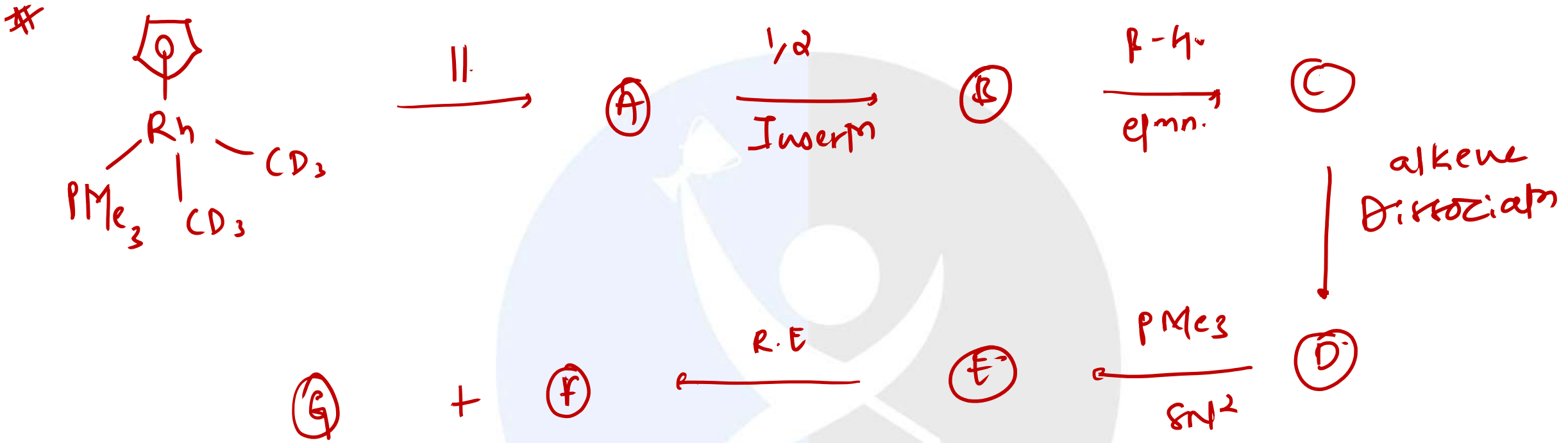
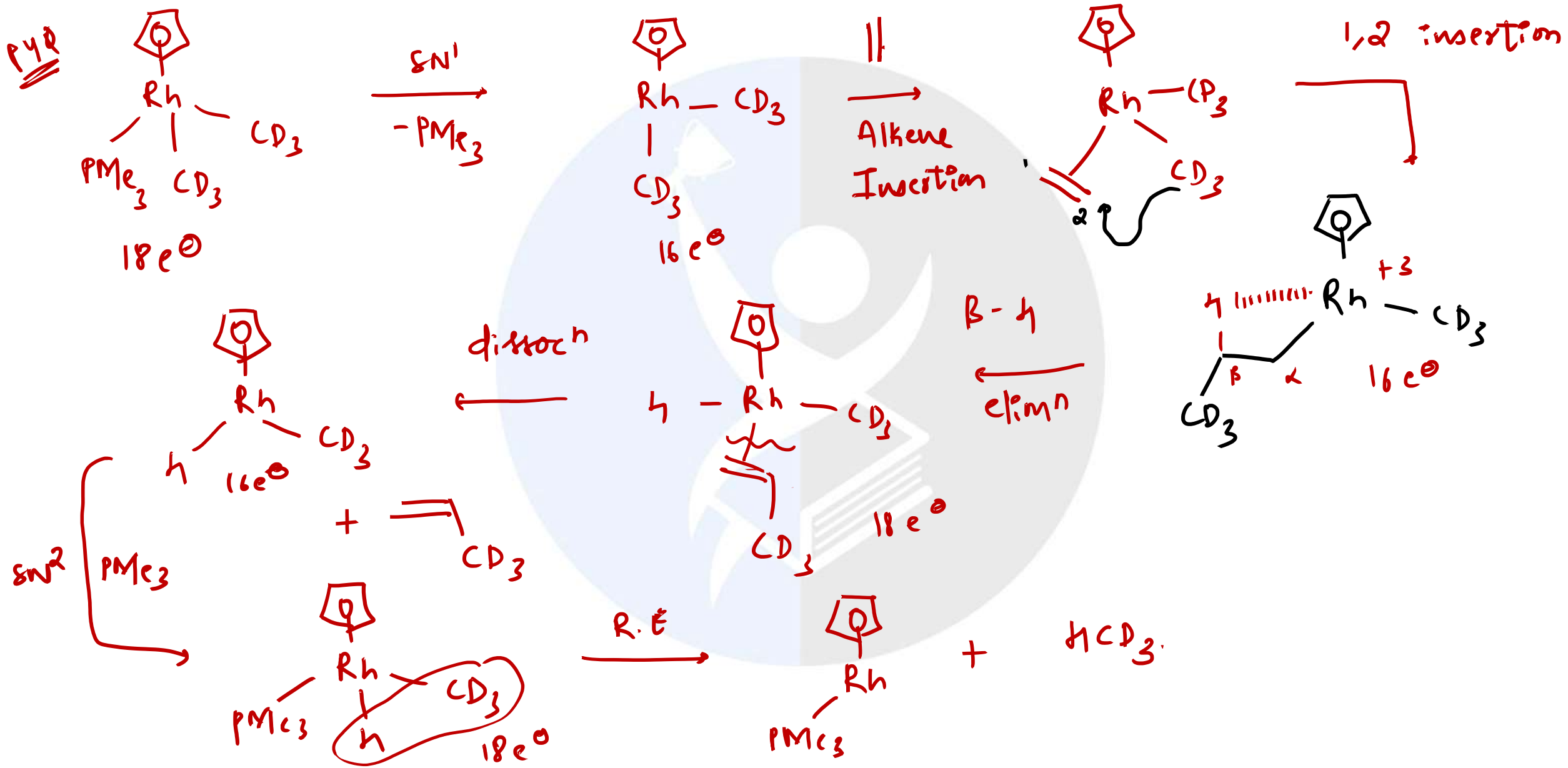
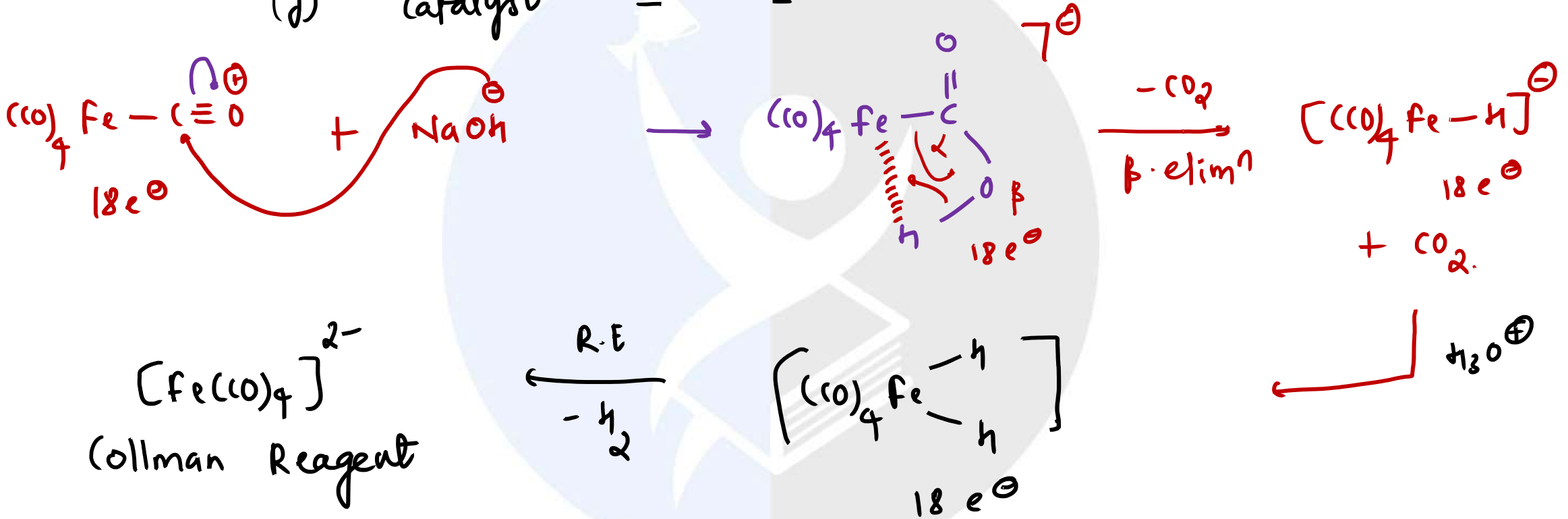

Rh
CD3
PMe3
CD3
II
A
1/2
Insertn
B
R-H
elmn.
C
alkene
Dissociatn
D
PMe3
SN2
E
R.E
F
G
+


PyP
SN1
-PMe3
Rh
CD3
PMe3
18e⊖
16e⊖
Alkene Insertion
1,2 insertion
+3
β
α
dissocn
elimn
β-H
SN2
PMe3
R.E
+ HCD3.

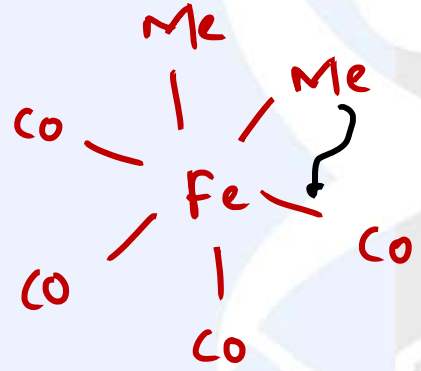
Water Gas Reaction :-

$$n\,CO_{(g)} \xrightarrow[\text{catalyst}]{Ni/Fe} [CO_2 + H_2]$$



Q. $[Fe(CO)_4]^{2-}$ $\xrightarrow{2MeI}$ (A) $\xrightarrow[1,1]{PPh_3}$ (B)

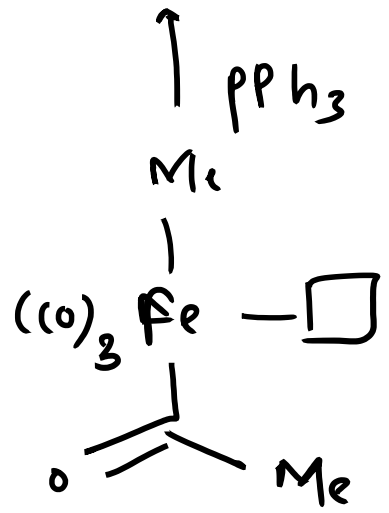
18 e⊖



$\xrightarrow{PPh_3}$ 1,1 Migration

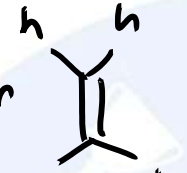
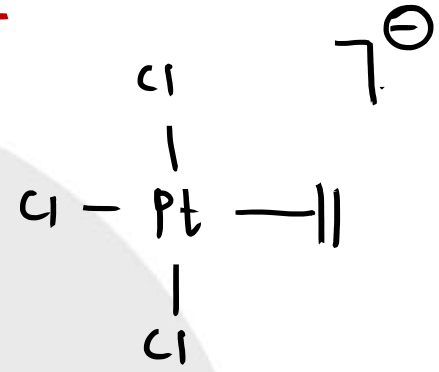
$[PPh_3Fe(COMe)(Me)(CO)_3]$

18 e⊖



Metal – Olefin Complex :-

Rxn :

$K_2[PtCl_4]$ + C_2H_4 or  →  + KCl

Pt^{+2}

$5d^8$

free olefin

Zeise's salt

Pt^{+2}

$5d^8$

Free Olefin

(Metal Olefin)

Coordinated Olefin.

① Nucleophilic nature

= + Br_2 → 

① 

Electrophilic in nature

② free olefin shows E^+ addn rxn

③ I.R stretching freq νcm^{-1} high (B.O = 2)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

④ Bond strength of free olefin higher

⑤ Less C—C Bond length.

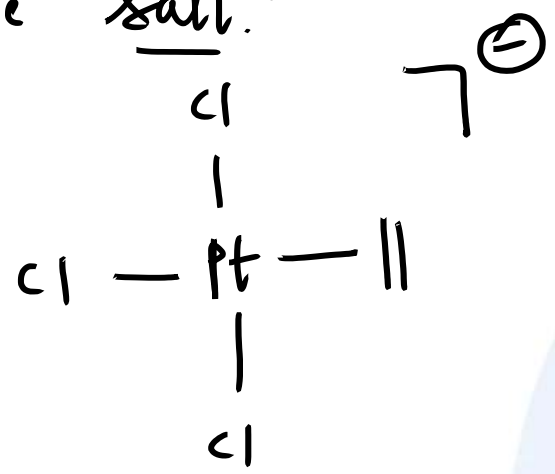
② Coordinated olefin shows $Nu^{\ominus}$ addn rxn.

③ I.R stretching freq less (B.O = 1 & 2 betn due to B.B)

④ B.S of coordinated olefin is low

⑤ More C—C B.L.

Zeise salt:



→ Pseudo · sq. planar

→ Pt^{+2} : $5d^8$

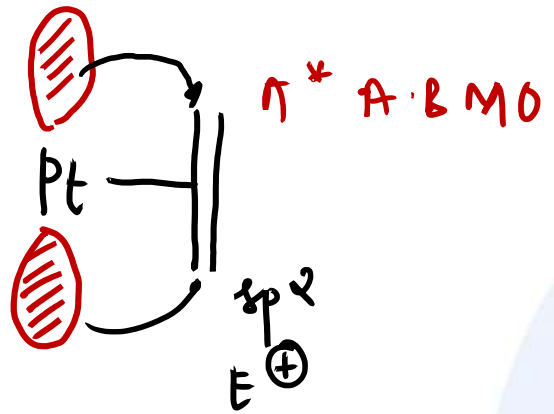
low spin complex

dsp^2 Hybrid.

→ B.O : 1 & 2 both

→ In Zeise salt, All Cl – Pt B.L not same [∵ of trans effect ⟹ Cl]

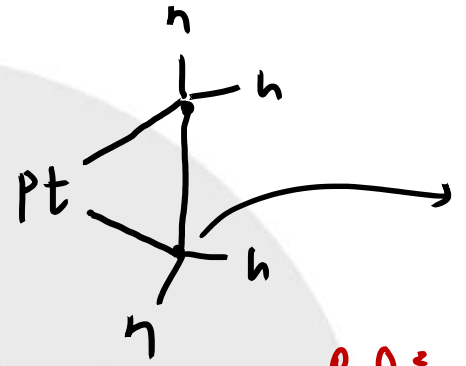
PYQ



B.O = 1 & 2

1550 cm^{-1}

B.L less

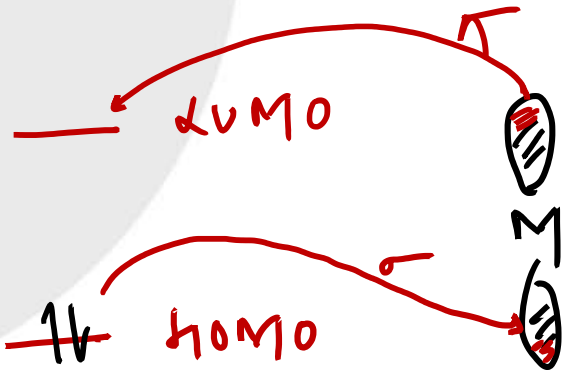


sp^3

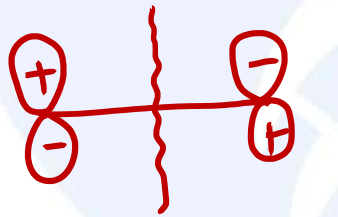
B.O = 1

I.R = 1335 - 1900 cm^{-1}

C-C B.L ↑



d_{xz}/d_{yz}



π_g n = 1

n = 0 π_u

=

① π acceptor

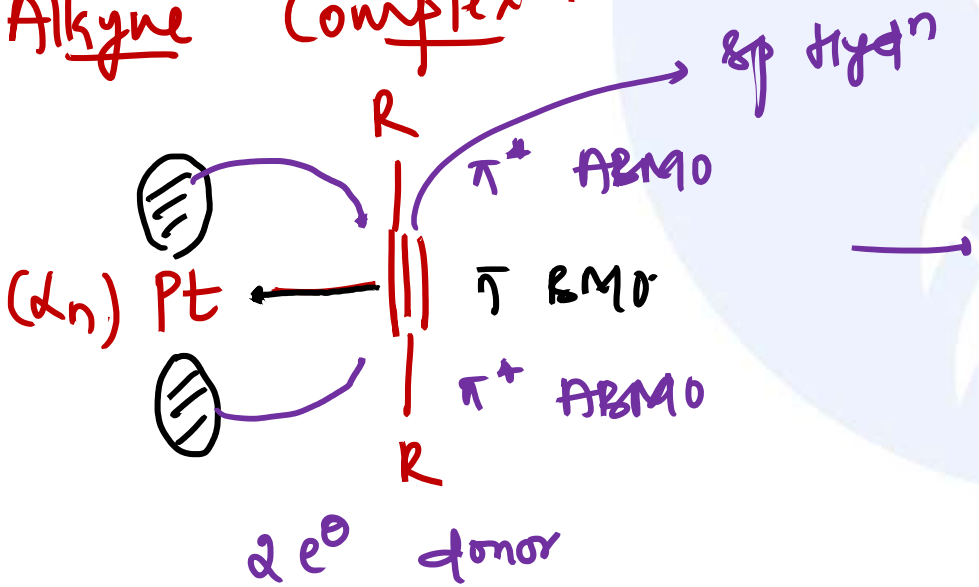
② 2 $e^{\ominus}$ donor

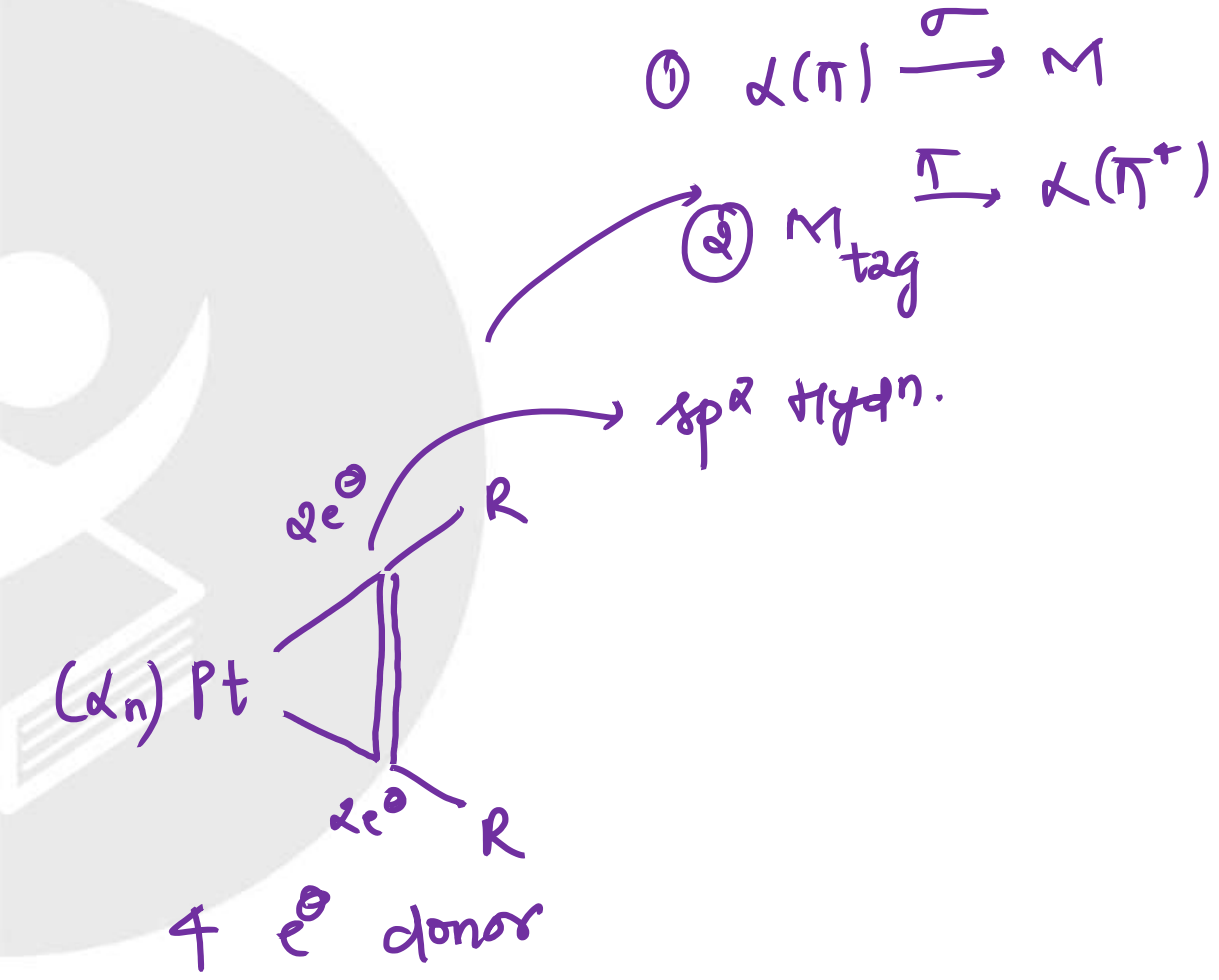
Interactn : 2 type

① $L(\pi) \xrightarrow{\sigma} (M)$

② $M_{tag} \xrightarrow{\pi} L(\pi^*)$

Alkyne Complex.

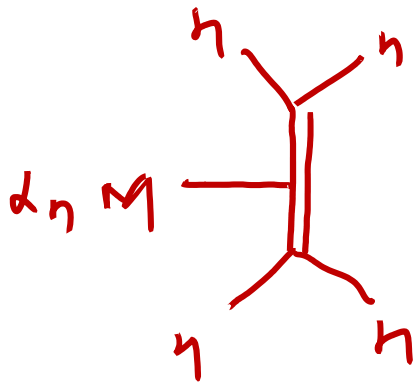


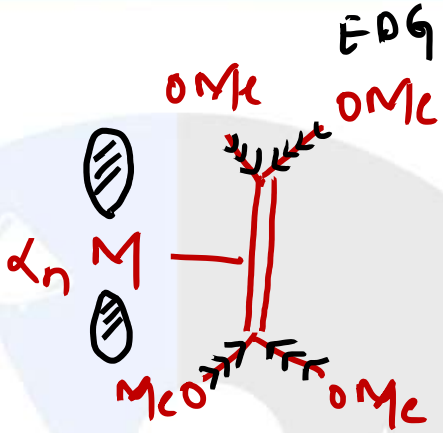


Factors affecting Metal Olefin :—

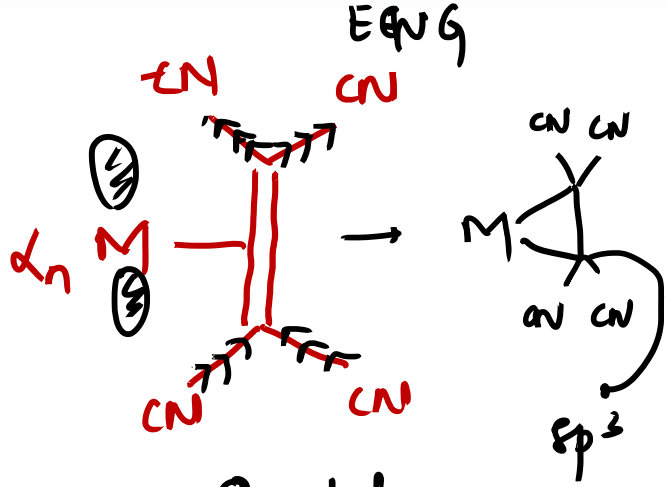
1. Back Bonding
2. IR - Stretching freq.
3. Bond Length
4. Rate of Coordinate Olefin

① Back Bonding :-

① 

② 

π^* ARMO $e^\ominus$ rich
Less B.B

② 

π^* more $e^\ominus$ def.
∴ More B.B.

① If EDG present on alkene → B.B ↓ C–C ↓

② If EWG present on alkene → B.B ↑ C–C ↑

if B.B more
$sp^2 \longrightarrow sp^3$

① B.B : C > A > B
② B.L (C–C) : B > A > C
③ B.L (C–C) : C > A > B
④ γ_{cm}^{-1} : B > A > C

Q. Arrange in ↑ order of C–C B.L.

$[Ir(PPh_3)_2Cl(\alpha)]$

B.L : B > A > D > C

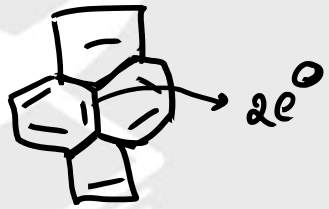
B.O : C > D > A > B

$\alpha \rightarrow$ (A) C_2H_4

(B) $C_2(CN)_4$ EWG B.B More

(C) $C_2(OMe)_4$ EDG B.B least

(D) $C_2(OPh)_4$ less EWG



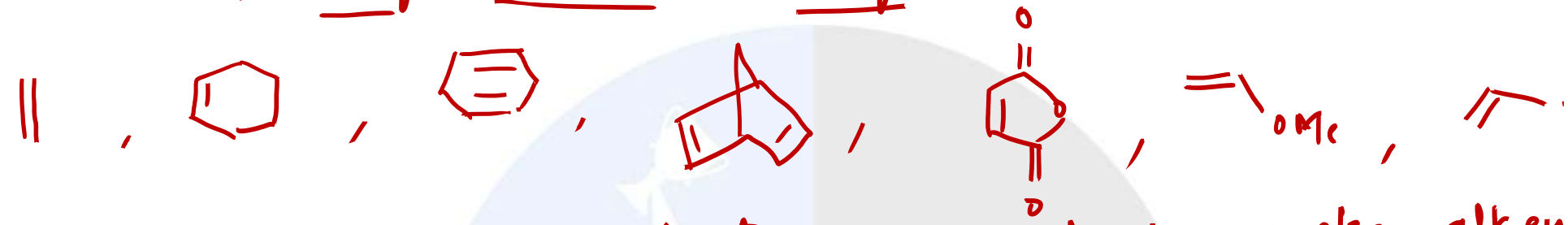
B.L : C > B > D > A

Q. Arrange ↑ order of C–C Bond length

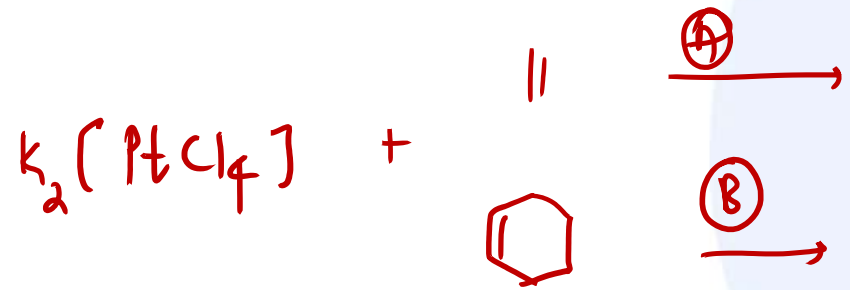
(A) C_{60} (B) $[IrCl(PPh_3)(\eta^2-C_{60})CO]$

(C) $[IrClCO(PPh_3)C_2(CN)_4]$ (D) $[IrCOCl(PPh_3)(C_2Me_4)]$ EDG

Rate of co-ordinate olefin :-

Ex: 

① free alkene faster coordinate compared to cyclic alkene



A > B

$K_2[PtCl_4]$ +

Q. $K_2[PtCl_4] + L \longrightarrow$

L_1 =  L_2 =  L_3 = 

[If no of π bond ↑, Rate of coordination ↑]

$$\boxed{L_3 > L_2 > L_1}$$

PYQ Q. Which of following ligand faster coordinate with. metals ?

$[Ni(bpy)_3] + L \longrightarrow$ (A)

(A) L = 

(B) L = 

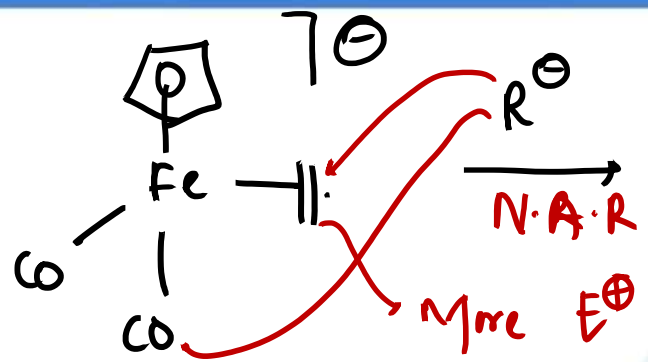
(C) ~~L =~~ 

More $E^{\oplus}$

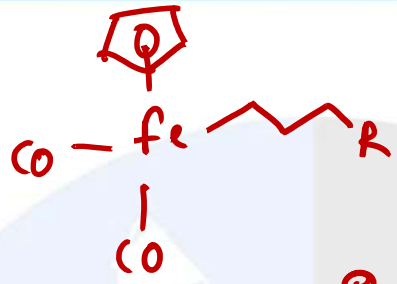
(D) L = 

More the conjugation, faster coordination

Q.



18e⊖



18e⊖

Coordinate Olefin → $Nu^{\ominus}$ Addⁿ Rxn

free Olefin → $E^{\oplus}$ Addⁿ Rxn.

DMG Rule

{ Devis. Mingo, Green }

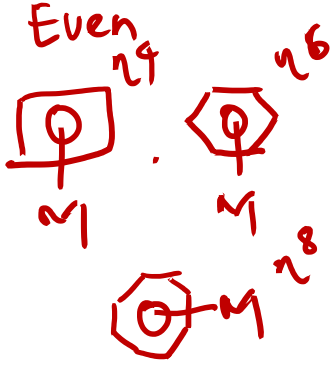
① DMG. rule used for $Nu^{\ominus}$ attack of polyene system.

② DMG. applicable for only 18 $e^{\ominus}$ complex.

Polyene

Closed Polyene

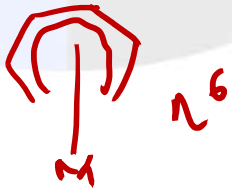
Even



Odd

Open Polyene

Even

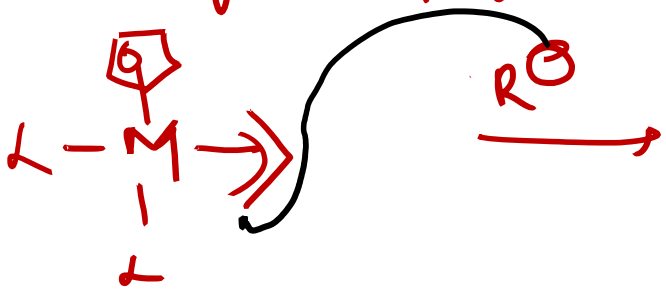


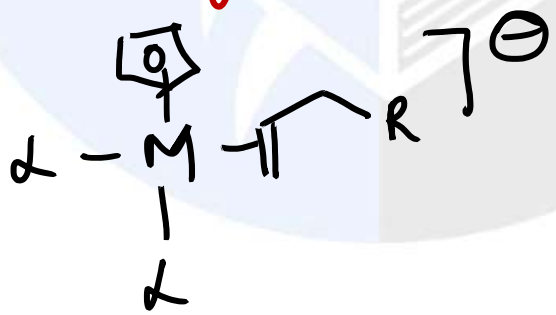
Odd

① Even polyene faster $Nu^{\ominus}$ attack than odd polyene

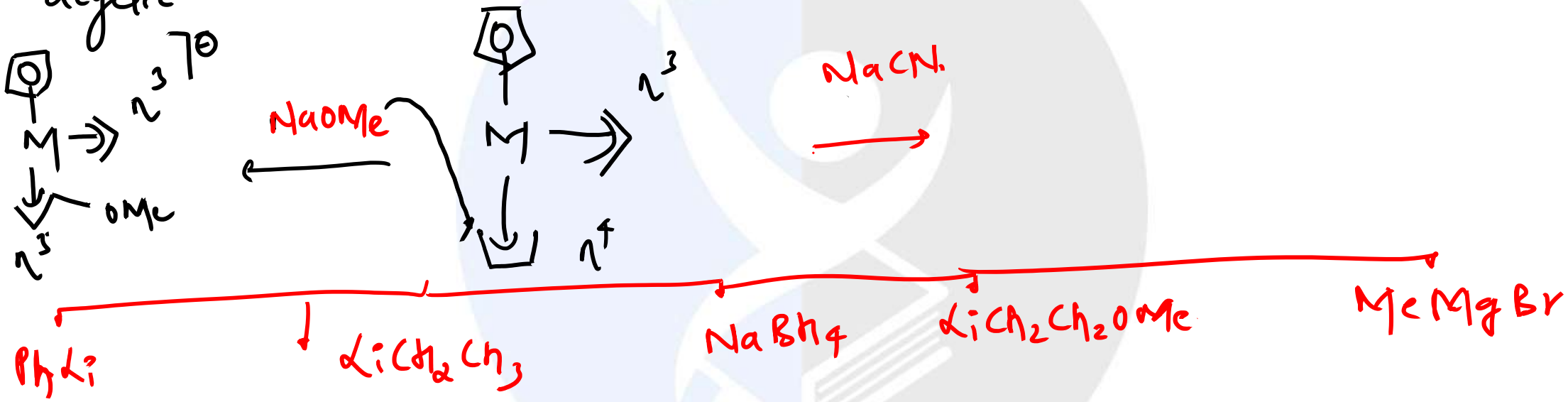
Eg:

② Acyclic polyene react faster than cyclic polyene.





③ If complex containing odd acyclic ring & even acyclic ring then even acyclic faster $Nu^{\ominus}$ attack than odd acyclic chain.



Reactivity Order :-

Acyclic even > Acyclic Odd > Cyclic even > Cyclic odd.