concentration of 60 ppm in the carbonaceous chondrites, which are 3% of all meteorites) have reached the earth, with 6×10^5 million tons arriving during a period when the earth was cold enough for the persistence of the amino acids.[2] Therefore, it seems possible that during development of life the earth was covered with matter (dust, meteorites, or comets) that stemmed from a region that was exposed to circularly polarized irradiation. The thus resulting enantiomeric excess of the amino acids might have tipped the scales towards the development of life. The global enantiomeric excess on earth—from racemization and dilution—was certainly less than in the meteorites. Bailey et al. guess that it might have been in the range of 5×10^{-3} to 10^{-7}% *ee*, and eventually higher in the vicinity of meteorite impacts.[5] These enantiomeric excesses are larger by orders of magnitudes than those explainable by the parity violation (10^{-17}%) or by stochastic effects.[1, 5] From this mechanism one might find molecules with opposite homochirality in other regions of the universe, depending on the polarization of the radiation.

Undoubtedly many questions on this topic are still unanswered and arguments are far from closed. Nevertheless, the herein presented perceptions possibly give new ideas as to where life might have originated.

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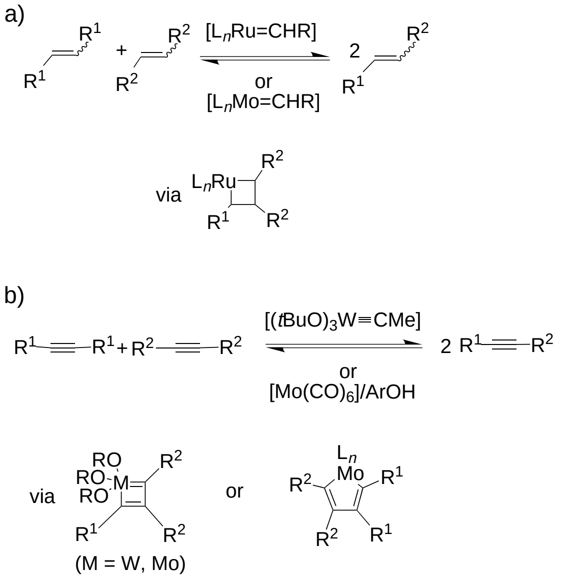
Alkyne Metathesis as a New Synthetic Tool: Ring-Closing, Ring-Opening, and Acyclic

Uwe H. F. Bunz* and Lioba Kloppenburg

In recent years alkene metathesis (Scheme 1a) has firmly established itself in the "tool box" of the organic chemist, and it is increasingly replacing other methods of C=C bond formation such as the Wittig reaction or the McMurry coupling. Schrock[1] and Grubbs[2] have developed active and efficient catalysts for metathesis which are commercially available and thus have made a major contribution to the spectacular success of this method in the preparation of complex natural products and novel materials. Recent reviews by Blechert[3a] and Fürstner[3b] summarize current developments in this area. An additional and important commercial aspect of the continuing interest in homogeneously catalyzed alkene metathesis is its potential for the synthesis of highly cross-linked polymers.[4]



Scheme 1. a) Alkene metathesis; b) alkyne metathesis.

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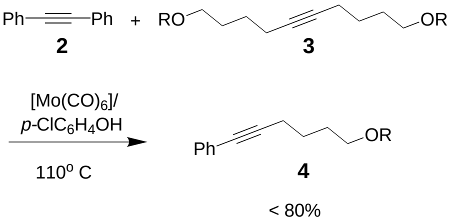
Basic Concepts

Until now, *alkyne* metathesis (Scheme 1 b) has remained in the shadow of alkene metathesis. The first example of a homogeneously catalyzed metathesis reaction of a C–C triple bond, described by Mortreux et al., was the statistical disproportionation of 4-methyltolan to tolan and 4,4′-dimethyltolan with a [Mo(CO)$_6$]/resorcinol catalyst formed in situ.[5] Attempts to convert terminal alkynes by metathesis were unsuccessful with this catalyst system. Instead, cyclotrimers and polymers of unknown constitution were isolated. However, the defined Schrock carbyne complex [(tBuO)$_3$-W≡CtBu] (**1**; see below) exhibits a certain activity in the metathesis of readily available terminal alkynes, where metathesis is accompanied by the evolution of gaseous acetylene during the first minute of the reaction. It has, however, not yet been possible to suppress the main reaction, which leads to the polymerization of the alkyne with the formation of polyacetylenes. If diethyl ether is used as solvent, the yield of metathesis product is about 90 %, although conversion is low (ca. 15%, 1-heptyne →6-dodecyne+$C_2H_2\uparrow$). This otherwise attractive variant (readily accessible substrate) suffers from the restriction of low conversion, and requires further development.[6]

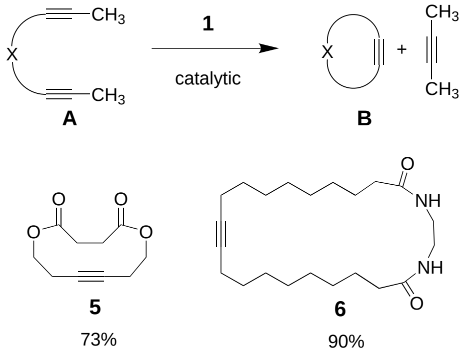
The metathesis of dialkylalkynes can be carried out photochemically at room temperature with catalyst systems that are generated in situ if both *meta*-chlorophenol and [Mo(CO)$_6$] are present in the reaction solution.[7] The catalytically active species in all these (thermally and photochemically activated) systems is unknown. However, experiments by Schrock, who prepared defined molybdenum-alkylidynes in 1984, suggest that the Mortreux catalysts may have a similar structure.[8] Analogously, the tungsten–carbyne complex **1**, obtained by Schrock in a multistep synthesis, is thermally stable, highly sensitive to water and atmospheric oxygen and is likewise superbly active in the metathesis of disubstituted alkynes.

Applications to Organic Synthesis

In 1995 Mori investigated the cross-metathesis of **3** with an excess of tolan (**2**, 11 equiv) in the presence of a Mortreux-type catalyst [Mo(CO)$_6$]/*para*-chlorophenol. She found that the corresponding mixed alkynes **4** are formed in yields of 50–80 %. The great advantage of catalysts that are prepared in situ is this simple experimental set up, which unfortunately did not always proceed in good yields.[10]



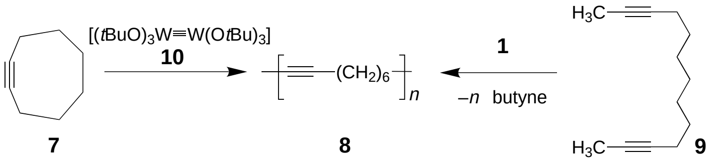
In a spectacular report, Fürstner[11] showed recently that functionalized diynes of type **A** could be converted in good yields into the corresponding macrocycles **B** (12- to 28-membered rings) with the concomitant expulsion of butyne (*r*ing-*c*losing *a*lkyne *m*etathesis, RCAM). Typically, however, high dilution conditions had to be employed to guarantee an efficient ring closure of **A**. The substrates used in this work carried either one or two ester groups (for example, the formation of **5**), but it was also possible to cyclize a bisamide to the macrocyclic lactam **6** in 90 % yield. This is a) the first published case of a ring-closing alkyne metathesis (for the identification of *meta*-coupled cyclophenylene-ethynylenes see reference [12]), and also b) an example of the unexpected compatibility of the tungsten–carbyne complex **1** with both polar ester groups and the amide functionalities in the lactam **6** and its precursors. Similar behavior, which underscores the excellent compatibility of Schrock carbyne complexes with ester groups, had been demonstrated previously by Weiss with the synthesis of the carbyne complex [EtO$_2$CC$_6$H$_4$C≡W-(OtBu)$_3$].[12]



According to Fürstner and Seidel, the RCAM method is valuable for the synthesis of cyclic alkenes, since the alkyne units can be converted stereoselectively into the corresponding *Z*- or *E*-alkenes by hydroboration and subsequent protonation, as well as by other methods.

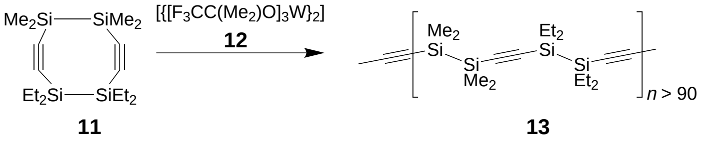
Polymers

Ring closing and ring opening are two sides of the same coin, so it is not surprising that ring opening of cycloalkynes by alkyne metathesis has been investigated. Schrock and Krouse[13] polymerized the strained cycle **7** by ring opening utilizing the catalyst precursor **10**, and obtained the almost insoluble elastomer **8**. The wide molecular weight distribution $M_w/M_n > 4$ suggests that this polymerization cannot be regarded as "living"; that is, initiation occurs only sluggishly, or, as is often observed in polymerizations by ring opening, the polymer already formed is partially degraded catalytically to form cyclooligomers. Schrock was able to demonstrate that the reaction of **7** with stoichiometric amounts of the dimer **10** takes place with the formation of well-defined carbyne complexes that can be detected by NMR spectroscopy. The corresponding polyoctynamer **8** can be obtained by ring-opening metathesis polymerization (ROMP) of **7** as well as by

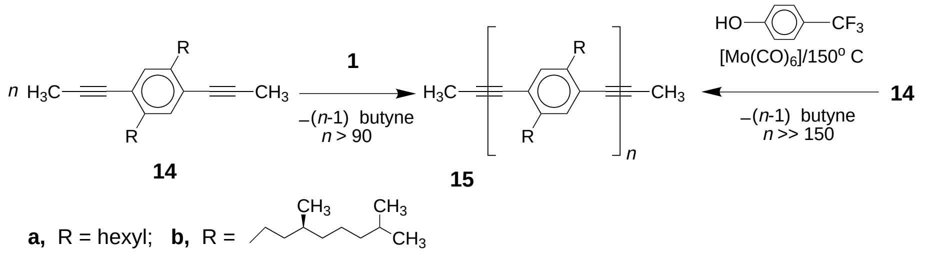


facile *a*cyclic *di*yne *met*athesis (ADIMET) of 2,10-dodecadiyne catalyzed by **1** under concomitant loss of 2-butyne.[14]

A further application of ring-opening alkyne metathesis has since been reported by Bazan,[15] who polymerized the somewhat exotic but stable cyclodiyne **11** stereospecifically to the head-to-tail coupled product **13** by employing catalyst precursor **12**. According to the authors, replacement of a methyl group in **10** by a trifluoromethyl group (**12**) is necessary to obtain a catalyst with increased activity. The silane polymer **13** becomes conducting when it is treated with SbF$_5$, and this semiconductor is also claimed to exhibit attractive optical properties.



In general, it should be possible to prepare completely conjugated organic polymers of the poly(*p*-phenyleneethynylene) (PPE) type **15** with the ADIMET reaction.[14] It has been shown that the ADIMET reaction of **14** to **15** is catalyzed by **1**, and the polymer **15a** (R = hexyl) is obtained in 68% yield and with a degree of polymerization *n* of greater than 90 and a M_w/M_n (polydispersity) value of 2.[14] This molecular weight distribution suggests that the reaction is a classical polycondensation. Only propynyl groups are present as end groups in **15a** when it is prepared by metathesis, which was demonstrated by model experiments and NMR studies. The ADIMET reactions are superior to classical Pd-catalyzed couplings in amine solvents[16] since not only is a higher degree of polymerization obtained, but the typical problems that are associated with the removal of Pd and phosphane-containing catalyst residues and the occurrence of butadiyne defect structures are elegantly avoided.[17] Owing to their extremely high fluorescence quantum yields, their thermal stability at temperatures of up to 200°C, and, with suitable substitution, their excellent solubility in organic solvents, PPEs are attractive potential emitter layers in light-emitting devices (LEDs)[18] for electroluminescent applications as organic "plastic" lasers,[17] and polarizers in liquid crystal display screens.[19] To circumvent the tedious synthesis of the carbyne complex **1** in the ADIMET reaction of **14**, and to develop a simple route to **15**, we treated monomer **14** with a modified Mortreux catalyst system prepared from *para*-trifluorocresol and [Mo(CO)$_6$] at 150°C.[20] The butyne formed during the reaction was removed from the reaction solution with a stream of nitrogen. The alkyl-substituted PPEs **15** were usually formed in quantitative yield. In a particularly good example we were able to show that chiral **14b**, doubly substituted by 3,7-dimethyloctyl groups, gave a highly soluble, optically active PPE (**15b**) with a degree of polymerization *n* of 150 or more. The big advantage of these catalyses lies in the application of commercially available catalyst precursors in solvents used without further purification or drying.



The highly promising developments described in this article should ensure that alkyne metathesis will emerge in the near future as an efficient method in both the arsenal of the organic chemist and in polymer synthesis. Alkyne metathesis will prove to be a useful complement and augmentation of the popular Cu- and Pd-catalyzed coupling reactions in alkyne chemistry. The efficient metathesis of terminal alkynes,[6] the reversibility of alkyne metathesis, which could lead to the degradation of polymers with integrated triple bonds, and the question of whether alkyne metathesis can be carried out efficiently in water as an environmentally friendly solvent, are important but poorly (if at all) investigated aspects of this fascinating reaction.

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Keywords: alkynes · carbyne complexes · metathesis · ring-opening polymerization

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