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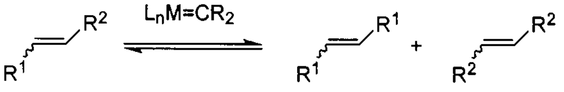
Foreword

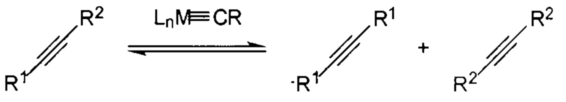
The formation of carbon–carbon double and triple bonds is one of the fundamental processes in organic as well as in organometallic chemistry. Conceptually, the formation of an unsaturated C–C bond can arise either by functional group manipulation, most notably by elimination to give carbon–carbon double/triple bonds, or by the coupling of two separate units. In ‘classic’ organic synthesis this is achieved by the Wittig reaction, by Peterson olefination, or by the addition of an organolithium/organomagnesium reagent to a C=O double bond followed by dehydration.

Organometallic chemistry now offers dramatically new and very efficient solutions to the old problems of double and triple bond formation by utilizing the ‘Metathesis’ reaction. In Olefin and Alkyne Metatheses, an equilibrium between three alkenes or three alkynes is established by using metal–carbene or metal–carbyne complexes as catalysts. Through judicious choices of the starting materials it is possible to obtain a single product in high yield, either by efficient removal of a volatile coproduct or by irreversible ring opening of a strained monomer/substrate. The development of these new and powerful catalyst systems began with Schrock’s tungsten carbene and carbynes and was recently expanded by Grubbs to ruthenium complexes. These catalysts are much more functional group tolerant, and are largely air and water stable. Very recently, nucleophilic carbenes of the Wanzlick type have become important as spectator ligands in the ruthenium carbene complexes utilized in alkene metathesis. This very interesting discovery was made by Herrmann and is now exploited on a wide scale. These developments taken together, show how the field of alkene metathesis has matured and developed into an indispensable reaction in the toolbox of modern organic, organometallic, and polymer chemists.



Olefin Metathesis

In contrast to the relative maturity of alkene metathesis, alkyne metathesis has only recently begun to attract attention, even though the process was discovered 26 years ago by Mortreux and was studied by Schrock and Bazan, who until recently provided the only examples of preparative scale alkyne metatheses. Alkyne metathesis has developed during the last two years into two different branches, both of which are represented in this issue. Fürstner has used and developed ‘high-tech’ catalyst systems based upon Schrock’s and Cummins’ types of compounds. These catalysts have very high activities and excellent functional group tolerance, but have to be made in multistep syntheses. They are also very sensitive toward air and moisture which makes their use a substantial investment. On the other hand, there are now the simple catalyst systems formed from molybdenum or tungsten hexacarbonyl and various phenols. These catalysts are formed in situ by using ‘off-the-shelf’ solvents. They were originally discovered by Mortreux, were used by Mori, and have been brought into high efficiencies by Bunz. The extreme simplicity of their application is paid for by the need for higher reaction temperatures and decreased functional group tolerance, but this is not necessarily a problem.



Alkyne Metathesis

This issue “Catalytic Metathesis of Organic Compounds” shows the very exciting and truly international cross section of the use and development of metathesis reactions in the formation of novel materials, polymers, natural products, raw materials for perfumes, and unusual organometallic topologies. Authors from the US, France, the UK, Germany, Belgium, the Netherlands, and Italy have contributed to this timely issue. The amazing breadth and applicability of the metathesis reaction is one of the surprising developments in this

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relatively new field. Unforeseeable only 10 years ago, it is now a well-documented science. In this issue the frontiers of organic metathesis are clearly revealed by many of the key players in the field. It is exciting to see what the early 21st century will bring out in this rich and very active field of research.

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Description of Cover Graphic

The cover page shows a structural diagram of the cation $[\mathrm{Ru{=}CH{-}CH{=}C(CH_3)_2(NCCH_3)(^tBu_2PCH_2P^tBu_2)Cl}]^+$. The catalytic ring opening metathesis polymerization (ROMP) activity of neutral Grubbs-type carbene complexes can be drastically enhanced by chloride instead of phosphine dissociation from appropriate *cis*-phosphine precursors. Solvent coordinated, monomeric ruthenium(II) carbene cations are presumed to be catalyst resting states. The ORTEP plot depicts an isolated monomeric acetonitrile adduct relevant to the mechanism of olefin metathesis. See report by Hofmann et al. in this issue for more details.