

11.2: Homogeneous Catalysis - II

Learning Objectives

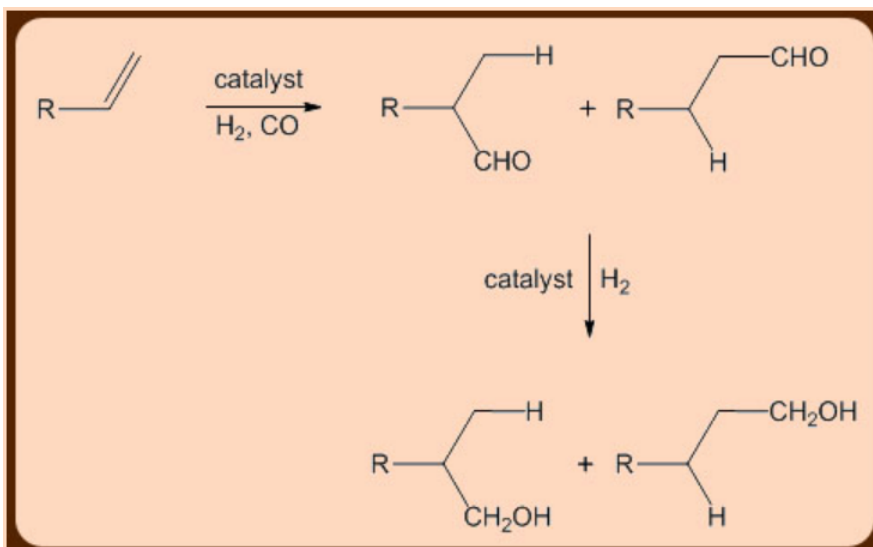
In this lecture you will learn the following

- The hydroformylation reaction and its mechanism.
- The C–C cross-coupling reactions and their mechanisms.

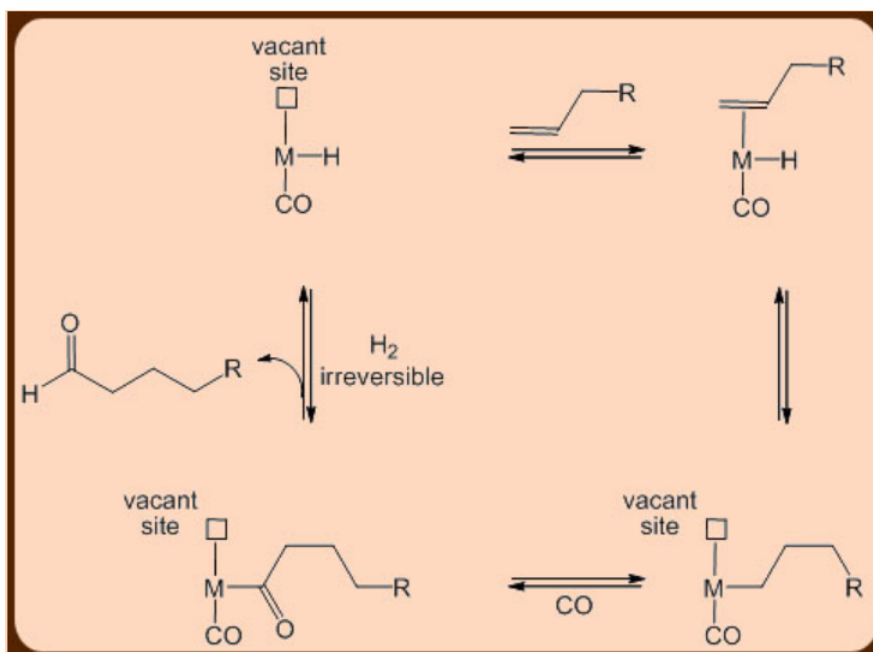
It is truly an exciting time for the field of organometallic chemistry as its potentials in homogeneous catalysis are being realized in an unprecedented manner. The growth in the field organometallic chemistry has been rightly acknowledged by the award of three Nobel prizes in over a decade in the areas of asymmetric hydrogenation (Noyori and Knowles in 2001), olefin metathesis (Grubbs, Schrock and Chauvin in 2006) and palladium mediated C–C cross coupling reactions (Suzuki, Negishi and Heck, 2010). A few representative examples of such landmark discoveries of homogeneous catalysis by organometallic compounds are discussed below.

Hydroformylation reaction

Hydroformylation, popularly known as the "oxo" process, is a Co or Rh catalyzed reaction of olefins with CO and H₂ to produce the value-added aldehydes.



The reaction, discovered by Otto Roelen in 1938, soon assumed an enormous proportion both in terms of the scope and scale of its application in the global production of aldehydes. The metal hydride complexes namely, the rhodium based $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and the cobalt based $\text{HCo}(\text{CO})_4$ complexes, catalyzed the hydroformylation reaction as shown below.



C-C 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 11.2.1).

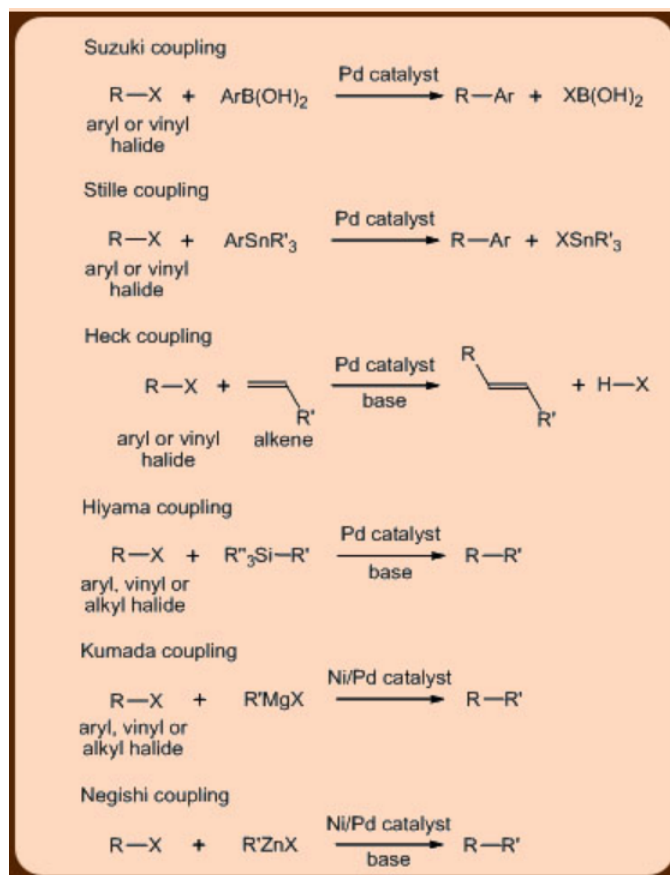


Figure 11.2.1: Various types of the palladium mediated C-C cross-coupling reactions.

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 (Figures 11.2.2 and 11.2.3).

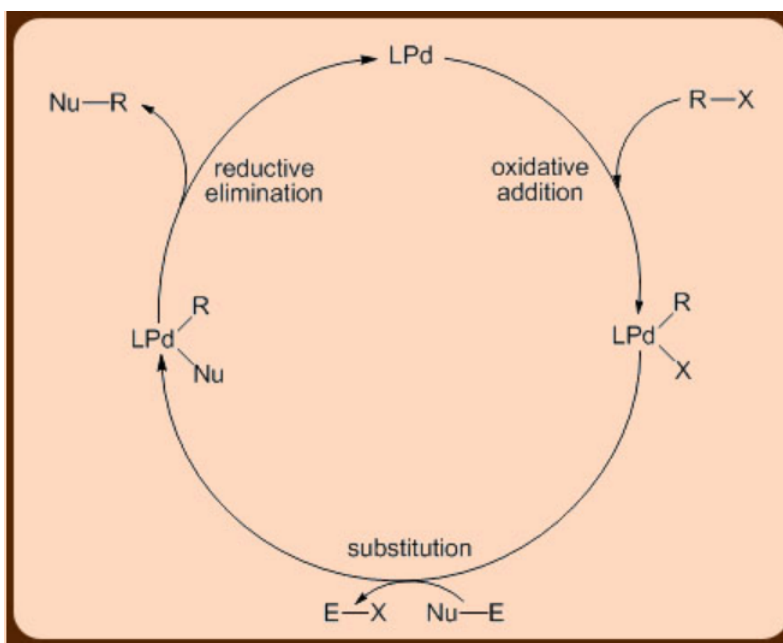


Figure 11.2.2: A general catalytic cycle for the palladium mediated C-C cross-coupling reactions.

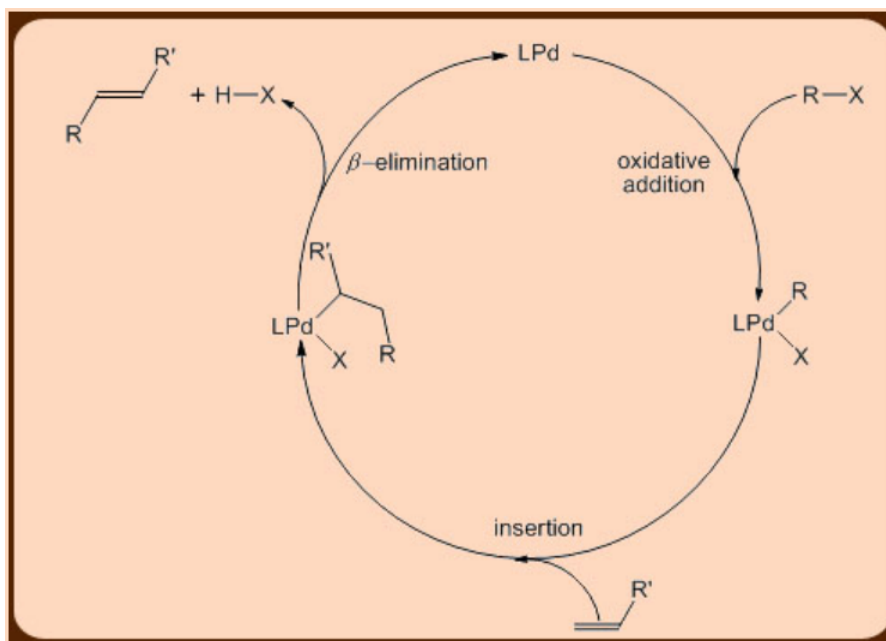


Figure 11.2.3: A catalytic cycle for the palladium mediated Heck coupling reaction.

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.

This page titled [11.2: Homogeneous Catalysis - II](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [M. S. Balakrishna & Prasenjit Ghosh](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.