Diyne Metathesis

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Catalytic Metathesis of Conjugated Diynes**

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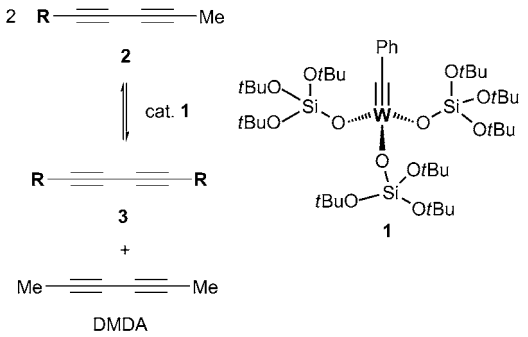
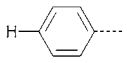
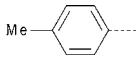
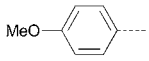
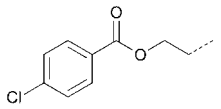
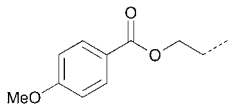
Alkyne metathesis has recently witnessed a significant growth in the number of homogeneous catalysts that are able to efficiently promote the formation and cleavage of carbon–carbon triple bonds.[1,2] All well-defined catalyst systems reported to date can be regarded as variants of Schrock-type molybdenum(VI) or tungsten(VI) alkylidyne complexes[3] in which the metal–alkylidyne moiety, M≡C–R, is supported by alkoxide,[4] arlyoxide,[5] amido,[6] imidazolin-2-iminato,[7] phosphoraneiminato,[8] or silanolate ligands.[9,10] With a few exceptions,[11] alkyne metathesis usually requires the presence of internal alkynes, such as RC≡CMe (R = alkyl or aryl), affording the symmetric alkynes RC≡CR and MeC≡CMe. To drive these equilibrium reactions to completion, the latter, 2-butyne (b.p. = 27 °C), can be continuously removed from the reaction mixtures under vacuum-driven conditions or, as recently shown by Fürstner and co-workers, advantageously by addition of molecular sieves (5 Å M.S.) to adsorb 2-butyne.[9,12] For our part, the molecular-sieve-promoted method was also clearly superior when alkyne homocoupling and ring-closing alkyne metathesis (RCAM) reactions were studied in the presence of catalytic amounts of the tri(*tert*-butoxy)silanolate-supported tungsten benzylidyne complex **1** (Scheme 1).[10]



Scheme 1. Metathesis of diynes catalyzed by **1**. For a definition of the R groups, see Table 1; DMDA = dimethyldiacetylene.

With this highly active alkyne metathesis catalyst at hand, we became interested in the metathesis of conjugated diynes of the type RC≡C–C≡CMe (**2**), which could potentially lead to symmetric triynes RC≡C–C≡C–C≡CR[13] if 2-butyne was likewise formed. Therefore, we initially exposed 1,3-pentadiyn-1-ylbenzene **2a** (R = Ph) to our standard alkyne metathesis (Table 1) by stirring a toluene solution (4 mL) of **2a** (1.0 mmol) and the catalyst **1** (2 mol %) for two hours at room temperature in the presence of activated 5 Å molecular sieves. The conversion was monitored by gas chromatography and, after full consumption of **2a**, the reaction mixture was filtered through alumina. Evaporation of the solvent afforded a white solid, the spectroscopic characterization of which indicated, much to our surprise, almost quantitative formation of 1,4-diphenyl-1,3-butadiyne (**3a**) instead of the anticipated triyne.[14] Clearly, the isolation of **3a** requires the formation of 2,4-hexadiyne (dimethyldiacetylene, DMDA)[15] in equal amounts (Scheme 1), which is likely to be adsorbed by the molecular sieves. Its formation could be unambiguously confirmed by performing the metathesis of **2a** at room temperature under vacuum-driven conditions (0.1 mbar) in 1,2,4-trichlorobenzene solution. The reaction flask was connected to a cold trap (liquid N_2), and volatile DMDA was collected by sublimation.[15] Under these conditions, **3a** could be isolated in 82 % yield, indicating again the preferability of the molecular-sieve-promoted method.

Table 1: Diyne metathesis of R-C≡C–C≡C-Me (**2**) catalyzed by **1**.[a]

Reagent	Product R-C≡C–C≡C-R	R	Yield[b] [%]
2a	**3a**		97
2b	**3b**		95
2c	**3c**		97
2d	**3d**		95
2e	**3e**		96
2f	**3f**		80[c]

[a] Conditions: Substrate (1.0 mmol), catalyst **1** (21 mg, 2 mol %), toluene (4 mL), 5 Å M.S. (1.0 g), room temperature, $t = 2$ h. [b] Yield of product isolated after filtration through alumina and purification by column chromatography (if required). [c] The decreased yield arises from the volatility of **3f**.

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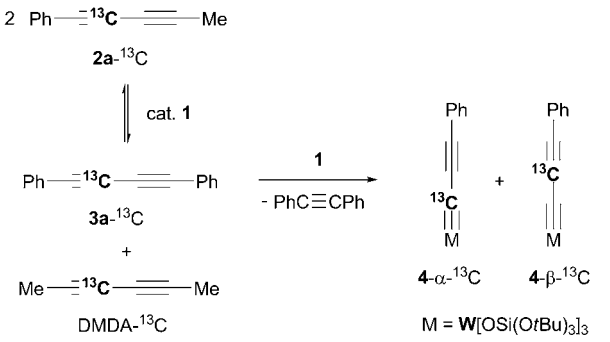
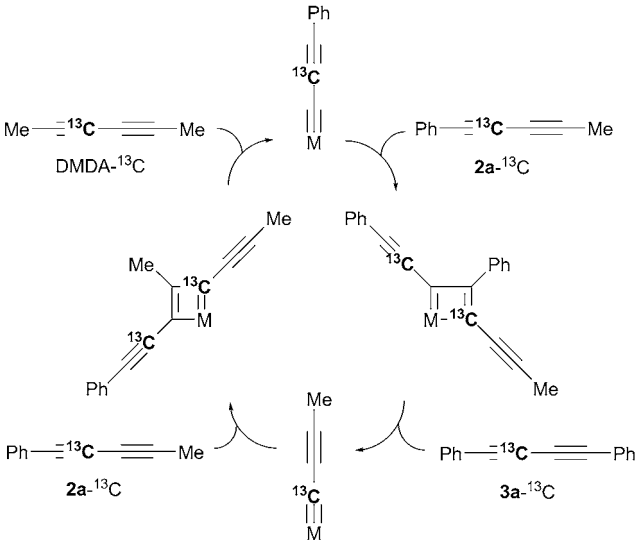
At first glance, the conversion of **2a** into the symmetric diyne **3a** and DMDA might suggest that the metathesis proceeds by an exchange of the alkynyl groups by C–C activation[16] and cleavage of the internal carbon–carbon single bond, similar to the mechanism established for the titanocene-mediated and photocatalyzed cleavage and recombination of disubstituted butadiynes.[17] In the presence of the alkylidyne complex **1**, however, such a mechanism is clearly unlikely, and metathesis should proceed by exchange of the alkylidyne groups by the formation of metallacyclobutadiene intermediates according to the established mechanism.[7c,18] To unequivocally preclude C–C σ-bond metathesis, the ^{13}C-labeled pentadiyne **2a**-^{13}C was synthesized from the corresponding phenylacetylene, PhC≡^{13}CH, and subjected to catalytic alkyne metathesis.[13] Under the conditions described above, the product PhC≡^{13}C–C≡CPh (**3a**-^{13}C) was isolated in high yield and shown by mass spectrometry and ^{13}C NMR spectroscopy to contain only one ^{13}C atom residing exclusively in the 2-position (Scheme 2).[19] Accordingly, the absence of any detectable amounts of the doubly ^{13}C-labeled butadiyne PhC≡^{13}C–^{13}C≡CPh rules out a mechanism involving alkynyl group exchange.



Scheme 2. Metathesis of the ^{13}C-labeled diyne **3a**-^{13}C and formation of ^{13}C-labeled phenylalkynylalkylidyne complexes.

To substantiate a possible mechanism for the observed diyne metathesis, the ^{13}C-labeled product **3a**-^{13}C was treated with an equimolar amount of **1** in C_6D_6. The ^{13}C NMR spectrum indicated full conversion into the phenylalkynylalkylidyne complexes **4**-α-^{13}C and **4**-β-^{13}C and unlabeled diphenylacetylene (tolane). The M≡^{13}C–C≡C and M≡C–^{13}C≡C signals in the NMR spectrum are found at 252.3 and 95.8 ppm, with the tungsten satellites revealing coupling constants of $^1J(^{13}C–^{183}W) = 298.1$ Hz and $^2J(^{13}C–^{183}W) = 60.5$ Hz, which is in very good agreement with the values reported for the quinuclidine adduct of the related complex [(*t*BuO)$_3$W≡C–C≡C–Et].[20,21] Furthermore, the signals for C_α and C_β are flanked by carbon satellites, revealing a $^1J(^{13}C–^{13}C)$ coupling constant of 94.6 Hz. Isolation of **4** on a preparative scale was however not achieved, as slow conversion into other reaction products, presumably dinuclear species, was observed.[20,22]

In view of the rapid formation of alkynylalkylidyne species such as **4**, we favor the mechanism outlined in Scheme 3, which involves metallacyclobutadiene intermediates bearing the alkynyl groups exclusively in the α-positions. As shown, this mechanism allows us to rationalize the exclusive formation of the monolabeled diyne **3a**-^{13}C, while DMDA-^{13}C is adsorbed on 5 Å M.S. It should be noted, however, that an alternative catalytic cycle with β-alkynylmetallacyclobutadiene species can also account for these observations (see the Supporting information).[14] At the present stage, an unambiguous decision in favor of one of these mechanisms, or another one altogether, is not possible and requires additional experimental and theoretical support.[23]



Scheme 3. Proposed catalytic cycle for the metathesis of diynes.

To study the scope of the new diyne metathesis reaction, *para*-(1,3-pentadiyn-1-yl)toluene (**2b**) and *para*-(1,3-pentadiyn-1-yl)anisole (**2c**) were synthesized and subjected to the standard metathesis (Table 1). For both substrates, the reaction was completed within less than one hour, and Figure 1 shows a representative conversion–time diagram

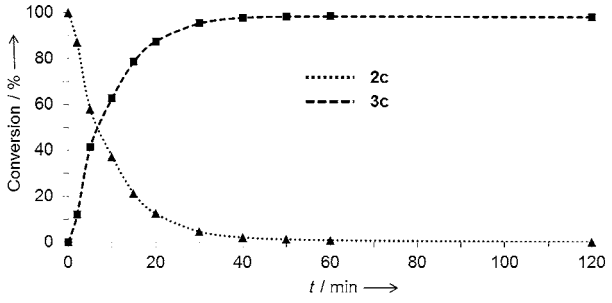


Figure 1. Conversion–time diagram for the metathesis of **2c**. For reaction conditions, see Table 1.

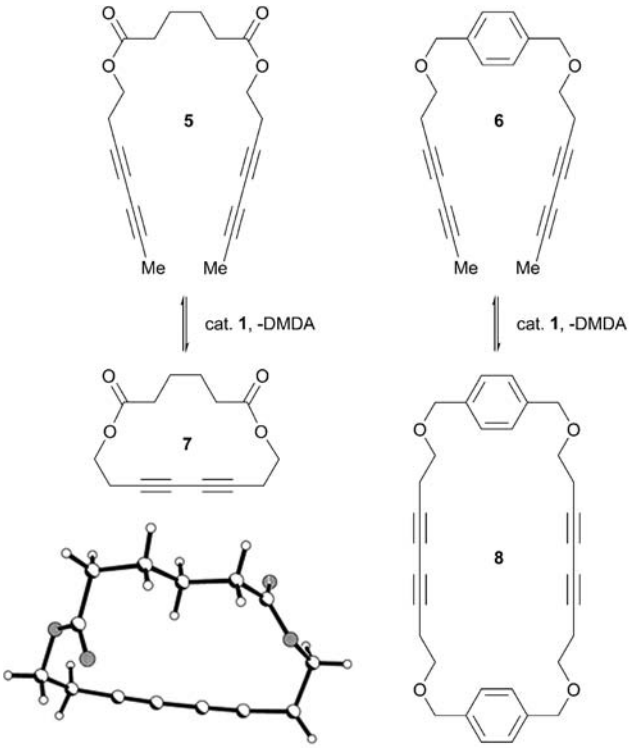
for the metathesis of **2c**. It should be emphasized that prolonged reaction times ($t > 3$ h) afford lower yields of **3b** and **3c**, as trace amounts of other species such as the corresponding mono- and triacetylenes are formed, as indicated by GC/MS analysis and ^{13}C NMR spectroscopy.

Along with the arylpentadiynes **2a**–**2c**, the homocoupling of the aliphatic 3,5-heptadiyn-1-yl benzoates **2d** and **2e** was studied under the same reaction conditions. The dibenzoates **3d** and **3e** were isolated as white crystalline solids in excellent yield (Table 1), confirming the functional group tolerance that had previously been established for catalyst **1**.[10] Compatibility with the trimethylsilyl group was also found by cleanly converting 1-trimethylsilyl-1,3-pentadiyne (**2f**) into 1,4-bis(trimethylsilyl)butadiyne (**3f**). The slightly reduced yield (80%) can be attributed to the volatility of **3f** and its loss during solvent evaporation.

Admittedly, several arguments could be raised to question the usefulness and applicability of the newly discovered diyne metathesis reaction: 1) The preparation of the symmetric diynes **3** (Table 1) by metathesis is not an atom-economic transformation, as stoichiometric amounts of 2,4-hexadiyne are formed; 2) the diyne substrates **2** have to be synthesized in a rather elaborate manner, for example by treatment of terminal alkynes with EtMgBr followed by reaction with propargyl bromide and isomerization;[14] 3) copper-mediated transformations, such as Glaser, Eglinton, or Hay coupling of terminal alkynes usually provide a convenient and direct access to symmetric diynes and polyynes.[24] In the latter reactions, however, C–C bond formation proceeds irreversibly, which limits the development of high-yielding procedures for the construction of macrocyclic diyne or oligo(diyne) scaffolds.[24,25] In contrast, the reversibility of carbon–carbon triple-bond formation by catalytic ring-closing diyne metathesis (RCDM) offers, similarly to conventional RCAM,[7b] the possibility of synthesizing cyclodiynes under thermodynamic control, providing the potential for increased selectivity in macrocyclic product formation.[26]

Thus, the bis(diynes) **5** and **6** were prepared by esterification or etherification of 3,5-heptadiyn-1-ol with adipoyl dichloride or 1,4-di(bromomethyl)benzene, respectively, and subjected to catalytic diyne metathesis under similar conditions as described above, albeit at significantly higher dilution (Scheme 4). In the case of **5**, the cyclic adipate **7** was isolated as a white crystalline solid in 90% yield. Characterization by NMR spectroscopy and gas chromatography indicated the selective formation of monomeric **7**, which could be qualitatively confirmed by X-ray diffraction analysis. However, the crystal structure suffers from modulation; the apparent cell contains twelve independent molecules, and refinement is unsatisfactory. The exact nature of the modulation has not yet been established.

Under similar conditions, RCDM of **6** afforded the bis(diyne) **8** as a crystalline white solid in 80% yield after chromatographic purification. Single crystals of **8** suitable for X-ray diffraction analysis were obtained from CH_2Cl_2/toluene solution at 3°C. The molecular structure is shown in Figure 2,[14] confirming the formation of a [12.12]paracyclophane.[27] The molecule has crystallographic inversion symmetry and contains two parallel, linear diyne moieties with C1–C2, C2–C3, and C3–C4 bond lengths of 1.2037(17), 1.3794(17), and 1.2029(17) Å, which is in good agreement with the structures established for other bis(diyne)-bridged cyclophanes.[28] Furthermore, the selective formation of dimeric **8** and the absence of any detectable amounts of the



Scheme 4. Ring-closing diyne metathesis (RCDM). Reaction conditions: substrate (0.5 mmol), catalyst (21 mg, 4 mol%), toluene (25 mL), 5 Å M.S. (1.0 g), room temperature, $t = 16$ h; yields of isolated products: 90% (**7**), 80% (**8**). Ball-and-stick drawing of one of twelve crystallographically independent molecules of **7**.

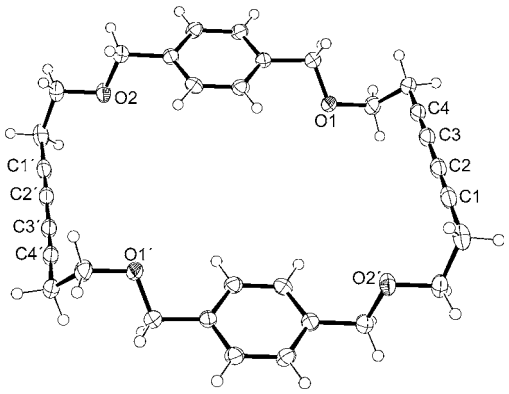


Figure 2. ORTEP diagram of **8** with ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: C1–C2 1.2037(17), C2–C3 1.3794(17), C3–C4 1.2029(17); C1-C2-C3 178.46(12), C2-C3-C4 177.34(11).

corresponding monomeric [12]paracyclophane is fully consistent with the exclusive formation of a closely related [10.10]paracyclophane under thermodynamically controlled RCAM reaction conditions.[7b]

The results presented herein demonstrate the ability of the tungsten benzylidyne complex **1** to promote the catalytic metathesis of methyl-capped conjugated diynes, affording symmetric diynes with a 1,4-butadiyne core. ^{13}C-labeling experiments provide clear evidence that these reactions

proceed in a similar fashion to that established for conventional metal-catalyzed alkyne metathesis, which involves cleavage and formation of carbon–carbon triple bonds via metallacyclobutadiene intermediates.[18] This procedure can be adapted to the preparation of cyclodiynes by ring-closing diyne metathesis (RCDM), and the reversibility of the catalytic reaction steps provides the possibility of obtaining a high degree of thermodynamic control and selectivity in macrocyclic diyne and oligo(diyne) construction. Therefore, we feel that this new method will be a useful and versatile addition to the methods available in preparative acetylenic chemistry,[29] for example in natural product and polymer synthesis.[30,31]

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[14] See the Supporting Information for full experimental details and spectroscopic characterization of all compounds together with a presentation of selected NMR spectra.

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[19] The ^{13}C NMR spectra of **3a**-^{13}C exhibits for instance two doublets at 81.7 ppm for the 1,4-carbon atoms ($C\equiv{}^{13}\mathbf{C}-C\equiv C$) with $^{1}J(^{13}C–^{13}C) = 197.4$ Hz and $^{2}J(^{13}C–^{13}C) = 19.1$ Hz. Similarly, two doublets are found at 121.9 ppm for the *ipso*-carbon atoms with $^{2}J(^{13}C–^{13}C) = 14.0$ Hz and $^{3}J(^{13}C–^{13}C) = 3.6$ Hz. As expected, the main resonance for the labeled carbon atom (100% intensity) at 74.1 ppm shows the corresponding ^{13}C–^{13}C couplings as satellites in about 1.1% intensity according to the natural abundance of the ^{13}C isotope. The full ^{13}C NMR spectrum of **3a**-^{13}C is shown in the Supporting information together with its simulated ^{13}C NMR spectrum.

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