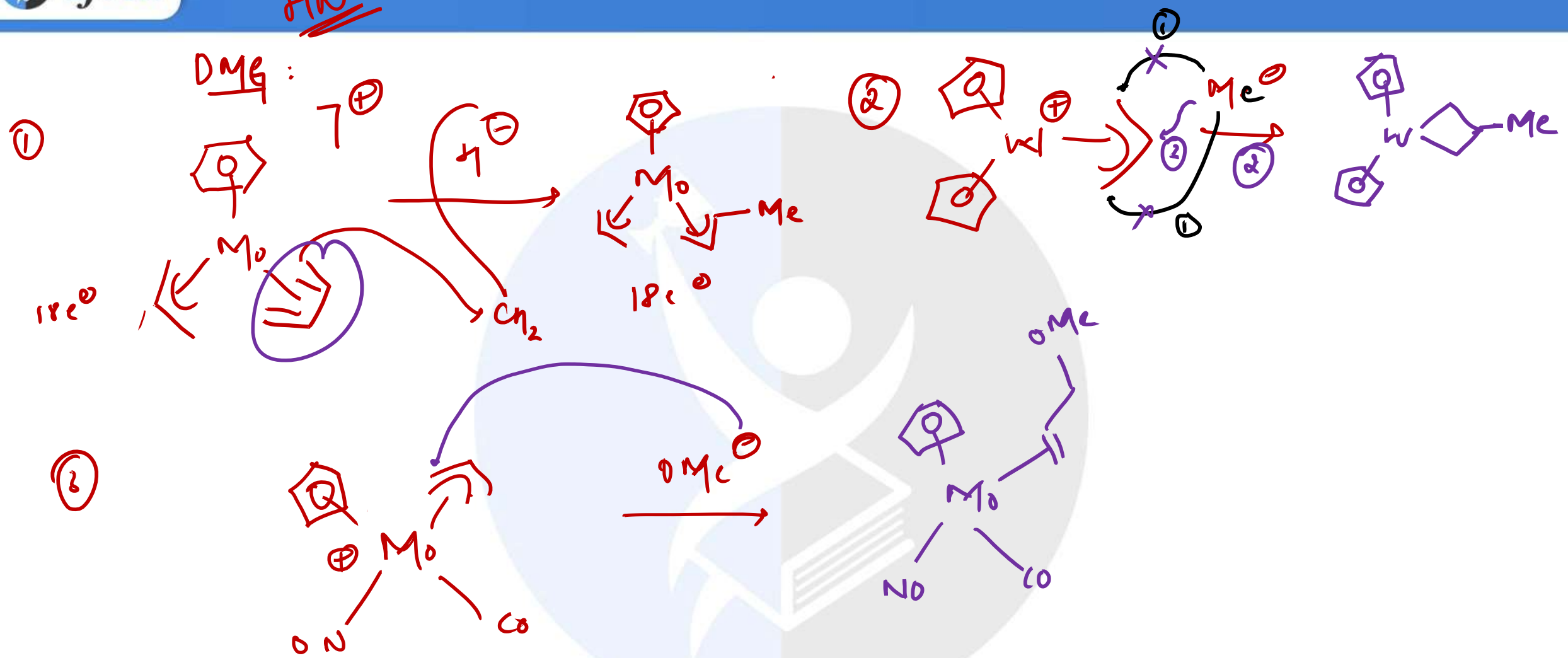
HW

DME :



* In the case of even open polyenes, $Nu^{\ominus}$ attack always occurs at the terminal C atom. for odd open polyenyls, attack at the terminal carbon occurs only if $ArN^{\oplus}$ is a relatively stronger withdraw -ing fragment.

Q. June 2016 (FM)

Correct order of M-C Bond Length of metallocene's (a-c)

a. $[Fe(\eta^5\text{-}Cp)_2]$

b. $[Ni(\eta^5\text{-}Cp)_2]$

c. $[Co(\eta^5\text{-}Cp)_2]$

(1) a > b > c

(2) b > c > a

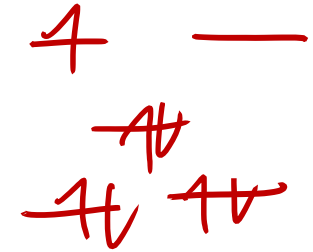
(3) c > b > a

(4) a > c > b

(a) $Fe^{+2} \rightarrow 6$

(b) $Ni^{+2} \rightarrow 8$

(c) $Co^{+2} \rightarrow 7$



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

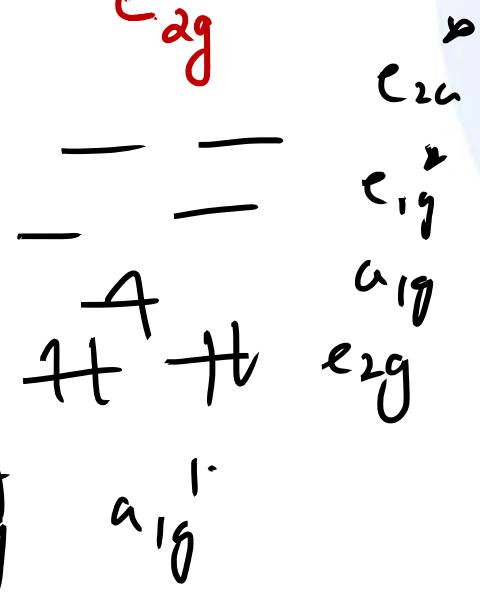
Q. Correct E.C of frontier M.O is of $Mn(\eta^5-C_5Me_5)_2$ is {Nov 2020 4M}

(a) $e_{2g}^1\ a_{1g}\ a_{1g}^2$

(b) $e_{2g}^4\ a_{1g}^1$

(c) $e_{2g}^3\ a_{1g}^2$

(d) $e_{1g}^2\ e_{2g}^3$



$e_{2g}^4\ a_{1g}^1$

The no. of unpaired $e^\ominus$ in (Cp_2Fe), Cp_2Ni & Cp_2Co are

June 2023 4M

(a) 0, 0, 1

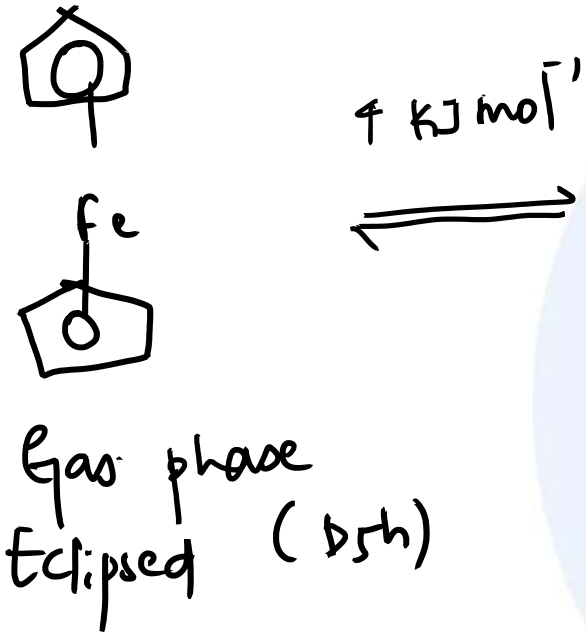
(b) 0, 2, 1

(c) 0, 1 & 2

(d) 2, 2 & 1

Reactions of Metallocenes :—

(1)



Gas phase
Eclipsed (D_{5h})

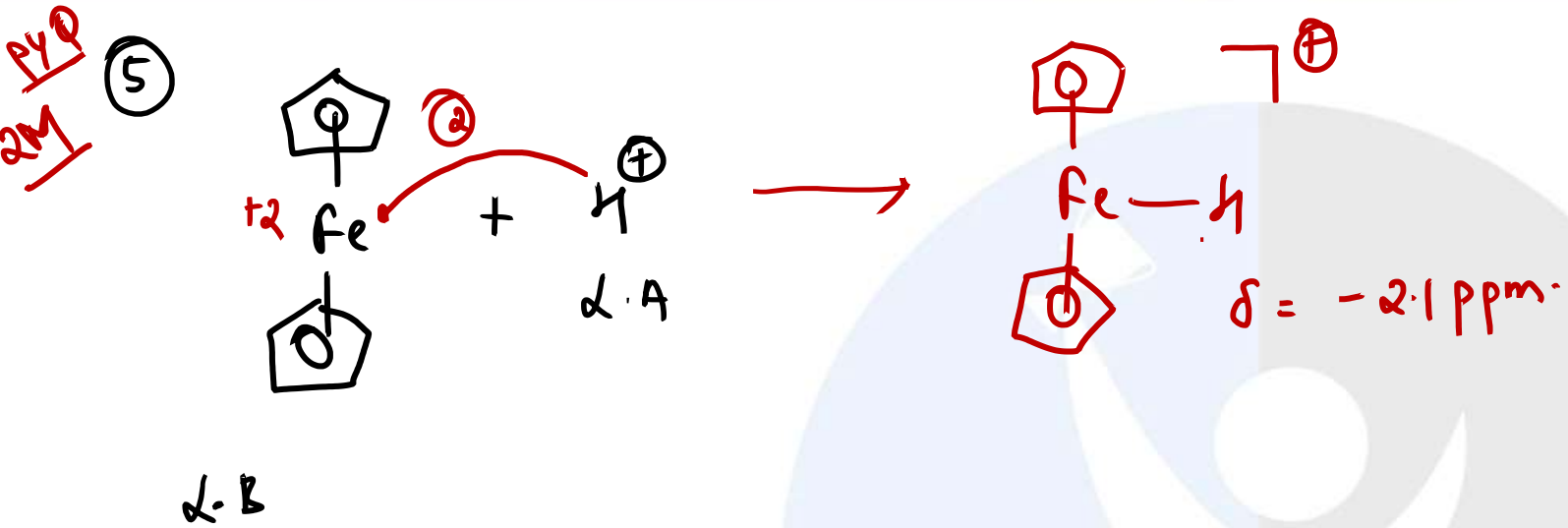
Staggered
Solid state (D_{5d})

(1) Diamagnetic

(2) Camphor like odour

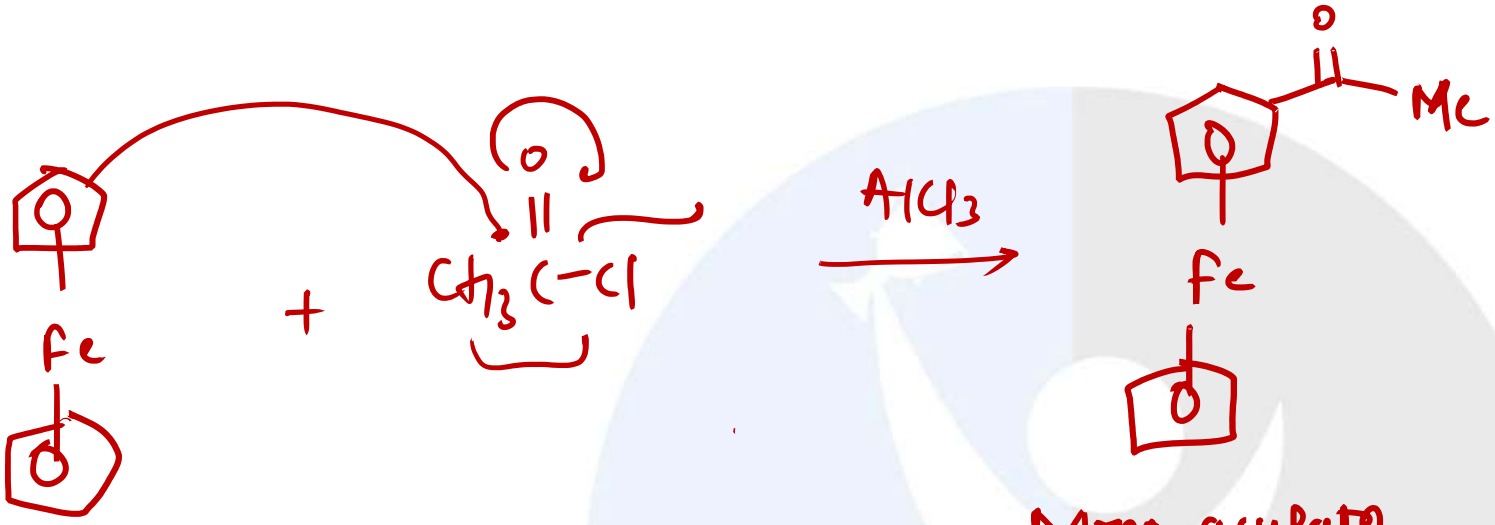
(3) M.P : 174°C
B.P : 249°C
} Stable

(4) Insoluble in H_2O
Soluble in org solvents.



→ Reactions of Ferrocene :—

① F.C. Acylation :—

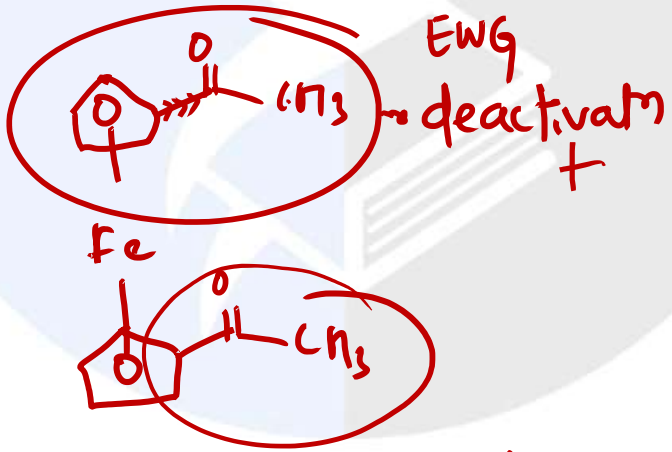


Mono acylation

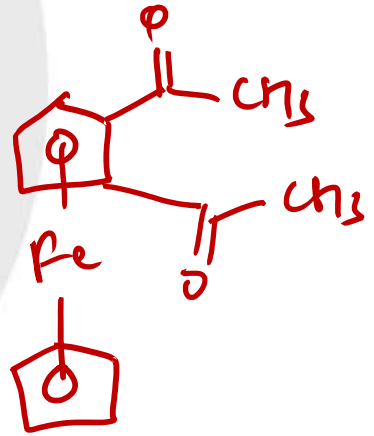
Ellicysed

Excess CH_3COCl

$AlCl_3$



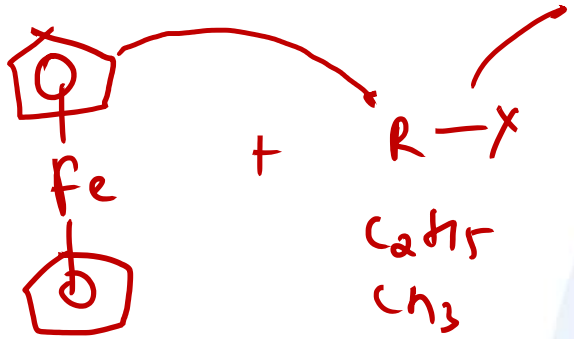
1,1 disubstituted (Major)

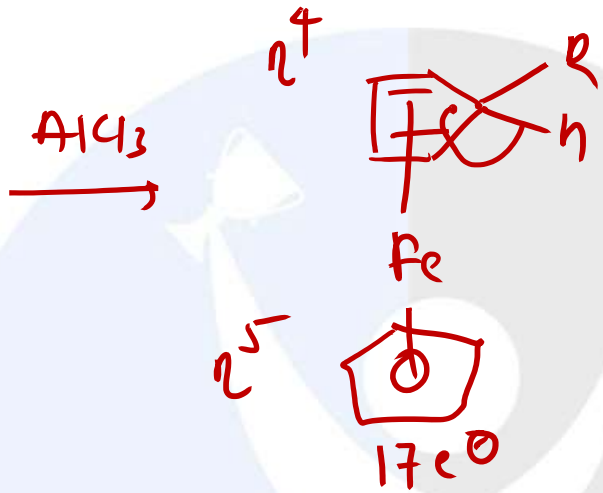


1,2 disubstituted (Minor)

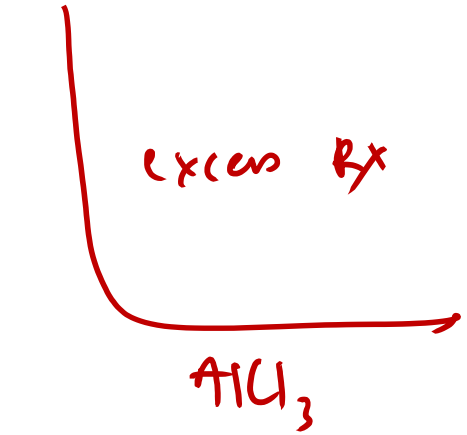
(60 : 1)

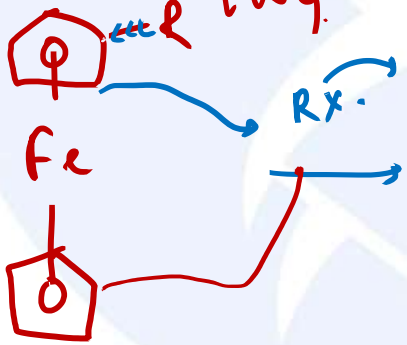
② F.C Alkylation e–





Rearomat: -zation





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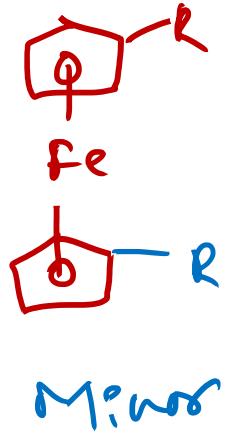
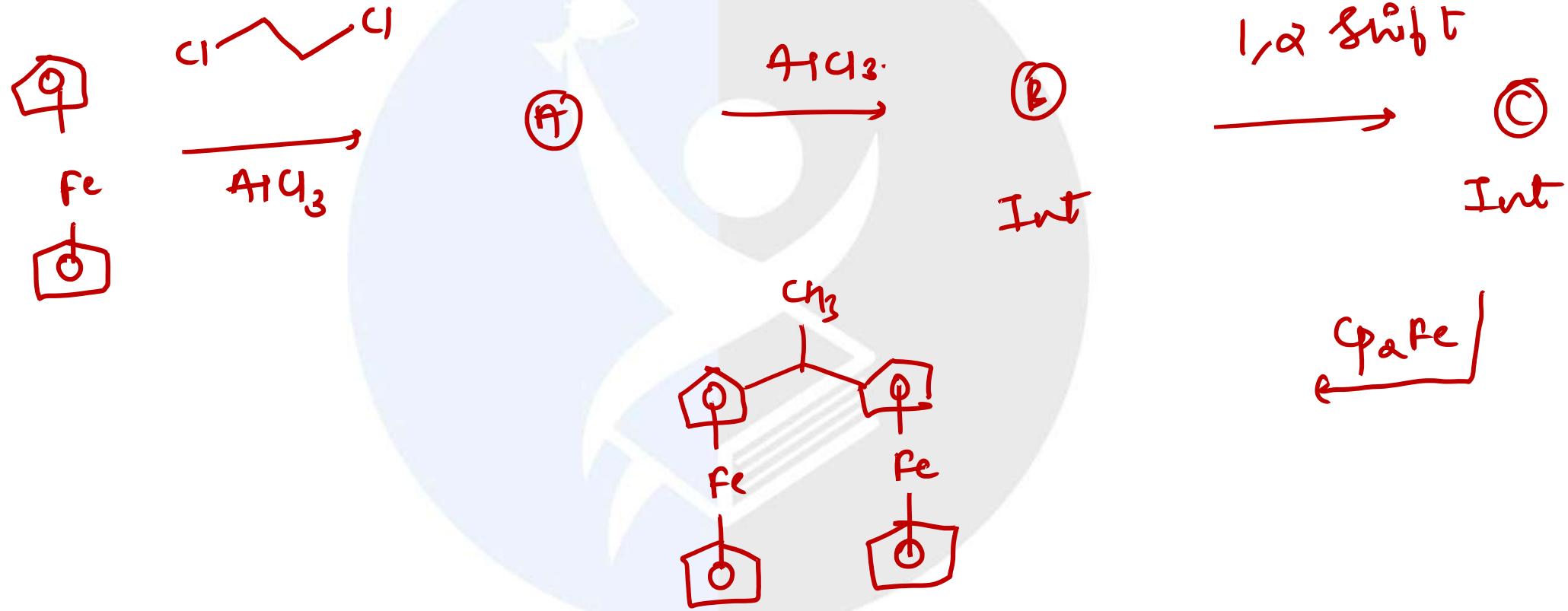


Whenever possible; Carbocation rearranges itself into more stable one

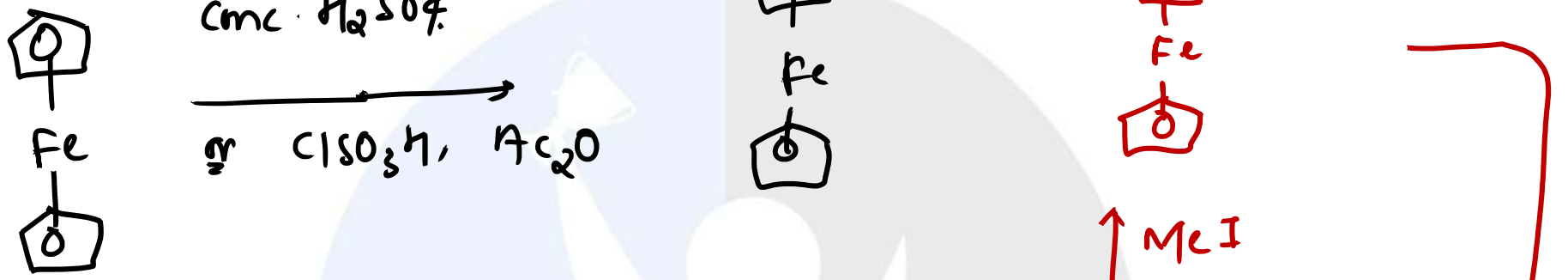
$3^0 > 2^0 > 1^0$

HW

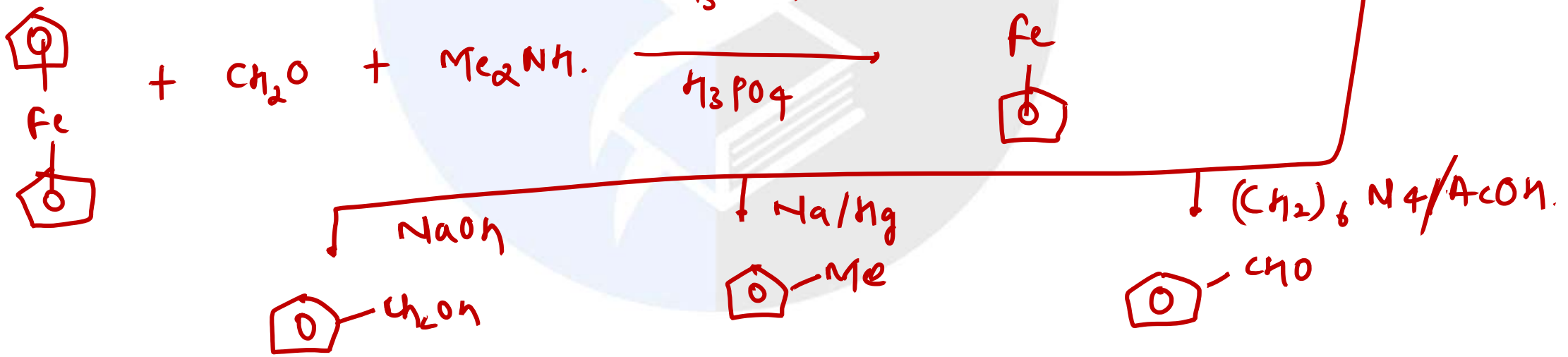
Ex:



(3) Sulphonation :—



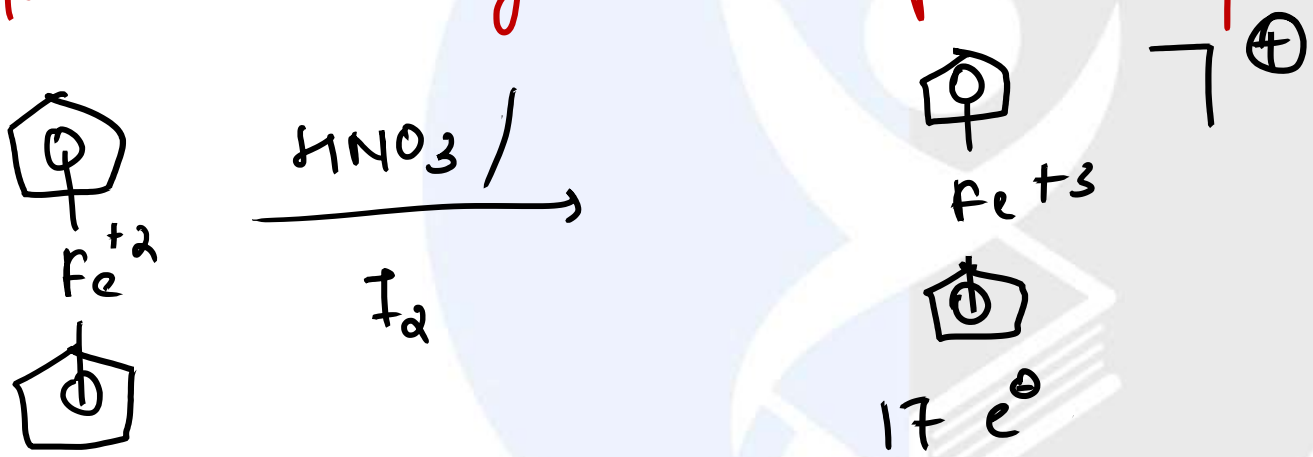
(4) Mannich Rxn :—



Nitration & Halogenation

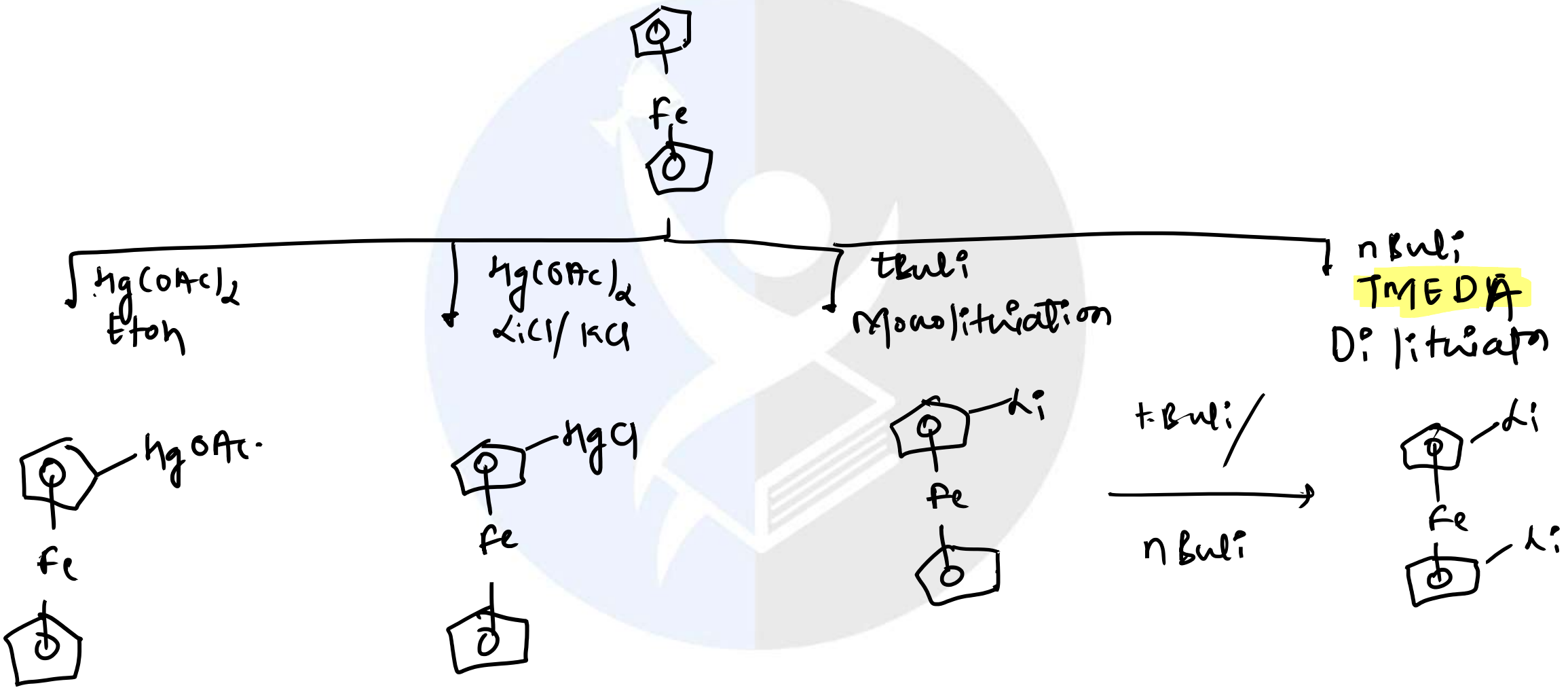
① Direct introduction of $-NO_2$ & $-X$ not possible.

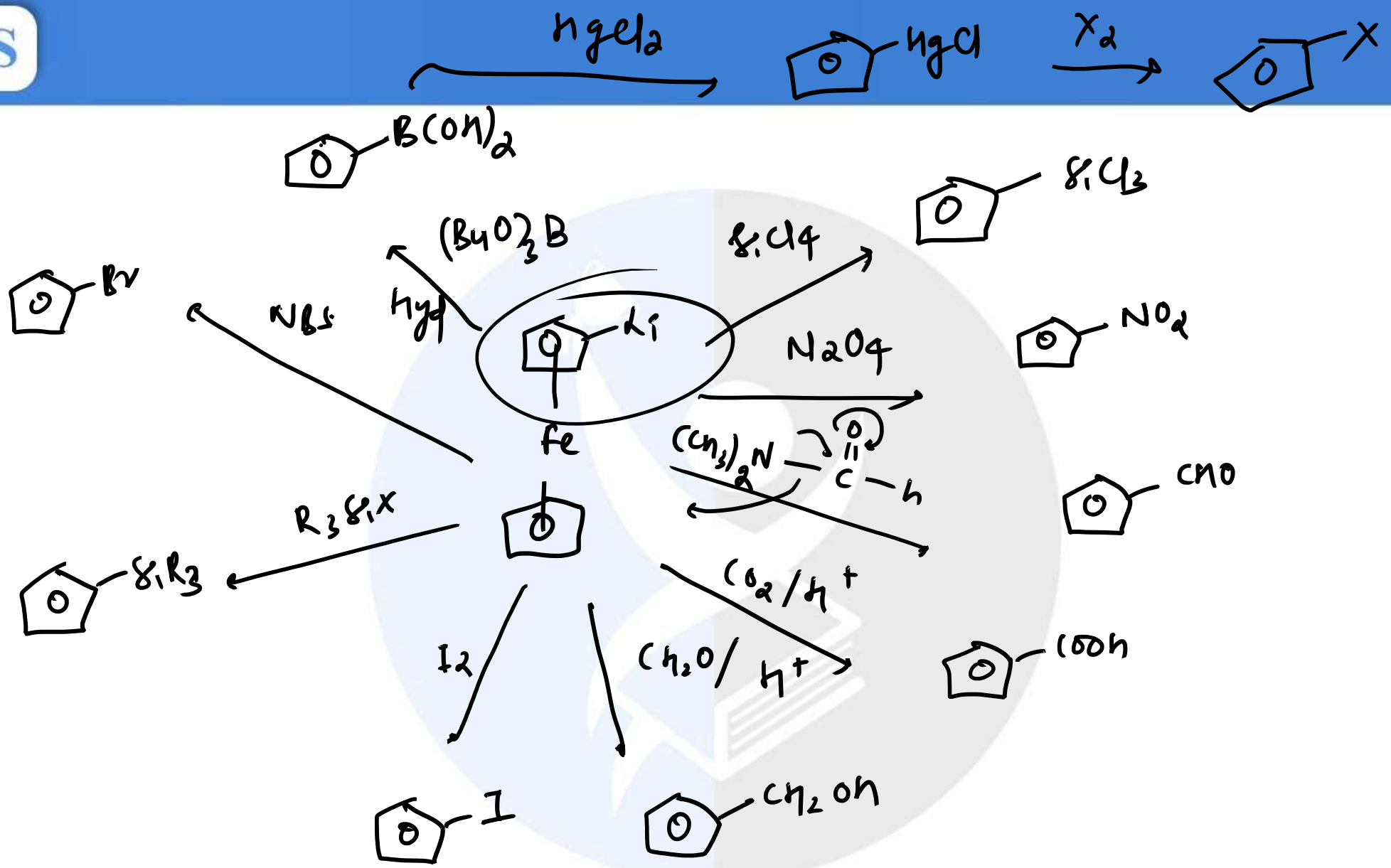
because ferrocene is readily oxidized to ferrocenium ion by the oxidizing electrophile & makes it inactive



{ ∴ $-NO_2$ & $-X$ group introduced indirectly through metallation }

Metallation :- Introduction of metal on ring

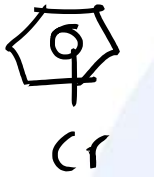


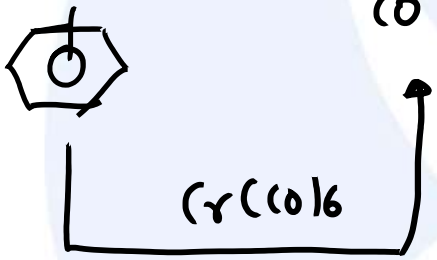

HgCl2
HgCl
X2
X
B(OH)2
(BuO)3B
SiCl4
SiCl3
Br
NBS
Hg
Li
NO2
N2O4
Fe
(CH3)2N
O
C
H
CHO
R3SiX
SiR3
CO2/H+
I2
CH2O/ H+
COOH
I
CH2OH

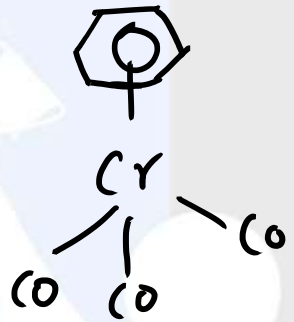
Arene Complexes :-

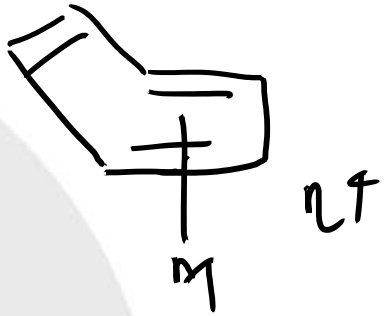
Benzene / its derivatives

Ex:



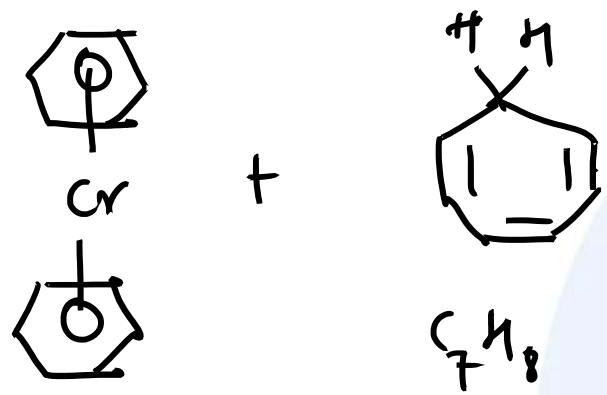






M = Cr, W, Mo

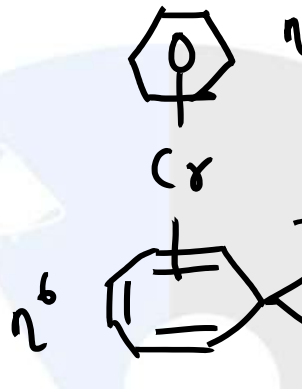
→ $Cr(\eta^6-C_6H_6)_2$



+

C_7H_8

→

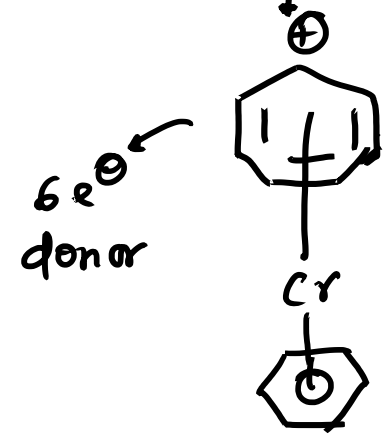


$[(\eta^6-C_7H_8)(\eta^6-C_6H_6)Cr]$

+ C_6H_6

Nonplanar

$Ph_3C^{\oplus}\ BF_4^{\ominus}$



6e⊖ donor

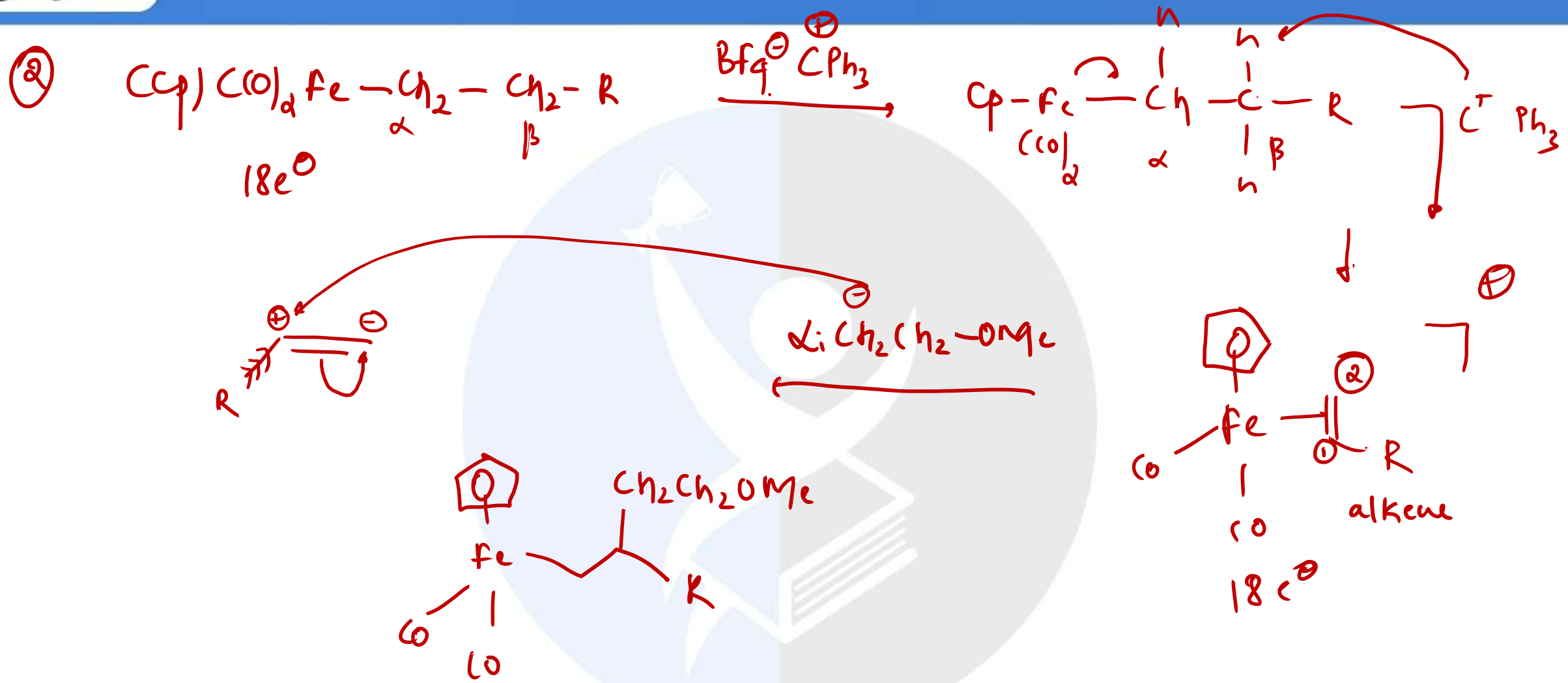
η^6 → Planar

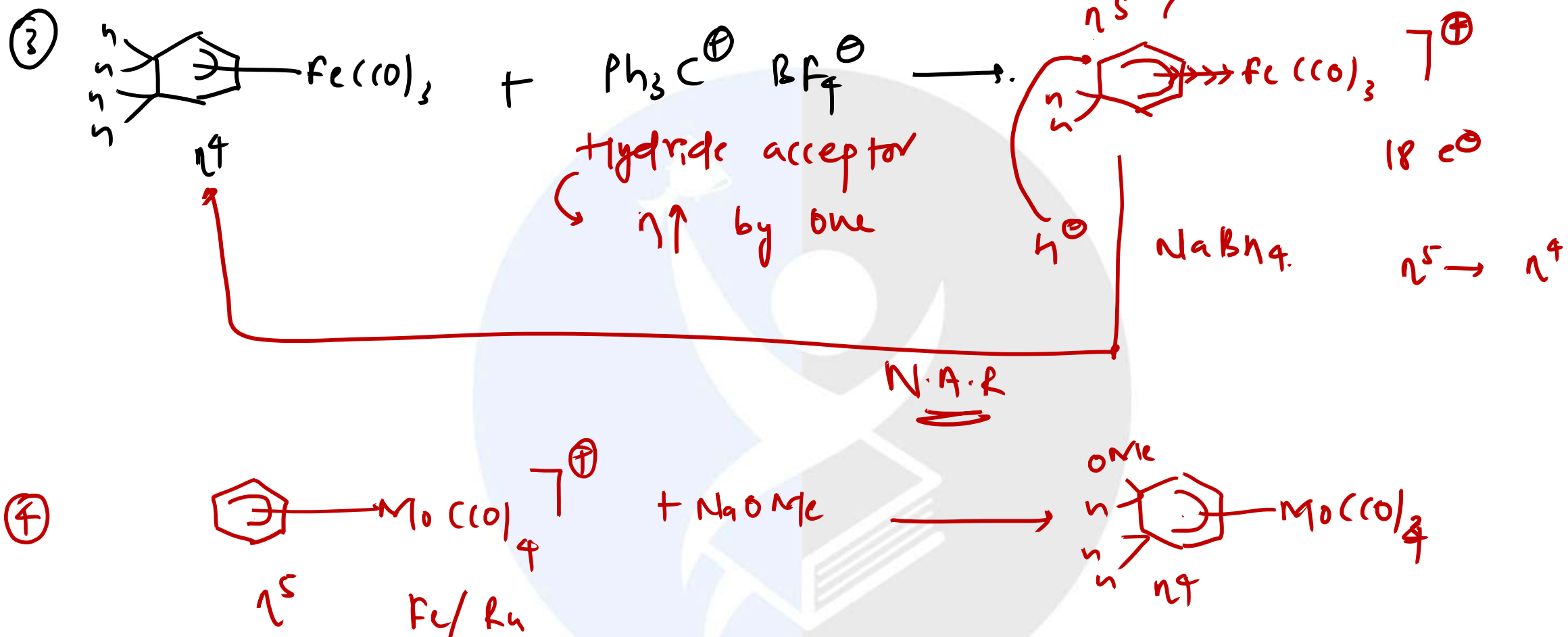
η^6

+ Ph_3CH

Hydride acceptor reagent:

$Ph_3C^{\oplus}\ BF_4^{\ominus}$ —H→ Ph_3CH


②
Cp(CO)2Fe–CH2–CH2–R
α
β
18e⊖
BF4⊖ ⊕CPh3
Cp–Fe(CO)2–CH(α)–C(β)(n)–R
n
n
C+Ph3
R
Li CH2CH2–OMe
CH2CH2OMe
Fe
CO
CO
R
alkene
CO
18e⊖


③
Fe(CO)3
+
Ph3C⊕ BF4⊖
Hydride acceptor
η↑ by one
η6
η5
Ring e⊖ def.
Fe(CO)3
18 e⊖
η4⊖
NaBH4
η5 → η4
N.A.R
④
Mo(CO)4
+ NaOMe
η5
Fe/ Ru
OMe
Mo(CO)3
η4


Thank you