

10.2.6: Organometallic Catalysts

Overview

The different types of organometallic reactions discussed in the previous sections can be combined together into catalytic cycles to produce valuable chemicals or perform otherwise difficult chemical reactions. While the organometallic catalyst will undergo a number of transformations over the course of the cycle, it will return to its original active state at the end of the reaction. By definition catalysts are reactive, because of this the metal complex added to a reaction is at times a more stable precatalyst which must undergo a reaction such as ligand dissociation to form the active catalyst.

Hydrogenation Catalysis

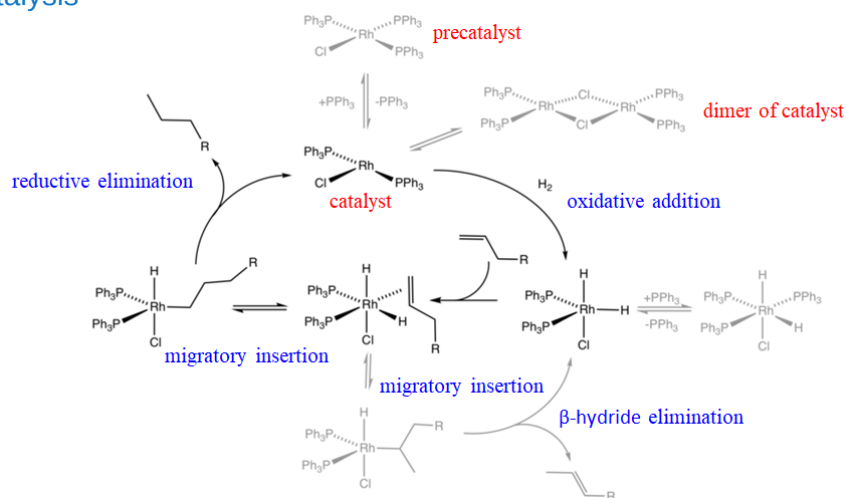


Figure 10.2.6.1: Mechanism of the Wilkinson hydrogenation catalyst (CC BY-SA; Smokefoot via Wikimedia Commons)

Migratory insertions play an important role in catalysis. For example a Rh-catalyst called Wilkinson's catalyst is an effective hydrogenation catalyst for olefins. The mechanism of the hydrogenation involves a combination of oxidative additions, olefin migratory (1,2) insertions, and reductive eliminations as shown in Figure 10.2.6.1. Wilkinson's catalyst is the square planar chloridotris(triphenylphosphine)rhodium(I) complex. This molecule is actually a precatalyst that becomes the active catalyst when it loses a triphenylphosphine ligand producing chloridobis(triphenylphosphine)rhodium(I). The loss of this ligand is a reversible reaction, and thus the catalyst is in chemical equilibrium with the precatalyst. The active catalyst is also in chemical equilibrium with its dimer. The chloridobis(triphenylphosphine)rhodium(I) catalyst can undergo an oxidative addition in the presence of hydrogen to form a trigonal bipyramidal chlorodihydridobis(triphenylphosphine)rhodium(III) complex. This species is in chemical equilibrium with an octahedral chlorodihydridotris(triphenylphosphine)rhodium(III) species that can form due to the presence of free triphenylphosphine ligands in the system. The trigonal bipyramidal species can then add an olefin ligand that binds side-on to the Rh. Because the olefin is in cis-position to the hydride ligand it can undergo a 1,2 insertion. The Rh-C bond can either form with the first or the second carbon in the carbon chain of the olefin, giving a linear and a branched alkyl complex, respectively. The branched complex can undergo a β -hydride elimination thereby reforming the trigonal bipyramidal Rh-complex, and an olefin. This reaction is a side-reaction because the branched alkyl complex is sterically more crowded than the linear complex. The linear alkyl Rh complex can undergo a reductive elimination to form the linear alkane and the $\text{RhCl}(\text{PPh}_3)_2$ catalyst. This completes the catalytic cycle, and a new cycle can start.

Ziegler-Natta Polymerization

Another example of an organometallic catalytic reaction is the Ziegler-Natta olefin polymerization. This reaction is of high industrial importance for the production of polymers like polyethylene. There are both heterogeneous and homogeneous Ziegler-Natta catalysts. The mechanism for the homogeneous catalysts is generally well understood. Homogeneous catalysts are typically metallocene catalysts.

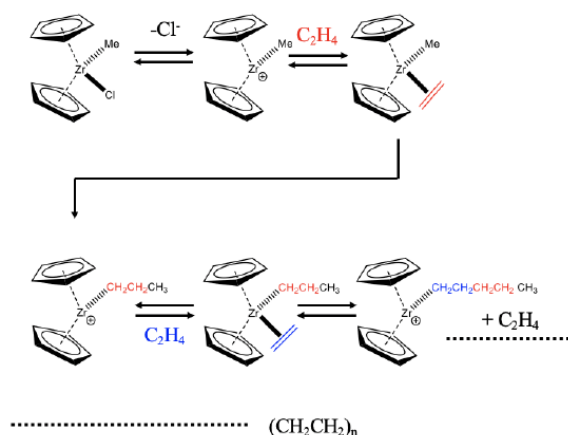


Figure 10.2.6.2: Mechanism for Zirconium-based Ziegler-Natta catalysis (Attribution: A. Vedernikov, U Maryland (modified).)

An example of a zirconium-based catalyst is shown in Figure 10.2.6.2. The catalyst is a coordinatively unsaturated complex cation with two cyclopentadienyl rings and a methyl group. The catalyst is formed from its precatalyst, a neutral molecule with an additional chloride ligand. The catalyst oxidatively adds an olefin like an ethylene molecule to the coordinatively unsaturated site. This step is followed by a 1,2b insertion step that produces a propyl group. The migratory insertion leads to the formation of a vacant site, that can be reoccupied by another ethylene molecule. This molecule can insert into the propyl chain thereby prolonging the propyl chain to a pentyl chain. The olefin insertion step generates another vacant site that can be reoccupied by a new ethylene molecule. Repeating the catalytic cycle many times eventually leads to polyethylene.

Catalytic Olefin Hydroformylation

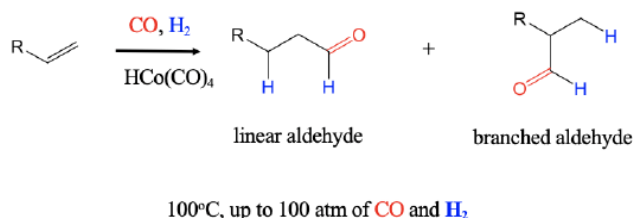


Figure 10.2.6.3: Scheme for catalytic olefin hydroformylation

A further important industrial reaction is the catalytic hydroformylation reaction, also known as oxo-process. It was discovered in 1938 by Otto Roelen at BASF. In the hydroformylation reaction an H atom and a formyl group are added to an alkene to form aldehydes. The reaction can produce both branched and linear aldehydes from terminal alkenes, CO, and H₂ using a carbonyl hydrides such as HCo(CO)₄ as a catalyst. The reaction is performed at about 100°C at a pressure of up to 100 atm.

Mechanism

How does the hydroformylation work mechanistically?

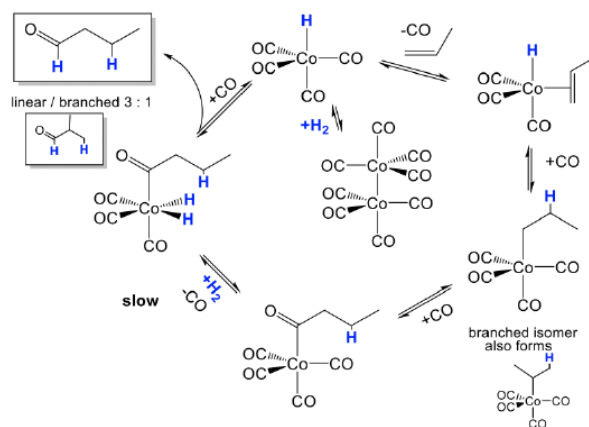


Figure 10.2.6.4: Mechanism of the catalytic olefin hydroformylation by HCo(CO)_4 (Attribution: A. Vedernikov, U Maryland (modified).)

The mechanism is illustrated for the hydroformylation of propene in Figure 10.2.6.4. The actual catalyst HCo(CO)_4 is first formed from its precatalyst $\text{Co}_2(\text{CO})_8$ in the presence of H_2 in a dinuclear oxidative addition reaction. The catalyst can undergo a substitution reaction in which a CO ligand is replaced by the olefin that binds side-on to the cobalt. This species can then undergo a migratory 1,2 olefin insertion reaction. This leads to a mixture of linear and branched alkyl groups attached to the Co. A new CO ligand can add to the vacant site. The alkyl group can then insert into a carbonyl group in another migratory insertion step, and the vacant site can be reoccupied by a new CO molecule. Then, H_2 is added in an oxidative addition. This is the slowest and rate-limiting step in the catalytic cycle. From the addition product the aldehyde can then be eliminated in a reductive elimination reaction. Addition of CO regenerates the catalyst, and the catalytic cycle can begin again.

Hydrocarbonylations

After the hydroformylation, a number of other hydrocarbonylations were developed, and industrially deployed.

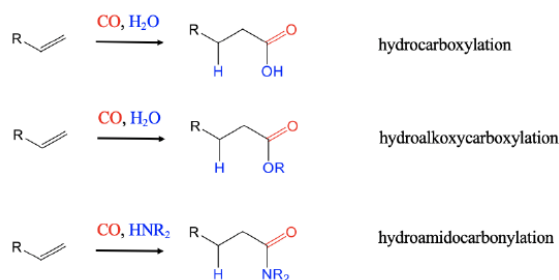


Figure 10.2.6.5: Hydrocarbonylation reactions

When hydrogen is replaced by H_2O hydrocarboxylations of alkenes lead to carboxylic acids (Figure 10.2.6.5). With an alcohol instead of H_2 hydroalkoxycarbonylations lead to esters. The employment of amines instead of H_2 leads to amides in hydroamidocarbonylation reactions.

Monsanto Acetic Acid Process

Another carbonylation reaction involving an organometallic catalyst is the Monsanto acetic acid process. It has been introduced by Monsanto in the 1970s for the industrial production of acetic acid from methanol. The reaction involves dual catalysis with HI and $[\text{RhI}_2(\text{CO})_2]^-$ as co-catalysts. How does this reaction work?

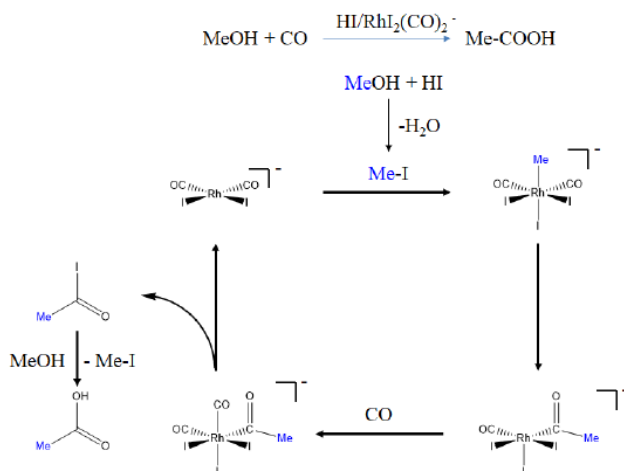


Figure 10.2.6.6: The catalytic cycle in the Monsanto acetic acid process

In the first step methanol reacts with HI to form methyl iodide. The methyl iodide then reacts with the Rh-catalyst in an oxidative addition reaction in which a methyl and an iodo group are added in trans-fashion to the square-planar Rh-complex to give an octahedral complex. The octahedral complex then undergoes a migratory insertion reaction with CO producing an acyl group and a vacant site. A CO molecule can then add to the vacant site. The acetyl iodide can then be eliminated in a reductive elimination to reform the Rh-catalyst thereby closing the catalytic cycle. The acetyl iodide can then react with methanol to form new methyl iodide and acetic acid. The methyl iodide can start a new catalytic cycle with the Rh-catalyst.

Olefin Metathesis

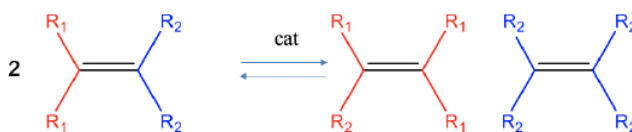


Figure 10.2.6.7: Scheme for olefin metathesis

Olefin metathesis is a reaction which allows to cut and rearrange C=C double bonds in olefins to make new olefins Figure 10.2.6.7. Formally, the carbon-carbon bond of the reactant is cleaved homoleptically and the two carbene fragments are combined in a different way. This reaction is typically an equilibrium reaction, and neither the reactants nor the products are clearly favored. This reaction is catalyzed by molybdenum arylamido carbene complexes or ruthenium carbene complexes.

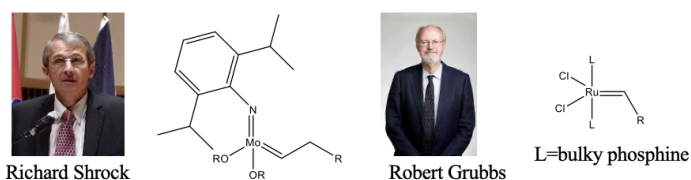


Figure 10.2.6.8: Shrock catalyst (left) (CC BY-SA; Materialschemist via Wikimedia Commons) and Grubbs catalyst (right) (CC BY-SA; The Royal Society via Wikimedia Commons)

The former are called Shrock catalysts, and the latter Grubbs catalysts named after their discoverers Richard Shrock and Robert Grubbs who received the Nobel prize for Chemistry in 2005 (Figure 10.2.6.8). The Shrock catalysts are more active, but also very sensitive to air and water. The Grubbs catalysts, while less active, are less sensitive to air and water.

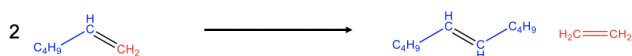


Figure 10.2.6.9: Scheme for regular metathesis

Olefin metathesis often allows for simpler preparation of olefins compared to other methods. Olefin metathesis is particularly powerful when one olefin product is gaseous because then it can be quite easily removed from the chemical equilibrium by purging. This drives the chemical equilibrium to the right side. An example is the preparation of 5-decene from 1-hexene. Cleavage of the C=C double bond in the hexene leads to C₅ and C₁ carbene fragments (Figure 10.2.6.9). The two C₁ fragments can combine

to form ethylene and the two C₅ fragments combine to 5-decene. The ethylene is volatile and can be purged from the reaction system thereby driving the chemical reaction to the right side.

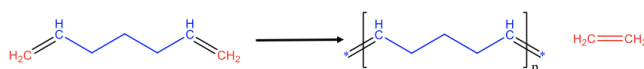


Figure 10.2.6.10: Acyclic diene metathesis (ADMET)

The same principles can also be applied to produce polymers from dienes with two terminal C=C double bonds at the chain ends. This is called acyclic diene metathesis (ADMET), Figure 10.2.6.10 For instance the cleavage of the two terminal double bonds in a diene with seven C atoms leads to C₁ and C₅ fragments. The C₁ fragments can combine to form ethylene, and the C₅ fragments can combine to make an unsaturated polymer of the type [CH(CH₂)₃CH]_n. Again, the reaction can be driven to the right side by removing the gaseous ethylene from the reaction mixture through purging.

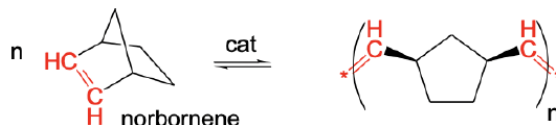


Figure 10.2.6.11: Ring-opening metathesis polymerization (ROMP)

Another variation of olefin metathesis is ring-opening metathesis polymerization (ROMP). It allows to make polymers from strained cycloolefins, for example norbornene. The reaction driving force is the relief of the strain. Because the strain is removed in the polymer, the chemical equilibrium lies far on the right side. The reaction product in norbornene is a polymer with 5-membered rings that are interconnected by ethylene -CH=CH- units (Figure 10.2.6.11).

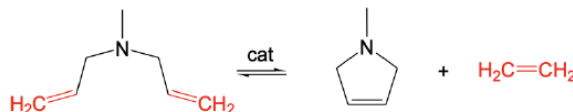


Figure 10.2.6.12: Ring-closing metathesis (RCM)

The opposite of ROMP is ring-closure metathesis (RCM). RCM allows for the preparation of unstrained rings with C=C double bonds from dienes with C=C double bonds that are five or six carbon atoms apart. This distance is suitable to produce unstrained rings. In the shown example a five-membered ring with a C=C double bond is formed from a diene with terminal C=C double bonds that are five atoms apart.

Mechanism

What is the mechanism of olefin metathesis?

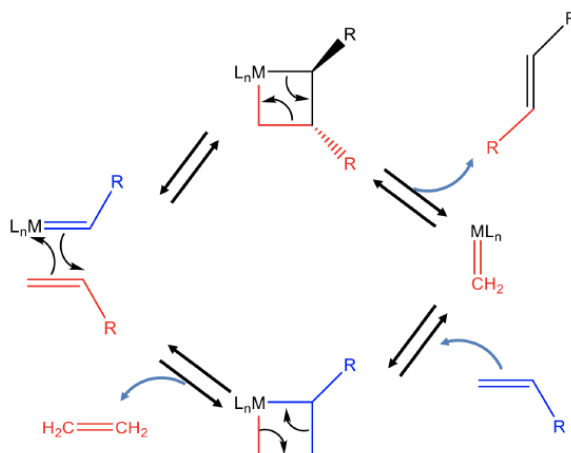


Figure 10.2.6.13: The mechanism of olefin metathesis

In the first step, the alkene adds to the the carbene fragment of the catalyst in a 2+2 cycloaddition reaction to produce an unstable intermediate with a highly strained four-membered ring (Figure 10.2.6.13). This four membered ring can open to produce the first

new alkene product $R-CH=CH-R$ and a metal carbene species. This metal carbene can react with another reactant olefin to form another highly strained 4-ring intermediate via a 2+2 cycloaddition reaction. This ring can then reopen again to produce the second alkene metathesis product, in this case ethylene, and the original catalyst. The regenerated catalyst can then start a new catalytic cycle.

Carbon-Carbon Cross Coupling Reactions

The palladium catalyzed cross-coupling reactions are a class of highly successful reactions with applications in the organic synthesis to have emerged recently. The reactions carry out a coupling of the aryl, vinyl or alkyl halide substrates with different organometallic nucleophiles and as such encompasses a family of C-C cross-coupling reactions that are dependent on the nature of nucleophiles like that of the B based ones in the Suzuki-Miyaura coupling, the Sn based ones in the Stille coupling, the Si based ones in the Hiyama coupling, the Zn based ones in the Negishi coupling and the Mg based ones in the Kumada coupling reactions (Figure 10.2.6.14).

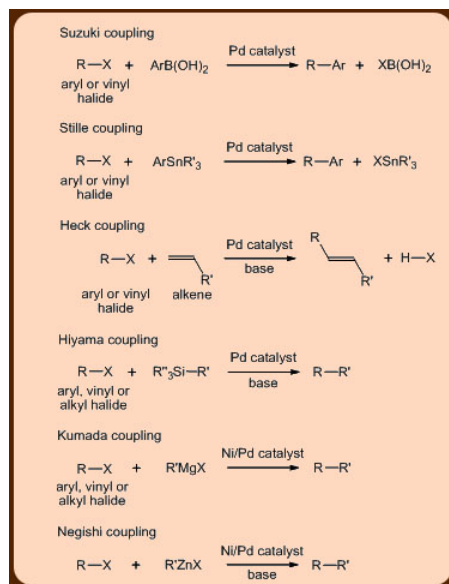


Figure 10.2.6.14: Various types of the palladium mediated C-C cross-coupling reactions.

An unique feature of these reactions is the exclusive formation of the cross-coupled product without the accompaniment of any homo-coupled product. Another interesting feature of these coupling reactions is that they proceed *via* a common mechanism involving three steps that include the oxidative addition, the transmetalation and the reductive elimination reactions (Figure 10.2.6.15 and 10.2.6.16).

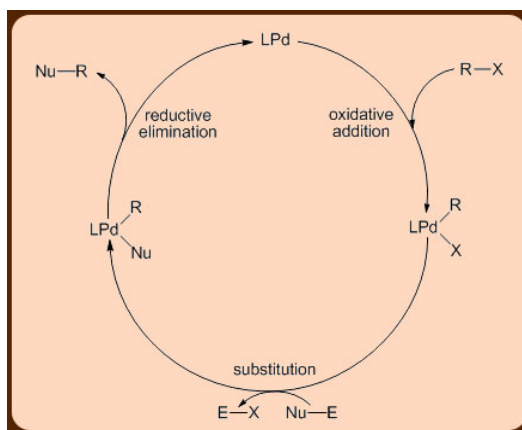


Figure 10.2.6.15: A general catalytic cycle for the palladium mediated C-C cross-coupling reactions.

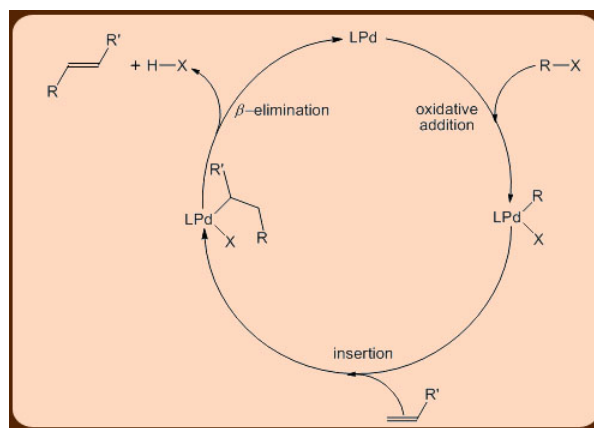


Figure 10.2.6.16: A catalytic cycle for the palladium mediated Heck coupling reaction.

Summary

Organometallic complexes play a pivotal role in several successful homogeneous catalysis reactions like that of the hydroformylation and the C-C cross-coupling reactions. These reactions are important because of the fact that both of the hydroformylation and the C-C cross-coupling reactions give more value added products compared to the starting reactants. The palladium catalyzed C-C cross-coupling reactions are a class of highly successful reactions that have permanently impacted the area of organic synthesis in a profound way to an extent that the 2010 Nobel prize has been conferred on one of these reactions thereby recognizing the importance of the C-C cross-coupling reactions.

Contributors and Attributions

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