Organometallic chemistry :-

It deals with molecules that contain metal carbon bond. It encompasses a wide variety of chemical compounds and their reactions, including compound containing both σ and π-bonds. b/w metal atom and carbon.

Organometallic Compounds :-

An Organometallic chemistry is generally defined as the one that posseses a metal-carbon bond. But it is not rigid condition. There are some compexes which do not contain any M-C bonds but are considered to the member of Organometallic compounds. For example Wilkinson catalyst, $[Rh(PPh_3)_3Cl]$ is used for Hydrogenation of alkene and alkyne. It is considered as Organometallic compound but it does not have any M-C bond.

- According to the defination given by the "American Chemical Society" (ACS) journal Organometallics —

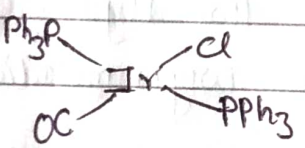
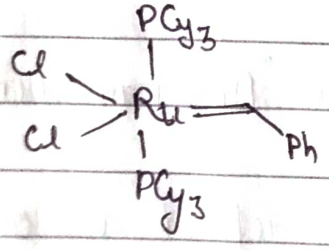
An Organometallic compounds will be defined as one in which There is an bonding interaction (ionic, or covalent, localised or delocalised) between one or more carbon atoms of an Organic groups or molecule and a main group, transition, Lantheride or actinide metal atom or (atoms).

- Boron and Silicon both are border-line metals; but Organoboron and Organosilicon compounds are considered as Organometallic compounds.

★ NaCN (Sodium cyanide) is not considered as Organometallic compounds even though it has a Metal carbon bond.

- $Ni(CO)_4$ is an Organometallic compounds though CO is not an Organic molecule / group.

Some Example of OMC :—

1. $Rh(PPh_3)Cl$ (Wilkinson's Catalyst)
2. $R-MgX$ (Grignard Reagent)
3. R_2CuLi (Gilmann Reagent/Organo copper Lithium)
4. $K[PtCl_3C_2H_4]$ (Zeise's salt)
5.  (Vaska's complex)
6.  (Grub's catalyst)

⇒ Importance of Organometallic chemistry :—

- Organometallic compounds act as catalyst and therefore various industrial process are based on homogeneous Organometallic compounds.
- Organometallic chemistry acts as a bridge between Organic and Inorganic chemistry.

Catalyst :-

A substance that brings reactants together and accelerates their interaction but does not permanently get changed during a reaction. classified in to two ways —

a) Homogeneous :-

They are soluble in reaction medium. (Catalyst and reactants are in the same phase.)

b) Heterogeneous :-

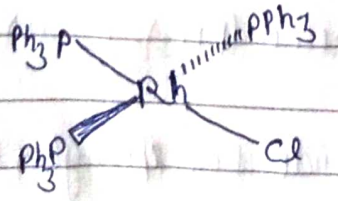
They are insoluble in reaction medium (catalyst and reactants are in different phases)

Wilkinson's Catalyst :- The chemical formula of wilkinson's catalyst is $[Rh(PPh_3)_3Cl]$ where Ph denotes a phenyl group.

IUPAC NAME — [chlorido tris(triphenyl phosphine) rhodium (I)]

- It is a co-ordination compound whose co-ordination centre is rhodium. and co-ordination number is '4'.
- It is extensively used as a catalyst in the hydrogenation of alkene.
- At ambient temp this comordination complexs exists as a reddish-brown solid.

- Wilkinson's catalyst is named after the english chemist ~~and Nobelaur~~ Sir "Geoffery Wilkinson" It's structure is illustrated below —



• according to single crystal X-ray (SCXRD) diffraction The compound adopts a slightly distorted square plannar structure.

• It analyzing the bonding, It is a complex of Rh(I), a d^8- transition metal ion.

• The Rhodium centre is bound to four ligands in this compounds.

• It has 16 e^- and as such the compound is Co-ordinative unsaturated.

Properties of wilkinson's catalyst :-

★ Physical properties :-

• Wilkinson's catalyst is Red-brown solid.

• It is insoluble in polar compounds such as water

• It is soluble in non-polar compounds such as benzene, dichloromethane, tetrahydrofuran etc.

• The molar mass of wilkinson catalyst is 925.22 $gmol^{-1}$.

• The melting point of the wilkinson catalyst is ranges from 518k to 523 K.

★ Chemical properties :-

• The wilkinson catalyst has a square plannar geometry

• The hybridisation of wilkinson catalyst is dsp^2.

Such complex is also called inner orbital complex.

• Wilkinson catalyst $[Rh(PPh_3)_3Cl]$ reacts with carbon monoxide (CO) and form $[RhCl(CO)(PPh_3)_2]$ as a product.

IUPAC → Cloride-bis(triphenyl phosphine) rhodium Carbonyl.

- This formed product compound can also be formed by the reaction with the aldehydes.

$$RhCl(PPh_3) + R-\overset{\overset{O}{\|}}{C}-H \longrightarrow RhCl(CO)(PPh_3)_2 + R-H + PPh_3$$

- Wilkinson catalyst can form a dimer when mixed in the benzene solution. This formed dimer $RhCl(PPh_3)_3$ is poorly soluble and red in colour.

Preperation :-

- It can be prepared by reacting $RhCl_3 \cdot 3H_2O$ with excess PPh_3 in EtOH.

$$RhCl_3(H_2O)_3 + \text{excess } PPh_3 \xrightarrow{EtOH} RhCl(PPh_3)_3 + Ph_3P=O + \text{solvent}$$

or

$$RhCl_3(H_2O)_3 + 4PPh_3 \xrightarrow{EtOH} RhCl(PPh_3)_3 + Ph_3P=O + 2HCl + 2H_2O$$

~~Mechanism~~ :-

Uses :- Wilkinson catalyst is used in the selective hydrogenation of alkenes and alkynes without affecting the functional groups like C=O, CN, NO_2, any, CO_2R etc.

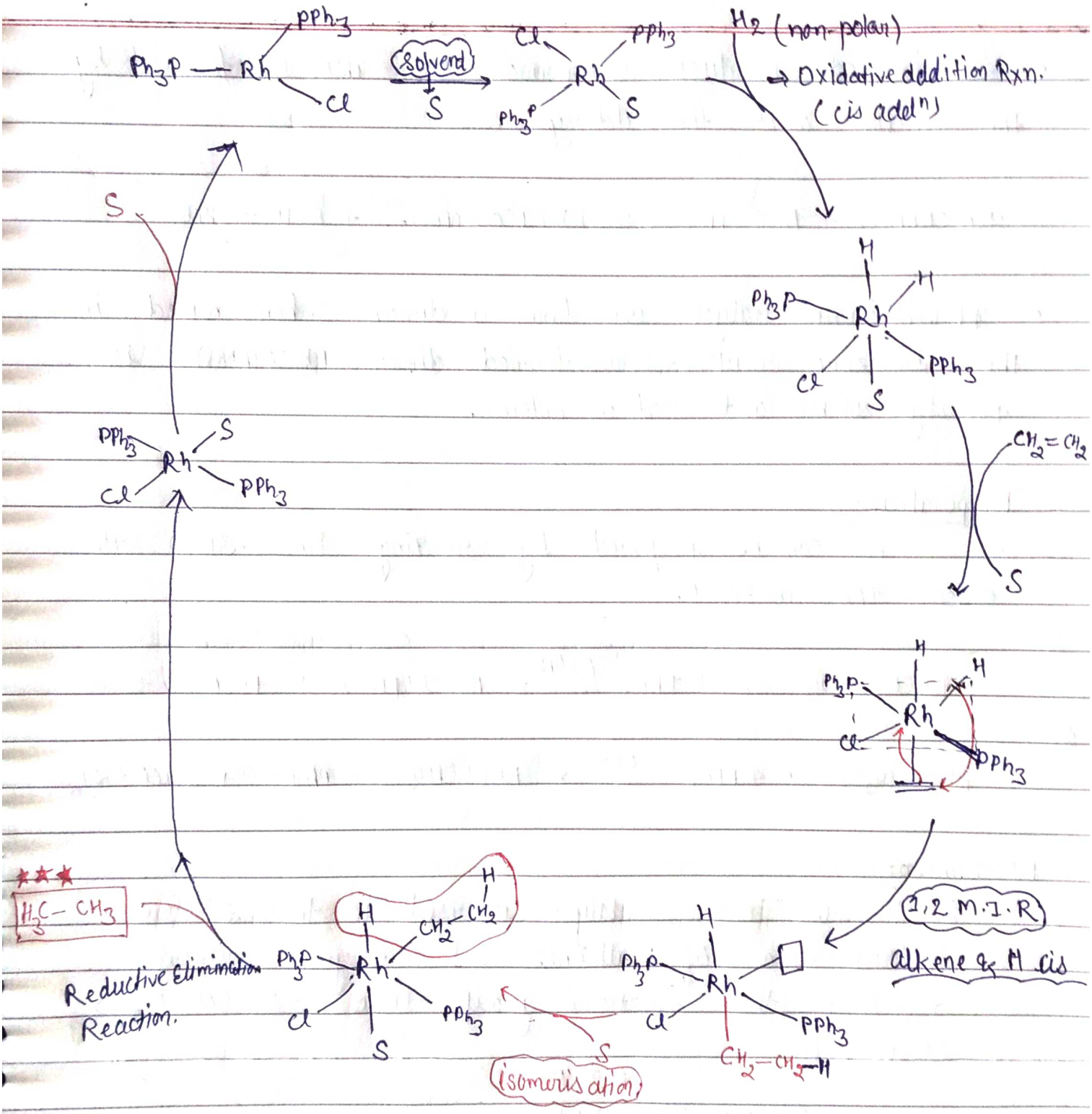
$$CH_2=CH_2 + H_2 \xrightarrow[\text{Wilkinson catalyst}]{RhCl(PPh_3)_3 + \text{Solvent}} H_2C-CH_2 \quad (H, H)$$

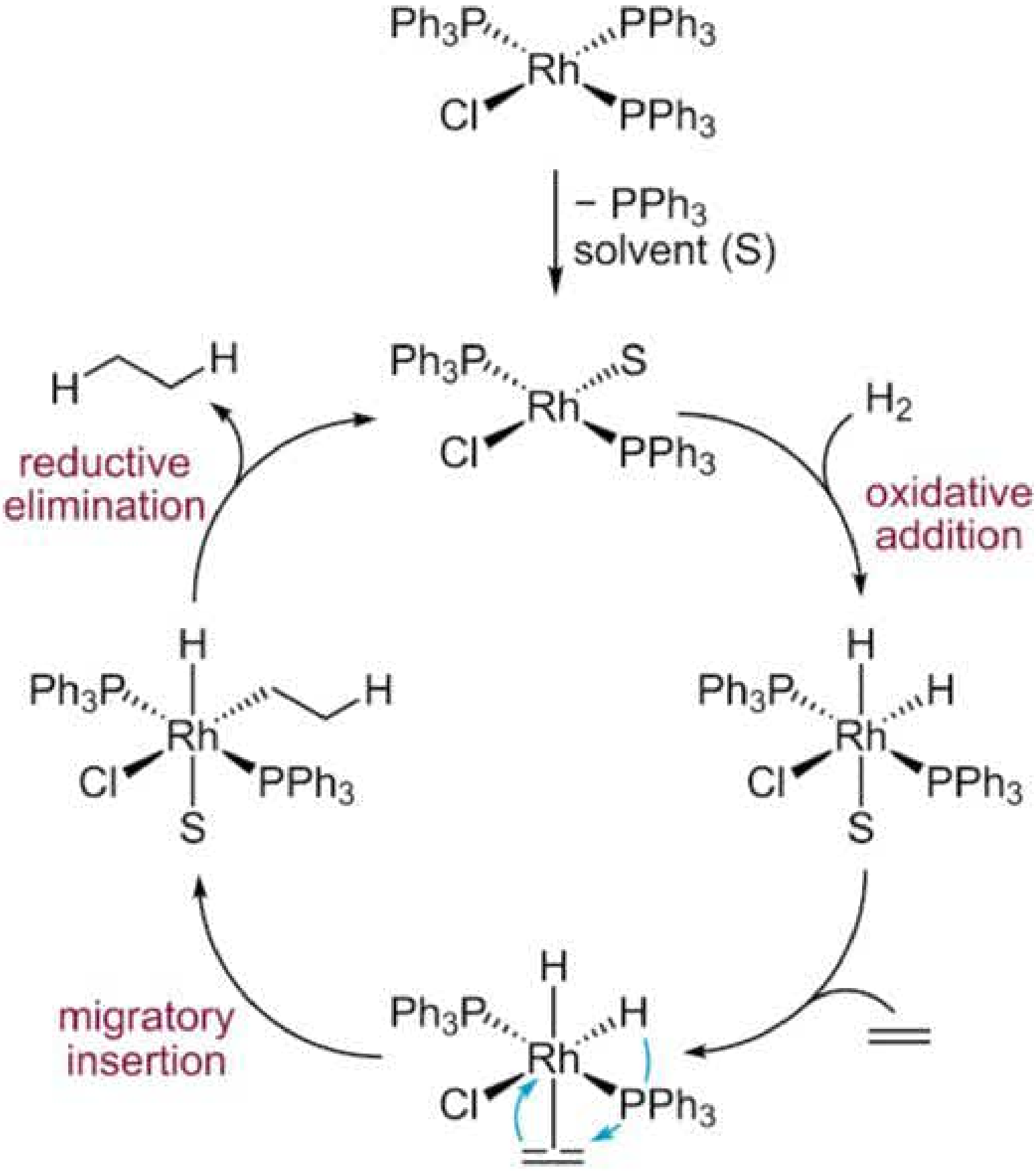
(benzene–EtOH)

Mechanism

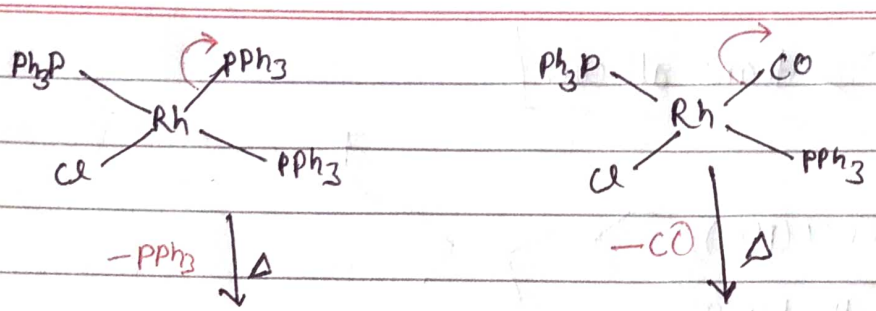
trigonal plannar (active form of catalyst)

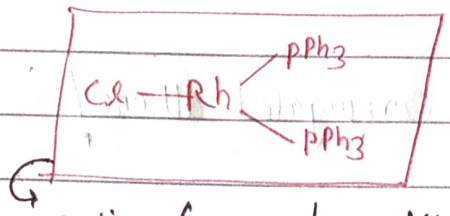
- 10^4 times fast.


Solvent
S
H_2 (non-polar)
→ Oxidative addition Rxn.
(cis addⁿ)
$CH_2=CH_2$
1,2 M.I.R
alkene & H cis
Reductive Elimination Reaction.
Isomerisation
H_3C-CH_3


Ph3P
PPh3
Rh
Cl
PPh3
– PPh3
solvent (S)
H
H
Ph3P
S
Rh
Cl
PPh3
H2
reductive
elimination
oxidative
addition
H
Ph3P
H
Rh
Cl
S
PPh3
H
Ph3P
H
Rh
Cl
S
PPh3
migratory
insertion
H
Ph3P
H
Rh
Cl
PPh3

Imp:-



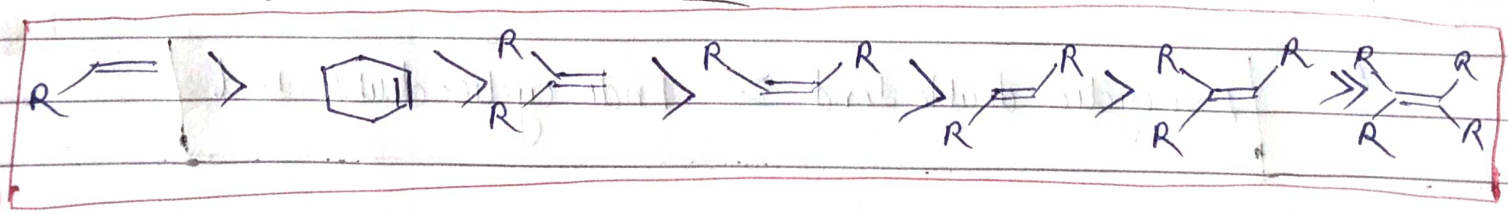


active form of wilkinson catalyst.

∴ both are wilkinson catalyst.

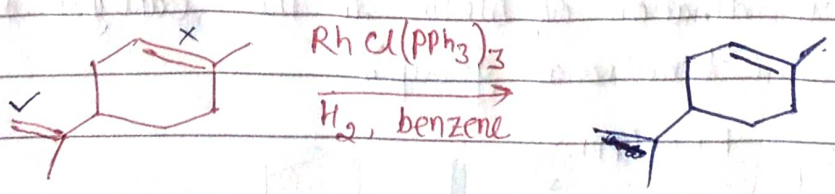
⇒ Rate of hydrogenation decreases with increases in the alkyl group substitution on double bond mirroring their relative binding affinities to the metal center. It is also partly due to steric factor.

Reactivity series of alkene :-



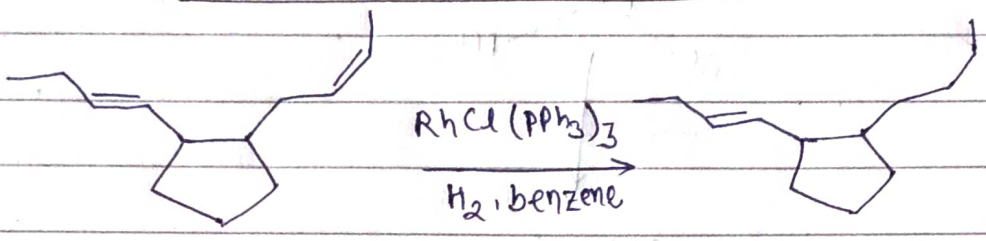
Selective Hydrogenation by wilkinson catalyst :-

1. Less substituted and sterically less hindered double bonds are selectively hydrogenated.



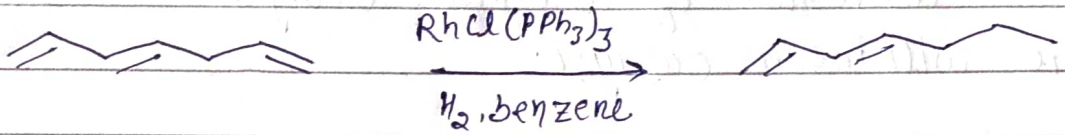
* { Terminal alkene >> Internal alkene }

2. cis alkene > trans alkene

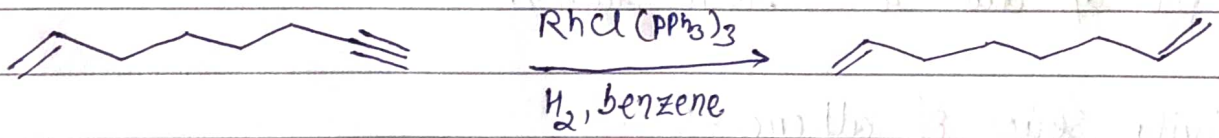


3. Isolated alkene >> Conjugated alkene

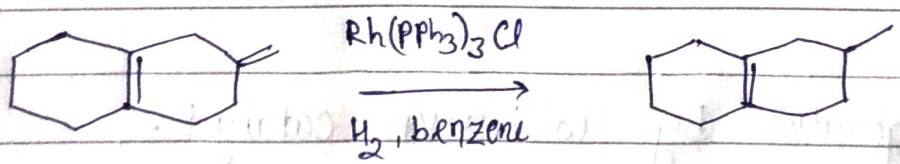
e.g.



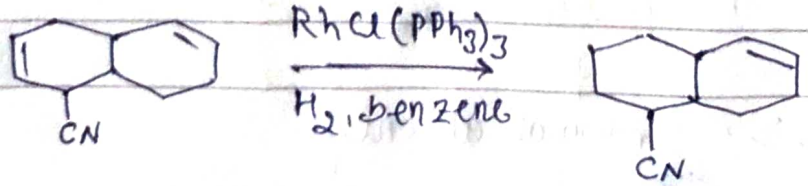
4. terminal alkyne >> terminal alkene



5. Exocyclic double bond >> Endo cyclic double bond



6. Unsaturated double bond containing polar functional group is more rapidly hydrogenated than other normal alkene. (due to easy coordination of olefin to the catalyst that is assisted by polar functional group.)



Question ①

The oxidation state of rhodium in Wilkinson's catalyst is:

a) +2 b) -1 c) +1 d) +3

Ans: (c) ✓ Rh → +1 Oxidation state.

Question-2 The co-ordination number of metal in wilkinson's catalyst is:

a) 4 b) 7 c) 5 d) 6

Ans: (a)

Question-3 Wilkinson catalyst formula —

a) $RhCl(Ph)_3$ b) $RhCl(PH_3)_3$ c) $RuCl(PPh_3)_3$ d) $RhCl(PPh_3)_3$

Answer- (d)

Question-4 Wilkinson catalyst contains:

a) Ruthenium b) cobalt c) Rhodium d) Zinc

Answer → (c)

Q-5 Wilkinson catalyst is used in;

a) Dehydrogenation of aliphatic compounds b) Hydrogenation of olefin
c) Reduction of aromatic compound d) Oxidation of alcohol.

Answer :- (b)

~~Q-6~~