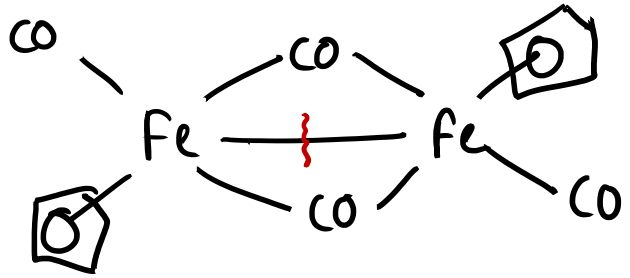
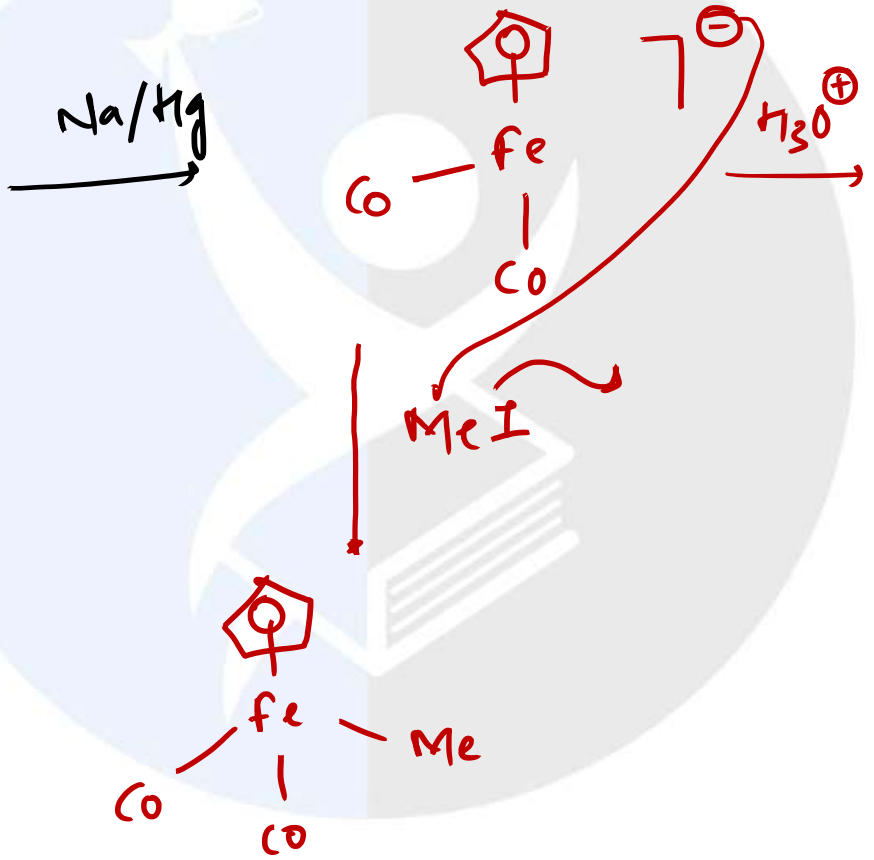
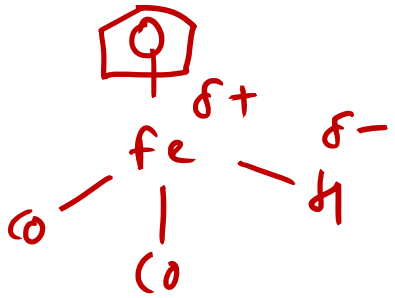
① Metalates:

① $[Fe_2(CO)_4(\eta^5\text{-}Cp)_2] + Na/Hg \xrightarrow[e^{\ominus}]{\text{Gain of}}$ (A)





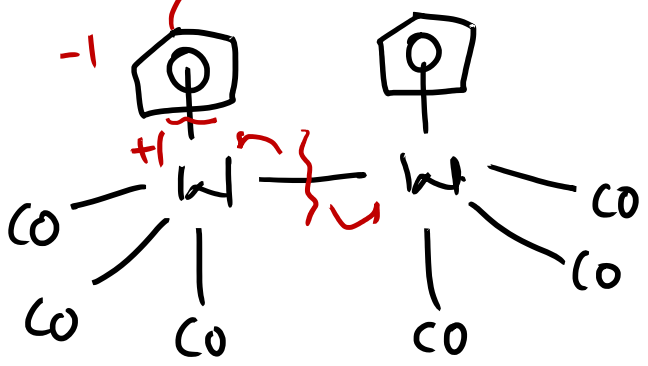


Metal Hydride, $18e^{\ominus}$

Chemical Shift = −ve

(Q) $[W_2(\eta^5\text{-}Cp)_2(CO)_6]$ $\xrightarrow{Na/Hg}$ (A) $\xrightarrow{Br_2}$ (B)

$5\pi e^\ominus + 1\pi e^\ominus = 6\pi e^\ominus$

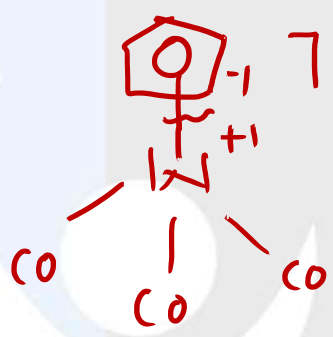


$18\,e^\ominus$

$W = +1$

$\{\eta^5\text{-}Cp \rightarrow (\eta^5\text{-}C_5H_5)\}$

Na/Hg → Reduction



$18\,e^\ominus$

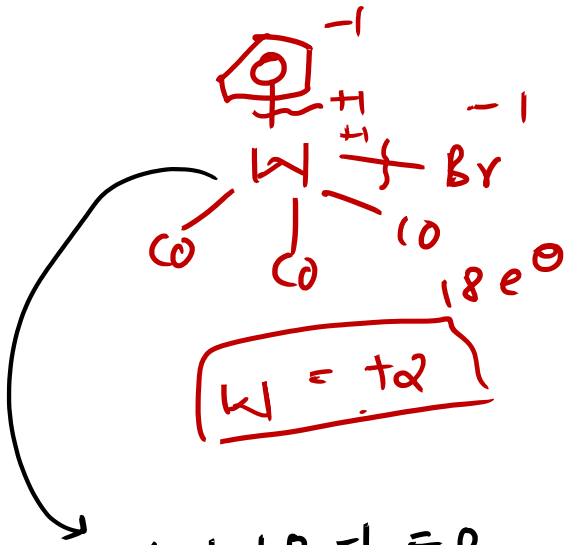
$W = 0 \cdot 0.5$

(A)

$x + 0 - 1 = -1$

$\boxed{x = 0}$

Br_2 →



③ $[V(CO)_6] + Na \longrightarrow [V(CO)_6]^{\ominus}$ (Na/liq NH_3, $-CO$) $\longrightarrow [V(CO)_5]^{3-}$

$17e^{\ominus}$

$18e^{\ominus}$

Carbonyl Metalate

Unstable

Super reduced metalate

$18e^{\ominus}$

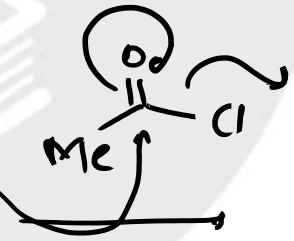
Highly unstable.

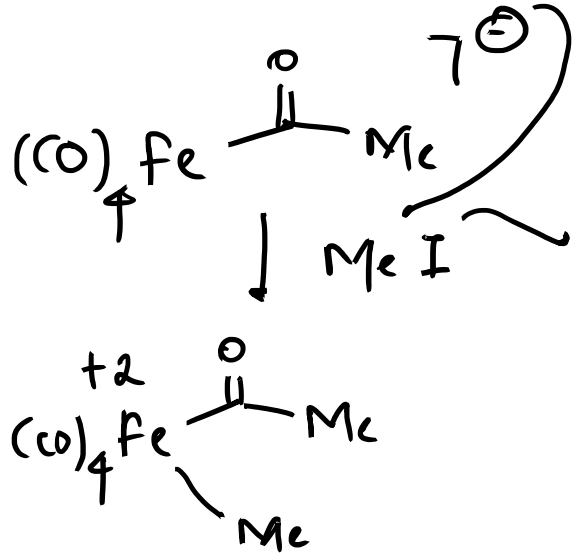
④

$Fe(CO)_5$

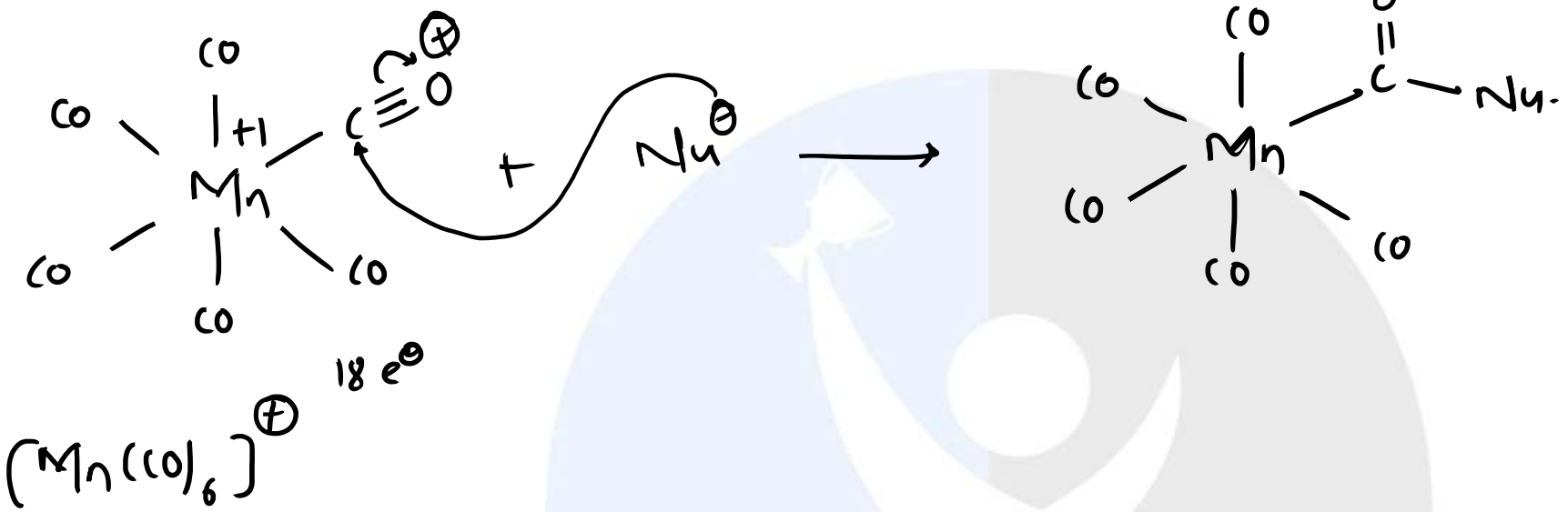
$-CO$ | Na/Hg

$[Fe(CO)_4]^{2-}$ $\xrightarrow{I_2}$ $[Fe(CO)_4I_2]$

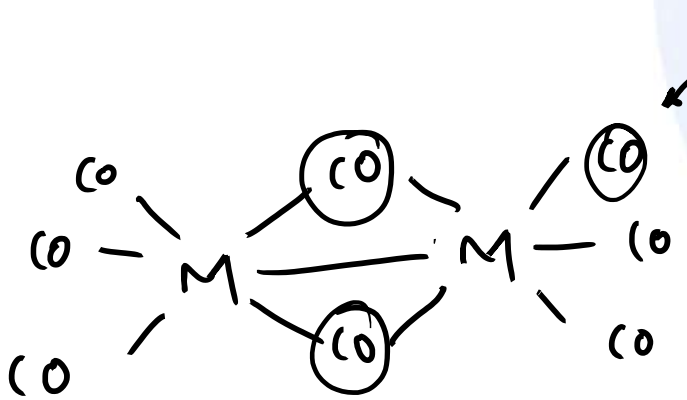




(5)



$[Mn(CO)_6]^{\oplus}$



Nu⊖

Nu⊖ Attack takes place on Terminal CO

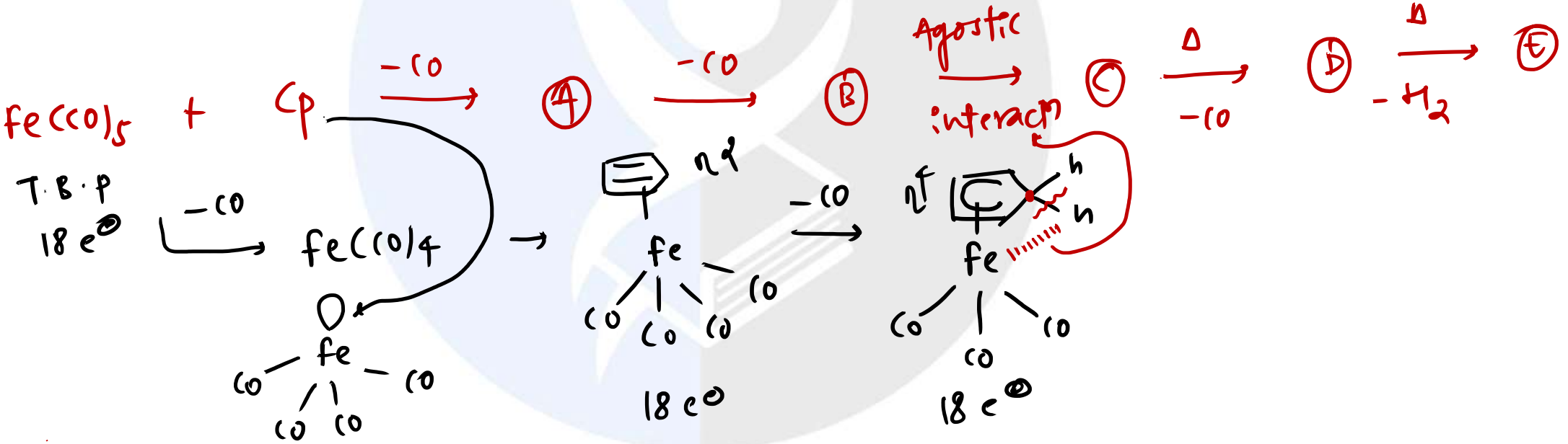
M-CO → 1860 – 1700 cm^{-1}.

Terminal → 2100 – 1860 cm^{-1} → $t^{\oplus}$ → Electrophilicity ↑

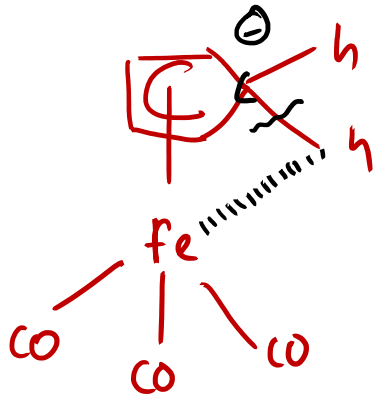
⑥ Metal-Hydride are unstable so after heating dimerization takes place.

Ex: $2\left[(CO)_5Mn-H\right] \xrightarrow[-H_2]{\Delta} \left[Mn_2(CO)_{10}\right]$

Q.



Cp →

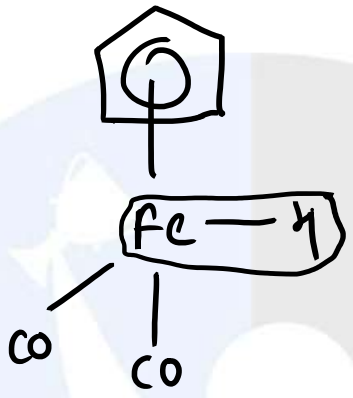


18 e⊖

$h\nu$ ↑

by 1

−CO

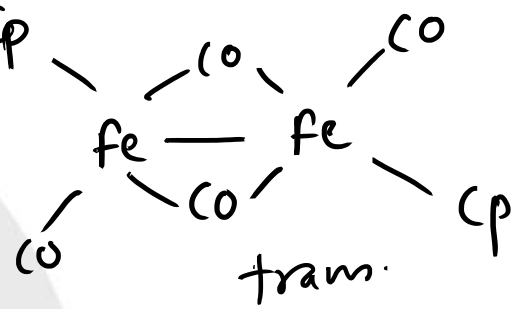


18 e⊖

^1H NMR = ②

Δ

$-H_2$



trans.

dimerisation

stable complex.

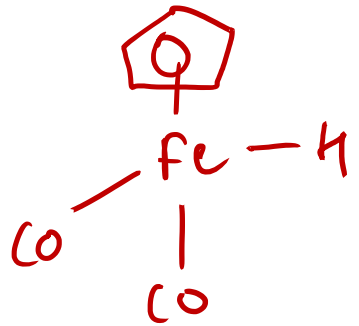
Q. $Fe(CO)_5$ +  $\xrightarrow{\text{Reflux}}$ (A) $\longrightarrow$ (B) + colourless gas ↑

(A) → 2 different ^1H NMR signal

C.S = -ve = -12 ppm

C.S = +ve = +5 ppm

(B) $\xrightarrow{Na/Hg}$ (C) $\xrightarrow{Me-I}$ (D)



Metal hydride

(A)

$\xrightarrow{-H_2}$ Dimerisation.

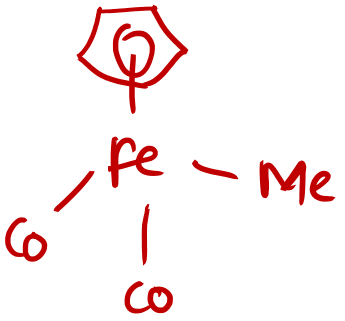
$[Fe_2(CO)_4(\eta^5\text{-}Cp)_2]$

(B)

$Na/Hg \rightarrow [Fe(CO)_2(Cp)]^{\ominus}$

(C)

$\xrightarrow{Me-I}$



(D)

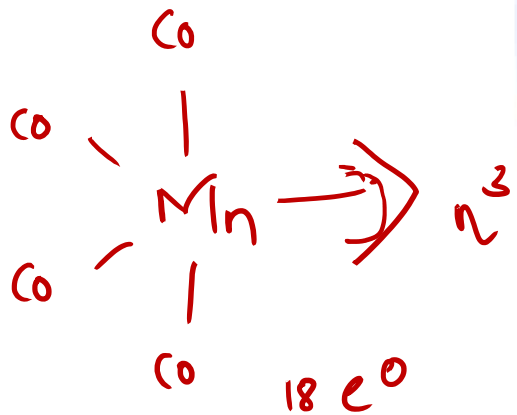
Q. $[Mn_2(CO)_{10}]$ + Na/Hg ⟶ (A) ⟶ (B) ⟶ (C)

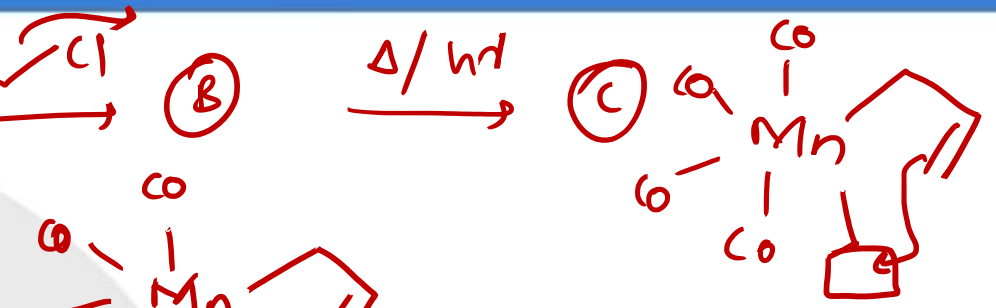
M–M : 1

$[Mn(CO)_5]^-$

(A) ⟶ (B) : I_2, Cl

(B) ⟶ (C) : Δ / hν





C.N : 6

18 e⁰

hν / Δ → −CO

{η¹ → η³}

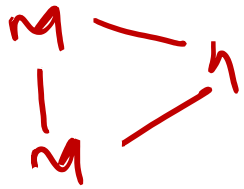
(7) Metal-Hydrides :-

(1) M — H → Terminal pair → More shielded

$3c-2e^{\ominus}$

$H^- \rightarrow 2e^{\ominus}$

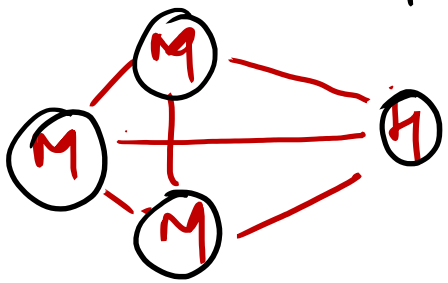
(2)



Bridging ↑

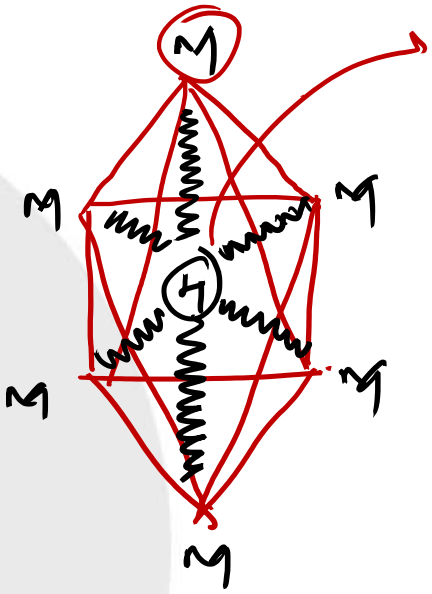
H is more deshielding

(3)



$4c-2e^{\ominus}$

(4)



encapsulated atom.

$7c-2e^{\ominus}$

As M ↑ deshielding ↑

Q $Co_2(CO)_8 + Na \longrightarrow [Co(CO)_4]^{\ominus} \xrightarrow{I_2} [Co(CO)_4 - I] \xrightarrow{LiAlH_4} [Co(CO)_4 - H^+]$

$\oplus K H^{\ominus}$ Acidic

$\downarrow$

$H_2 \uparrow + K^+[Co(CO)_4]^{\ominus}$

① The Carbonyl Hydrides of T.M behave as Both acid & base

② On descending down the group acidic character decreases.

{ thermal stability ↑

n ↑	T.S ↑

Ex. ① $H-Mn(CO)_5$

② $H-Tc(CO)_5$

③ $H-Re(CO)_5$

T.S : ③ > ② > ①

n ↑ T.S ↑

② ① $HCo(CO)_3(PF_3)$ > ② $HCo(CO)_3(PPh_3)$ > ② $HCo(CO)_3(PMe_3)$

Acidic Character : ① > ② > ③

EWG ↑ Acidic character ↑

③ Neutral CO hydrides → proton donor.

Anionic CO hydride → $H^{\ominus}$ donor not proton donor

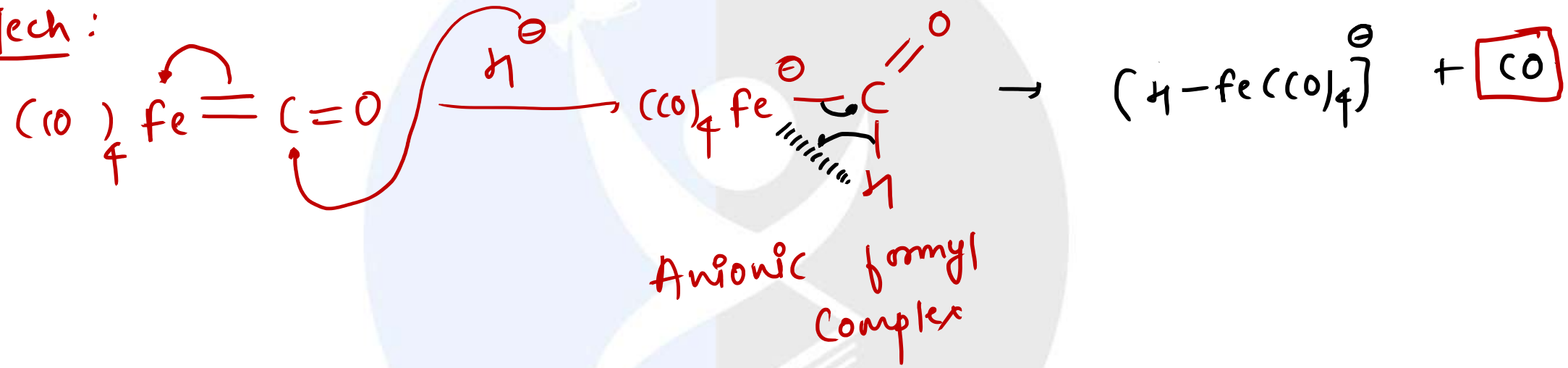
Ex:

$$RX + [H\text{-}Fe(CO)_4]^{\ominus} \longrightarrow RH + [XFe(CO)_4]^{\ominus}$$

X = Cl, Br, I

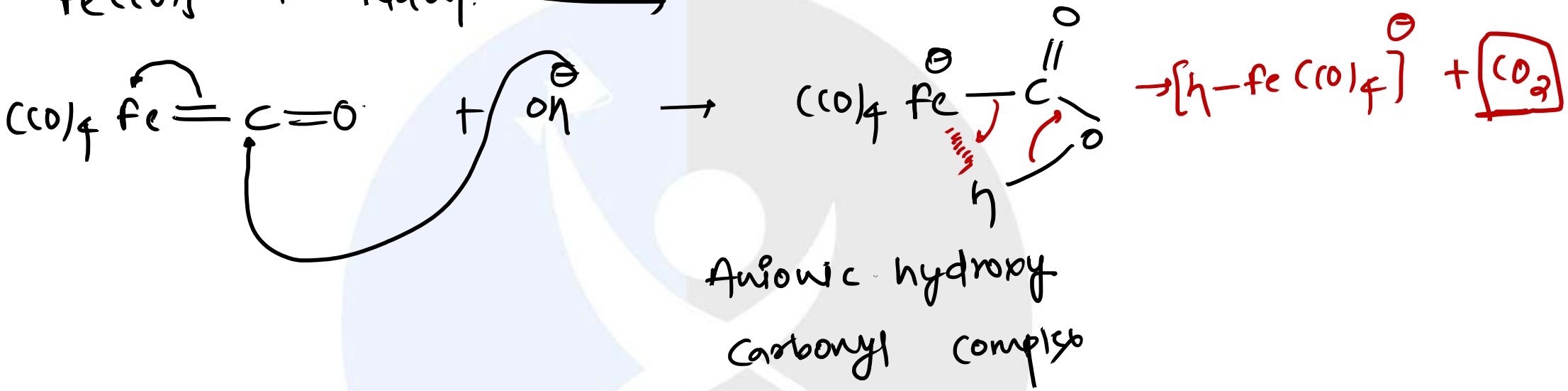
Q. $[Fe(CO)_5]$ $\xrightarrow{NaBH_4}$ $[HFe(CO)_4]^{\ominus}$ + CO

Mech:



Q. $FeI_2(CO)_4$ $\xrightarrow{NaBH_4}$ $[FeH_2(CO)_4]$

Q. $Fe(CO)_5 + NaOH \longrightarrow$



Anionic hydroxy carbonyl complex

Only for Rxn → of OMC Ajay Kumar

Metal halide complex:

① $Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$

$Fe(CO)_5X \rightarrow 19 \rightarrow$ Unstable

$X = Br, I$

$-CO$

$(Fe(CO)_4X) \rightarrow 17\ e^{\ominus} \rightarrow$ Unstable

② $(CO)_5Mn-Mn(CO)_5 + I_2 \longrightarrow 2\,Mn(CO)_5X$

(I–I)

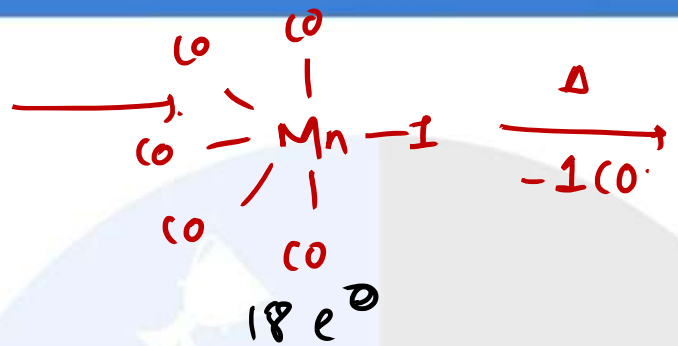
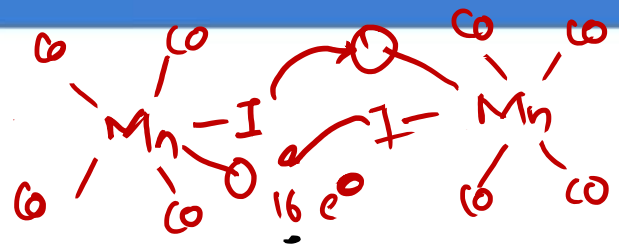
$\overset{+1}{Mn}\ \overset{-1}{X}$

$Mn = +1\ 0.5$

③ $Co_2(CO)_8 \xrightarrow{I_2} [\overset{+1}{Co}(CO)_4I]$

18 $e^{\ominus}$

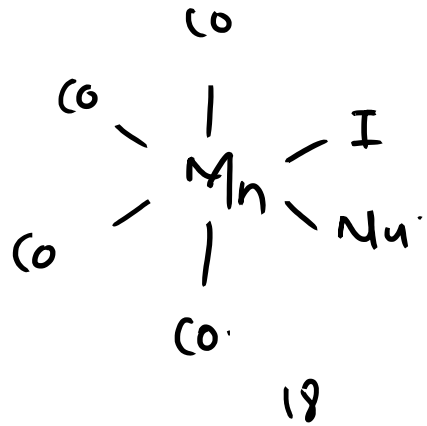
less B.B ν_{CO} ↑

Q. $Mn_2(CO)_{10} + I_2 \longrightarrow$  $\xrightarrow{\Delta}$ $\xrightarrow{-1CO}$ 

18 e⊖

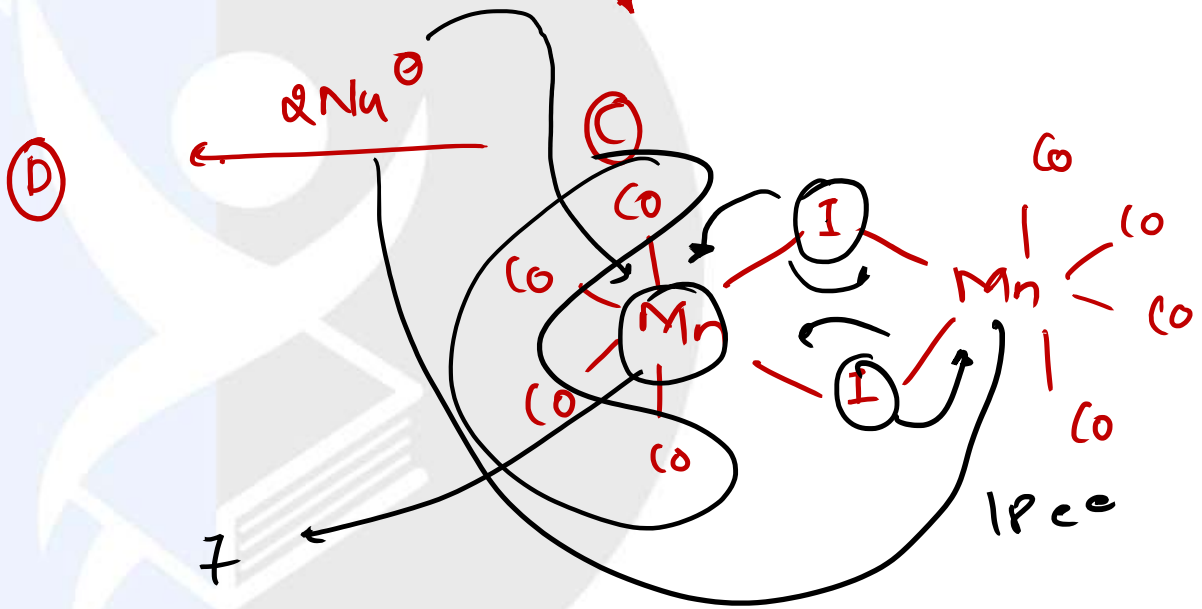
16 e⊖

Coupling



18

M–I → 1 e⊖ donor



18 e⊖

7

8

15

3

18

Q $Re_2(CO)_{10} + Br_2 \longrightarrow$ (A) $\xrightarrow{SN^1}$ (B) $\xrightarrow{\Delta, -CO}$ (C)

Dissociative step.

M – M. bond = 0

Thank you