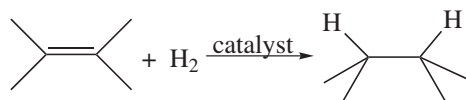


Hydrogenation of olefins

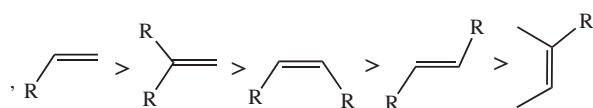
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Hydrogenation of olefins is one of the simplest reactions, where two hydrogen atoms add across a carbon-carbon double bond to give an alkane.



The ease of this reaction decreases with the increasing steric hindrance at the olefin as shown below.



Heterogeneous hydrogenation catalysts

They are present in a phase different from that of the reactants. Here, the reaction takes place at the surface of an insoluble solid catalyst. Some examples are 1% platinum on activated carbon or alumina, 5% ruthenium on activated carbon, and Raney nickel. When homogeneous catalysts are chemically attached to a solid surface, they are called heterogenized homogeneous catalysts.

Homogeneous hydrogenation catalysts

The activity of homogeneous catalysts can be adjusted

by changing the type and size of the ligands around the metal. Some simple homogeneous hydrogenation catalysts or precursors include: $[\text{M}_2(\text{cod})_2\text{Cl}_2]$ ($\text{M} = \text{Rh}, \text{Ir}$), $[\text{Ir}(\text{cod})(\text{pyridine})(\text{PPh}_3)]\text{PF}_6$, $[\text{RhClL}_3]$, $[\text{RuHClL}_3]$ and $[\text{RhH}(\text{CO})\text{L}_3]$, where $\text{L} = \text{PPh}_3$ and $\text{cod} = \text{cyclooctadiene}$.

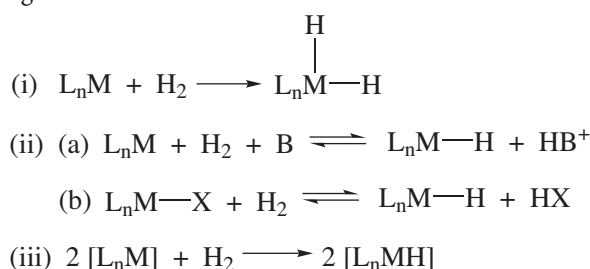
Asymmetric hydrogenation can be achieved by using chiral ligands such as DIOP, binaphthyl (BINAP), ferrocenyl (PPFA), phosphinooxazoline (PHOX) ligands *etc.* Some commercial processes of asymmetric hydrogenation are the synthesis of (i) L-Dopa (dihydroxy phenylalanine), used in the treatment of Parkinson's disease; (ii) the pain reliever Naproxen; (iii) N-acetyl L phenylalanine, the synthetic precursor to the sweetener aspartame *etc.*

Sources of hydrogen

Hydrogenation is one of the most extensively studied reactions using homogeneous catalysts. Dihydrogen (H_2), BH_4^- , HX and HCO_2H are the sources of hydrogen. Here, we will consider reduction reactions of olefins with **dihydrogen** in the presence of a suitable catalyst.

Dihydrogen can be activated *via* three methods. They are, (i) **oxidative addition** (ii) **heterolytic activation** & (iii) **homolytic activation**. General reactions for these

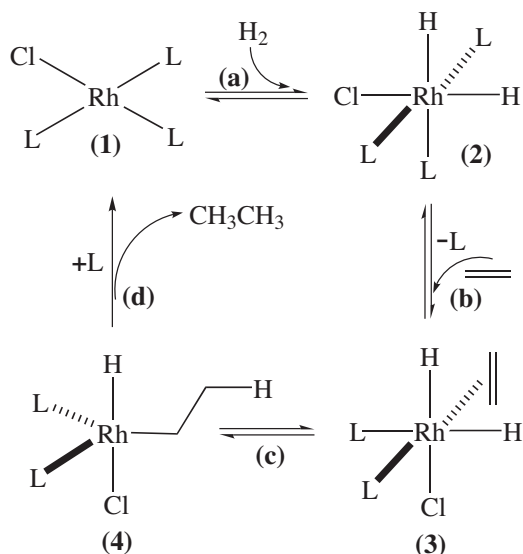
methods (i), (ii) and (iii) are given below. You should be able to determine the change in oxidation state of M; B is an external base and X is an internal monoanionic ligand.



In ii(b), the heterolytic activation of H₂ occurs in a single step without oxidising the metal. One can argue that this process involves oxidative addition of H₂ followed by the reductive elimination of HX.

Hydrogenation via oxidative addition

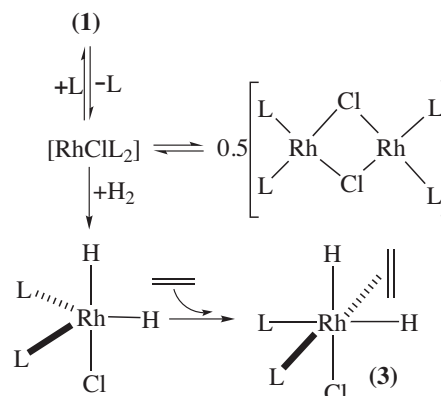
Hydrogenation of an olefin using the well-known 'Wilkinson's catalyst' [RhCl(PPh₃)₃] proceeds *via* this route as shown in scheme 1. (L = PPh₃)



Scheme 1 A possible mechanism for the hydrogenation of ethene by [RhCl(PPh₃)₃]. Note that other mechanisms/pathways exist.

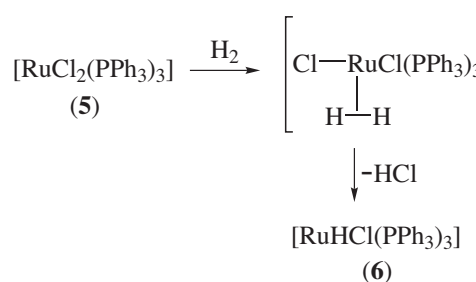
It is believed that the initial *cis* addition of H₂ to the Rh(I) centre (**step-a**) gives the Rh(III)-dihydride (2). Dissociation of PPh₃ and coordination of ethene (**step b**) gives (3). Insertion of ethene (**step c**) gives the alkyl derivative (4). Irreversible reductive elimination of ethane and coordination of PPh₃ (**step-d**) regenerates the catalyst (1).

Generation of other intermediates such as [RhCl(PPh₃)₂], the dimer [Rh(μ-Cl)(PPh₃)₂]₂ and [RhH₂Cl(PPh₃)₂] are also possible as shown below.



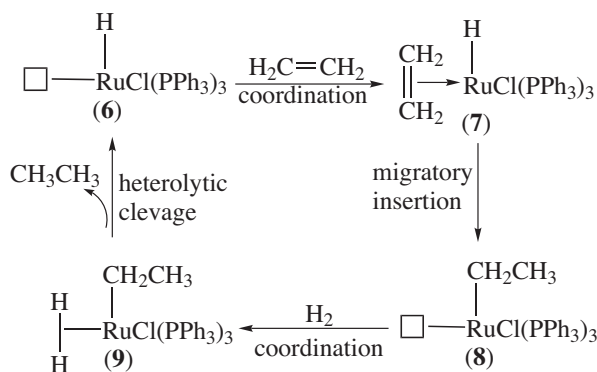
Hydrogenation via heterolytic activation

It is found that [RuCl₂(PPh₃)₃] (5) activates H₂ heterolytically as shown below.



(5) is a coordinatively unsaturated complex; H₂ coordination to (5) and the cleavage of H—H bond takes place rapidly to give the monohydride, [RuHCl(PPh₃)₃] (6). During this process, the oxidation state of Ru does not change and remains as +2.

The active catalyst (6) is also a coordinatively unsaturated complex and it catalyzes the hydrogenation of olefin as shown in scheme 2. The square (□) corresponds to a vacant site or a weakly coordinated solvent molecule.

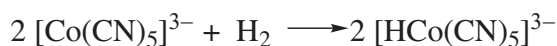


Scheme 2 A possible mechanism for the hydrogenation of ethene by [RuHCl(PPh₃)₃].

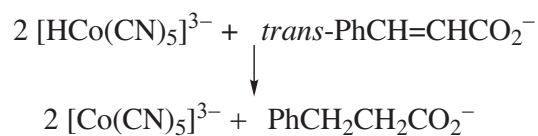
The first step involves coordination of ethene to the vacant site of the catalyst (**6**) to give the alkene-complex (**7**). Migratory insertion of ethene gives the ethyl-complex $[\text{RuCl}(\text{Et})(\text{PPh}_3)_3]$ (**8**). Coordination of H_2 gives the $\eta^2\text{-H}_2$ complex (**9**). This complex undergoes a heterolytic cleavage of H_2 , eliminating ethane and regenerating the active catalyst (**6**).

Hydrogenation via homolytic activation

The 17e Co(II)-complex $[\text{Co}(\text{CN})_5]^{3-}$ activates dihydrogen homolytically to give the Co(III) complex $[\text{CoH}(\text{CN})_5]^{3-}$.



This 18e-complex $[\text{CoH}(\text{CN})_5]^{3-}$ does not have a vacant site. However, it can transfer a hydrogen atom (H^\bullet) to an activated olefin, cinnamate (*trans* $\text{PhCH}=\text{CHCO}_2^-$), giving a moderately stable benzyl radical, $\text{Ph}^\bullet\text{CHCH}_2\text{CO}_2^-$ which abstracts another hydrogen radical (H^\bullet) to give 3 phenyl propionate ion, $\text{PhCH}_2\text{CH}_2\text{CO}_2^-$.



Problems

- The catalyst $[\text{MCl}(\text{PR}_3)_3]$ reacts with H_2 to give the octahedral M(III) dihydride (**A**). Replacement of PR_3 by $\text{MeCH}=\text{CH}_2$ in (**A**) gives the olefin-complex (**B**). In the presence of PR_3 , (**B**) undergoes migratory insertion to give the octahedral alkyl-complex (**C**). (**C**) reductively eliminates the alkane (**D**) to regenerate the catalyst $[\text{MCl}(\text{PR}_3)_3]$. Write the molecular formulae of (**A**), (**B**), (**C**) and (**D**).
- The active catalyst $[\text{RuHBr}(\text{PPh}_3)_3]$ coordinates with $\text{MeCH}=\text{CH}_2$ to give the olefin-complex (**P**). (**P**) undergoes migratory insertion to give the alkyl-complex (**Q**). (**Q**) reacts with H_2 to give the dihydrogen-complex (**R**) which eliminates (**S**) to regenerate $[\text{RuHBr}(\text{PPh}_3)_3]$. Identify (**P**), (**Q**), (**R**) and (**S**).