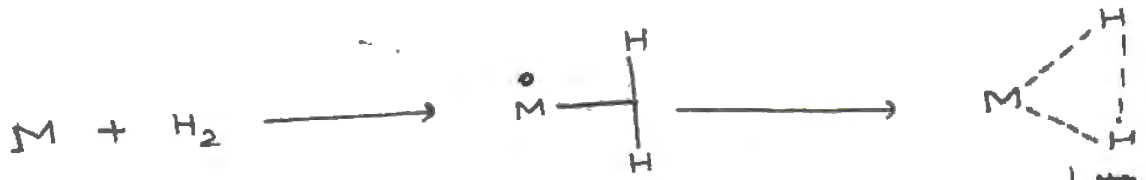
We need Ir +1

* $Ir^I \longrightarrow d^8$
* $CN \longrightarrow 4$
* $dsp^2 \longrightarrow$ Square planar

Agar ligand non-polar to addition hota h

cis





NO-N-classical

Due to addition of three membered transition state, addition of H_2 is always cis.

Classical

- $M(H_2) \rightarrow M^{0}$
- $M(H)_2 \rightarrow M^{+2}$

Ir^{+}

* d^8
* C.NO = 4
* $16e^-$
* dsp^2
* coordinatively unsaturated complex (CO)
* square planar

Ir^{+++}

d^6

C.N = 6

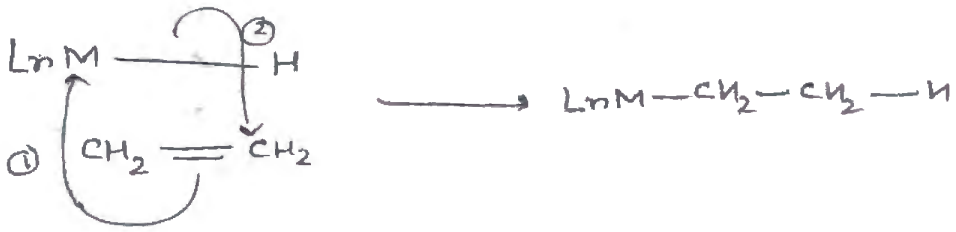
$18e^-$

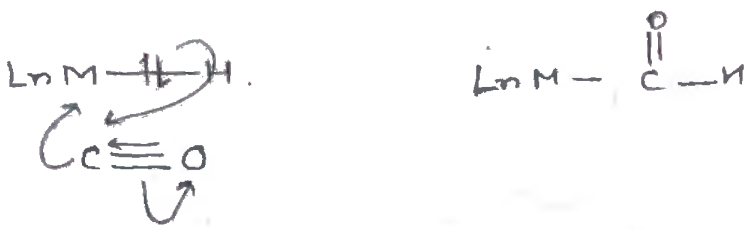
sp^3d^2 / d^2sp^3 one hybrid

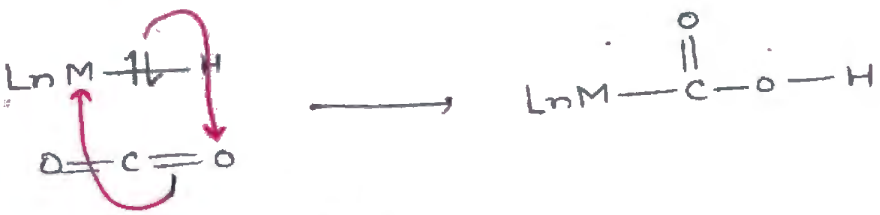
* Co-ordinatively saturated. (H^-)
* octahedral

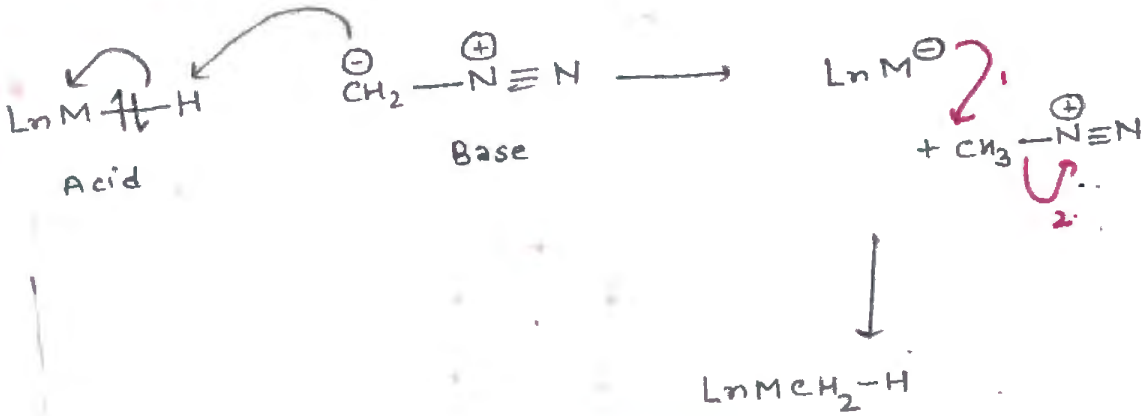
Insertion Reactions :→

(i). $LnM-H$ + $CO / CO_2 / CH_2N_2 / = / \equiv$

(i) 

(ii) 

(iii) 

(iv) 

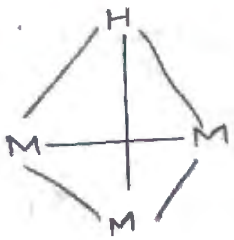
14/oct/2016

Bonding of Metal hydrides →

(I)

(II)

(3c-2e⁻)

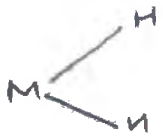


III

(4c-2e⁻)

(IV)

Non-classical Bonding

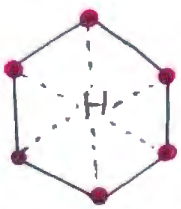


classical bonded

(V)

concerted Mechanism

● - Metal



Encapsulated

(μ₆-H)

→ Encapsulated Hydride

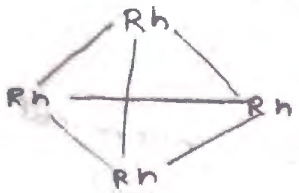
* 18 e⁻ Rule ≤ 4
* $M > 4 \rightarrow$ 18 e⁻ rule donot followed.

Prob-3 →

$$Rh_4(CO)_{12} \longrightarrow Rh_6(CO)_{12}$$

M-M = 6

B/M = 3



M-M = 12

B/M = 4

Kam bond s jada bond.
Bond break = Endothermic.

When cluster carbonylate anions are protonated a hydride ligand is encapsulated (thats why we only need one hydride) by a framework of metal atoms i.e. to form intersitial & e

$$[Co_6(CO)_{15}]^{--} \xrightarrow{H^+} [H\,Co_6(CO)_{15}]^{-}$$

Interstitial

Prob-15

$$Fe_3(CO)_{12} \longrightarrow [Fe(CO)_4]^{--} + [Fe(CO)_4]^{--}$$

$$\downarrow$$

$Fe^{--} \rightarrow 8+2 = 10$ + $[Fe(CO)_4]^{--}$

So ten wala dhudho
To Ni m ten h so,

Isolobal Analogies →

Iso = same

Isoelectronic = having same no of e⁻s.

Isostructure = " " hybridization

Isolobal = same less no of electrons.

- The species which have same less no of e⁻s from its valence shell are known as Isolobal fragments / clusters / species.
- These species have similar physical & chemical properties & denoted by a double headed tear drop (⟷)

Main Group ⟷ Transition elements

↓ ↓

Octet rule ⟷ 18 e⁻ rule

8-e⁻ ⟷ (18 - e⁻s)

8 ⟷ 18

7 ⟷ 17

6 ⟷ 16

5 ⟷ 15

4 ⟷ 14

} same e⁻ less

Prob - 16

(a) $CH_2 \longleftarrow \circ \longrightarrow Mn(CO)_4$

$6 \longleftarrow \circ \longrightarrow 15$

$8-6$ $\quad$ $18-15$

(2) $\quad$ 3

(b) $CH \longleftarrow \circ \longrightarrow Fe(CO)_4$

5

$4+1$ $\quad$ $8+8$

5 $\quad$ 16

(c) $CH_2 \longleftarrow \circ \longrightarrow Ni(CO)_2$

$4+2$ $\quad$ $10+4$

6 $\quad$ 14

$8-6$ $\quad$ $18-14$

2 $\quad$ 4

(d) $CH \longleftarrow \longrightarrow Co(CO)_3$

$4+1$ $\quad$ $9+6$

5 $\quad$ 15

$8 = CH_4$	$CH_3 = 7$	$CH_2 = 6$	$CH = 5$	$C = 4$
$Ni(CO)_4$	$Mn(CO)_5$ ✓	$Fe(CO)_4$	$[Co(CO)_3]$	$Fe(CO)_3$
$Fe(CO)_5$	$Co(CO)_4$	$Cr(CO)_5$	$Mn(CO)_4$	$Cr(CO)_4$
$Cr(CO)_6$	$[Fe\ Cp(CO)_2]$	$Ni(CO)_3$	$Cr(CO)_2Cp$	$Ni(CO)_2$
$^-CH_3$	H ✓	S	$NiCp$	$Co\ Cp$
	$^-CH_2$ ✓	^-CH	P	^+CH.
		$^+CH_3$	$^+CH_2$	
		~~Eee~~		
		$[Co(CO\ Cp]$		
	Hydrogen wale m, Ek ko (-) krege	$(8-1)=7$		

Wade - Mingo's Rule →

- Boranes & carboranes
- Higher Nuclear carbonyl complexes (HNCC)
  - TEC-PEC Method
  - 14n series
- Zintle ions → 4n series

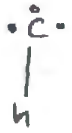
(n-1)	≡ 4n-2	≡ 14n-2	≡ $(BnHn)^{n-}$ → $(BnHn)^{+2}$	super closo / super Hyper closo
n	≡ 4n	≡ 14n	≡ $(BnHn)^{0}$	→ Hyper closo
(n+1)	≡ (4n+2)	≡ (14n+2)	≡ $(BnHn)^{2-}$	closo closed
(n+2)	≡ (4n+4)	≡ (14n+4)	≡ $(BnHn)^{4-}$	Nido (Nest)
(n+3)	≡ (4n+6)	≡ (14n+6)	≡ $(BnHn)^{6-}$	Arachno (spider's web)
(n+4)	≡ (4n+8)	≡ (14n+8)	≡ $(BnHn)^{8-}$	(Net) Hypho (Net)
(n+5) ← Carborane / Borane &	≡ (4n+10) ↓ zintle	≡ (14n+10) HNCC	≡ $(BnHn)^{10-}$	clado / conjuncto (Joined subunits)

Wade's Mingo for Carboranes & Boranes

$B_2H_6 \longrightarrow (B_nH_n)^{4-}$

$(B_2H_2)^{4-} \longrightarrow$ Nido

(i) BH ⟶ 2e⁻ only (donor) , (ii) CH = (3e⁻ donar)



(iii) ± charge (iv) Interstisial aton

H = 1

(i) $B_2H_6 \Rightarrow B_2H_6 + 4H$

(BH_2)

$(BH)_2 + 4H$

$2 \times 2 + 4 \times 1$

$4 + 4 =$ 8 ⟶ Pair ⟶ (4)

∴ n = 2 (Boron)

So to make it 4

(n+2).

eg. $(C_2B_7H_{13})$ → carboranes

$(CH)_2 + (BH)_7 + 4H$

↓

$3\times2 + 2\times7 + 4\times1$

$6 + 14 + 4$

(24) ⟶ pair (12)

~~∴ n = 9 (7+2)~~

So (9+3) ⇒ (n+3) ⇒ Arachno.

STYX code

---

1. $(B_{12}H_{12})^{2-}$ - closo

2- $C_2B_{10}H_{12}$ $(CH)_2 + (BH)_{10}$

$3\times2 + 2\times10$

$6 + 20 = 26 = 13$

$n = 12$ $(n+1) =$ closo

3- B_2H_6

$(B_2H_2)^{4-}$ Nido

(4) !

(4) B_4H_{10}

$[B_4H_4]^{-6}$ → Arachno

(5) B_5H_9 = $[B_5H_5]^{4-}$ = Nido ✓✓ (Y)

(6) B_5H_{11} = $[B_5H_5]^{-6}$ Arachno

(7) B_6H_{10} = $[B_6H_6]^{-4}$ → Nido

(14) $C_2B_4H_{11}^-$

$(CH)_2 + (BH)_4 + 5H + 1$ → -ve charge

$3\times2 + 2\times4 + 5 + 1$

$6 + 8 + 5 + 1$

$= 20$

↳ pair (10)

$\because n = 2 + 4 = 6$

$\Rightarrow (n+4)$ = (Hypho)

(8) $[B_{10}H_{14}]$

$[B_{10}H_{10}]^{-4}$ = Nido

(9) → $C_2B_7H_{13}$

$(CH)_2 + (BH)_7 + 4H$

$2\times3 + 7\times2 + 4\times1$

$6 + 14 + 4$

24 pair = 12

$n+3$ = Arachno

- Ya to total e^- count kro, then pair the $n+x$ then

Is se
$n-1$
n
$n+1$
$n+2$
$n+3$
$n+4$
$n+5$

(15) → P_4

$P = 5\ e^- = \underline{BH_2}$

$P_4 = (BH_2)_4 = [B_4H_8]$

$[B_4H_4]^{-4}$ = Nido

	(BH)	(BH_2)	(BH_3)
Valency	4	5	6
	C	N	O
	Si	P	S
	Ge	As	Se
	Sn	Sb	Te
	Pb	Bi	Po

Can be replaced by above

(16) closo $CB_4H_5^-$

$(CH) + (BH)_4 + 1$

$1\times3 + 2\times4 + 1$

$3 + 8 + 1$

$= 12$ pair = 6 $n+1$ closo

(11) $C_2B_4H_7^-$

$= (CH)_2 + (BH)_4 + H + 1$

$= 3\times2 + 2\times4 + 1 + 1$

$6 + 8 + 1 + 1$

$= 16$

$= 8$

$(n+2)$

= Nido

Ya to replace kro Sbko BH ki form m then apply $(B_nH_n)^{+2}$

0
-2
-4
-6

(12) - $C_2B_4H_8$

$(CH)_2 + (BH)_4 + 2H$

$= 3\times2 + 2\times4 + 2\times1$

$= 6 + 8 + 2$

$= 16 \longrightarrow$ pair = 8

$n = 6$

$\Rightarrow n+2 =$ Nido

$C_2B_4H_8$

$(BH)_2\ B_4H_8$

$B_2H_2\ B_4H_8$

B_6H_{10}

$B_6H_6^{-4}$

Nido

(13) $C_2B_4H_{10}$

$(CH)_2 + (BH)_4 + 4H$

$3\times2 + 2\times4 + 4\times1$

$6 + 8 + 4$

$18 \longrightarrow$ Pair = 9

$n = 6 \Rightarrow n+3$

Arachno

$C_2B_4H_{10}$

$(BH) + B_4H_{10}$

B_5H_{11}

$(B_5H_5)^{-6}$

Aracho

Wade- Mingo's Rules for HNCC →

- TEC- PEC
- 14n series

TEC- PEC → Total electron count + Polyhedral e^- counts

TVE = e^- provided by the free metal + e^- contributed by the surrounding ligands ± charge + e^- contributed by interstitial metal.

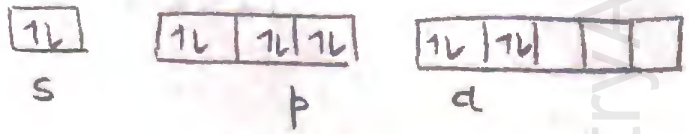
N = 5	e.g., (C = 4)	B = 3
P	Si	Al
As	Ge	Ga
Sb	Sn	In
Bi	Pb	Tl

PEC = Polyhedral e⁻ count ✓ ✓

PEC = TEC − 12n

Step - I → Calculate TEC

Step - II → PEC = TEC − 12n



Step -III → B PEC/2 = (n−1)
n
(n+1)
(n+2)
(n+3)
(n+4)

TEC-PEC Method →

- Calculate TEC
- Then PEC = TEC − 12N
- PEC/2

e.g. $Os_8(CO)_{23}$ →

TEC-PEC

Step-1 → 8×8 + 46
64 + 46
= 110

Step-2 - 110 − 12×8
110 − 96
14

Step - 14/2 = 7

∵ n = 8

⇒ (n−1) = Super Hyper closo

14n

TVE = 110

⇒ 14n = 14×8 = 112

TVE - 14n
110 − 112 = −2

⇒ (14n − 2) = 110

14×8 − 2 = 110

Super Hyper closo

(2) - $Os_6(CO)_{18}$

TVE = 8×6 + 36

= 48 + 36

= 84

∵ 14n 14×6 = 84 → Hypercloso

(3) $[Os_5C(CO)_{15}]$

TVE = 5×8 + 4 + 30

= 74

=

14×n = 14×5

= 70

⇒ 14n+4 = Nido

TEC-PEC

TEC = 5×8 + 4 + 30

= 74

PEC = 74 − 60 = 14

$\frac{PEC}{2} = \frac{14}{2} = 7$

⇒ ∵ n = 5

⇒ (n+2) = Nido

(4) $[Rh_6(CO)_{16}]$

TVE = 9×6 + 32

= 54 + 32

86

14n = 14×6 = 84

14n+2 = Closo

TEC-PEC

TEC = 5×8 + 4 + 30

= 74

PEC = 74 − 72 = 2

(5) $[Ni_5(CO)_{12}]^{2-}$

TVE = $10 \times 5 + 24 + 2$

$= 50 + 24 + 2$

$= 76$

$14 \times n = 14 \times 5 = 70$

$\Rightarrow 14n + 6 =$ Arachno

(6) $[C_6(CO)_{16}]$

TVE = $9 \times 6 + 32$

$= 54 + 32$

$= 86$

$14n = 14 \times 6$

$= 84$

$(14n + 2) =$ closo

(7) $[Ru_6C(CO)_{17}]$

TVE = $6 \times 8 + 4 + 34$

$= 48 + 4 + 34$

$= 86$

$14n = 14 \times 6$

$= 84$

$14n + 2 =$ closo

(8)- $[Ru_5 N (CO)_{14}]^-$

TVE = 5×8 + 5 + 28 + 1

= 40 + 5 + 29

= 74

40
5
29
4

14n = 14×5

= 70

14n + 4

Nido

(9) $[Fe_4 C (CO)_{12}]^{2-}$ ⇒

TVE = 8×4 + 4 + 24 + 2

= 32 + 4 + 24 + 2 = 62

14 + n = 14×4 = 56

(14n + 6) Arachno

(10) → $[Os_5 (CO)_{16}]$

TVE = [8×5 + 32]

= 40 + 32

= 72

14n = 14×5

70

(14n + 2)

closo

(11) → $[OS_5(CO)_{15}]^{2-}$

TVE = (5×8 + 30 + 2)

= 40 + 32

= 72

14n = 14 × 5

70

14n+2 = c10so

(12) → $[HOS_5(CO)_{15}]^{-}$

TVE = 1 + 40 + 30 + 1

= 72

14n = 14 × 5

= 70

14n+2 = c10so

(13) → $[H_2OS_5(CO)_{15}]$

TVE = 2 + 40 + 30

= 72

14n = 14 × 5 = 70

14n+2 = c10so

(14) $[Ru_5C(CO)_{16}]$

TVE = 40 + 4 + 32

= 76

PEC = 76 − 12×5

76 − 60

16

$\frac{PEC}{2} = \frac{16}{2} = 8$

Arachno

14n (Y)

76

14×5

70

n+2
n+6
n+6

n+6

Arachno

(15) $[Os_6(CO)_{18}]^{--}$

TEC = 48 + 36 + 2 = 86

PEC = 86 − 72

= 14

$\frac{PEC}{2} = \frac{14}{2} = 7$

n+1

Closo

14n

14×6

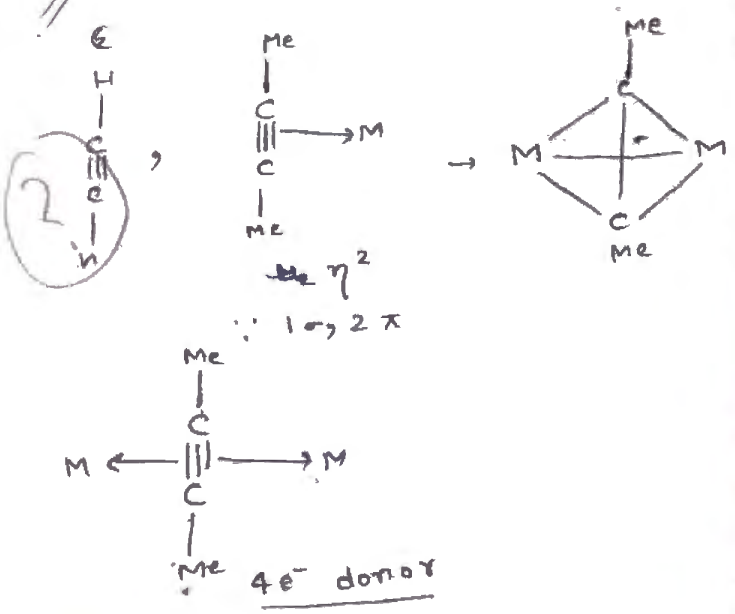
= 84

TEC = 86

14n + 2

Closo

(16) → $[Os_4(CO)_{12}(\mu_4\text{-}C_2Me_2)]$



TEE = 32 + 24 + 4 = 60

PEC = 60 − 12×4 = 12

$\frac{PEC}{2}$

$\frac{12}{2} = 6$

n+2 ⇒ Nido

TEC = 60

14n = 56

14n + 4

Nido

(17) $[Os_6(CO)_{17}\{P(OMe)_3\}_2]$

TEC = 48 + 34 + 2×2

= 86

PEC = 86 − 72 = 14

$\frac{PEC}{2} = \frac{14}{2} = 7$

TEC = 86

14n = 14×6 = 84

14n − 2

14n

14n + 2

(18) $[Os_4N(CO)_{12}]^-$

TEC = 32 + 5 + 24 + 1

= 62

PEC = 62 − 12

Wade's Mingos Rule for Zintle Ion

{= Naked clusters}

clusters of main group elements are known as zintle ions or naked clusters

(i) Pb_5^{2-}

(ii) Sn_9^{4-}

(iii) Sb_4^{2-}

(iv) Sn_4^{2-}

(v) Ge_4^{2-}

(vi) Bi_3^{3-}

(vii)- Sn_5^{2-}

(viii) Bi_5^{3+}

(ix) Te_6^{2+}

(x) Sb_7^{3-}

① Pb_5^{2-}

TVE = $5 \times 4 + 2$

$= 22$

$\because 4n = 4 \times 5 = 20$

$\Rightarrow 4n+2$, closo

② Sn_4^{4-}

TVE = $4 \times 4 + 2 = 18$

$4n = 4 \times 4 = 16$

$4n+2 =$ closo

③ Ge_4^{2-}

TVE = $4 \times 4 + 2 = 18$

$4n = 4 \times 4 = 16$

$4n+2 =$ closo

② Sn_9^{4-}

TVE = $9 \times 4 = 36 + 4$

$4n = 4 \times 9 = 36$

$4n+4$ ⇒ Nido

⑥ Bi_3^{3-}

TVE = $5 \times 3 + 3 = 18$

$4n = 4 \times 3 = 12$

$4n+6$ Arachno

Zintle Ion

K Liye

4n

⑦ Sn_5^{2-}

TVE = $4 \times 5 = 20 + 2 = 22$

$4n = 4 \times 5 = 20$

$4n+2$ ∴ closo

⑧ → Bi_5^{3+}

TVE = $5 \times 5 - 3 = 22$

$4n = 20$

~~TVE - 4n~~ = $4n+2$, ∴ closo

⑨ Te_6^{+2}

TVE = $6 \times 6 - 2 = 34$

$4n = 4 \times 6 = 24$

TVE − 4n = 10

$4n+10$ ∴ conjuncto / Klado.

(10) → Sb_7^{3-}

TVE = $5 \times 7 = 35 + 3 = 38$

$4n = 4 \times 7 = 28$

TVE $- 4n = 38 - 28 = 10$

$4n + 10$ ∴ conjuncto

Concept of PSEPT →

Polyhedral skeleton Electron pair theory

~~TEC-12~~ = TEC-12

TVE-12 ↙ non-skeletal

NO of valence e^- provided by the fragments = TVE-12 or TEC-12

or, $\chi = V + n - 12$

V = valence shell e^- provided by the

n = valence shell e^- by ligand.

2.

Cluster fragement	Group-6 M=Cr, Mo, W	Group 7 M=Mn, Tc, Re	Group 8 M=Fe, Ru, Os	Group 9 M=Co, Rh, Ir
$M(CO)_2$	-2	-1	0	1 (9+4-12 = TRE -12)
$M(CO)_3$	0	1	2	3
$M(CO)_4$	2	3	4	5
$M(\eta^5\text{-}Cp)_2$ Metallacene ↓ Metallocene fragment+ $M(\eta^5\text{-}Cp)$	-1	0	+1	+2
$M(\eta^6\text{-}C_6H_6)$	0	1	2	3
$M(CO)_2(PR_2)$	1	2	3	4

Prob-1 →

B_2H_6 ⟷ $[OS_6(CO)_{18}]^{--}$

$[B_2H_2]^{4-}$

↓

Nido

Not isolabal

$8\times6 + 18\times2 + 2 = 86$

$14n = 14\times6 = 84$

$14n+2$

closo

B_6H_8 ←o✓→ $[Ru_6(CO)_{18}]^{--}$

$[B_6H_6]^{2-}$ ←o→

TVE = 84

$14n = \frac{84}{2}$

Closo

Closo

Problem-3

$B_3H_7[Fe(CO)_3]_2$

$B_3H_7[14]_2$

$B_3H_7[BH]_2$

$= B_5H_9$

$[B_5H_5]^{-4}$

= Nido

18 ←o→	8 ←→	BH_5
17 ←o→	7 ←o→	BH_4
16 ←o→	6 ←o→	BH_3
14 ←o→	4 ←o→	BH
15 ←o→	5 ←o→	BH_2

Prob- S_8 $[BH_3]_8$

B_8H_{24} ✗

B = B_{12} → Icosahedron

S = S_8 → crown

P = P_4 → Tetrahedral

Prob →

(I)- $[Fe(CO)_4]$ ←o→ $[Cp\,Fe(CO)]^-$ ←o→ $[CpRh(CO)]$

True

(II)→ CH ←o→ P , As ←o→ BH^{--}

(CH ↓ 5, P ↓ 5, As ↓ 5, BH^{--} ↓ 6)

False

(III) CH_2 ←o→ $[Fe(CO)_4]$ ←o→ SiH_2

6 ←o→ 16 ←o→ 6

6 ↓o 16

SiH_2 ↓o $[Ru(CO)_4]$

True

(IV)→ $[HCo_6(CO)_{15}]^-$ ←o→ $[Fe_5(CO)_{15}]^{4-}$

$[HCo_6(CO)_{15}]^-$ ↓ closo

$[Fe_5(CO)_{15}]^{4-}$ ↓ Nido

$[Fe_5(CO)_{15}]^{4-}$ ↕o $[B_5H_5]^{4-}$

$[B_5H_5]^{4-}$ ↓ Nido

False.

(V)→ $[HCo_6(CO)_{15}]^-$ ←o→ $[Co_6(CO)_{15}]^{--}$ → closo

$[HCo_6(CO)_{15}]^-$ ↓ closo

TVE = 48 + 32 + 2

82

14n = 14 × 6 = 84

$[Co_6(CO)_{15}]^{--}$ ↕o $[Fe_6(CO)_{16}]^{2-}$

$[Fe_6(CO)_{16}]^{2-}$ ↕ $[B_6H_8]$ → closo

(2) SM.C mine ~~super hyper closo~~

(I) → $CH_3 \leftarrow\!\!\circ\!\!\rightarrow \bar{B}H_3 \leftarrow\!\!\circ\!\!\rightarrow [Fe(CO)_5]^+ \leftarrow\!\!\circ\!\!\rightarrow [Mn(CO)_5]$

(II) $\overset{+}{C}H_3 \leftarrow\!\!\circ\!\!\rightarrow BH_3 \leftarrow\!\!\circ\!\!\rightarrow [Cr(CO)_5]^- \leftarrow\!\!\circ\!\!\rightarrow [Mn(CO)_5]^+$

(III) $\overset{+}{C}H \leftarrow\!\!\circ\!\!\rightarrow [Fe(CO)_3] \leftarrow\!\!\circ\!\!\rightarrow CoCp \leftarrow\!\!\rightarrow [NiCPR_3)_2]$

(IV) $[NiCCO_3] \leftarrow\!\!\circ\!\!\rightarrow CH_2 \leftarrow\!\!\circ\!\!\rightarrow \overset{+}{C}H_3 \leftarrow\!\!\circ\!\!\rightarrow CH_2$

(I), III & IV are correct but, IInd is wrong

Metal carbonyl Halide complexes → (63)

carbonyls → $NU^{\ominus}$ → Metal carbonylate anion like $[Fe(CO)_4]^{--}$

carbonyls → $E^{\oplus}$ → Metal carbonyl halide complex

$[M_x(CO)_y]^{z-}$ → Metal carbonylate anion = $[M^{z-}]$

e.g. $[Mn(CO)_5]^- = [Mn^-]$ $[Mn^-(CO)_5] \rightarrow NU^-$

$[(CO)_5Mn^-Cl] \rightarrow EU^{\oplus}$

Methods

① - By the reaction of metal carbonyl with halogen or breaking Metal-metal bonds

- $Mn_2(CO)_{10} \xrightarrow{X_2} Mn(CO)_5X + Mn(CO)_5X$

- $(CO)_5Mn\{-Mn(CO)_5$ (X bridging)
  18e⁻ 18e⁻

- $[Co_2(CO)_8] \equiv (CO)_4Co\{-Co(CO)_4$ (X bridging)

  we took so with form

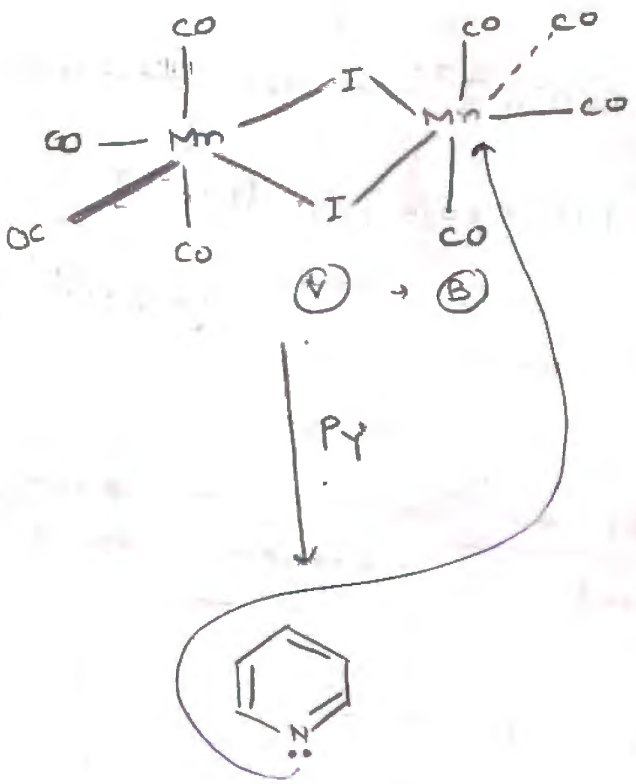
  $= [Co(CO)_4X]_2$

Prob-18 →

$Mn_2(CO)_{10} \xrightarrow{I_2} 2[Mn(CO)_5 I]$

(A) II

$\xrightarrow[120°C]{-CO,\ \Delta}$



(V) → (B)

$\xrightarrow{Py}$

$[Py\text{-}Mn(CO)_4]$

(C)

Method-II → By the direct reaction of metal halides with CO.

$2MCl_2 + 2CO \longrightarrow [M(CO)Cl_2]_2$

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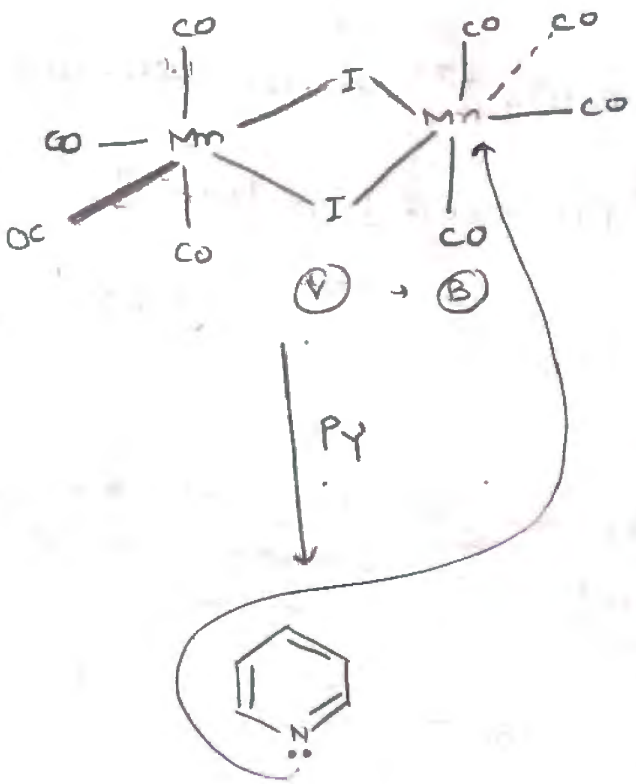

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