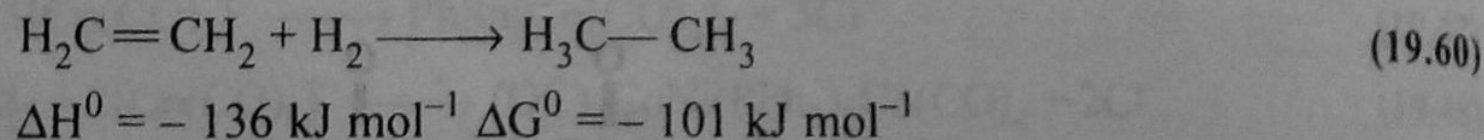## Alkene Hydrogenation

Although the reaction of hydrogen gas with ethylene is thermodynamically favorable, it does not take place at room temperature and pressure.

$$H_2C=CH_2 + H_2 \longrightarrow H_3C-CH_3 \tag{19.60}$$

$$\Delta H^0 = -136 \text{ kJ mol}^{-1} \quad \Delta G^0 = -101 \text{ kJ mol}^{-1}$$

However, in the presence of metallic nickel, copper, palladium, or platinum, the reaction is fast and complete. The metal may be deposited on the inert solid support such as alumina or calcium carbonate, but the reaction is with the metal surface and therefore is heterogeneously catalyzed.

The first effective homogeneous catalyst to be discovered for hydrogenation was the square planar 16-electron $d^8$ complex chlorotris (triphenylphosphine) rhodium (I), $(Ph_3P)_3RhCl$ (Fig. 19.2), which is known as Wilkinson's catalyst, In Chapter 14 we saw that this geometry and electron configuration are an especially favorable combination. These species also have wide possibilities for oxidative addition. They can become five-coordinate through simple addition of a ligand or six-coordinate through addition combined

## ∧ Synthesis

Wilkinson's catalyst is usually obtained by treating rhodium(III) chloride hydrate with an excess of triphenylphosphine in refluxing ethanol.[8][9][1] Triphenylphosphine serves as a two-electron reducing agent that oxidizes itself from oxidation state (III) to (V). In the synthesis, three equivalents of triphenylphosphine become ligands in the product, while the fourth reduces rhodium(III) to rhodium(I).

$$RhCl_3(H_2O)_3 + 4\ PPh_3 \rightarrow RhCl(PPh_3)_3 + OPPh_3 + 2\ HCl + 2\ H_2O$$
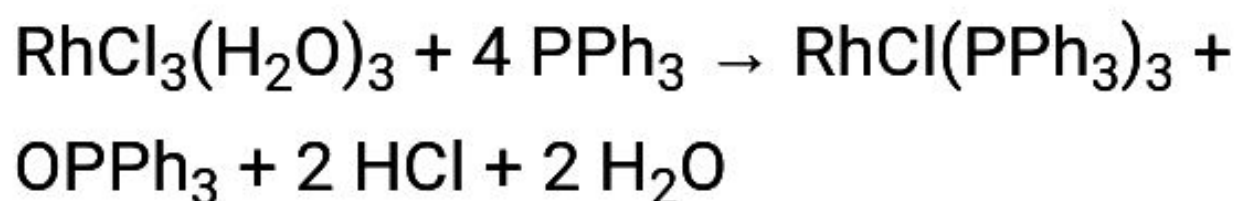
$RhCl(PPh_3)_3$ -
Chlorotris(triphenylphosphine)rhodium(I), is known as Wilkinson's catalyst. It is used as a homogeneous hydrogenation catalyst. It is a square planar 16-electron complex. The oxidation state of Rhodium in it is +1.
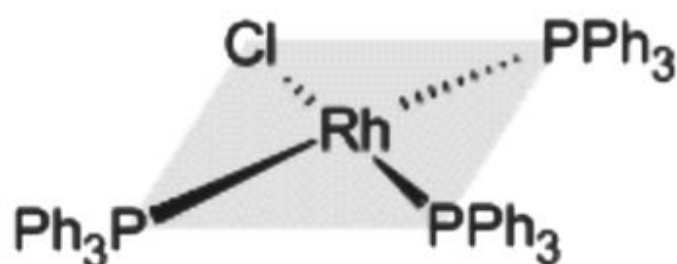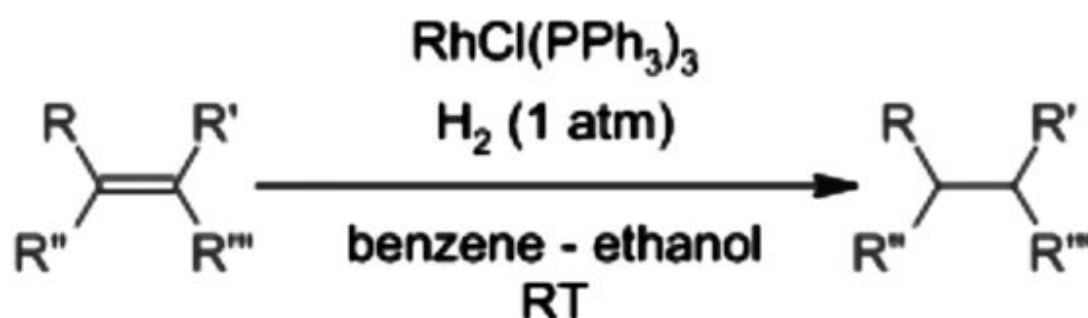


## Preparation:

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

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

## Uses:

It is used in the selective hydrogenation of alkenes and alkynes without affecting the functional groups like: C=O, CN, $NO_2$, Aryl, $CO_2R$ etc.

# MECHANISM OF HYDROGENATION - CATALYTIC CYCLE

Indeed, Wilkinson's catalyst is a pre-catalyst that is converted to an active form by losing one triphenylphosphine ligand before entering the catalytic cycle. Usually, the solvent molecule fills the vacant site.

Initially, the catalyst activates the molecular dihydrogen by oxidative addition mechanism to give a 18 valence electron dihydrido complex. The oxidation state of Rh is increased to +3. Thus formed dihydrido complex binds to the olefin in the next step with the concomitant loss of solvent or $PPh_3$ ligand. Since the activation of dihydrogen occurs before addition of olefin, this path is referred to as dihydride path .

Now one of the hydrogen undergoes migratory insertion at the double bond. This is a slow step i.e., Rate Determining Step (RDS).

Immediately and finally, the alkane is released rapidly by an irreversible reductive elimination step that completes the catalytic cycle. The oxidation state of Rh is decreased to +1 and the catalyst is regenerated.

However, other paths and intermediates are also possible under the given reaction conditions (see below).
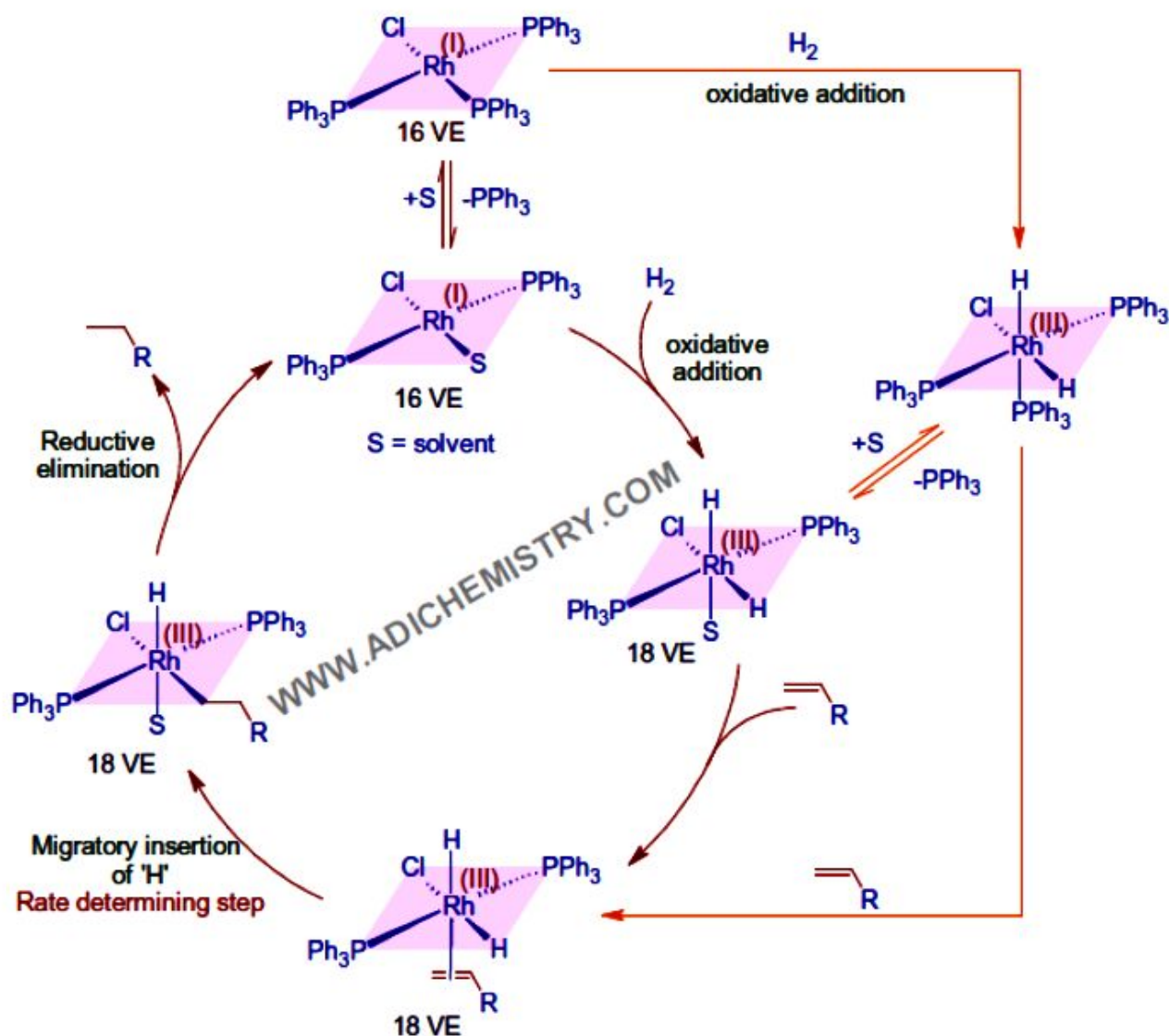
Above mechanism is supported by following observations.

* The rate of reaction decreases when excess of $PPh_3$ is added; indicating the initial dissociation of one of the $PPh_3$ ligand before dihydrogen activation.

* It is observed that strong π-acids like ethylene act as poisons by binding strongly with the electron rich Rh metal center and inhibit hydrogenation.
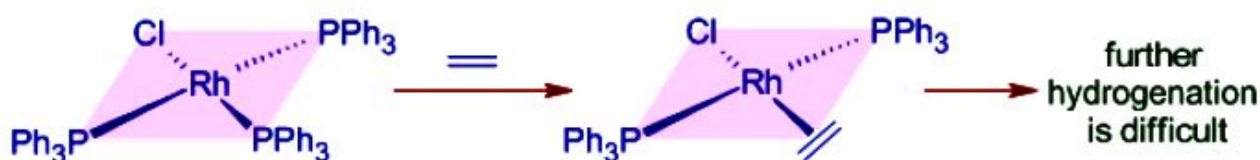
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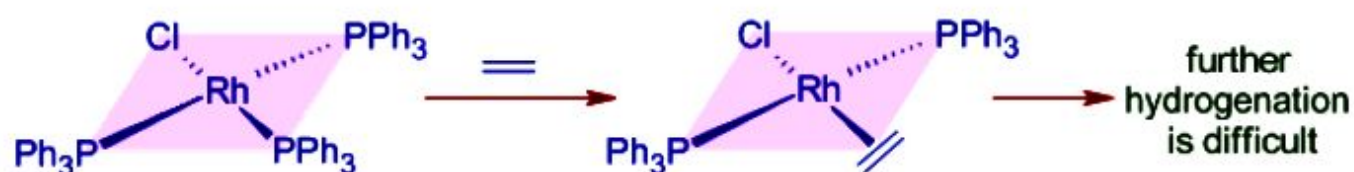


Though ethylene cannot be hydrogenated in presence of Wilkinson's catalyst under normal conditions, hydrogen transfer can be achieved with preformed dihydrido complex.



The rates of hydrogenations decrease with increase in the alkyl group substitution on double bond mirroring their relative binding affinities to the metal center. It is also partly due to steric factors.
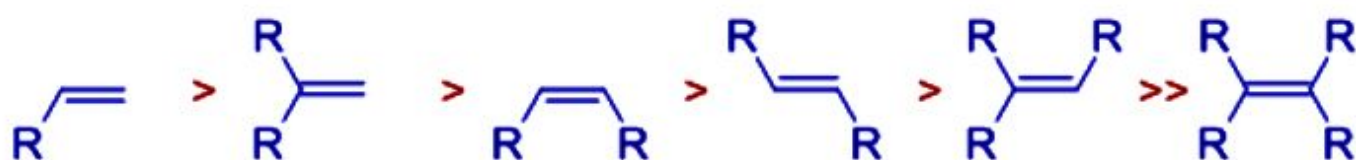
Ethylene is commonly chosen to illustrate homogeneous hydrogenation with Wilkinsons's catalyst, but the process is actually very slow with this alkene. The explanation lies with the formation of a stable rhodium ethylene complex, which does not readily undergo reaction with $H_2$. Ethylene competes effectively with the solvent for the vacant coordination site created when triphenylphosphine dissociates from Wilkinson's catalyst and thus serves as an inhibitor to hydrogenation.

$$(Ph_3P)_3RhCl + H_2C=CH_2 \longrightarrow (PH_3P)_2RhCl(\eta^2\text{-}C_2H_4) + Ph_3P \tag{19.67}$$