

## Module 14 : Metathesis

### Lecture 1 : Catalytic Applications of Organometallic Compounds: Alkene Metathesis

#### Objectives

#### In this lecture you will learn the following

- The alkene metathesis reactions and their different variants.
- The application of metal carbenes in alkene metathesis reactions.
- The functional group tolerance, air and moisture sensitivity and high efficiency as important catalyst attributes for the alkene metathesis reactions.

The application of organometallic chemistry in homogenous catalysis is progressively increasing with the fast pace of discovery of new catalysts in the area. The benefits of organometallic catalysis have now percolated to all facets of the chemical world that span from the confines of the industry to the day-to-day small scale use in organic synthesis in academic laboratories. Quite a few of these applications of organometallic complexes in homogeneous catalysis have made a permanent imprint on the ever going developmental process that is constantly transforming our day-to-day life. An example of such a success story is of alkene metathesis, which is described in this chapter.

#### Alkene metathesis

Alkene metathesis reactions are gaining wide popularity in synthesizing unsaturated olefinic compounds as well as the unsaturated polymeric counterparts. Central to this catalysis is a metal carbene intermediate that reacts with olefins to give different olefinic compounds or even the unsaturated olefinic polymers depending upon the reaction conditions of the metathesis reaction. Metathesis is an unusual transformation in which a C=C is broken and also formed during catalysis to generate new unsaturated olefins.



Though a large variety of metal-carbene catalysts have been developed for the metathesis reaction, only a few have been found to be functional group tolerant. Thus a critical step in broadening the utility of metathesis reaction has been in developing catalysts that are functional group tolerant. In this regard, the early-transition metal based carbene catalysts like that of the Ti based ones are highly oxophilic and hence are intolerant to the functional groups. On the other hand, the more electron-rich Mo and W based catalysts are of intermediate character. Finally, the late-transition metal based Ru catalysts are found to be exceptionally tolerant toward functional groups but all the while exhibiting high reactivity toward olefinic bonds. In this context notable are the Grubb's Ru catalyst, which is easy to handle, and the Schrock's Mo catalyst, which display high activity.

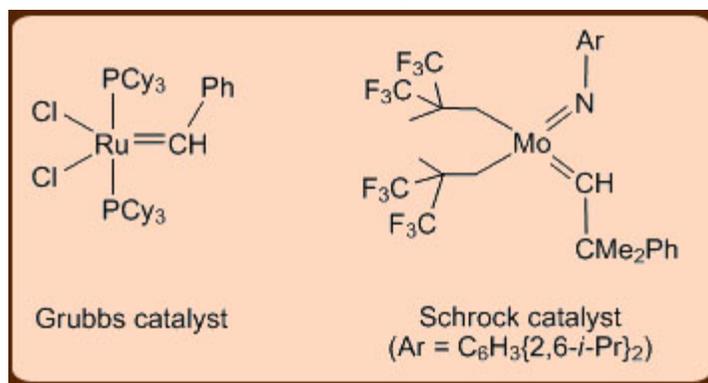
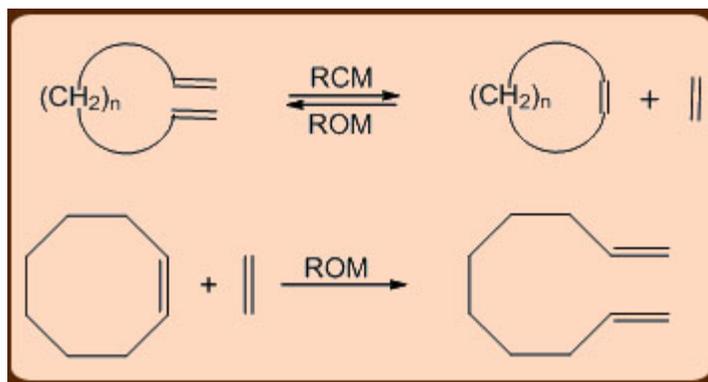


Figure 1. The Grubb's and the Schrock's catalyst.

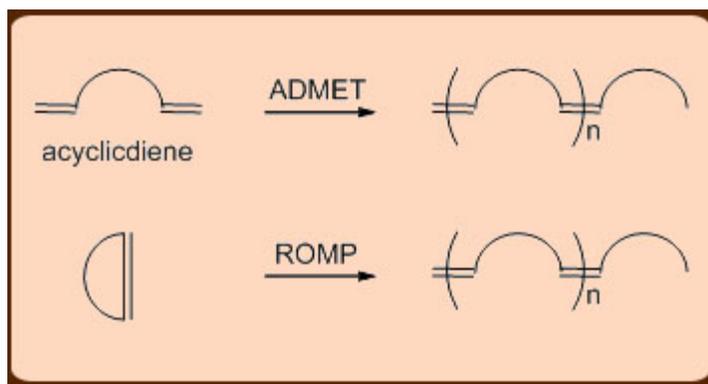
The metathesis reaction as such stands for a family of related reactions all of which involve a "cutting and stitching" of olefinic bonds leading to different unsaturated products. When two different olefin substrates are used, the reaction is called the "cross metathesis" owing to the fact that the olefinic ends are exchanged.



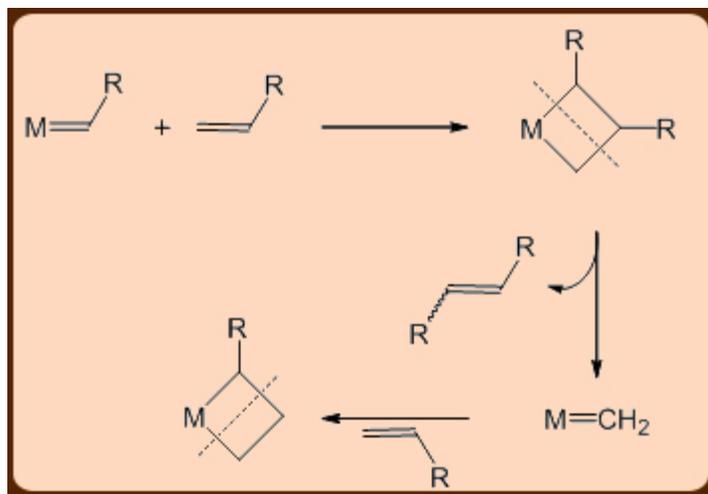
The metathesis reactions can even extend further to the conjugated dienes that can undergo Ring Closing Metathesis (RCM) in systems where the ring strain is not too high in the final product. The reverse of Ring Closing Metathesis (RCM) is called the Ring Opening Metathesis (ROM), and which is usually favored in the presence of large excess of C<sub>2</sub>H<sub>4</sub>.



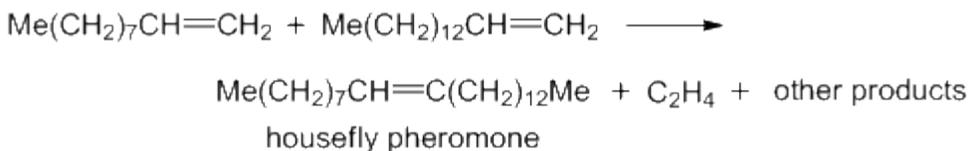
The variants of metathesis often used in producing polymers are, (i) the Acyclic Diene Metathesis (ADMET) and (ii) the Ring Opening Metathesis Polymerization (ROMP), in which the relief of ring-strain of cycloalkenes drives the polymerization reaction forward. Both of these reactions, produce long chain polymers in a living fashion and as a result of which these reactions are useful for producing block copolymers  $-(\text{AAABBB})_n-$ .



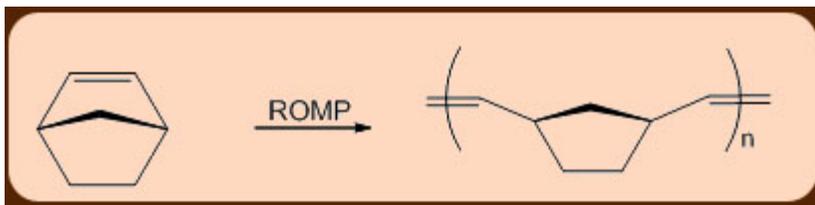
Though several possibilities have been debated for the mechanism of the metathesis reaction, the one proceeding *via* a metalacyclobutane intermediate has gained credence.



Several important industrial applications have emerged out of the metathesis reaction like that of the commercial synthesis of the housefly pheromone.



Similarly, the polycyclopentadiene polymer, which is formed from the Ring Opening Metathesis Polymerization (ROMP) of dicyclopentadiene substrate, is used for bullet proof related applications because of its exceptional strength owing to its cross-linked nature.



## Summary

Alkene metathesis represents a distinct class of related chemical reactions that involve the “cutting and stitching” of olefinic bonds to give unsaturated organic products. Depending upon the nature of the product formed, different type of alkene metathesis reactions exist like the alkene metathesis, cross-metathesis, Ring Closing Metathesis (RCM), Ring Opening Metathesis (ROM), Acyclic Diene Metathesis (ADMET), and the Ring Opening Metathesis Polymerization (ROMP). A commonality that runs through all of these different varieties of the metathesis reaction is its mechanism that involves a catalytically active metal–carbene species. The mechanism is said to be proceed *via* a 4–membered metalacyclobutane intermediate. The alkene metathesis has found important applications in organic synthesis as well as in the chemical industry.