

11.1: Homogeneous Catalysis - I

Learning Objectives

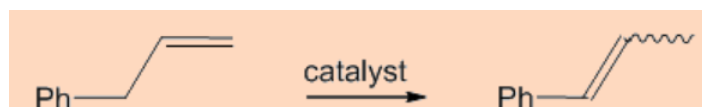
In this lecture you will learn the following

- The application of organometallic complexes in homogeneous catalysis.
- Alkene isomerization.
- Alkene and the arene hydrogenations.
- Transfer hydrogenation.

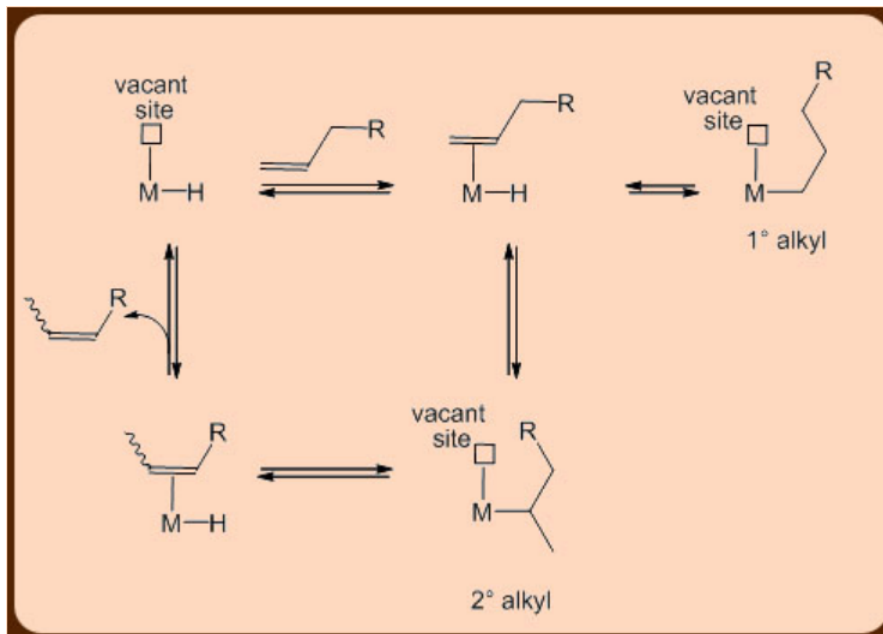
One of the most important exploits of the organometallic chemistry is its application in the area of homogeneous catalysis. The field has now expanded its territory to accommodate in equal measures many large-scale industrial processes as well as numerous small scale reactions of the day-to-day organic synthesis. A few representative examples of organometallic catalysis are outlined below.

Alkene Isomerization

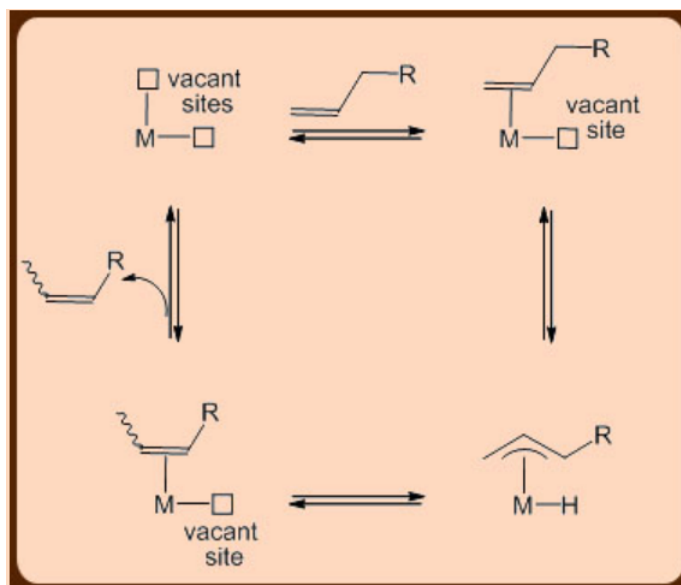
Alkene isomerization is a transformation that involve a shift of a double bond to an adjacent position followed by 1,3-migration of a H atom. The isomerization reaction is transition metal catalyzed.



The alkene isomerization reaction may proceed by two pathways, (i) one through a η^1 -alkyl intermediate and (ii) the other through η^3 -allyl intermediate. In the η^1 -alkyl pathway, an alkene first binds to a metal at a vacant site next to M-H bond and then subsequently undergoing an insertion into the M-H bond thus creating back the vacant site. The resultant species then undergoes a H atom transfer from the alkyl moiety to give the isomerized olefin along with the regeneration of the M-H species.



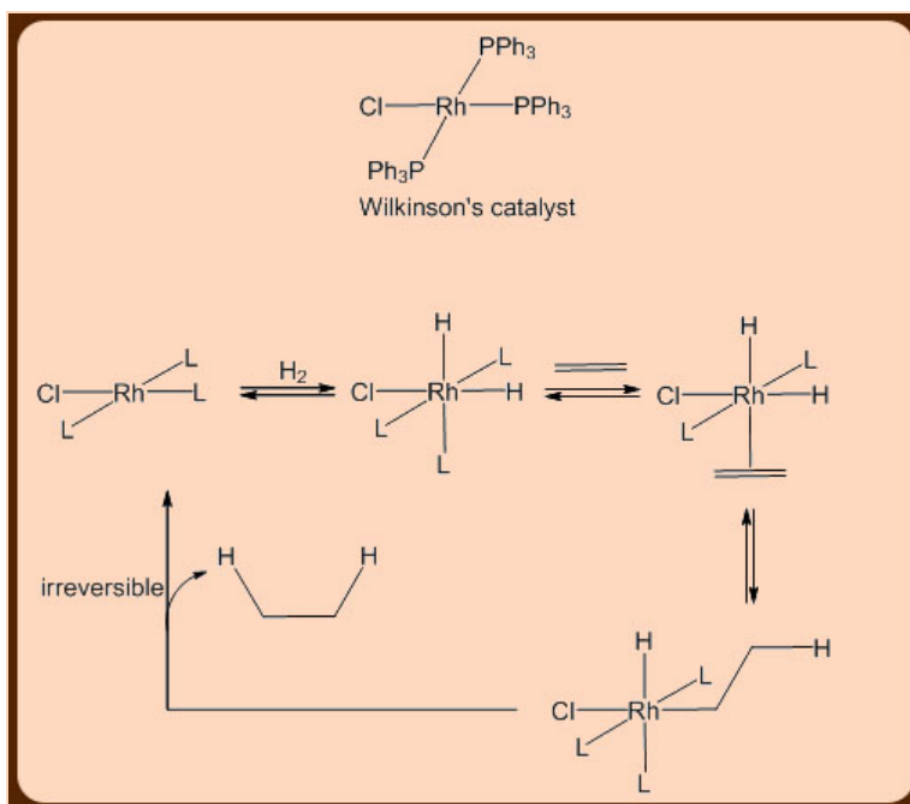
The η^3 -allyl mechanism requires the presence of two vacant sites. This mechanism goes through a η^3 -allyl intermediate formed by a C-H activation at the allylic position of the olefin formed after binding to the metal and alongside leads to the formation of a M-H bond. Subsequent H transfer from the metal back to the η^3 -allyl moiety leads to the alkene isomerized product.



Alkene Hydrogenation

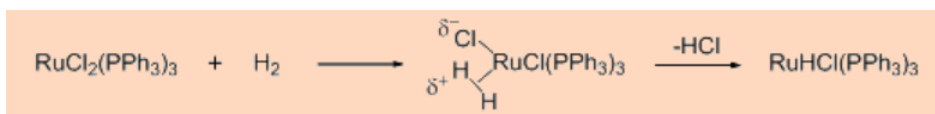
The transition metal catalyzed alkene hydrogenation reactions are of significant industrial and academic interest. These reactions involve the H_2 addition on a $C=C$ bond of olefins to give alkanes. The alkene hydrogenation may proceed by three different pathways namely the (i) oxidative addition (ii) heterolytic activation and (iii) the homolytic activation of the H_2 molecule.

The oxidative addition pathway is commonly observed for the Wilkinson's catalyst $(PPh_3)_3RhCl$ and is the most studied among all of the three pathways that exist. The catalytic cycle initiates with the oxidative addition of H_2 followed by alkene coordination. The resultant species subsequently get converted to the hydrogenated product.

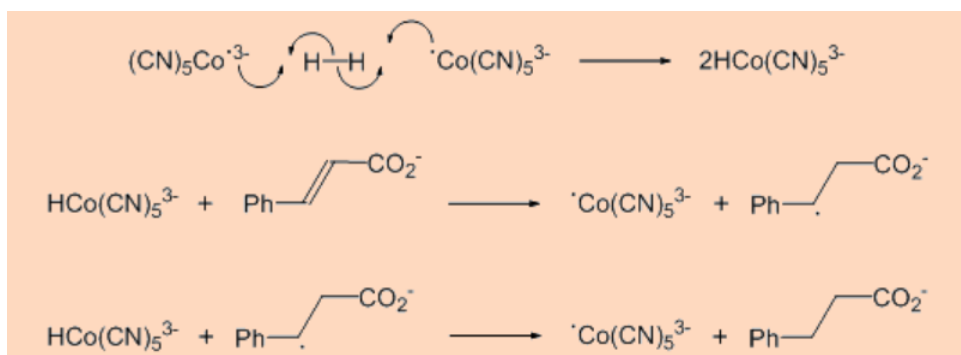


The second pathway proceeds by the heterolytic activation of the H_2 molecule and requires the presence of a base like NEt_3 , which facilitates the heterolytic cleavage by abstracting a proton from the H_2 molecule and leaving behind a hydride H^- ion that

participates in the hydrogenation reaction. This type of mechanism is usually followed by the $(\text{PPh}_3)_3\text{RuCl}_2$ type of complexes.

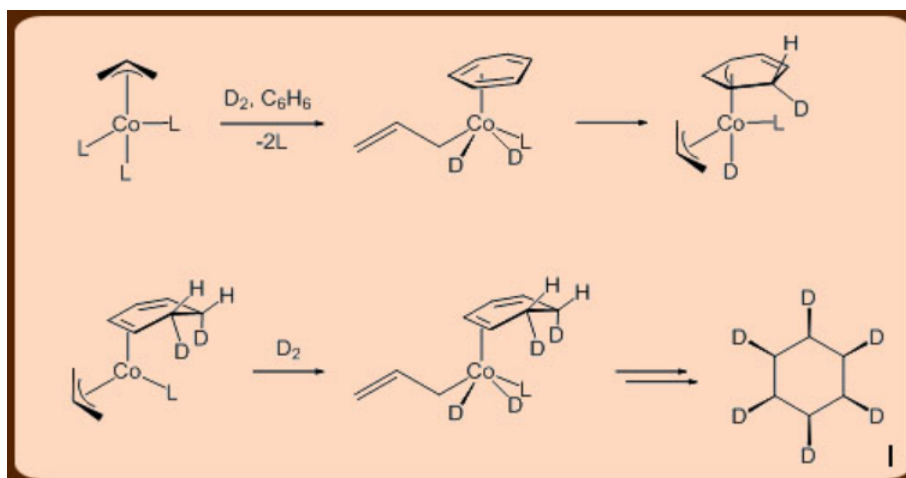


Homolytic cleavage of H_2 is the third pathway for the alkene hydrogenation. It is the rarest of all the three methods and proceeds mainly in a binuclear pathway. Paramagnetic cobalt based $\text{Co}(\text{CN})_5^{3-}$ type catalysts carry out alkene hydrogenation by this pathway via the formation of the $\text{HCo}(\text{CN})_5^{3-}$ species.



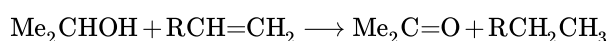
Arene hydrogenations

Examples of homogeneous catalysts for arene hydrogenation are rare though it is routinely achieved using catalysts like Rh/C under the heterogeneous conditions. A representative example of a homogeneous catalyst of this class is $(\eta^3\text{-allyl})\text{Co}[\text{P}(\text{OMe})_3]_3$ that carry out the deuteration of benzene to give the all-*cis*- $\text{C}_6\text{H}_6\text{D}_6$ compound.



Transfer hydrogenation

This is a new kind of a hydrogenation reaction in which the source of the hydrogen is not the H_2 molecule but an easily oxidizable substrate like isopropyl alcohol. The method is particularly useful for the reduction of ketones and imines but not very effective for the olefins.



Summary

The applications of organometallic compounds in homogeneous catalysis have transcended the boundaries of industry to meet the day-to-day synthesis in laboratory scale reactions. The alkene isomerization is one such application of homogeneous catalysis by the transition metal organometallic complexes. The hydrogenation reactions of alkene, arene, ketone and imine substrates are

achieved by several types of the transition metal organometallic catalysts. They also proceed by different mechanisms involving oxidative addition, heterolytic and homolytic cleavages of the H-H bond. The transfer hydrogenation reaction uses easily oxidizable substrates like *i*-PrOH instead of H₂ as the hydrogenation source.

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