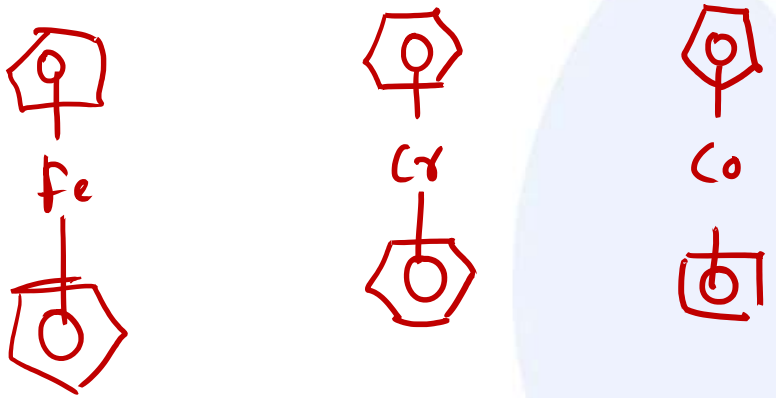
Metallocene :-

→ ✓ Metallocene contain cyclic polyene ligand.

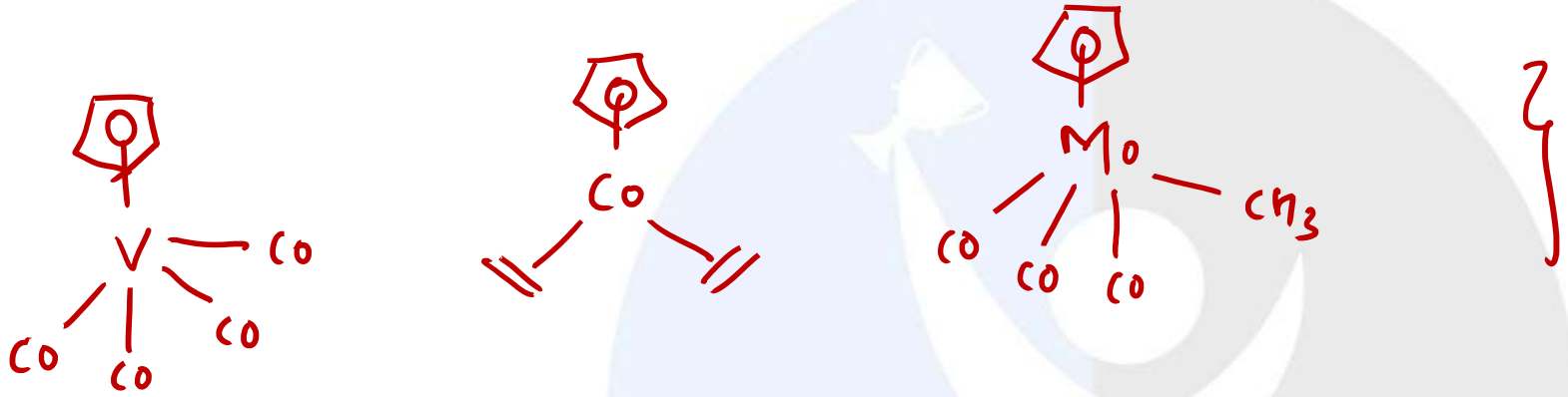


→ {Sandwich Compound}

Ferrocene

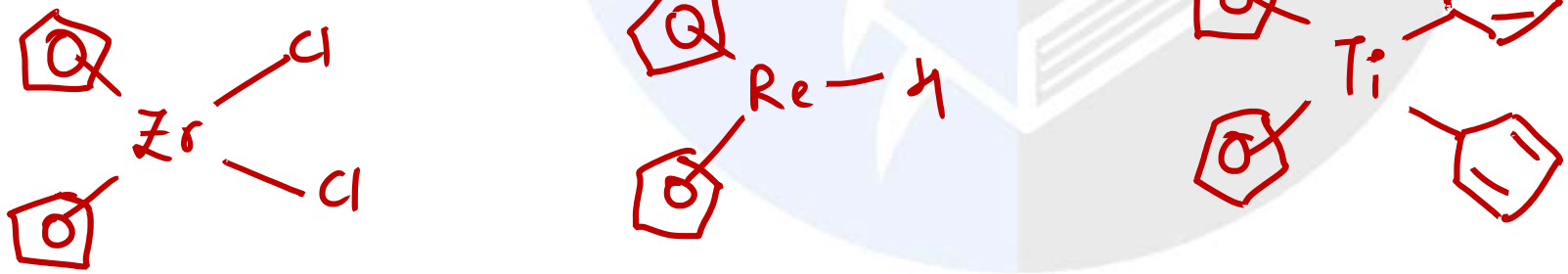
Metallocene

Half sandwich compound :—



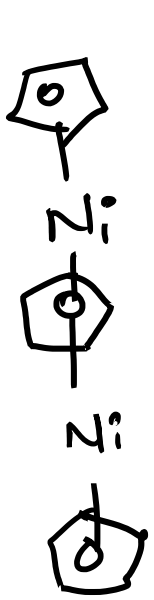
} Half sand wich Compounds.

✓ Bent Metallocene :—

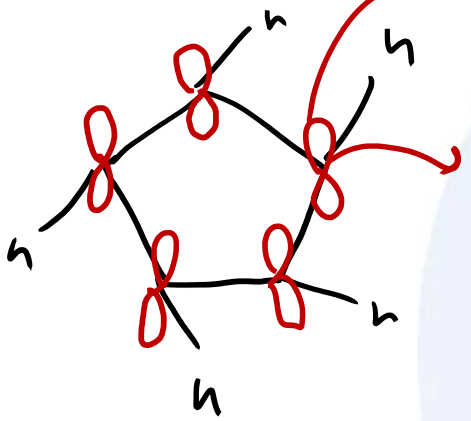


{ Due to steric hindenerance cp rings are tilted towards each other }

Triple Deckers:

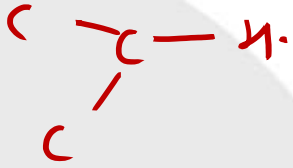


Metallocenes $\{M(Cp)_2\}$



p_z orb.

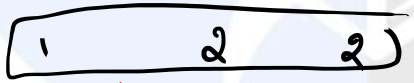
sp^2 hybrid



2 C—C. } 3 sp^2 hybrid orb of
1 C–H } C are utilized.

Total (5) p_z / $p\pi$ orbitals on 5 carbon → 5 π-M.O

L.E.O



$e_1 < e_2$

Symmetries : energy

1st $C_5H_5^-$ → $a_1 < e_1 < e_2$ 2nd $C_5H_5^-$ → $a_1 < e_1 < e_2$

10 M.O / L.C.C

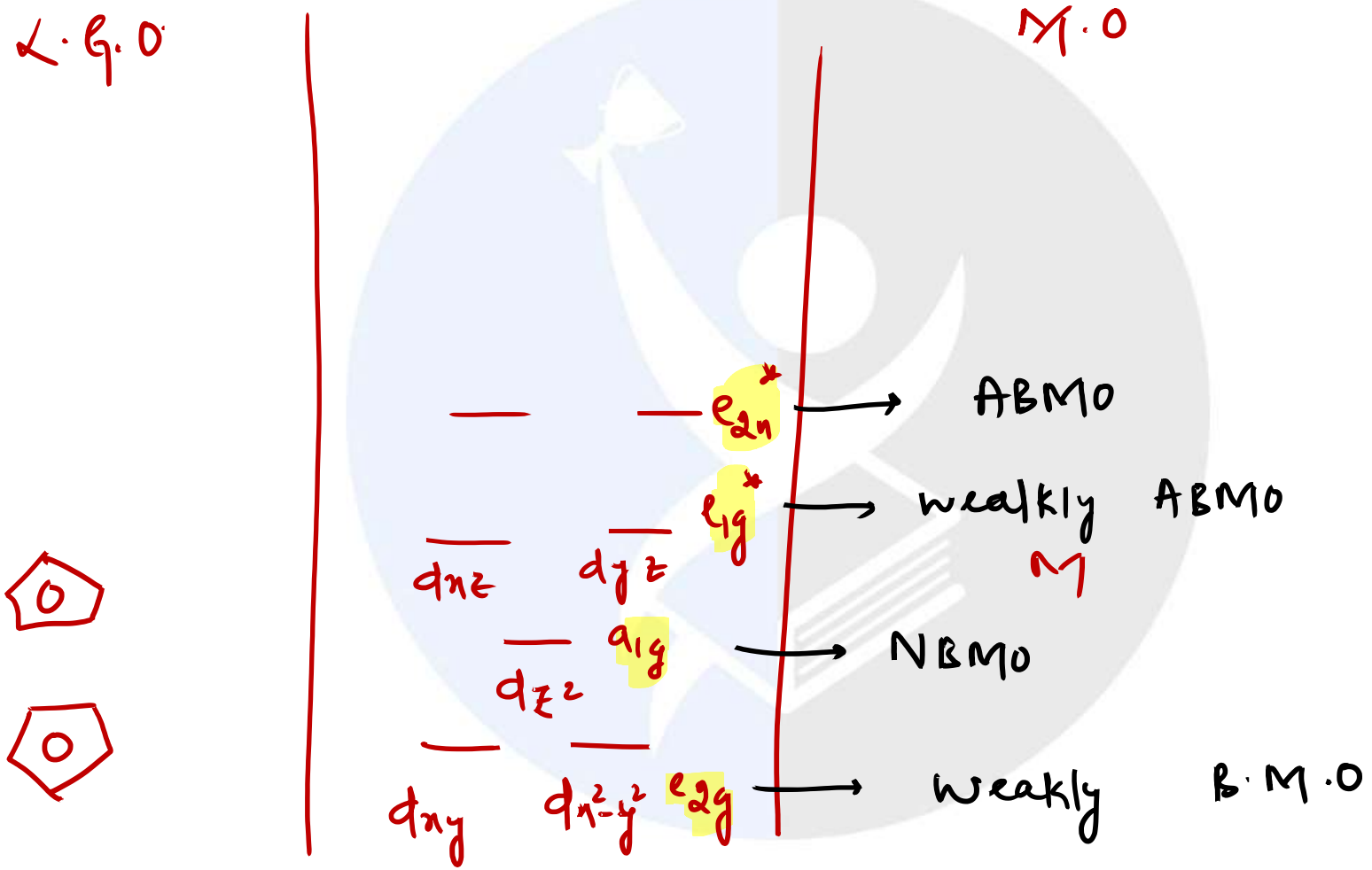
L.C.O a_{1g} + $2e_{1g}$ + $2e_{1u}$ + $2e_{2g}$ + $2e_{2u}$ + a_{2u}

↓

Metal Orbital. s $\{ d_{z^2}$ d_{xz} $\{$ p_x $\{$ d_{xy} No orb p_z

p_y d_{yz} $+d_{x^2-y^2}$ on Metal

M.O. diagram of Metallocene :-



① $Fe(Cp)_2$

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

$2Cp^{\ominus}$: $12e^{\ominus}$

$18e^{\ominus}$

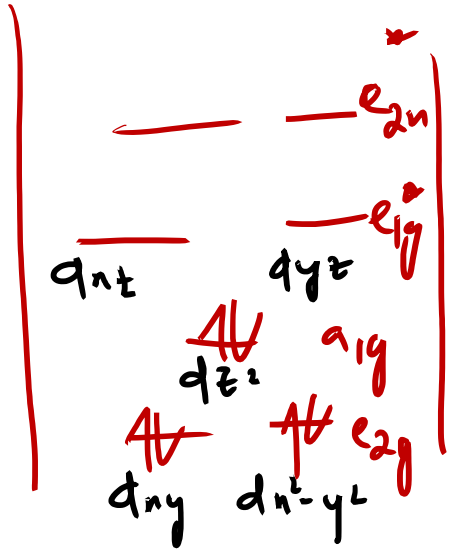
① HOMO : $(a_{1g})^2 (d_{z^2})^2$

LUMO : $(e_g)^{*0} (d_{xz} = d_{yz})^0$

② Magnetism : Diamag

③ $E^{\ominus}$ config : $(e_g^*)^0 > (a_{1g})^2 > (e_{2g})^4$

$(d_{xz} = d_{yz})^0 > (d_{z^2})^2 > (d_{xy}\ d_{x^2-y^2})^4$



M-C Bond Length :

$[Fe(CO)_2]$
18 $e^\ominus$
dia

$[Fe(CO)_2]^\oplus$
17 $e^\ominus$
para

*

→ ① If $e^\ominus$ removed in BMO / NBMO

→ M-C B.L ↑

② If $e^\ominus$ remove in ABMO.

M-C B.L ↓

② No. of unpaired $e^{\ominus}$ ↑ M–C B.L ↑

③ Paramagnetic > Diamag

④ If $e^{\ominus}$ present in ABMO, M–C B.L ↑

Q. Stability Order

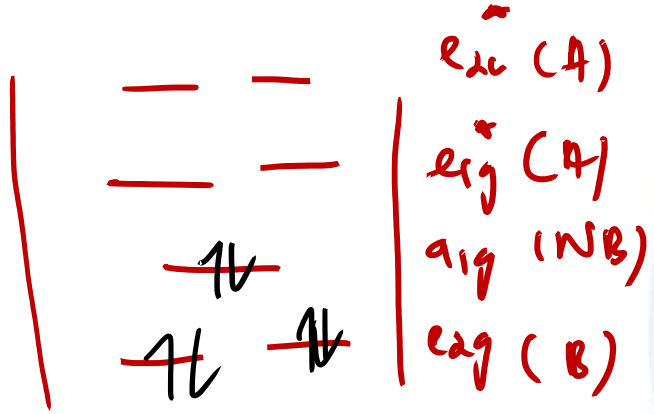
Q. Bond Enthalpy ∝ M–C B.S
M–C B.O

Q. No. of unpaired in metallocene

Q. Mag. moment of Metallocene

① $Fe(CO)_2$

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



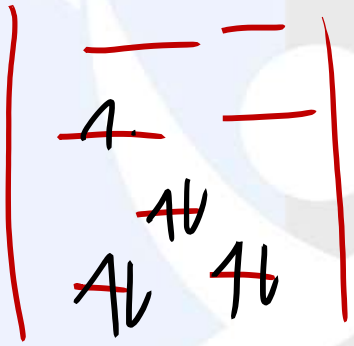
HOMO : $(a_{1g})^2$

LUMO : $(e_{1g}^*)^0$

② Mag. : Dia

② $Co(CO)_4$

Co^{+2}: $3d^7$



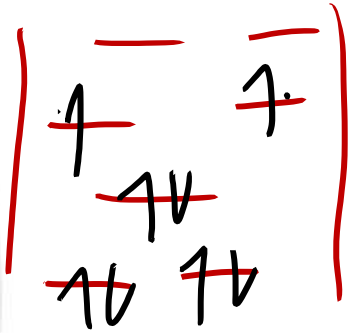
HOMO e_{1g}^*

LUMO e_{2u}^*

Para

③ $Ni(CO)_4$

Ni^{+2}: $3d^8$



e_{1g}^*

e_{2u}^*

Para

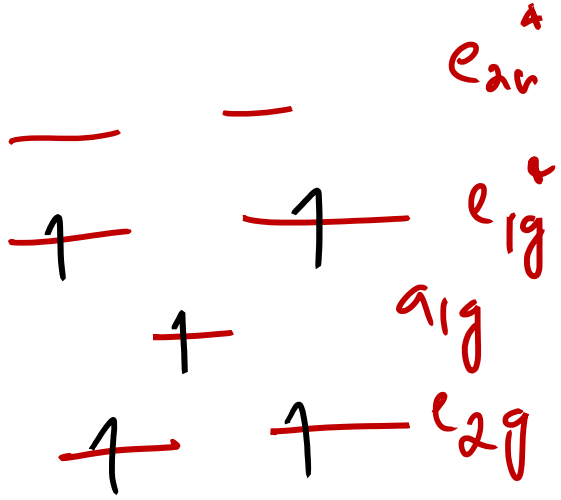
③	No. of unpaired :	0	1	2
④	M.M. $\sqrt{n(n+2)}$ BM	0 BM	1.73 BM	2.87 BM
⑤	E.C :	$(e_{2g})^4 < (a_{1g})^2 < (e_{1g}^*)^0$	$(e_{2g})^4 < a_{1g}^2 < (e_{1g}^*)^1$	$(e_{2g})^4 < a_{1g}^2 < (e_{1g}^*)^2$
⑥	M-C B.L	$Fe(CO)_6$ <	$Co(CO)_6$	< $Ni(CO)_6$
⑦	B.E	$Fe(CO)_6$ >	$Co(CO)_6$	> $Ni(CO)_6$
⑧	Stability order		n.	

0 → 0 BM
1 → 1.73
2 → 2.87
3 → 3.87
4 → 4.92
5 → 5.92

* $Mn(Cp)_2$

→ High spin complex

Mn^{+2} : $3d^5$



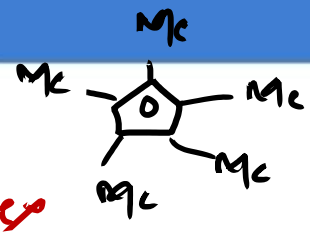
n = 5

① HOMO : e_{1g}^*

LUMO : e_{2u}^*

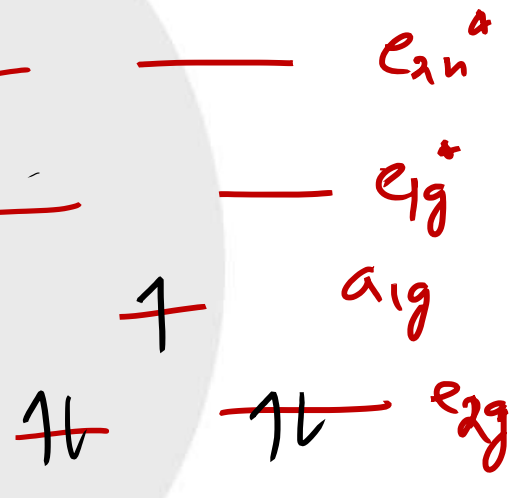
② Mag : Para

$[Mn(Cp^*)_2]$



Low spin complex

Mn^{+2} : $3d^5$



n = 1.

a_{1g}

e_{1g}^*

Para

IfAS

② $\eta = 5^-$

④ M.M : 5.92 BM

⑤ E.C

⑥ M–C B.d :

⑦ B.t :

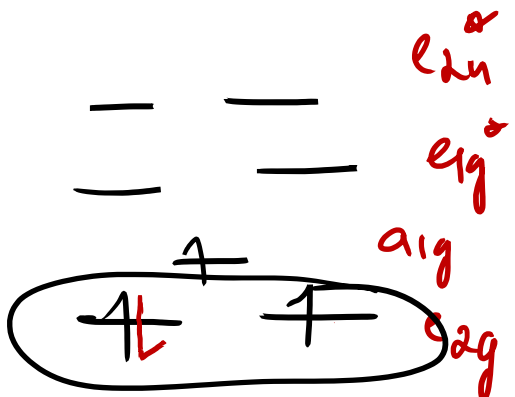
$Mn(CO)_a > Mn(CO^*)_a$

$Mn(CO^*)_a > Mn(CO)_a$

$\eta = 1$

1.73 BM

$Cr(CO)_2$ Cr+2 : $3d^4$

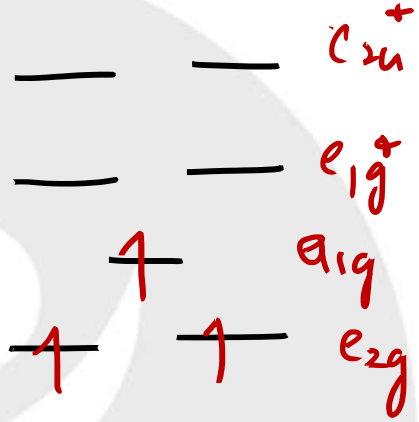


$n = 2 \rightarrow$ ~~2.84 BM~~

3.20 B.M

+ Orbital Contribution

$V(CO)_2$



$n = 3$

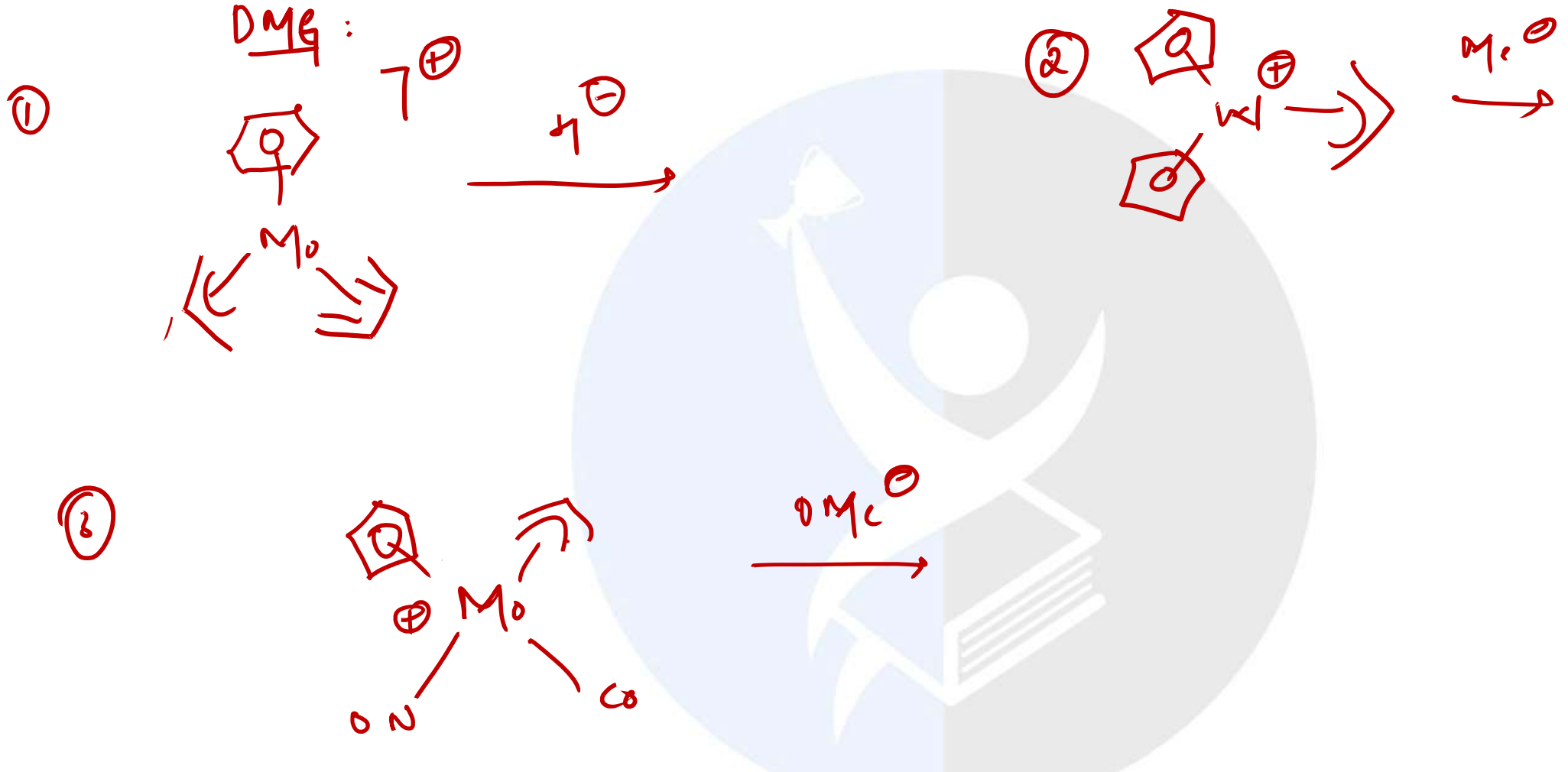
M.M : 3.87 BM

No orbital Contribution

→ Cp^4 is stronger π donor and weaker π acceptor ligand compared to Cp

HW

DMG :




Thank you