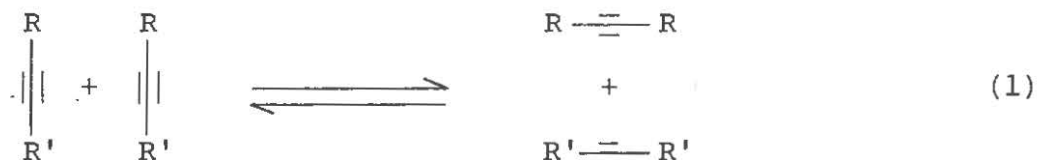


ALKYNE METATHESIS REACTIONS

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Literature Seminar

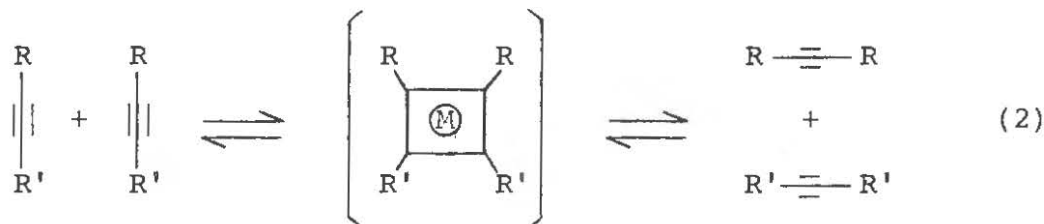
November 10, 1983



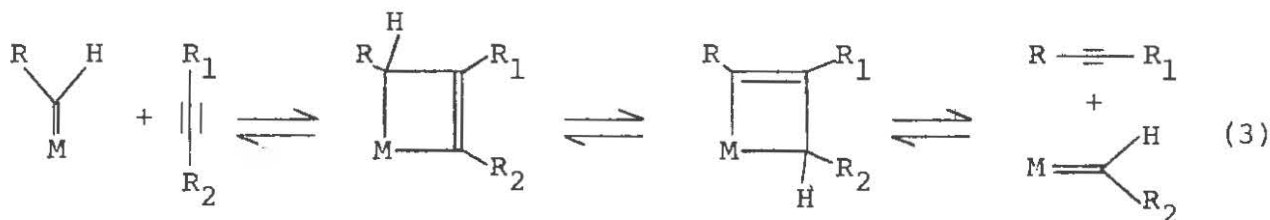
The first alkyne metathesis reactions (Fig. 1) were reported by Pennella [1] in 1968. Since then a limited number of heterogeneous and homogeneous catalytic systems have been found. The heterogeneous catalytic systems, such as $\text{MoO}_3/\text{SiO}_2$ and WO_3/SiO_2 [1-5], also function as olefin metathesis catalysts, but the conditions for these reactions are normally harsher than the related olefin reactions. In homogeneous catalytic systems, Mortreux [6-8] has observed that $\text{Mo}(\text{CO})_x\text{L}_y\text{-PhOH}$ combinations and $\text{O}_2\text{Mo}(\text{acac})_2\text{-AlEt}_3\text{-PhOH}$ combinations catalyze alkyne metathesis while Schrock [9-11] has observed similar reactions with tungsten alkylidyne complexes.

The homogeneous systems have been investigated more thoroughly than the heterogeneous systems. A number of mechanisms for this reaction have been suggested. These include the following (Eq. 2-5):

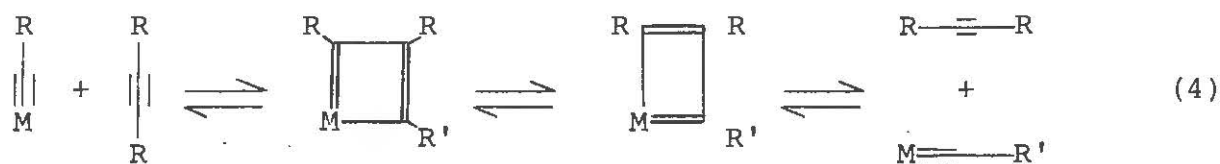
A. Cyclobutadiene Complex Intermediates [1]



B. Metal-carbene and Metallacyclobutene Intermediates [8]

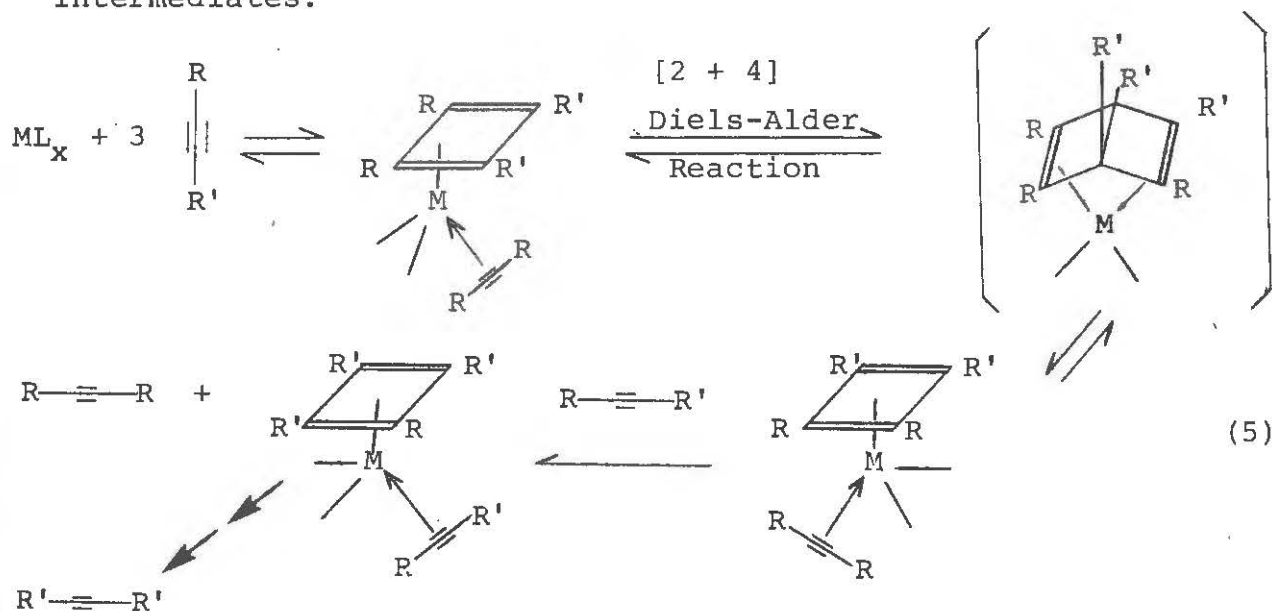


C. Metal-carbyne and Metallacyclobutadiene Intermediates [12]



The preparation and reactivities of cyclobutadiene-metal complexes reported by Hubel [13] and Criegee [14-16] suggest that another mechanism for alkyne metathesis might also be possible:

D. Diels-Alder Reactions on the Acetylene Cyclobutadiene Complex Intermediates.



Some catalysts (eg. $(\text{Bu}^t\text{O})_3\text{W}(\text{C}^t\text{Bu}^t)$ and $\text{O}_2\text{W}(\text{acac})_2\text{-AlEt}_3\text{-PhOH}$) show outstanding activity (300 turnovers/min) and selectivity (97% alkyne products) suggesting that alkyne metathesis may become a viable process in industry. However, the exact mechanism is still open to much speculation. It appears that the mechanism may be dependent on the specific reaction system, such as the specific catalyst and alkynes being utilized. The details remain a considerable challenge to organometallic chemists.

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