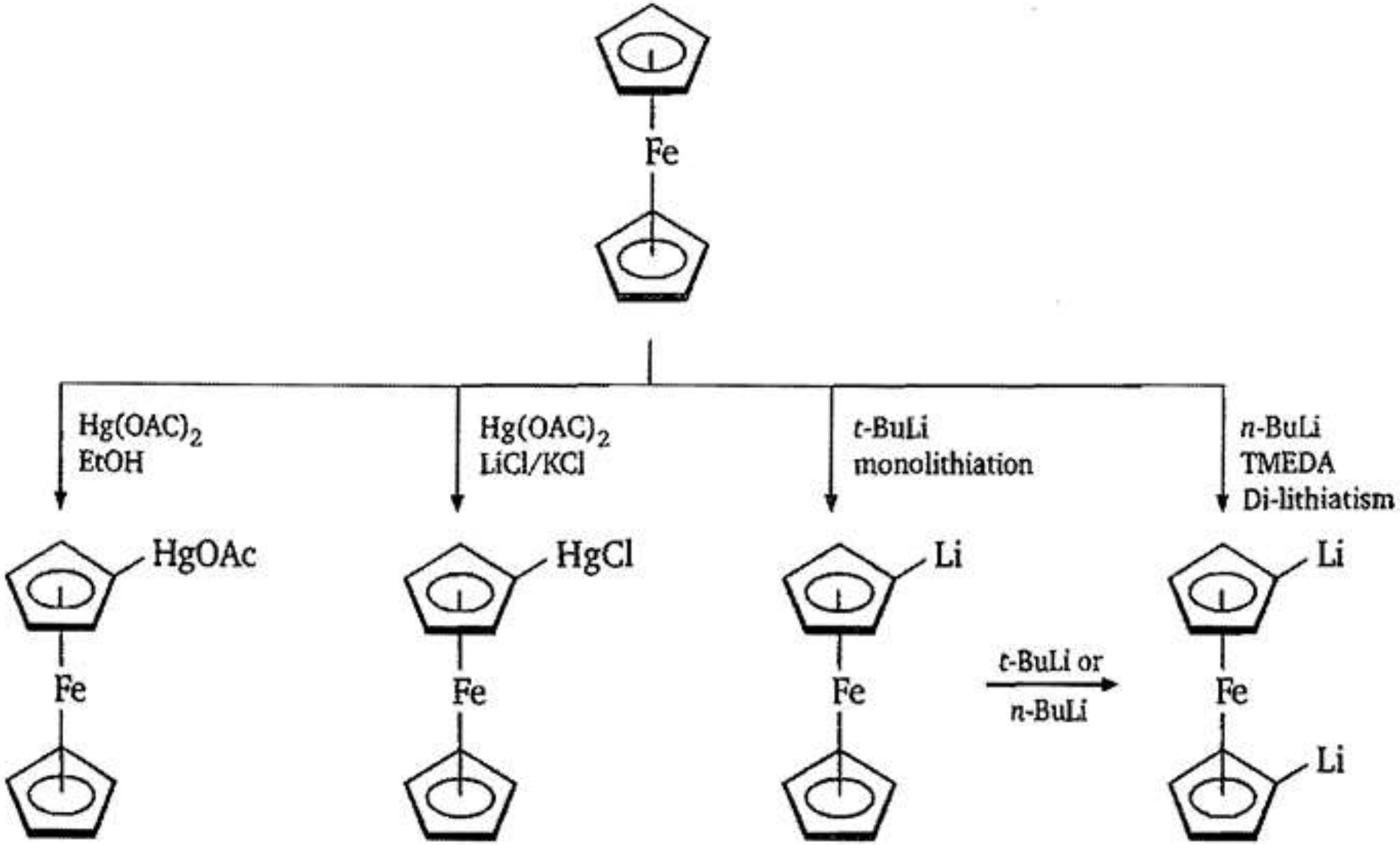

Fe
Hg(OAC)$_2$
EtOH
Hg(OAC)$_2$
LiCl/KCl
t-BuLi
monolithiation
n-BuLi
TMEDA
Di-lithiatism
HgOAc
Fe
HgCl
Fe
Li
Fe
t-BuLi or
n-BuLi
Li
Fe
Li

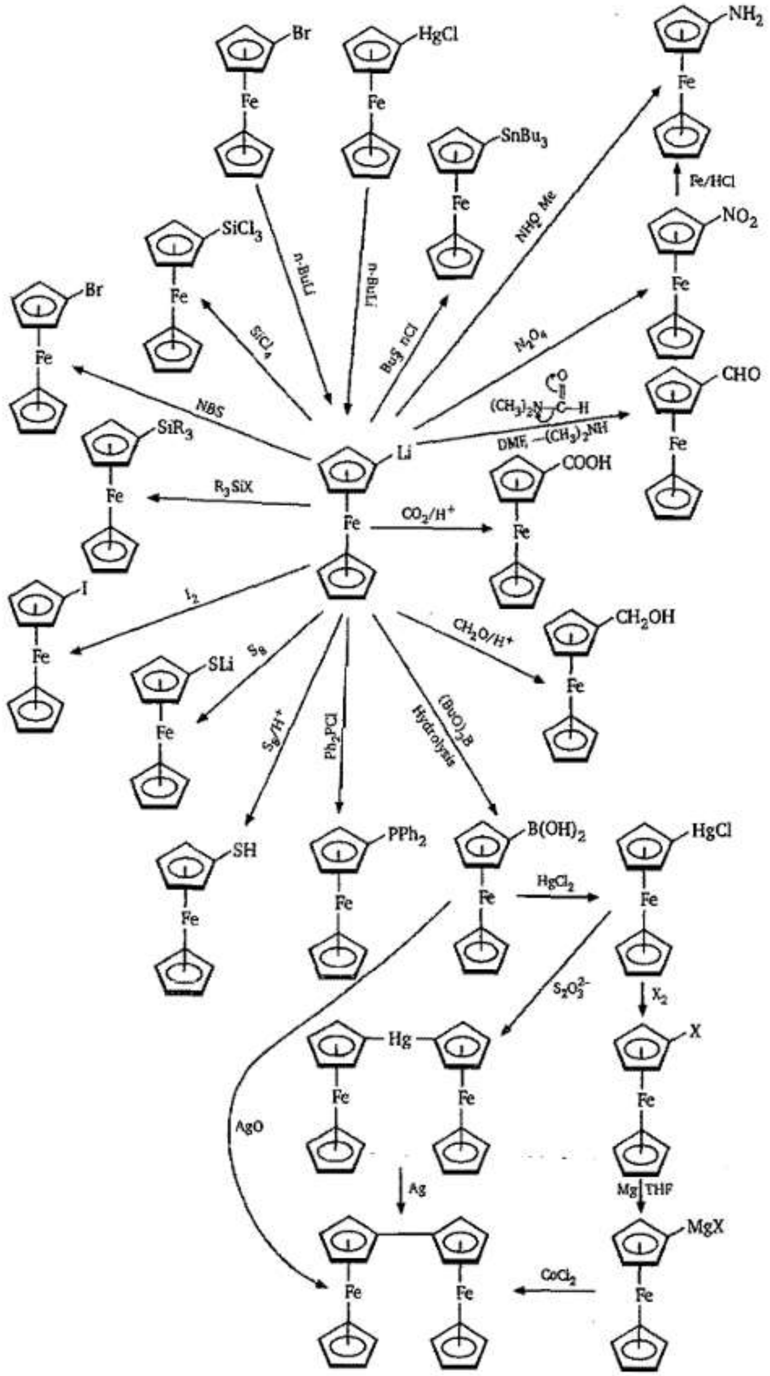


Fig. 6.14 Synthesis and reaction of mono-lithiated ferrocene

Ajay Kumar

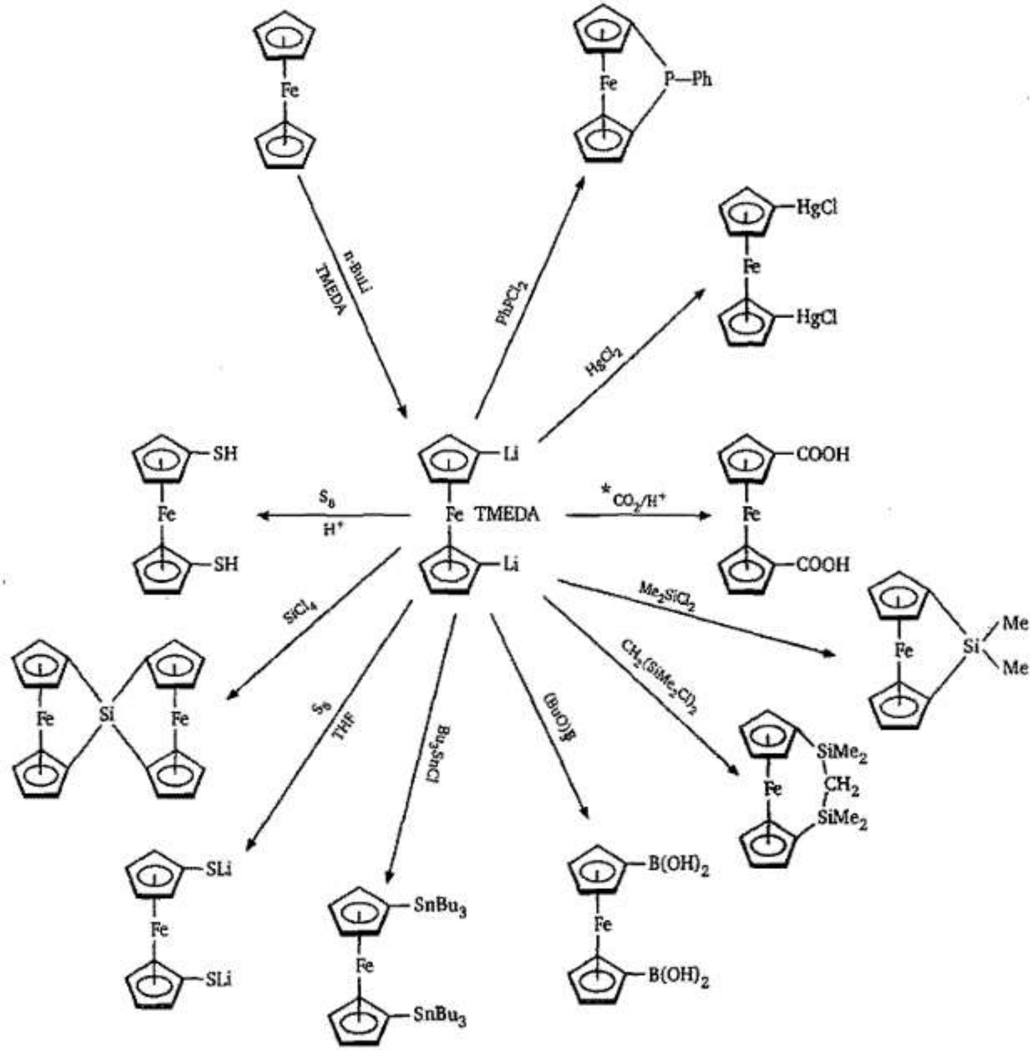
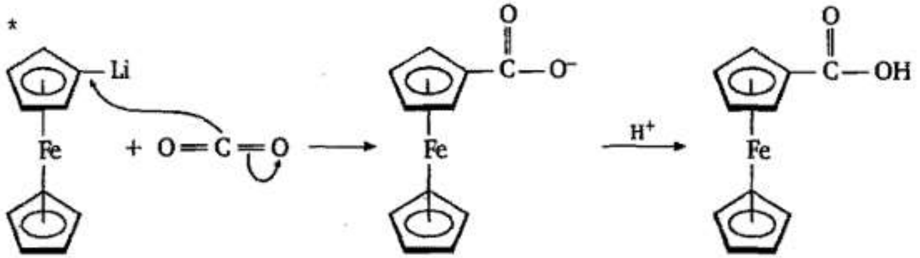
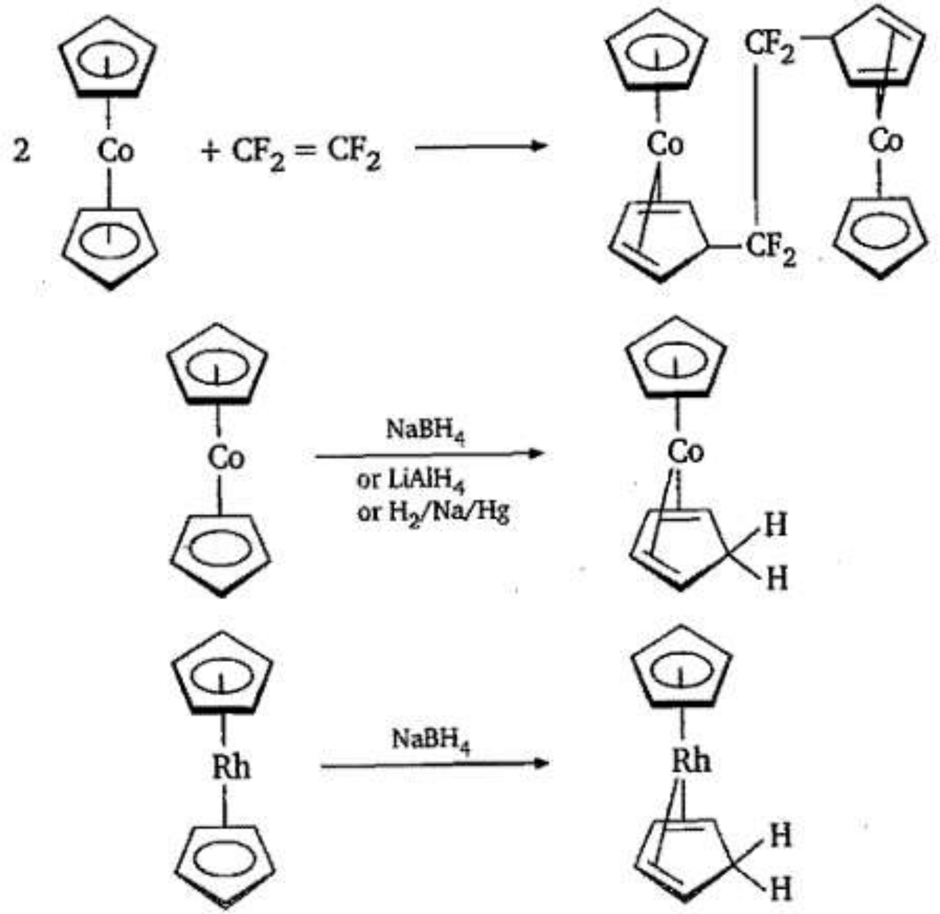
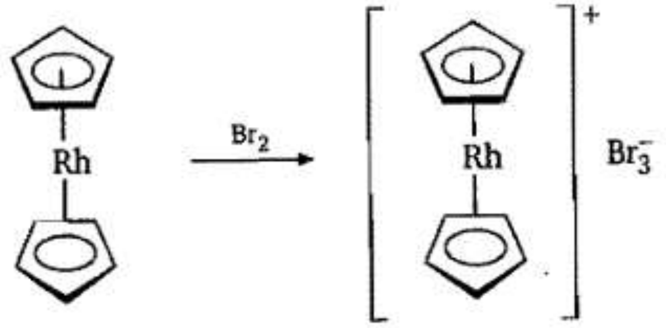


Fig. 6.15 Synthesis and Reaction of 1,1'-dilithio ferrocene





$$Cp_2Rh \xrightarrow{> -196^\circ C} [CpRh(\eta^4-C_5H_4)]_2$$



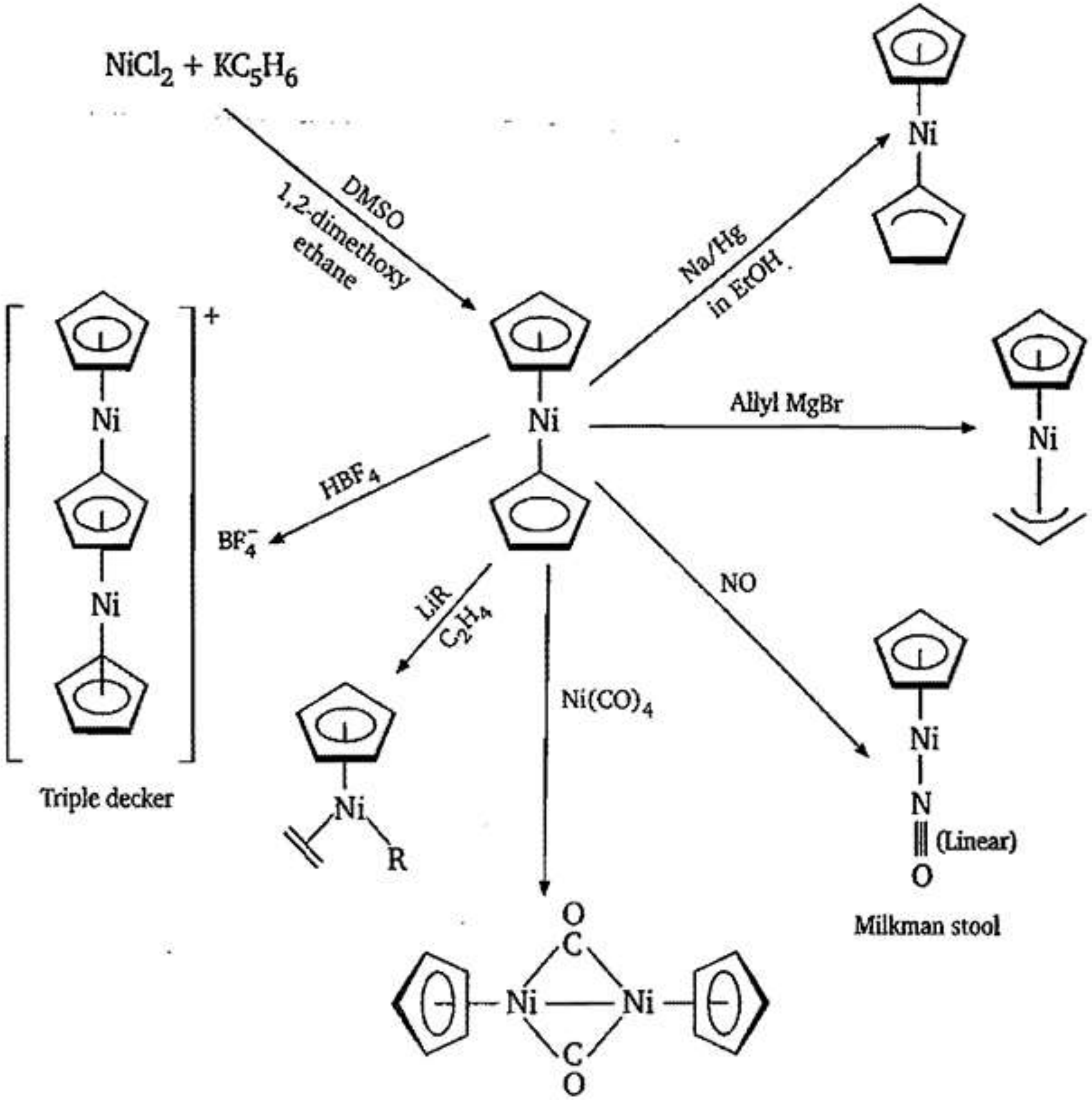
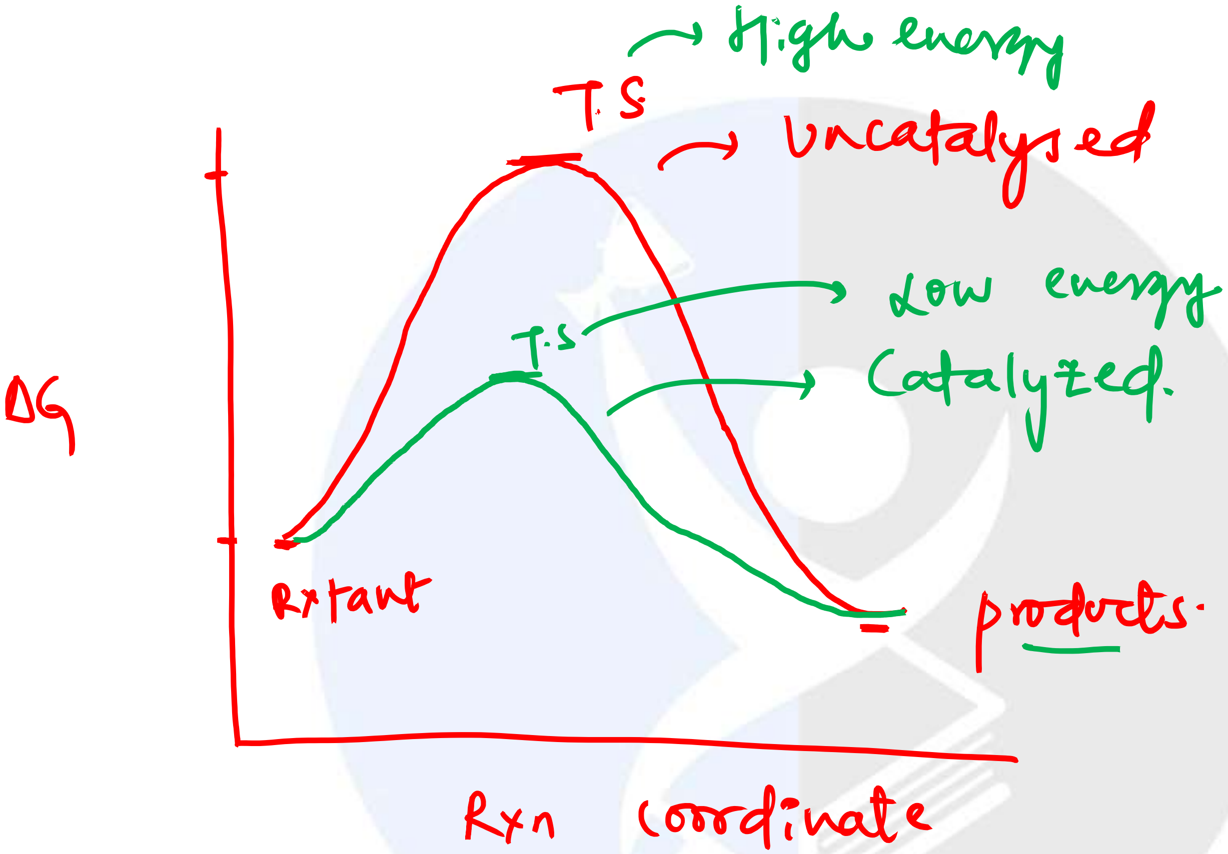


Fig. 6.19 Synthesis and reactions of Cp_2Ni

Organometallic Catalysts

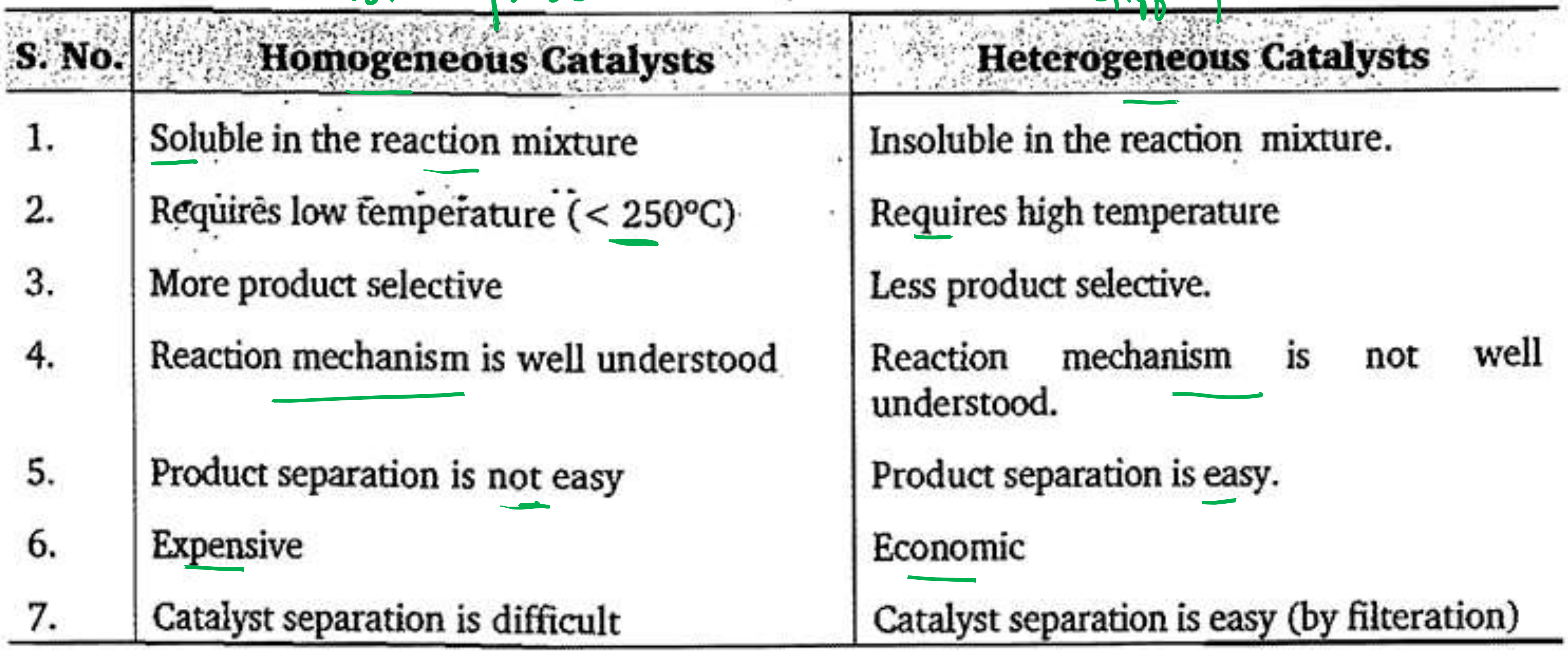
1. A thermodynamically favourable reactions may be slow at modest temperatures and, therefore, are not of much value for synthesis. The rate of reaction can be accelerated by increasing temperature but it requires high energy and, therefore, it is very expensive. Higher temperatures may also induce competing side reactions that will cause the reduction in yield of the required product. The rate of reaction of such thermodynamically favourable reactions can be accelerated using a catalyst.
2. A catalyst is a substance that increases the rate of a such thermodynamically allowed reaction by lowering the activation energy of barrier for the process without itself being consumed. A catalyst does not affect the Gibbs free energy of the overall reaction because G is a state function. The reaction which are not thermodynamically favourable can not be made favourable using catalyst. A catalyst is used in sub stoichiometric amount to bring about a reaction at a temperature below that required for uncatalyzed thermal reaction. If several reaction paths are possible, a catalyst may increase product specificity by lowering activation energy for desired path or by raising it for another.
3. A catalyst combines with the reactants or substrates to form transition state which finally produces the reaction products and regenerates the catalyst. The catalyst further enters the catalytic cycle and combines the reactants again and again. A typical catalyst may participate in a catalytic cycle 10^1-10^6 times or more.


High energy
T.S
Uncatalysed
Low energy
T.S
Catalyzed.
ΔG
Rxtant
products.
Rxn coordinate

Catalysts are classified into two categories-homogeneous ① and hetergeneous ②.

same phase

diff phase



S. No.	Homogeneous Catalysts	Heterogeneous Catalysts
1.	Soluble in the reaction mixture	Insoluble in the reaction mixture.
2.	Requires low temperature (< 250°C)	Requires high temperature
3.	More product selective	Less product selective.
4.	Reaction mechanism is well understood	Reaction mechanism is not well understood.
5.	Product separation is not easy	Product separation is easy.
6.	Expensive	Economic
7.	Catalyst separation is difficult	Catalyst separation is easy (by filteration)

Catalytic Cycles :—

$$\underline{\text{Turn Over Number}}\ (\text{TON}) = \frac{\text{Moles of rxtant}}{\text{Moles of catalyst}} \times \%\ \text{yield of product}$$

TON Higher; life of catalyst is longer.

$$\underline{\text{TOF}} = \frac{\text{Moles of rxtant}}{\text{Time} \times \text{Moles of catalyst}} \times \%\ \text{yield of product}$$

$$\text{TOF} = \frac{\text{TON}}{\text{Time}} \rightarrow \text{Unit } (\text{time}^{-1})$$

Catalyst

* Homogeneous Catalyst

Ex: ① Hydroformylation $HCo(CO)_4$
oxo- process

② Monsanto Acetic Acid.
$[RhI_2(CO)_2]^{\ominus}$, $[IrI_2(CO)_2]^{\ominus}$

③ Wikinson Catalyst
$[RhCl(PPh_3)_3]$

Heterogeneous Catalyst

① Ziegler–Natta Catalyst
$[TiCl_4 + (AlEt_3)]$

② ZSM-5

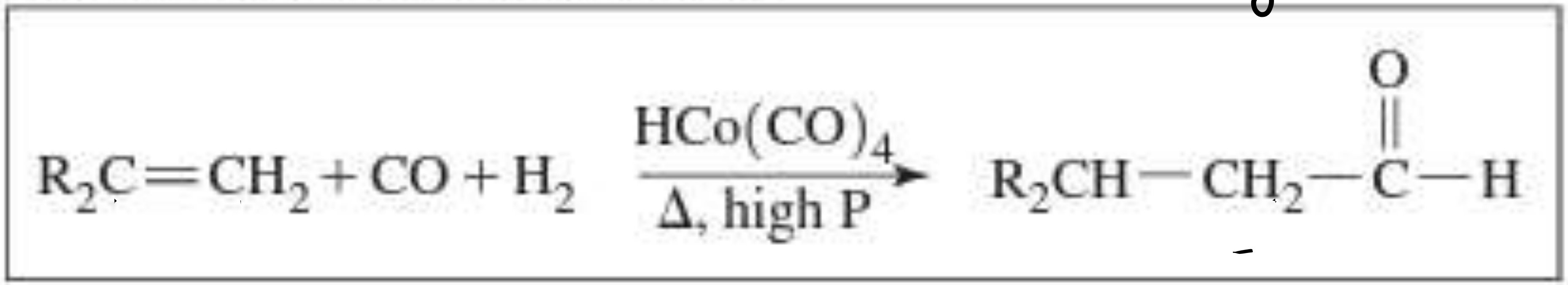
③ Water-Gas Rxn.

Hydroformylation 1938

no. of carbon ↑ by ①

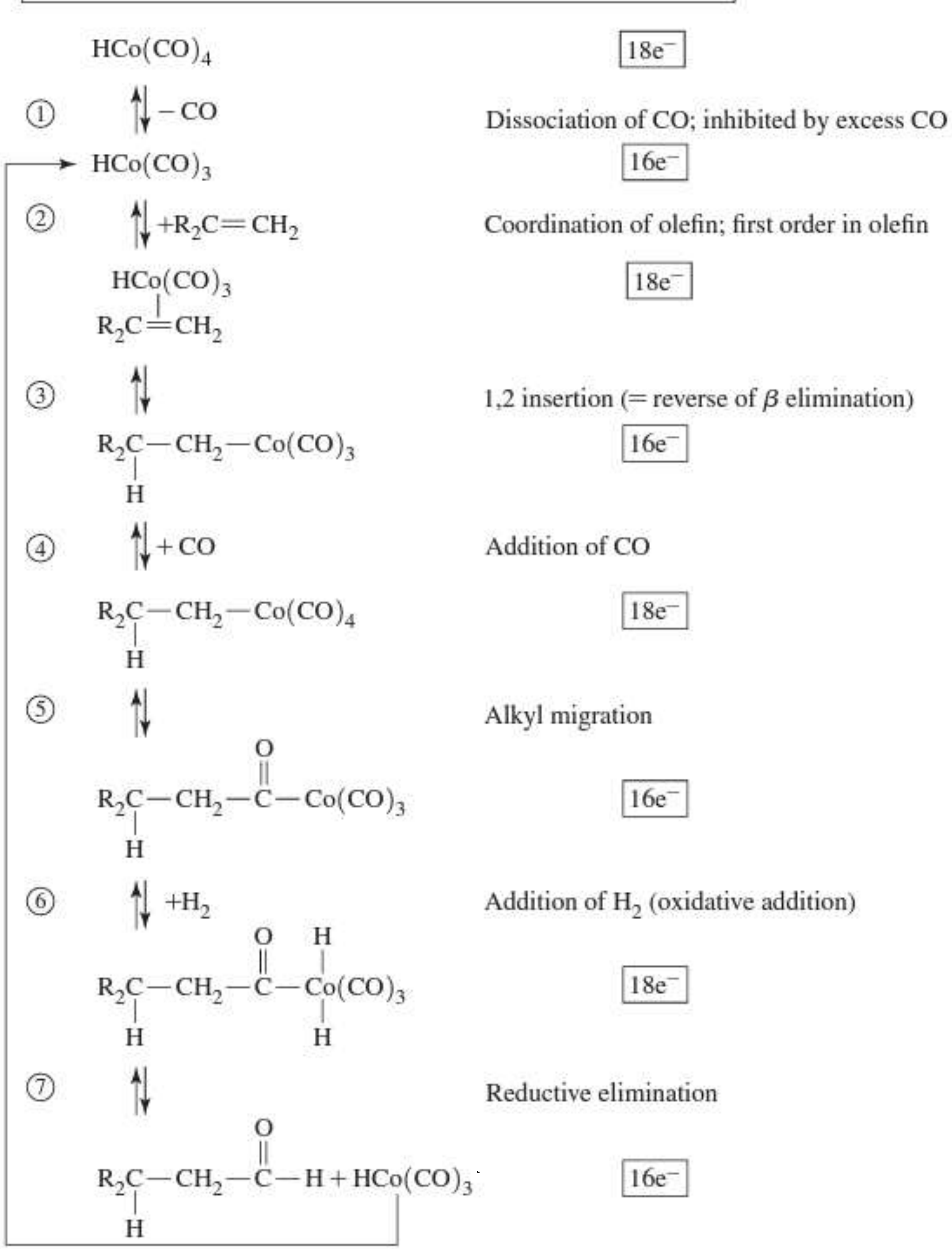
Hydroformylation (Oxo) Process

'Aldehyde'



$$R_2C{=}CH_2 + CO + H_2 \xrightarrow[\Delta,\ \text{high P}]{HCo(CO)_4} R_2CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}H$$

→ Addn of formaldehyde to alkene



$HCo(CO)_4$ $\boxed{18e^-}$

① $\updownarrow -CO$ Dissociation of CO; inhibited by excess CO

$HCo(CO)_3$ $\boxed{16e^-}$

② $\updownarrow +R_2C{=}CH_2$ Coordination of olefin; first order in olefin

$HCo(CO)_3(R_2C{=}CH_2)$ $\boxed{18e^-}$

③ $\updownarrow$ 1,2 insertion (= reverse of β elimination)

$R_2CH{-}CH_2{-}Co(CO)_3$ $\boxed{16e^-}$

④ $\updownarrow +CO$ Addition of CO

$R_2CH{-}CH_2{-}Co(CO)_4$ $\boxed{18e^-}$

⑤ $\updownarrow$ Alkyl migration

$R_2CH{-}CH_2{-}C({=}O){-}Co(CO)_3$ $\boxed{16e^-}$

⑥ $\updownarrow +H_2$ Addition of H_2 (oxidative addition)

$R_2CH{-}CH_2{-}C({=}O){-}CoH_2(CO)_3$ $\boxed{18e^-}$

⑦ $\updownarrow$ Reductive elimination

$R_2CH{-}CH_2{-}C({=}O){-}H + HCo(CO)_3$ $\boxed{16e^-}$

$18 + 16 = \boxed{34} \rightarrow 1$ M–M bond

$Co_2(CO)_8 \longrightarrow$

$\downarrow \{H_2\}$

$HCo(CO)_4$

① Dissociatn of CO

② Alkene Insertn (R.D.S)

③ 1,2 Insertn

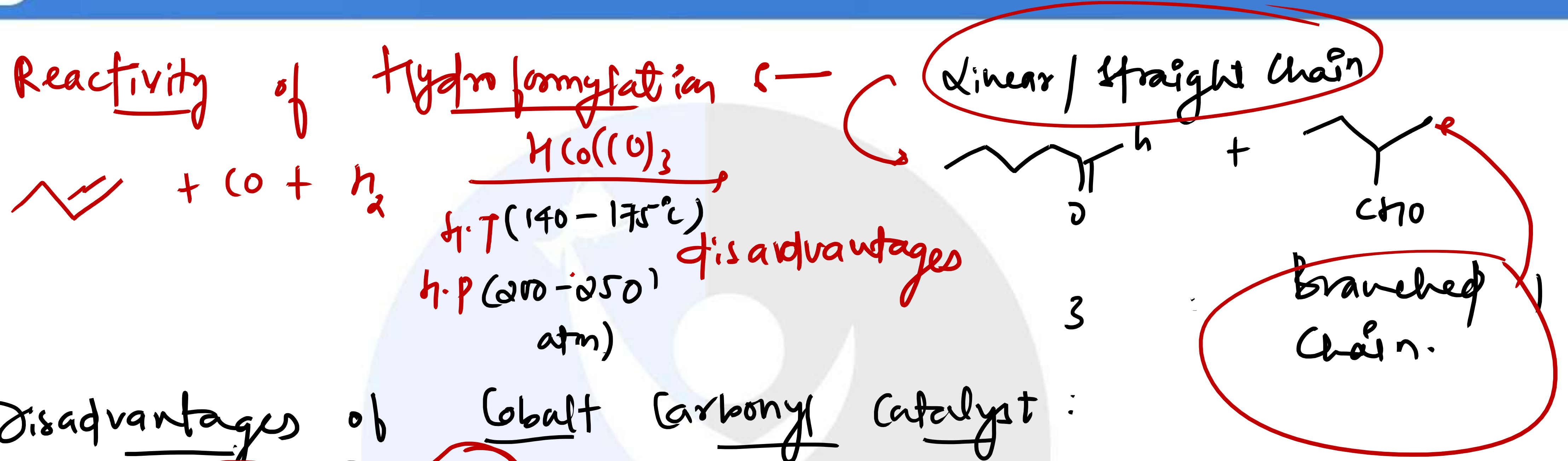
④ CO addn

⑤ Alkyl / 1,1 - Migratn.

⑥ O.A of H_2

⑦ R.E

Reactivity of Hydroformylation



① Disadvantages of Cobalt Carbonyl Catalyst :

H.T & H.P

② Along with Linear chain; branched chain also obtained in 3 : 1 ratio which is not good as this ratio should be high.

$$HCo(CO)_4 \xrightarrow[-PBu_3]{-CO} HCo(CO)_3(PBu_3)$$

②

(n-Butyl)

$\downarrow$ $P(t-Bu)_3$

t-Butyl

$HCo(CO)_3(P(t-Bu)_3)]$

①

$\downarrow$

9 : 1

Linear ← → Branched

→ Linear

→ Disadvantage : Rate of Rxn ↓

∴ 175°C , 50-100 atm.

linear 90%

Brached 10%

If Bulkier group substituted By CO ; selectivity for Linear product ↑

Q. Which of following Catalyst gives predominant linear aldehyde ?

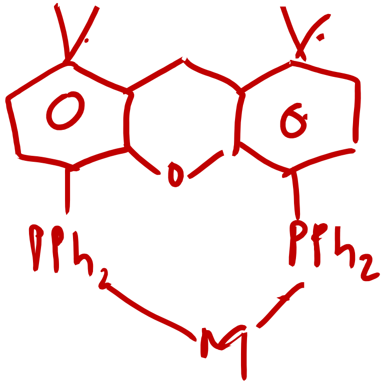
① $[HCo(CO)_2(PEt_3)]$

② $[HCo(CO)_2(P(nBu)_3)]$ → More Bulky

③ $[HCo(CO)_3]$

④ $[HCo(CO)_2(PMe_3)]$

①



②

③

④ PPh_3

$$HCo(CO)_4 \xrightarrow[H.P]{H.T} \text{less selective}$$

$$HRh(CO)_4 \xrightarrow[L.P]{L.T} \text{More selective}$$

$$\begin{tikzcd}
H-Rh(CO)_4 \arrow[r, "-CO", "PR_3"'] & \underline{H-Rh(CO)_3(PR_3)} \arrow[r, "-CO", "+PR_3"'] & H-Rh(CO)_2(PR_3)_2 \arrow[d, "-CO", "+PR_3"'] \\
 & {[H\cdot Rh(PR_3)_4]} & H-Rh(CO)_1(PR_3)_3 \arrow[l, "-CO"', "+PR_3"]
\end{tikzcd}$$

$H-Rh(CO)_3(PR_3)$: Active Catalyst (A.C)

$H-Rh(CO)_2(PR_3)_2$: A.C

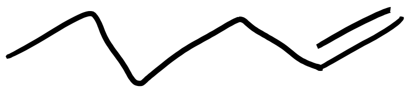
$H-Rh(CO)_1(PR_3)_3$: A.C

$[H\cdot Rh(PR_3)_4]$ Inactive

↓ Rate of Hydroformylation

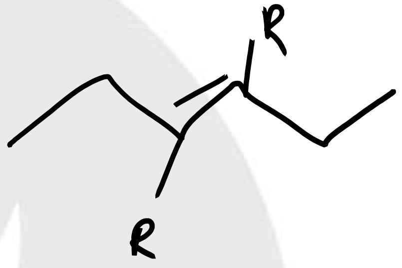
Selectivity of formatn of oxo group & hydroformylatn

→ less steric crowding alkene ; fast insertion.



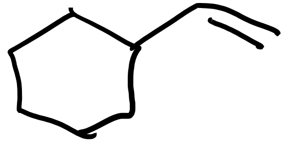
① terminal

②

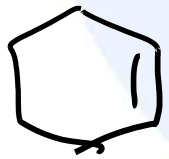


Rate order : ① > ② > ③

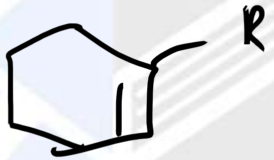
②.



①



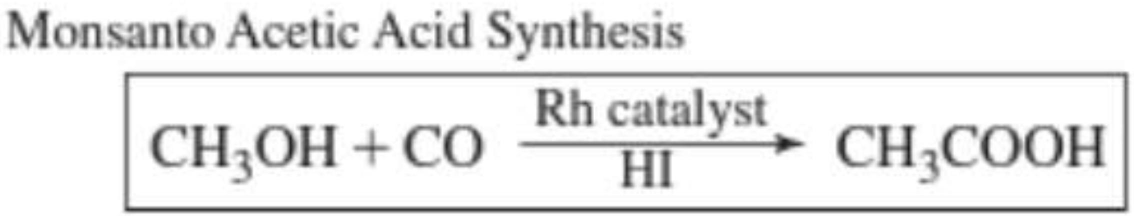
②



③

① > ② > ③

Monsanto Acetic Acid Process

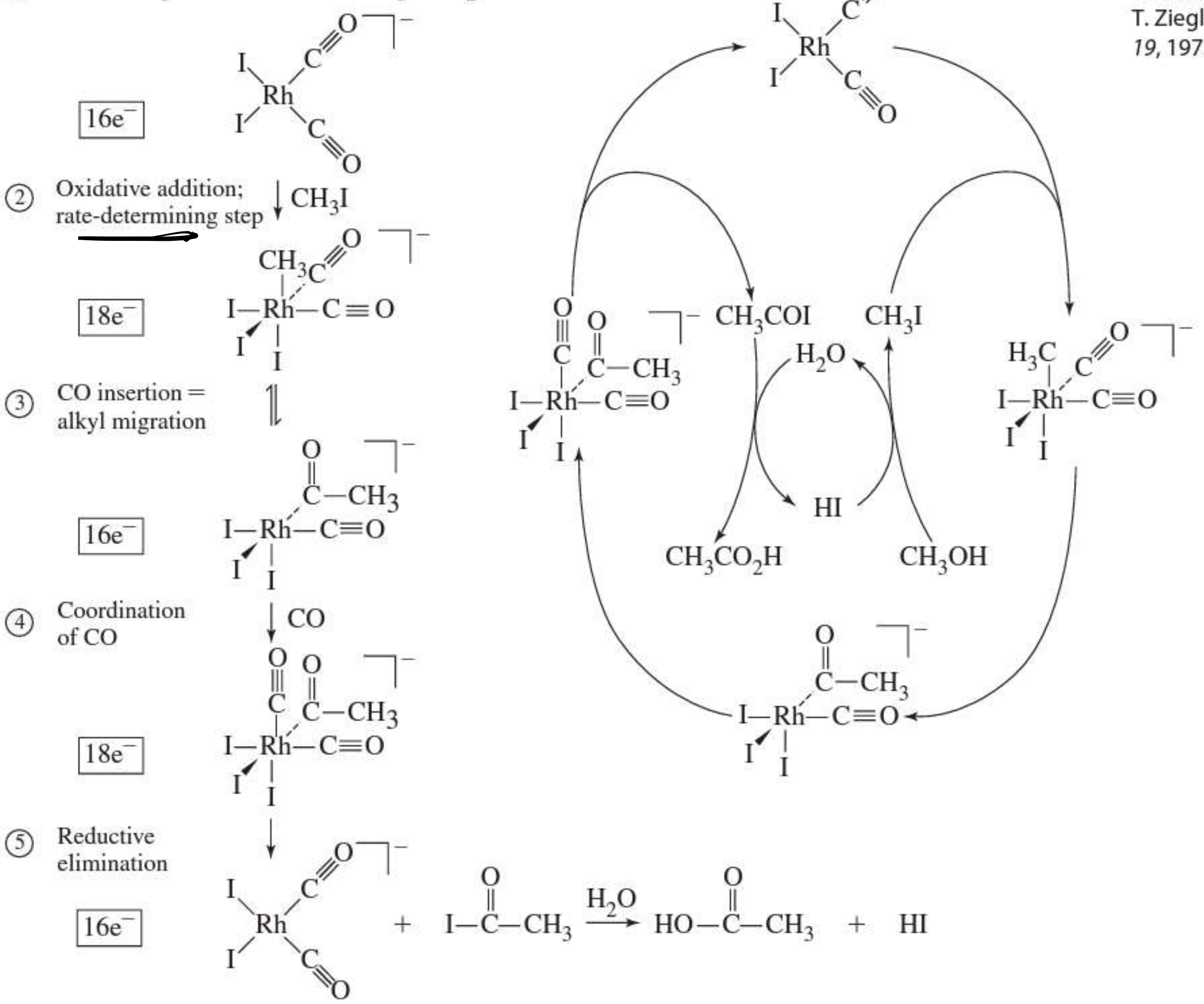


Monsanto Acetic Acid Synthesis

$$\boxed{CH_3OH + CO \xrightarrow[HI]{\text{Rh catalyst}} CH_3COOH}$$

Possible mechanism:

① $CH_3OH + HI \rightarrow CH_3I + H_2O$

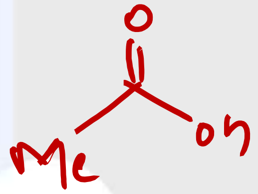


Gulliver,
J. Am. Ch
8567; M.
T. Ziegle
19, 1973

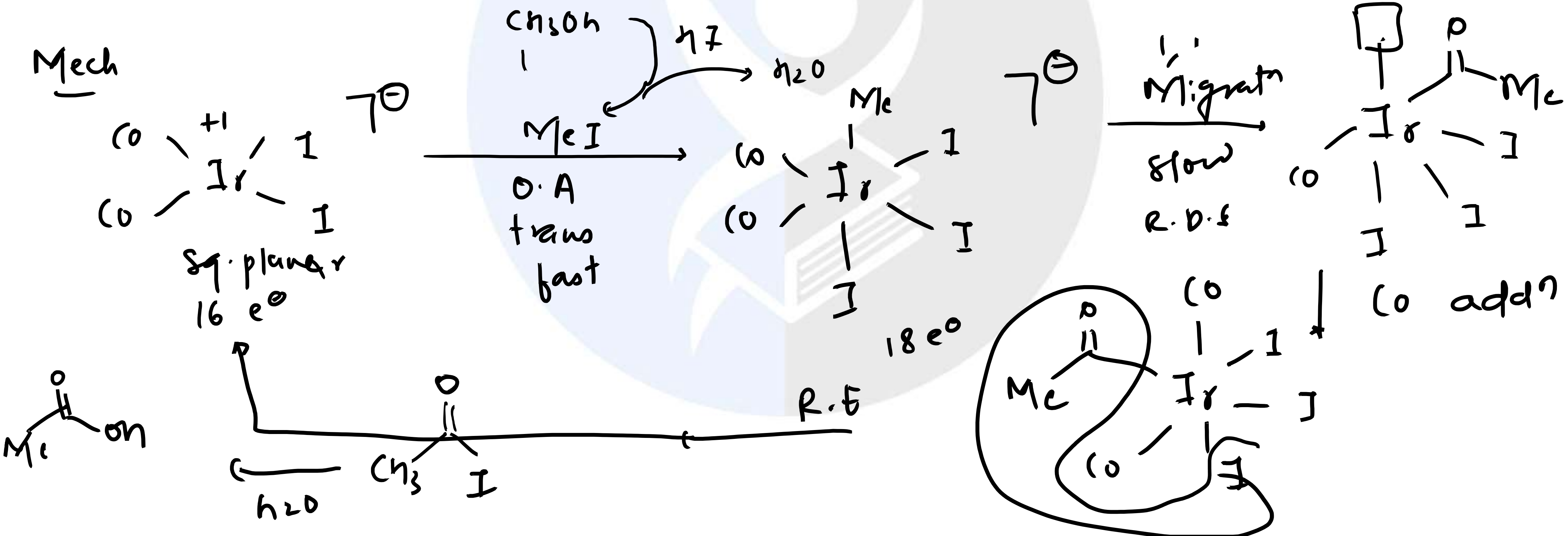
Cativa Process :-

$$[RhI_2(CO)_2]^{\ominus} \xrightarrow{Ir} [IrI_2(CO)_2]^{\ominus}$$

$$CH_3OH + HI \xrightarrow{[IrI_2(CO)_2]^{\ominus}}$$



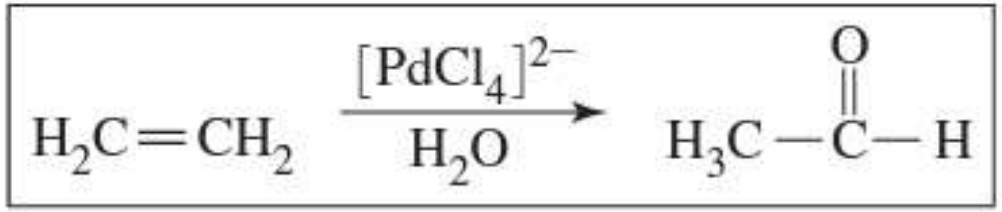
Mech



Cativa process fast than Monsanto.

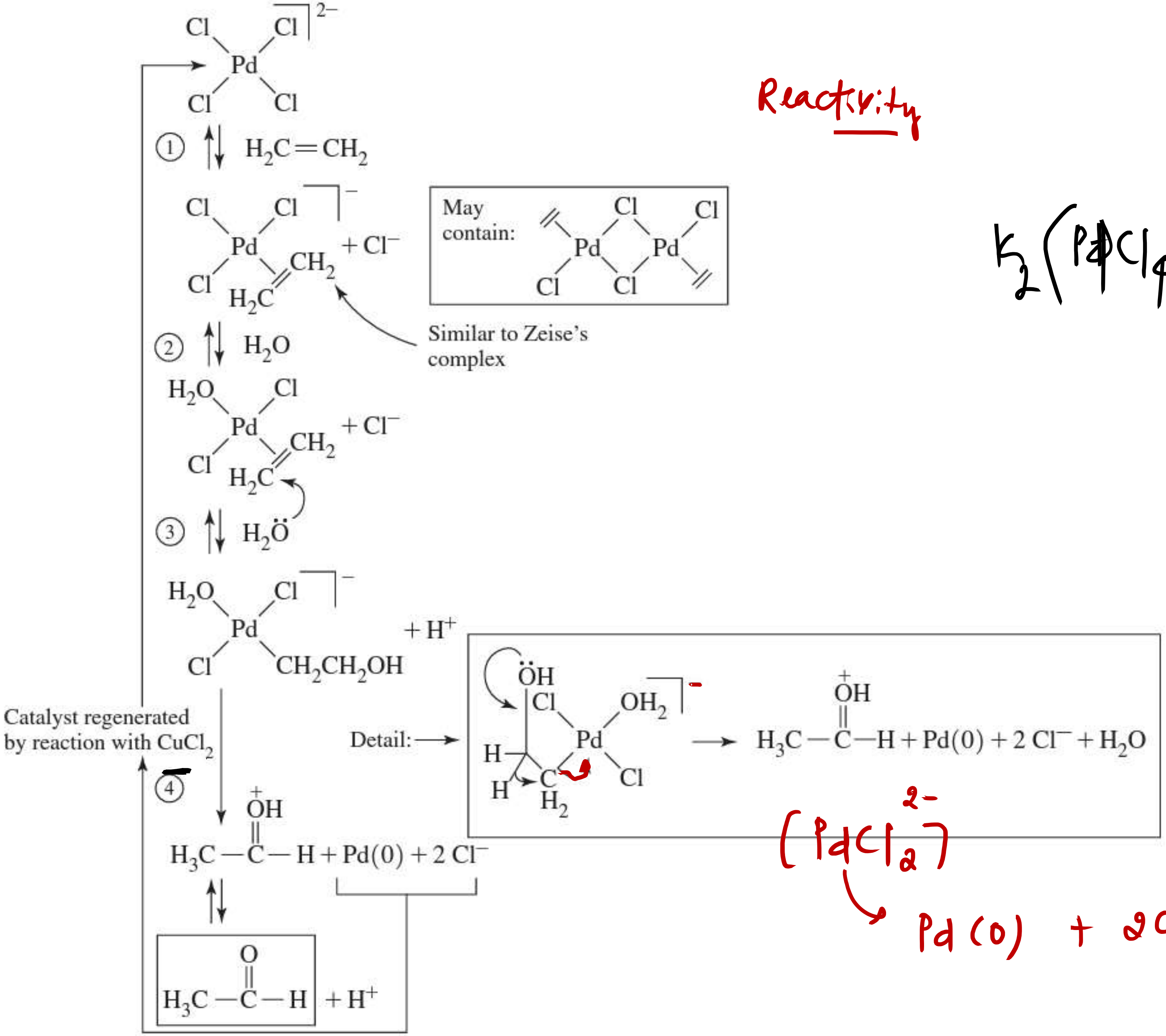
Wacker (Smidt) Process : no.of carbon same

Wacker (Smidt) Process

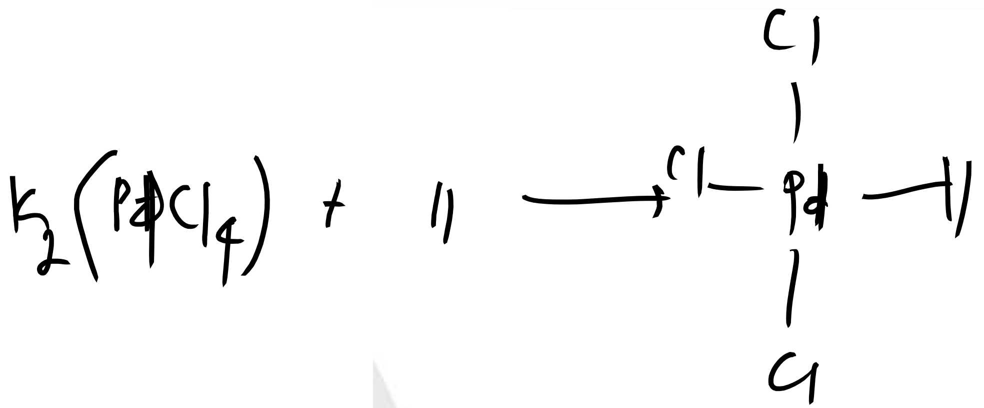


$$H_2C=CH_2 \xrightarrow[H_2O]{[PdCl_4]^{2-}} H_3C-\overset{\overset{\Large O}{\|}}{C}-H$$

Possible mechanism:

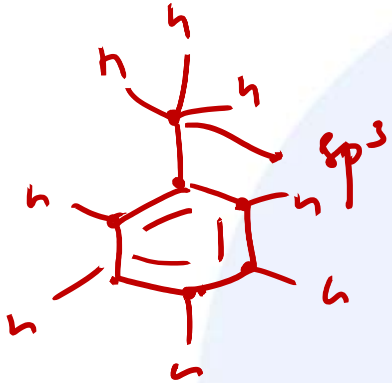


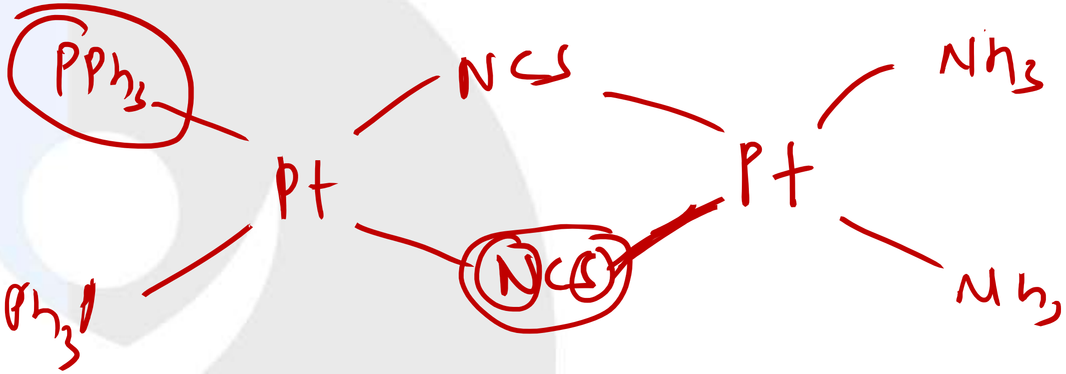
Reactivity



$[PdCl_2]^{2-}$

$\rightarrow Pd(0) + 2Cl^{\ominus}$





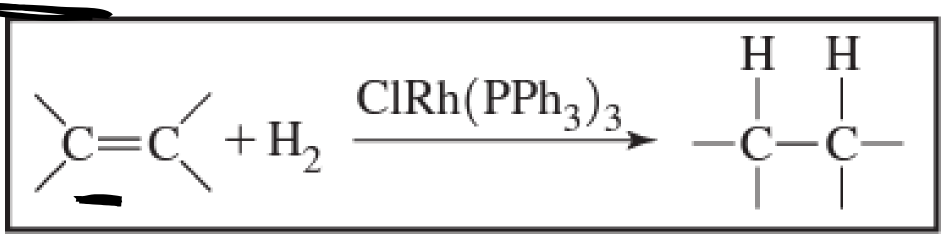
$NH_3 \rightarrow \cancel{\pi}$

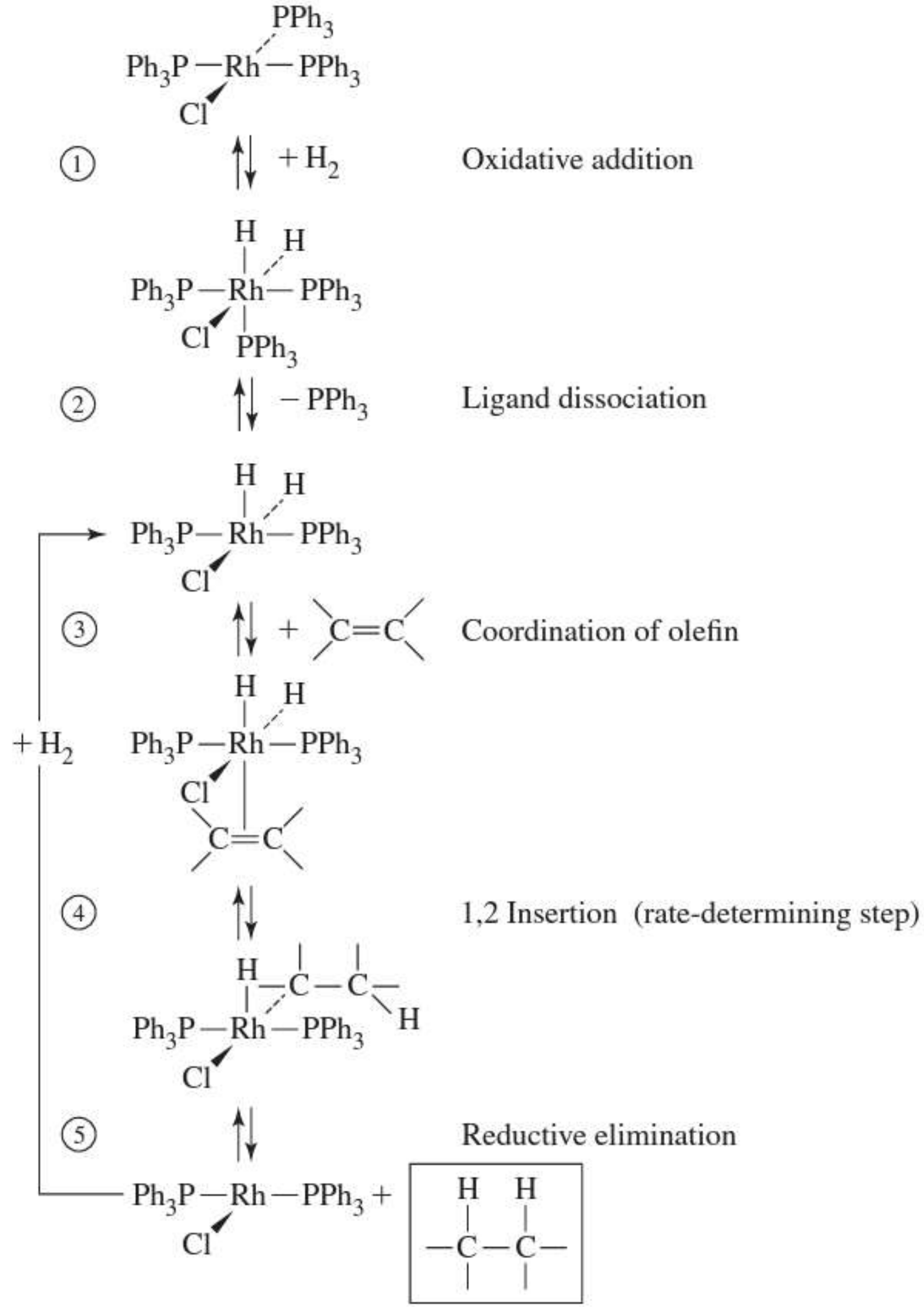
$S \rightarrow \pi$ ✓

$P \rightarrow \pi$ ✓

Hydrogenation by Wilkinson’s Catalyst

Hydrogenation using Wilkinson’s Catalyst




① Oxidative addition
+ H_2
② Ligand dissociation
− PPh_3
③ Coordination of olefin
④ 1,2 Insertion (rate-determining step)
⑤ Reductive elimination
+ H_2
Rh
Ph_3P
PPh_3
Cl
H

Thank you