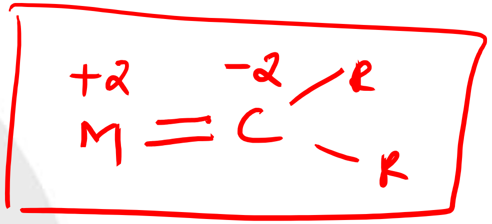
①

Neutral → $\underline{0}$ O.S

$M \leftarrow :NR_3$ Amine → $2e^{\ominus}$ donor

$M \leftarrow \overset{\ominus}{\cancel{\cdot}}NR_2$ → {$\underline{1}$ $e^{\ominus}$ donor}.

$\overset{+1}{\underline{M}} - \overset{-1}{\underline{NR_2}}$



$\overset{+2}{M} = \overset{-2}{C}R_2$

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

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.

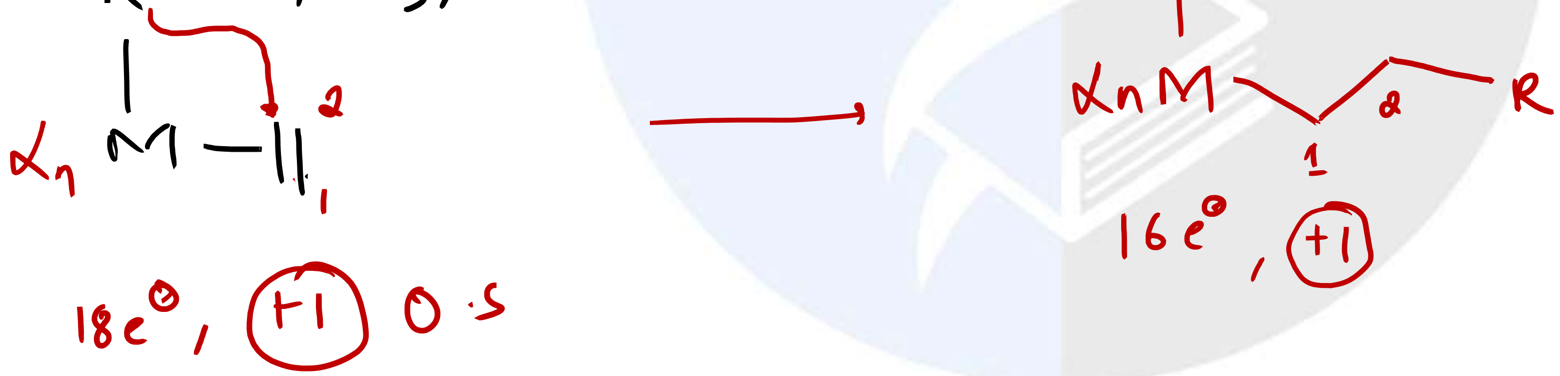
⑤ In Migratory Insertion, 5 coordinate int is formed.

1,2 Migratory Insertion :

Condn :- 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.

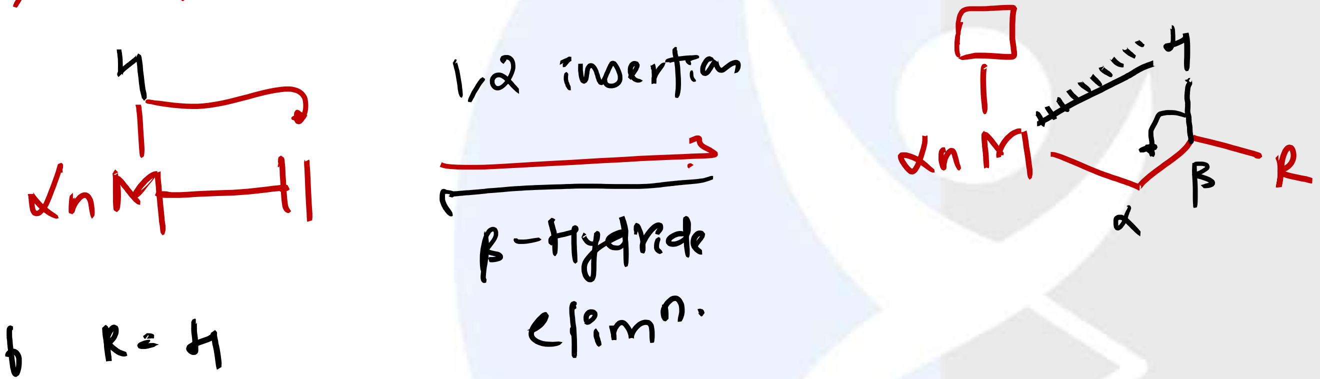
R → H, CH_3, CR_3, C_2H_5



③ O.S remains same

④ 18 e⊖ complex ⟶ 16 e⊖ comp.

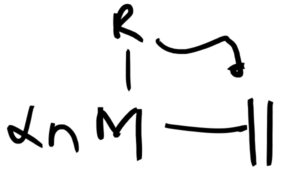
⑤ 1,2 Insertion rxn reversible to β-Hydride elimination

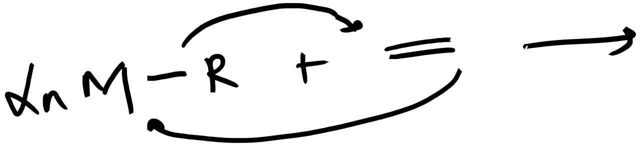


if R = H

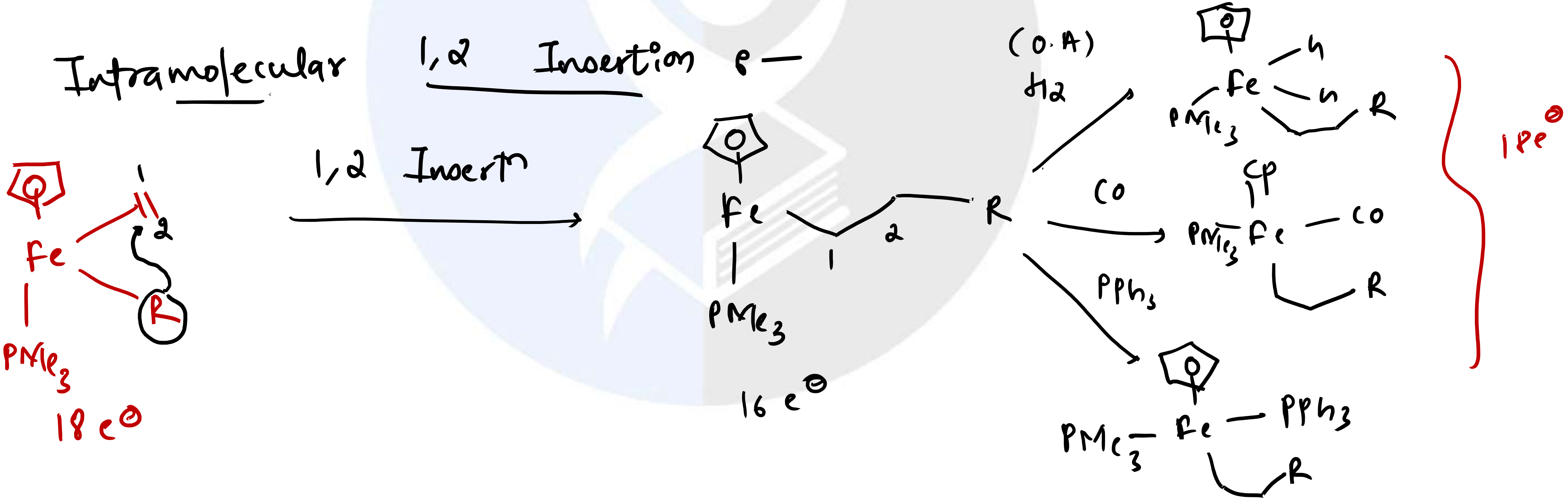
Intramolecular 1,2 Insertion

Intermolecular 1,2 insertion.

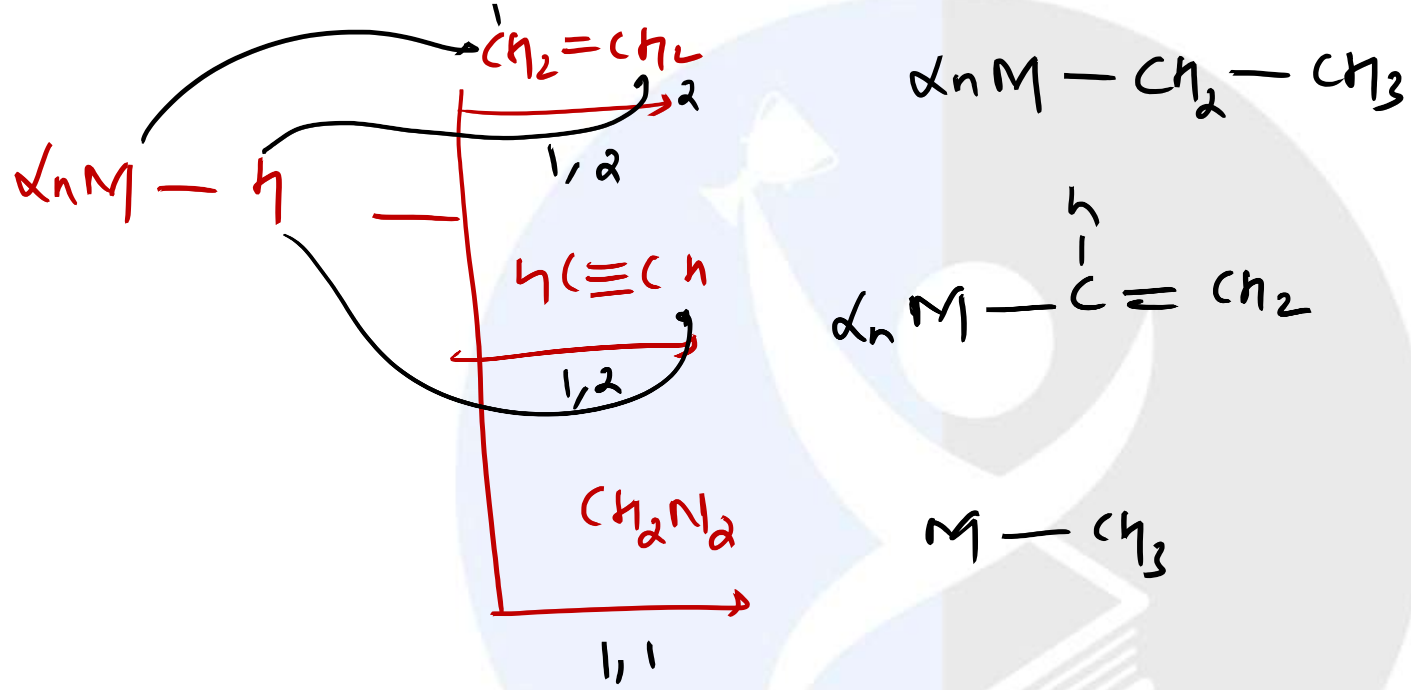




① Intramolecular 1,2 Insertion e —



② Intermolecular 1,2 Insertion :-



$$L_nM-CH_2-CH_3$$

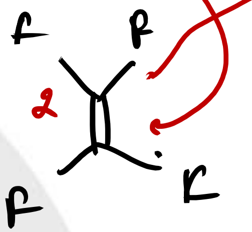
$$L_nM-\overset{H}{\overset{|}{C}}=CH_2$$

$$M-CH_3$$

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

$(CO)_4Co—H$.

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



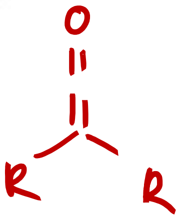
1,2 Insertn.

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

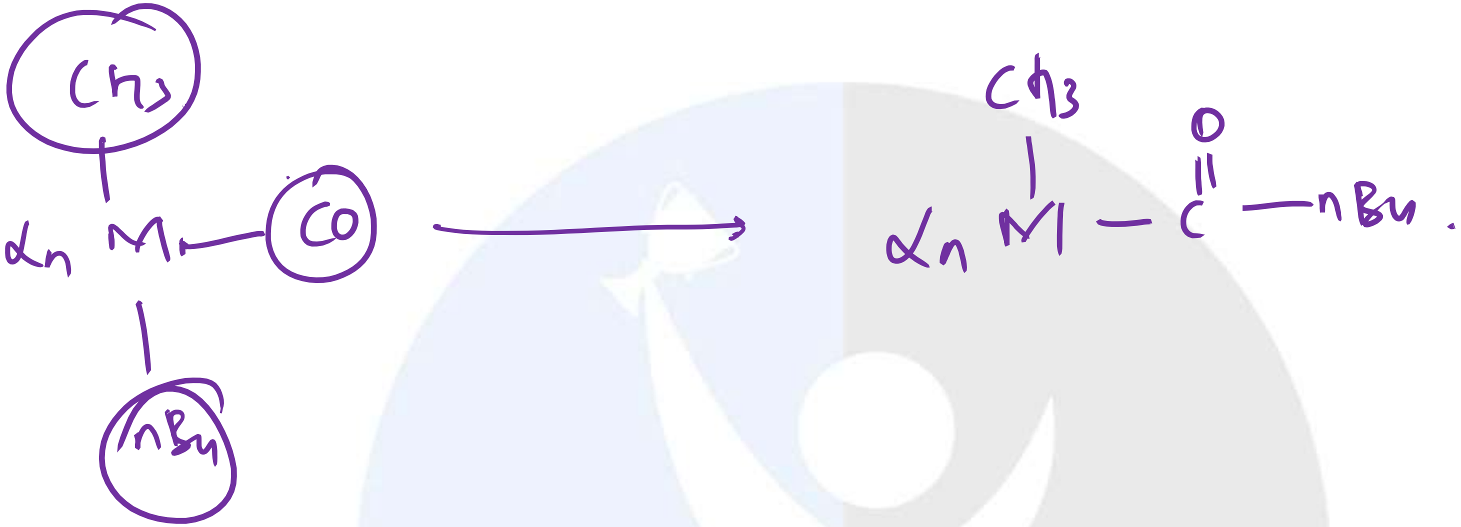
HW

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

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



Q



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

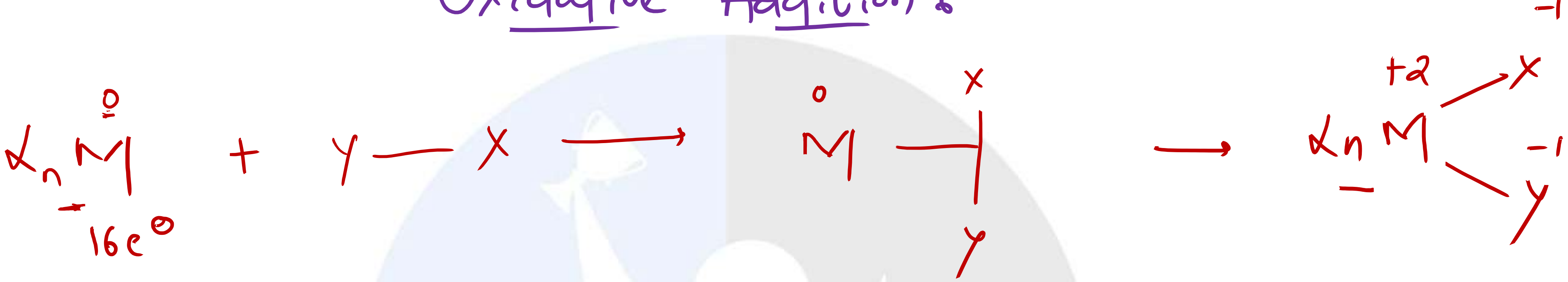
Migratory Aptitude :-

$H > nBu \approx CH_2CH_2CH_3 > CH_3 > C_2H_5^-$

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

→ EWG will not migrate.

Oxidative Addition :—



Criteria :

① All $16\,e^{\ominus}$ complex can show O·A

② In O·A, O·S & CN ↑ by 2 unit

③ Metal should be in lower O·S / $e^{\ominus}$ rich.

④ If EDG ↑ on comp., Rate of O·A ↑

✓

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

O·A

Polar O·A

→ If EN diff betn 2 atoms > 0.5

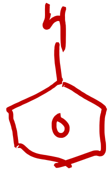
Ex: $\overset{\delta+}{Me}\overset{\delta-}{I}$, $\overset{\delta+}{Me}\overset{\delta-}{Br}$, $\overset{\delta+}{Me}\overset{\delta-}{Cl}$, $\overset{\delta+}{H}\overset{\delta-}{Cl}$

→ Concerted Mech (S_N2)

→ Trans addn

Non polar O·A

→ EN diff betn atom < 0.5

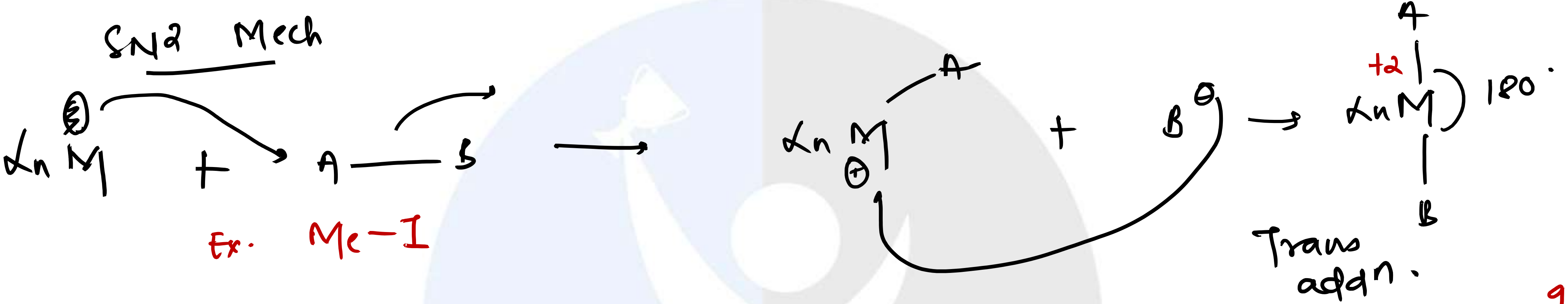
Ex: H_2, O_2, N_2,  , $H-C\equiv C-H$

→ Free Radical mech

→ Cis addn.

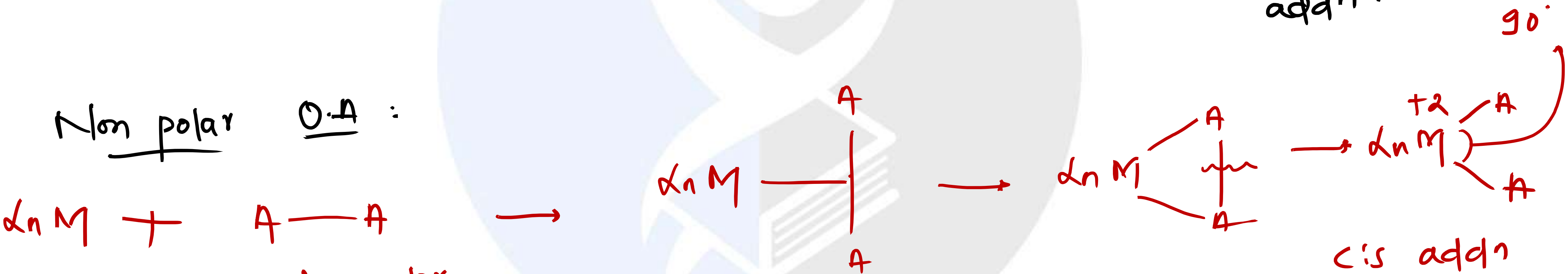
Polar O.A :

SN2 Mech



Ex. Me—I

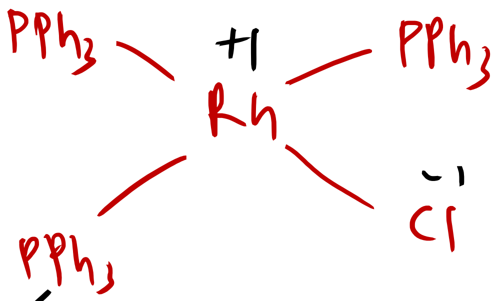
Non polar O.A :



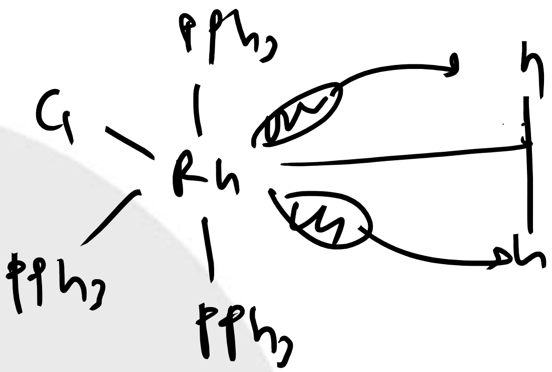
Non polar

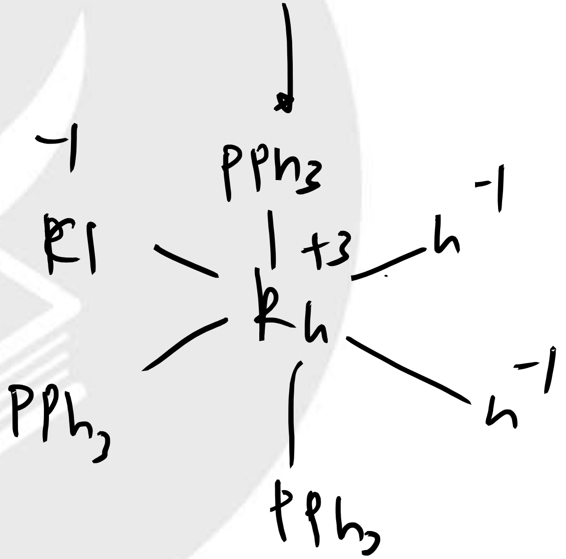
Ex: H_2

Q.



$+ \; H_2 \longrightarrow$





16 $e^{\ominus}$

Sq. planar

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

C.N = 4

Non polar

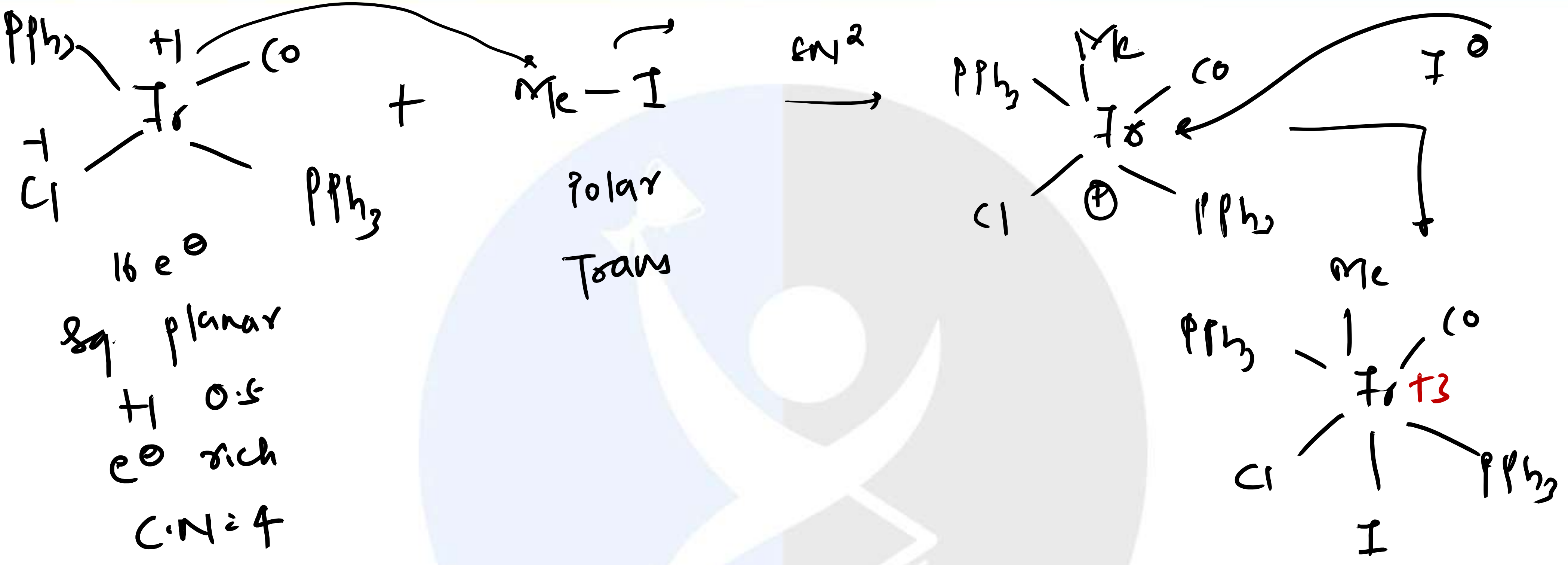
Cis add^n

O.S ↑ by 2

C.N ↑ by 2

C.N = 6

Q.



16 $e^{\ominus}$

Sq planar

+1 O.S

$e^{\ominus}$ rich

C.N = 4

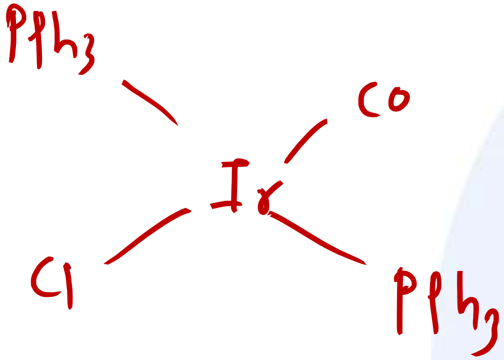
Polar

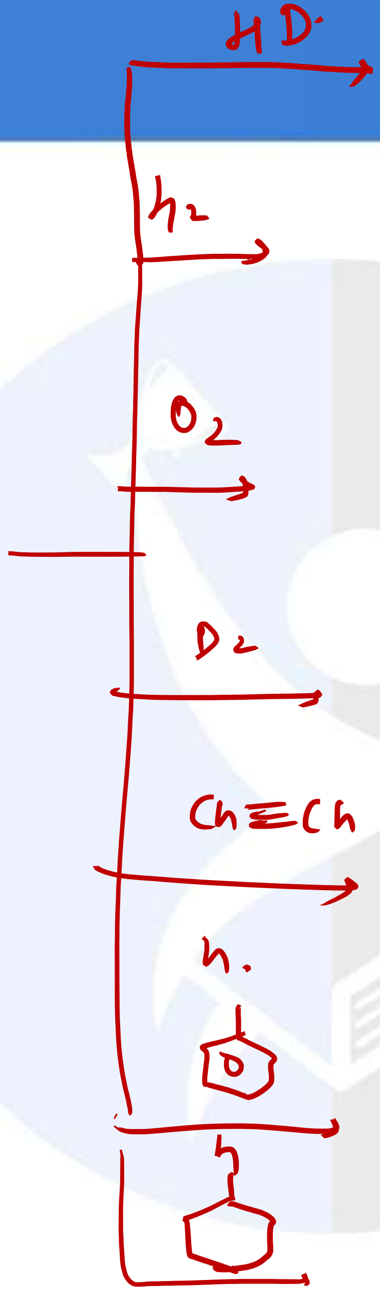
Trans

C.N = 6

Q.

HW

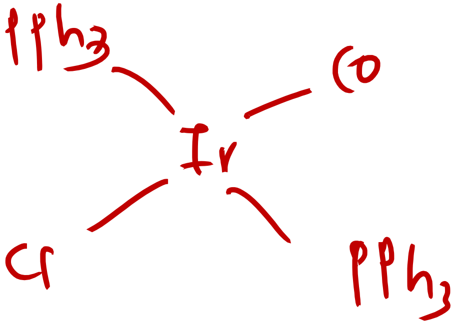




Cis addn

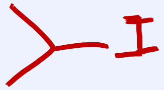
Non polar

Q ^{hw}



MeI

C_6H_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 ?

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

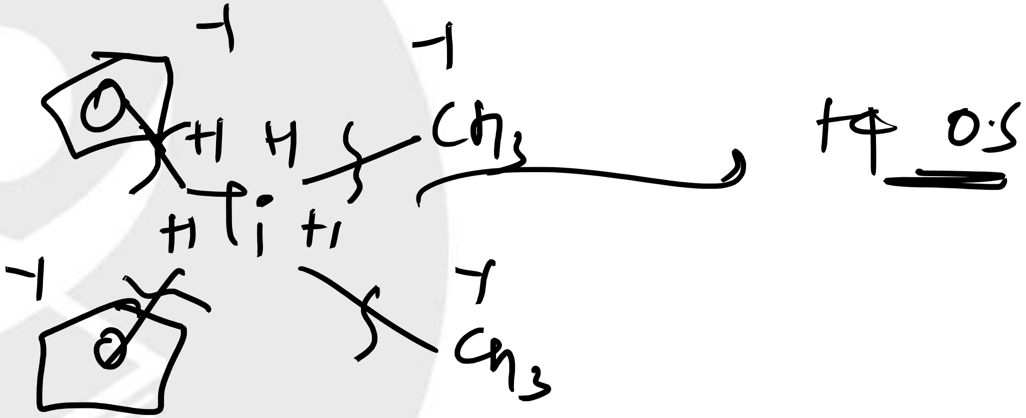
ⓑ $[\overset{+1}{Ir}(CO)Cl(PMe_3)_2] \rightarrow 16e^{\ominus}$ ✓

ⓒ $[RhCl(PPh_3)_3]$ $16^{\ominus}$ ✓

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

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

→ M high 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 ?

Ⓐ $[Co(CO)Cl(PPh_3)_2]^-$

Ⓑ $[RhCOCl(PPh_3)_2]$

Ⓒ $[IrCOCl(PPh_3)_2]$

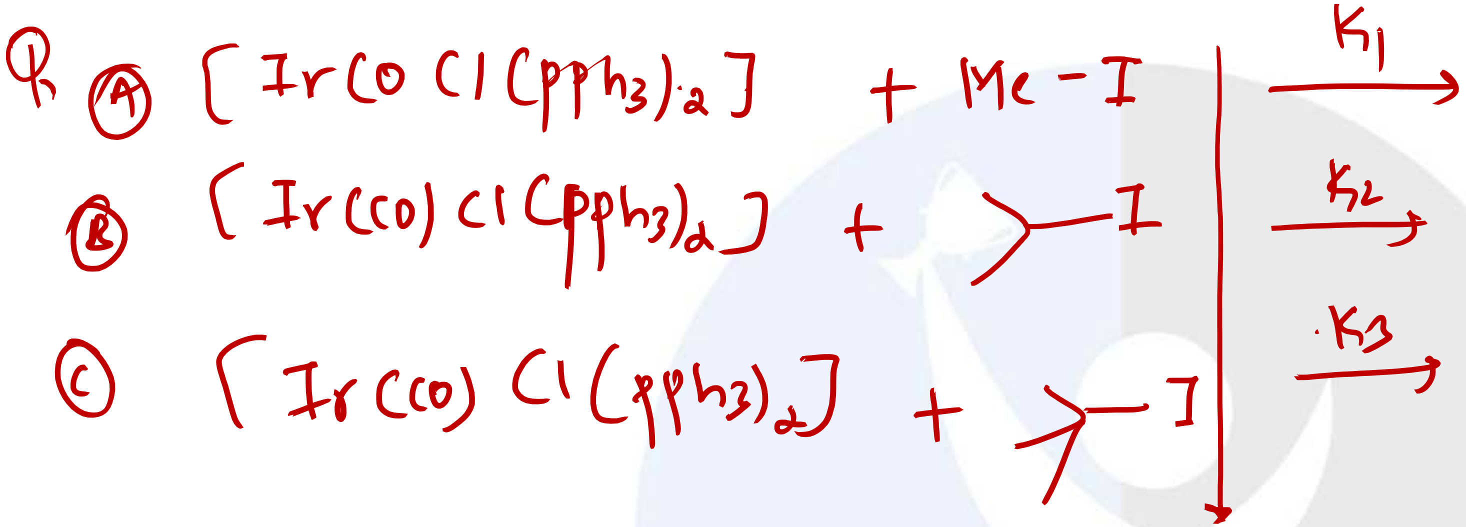
n ↑ O.A ↑

$\boxed{C > B > A}$

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

Ⓑ $[Ir(CO)Cl(PPh_3)_2] +$

Ⓒ $[Ir(CO)Cl(PPh_3)_2] +$



$k_1 > k_2 > k_3$

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>

$k_1 > k_2 > k_3 > k_4$

If L·G ability ↑

Rate of O·A ↑

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

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.

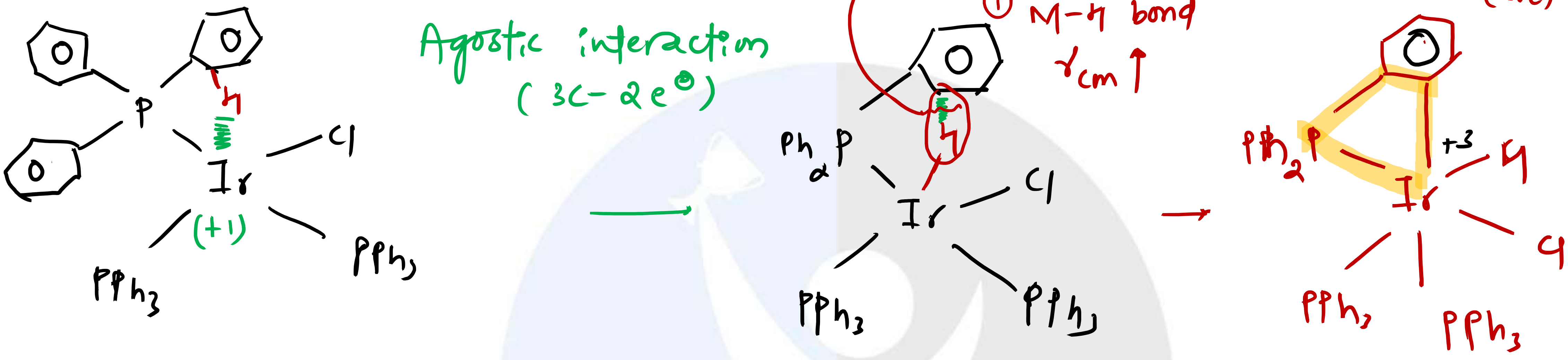
Agostic interaction

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

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

① M-H bond

ν_{cm} ↑



[5 mem T.S]

4 mem Ring

O.S ↑ by +2

③ Sigma bond Metathesis σ-

Condn :

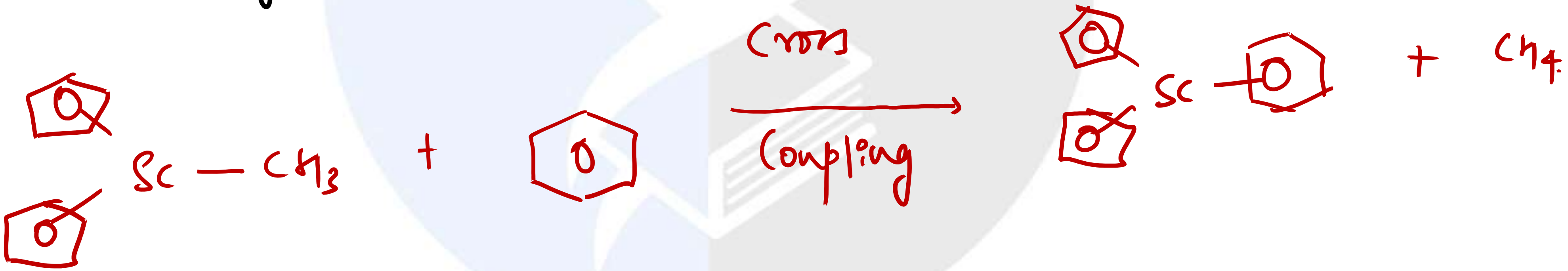
① The E.C of metal d^0

② formation of a 4 - membered T.S.

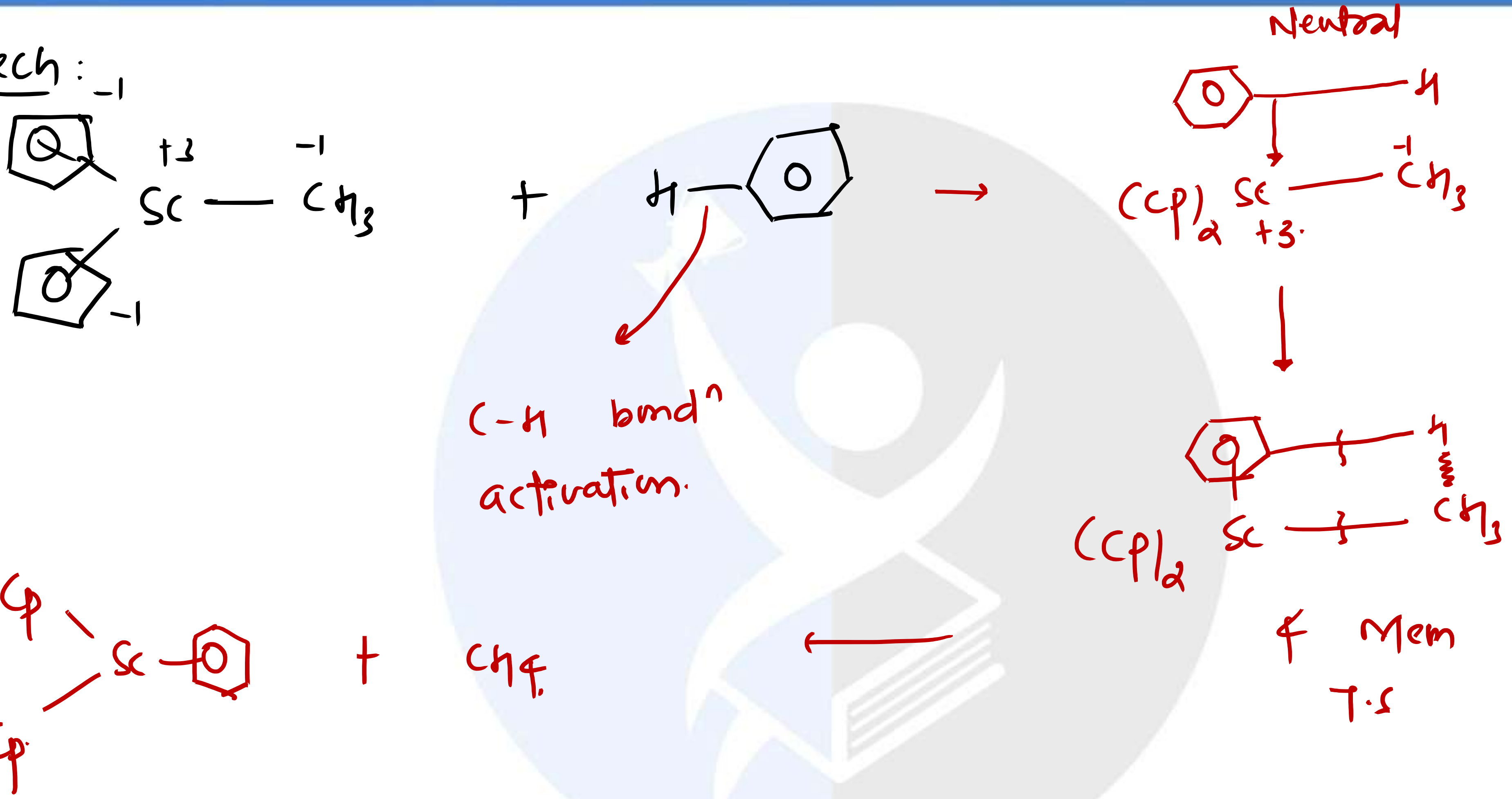
③ No change in O.S.

④ Metal exists in high O.S.

Rxn.



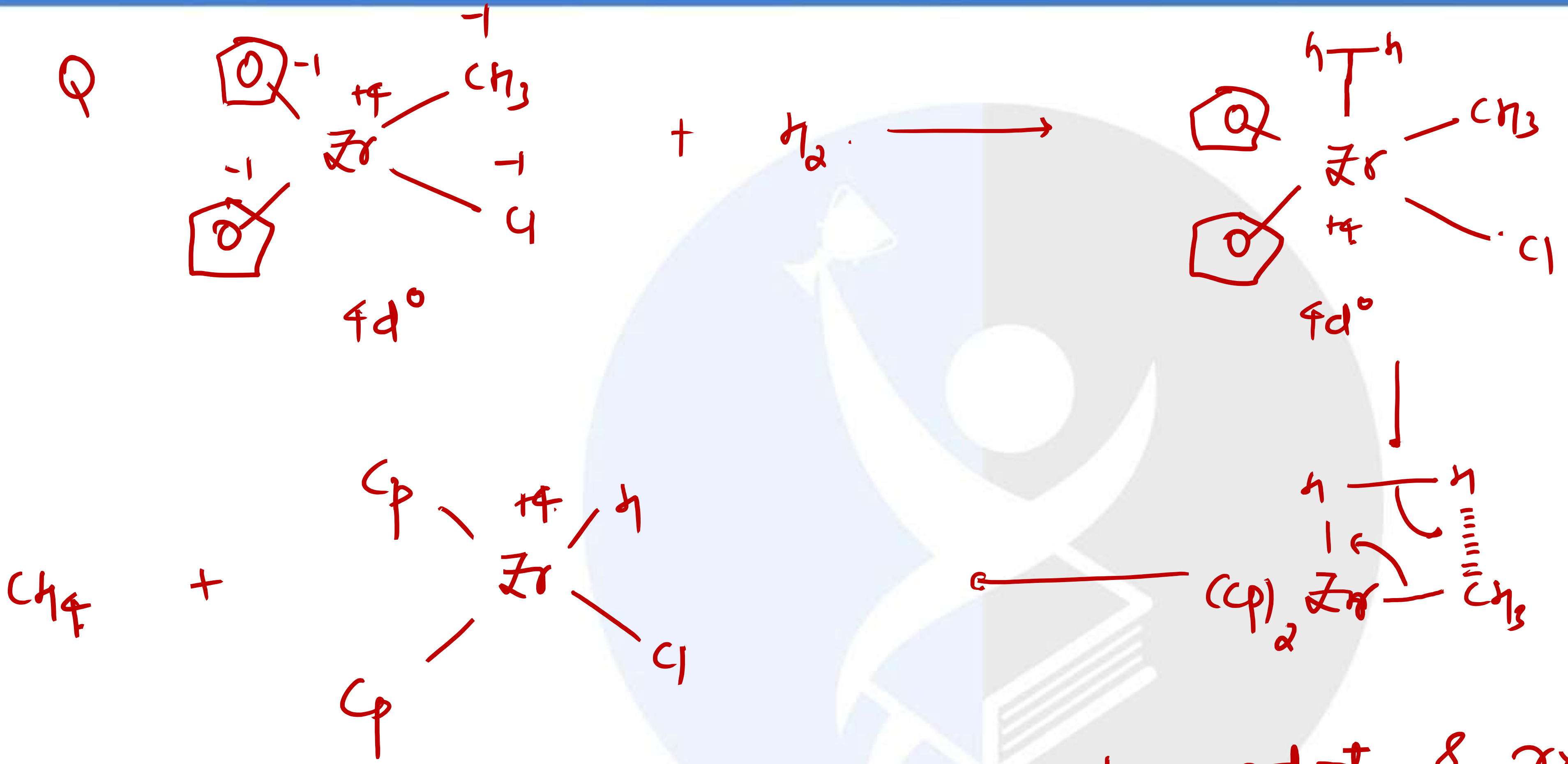
Mech :



C-H bond^n activation.

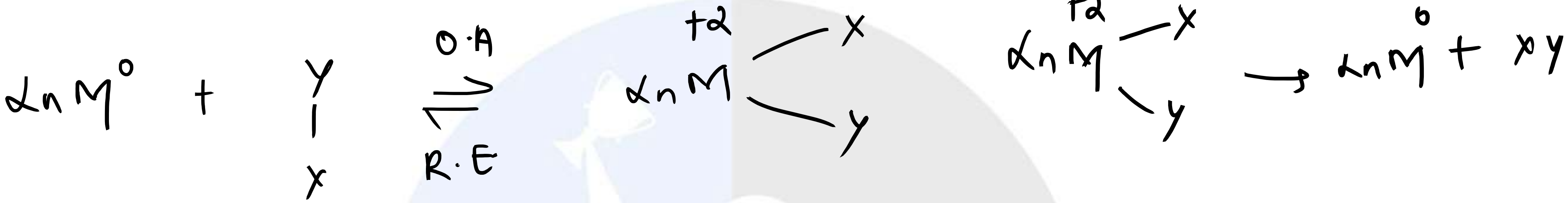
4 Mem T.S

Q



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

④ Reductive Elimination :-



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

$$L_nM^{+2}\begin{smallmatrix}X\\Y\end{smallmatrix} \longrightarrow L_nM^0 + XY$$

Condn:

(i) Metal should be e^- def. / higher O.S.

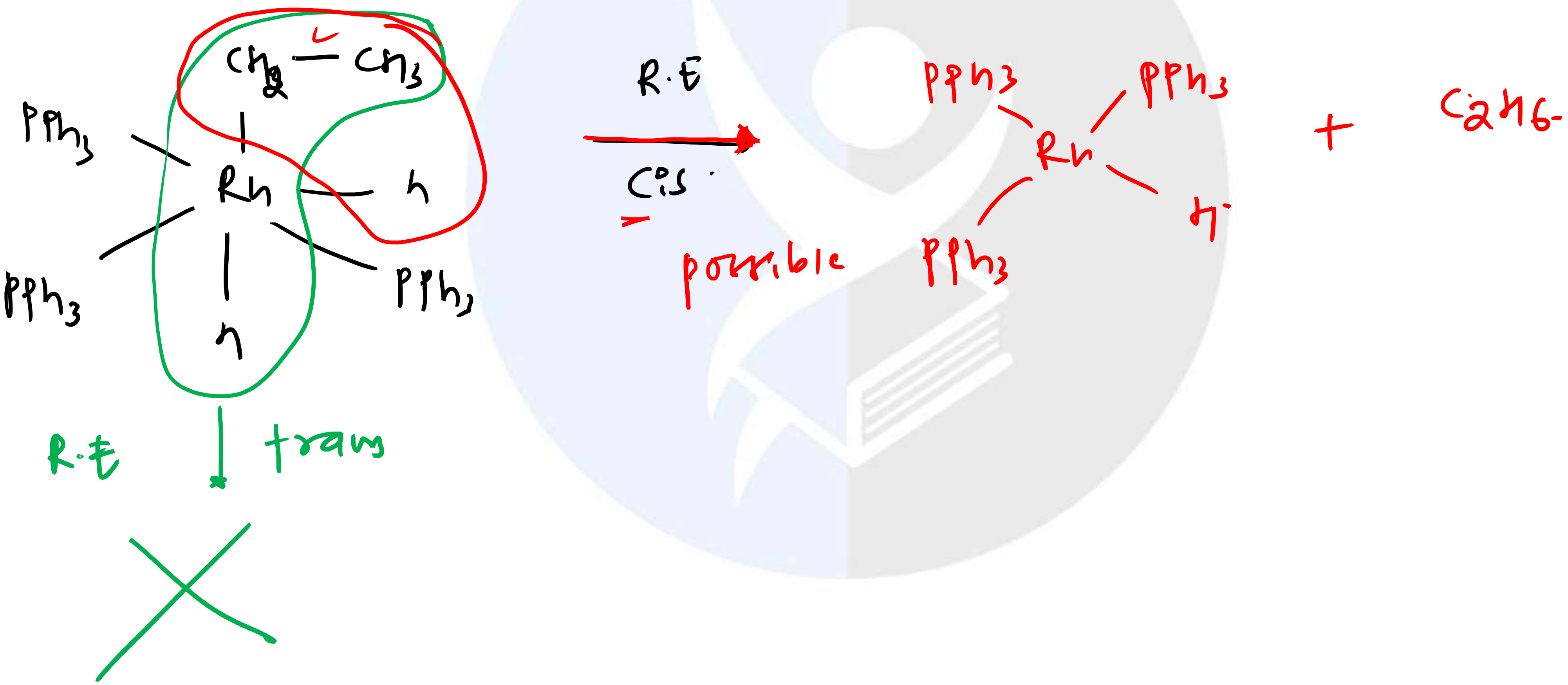
② C.N / O.S ↓ by 2 unit.

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:



Thank you