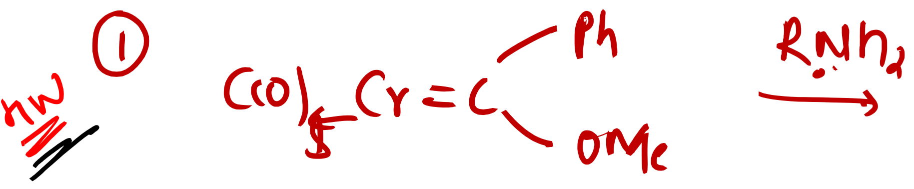
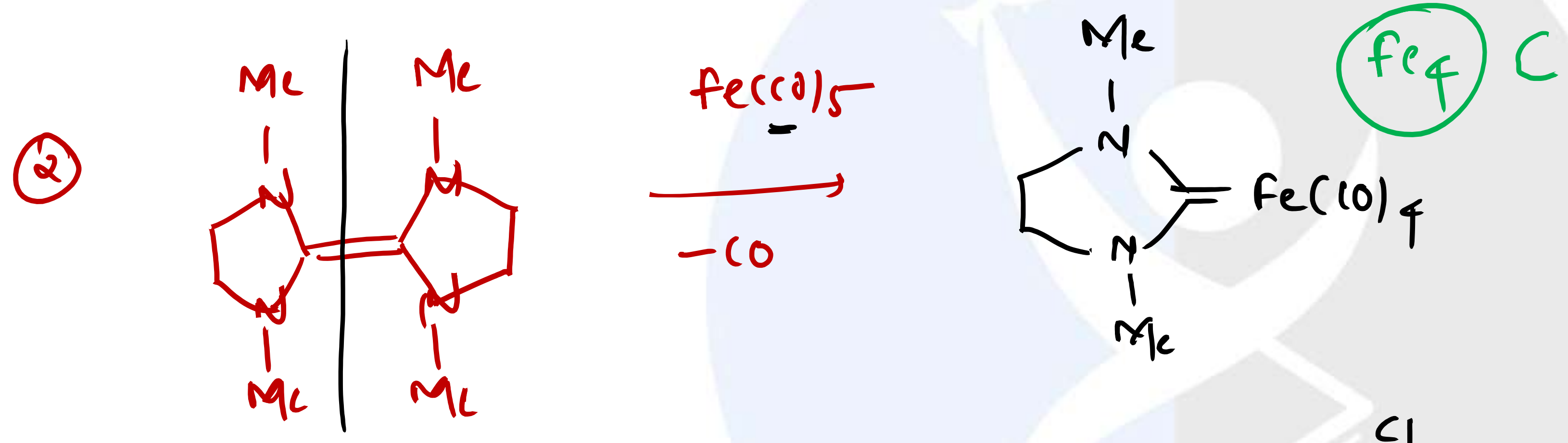
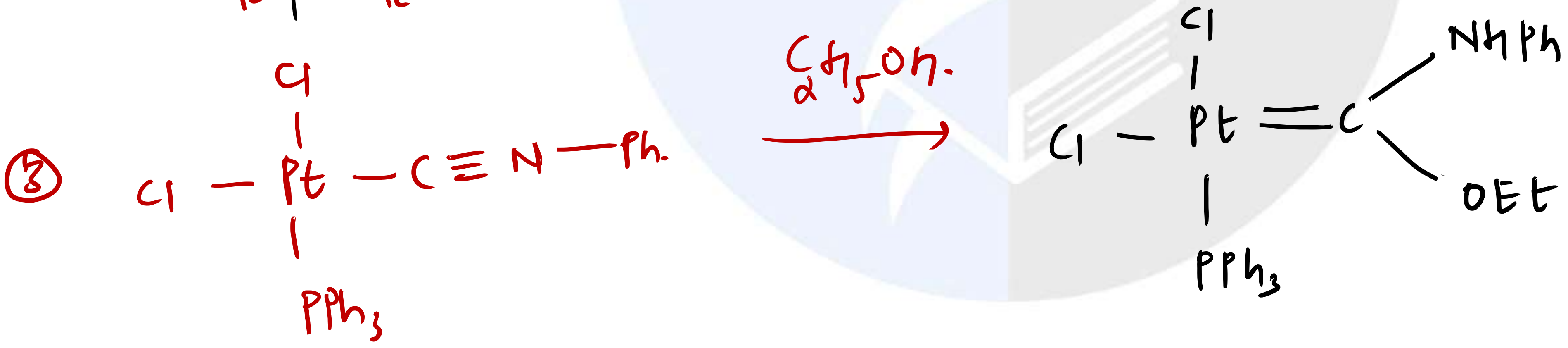
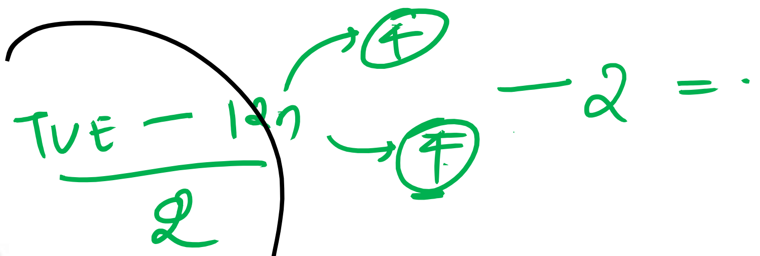




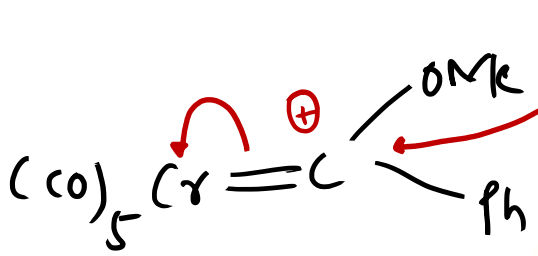


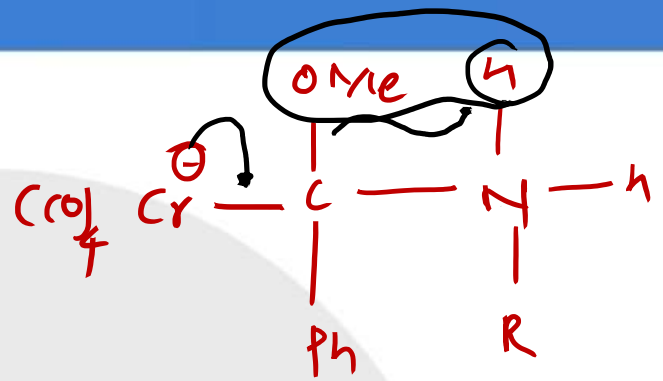


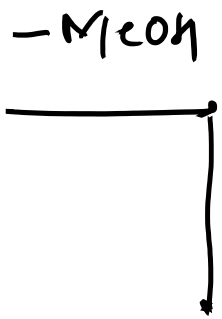
Fischer Carbene (singlet)

HW *

Q.





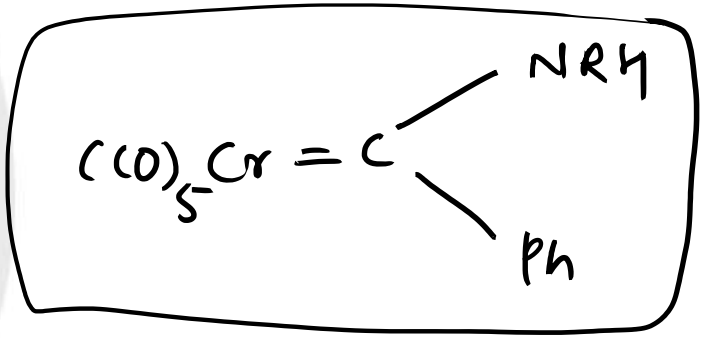


↳ Addn elimination Rxn.

$NH_3 \rightarrow -NH_2$

$NRH_2 \rightarrow -NRH$

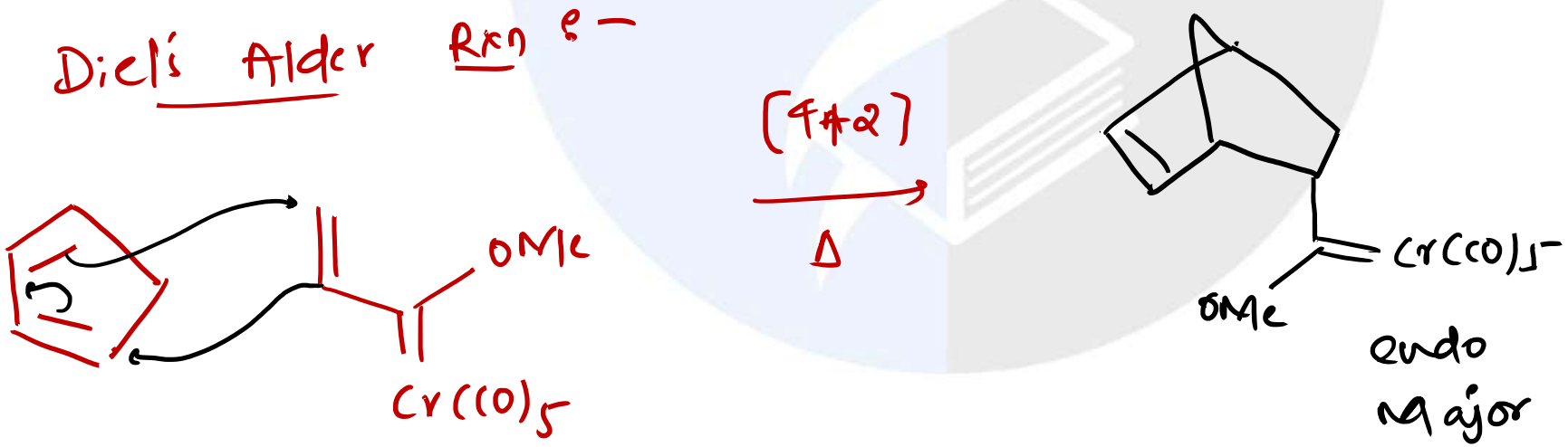
$NR_2H \rightarrow -NR_2$



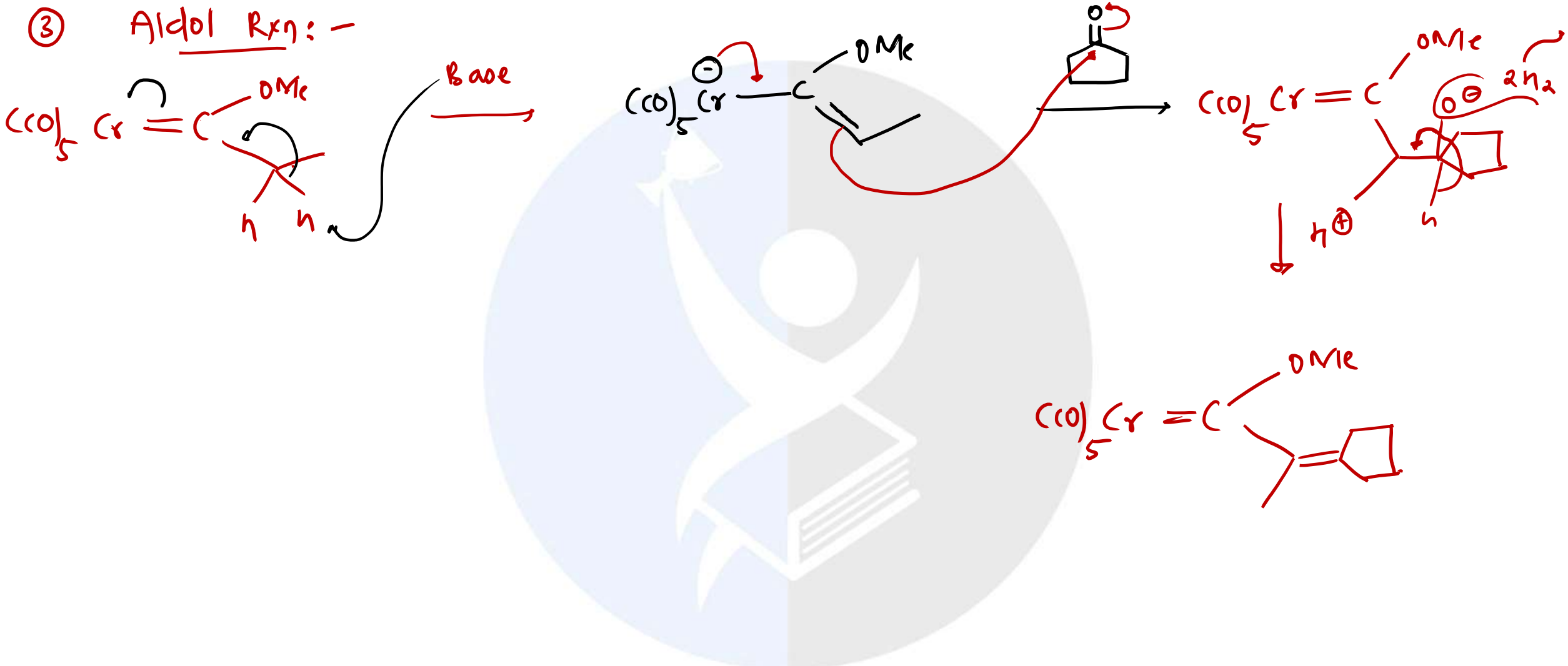
Applicatim of fischer Carbene :-

1. Acts as dienophile in Deil's Alder Rxn
2. f.C shows addn / elimination rxn ☆
3. f.C acts as Micheal acceptor
4. Can be used in Mannich Rxn.

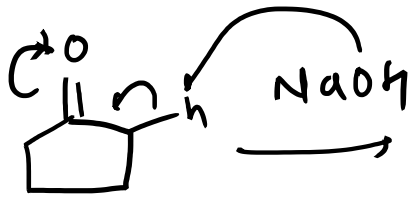
1 Diel's Alder Rxn :-

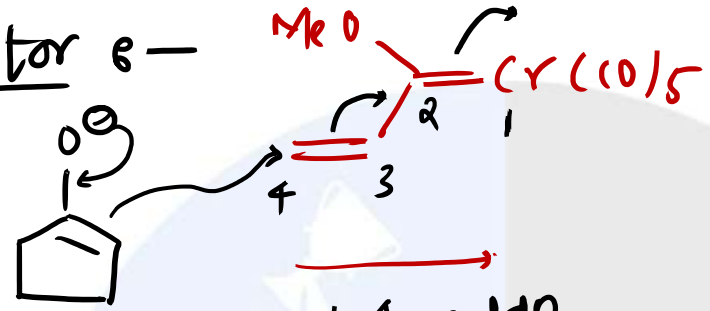


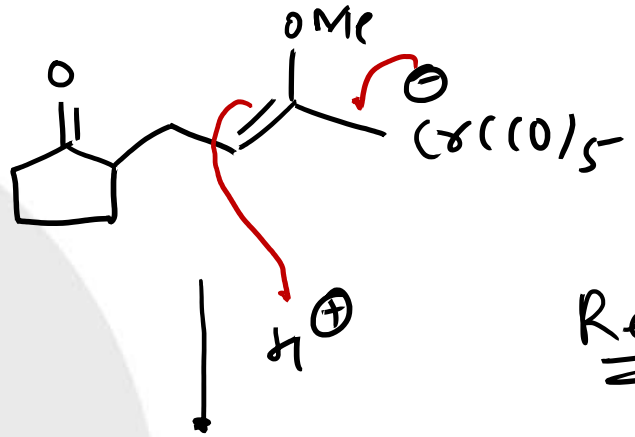
③ Aldol Rxn:-

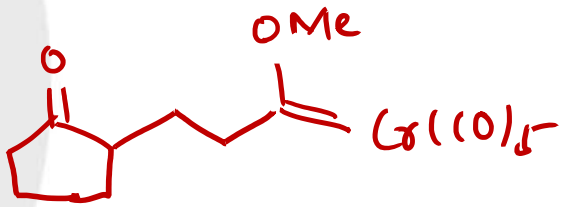


④ Micheal Acceptor :-

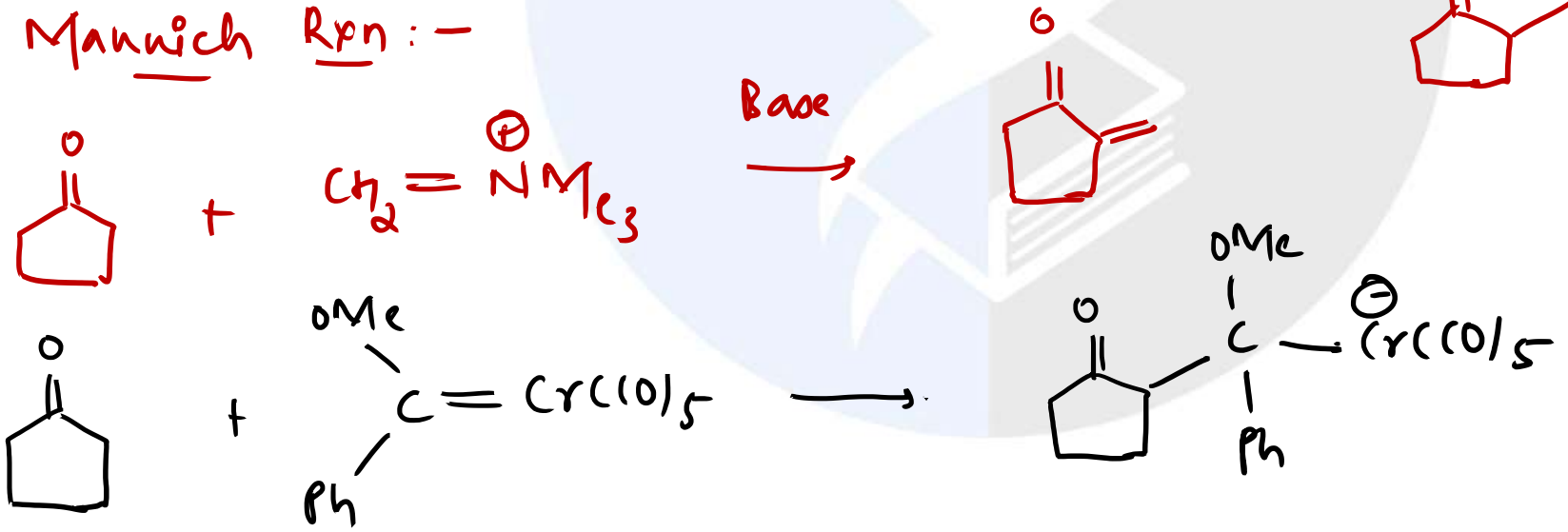








⑤ Mannich Rxn :-



Schrock Carbene :

① Does not follow 18 $e^{\ominus}$ rule.

② Early transition metals used in Schrock carbene

Ex: Ti^{+4} & Ta^{+5}

③ In S.C, metal must be in higher O.S.

④ S.C is triplet Carbene & nucleophic in nature

⑤ ✱ Hybn of C in S.C is sp^2 hybn (to be checked)

⑥ In S.C, carebene C contains σ-donor ligand.

⑦ In S.C, metal attached to σ donor & π donor ligands

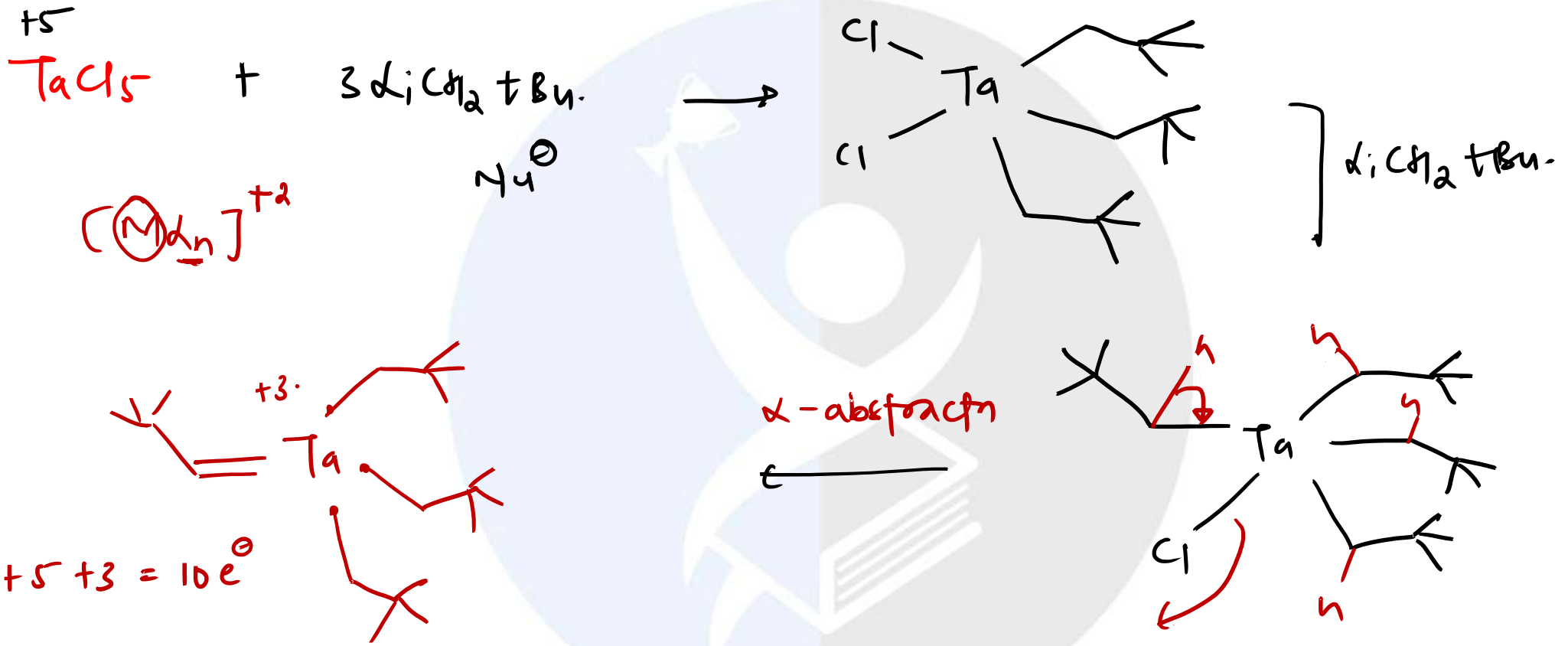
⑧ High Rotational barrier.

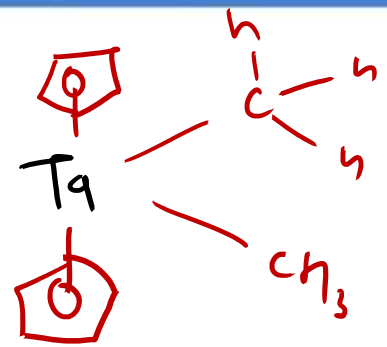
Ta, Ti → less EN

C → High EN

$M^{\delta+} - C^{\delta-} \rightarrow Nu^{\ominus}$

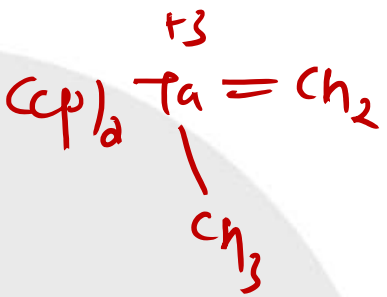
① Preparation of Schrock Carbene :-



② 

M = Ta / Ti / Zr

α-H-abstraction



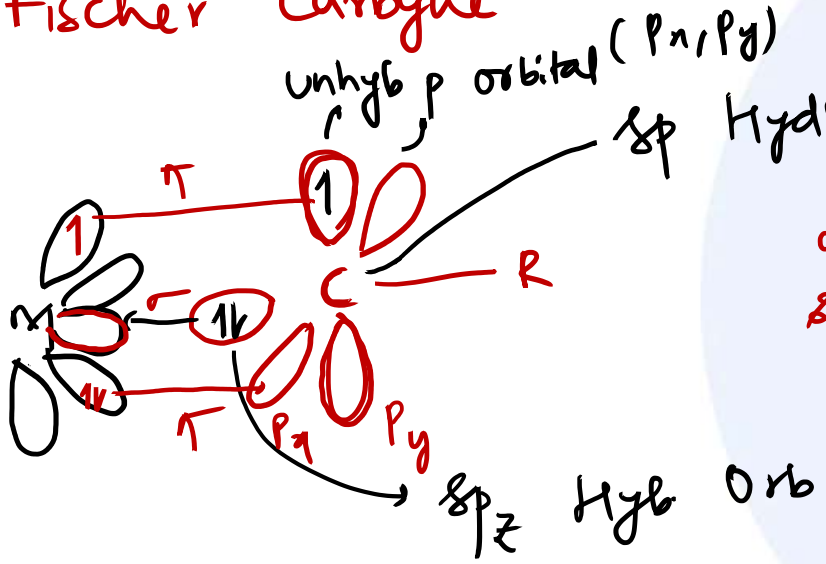
Application of Schrock Carbene :-

① $(\eta^5\text{-}Cp)_2Ta(CH_3)=CH_2 + AlMe_3$ (L.A) $\longrightarrow (\eta^5\text{-}Cp)_2MeTa^{\oplus}-CH_2-Al^{\ominus}Me_3$.

② $(\eta^5\text{-}Cp)_2MeTa^{\oplus}=CH_2 + Me_3SiBr \longrightarrow [(\eta^5\text{-}Cp)_2MeTa^{\oplus}.(CH_2SiMe_3)] + Br^{\ominus}$

Carbyne :- (CH / CR)

Fischer Carbyne



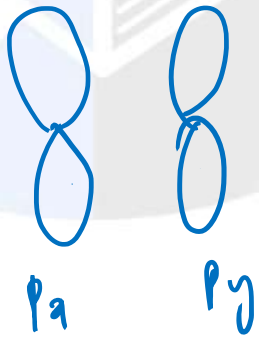
$M \equiv C$ (triple bond)

Doublet Carbyne

$2S+1$

$2\frac{1}{2}+1 = 2$

doublet

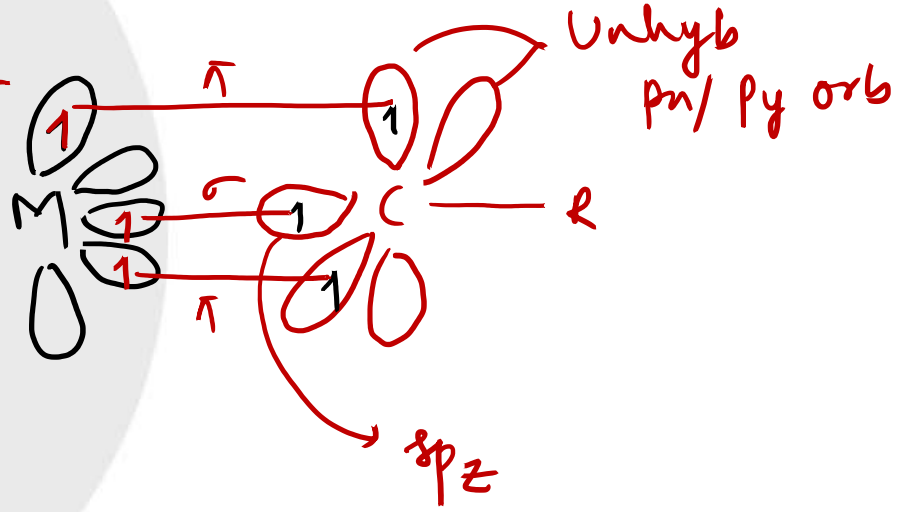


$2(\frac{3}{2})+1$

4

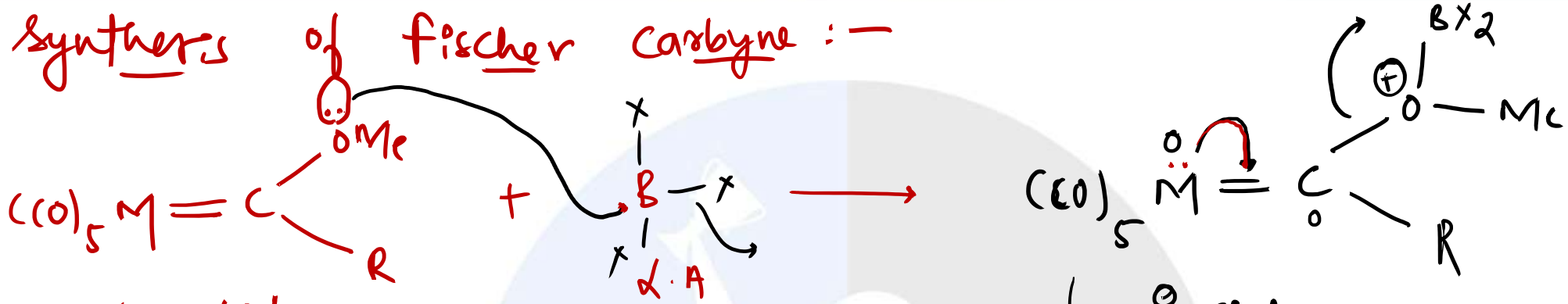
Quartet

Schrock Carbyne



Quartet Carbyne

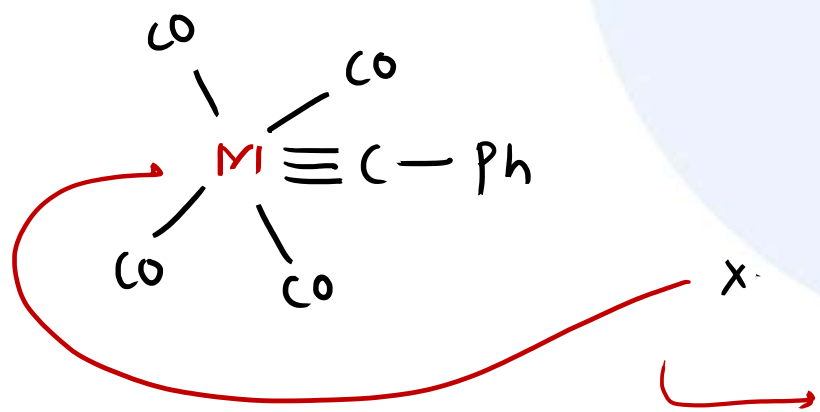
Synthesis of fischer carbyne :—

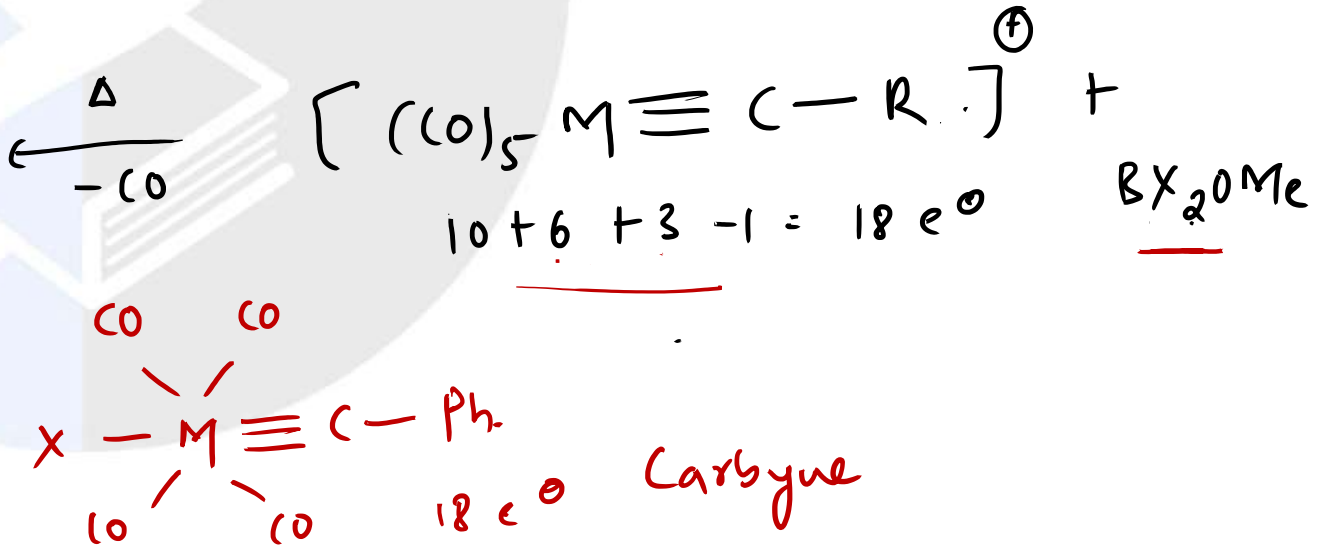


M = Cr / Mo / W

X = Cl, Br, I

R = Me, Et, Ph



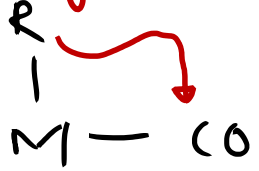


Migration / Insertion Reaction :-

- 1,1 Migration
- 1,1 Insertion

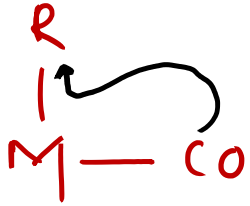
- 1,2 Migration
- 1,2 Insertion.

Migration



If anionic ligand migrate towards neutral ligand

Insertion



If neutral ligand migrate toward → Anionic ligand

1,1 Migration & Insertion

Condns.

1. Complex follow 18 $e^{\ominus}$ rule
2. Metal attached to σ donor ligand & next to carbonyl.
3. In 1,1 migration / Insertion, O.S remains same.

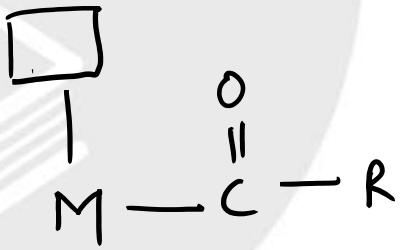
R → CH_3, CD_3, C_2H_5-, CH_2-CH_2-Br → σ donor

M — CO

18 $e^{\ominus}$

Saturated Complex

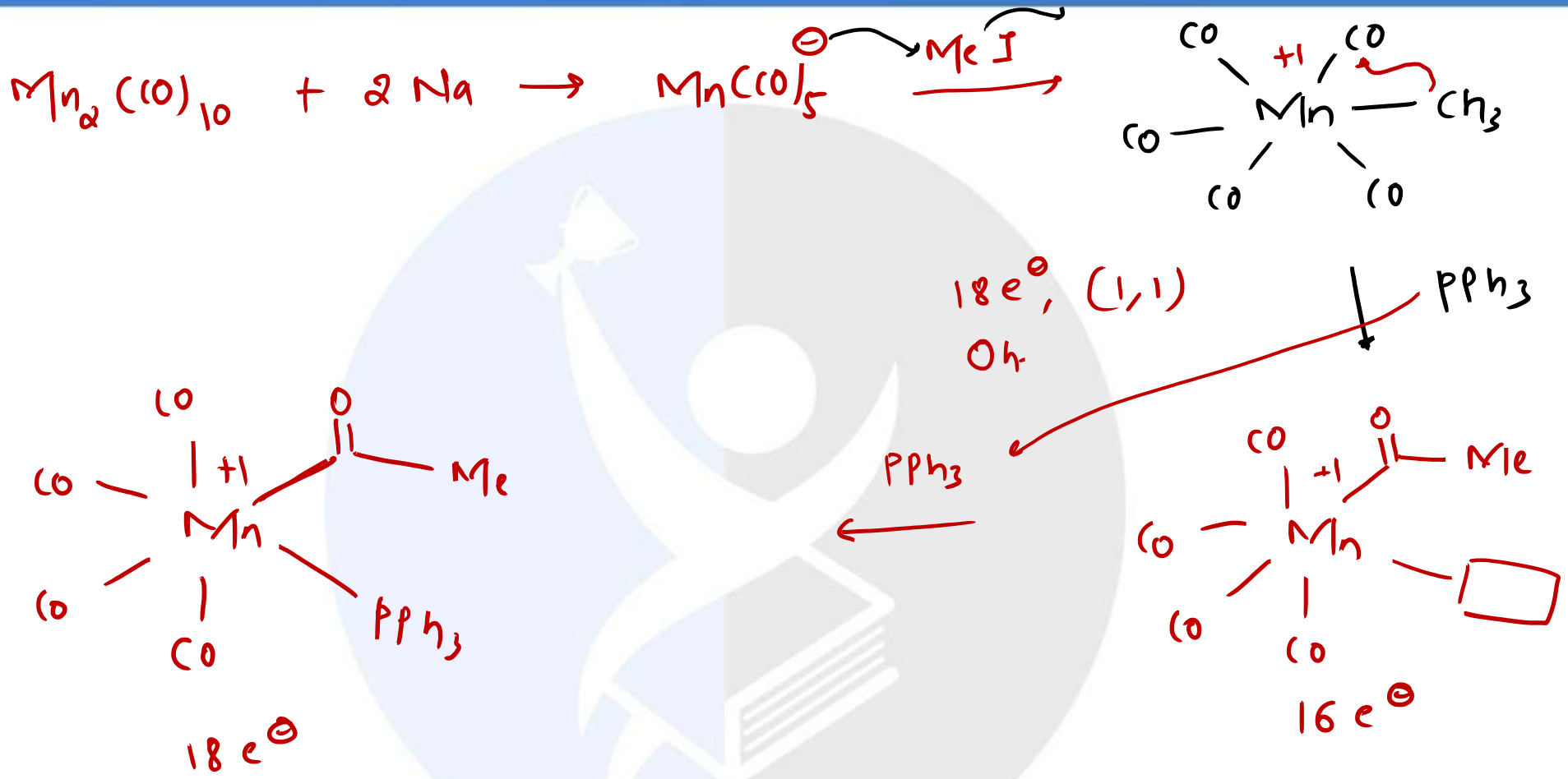
1,1 Migration



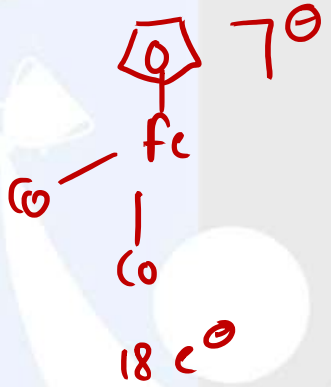
16 $e^{\ominus}$

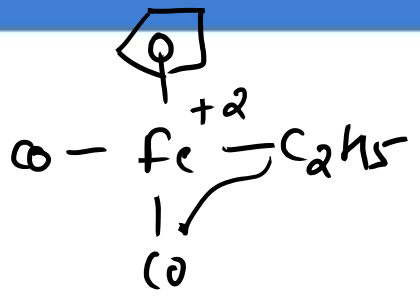
Unsaturated Complex

Ex: ①

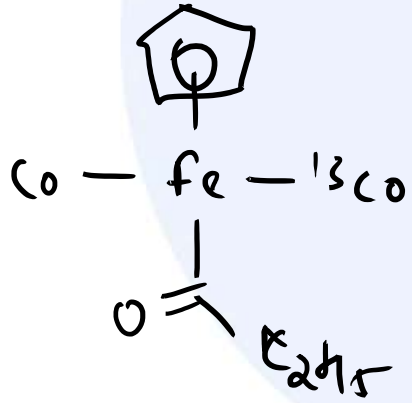

$Mn_2(CO)_{10} + 2Na \rightarrow Mn(CO)_5^{\ominus}$
MeI
+1
CO
Mn
CH_3
18 e⊖, (1,1)
Oh
PPh_3
Me
18 e⊖
16 e⊖

② $[Fe_2(CO)_4(Cp)_2] + 2Na \longrightarrow$ (A) $\xrightarrow{C_2H_5-I}$ (B)

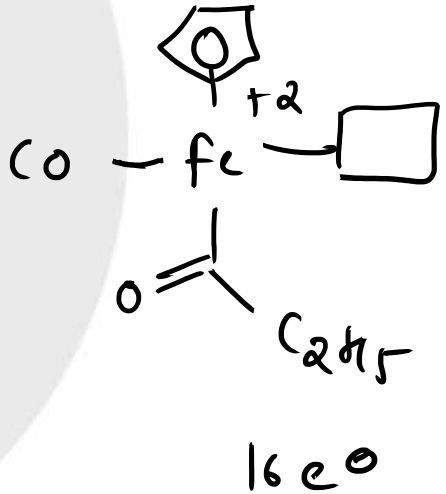




^{13}CO

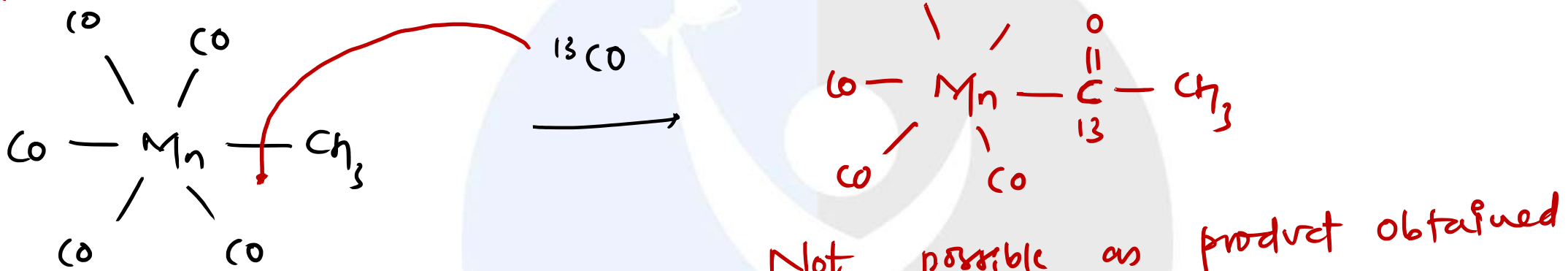


^{13}CO



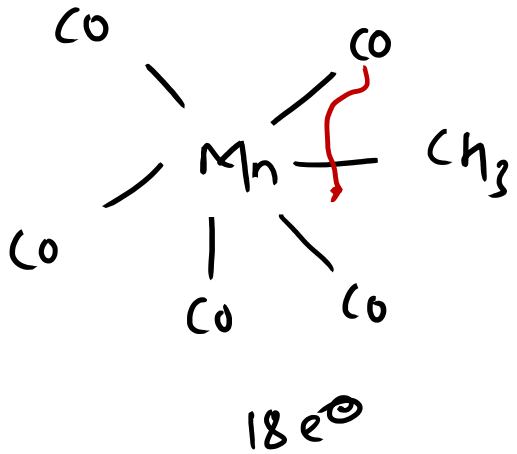
1.1 Migration Mechanism :-

① Direct CO Insertion :-

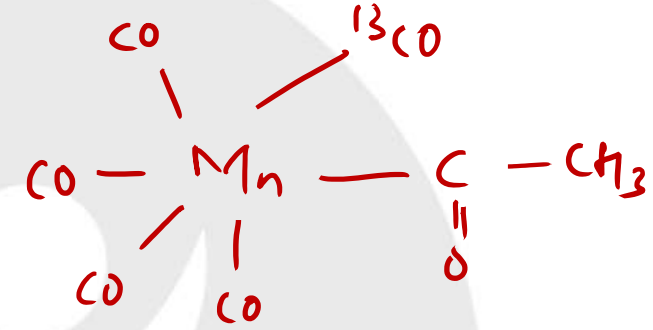


Not possible as product obtained expirementally is not labelled.

② Intramolecular CO Insertion.



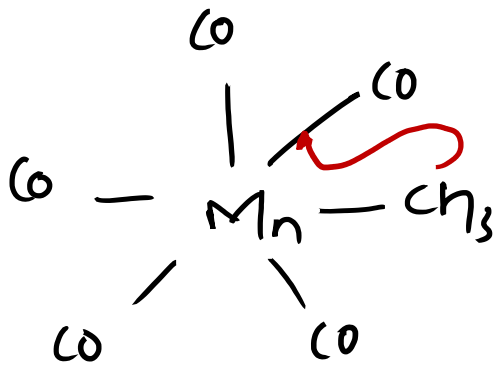
^{13}CO →



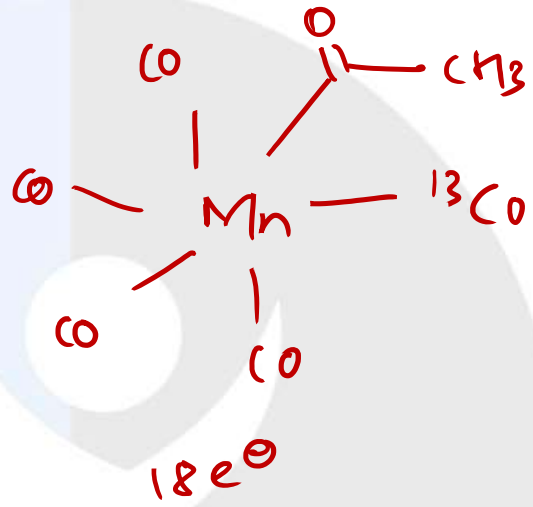
Possible

Non labelled acyl group

(3) Methyl Migration :-

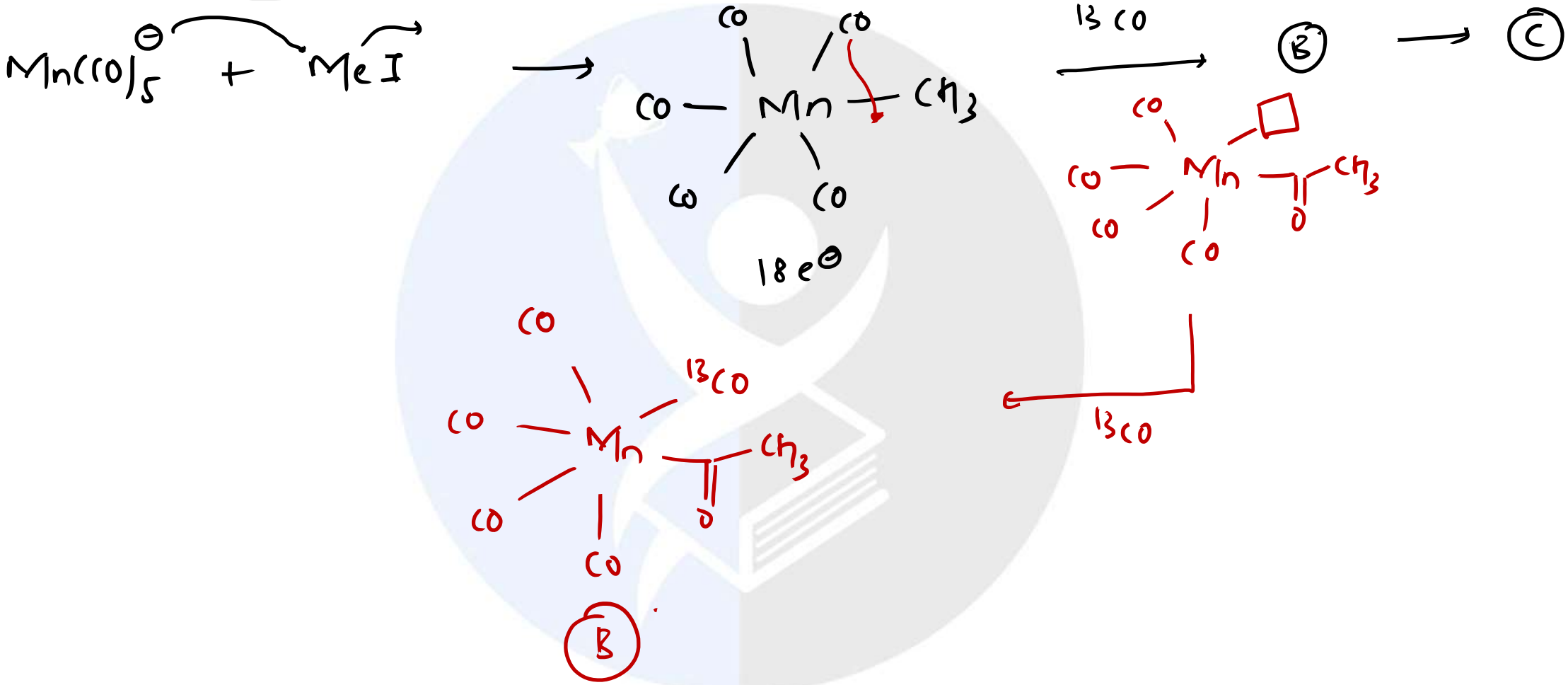


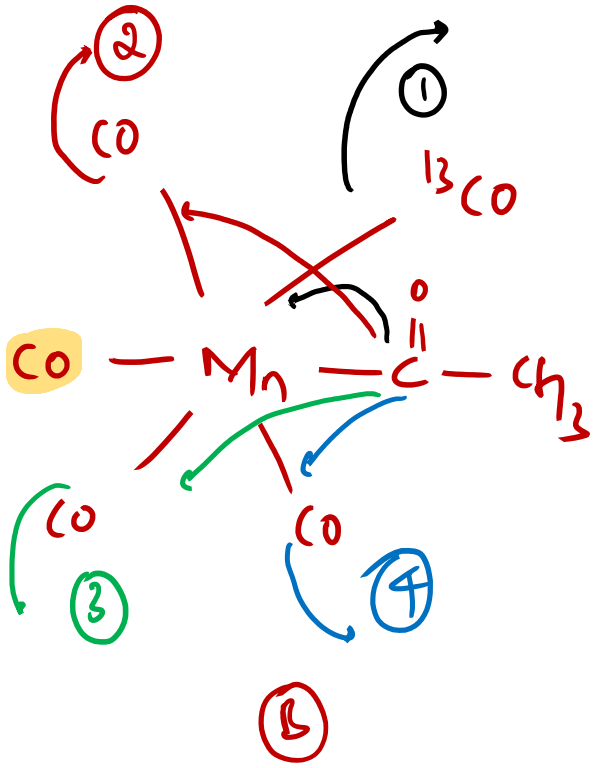
^{13}CO →

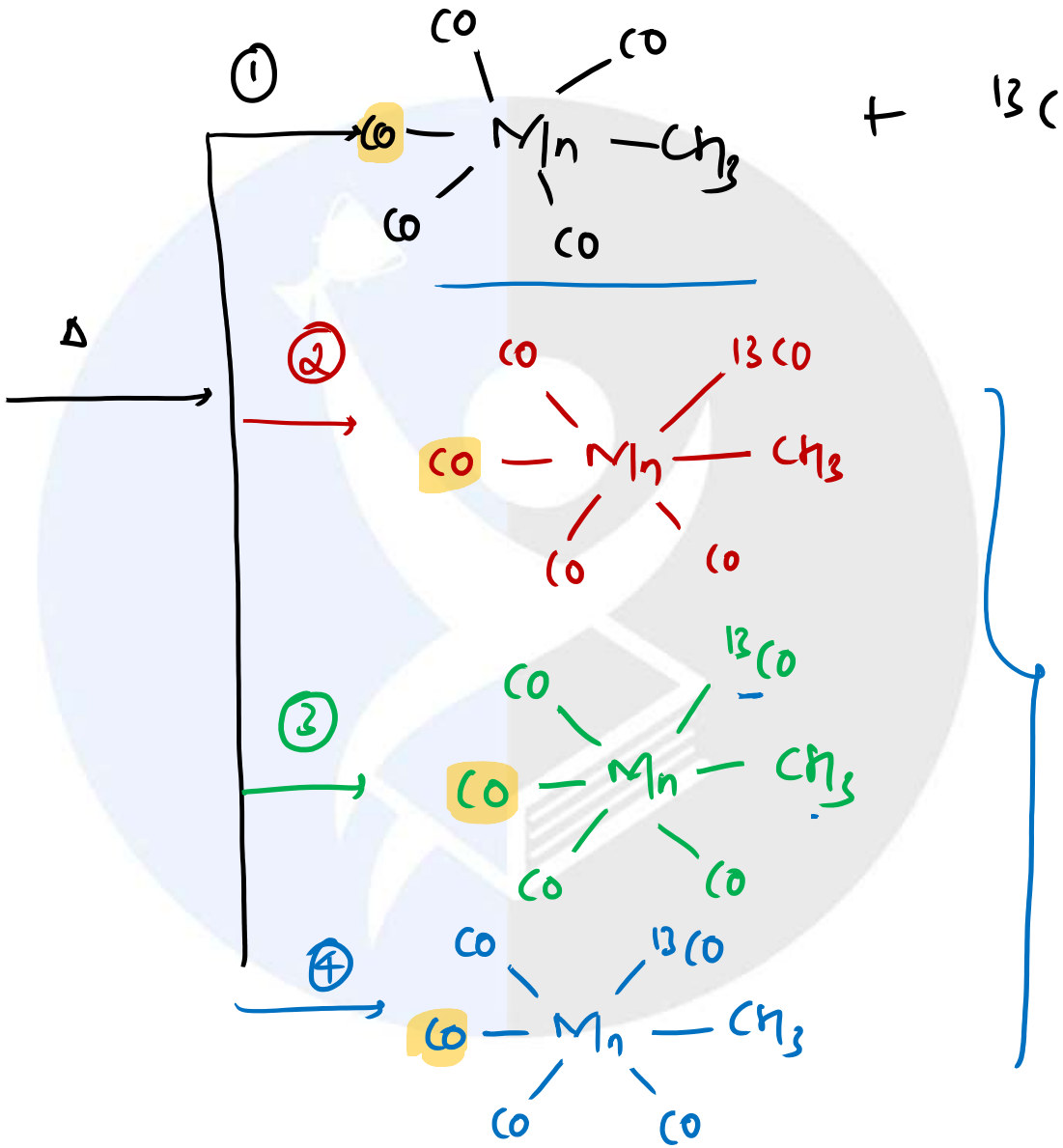


possible as product contains non labelled acyl group.

Intramolecular CO Insertion :-



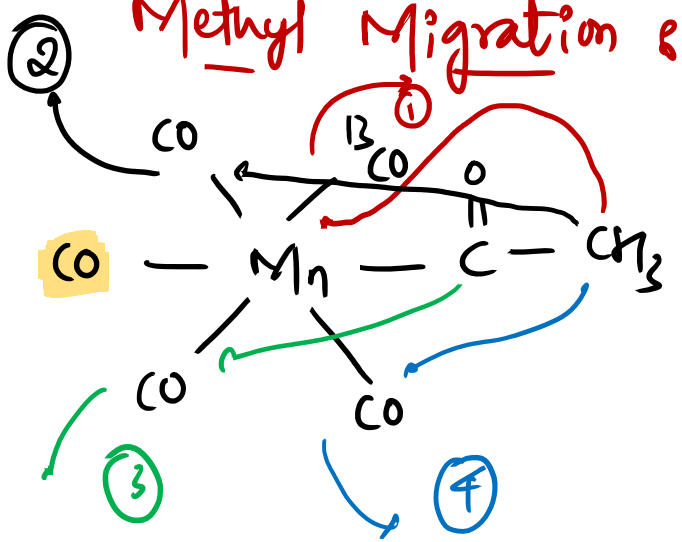




25 % Non labelled product (cis)

75 % labelled product (cis)

Methyl Migration :-

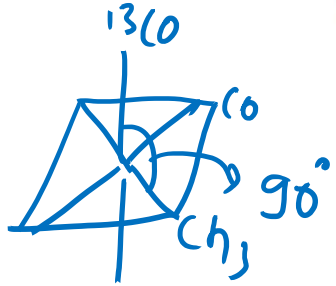


1 : 2 : 1

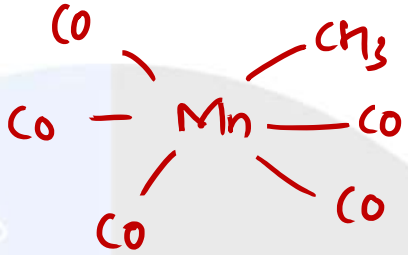
25% non labelled

50% cis

25% trans

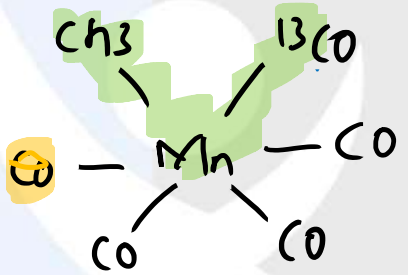


1 + ^{13}CO



25% Non labelled

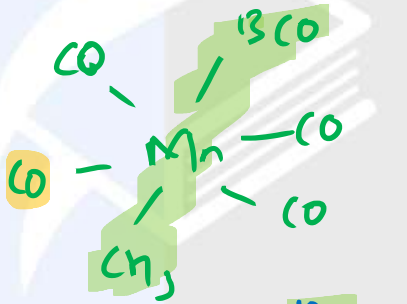
2



25% labelled product

cis

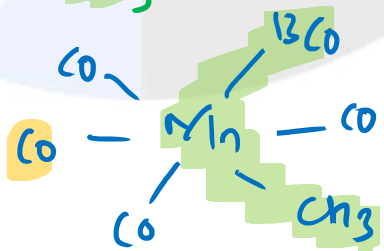
3



25% labelled.

trans

4



25% labelled

cis

Thank you