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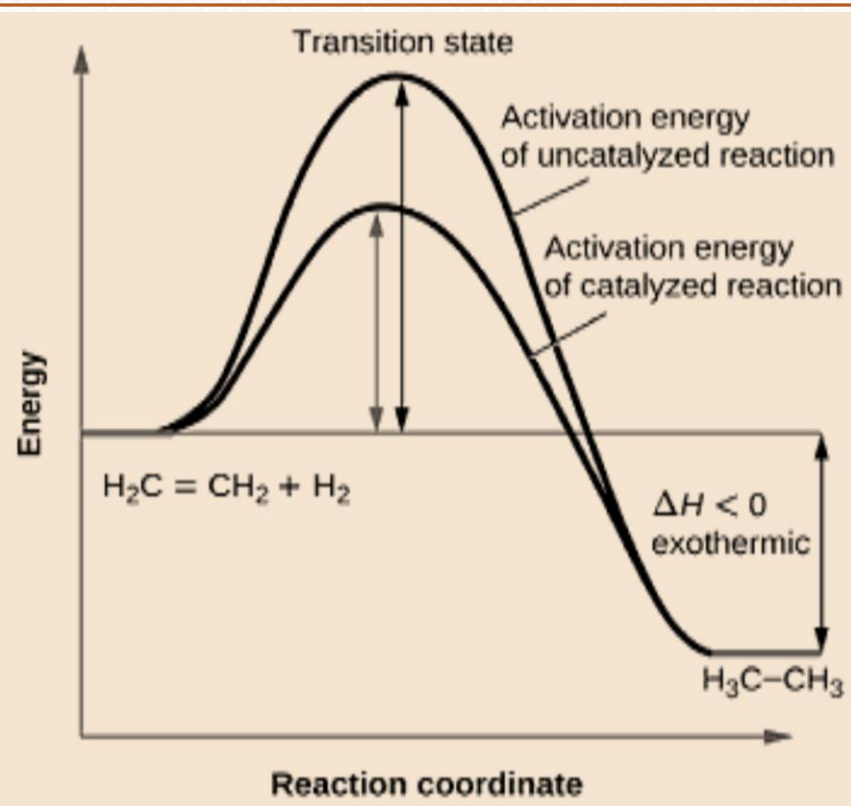
by

Dr. S. KALAIMANI

Asso. Prof. of Chem.,
Periyar Govt. Arts College,
Cuddalore-1

UNIT-II

Organometallic Chemistry-II

Catalysis by organometallic compounds

❖ **A thermodynamically favorable reaction may be slow at room temperature and therefore, it has no value for synthesis.**

❖ **By increasing temperature and pressure of the reaction, may significantly accelerate its rate, but providing the energy to do so is highly expensive. Moreover, high temperature may induce competing side reactions that will greatly reduce the product yields.**

❖ **A more attractive approach to increase the rate of a reaction is to use a catalyst. Catalysts are the substances which increase the rate of the reaction, but itself not consumed in the reaction. A catalyst typically increases the reaction rates by lowering the activation energy, E_a of the reaction by proving a different pathway with lower activation energy, E_a.**

Transition state

Activation energy of uncatalyzed reaction

Activation energy of catalyzed reaction

Energy

$H_2C = CH_2 + H_2$

$\Delta H < 0$ exothermic

H_3C-CH_3

Reaction coordinate

❖ **Catalysts** are **classified** as **homogeneous** if they are present **in the same phase** as the reactants and **heterogeneous** if they are present **in a different phase** from that of reactants.

❖ **Each type has its own advantages and disadvantages.**

❖ **Heterogeneous catalysts** are **easily separated** from the products (**a positive** feature), but **require high T & P** and so frequently lead to mixture of products, i.e., **low selectivity** (**a negative** feature)

❖ **Homogeneous catalysts** are **difficult to separate** from the products (**a negative** feature), but they operate at low T & P (**a positive** feature) and usually give good selectivity (**another positive** aspect).

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❖ In large-scale industrial processes, homogeneous catalysts are preferred for exothermic reactions because it is easier to dissipate heat from a solution than from the solid bed of a heterogeneous catalyst.

Catalytic efficiency and life time

❖ A highly active catalyst is the one, which results in a fast reaction even at low concentrations, and it should possess a high turn-over frequency 'f'. An efficient catalyst must be able to survive a large number of catalytic cycles, i.e., the catalyst must have a large a large turn-over number(N).

❖ The turn-over frequency(f) is often used to express the efficiency of a catalyst.

❖ For the conversion of A→B, catalyzed by 'Q' and with rate 'v'= d[B]/dt . The turn-over Number(N) = v/[Q] = rate of catalyzed rn. / [catalyst]. If N is high, the catalyst is good, because for small concentration of the catalyst, the rate is high.
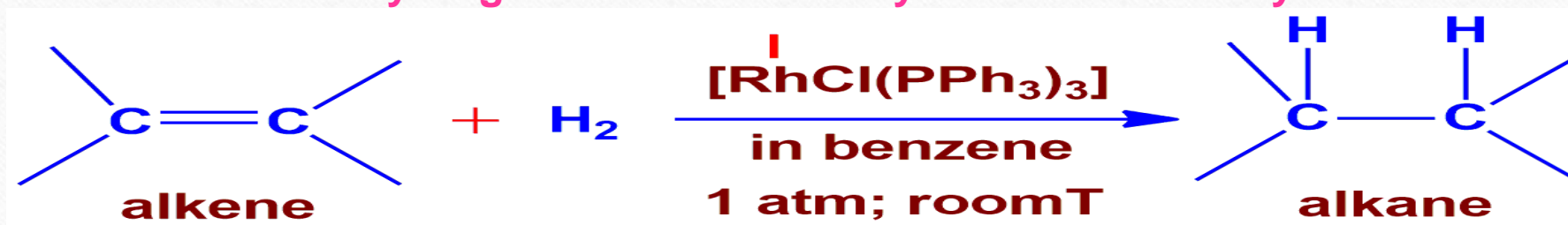
Turn-over frequency (f) = Turn-over number (N) / hour

❖ **So the TOF is the total number of moles of the reactant that has been transformed into the desired product by one mole of catalyst per hour.**

❖ **In catalysis by organometallic systems, the catalyst brings together substrates within the coordination sphere. This means that the catalyst must have a vacant coordination site, or at least be able to free-up a coordination site by ligand dissociation or isomerization. The substrates are activated in some way by the process of coordination and a reaction takes place.**

❖ **Some organometallic compounds of transition metals are of great utility as homogeneous catalysts in organic chemistry and also in some industrial processes. Examples include,**

① **Hydrogenation of olefins by Wilkinson's catalyst, [Rh^{I}Cl(PPh$_3$)$_3$]**

② **Hydroformylation of olefins using cobalt, [Co$_2$(CO)$_8$] and rhodium catalyst, [Rh^I(H)(CO) (PPh$_3$)$_3$] (Oxo process)**

③ **Oxidation of olefins to aldehydes and ketones by organo platinum catalyst (Wacker process)**

④ **Polymerization of olefins using organoaluminium-titanium catalysts(Zeigler-Natta catalysis)** **to give stereo regulated polymers.**

⑤ **Cyclo-oligomerization of acetylenes using nickel(II) catalysts(Reppe's catalysis)**

⑥ **Polymer bound catalysis.**

⑦ **Monsanto Acetic acid synthesis from methanol and CO using $[Rh^I(CO)_2 I_2]^-$ & HI.**

① Hydrogenation of olefins by Wilkinson's catalyst, $[Rh^I Cl(PPh_3)_3]$

❖ **Hydrogenation of olefins is a reaction, being used in the petrochemical industries and in the pharmaceutical industries where the preparation of drugs often involves the hydrogenation of specific double bonds. One very successful catalyst for this process is Wilkinson's catalyst $[Rh^I Cl(PPh_3)_3]$. This is an effective homogeneous catalyst in solutions of aromatic hydrocarbons such as benzene and toluene.**

❖ **The net reaction of hydrogenation of olefins by Wilkinson's catalyst is**

$$\text{alkene} \quad C{=}C \quad + \quad H_2 \quad \xrightarrow[\substack{\text{in benzene} \\ \text{1 atm; roomT}}]{[RhCl(PPh_3)_3]} \quad \underset{\text{alkane}}{\overset{H \quad H}{C{-}C}}$$

❖ **The bulky phosphine ligands in the catalyst play an important role in making the reaction selective, for example, they restrict the coordination of rhodium to unhindered positions (least substituted double bond) on alkenes.**

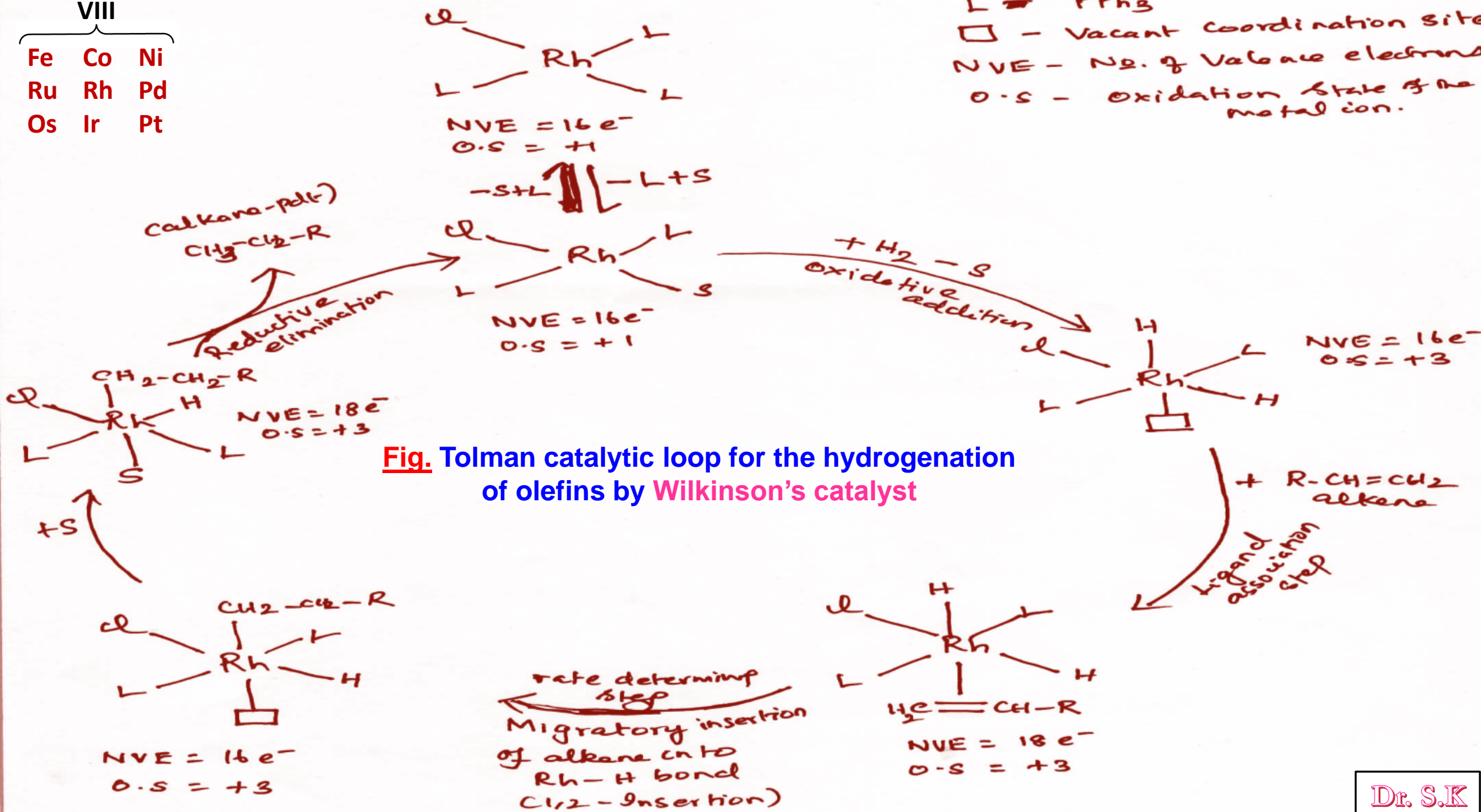## Mechanism of hydrogenation of olefins using Wilkinson's catalyst

Role of Rhodium metal in the catalytic process

❖ **The role of 'Rh' metal in the catalytic process is three fold. (i) Firstly, the metal provides a low energy path for cleaving the H-H bond in H_2. (ii) Secondly, the metal coordinates with the alkene, thereby weakening the bond between carbon atoms. (iii) Thirdly, the metal provides a mechanism for transferring the two H fragments to the alkene carbon atoms, yielding an alkane.**

Fig. Tolman catalytic loop for the hydrogenation of olefins by Wilkinson's catalyst

VIII

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

L = PPh₃
□ — Vacant Coordination site
NVE — No. of Valence electrons
O.S — Oxidation State of the metal ion.

NVE = 16 e⁻
O.S = +1

−S+L   −L+S

NVE = 16 e⁻
O.S = +1

+ H₂ − S
Oxidative addition

NVE = 16 e⁻
O.S = +3

C(alkane-Pd(-))
CH₃−CH₂−R

Reductive elimination

CH₂−CH₂−R
NVE = 18 e⁻
O.S = +3

+ R−CH=CH₂
alkene

ligand association step

+S

CH₂−CH₂−R
NVE = 16 e⁻
O.S = +3

rate determining step

Migratory insertion of alkene into Rh−H bond
(1,2 − Insertion)

H₂C=CH−R
NVE = 18 e⁻
O.S = +3

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Step-1 :

❖ It involves a **reversible dissociation** of **one PPh$_3$** ligand from the catalyst, leaving the species, **[Rh^{I}Cl(PPh$_3$)$_2$]**. This tri-coordinate complex is very reactive and **real catalytic active species.**

❖ **The evidence for dissociation of a PPh$_3$ ligand from [Rh^{I}Cl(PPh$_3$)$_3$] is indirect but convincing.**

  (i) For complexes with less sterically hindered phosphines (e.g. PEt$_3$), the catalytic effect disappears, because steric repulsion is necessary for dissociation.

  (ii) With the corresponding Iridium complex in which Ir-PPh$_3$ bond is stronger, no dissociation takes place and no catalysis is observed.

Step-2 :

❖ In this step, the tri coordinate molecule, possibly solvated, can **undergo oxidative addition** with a molecule of hydrogen to form dihydrido complex. Here, Rh(I) complex is oxidized to Rh(III) complex and the **Co.No.** is increased from **3 to 5.** This step is also reversible and in this step, the first role of the metal i.e. the cleavage of the **H-H** bond is accomplished.

Step-3 :

❖ This step involves the **coordination of the alkene** to the vacant site on the 5-coordinate dihydrido complex to form the 6-coordinate (**18e⁻**)species. In this step, the **metal weakens the alkene double** bond by coordination, and also **brings the alkene and H atoms into close** proximity, where they react. So in this step, the 2nd role of the catalyst namely the weakening of the bond between the two C atoms is accomplished.

Step-4 :

❖ This step is a **migratory insertion** reaction. It involves **the insertion of olefin into M-H bond** to give the metal-alkyl derivative, which is again a **16e⁻** species. This step is the **rate determining** step. This reaction is a **1,2-insertion** because the H-group that was one bond away from the metal atom ends up on an atom that is two bonds away from the metal.

Step-5 :

❖ This step is the **reductive elimination** step. Here, the metal is reduced from +3 oxidation state to +1 oxidation state and the **Co.No.** of the metal ion is decreased from **6 to 4.**

❖ **In this step, the product, alkane is formed. Here, the 3ʳᵈ role of the catalyst, namely, the transfer of hydrogen fragments to the alkene yielding the product alkane is achieved in steps 4 & 5.**

Advantages of this catalysis:

❖ **In molecules containing several double bonds, the least hindered double bonds are reduced by this catalyst. The most hindered positions cannot coordinate efficiently to 'Rh' (largely because of the bulky phosphines) and hence do not react rapidly. Consequently, Wilkinson's catalyst is useful for selective hydrogenation of C=C bonds that are not sterically hindered. That is why this catalyst is specific for the hydrogenation of terminal olefins.**
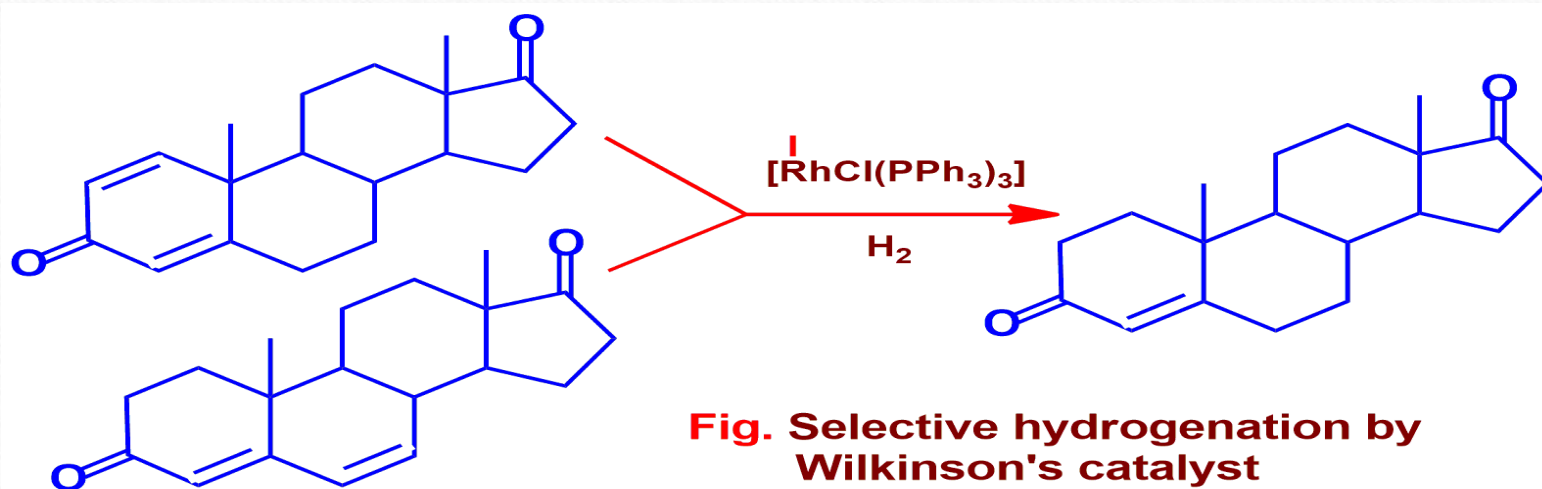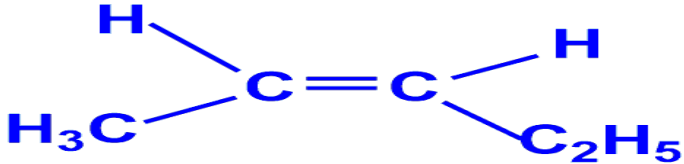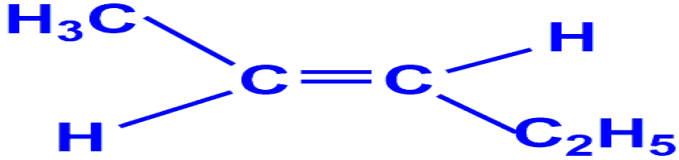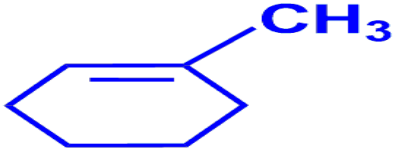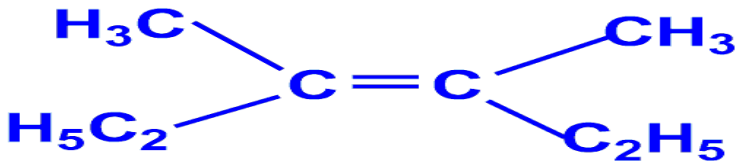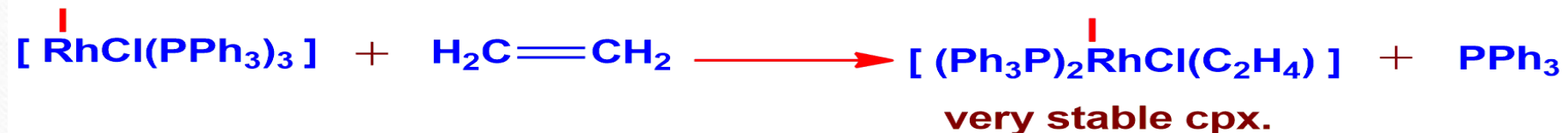
Fig. Selective hydrogenation by Wilkinson's catalyst

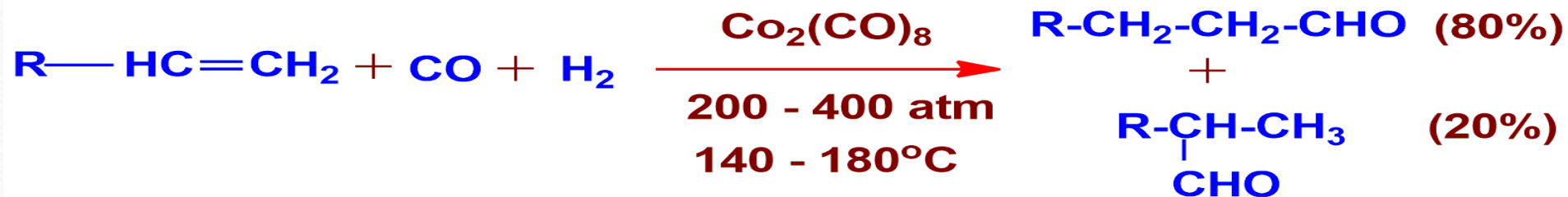**Fig.** Relative rates of hydrogenation using Wilkinson's catalyst

Note:

- ❖ **Hydrogenation of ethylene by Wilkinson's catalyst is very slow. Because, ethylene competes effectively with the solvent for the vacant coordination site created when PPh$_3$ dissociates from the catalyst to form a stable Rh-η^2-ethylene complex and thus serves as an inhibitor in hydrogenation.**

$$[\,\overset{|}{Rh}Cl(PPh_3)_3\,] \;+\; H_2C{=\!=}CH_2 \longrightarrow [\,(Ph_3P)_2\overset{|}{Rh}Cl(C_2H_4)\,] \;+\; PPh_3$$

$$\text{very stable cpx.}$$

② **Hydroformylation of olefins (OXO Process)**

- ❖ **The reaction of a terminal alkene with CO and H$_2$, catalyzed by cobalt or rhodium organometallic compounds to form an aldehyde is called 'hydroformylation' (or 'oxo process') reaction. The net reaction is**
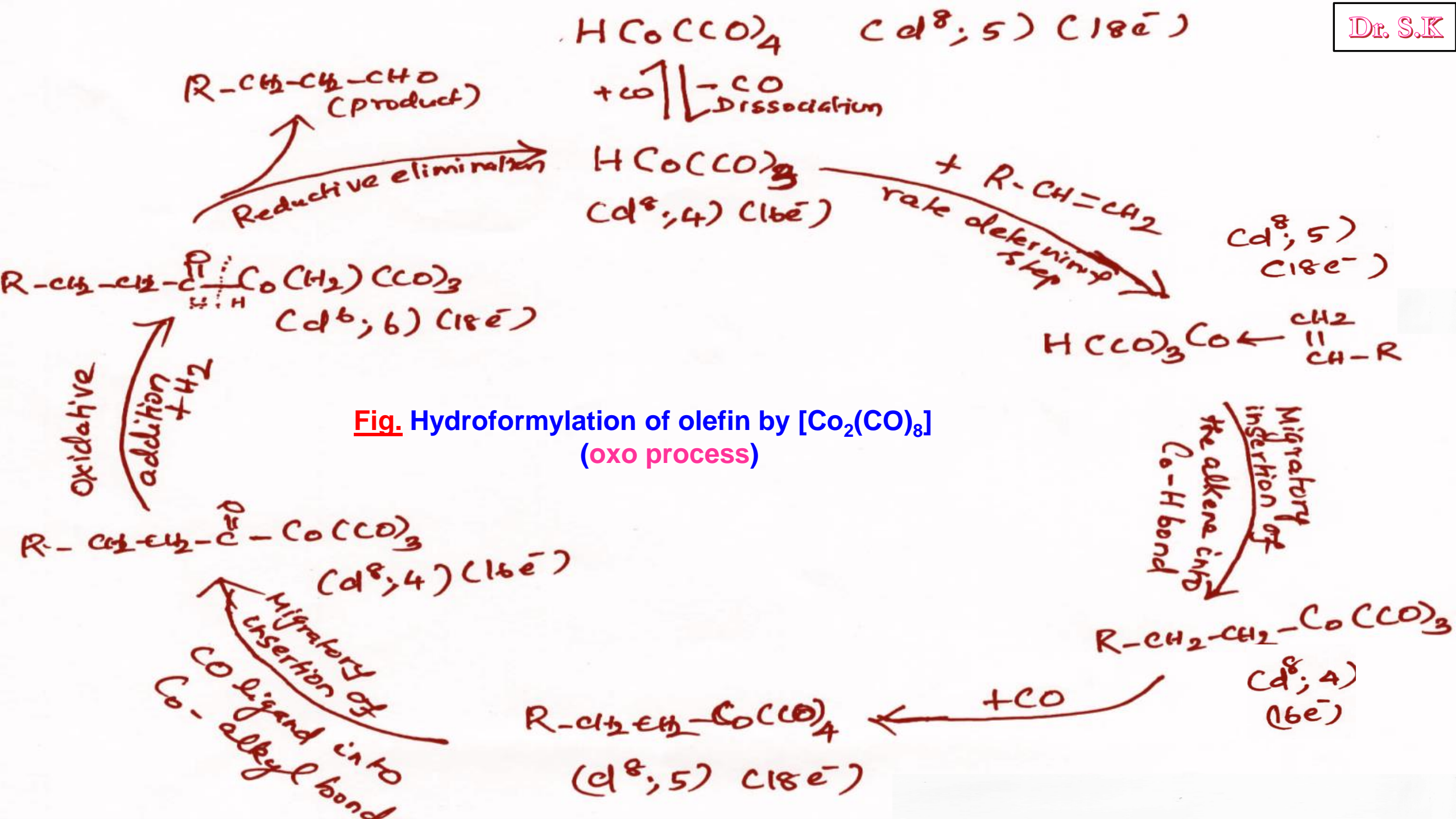
$$R{-\!-}HC{=\!=}CH_2 + CO + H_2 \xrightarrow[\substack{200-400 \text{ atm} \\ 140-180°C}]{Co_2(CO)_8} \begin{array}{l} R\text{-}CH_2\text{-}CH_2\text{-}CHO \;\; (80\%) \\ \qquad\qquad + \\ R\text{-}\underset{|}{CH}\text{-}CH_3 \qquad (20\%) \\ \quad\;\; CHO \end{array}$$

❖ **The name 'hydroformylation' arises from the fact that a hydrogen atom and a formyl group (CHO) are added across a double bond. The net result of the process is the extension of the carbon chain by one and introduction of oxygen into the molecule, that is why it is called 'oxo process'**

Mechanism of oxo process

❖ **The kinetic study of oxo process reveals that it is first order with respect to olefin and approximately first order in the amount of catalyst used. The reaction rate increases with increasing H_2 pressure and decreases with CO pressure. It is faster for terminal olefins than for internal olefins.**

❖ **Under the reaction conditions, The cobalt is presumed to be in the form of $[Co_2(CO)_8]$ & $[HCo(CO)_4]$ these compounds being related by an equilibrium reaction involving H_2 .**

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\,HCo(CO)_4 \quad (18e-)$$

tetracarbonylhydridocobalt(I)

Fig. **Hydroformylation of olefin by [Co₂(CO)₈]**
(oxo process)

❖ **The different steps involved in this catalytic process are:**

STEP-1: The first step involves the dissociation of one CO from the five coordinate 18e$^-$ species [HCo(CO)$_4$], to give the four coordinate [HCo(CO)$_3$], 16e$^-$ species. This is coordinatively unsaturated and it is the actual reactive catalytic species in this mechanism. The dissociation CO in this step is inhibited by high CO pressure.

STEP-2: The step involves the addition of olefin to the coordinatively unsaturated [HCo(CO)$_3$] to form a coordinatively saturated 18e$^-$ alkene π–complex. This step is the rate determining step.

STEP-3: The step involves the migratory insertion of alkene into the Co-H bond (1,2-insertion) via the four center transition state to give an alkyl-Co intermediate which is again a 16e$^-$ species.

STEP-4: The step involves the addition of CO to the coordinatively unsaturated alkyl-Co intermediate to form alkyl-Co(CO)$_4$ species(18e$^-$).

STEP-5: This step is another insertion reaction(1,1-insertion), namely carbonyl insertion into Co-alkyl bond to give an Co-acyl complex which is again a 16e$^-$ species. (R-CH$_2$-CH$_2$-CO-Co(CO)$_3$)

STEP-6: In this step, the acyl complex undergoes an oxidative addition reaction with a molecule of H$_2$ to form acyl dihydrido six coordinate complex which is a 18e$^-$ species.

STEP-7: This step involves the reductive elimination of dihydrido acyl cobalt complex to give the product, aldehyde and return the cycle to the catalytically active species [HCo(CO)$_3$].

Importance of oxo process:

(i) The oxo process may be carried out so that the aldehyde products are reduced to give alcohol such as 1-butanol or higher alcohols used for making detergents or other plasticizers.

(ii) The product, aldehyde can be converted to acids (by oxidation) or esters (by allowing the alcohols to react with acids formed by the reduction and oxidation of aldehydes respectively).

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Disadvatages of this catalyst:

(i) This cobalt catalyst works well at high T & P. This requires the use of a vessel which can withstand this high T & P. This leads to a high cost for the industrial process.

(ii) This catalyst also catalyses hydrogenation of olefins under these conditions. Hence, a part of the olefin is lost as alkane.

(iii) Volatility of $[HCo(CO)_4]$ leads to recovery problem.

(iv) Addition of $[HCo(CO)_4]$ to unsymmetrical olefins leads to the formation of mixture of linear and branched chain aldehydes. In general, linear chain aldehydes are more desirable, because linear detergents are more bio-degradable than the branched ones

Modification over the catalyst:

Among the various modified catalysts, the most important is the rhodium catalyst of composition, $[Rh^I(H)(CO)(PPh_3)_3]$

Advantages of Rhodium catalyst : $[Rh^I(H)(CO)(PPh_3)_3]$

(i) This complex is catalytically active even at 25°C and one atmospheric pressure.

(ii) Due to steric reasons, it produces only linear aldehydes.

Mechanism of hydroformylation of olefins by Rhodium catalyst

$$R-HC=CH_2 + CO + H_2 \xrightarrow{[Rh^I(H)(CO)(PPh_3)_3]} R-CH_2-CH_2-CHO$$

Linear aldehyde
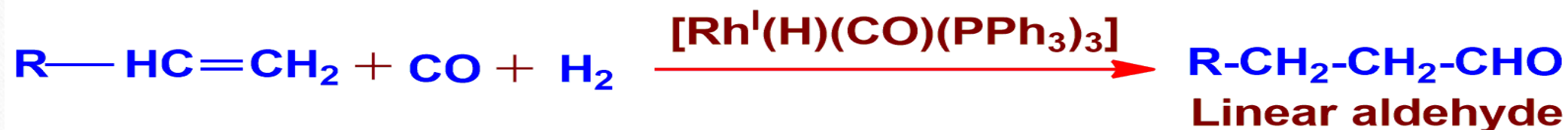
STEP-1: It involves the reversible loss of one molecule of PPh_3 to give 4-coordinated 16e⁻ catalytic active species.

STEP-2: It involves olefin addition to give 5-coordinated Rh-π-complex 18e⁻ species.

STEP-3: It involves the insertion of alkene into the Rh-H bond (1,2-insertion) to give 4-coordinated, 16e⁻ alkyl derivative.

Fig. Hydroformylation of olefin by [Rh^I(H)(CO)(PPh$_3$)$_3$]

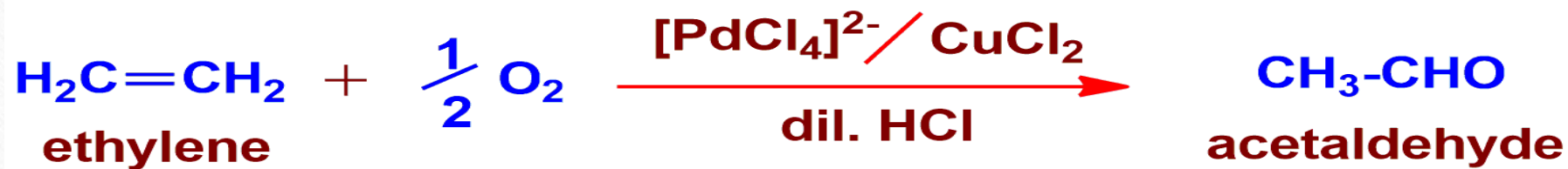**STEP-4:** It involves the carbonyl addition to give 5-coordinated, 18e⁻ species.

STEP-5: It involves the carbonyl insertion into the Rh-alkyl bond to give a 4-coordinated, 16e⁻, acyl complex.

STEP-6: It is the rate determining step which involves the oxidative addition of H_2 to yield 6-coordinated, 18e⁻ species, the dihydridoacyl complex.

STEP-7: It is the reductive elimination step which involves one hydrogen transfer to the carbon atom of the acyl group followed by the loss of aldehyde and regeneration of the 4-coordinated catalytic active species which is used to restart the whole catalytic cycle again.

## ③ Oxidation of olefins (Wacker's Process) or (Smidt reaction)

❖ The palladium chloride-catalyzed production of acetaldehyde from ethylene was first carried out commercially by Smidt at Wacker Chemie in Germany. In this process, copper(II) chloride is used as Co-catalyst in the presence of dil.HCl.

$$H_2C{=}CH_2 \ + \ \frac{1}{2} \ O_2 \xrightarrow[\text{dil. HCl}]{[PdCl_4]^{2-}\big/\,CuCl_2} CH_3\text{-}CHO$$

ethylene   acetaldehyde

Basically, three reactions are involved in the overall process.

(i) <u>Product formation reaction</u>.

❖ **When ethylene is passed into a slightly acidic solution of Pd(II) chloride, the product, acetaldehyde and palladium metal are formed.**

$$C_2H_4 + [PdCl_4]^{2-} + H_2O \longrightarrow CH_3CHO \ + \ Pd(0) \ + \ 2HCl \ + \ 2Cl^-$$
(catalyst)
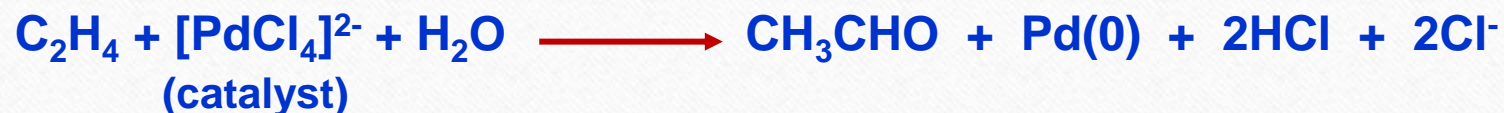
(ii) <u>Catalyst regeneration reaction</u>.

❖ **The palladium metal formed cannot be reused directly as the catalyst. It has to be reoxidized to Pd(II). It can be done by using Cu(II) salt as co-catalyst. Cu(II) is reduced to Cu(I) salt.**

$$Pd(0) + 2CuCl_2 + 2Cl^- \longrightarrow [PdCl_4]^{2-} + 2CuCl$$

(Cupric chloride)   (catalyst)   (cuprous chloride)

(ii) <u>Co-Catalyst regeneration reaction</u>.

❖ **If the solution is acidic, the Cu(I) salt produced can be re-oxidized to Cu(II) salt by blowing molecular oxygen. This is the reason for operating this process at low pH.**

$$2CuCl + 2HCl + \tfrac{1}{2} O_2 \longrightarrow 2CuCl_2 + H_2O$$

(Co-catalyst)

<u>Mechanism of Wacker's process</u>

❖ **Kinetic studies of Wacker's process in aqueous solution suggest the following rate law:**

$$\text{rate} = \frac{d\,[CH_3CHO]}{dt} = \frac{k\,[C_2H_4]\,[PdCl_4]^{2-}}{[H^+]\,[Cl^-]^2}$$

❖ **Thus, there is a first order dependence on ethylene and the palladium halide, an inverse dependence on H^+, and an inverse square dependence on Cl^-**

❖ **When D_2O is used as a solvent, the rate is slowed. However, no Deuterium appears in the product, thereby indicating that all of the hydrogen atoms in the product must have originated from the olefin only. On the basis of the above informations, the following sequence of reactions is proposed.**

STEP-1: This step involves the formation of a metal-olefin π-complex. This π-complex is similar to Zeise's salt. This step is further supported by the observation that addition of Cl^- decreases the rate of oxidation.
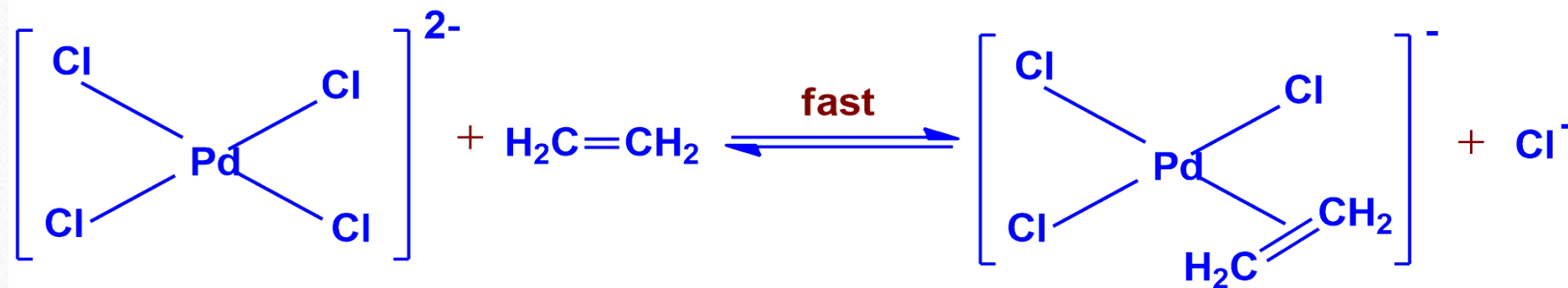
STEP-2: This step involves the substitution of second Cl⁻ by H₂O. Since Cl⁻ is eliminated in this step and in the previous step, this accounts for the **inverse square dependence** on Cl⁻ ion concentration in the rate law.
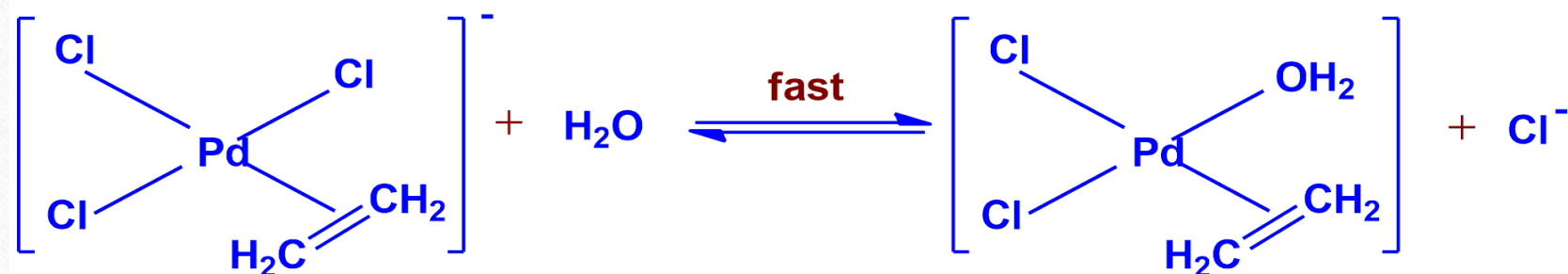

STEP-3: This step is deprotonation step. This step involves the loss of **H⁺** ion to form a hydroxo-metal complex. It is the step that accounts for the rate retardation in **D₂O** and for the inverse dependence of rate on **H⁺** ion concentration.


hydroxo-metal cpx
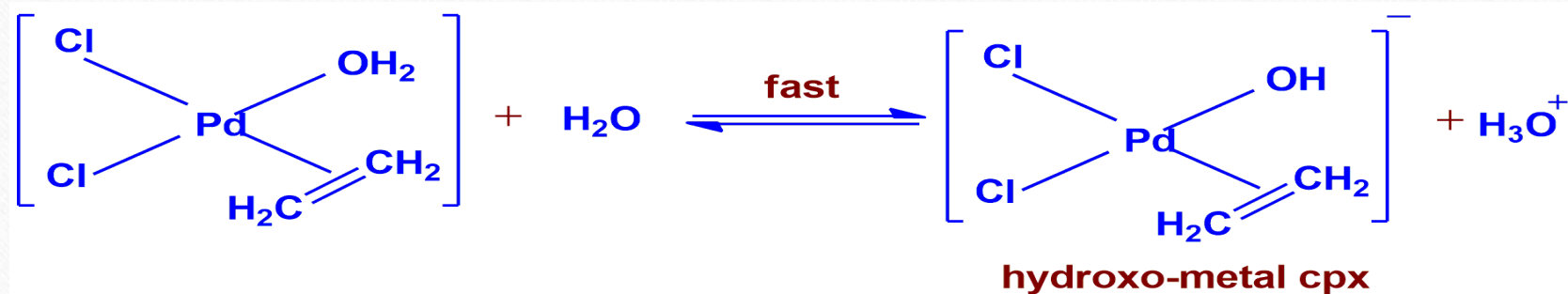
STEP-4: This step is the **rate determining step. This step involves the migration of the hydroxyl ligand to one carbon of the coordinated olefin and the other carbon adopts a σ–donor arrangement with the palladium to give 2-hydroxyethyl palladium complex.**

hydroxo-metal cpx

slow

+ solvent
(nucleophilic
attack of OH⁻
on C_2H_4)

2-hydroxyethylpalladium cpx
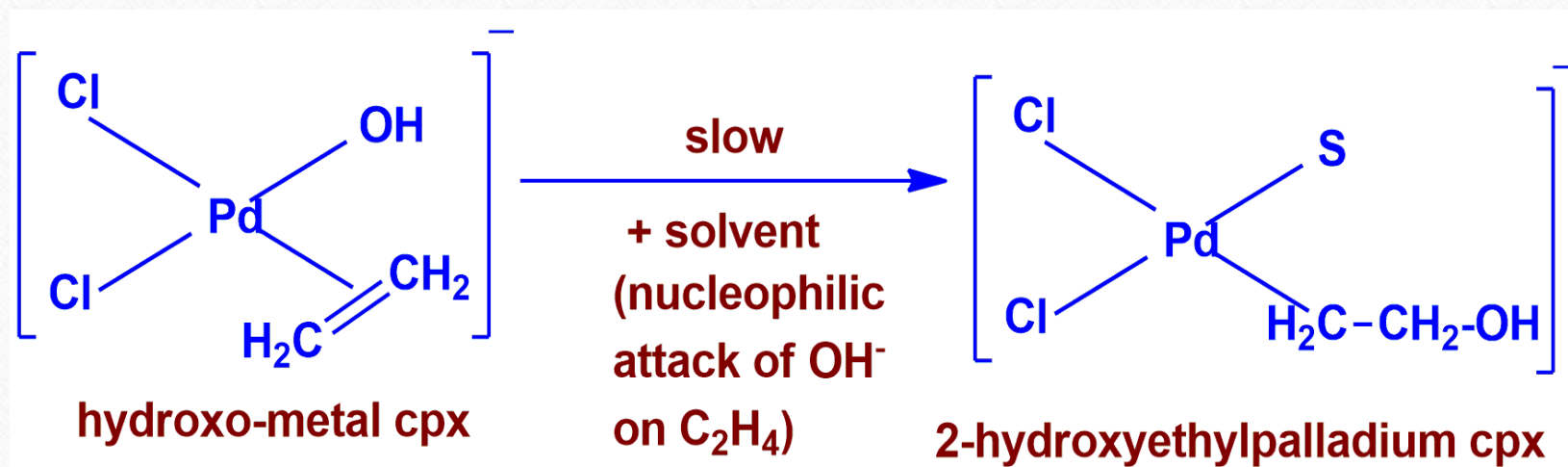
STEP-5: **An important feature of palladium chemistry is the affinity of the metal for hydrogen. Therefore, this step involves β–elimination with simultaneous formation of the metal hydride to produce π-vinyl alcohol complex, which then reinserts into the Pd-H bond in the opposite sense(1,2-insertion) to form 1-hydroxyethyl palladium complex.**
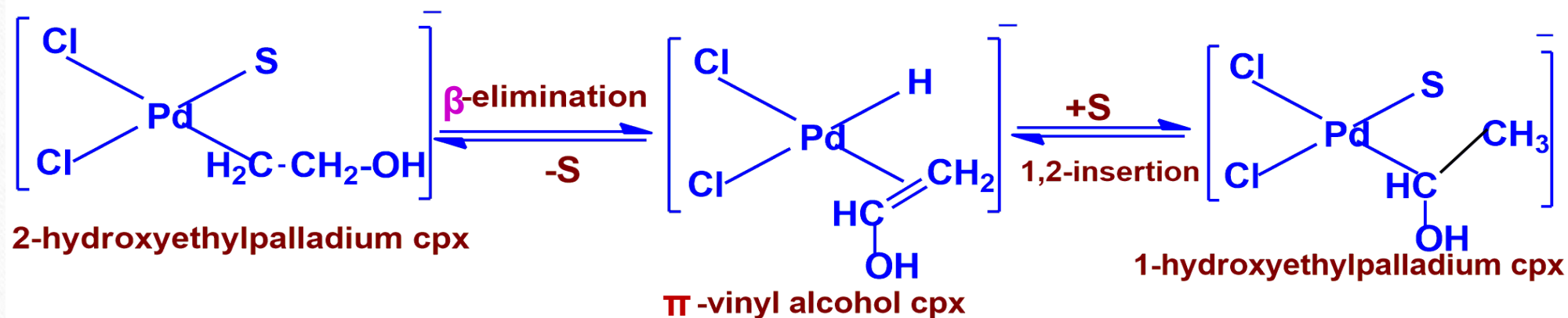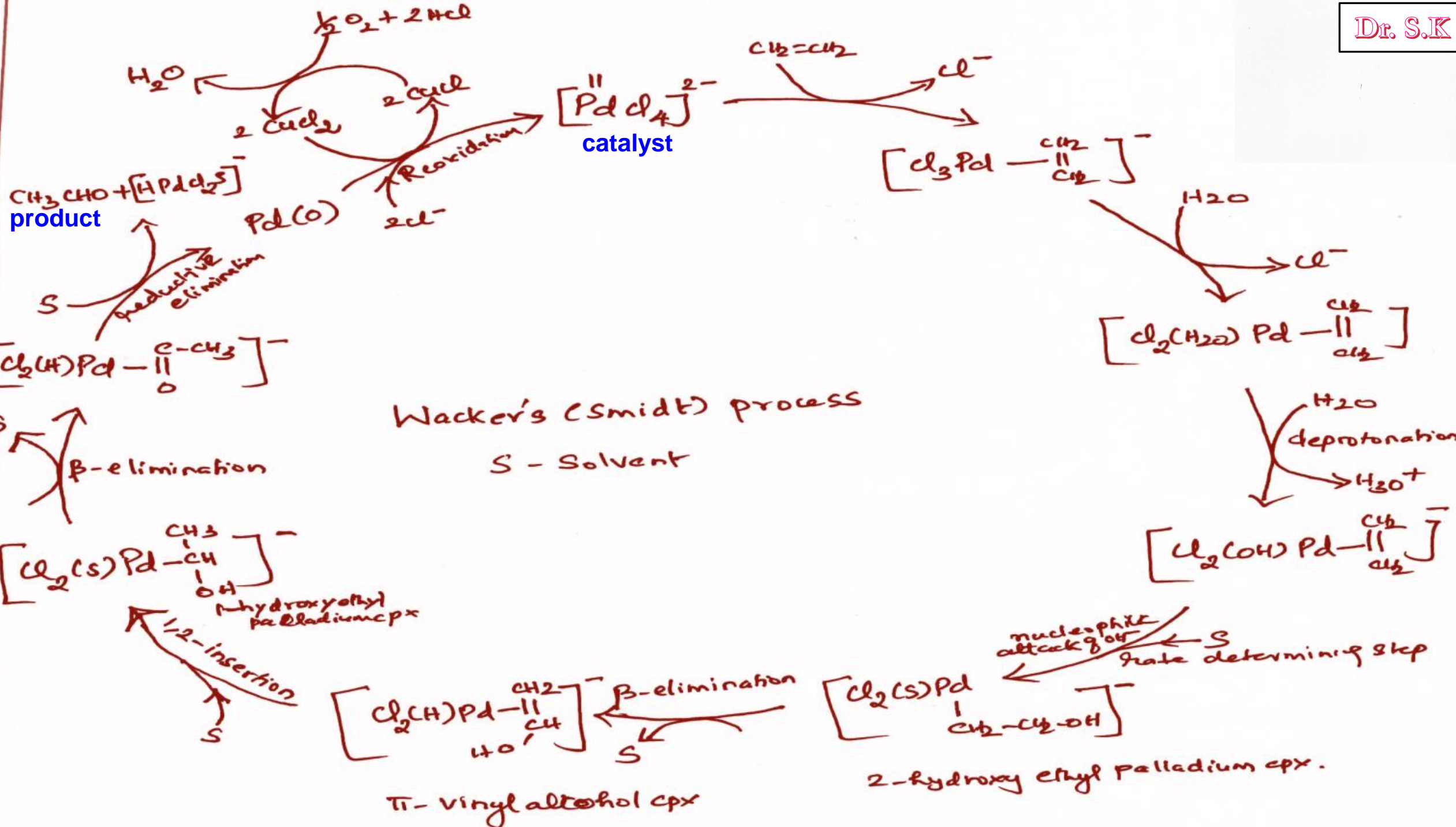
STEP-6: This step involves another **β–elimination** in which acetaldehyde is produced. Then, it is followed by a reductive elimination reaction of [HPdCl$_2$S]$^-$ to give Pd(0), HCl, Cl$^-$ and S.
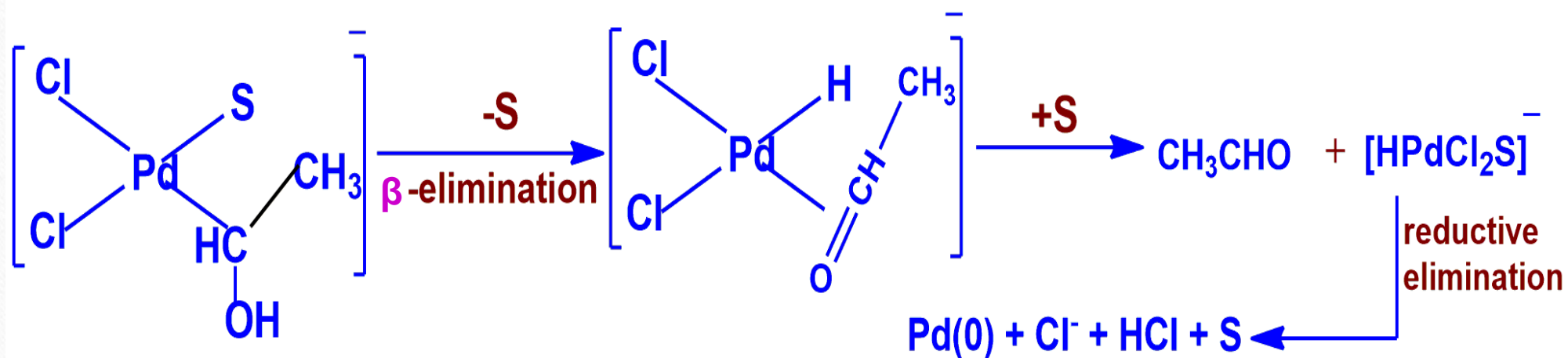
Role of Palladium in catalysing the oxidation of ethylene to acetaldehyde

1. Pd coordinates with ethylene, thereby weakening the $C=C$ bond

2. Pd also coordinates with OH^- ion (initially in the form of H_2O which is then deprotonated) thereby ensuring that the alkene and OH^- ion are held close together and thus facilitating the reaction between them.

3. The coordination of alkene to 'Pd' removes more e^- density from the π–bonding orbital of alkene, thereby rendering the alkene more susceptible to nucleophilic attack by OH^- than in the uncoordinated state.

Wacker's (Smidt) process
S – Solvent

$\frac{1}{2}O_2 + 2HCl$

H_2O

$2\ CuCl_2$

Reoxidation

$2\ CuCl$

$Pd(O)$

$2Cl^-$

$CH_3CHO + [HPdCl_2]^-$
product

reductive elimination

S

$\left[Cl_2(H)Pd - \overset{C-CH_3}{\underset{O}{\|}}\right]^-$

S

β-elimination

$\left[Cl_2(S)Pd - \overset{CH_3}{\underset{OH}{C}H}\right]^-$
r–hydroxyethyl palladium cpx

1,2-insertion

S

$\left[Cl_2(H)Pd - \overset{CH2}{\underset{HO}{\underset{CH}{\|}}}\right]^-$
π–vinyl alcohol cpx

β-elimination

S

$\left[Cl_2(S)Pd - \underset{CH_2-CH_2-OH}{|}\right]^-$
2–hydroxy ethyl palladium cpx.

nucleophilic attack of OH
$\leftarrow S$
rate determining step

$\left[Cl_2(OH)Pd - \overset{CH_2}{\underset{CH_2}{\|}}\right]^-$

H2O
deprotonation
H_3O^+

$\left[Cl_2(H_2O)Pd - \overset{CH_2}{\underset{CH_2}{\|}}\right]$

Cl^-

H_2O

$\left[Cl_3Pd - \overset{CH_2}{\underset{CH_2}{\|}}\right]^-$

$CH_2=CH_2$

Cl^-

$\left[Pd\ Cl_4\right]^{2-}$
catalyst

Polymerization of olefins (Ziegler-Natta Catalysis)

$$n \ HC \overset{\displaystyle CH_3}{=\!=} CH_2 \xrightarrow[\text{60°C; 1 atm P}]{\text{Ziegler-Natta catayst}} \left[HC \overset{\displaystyle CH_3}{-\!-} CH_2 \right]_n$$

propylene

stereo-regulated polypropylene

❖ **One of the great discoveries of organometallic chemistry was the Ziegler-Natta catalyzed polymerization of α–alkenes at one atmospheric pressure and at ambient temperature. Because, the conventional free radical polymerization of ethylene is carried out under severe conditions of about 200^oC and 1500 atmospheres of pressure.**

❖ **The polyethylene obtained by this free radical polymerization method has lower density, lower melting point, relatively lower molecular weight, relatively softer and consists of branched chains as compared to polyethylene produced by Ziegler-Natta catalysis.**

❖ **Polyethylene produced by Ziegler-Natta catalysis is superior to that produced by free radical polymerization.**

❖ **A typical Ziegler-Natta(ZN) catalyst system usually contains two parts: a transition metal (Group IVB metals, like Ti, Zr, Hf) compound and an organo aluminum compound (co-catalyst). The common examples of ZN catalyst systems include $TiCl_4 + Et_3Al$ and $TiCl_3 + AlEt_2Cl$.**

❖ **Ziegler and Natta were jointly awarded Nobel Prize in Chemistry in 1963.**

❖ **Ziegler-Natta catalysis of alkene polymerization leads to stereo-regulated (isotactic or syndiotactic) polymers. This is, in direct to contrast to the high 'T' and high 'P' polymerization. Stereo regularity often introduces some desirable properties into the polymer. In this process, the α–alkenes polymerize in such a way to yield long, unbranched, linear chains with high and controllable molecular weights. Because of orderly arrangement of isotactic polymer, the polymeric chains can lie closer, thus it imparts greater mechanical strength to the polymer enabling it to be used in making string and rope as well as more rigid articles.**

Mechanism of Ziegler-Natta Catalysis

❖ **The full details of the mechanism of Ziegler-Natta catalysis are still uncertain, but the Cossee-Arlman mechanism has been largely accepted**

❖ **The catalyst ($TiCl_4$ + Et_3Al) first react to give polymeric $TiCl_3$.**

$$TiCl_4 + Al(C_2H_5)_3 \longrightarrow Al(C_2H_5)_2Cl + TiCl_3(C_2H_5)$$

$$TiCl_3(C_2H_5) \longrightarrow HCl + C_2H_4 + TiCl_2$$

$$TiCl_3(C_2H_5) + HCl \longrightarrow C_2H_4 + TiCl_4$$

$$TiCl_2 + TiCl_4 \longrightarrow 2TiCl_3$$

atactic

isotactic
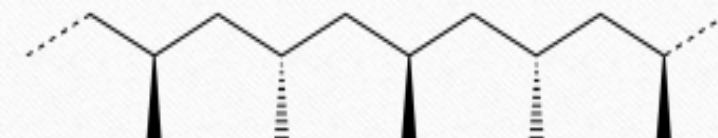
syndiotactic

❖ **To understand how the catalyst works, we must look at the crystal structure of TlCl$_3$. In solid TlCl$_3$, each Ti atom is surrounded octahedrally by six chlorine atoms and this each chlorine atom is further bound to a Ti atom. However, while the internal Ti ions octahedrally coordinated, the surface Ti ions are not, they have only 5 Cl atoms around them and so possess a vacant site.**

(i) Activation of Ziegler-Natta catalyst

On treating such a crystal of TiCl$_3$ with Et$_3$Al, this vacant site is alkylated, meanwhile, one surface chlorine atom from titanium is kicked out during this process. Thus, the catalyst system still posses a vacant site. Thus, the catalyst is activated by the coordination of AlEt$_3$ to Ti atom.

Catalytically active species
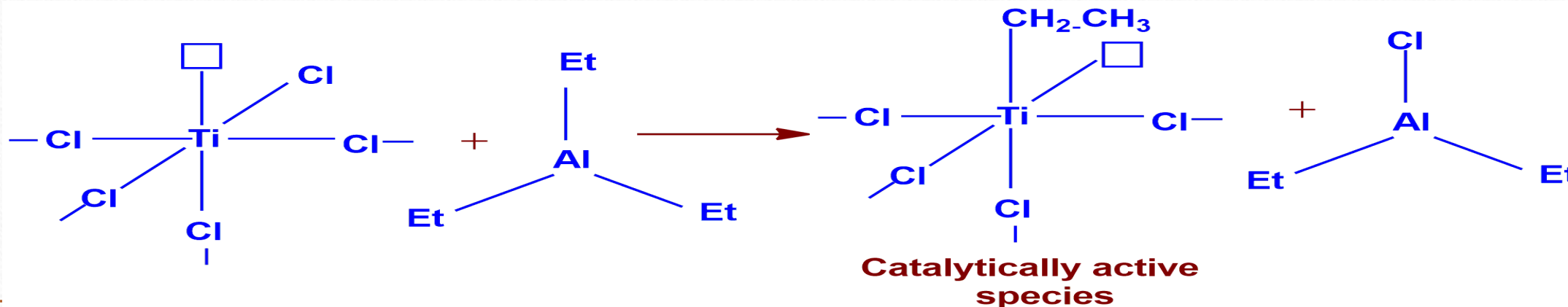
Note:

☐ - vacant coordination site
-Cl - a Cl bound to a second Ti
Cl - a Cl atom lie on the surface of the crystal (not bound to a second Ti)

(ii) Initiation step:

❖ This vacant site is potentially capable of coordinating an alkene. The polymerization reaction is initiated by forming alkene-metal π-complex. The electropositive nature of the Ti atom allows the electrons in the $Ti-C_2H_5$ bond to flow towards C_2H_5 group. This weakens the bond which is labile and it is cis to the newly arrived alkene π- bond.

❖ When the alkene and the alkyl groups are bound to adjacent sites on the metal atom, they react to give what is known as an insertion product (insertion of alkene into the Ti-alkyl bond) through a concerted four-centred rearrangement. This is step is assumed to be the rate determining step. When the insertion is complete, a new vacant coordination site is generated on the Ti atom, which is cis to the newly longer alkyl group.
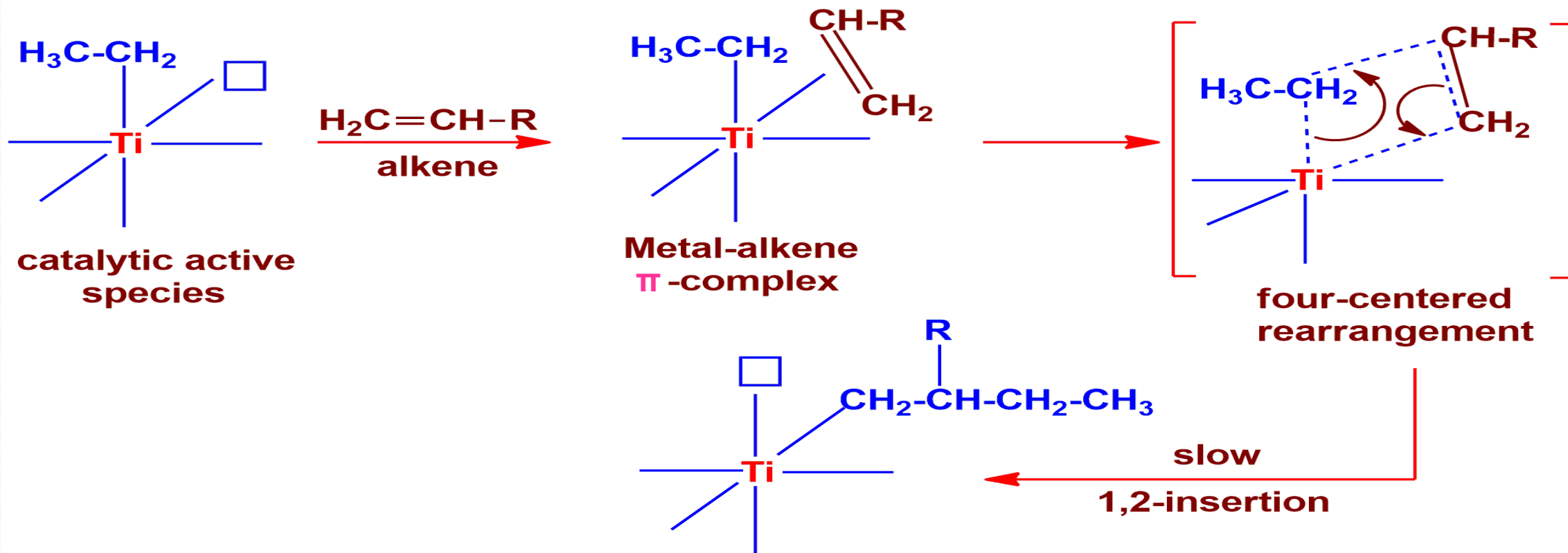
(iii) Propagation step:

❖ **The presence of vacant site enables the chain to continue growing** **by switching back and forth between the two sites. When other alkene molecules come in, this process starts over and over, giving linear poly alkene.**
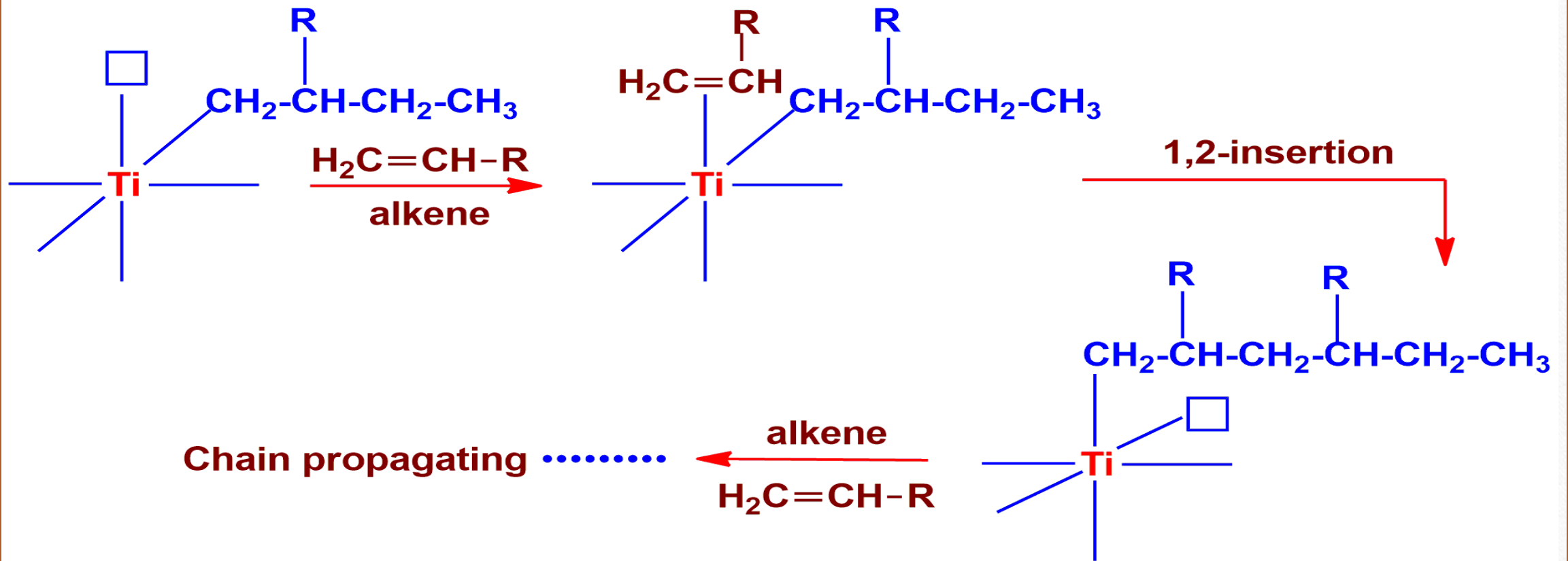
(iv) Termination step:

❖ **Termination is the final step of a chain-growth polymerization, forming "dead" polymers (desired products). Termination would occur by β–hydride elimination.**

β-hydride elimination

polymer
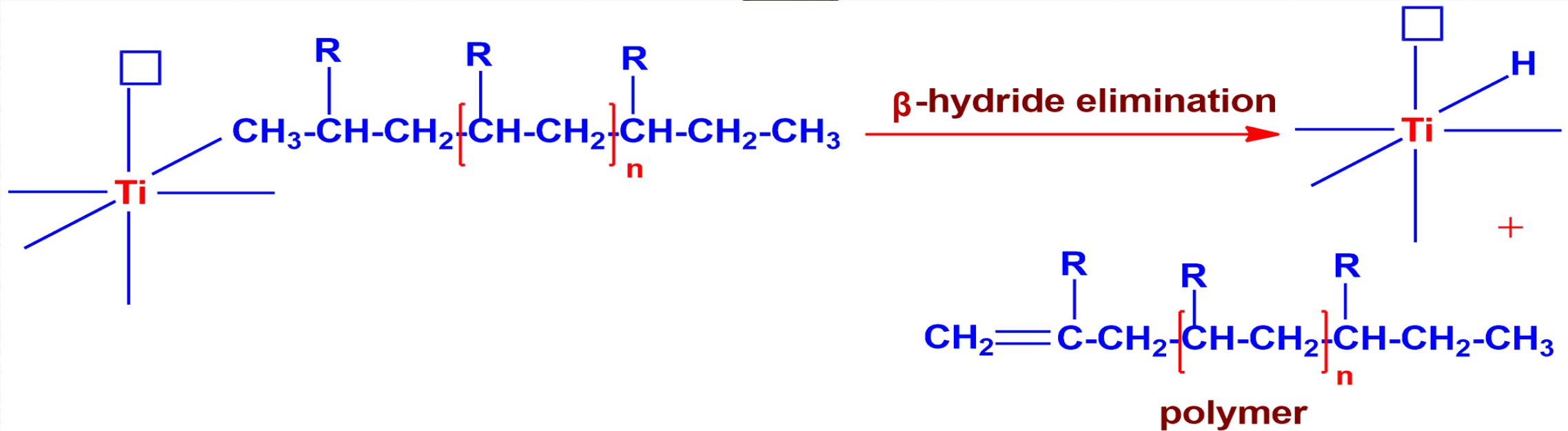
Note:

❖ **When the double bond of the propylene attaches to Ti, the methyl group must always point away from the surface of the crystal** because the reaction occurs on the surface. When the molecule migrates and get inserted into the Ti-C bond, it always has the same orientation. This is called **cis-insertion of the alkene** and explains why the polymers produced **are stereo-regulated.**

Applications of Ziegler-Natta polymerization

Production of:

► High density polyethylene (HDPE)

► Linear low density polyethylene (LDPE)

► Ultra-high molecular weight polyethylene (UHMWPE)

► Thermoplastic polyolefins (TPO's)

► Polybutylene (PB)

► Shiny lustrous polyacetylene film which have semiconducting properties

► Crystalline polypropylene

► Carbon nanotubes nanocomposites

Limitations of Ziegler-Natta polymerization

❖ ZN catalysts are effective for polymerization of α-Olefins (ethylene, propylene) and some dienes (butadiene, isoprene). However, they don't work for some other monomers, such as 1,2 disubstituted double bonds. Vinyl chloride cannot be polymerized by ZN catalyst because, free radical vinyl polymerization is initiated during the reaction. Another situation that ZN catalysts don't work is when the substrate is acrylate.

Cyclo-Oligomerization of Acetylenes-Reppe's catalysis

❖ When many monomers units combine to give a macromolecule, the process is called polymerization. But, when two to about nine or ten monomer units combine to give a single molecule, then the process is referred to as oligomerization. If oligomerization process is accompanied by cyclisation (ring closure) then it is called cyclo- oligomerization.

❖ **The catalysis for alkyne cyclo- oligomerization involve organometallic compounds of VIII-group transition elements. The classical examples, discovered by Reppe, involve Ni(II) salts with ligands such as acetylacetone and salicylaldehyde which are bidentate ligands. Such ligands can be partially displaced by the acetylene, the number of vacatable sites determining the type of product formed as shown below. (Where L-L is a bidentate ligand and S is solvent)**
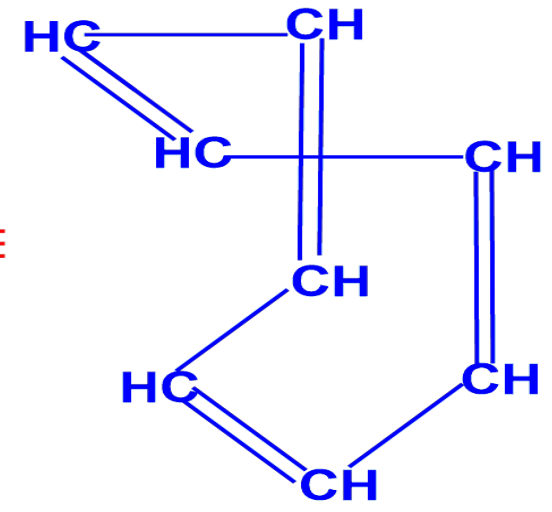
$$L-L = H_3C-\overset{\displaystyle O^-}{C}=CH-\overset{\displaystyle \underset{\|}{O}}{C}-CH_3 \quad \text{(or)}$$
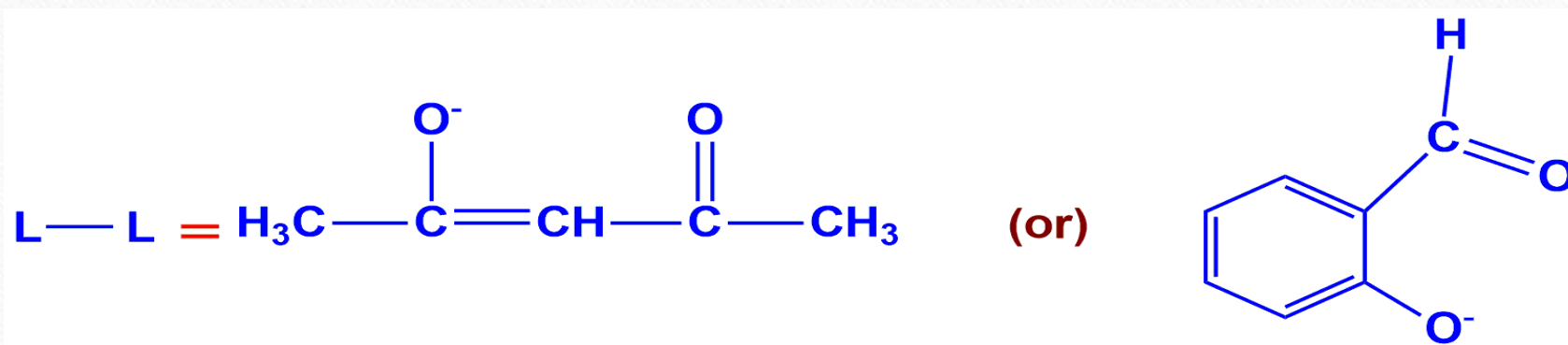
(i) Catalyst with four vacatable sites gives mainly cyclooctatetraene (cyclo-tetramerization product)
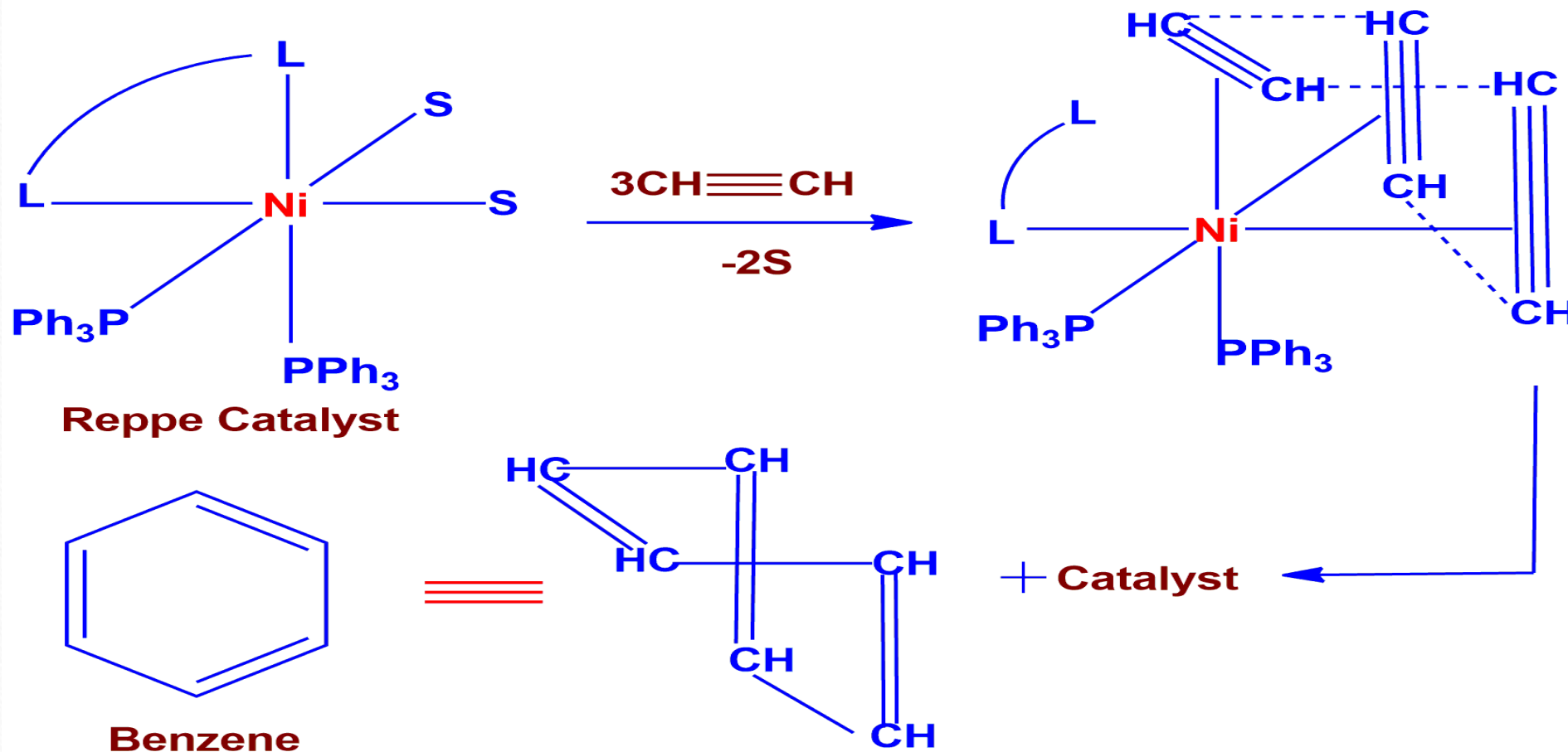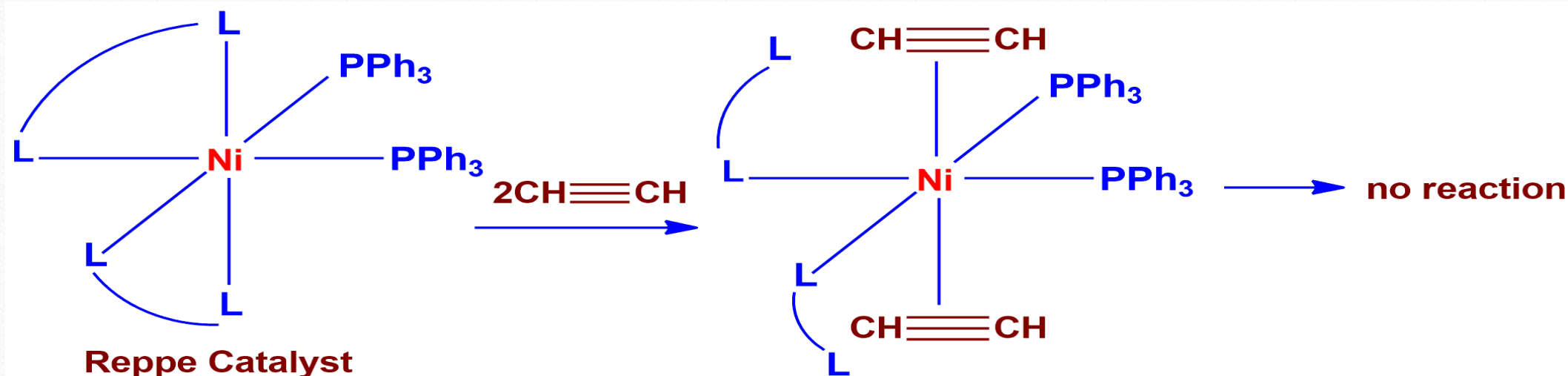
Reppe Catalyst

4CH≡CH
-2S
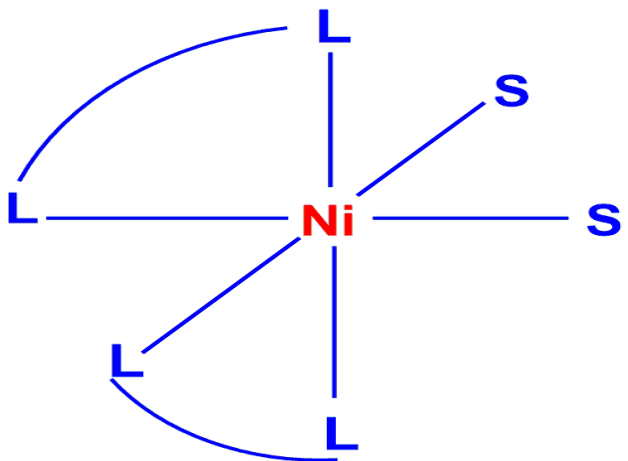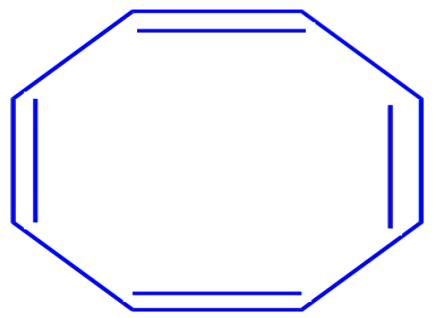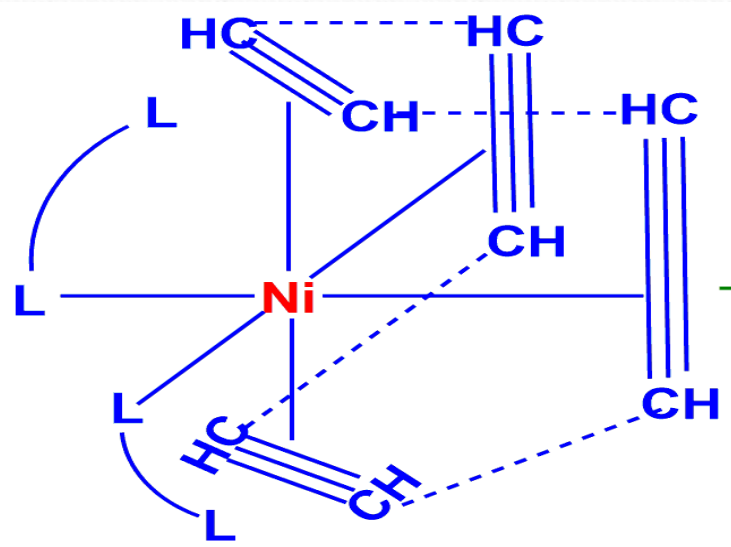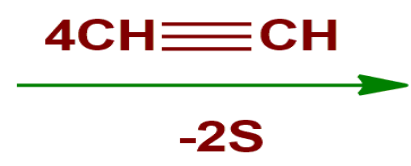
Cyclooctatetraene

+ Catalyst

(ii) If a **less labile ligand** such as **PPh₃** is incorporated, the coordination sites required for tetramerization are not available and **cyclo-termerization** predominates to give **benzene.** Substituted benzene derivatives can be obtained from the appropriately substituted acetylenes.

(iii) If only the two trans positions are vacated, then there will be no reaction.

Reppe Catalyst

Polymer bound catalysis

❖ One of the problems of homogeneous catalysis has been the **separation of the catalyst from the products.** However, when 'the homogeneous catalyst' is bound to a polymer, it is possible to simply decant (filter) the products and free the catalyst for future use. Because, the resulting **'polymer supported catalyst' is a solid and hence it can be easily filtered off at end of the catalytic process.**

❖ **This process of converting a homogeneous catalyst into a heterogeneous one is called 'anchoring of catalyst'.**

❖ **When a homogeneous catalyst is heterogenized in such a way that it can react mechanically in the same manner as its homogeneous counter-part, the greater selectivity and activity of the homogeneous catalyst are thus preserved.**

❖ **Polymer supported Wilkinson's catalyst is prepared as follows. Phosphine groups are introduced on to the polymer support by the following series of reactions.**

Dr. S.K

Polystyrene + MeOCH$_2$Cl $\xrightarrow[\text{-MeOH}]{\text{SnCl}_4}$

Li$^+$PPh$_2^-$

-LiCl

$[\text{RhCl}(\text{PPh}_3)_3]$

2-4 Weeks | benzene, 20°C

CH$_2$-PPh$_2$ → RhCl(PPh$_3$)$_2$ + PPh$_3$

Polymer-supported Wilkinson's catalyst

The resulting polymer supported catalyst is a solid and hence can be easily filtered at the end of the catalytic process.
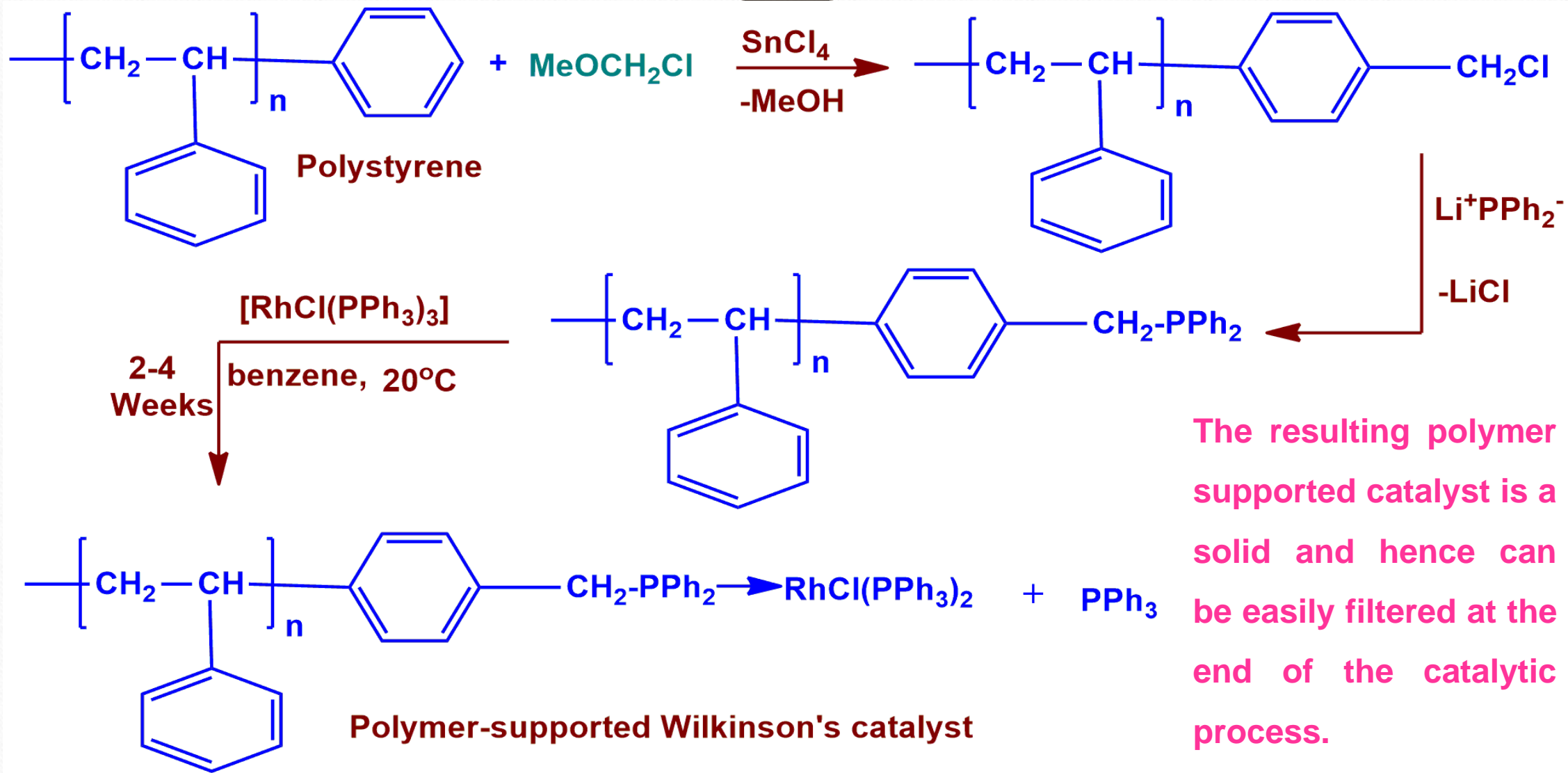
Monsanto Acetic acid process

❖ **One of the great successes of homogeneous catalysis is the synthesis of acetic acid from Methanol and CO by Monsanto.**
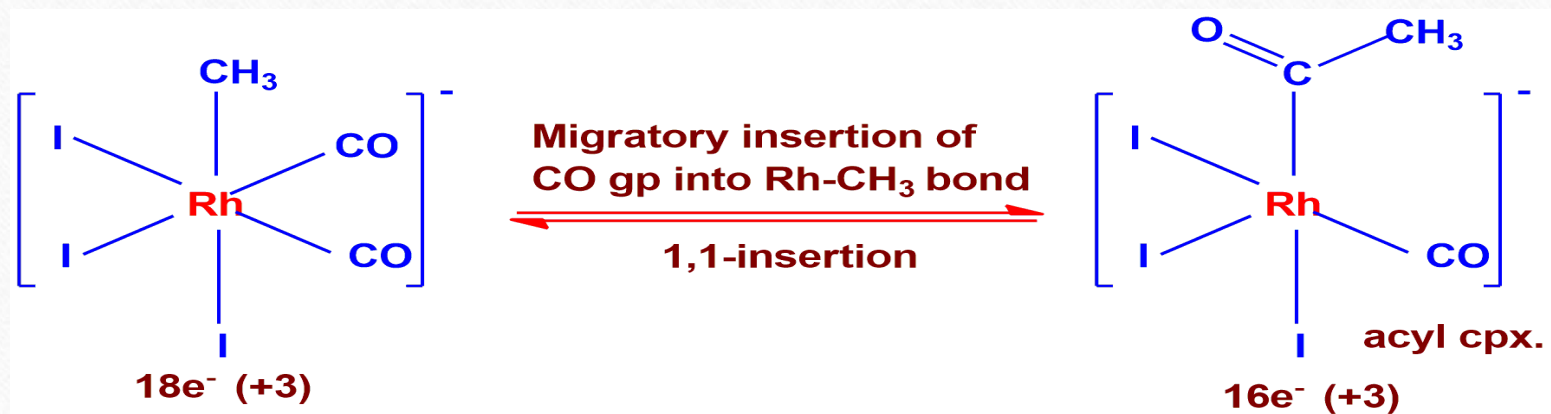
$$CH_3OH + CO \xrightarrow[HI]{[Rh(CO)I_2]^-} CH_3COOH$$

Methanol → Acetic acid

Mechanism:

STEP-1: It involves the oxidative addition of CH_3I to the active catalyst $[Rh^I(CO)_2I_2]^-$, which is rate determining step. The methyl iodide arises from the reaction of methanol and HI.

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$
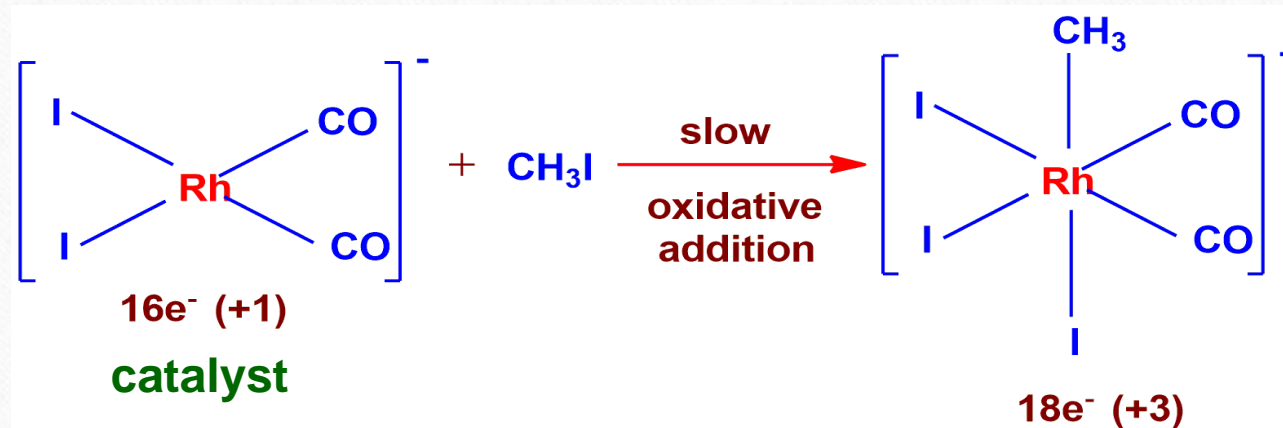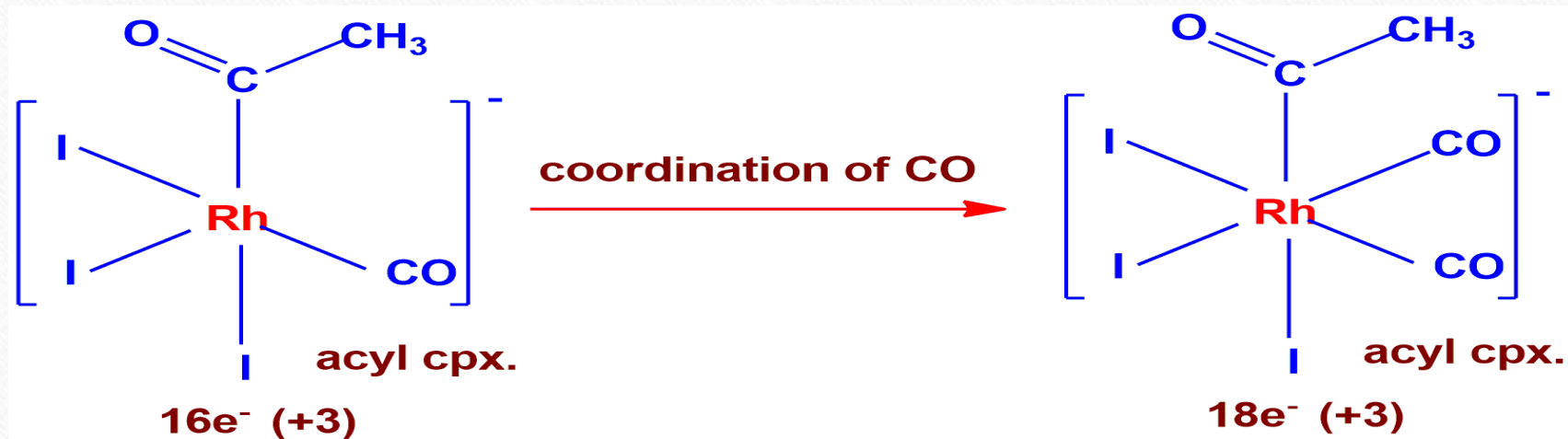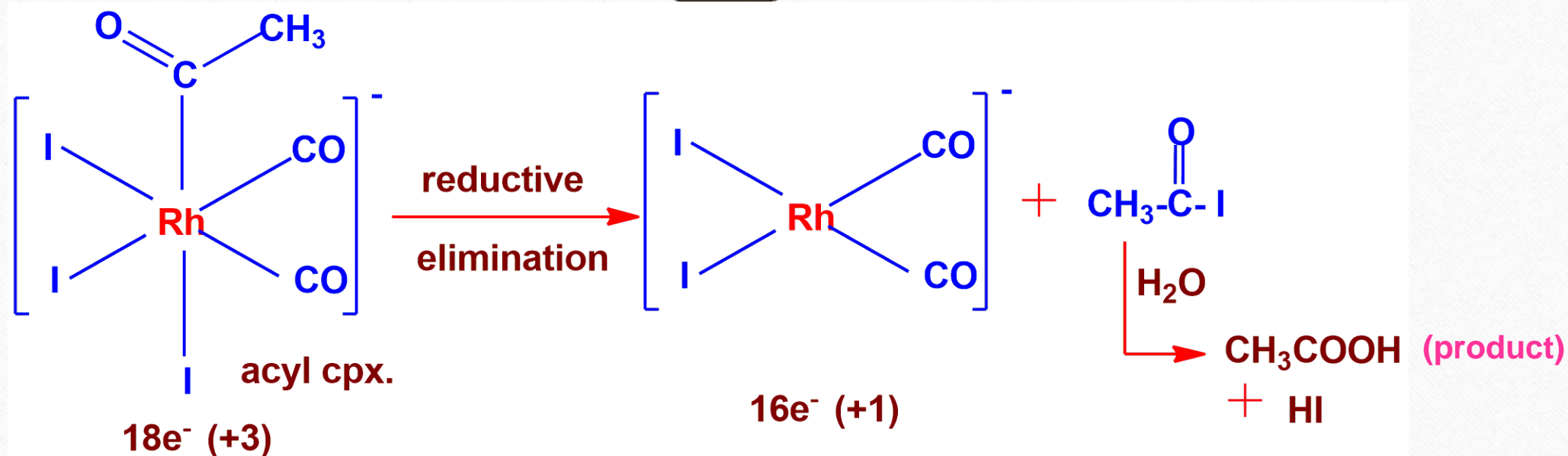
STEP-2: It involves carbonyl insertion to give 5-coordinate 16e⁻ species.

STEP-3: It involves coordination of **CO** to give again 18e⁻ species.

STEP-4: It involves reductive elimination to give the active catalytic species for reuse and acetyl iodide which on hydrolysis produces acetic acid and HI.

- ❖ **In the catalytic loop, CH_3OH (reactant) is present at the lower right side and it end with the product, CH_3COOH, at the lower left side.**

- ❖ **In addition to rhodium-based catalyst, Iridium-based catalysts have also been developed ($[Ir^I(CO)_2I_2]^-$) in a process known as Cativa process.**
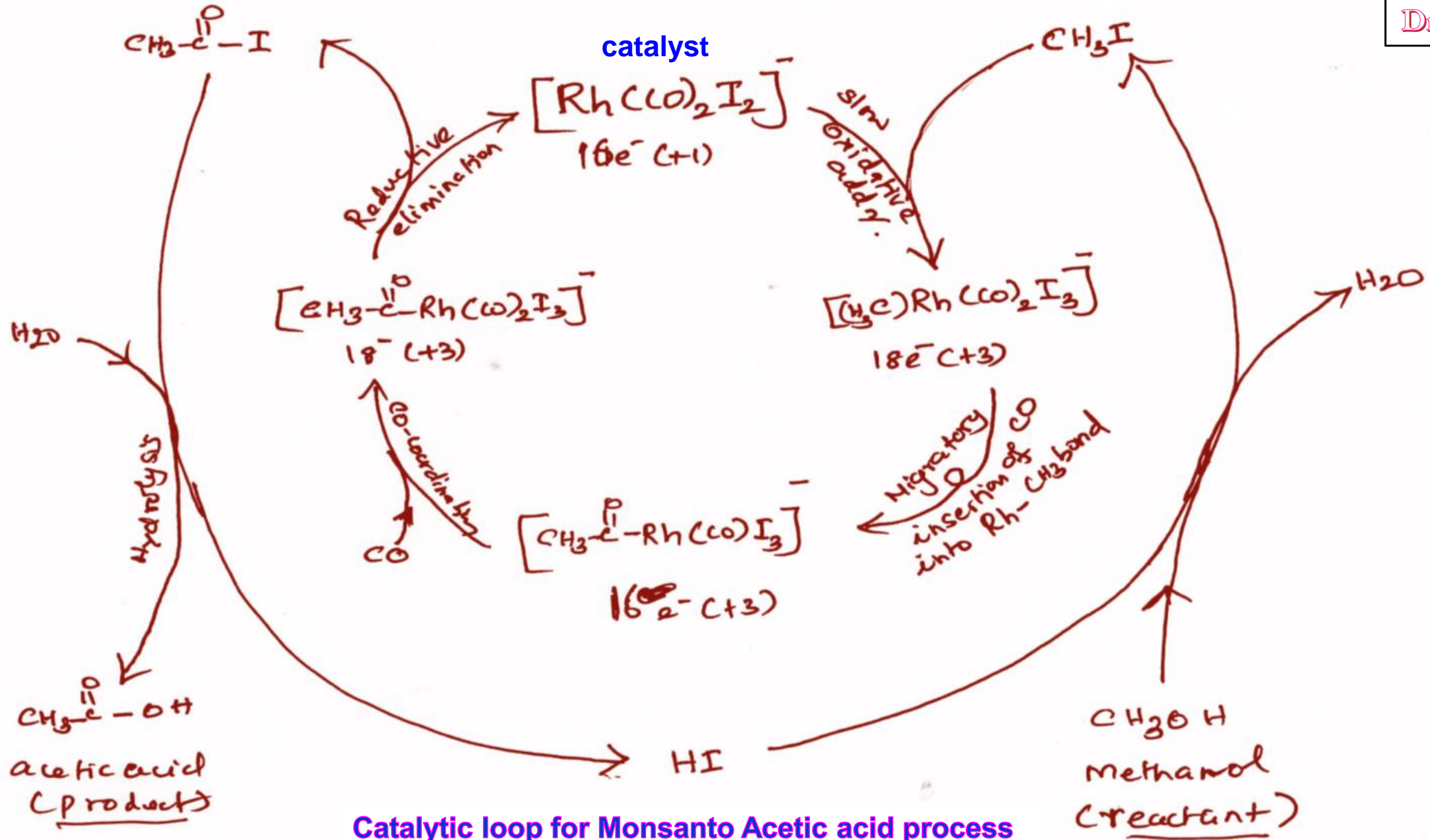
Catalytic loop for Monsanto Acetic acid process

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THANK YOU