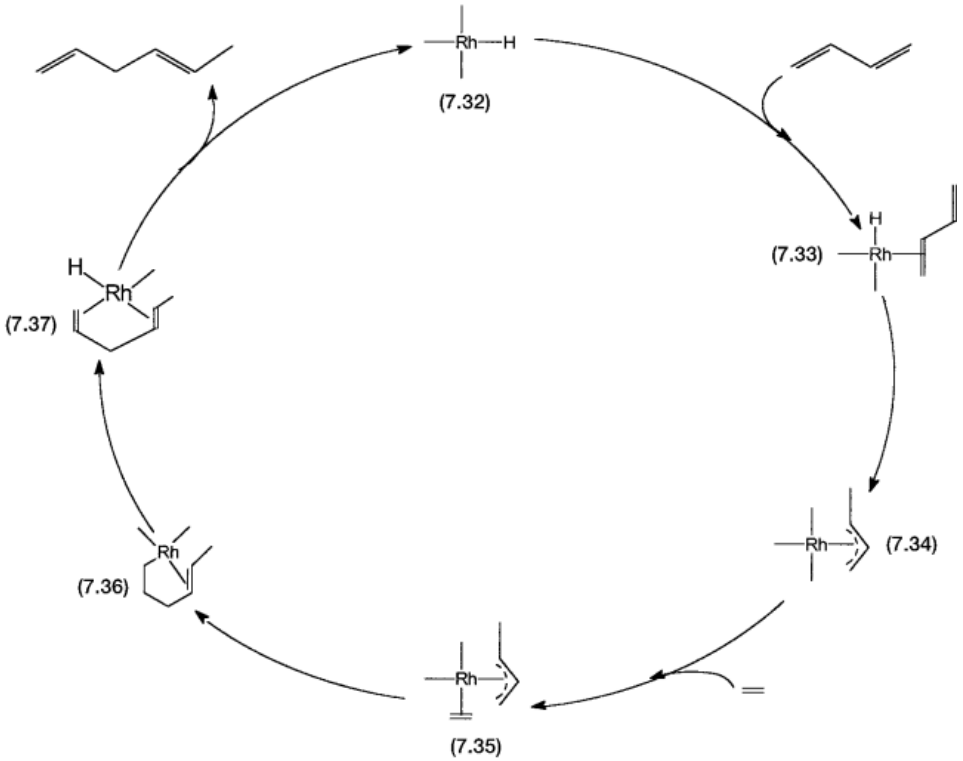
METATHESIS REACTIONS

Alkene metathesis is basically a sequence of reactions in which there is an exchange of C atoms between pairs of double bonds. The reactions mentioned in Fig display only a few representative examples. 7.10. 7.10. The industrial use of metathesis reactions to date has been restricted mainly to the exchange of metathesis (Fig. 7.10, top, backward reaction) as in the SHOP process, and the polymerization of ring-open metathesis (ROMP). Nearly all industrial processes involve heterogeneous catalysts based on metathesis reactions. These are produced by promoting the high oxidation state of molybdenum, tungsten, or rhenium on an inorganic help such as alumina. Hercules recently reported a liquid-phase process involving a Ziegler type of ruthenium-based catalytic system for the development of a specialty polymer made from dicyclopentadiene.

The value of homogeneous catalytic systems as applied on a laboratory scale is that they have a detailed understanding of the mechanism of metathesis at a molecular level. All metathesis reactions have a mechanism consisting of three basic steps. The first step is the formation of metal–alkylidene complexes. The second step is the formation of metallocyclobutanes. The third step is the opening of the metallocyclobutane rings, which leads to product formation.



The alkylidene species 7.38 or 7.40 is formed by precatalyst M reactions, with the two hypothetical alkenes. The most likely way this will happen is by metal-alkyl formation followed by some β-elimination, as reaction 7.11 indicates. The thus produced primary alkylidiene species that undergo reactions 7.12 and 7.13. The alkenes that are generated in reaction 7.12 and 7.13 are obviously not the products of the catalytic cycle; they are generated only initially when the

precatalyst is converted into the active catalytic intermediates. Note that similar pathways involving the other alkene also exist

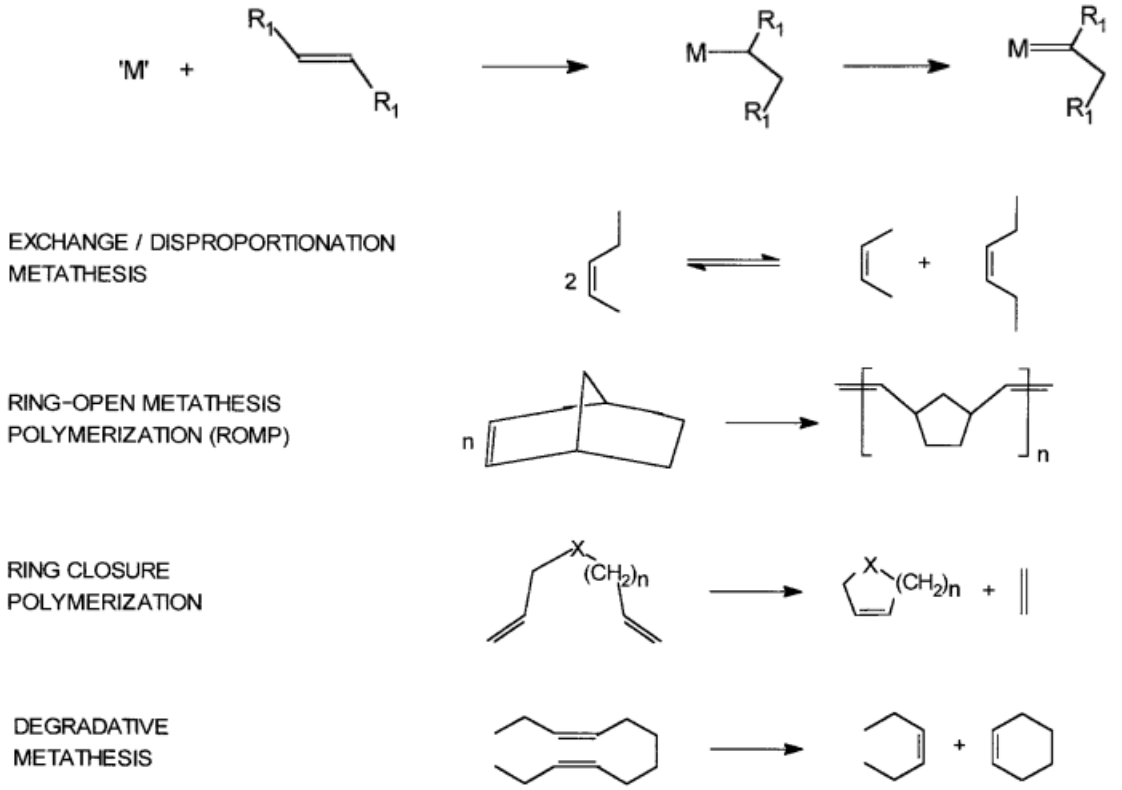


Figure Different types of metathesis reaction. The first two have found significant use in industry.

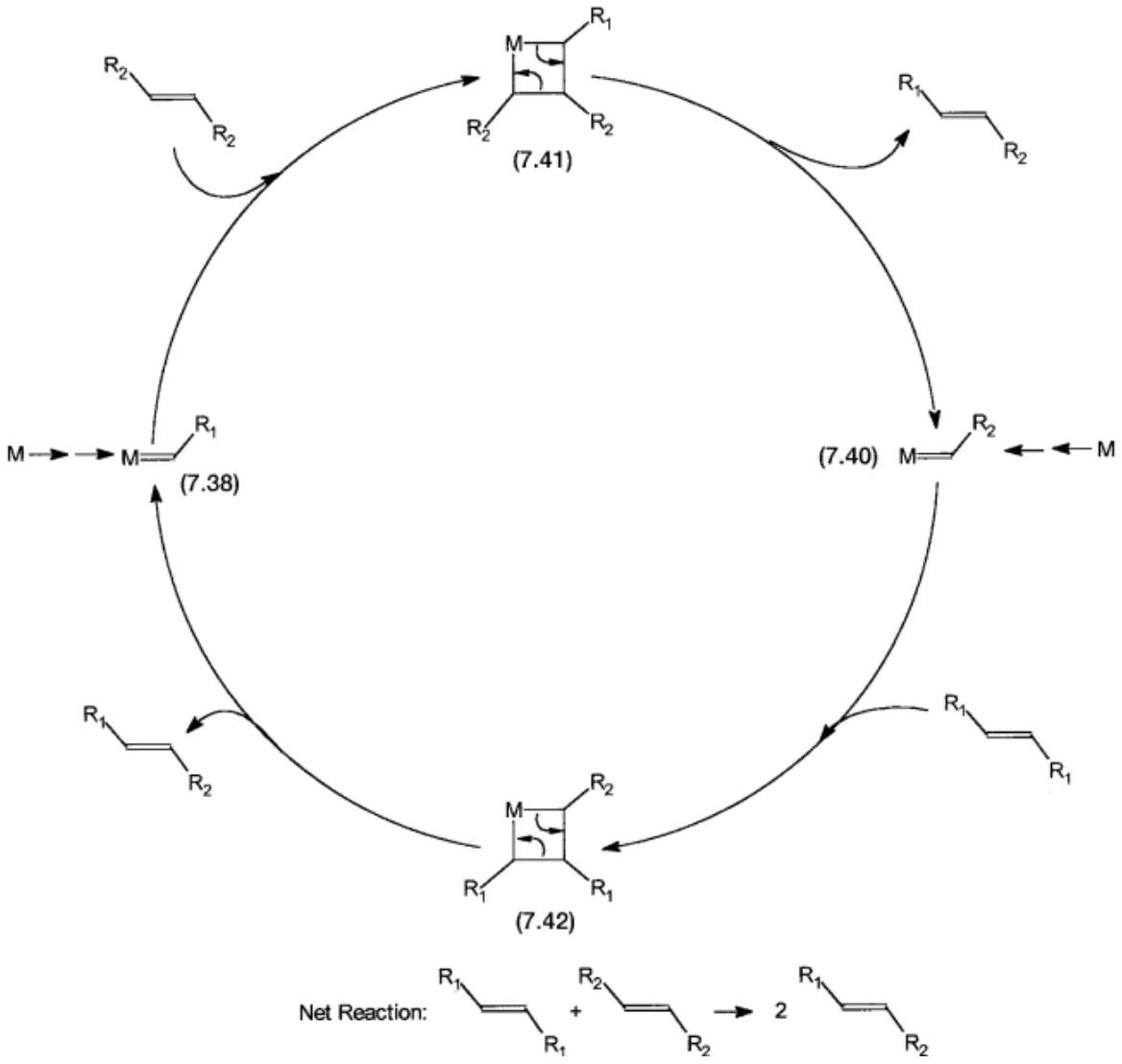


Figure A general cycle for alkene metathesis. Note that both the carbenes 7.38 and 7.40 can catalyze the metathesis reaction.