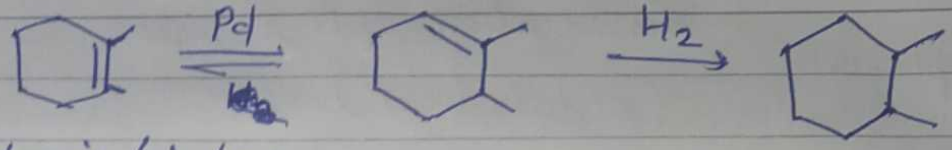
Homogeneous Hydrogenation

Disadvantages of heterogeneous Hydrogenation:-

- lack of selectivity
- Migration of double bond



Steric hindrance

- Some times easy hydrogenolysis

To overcome these problems, metal is replaced by a soluble complex of metal.

= Homogeneous catalyst

- Soluble in reacⁿ mix.
- Catalysis occurs not at the surface of a metal, but throughout the solution.
- Catalyst :- transition metal complex containing organic ligands

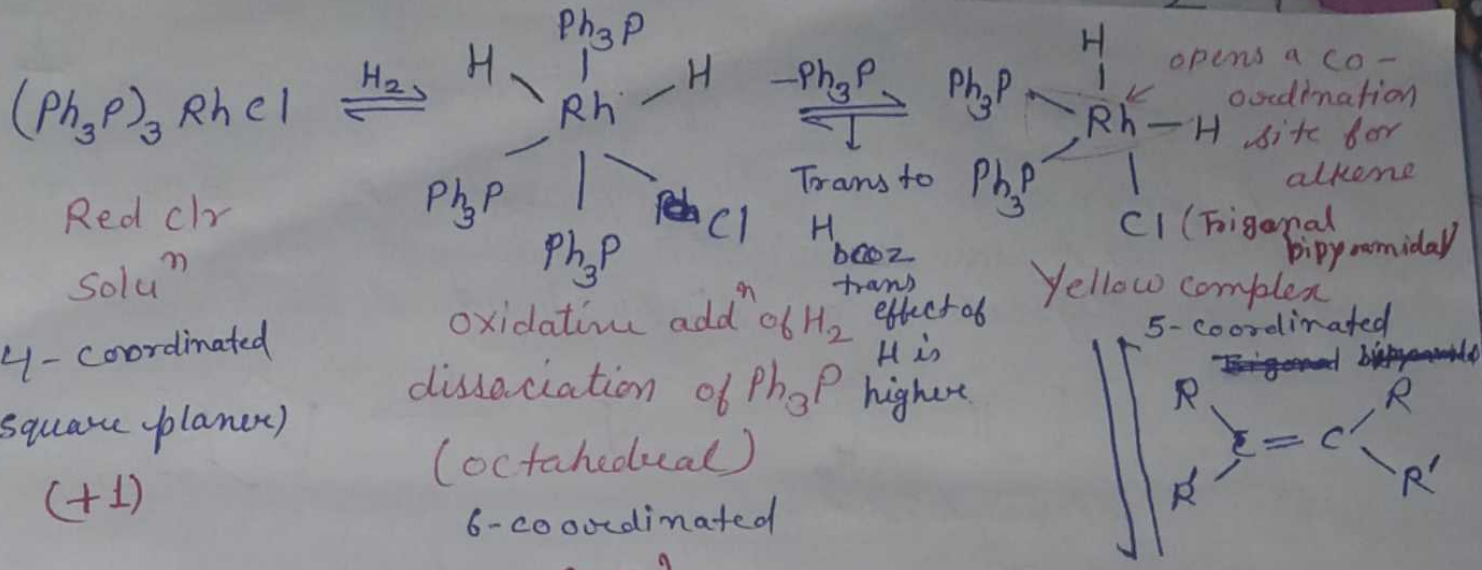
1. Tris (triphenyl phosphine) rhodium(I) chloride
   $[(C_6H_5)_3P]_3RhCl$
2. Hydrido chlorotris (triphenyl phosphine) Ruthenium
   $[(C_6H_5)_3P]_3RuClH$

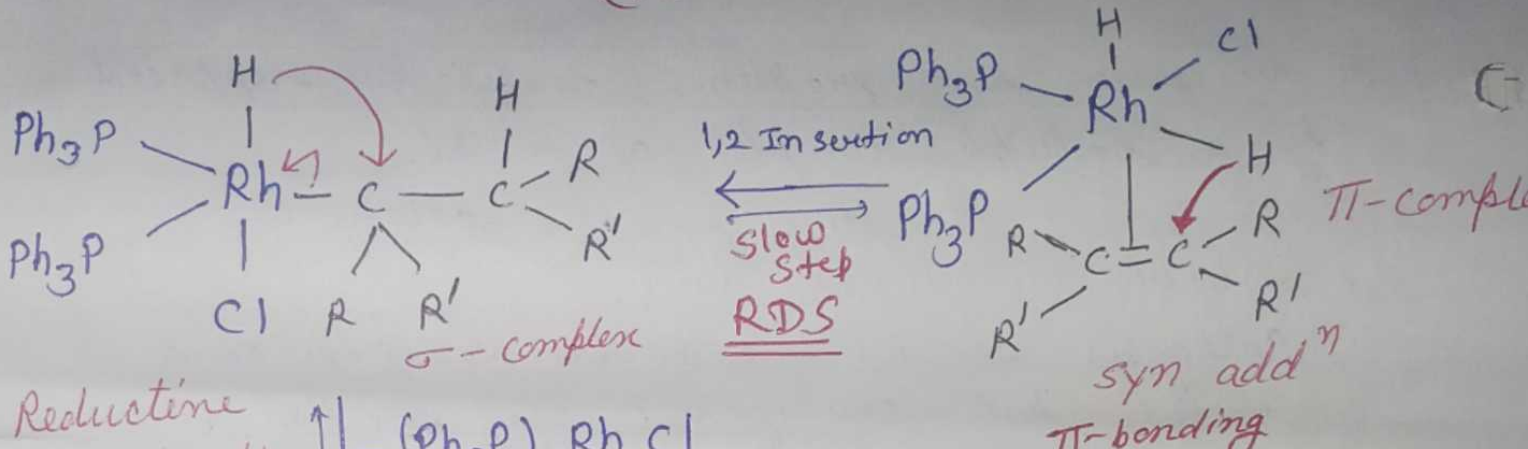
Wilkinson's catalyst :- $(Ph_3P)_3RhCl$

- Soluble in methanol / ethanol

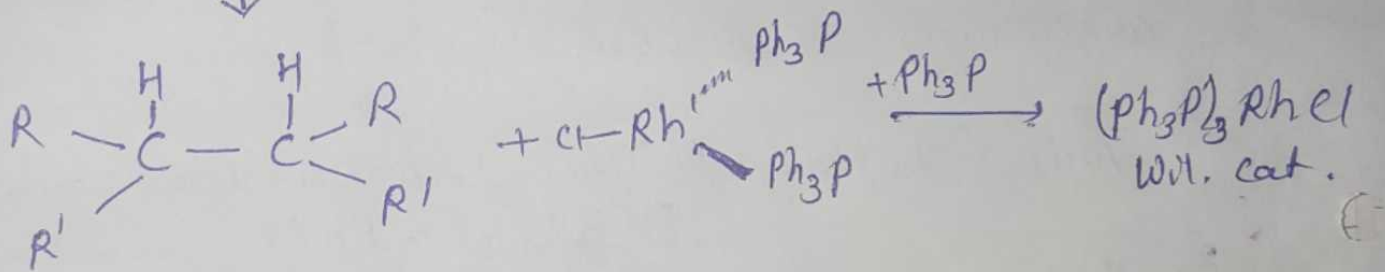
$$RhCl_3 \cdot 3H_2O + Ph_3P \xrightarrow[\text{Reflux}]{EtOH} (Ph_3P)_3RhCl$$

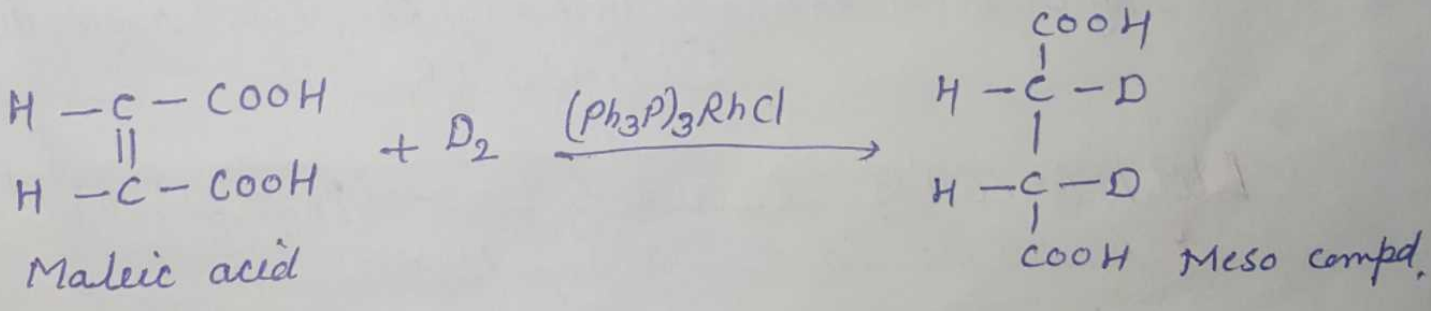
- Reduced terminal double bond
- Reduce non conjugated alkenes and alkynes in boiling C_6H_6.
- Functional gp like oxo, cyano, nitro, azo are not effected by this under ordinary Temp. and pressure.

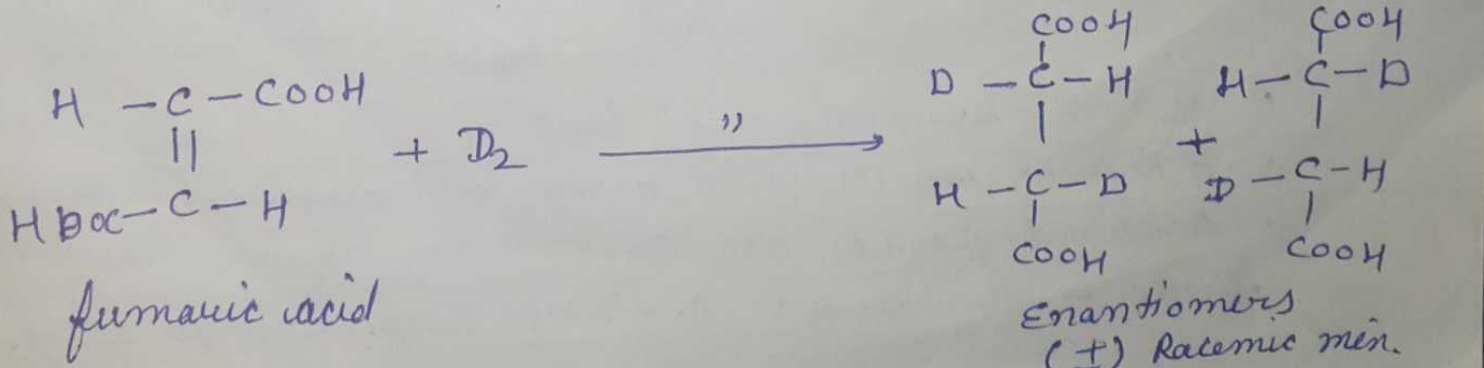




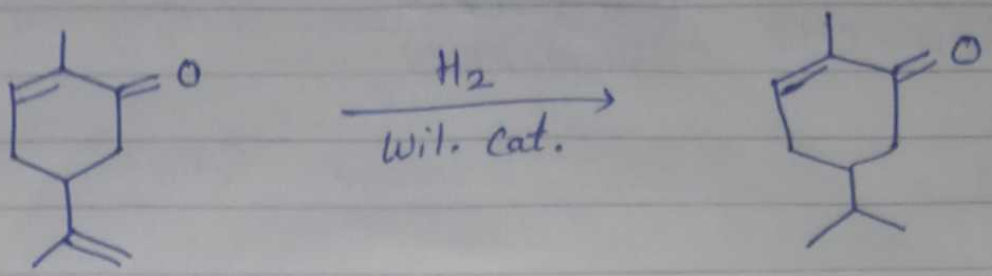
Reductive elimination $\rightleftharpoons$ $-(Ph_3P)_2RhCl$

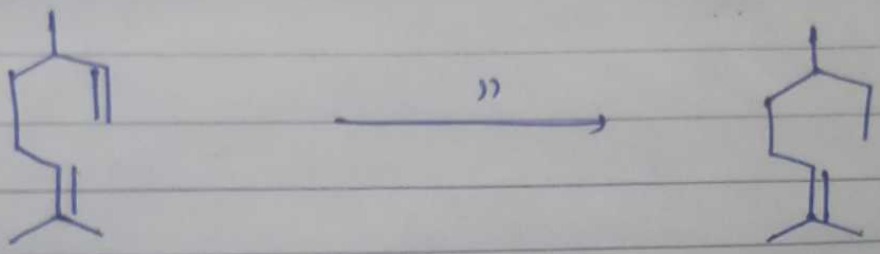




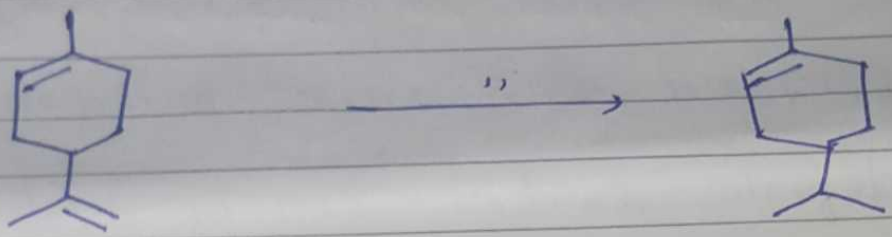


Wilkinson's catalyst used for the hydrogenation of non-conjugated double bond.

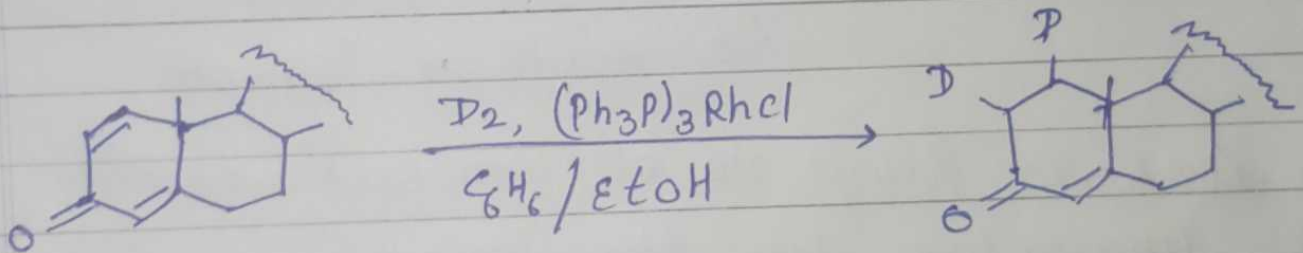




Mono/di substituted reduced more rapidly



$CH_3-CH=CH-CH_2NO_2 \xrightarrow{"} CH_3-CH_2-CH_2-CH_2-NO_2$



$C_6H_5-CH=CH-COOC_6H_5 \xrightarrow["]{H_2 \ "} C_6H_5-CH_2-CH_2-COOC_6H_5$

Benzyl cinnamate

$CH_2=CH-CH_2S-C_6H_5 \xrightarrow{"} CH_3-CH_2-CH_2-S-C_6H_5$

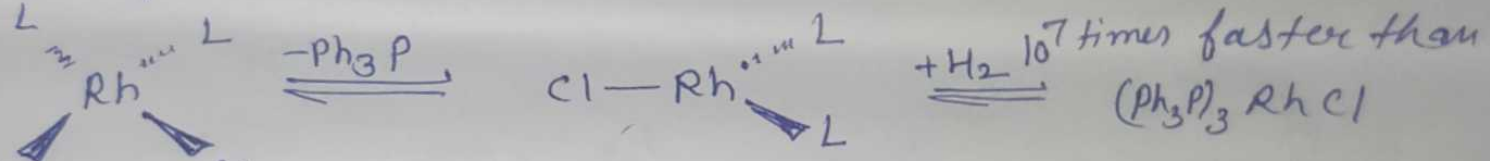
allyl phenyl sulfide — Phenyl Propyl thio sulfide

$RhCl(PPh_3)_3$ Chloro tris (triphenyl phosphine) rhodium (I)

- Square planar complex
- 16 electron complex
- oxidation state of Rh is +1. $Rh = 4d^9$ $Rh^{+1} = 4d^8$ sp

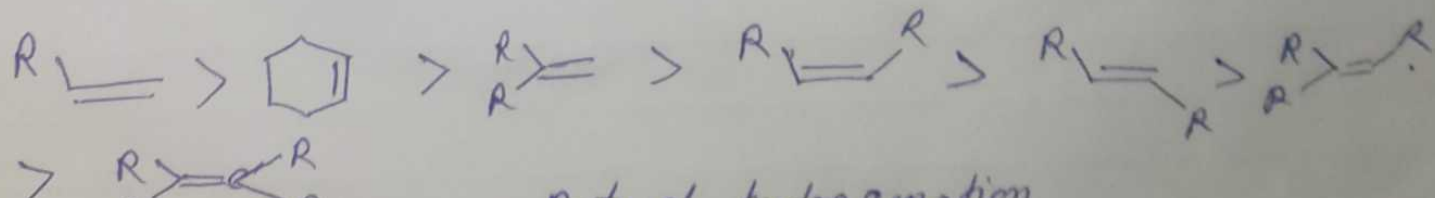
tetra co-ordinate

- It is a pre-catalyst
- converted to an active foorm by losing one Ph_3P ligand before entering the catalytic cycle.



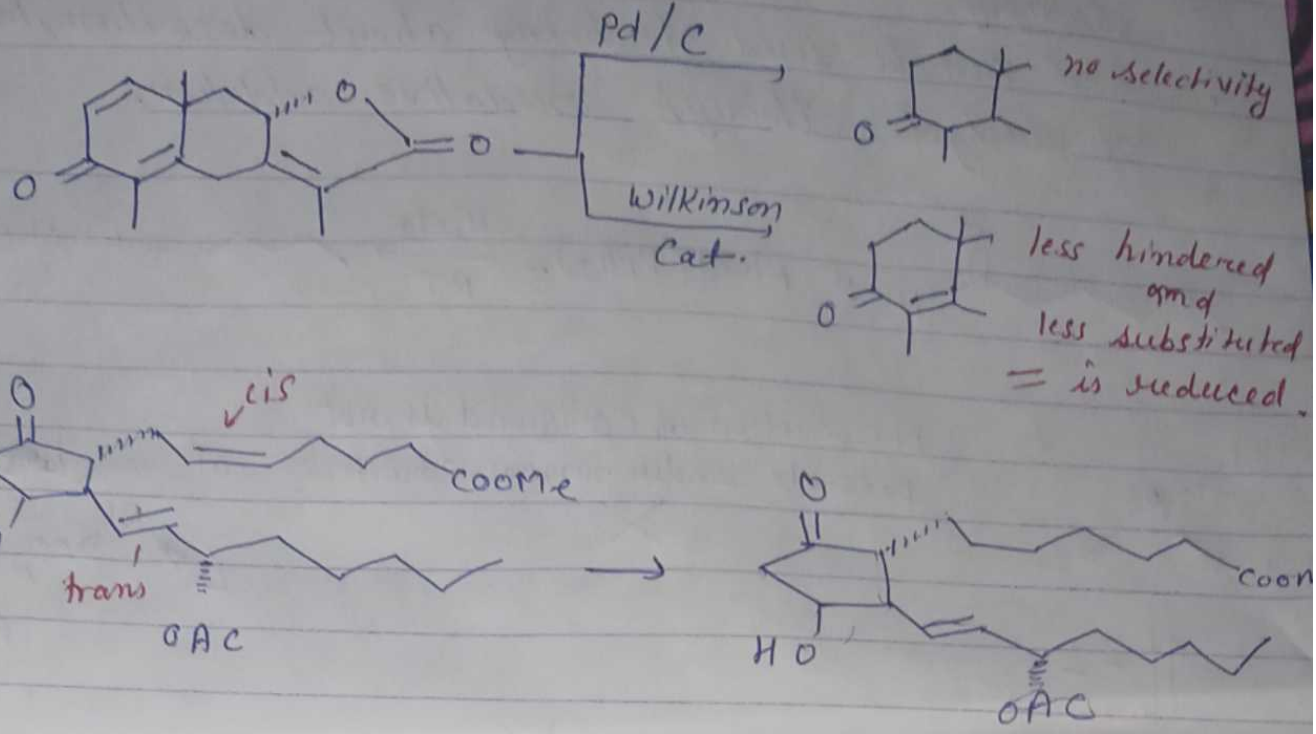
* Active foorm
Net

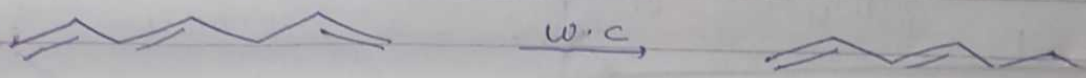
- Less hindered site → moore preffered.
- Less substituted alkene "
  mono > Di > tri > tetra
- Terminal alkyne > Terminal Alkene
- Polar gr. containing alkene "
- Cis alkene > trans alkene



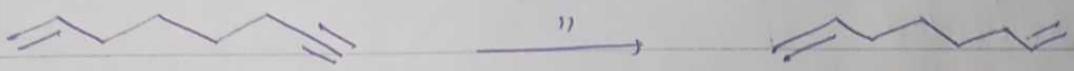
Rate of hydrogenation

- $[Ir(PPh_3)_3Cl]$ can not be used for hydrogenation. bcoz $Ir-PPh_3$ is much more strong than $Rh-PPh_3$.

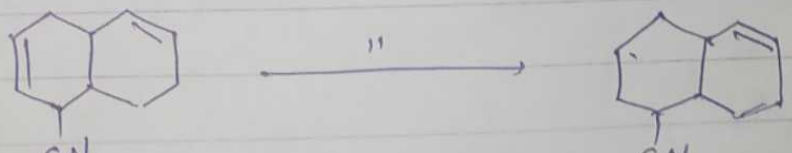




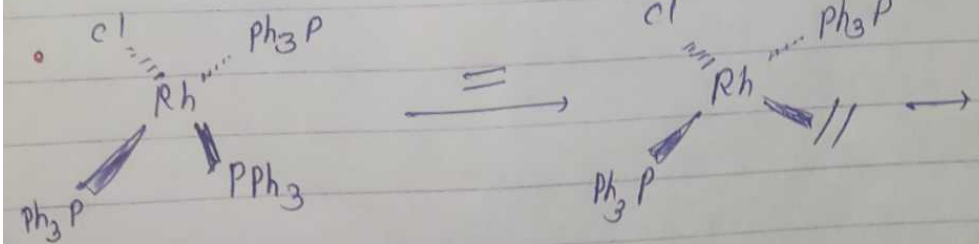
isolated = reduced rapidly



Terminal alkynes are hydrogenated more Rapidly.



Polar functionality are reduced more rapidly due to easy coordinating of olefin.

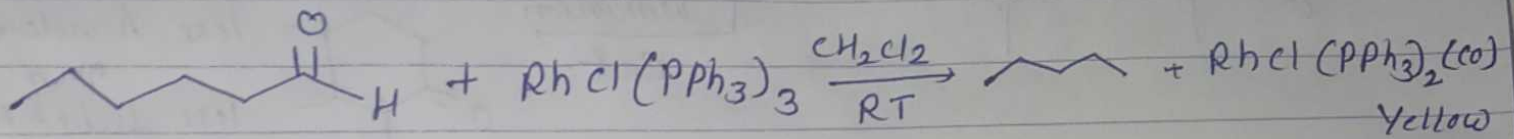


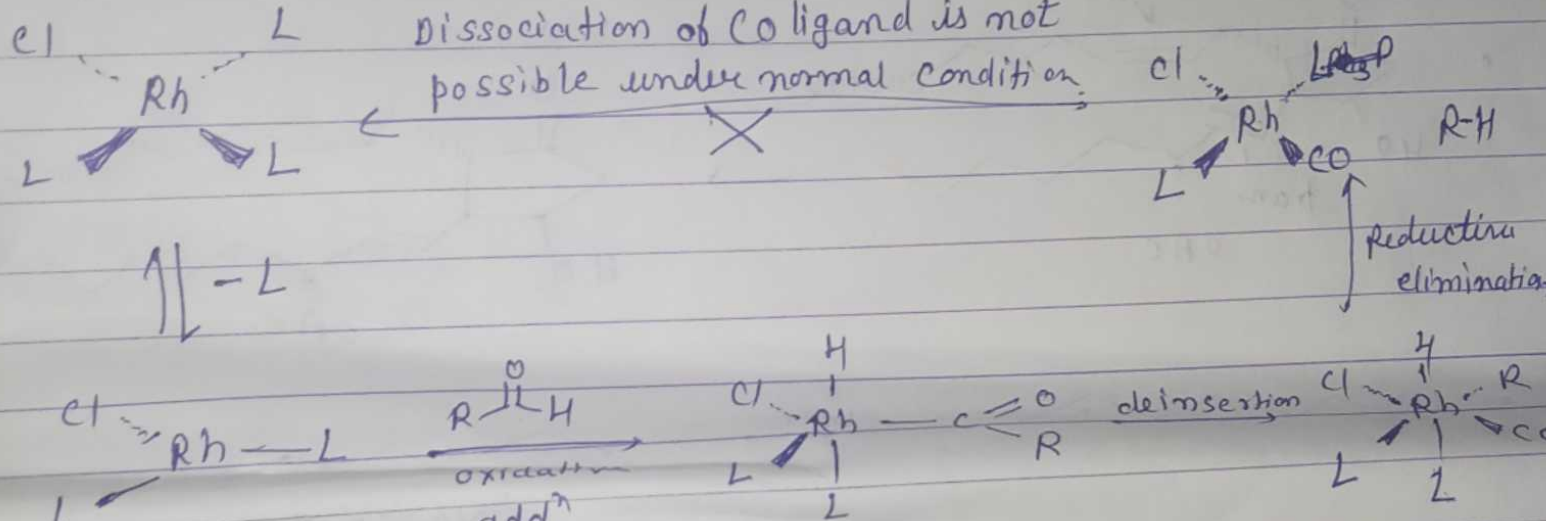
further hydrogenation is difficult bcoz = acts as poison.

Decarbonylation with Wilkinson's catalyst

Tsuji-Wilkinson decarbonylation reaction.

- Rh (II) is a low valent and coordinately unsaturated metal and can bind to CO strongly.
- and can be used to bring about decarbonylation of aldehydes through oxidative addition.





- This process is non-catalytic, since the catalyst can't be regenerated.
- The complex $RhCl(PPh_3)_2(CO)$ formed is quite stable and not possible to dissociate (CO) ligand at mild conditions.

* ~~Rhenium catalysts~~ :- $(Ph_3P)_3RhCl$ → Decarbonylation decarbonates aldehyde.

due to the strong affinity of $(Ph_3P)_3RhCl$ for CO.

$C_6H_5CH=CH-CHO \xrightarrow[(Ph_3P)_3RhCl]{} C_6H_5-CH=CH_2$

$C_6H_5COCl \longrightarrow C_6H_5Cl$