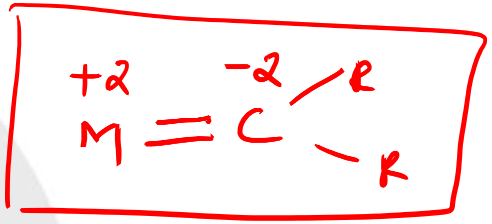
①

Neutral → $\underline{0}$ O.S

$M \leftarrow \ddot{N}R_3$ Amine → $2e^{\ominus}$ donor

$M \leftarrow \cancel{\cdot}\overset{\ominus}{N}R_2$ → { $\underline{1}$ $e^{\ominus}$ donor }.

$\underline{\overset{+1}{M}} - \underline{\overset{-1}{N}}R_2$



$\overset{+3}{M} \equiv \overset{-3}{C} - R$

② Impt pts of 1,1 Migratory Insertion:

① In 1,1 migration O.S. never changes.

② " " " . mechanism is always cis.

③ 1st Order Rxn

$$\underset{Oh}{Mn(CO)_5Me} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn(CO)_4(COMe)$$

slow/ R.D.S

$$\boxed{Rxn \propto [Mn(CO)_5\text{-}Me]}$$

$$Mn(CO)_4(COMe) + {}^{13}CO \xrightarrow{fast} [Mn(CO)_4(COMe)({}^{13}CO)].$$

③ ~~④~~

Me Migratn } same product
CO Insertion

(IR studies) → Me migration is favoured over CO Insertion.

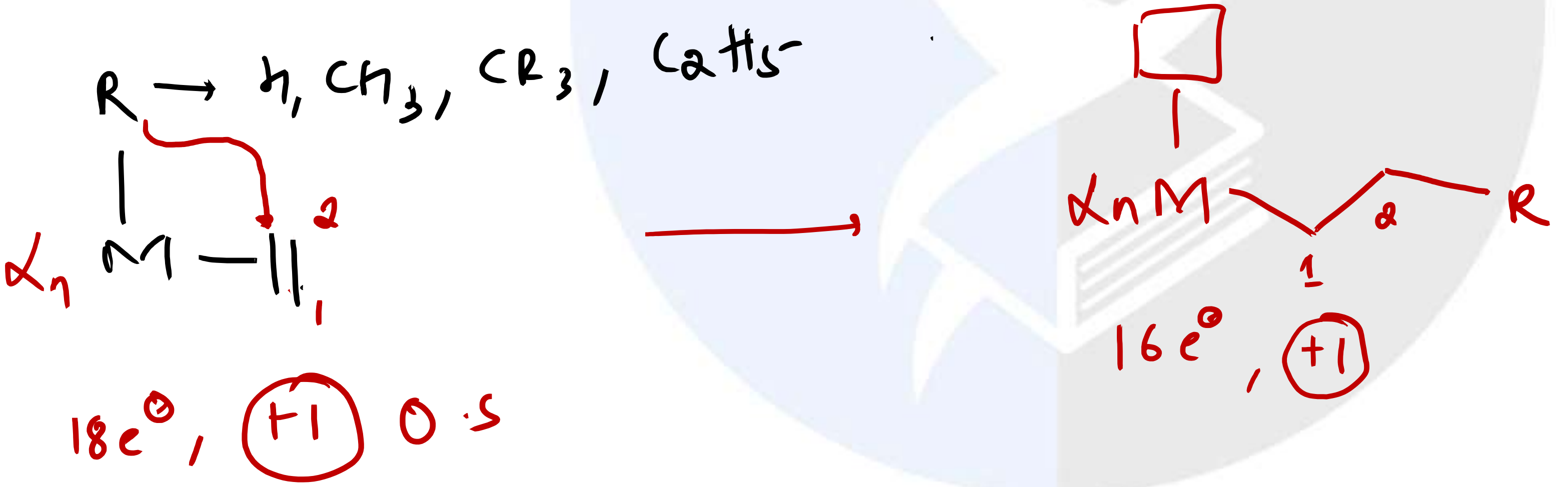
⑤ In Migratory Insertion, 5 coordinate int is formed.

1,2 Migratory Insertion :

Cond^n :- ① 18 $e^{\ominus}$ complex shows 1,2 migratory Insertion.

② In 1,2 Migratory Insertion; metal attached to alkene & next to σ donor ligand.

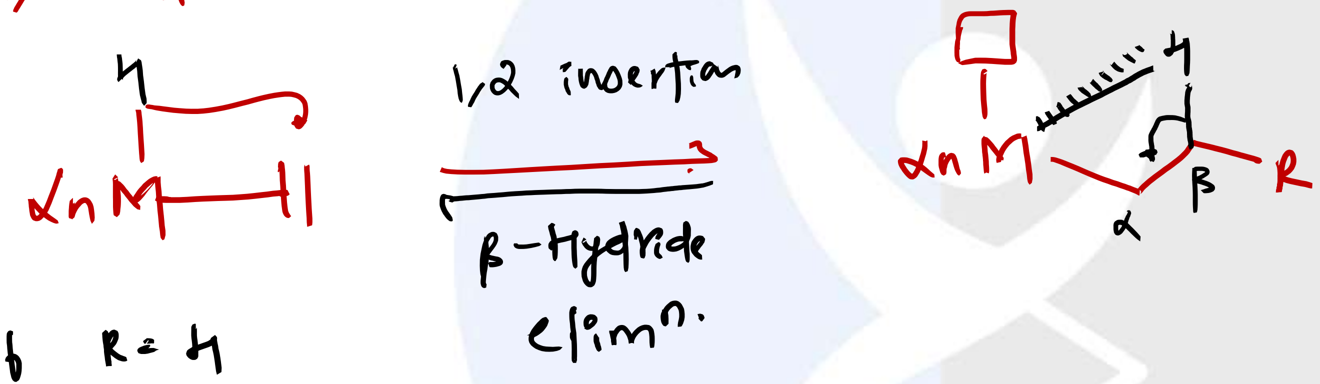
R → H, CH_3, CR_3, C_2H_5



③ O.S remains same

④ 18 $e^{\ominus}$ complex ⟶ 16 $e^{\ominus}$ comp.

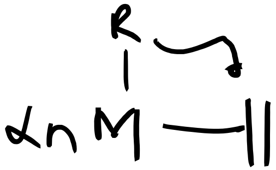
⑤ 1,2 Insertion rxn reversible to β-Hydride elimination

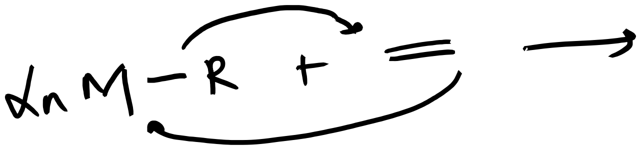


if R = H

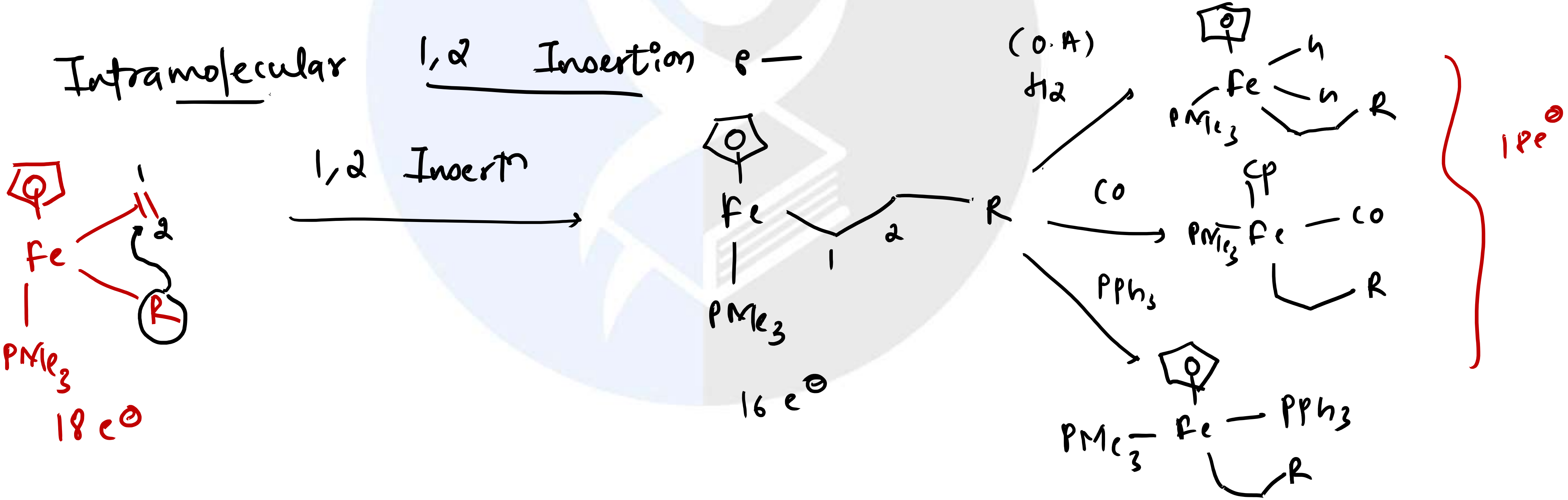
Intramolecular 1,2 Insertion

Intermolecular 1,2 insertion.

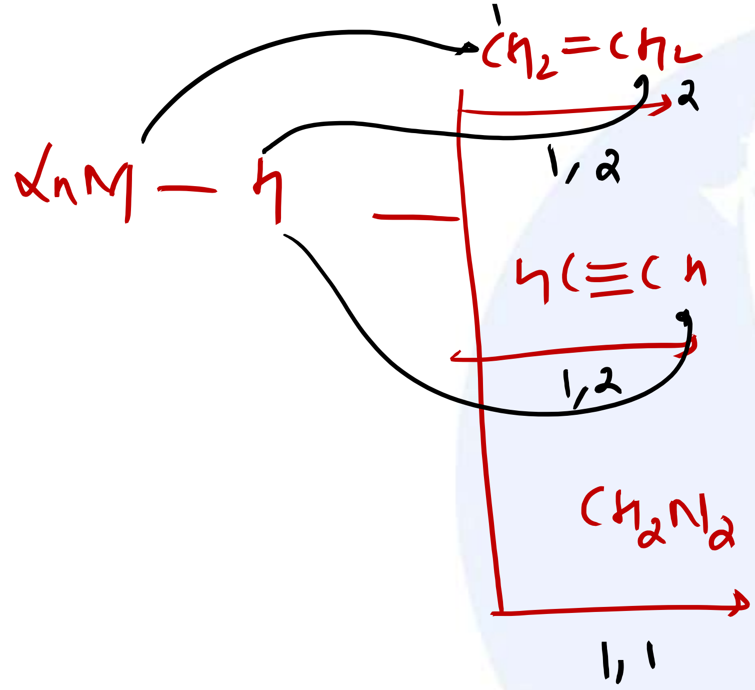




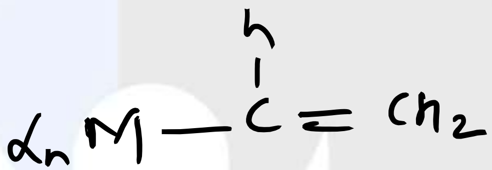
① Intramolecular 1,2 Insertion e—



② Intermolecular 1,2 Insertion :-



$L_nM-CH_2-CH_3$



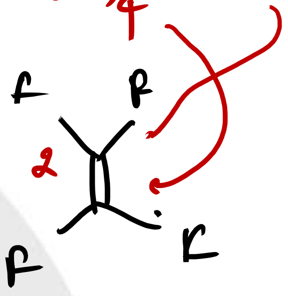
$L_nM-\overset{\overset{H}{|}}{C}=CH_2$

$M-CH_3$

Q. $Co_2(CO)_8 + 2Na \longrightarrow$ Ⓐ $\xrightarrow{H_3O^{\oplus}}$ Ⓑ.

$(CO)_4Co-H.$

$Na[Co(CO)_4]^{\ominus}$



1,2 Insertn.

$\downarrow$

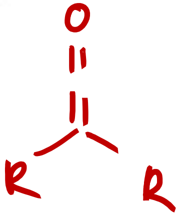
Ⓒ

$(CO)_4Co-CF_2-CF_2-H$

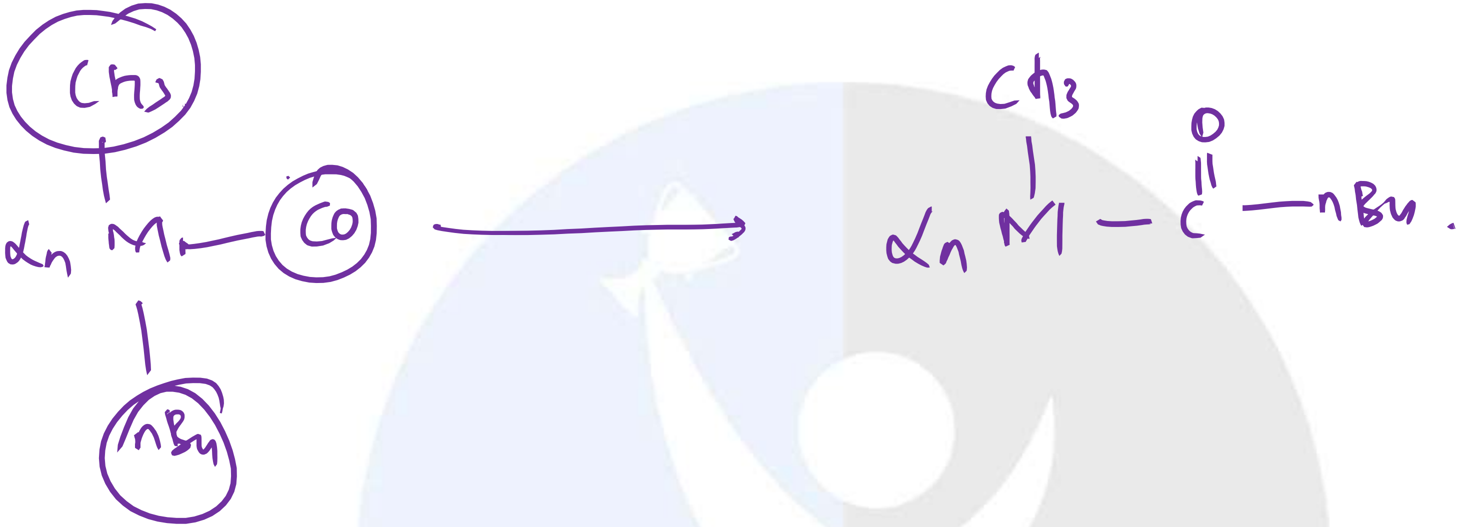
HW ✓

Q. $Co_2(CO)_8 + 2Na \longrightarrow$ Ⓐ $\xrightarrow{H_2O}$ Ⓑ $\longrightarrow$ Ⓒ

$\xrightarrow{2Na}$ Ⓐ $\xrightarrow{H_2O}$ Ⓑ $\xrightarrow{CH_2N_2}$ Ⓒ. $\xrightarrow{PPh_3}$ Ⓓ



Q



$$L_nM(CH_3)(nBu)-CO \longrightarrow L_nM(CH_3)-\overset{O}{\overset{\|}{C}}-nBu$$

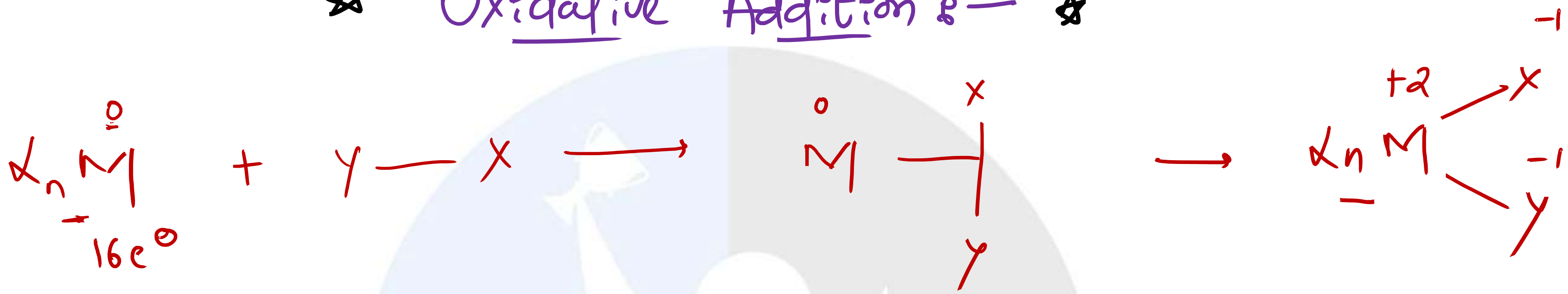
Migratory Aptitude :-

$H > nBu \simeq CH_2CH_2CH_3 > CH_3 > C_2H_5$

→ $\boxed{e^{\ominus} \text{ rich group migrates first}}$

→ EWG will not migrate.

★ Oxidative Addition :- ★



Criteria :

① All 16 e⁻ complex can show O·A

② In O·A, O·S & CN ↑ by 2 unit

③ Metal should be in lower O·S / e⁻ rich.

④ If EDG ↑ on comp., Rate of O·A ↑

⑤ EWG / ↑ acceptor ligand, Rate of O·A ↓

$\boxed{\text{O·A}}$

Polar O·A

→ If EN diff betn 2 atoms > 0.5

Ex: $\overset{\delta+}{Me}\overset{\delta-}{I}$, $\overset{\delta+}{Me}\overset{\delta-}{Br}$, $\overset{\delta+}{Me}\overset{\delta-}{Cl}$, $\overset{\delta+}{H}\overset{\delta-}{Cl}$

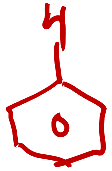
→ Concerted Mech (S_N2)

→ Trans addn

Non polar O·A

→ EN diff betn atom < 0.5

Ex: H_2, O_2, N_2,



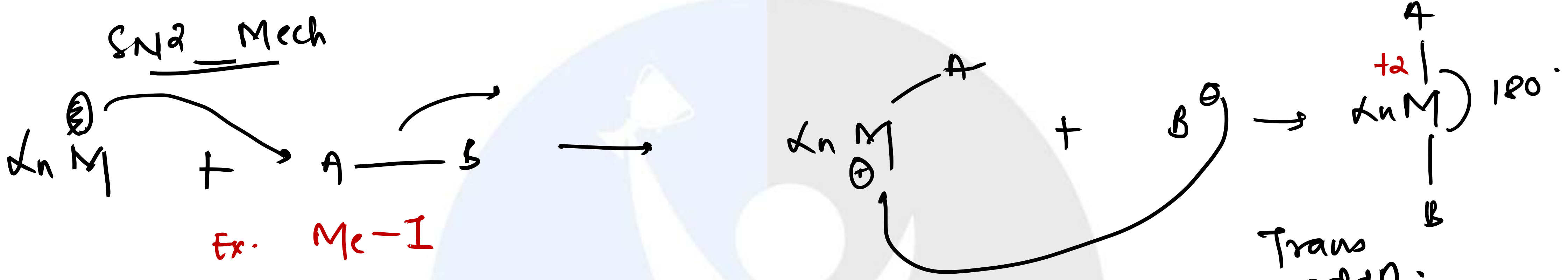
, $H-C\equiv C-H$

→ Free Radical mech

→ Cis· addn.

Polar O·A :

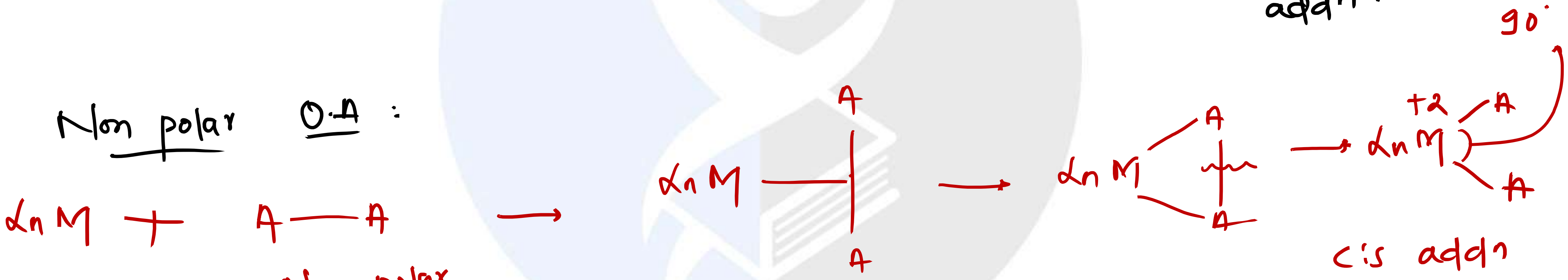
SN2 Mech



Ex. $Me-I$

Trans addn.

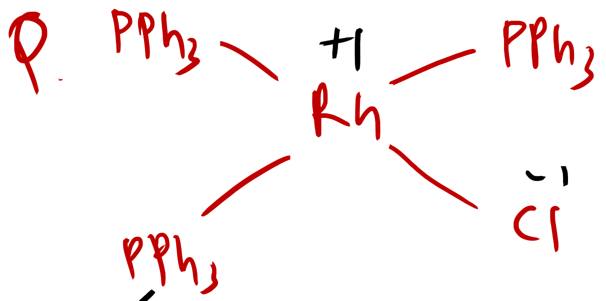
Non polar O·A :



Non polar

Ex: H_2

cis addn



$+ \; H_2 \longrightarrow$

16 $e^{\ominus}$

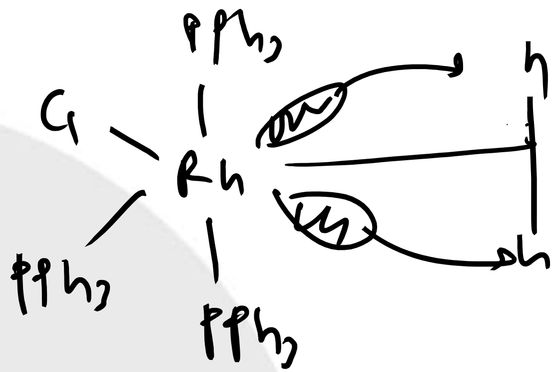
Sq. planar

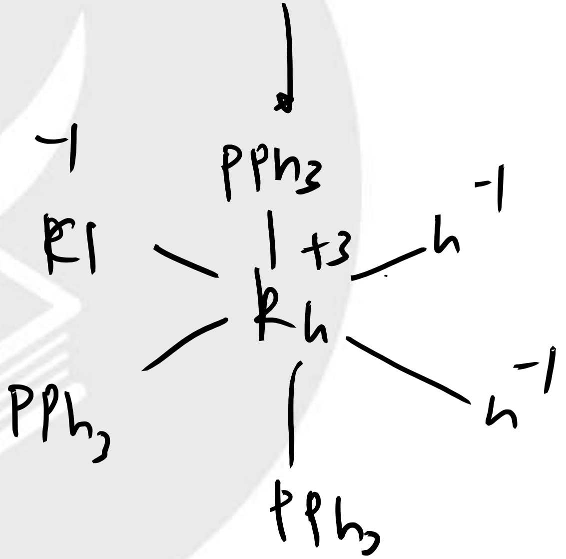
low O.S / M $e^{\ominus}$ rich

C.N = 4

Non polar

Cis addⁿ



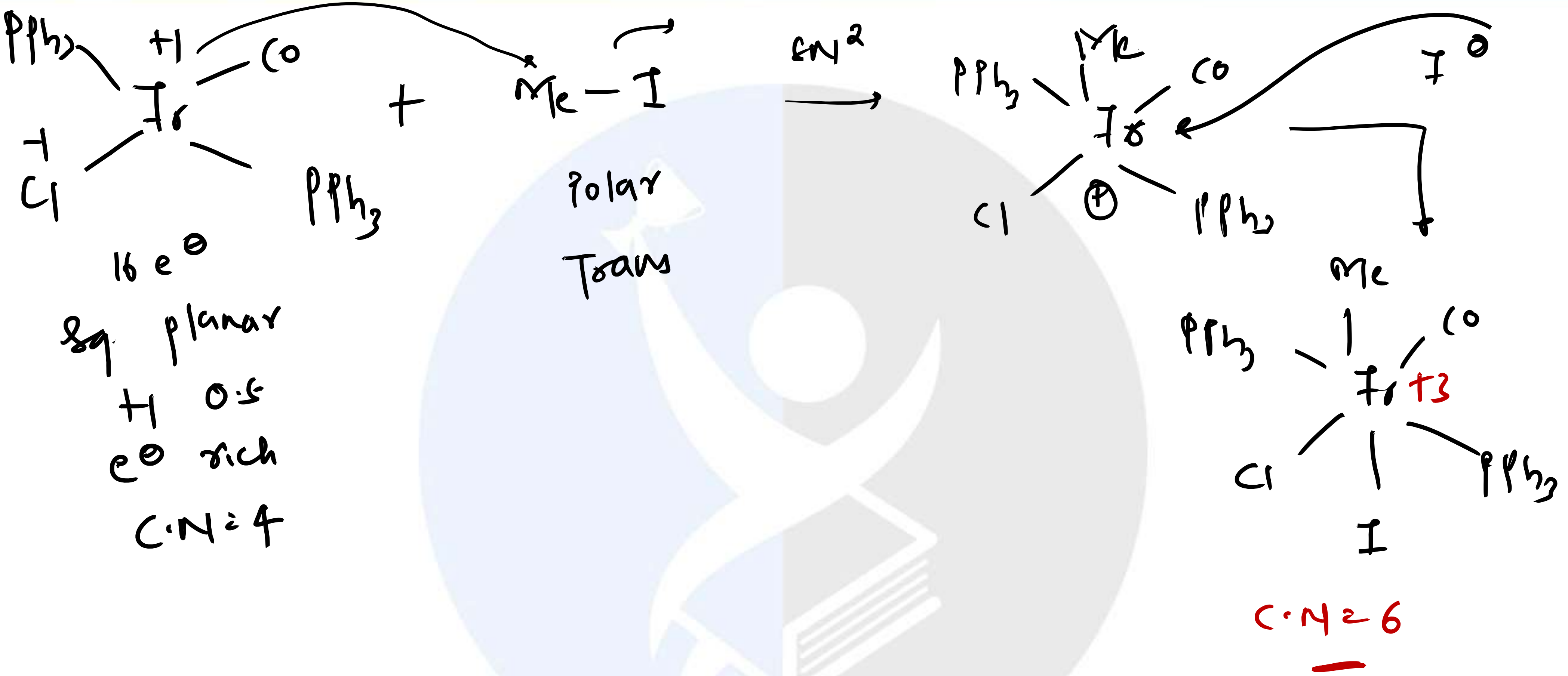


O.S ↑ by 2

C.N ↑ by 2

C.N = 6

Q.



16 e⊖

sq. planar

+1 O.S

e⊖ rich

C.N = 4

Polar

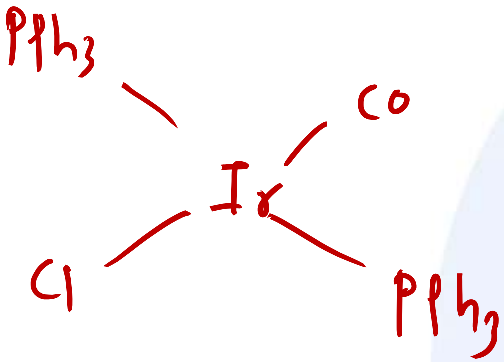
Trans

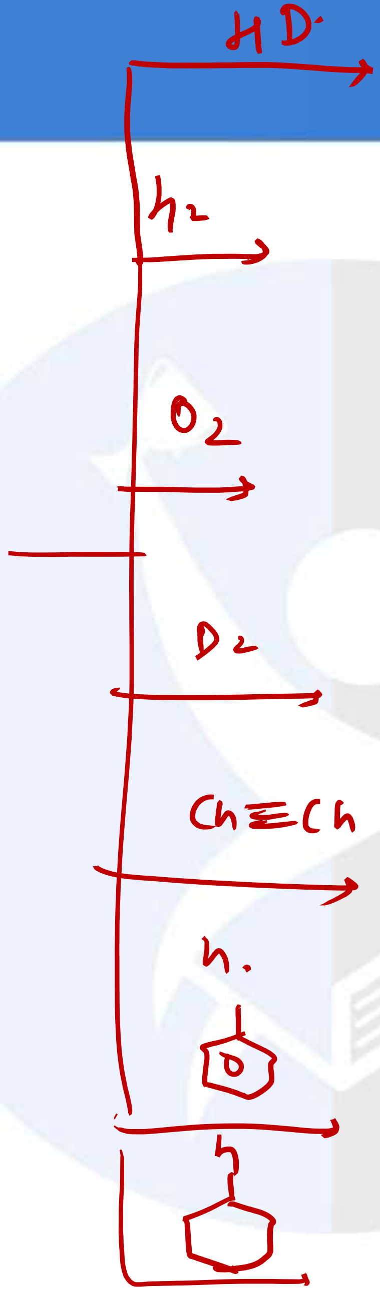
S_N2

C.N = 6

Q.

HW

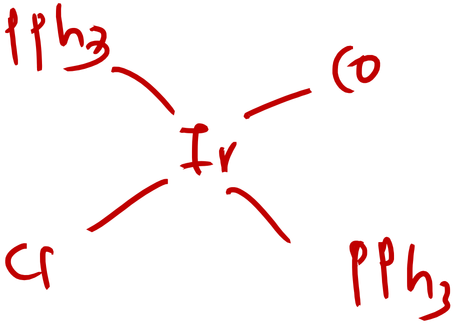




Cis addn

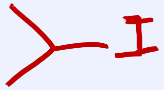
Non polar

φ hw



MeI

C_2H_5Cl



} trans addⁿ

$\boxed{HI}$

EN diff

∴ cis addⁿ

More C.C / More polarisatⁿ.

HF
HCl
HBr

} trans addⁿ

less C.C (cov. character)

less polarisatⁿ

Q. Which of following donot show O.A ?

ⓐ [$\overset{0}{\text{Ni}}(CO)(PPh_3)_2$] → 16 $e^{\ominus}$ ✓

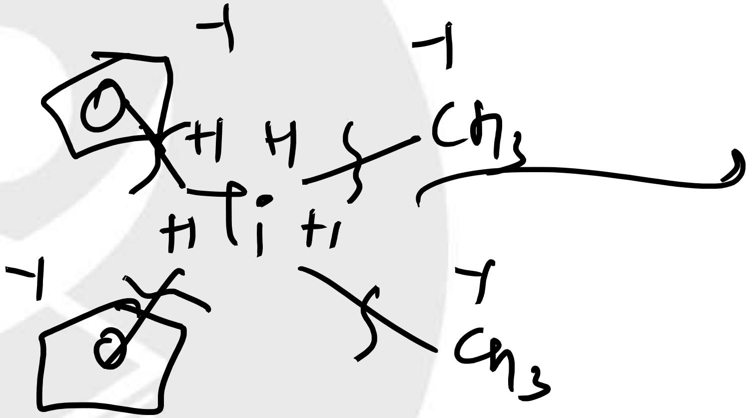
Ⓑ [$\overset{+1}{\text{Ir}}(CO)Cl(PMe_3)_2$] → 16$e^{\ominus}$ ✓

ⓒ [$RhCl(PPh_3)_3$] $16^{\ominus}$ ✓

ⓓ [$\overset{+1}{\text{Rh}}I_2(CO)_2]^{\ominus}$ 16 $e^{\ominus}$ ✓

ⓔ [$\overset{+4}{\text{Ti}}(Cp)_2.(CH_3)_2$] → $16^{\ominus}$ ✗

M high O.S



+4 O.S

Reactivity O.A :

① d^8 Metal show O.A

3d	Fe^0	Co^{+1}	Ni^{+2}
4d	Ru^0	Rh^{+1}	Pd^{+2}
5d	Os^0	Ir^{+1}	Pt^{+2}
	d^8	d^8	d^8

↓ Principal Q. no ↑

Rate of O.A ↑

→

O.S ↑ $e^{\ominus}$ denisty ↓ O.A rate ↓

Q. Which among gives faster O.A ?

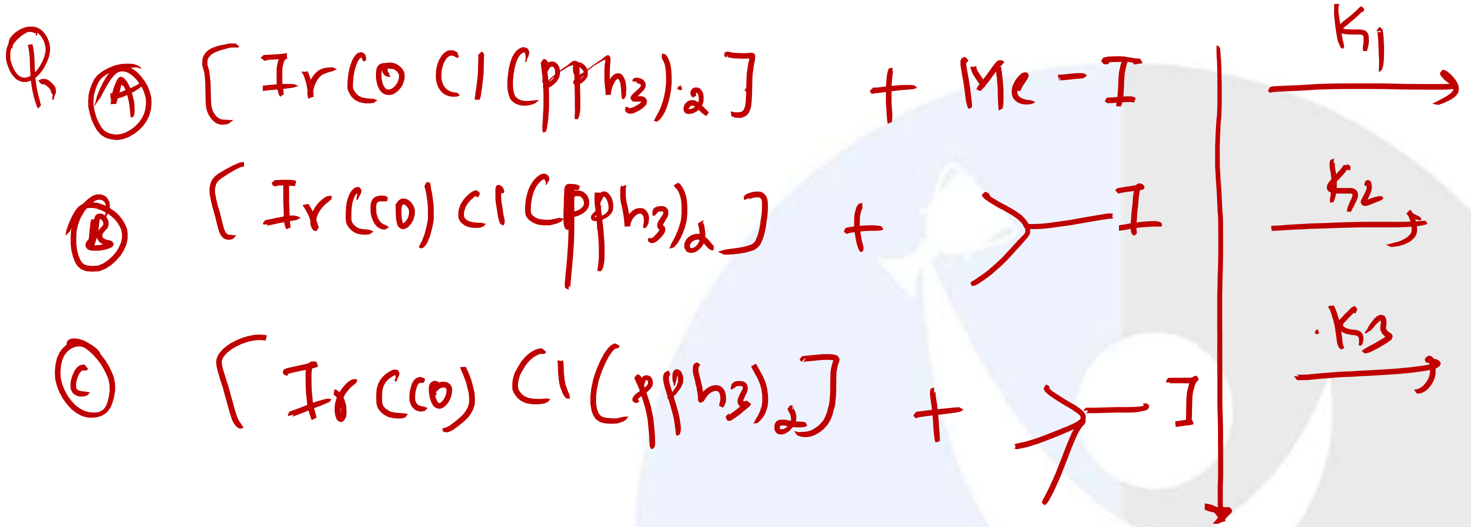
Ⓐ $[Co(CO)Cl(PPh_3)_2^{-}]$

Ⓑ $[RhCOCl(PPh_3)_2]$

Ⓒ $[IrCOCl(PPh_3)_2]$.

$n \uparrow$ O.A $\uparrow$

$\boxed{C > B > A}$



Q. Ⓐ $[Ir(CO)Cl(PPh_3)_2] + Me-I \xrightarrow{k_1}$

Ⓑ $[Ir(CO)Cl(PPh_3)_2] + \; -I \xrightarrow{k_2}$

Ⓒ $[Ir(CO)Cl(PPh_3)_2] + \; -I \xrightarrow{k_3}$

$k_1 > k_2 > k_3$

Steric crowding ↑ of polar group

Rate of O.A ↓

Q. Ⓐ $[Ir(CO)Cl(PPh_3)_2]$ + $CH_3-OTs \xrightarrow{k_1}$

Ⓑ $CH_3-I \xrightarrow{k_2}$

Ⓒ $CH_3-Br \xrightarrow{k_3}$

Ⓓ $CH_3-Cl \xrightarrow{k_4}$

<u>Rate of O·A</u>

$k_1 > k_2 > k_3 > k_4$

$$\boxed{\begin{array}{c} \text{If L.G ability} \uparrow \\ \text{Rate of O·A} \uparrow \end{array}}$$

$-OTs > -I > -Br > -Cl$

Ortho Metallation / Cyclometallation :—

① 16 $e^{\ominus}$ complex show Orthometallation

② Ortho Hydrogen must be present.

③ In final product, 4 mem ring is formed.

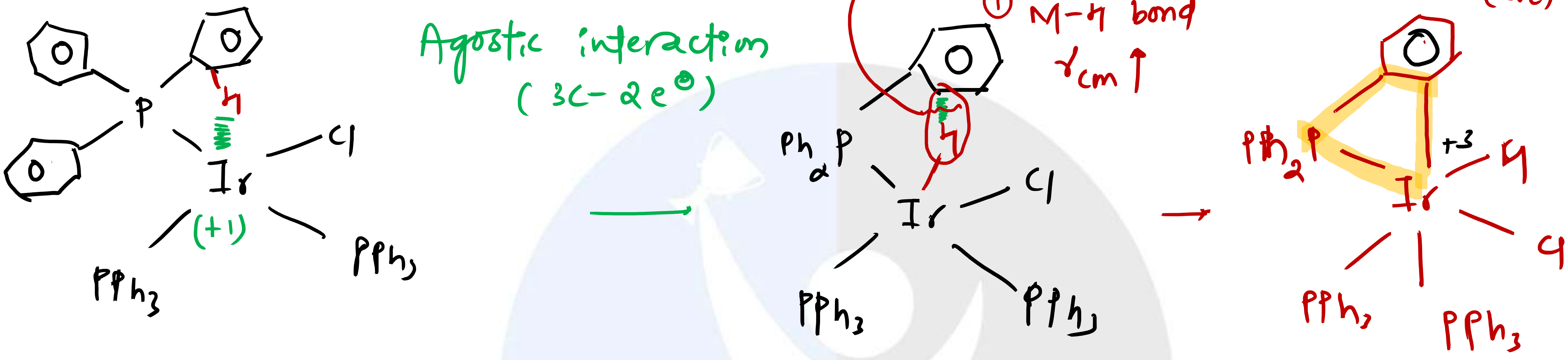
④ Orthometallation is similar to O.A. as it also requires Lower O.S.

B.L ↑, C-H acidity [Upfield region shielding (-ve)]

Agostic interaction (3C- 2e$^{\ominus}$)

① M-H bond

ν_{cm} ↑



[5 mem T.S]

4 mem Ring

O.S ↑ by +2

③ Sigma bond Metathesis σ—

Condn :

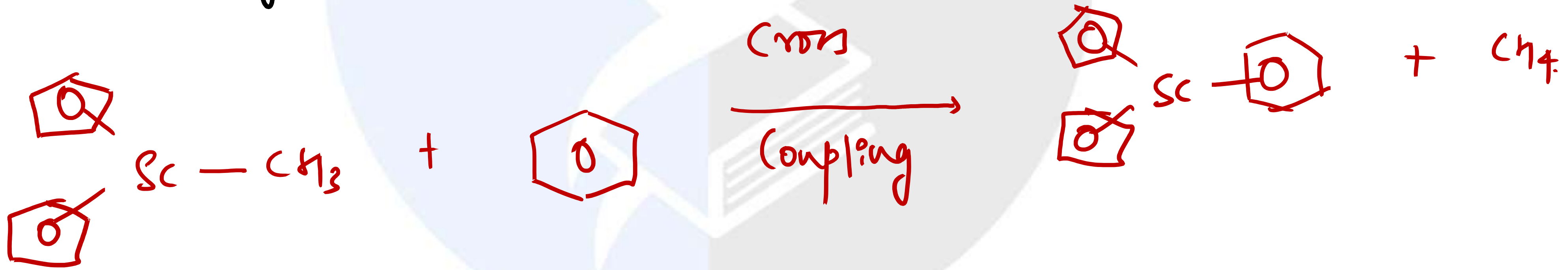
① The E.C of metal d^0

② formation of a 4 - membered T.S.

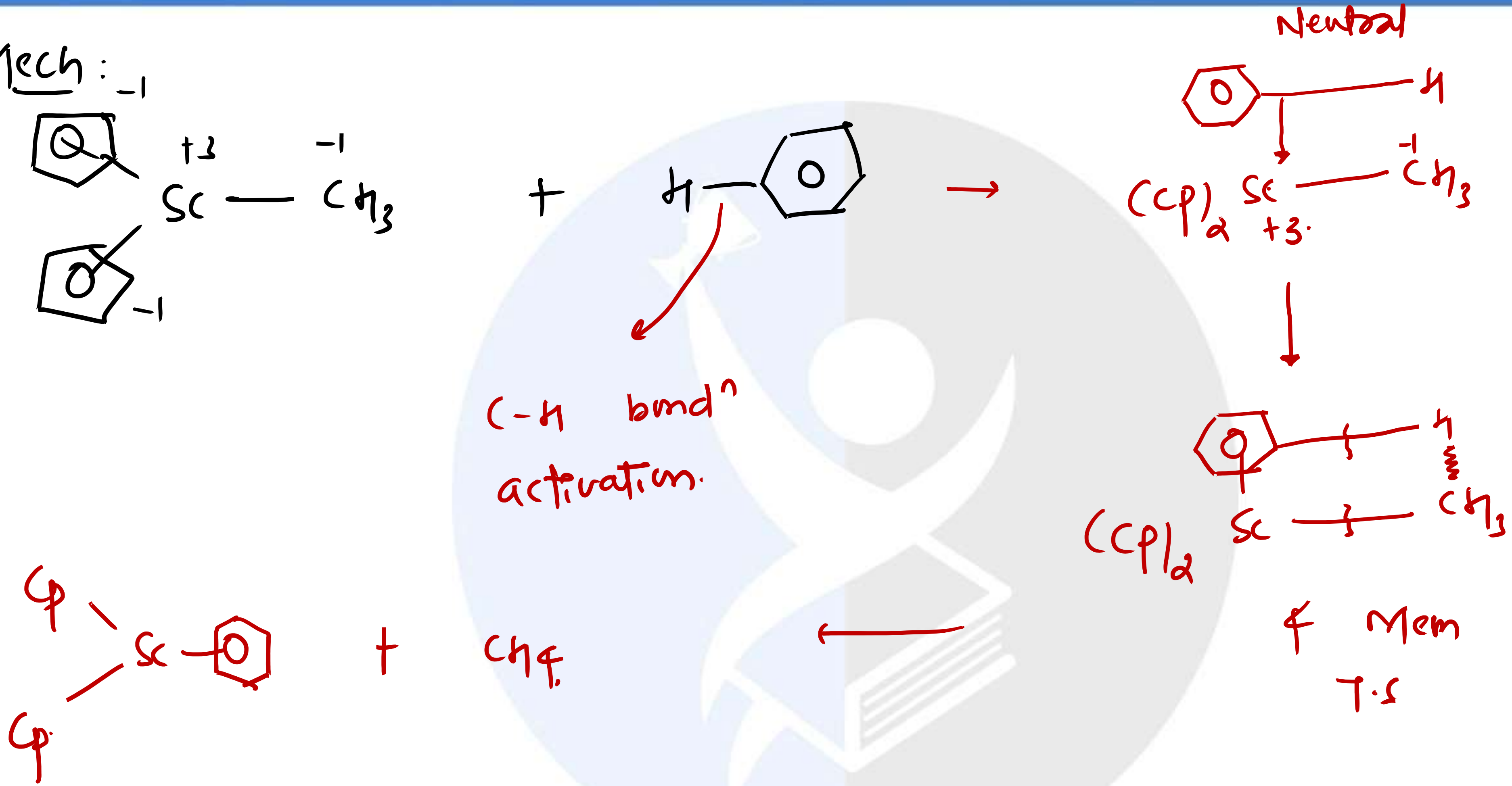
③ No change in O.S.

④ Metal exists in high O.S.

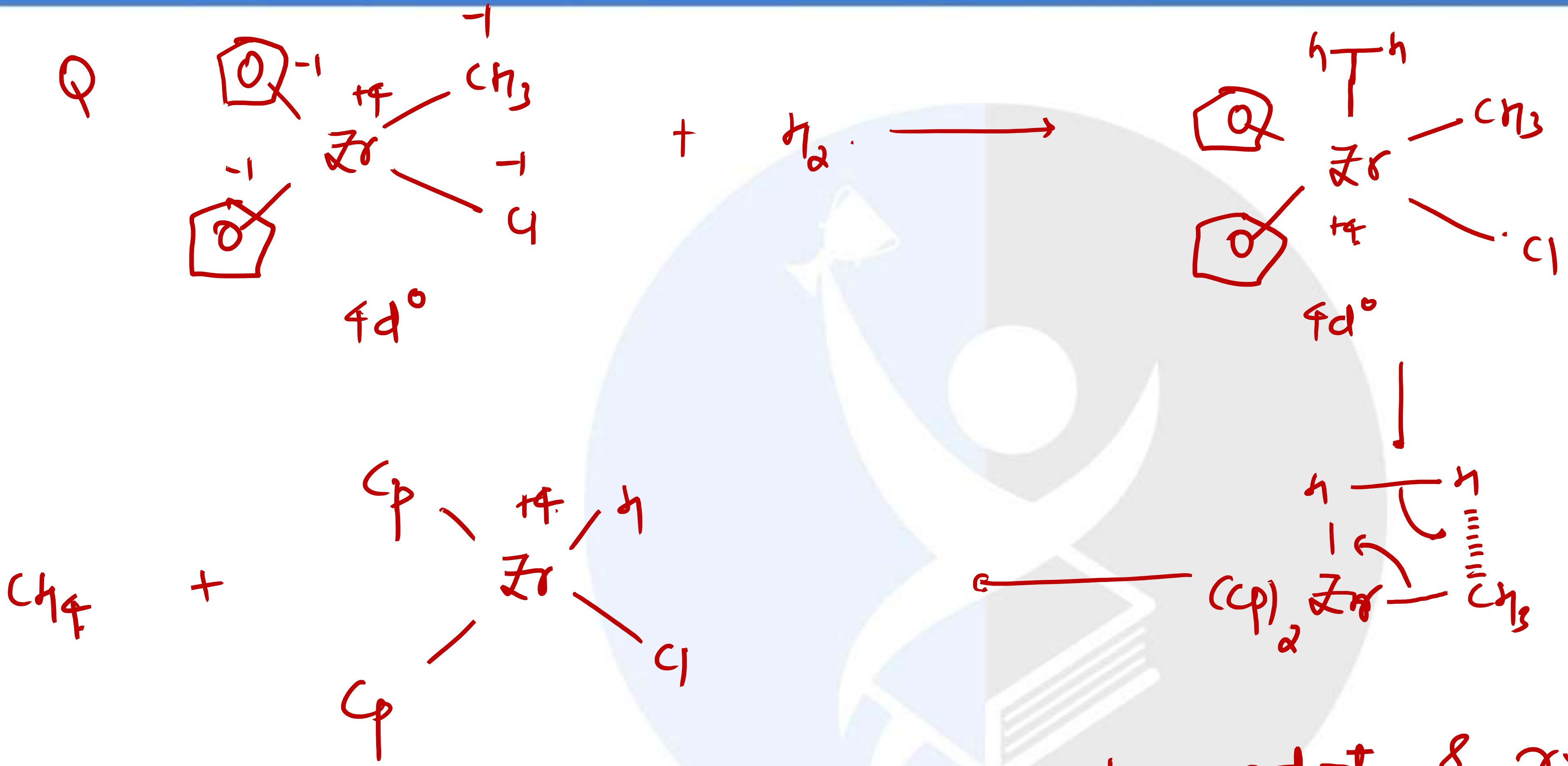
Rxn .



Mech :


-1
+3
-1
Sc
CH_3
-1
+
H
→
C-H bond^n activation.
Neutral
H
CH_3
-1
$(Cp)_2$ Sc
+3.
H
CH_3
$(Cp)_2$ Sc
4 Mem T.S
←
Cp
Sc
Cp
+
CH_4

Q



→ In σ bond metathesis O.S. of product & rxtant remains same.

④ Reductive Elimination :-

$$L_nM^0 + \begin{matrix}Y\\|\\X\end{matrix} \underset{R.E}{\overset{O.A}{\rightleftharpoons}} \overset{+2}{L_nM}\begin{matrix}X\\Y\end{matrix}$$

$$\overset{+2}{L_nM}\begin{matrix}X\\Y\end{matrix} \xrightarrow{R.E} L_nM^0 + XY$$

Condn:

ⓘ Metal should be $e^{\ominus}$ def. / higher O.S.

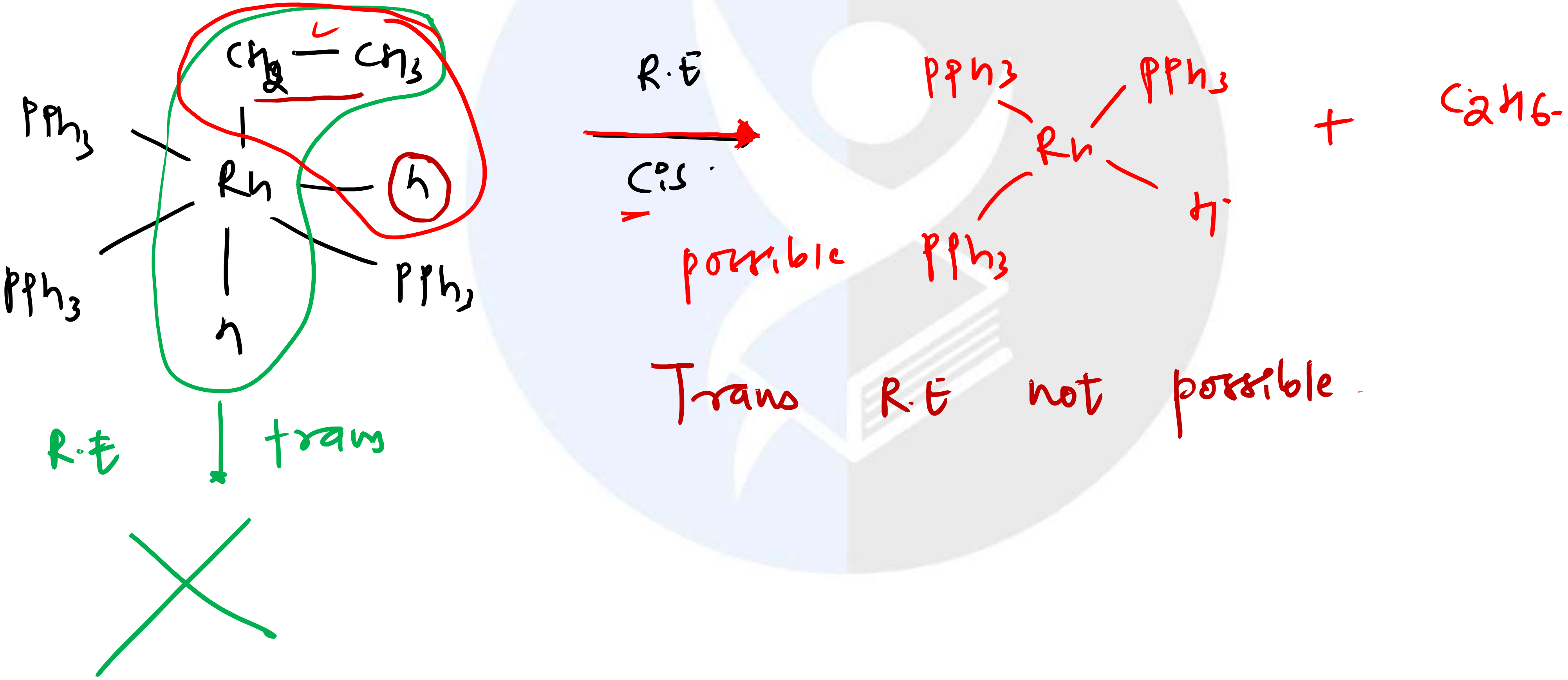
② C.N / O.S ↓ by 2 unit.

③ . If π- acceptor ligand attach to metal, Rate of R.E ↑

④ If σ donor ligand ↑ Rate of R.E ↓

⑤ Only cis R.E is possible, Trans R.E is not possible [Req. more Eq.].

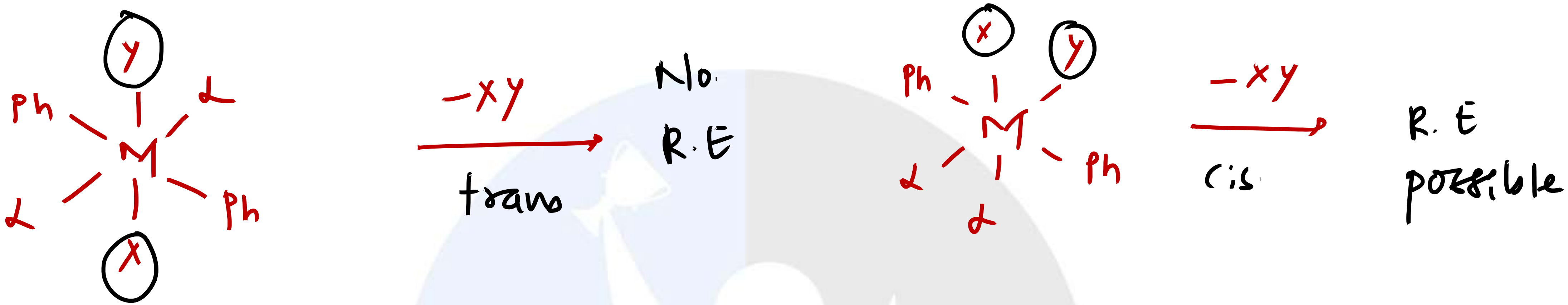
Ex:



Trans R.E not possible.

{1st slide}

Q.

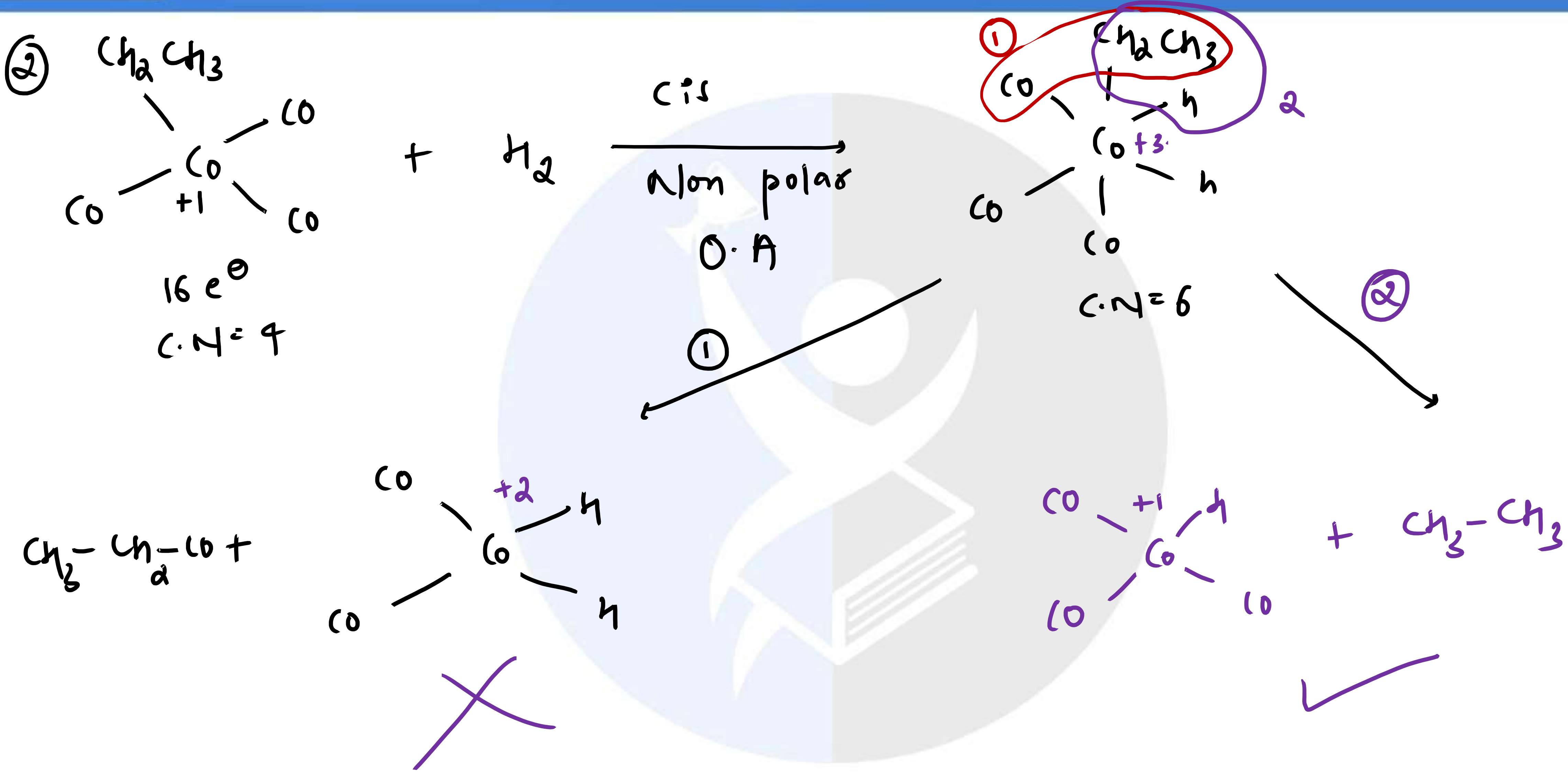


① In R.E, L.G should be anionic (Cleavage group)

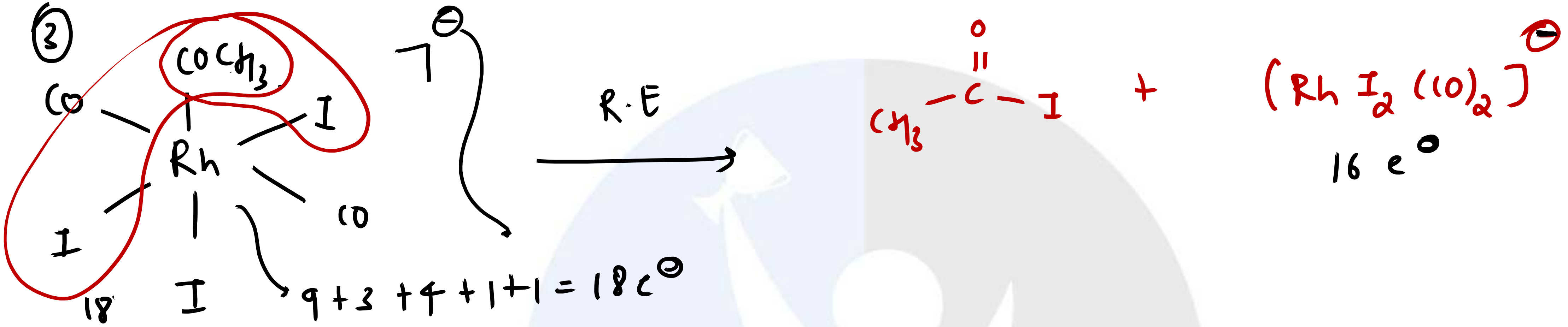
Ex. $[\overset{0}{Pd}(PPh_3)_4] \xrightarrow{-PPh_3} [\overset{0}{Pd}(PPh_3)_3] \xrightarrow{-PPh_3} [\overset{0}{Pd}(PPh_3)_2]$

$18e^{\ominus}$

Not a R.E
[O.S remaining same].


②
CH2CH3
CO
Co
+1
CO
CO
16 e⊖
C.N = 4
+
H2
cis
Non polar
O.A
①
CO
CH2CH3
H
2
Co +3
H
CO
CO
C.N = 6
①
②
CH3-CH2-CO +
CO
+2
H
Co
H
CO
CO
+1
H
Co
CO
CO
+ CH3-CH3
✓

③

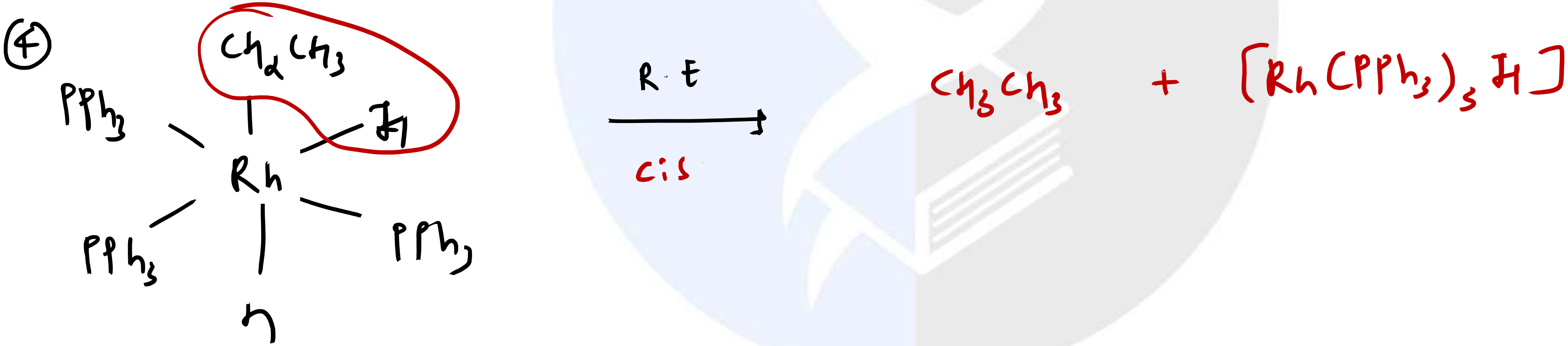


$9+3+4+1+1 = 18e^{\ominus}$

$$[Rh(CO)_2I_3(COCH_3)]^{\ominus} \xrightarrow{R.E} CH_3-\overset{O}{\overset{\|}{C}}-I + [RhI_2(CO)_2]^{\ominus}$$

$16\ e^{\circ}$

④



$$\xrightarrow[cis]{R.E} CH_3CH_3 + [Rh(PPh_3)_3H]$$

R.E for Sq planar Complex :-

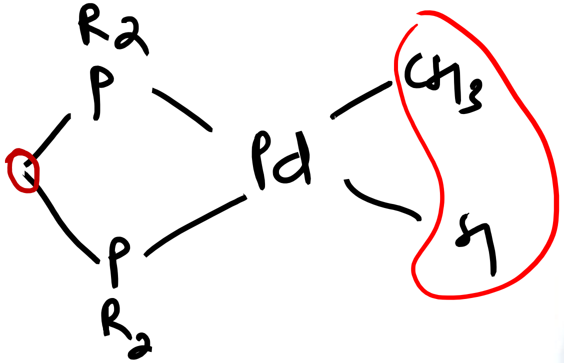
$L = PPh_3$

Reactivity of R.E :

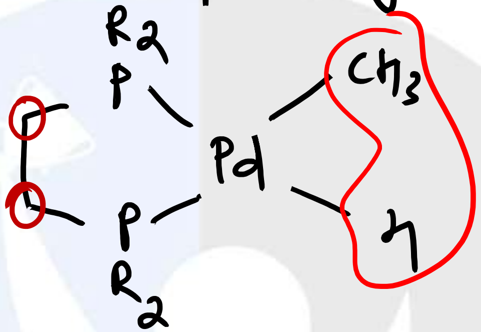
* Steric Crowding ↑ Cone Angle ↑ R.E ↑
(Bite Angle

Q. Which of following complex gave faster R.E

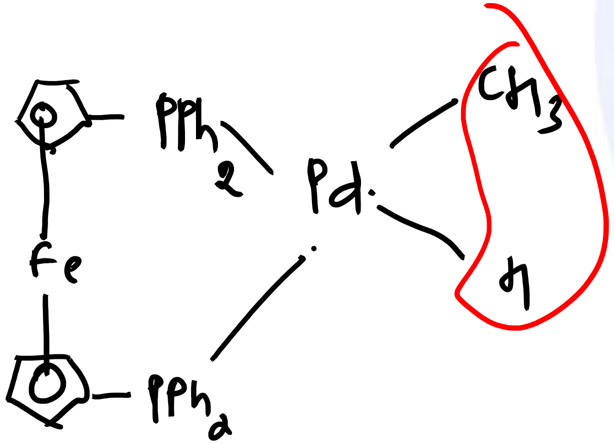
Ⓐ



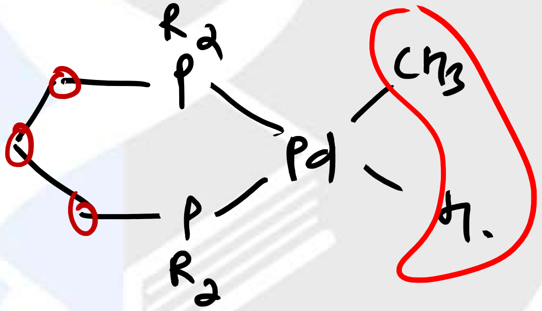
Ⓑ



Ⓒ

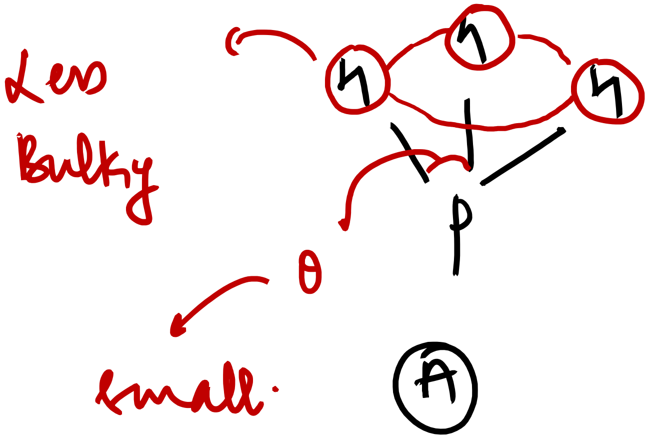


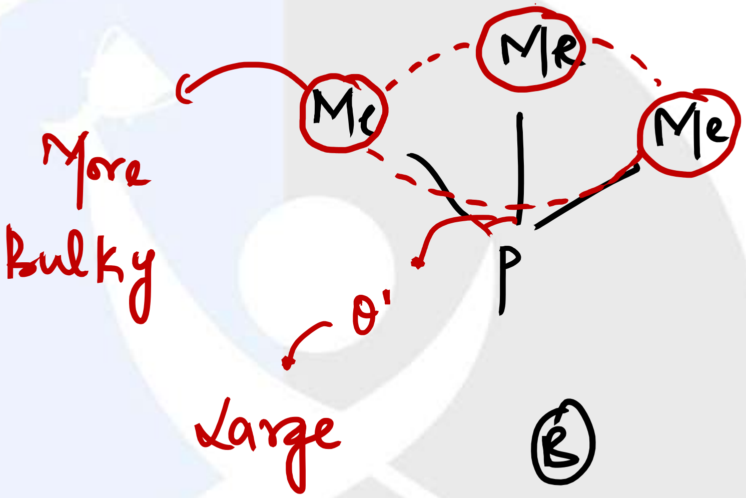
Ⓓ



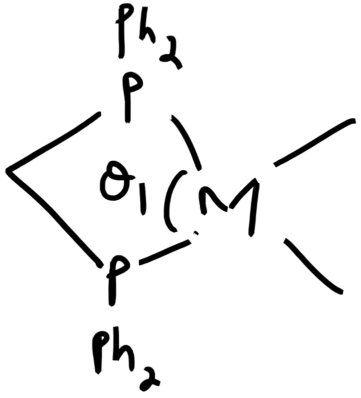
Order: Cone Angle ↑ R.E ↑

Ⓒ > Ⓓ > Ⓑ > Ⓐ

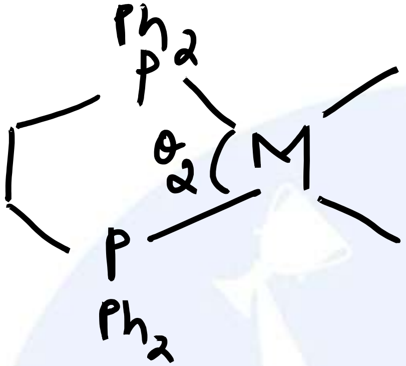

Less Bulky
H
H
H
P
θ
small.
A


More Bulky
Me
Me
Me
P
θ'
Large
B

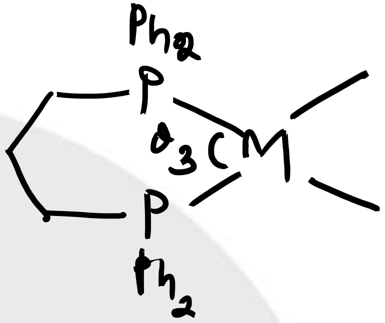
Q



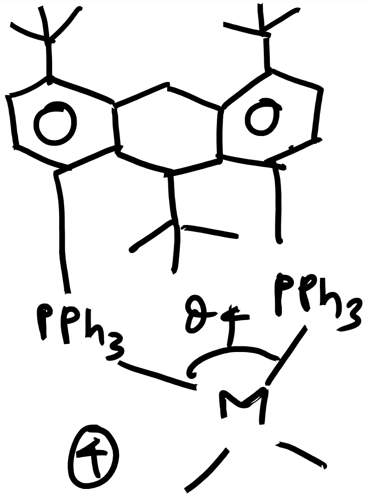
①



②



③



④

R.E <u>order</u> :- $\{ \theta_4 > \theta_3 > \theta_2 > \theta_1 \}$

No. of CH_2 ↑ Cone angle ↑ R.E ↑

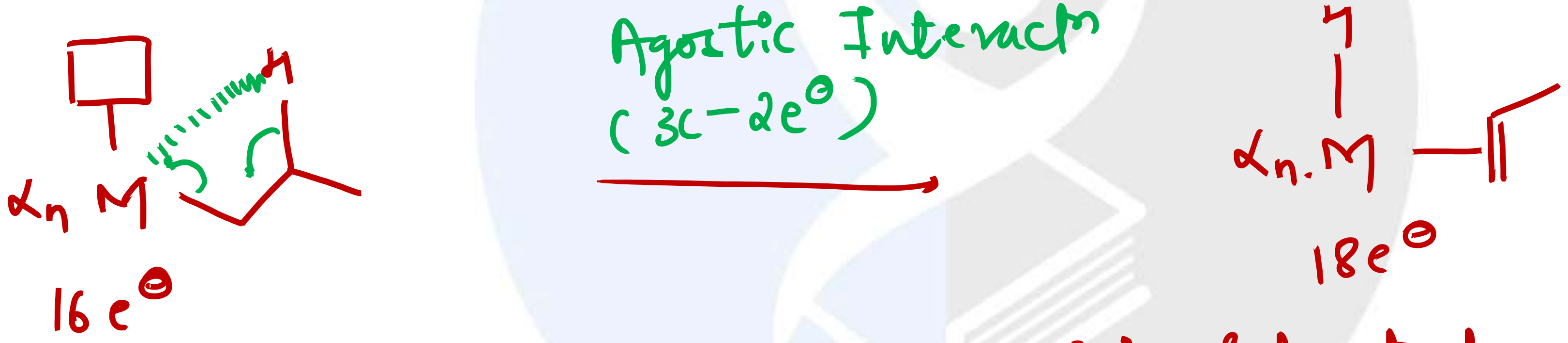
β- Hydride Elimination :—
(β- Hydrogen Elimination) :—

Condn :—

① Complex must follow 16 $e^{\ominus}$ rule (Unsaturated coordn site)

② Atleast 1 β-H should be present.

③



→ Unsaturated complex

→ Lower O.S of M

→ saturated.

→ Oxdn of metal not change

④ Metal should be in lower o.s.

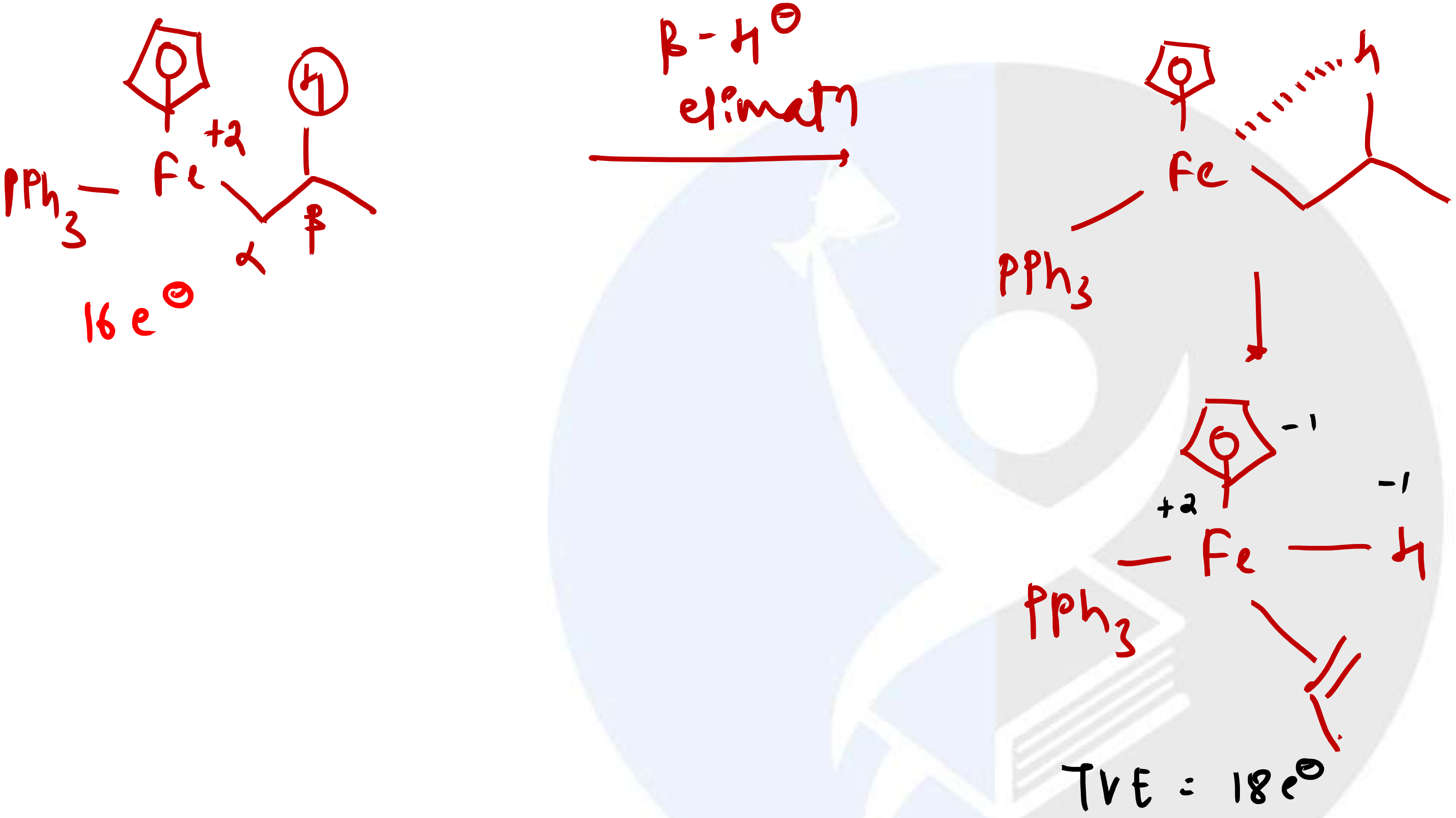
⑤ β- Hydride elimination reversible to 1,2 insertion.

*** ⑥ In β- Hydride elimination, β- Hydrogen must be cis/syn to the metal.

⑦ Trans β- Hydride eliminatn not possible

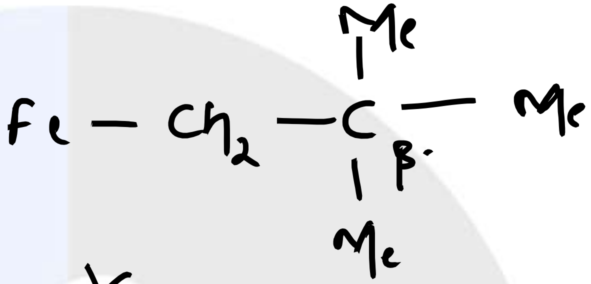
*** ⑧ If complex shows β- Hydride elimination that complex is thermally unstable.

Ex:



Q. Which of following complex show β-Hyd. elimⁿ ?

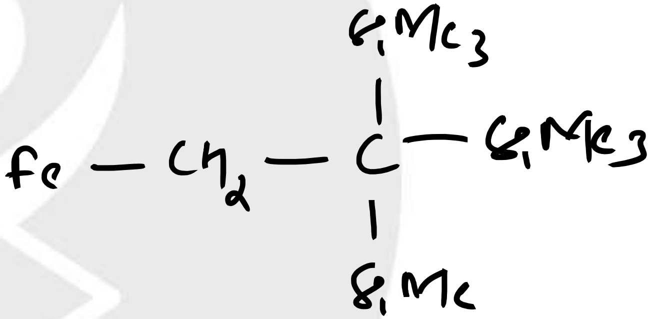
Ⓐ $[Fe(Cp)(PPh_3)(CH_2C(CH_3)_3)]$



Ⓑ $[Fe(Cp)(PPh_3)(CH_3)]$

$Fe-CH_3$ ✗

Ⓒ $[Fe(Cp)(PPh_3)(CH_2-(SiMe_3)_3)]$



Ⓓ ✓ $[Fe(Cp)(PPh_3)(nBu)]$

$\hookrightarrow Fe-CH_2-\underset{\beta\text{-H}}{CH_2}-CH_2-CH_3$

Q. Which of following doesnot show R.E ?

↳ $e^{\ominus}$ count

Ⓐ $[Fe(\eta^5-Cp)(PPh_3)(CO)(C_2H_5^-)] \rightarrow 18\,e^{\ominus}$ ✗

Ⓑ $[Ru(\eta^5-Cp)(PPh_3)_2(C_2H_5)] \rightarrow 18\,e^{\ominus}$ ✗

$8 + 5 + 4 + 1$

Ⓒ $[Rh(\eta^5-Cp)(PPh_3)_2(C_2H_5)]^{\oplus} \rightarrow 18\,e^{\ominus}$ ✗

$9 + 5 + 4 + 1 - 1$

Ⓓ $[Ru(\eta^5-Cp)(PPh_3)(C_2H_5)] \rightarrow 16\,e^{\ominus}$ ✓

$8 + 5 + 2 + 1$

Ⓔ $[Co(\eta^5-Cp)(CO)_2(C_3H_7)]^{\oplus} \rightarrow 18\,e^{\ominus}$ ✗

$9 + 5 + 4 + 1 - 1$

Ⓕ $[Ir(\eta^5-Cp)(PPh_3)(C_2H_5)]^{\oplus} \rightarrow 16\,e^{\ominus}$ ✓

$9 + 5 + 1 + 1.$

Q. Which of following complex are thermally unstable ? (T.U)

(A) ✓ $[Fe(\eta^5\text{-}Cp)(PPh_3)(C_2H_5)]$ → $16e^{\ominus}$ → β H present (T.U)

$8 + 5 + 2$ 16

(B) $[Rh(\eta^5\text{-}Cp)(PPh_3)_2C_2H_5]^{\oplus}$ → $\underline{18}\,e^{\ominus}$ → β H → (T.S)

$9 + 5 + 4 + 1 - 1$

(C) $[Rh(\eta^5\text{-}Cp)(PPh_3)(CH_2CMe_3)]^{\oplus}$ → $\underline{16}\,e^{\ominus}$ → No β-H → (T.S)

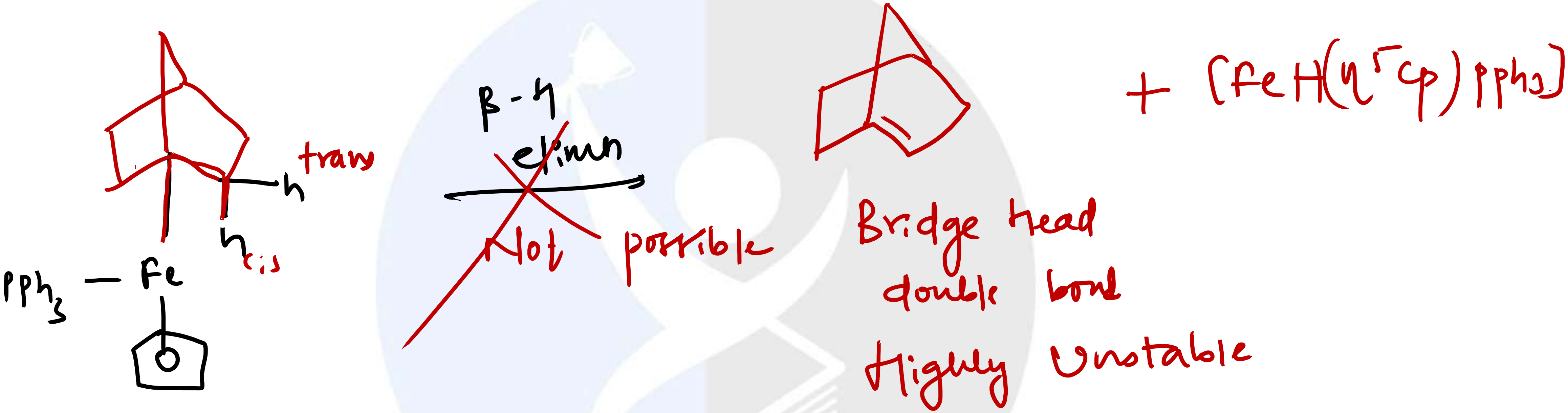
$9 + 5 + 2 + 1$

(D) ✓ $[Rh(\eta^5\text{-}Cp)(PPh_3)(CH_2CH_3)]^{\oplus}$ → $16e^{\ominus}$ → β H present → T.U

β-H present, complex thermally Unstable.

Cases where β-Hyd elimination Not possible :-

Case ①



Bridge head double bond

Highly unstable

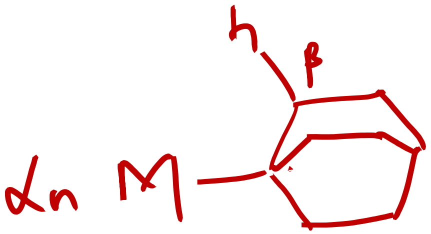
② trans

$L_nM-\underset{\alpha}{C}\equiv\underset{\beta}{C}-H$ $\longrightarrow$ No β-H elimination

β-H

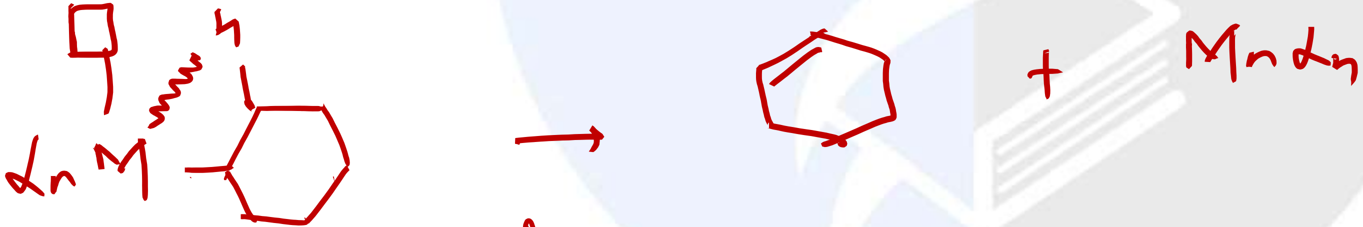
$16e^{\ominus}$

③

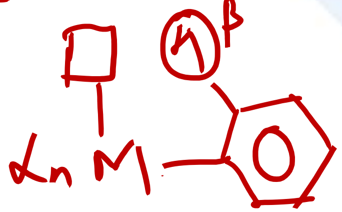


$\longrightarrow$ No β-H elimination

④



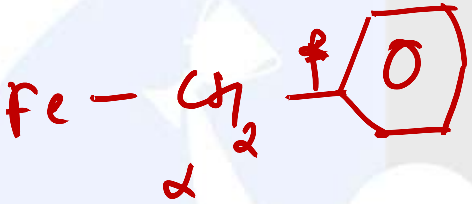
$16e^{\ominus}$



$16e^{\ominus}$

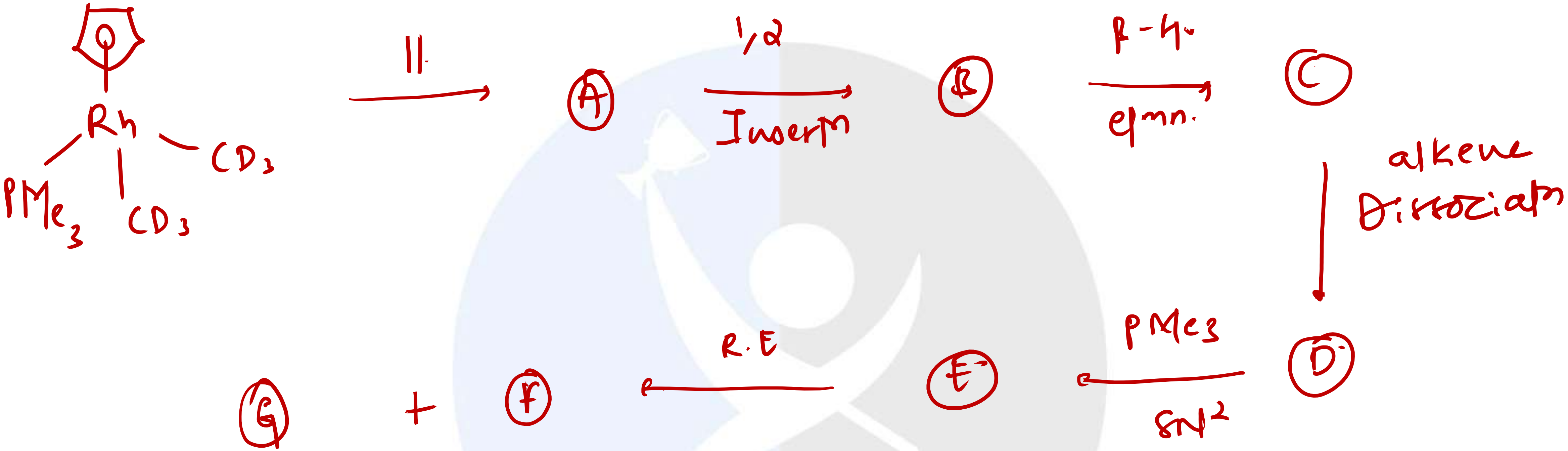
$\longrightarrow$ No Rxn.

⑤ $[Fe(Cp)(PPh_3)(CH_2Ph)]$



No β-H

No β- elimination


Rh
PMe3
CD3
CD3
||
A
1,2
Insertn
B
β-H
elmn.
C
alkene
Dissociatn
D
PMe3
SN2
E
R.E
F
+
G