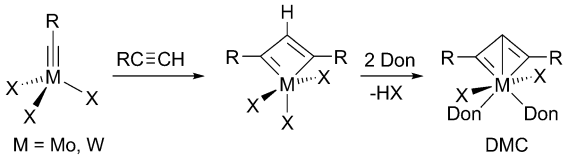
DOI: 10.1002/anie.201207772

Alkyne Metathesis

Efficient Metathesis of Terminal Alkynes

*Birte Haberlag, Matthias Freytag, Constantin G. Daniliuc, Peter G. Jones, and Matthias Tamm**

Despite remarkable recent advances in the development of well-defined homogeneous catalysts for alkyne metathesis with regard to their activity, functional-group tolerance, and required reaction temperature,[1] this method is largely limited to the use of internal alkynes, RC≡CR′ (R = alkyl, aryl; R′ ≠ H). Commonly, methyl-capped alkynes (R′ = Me) are employed,[2] resulting in the formation of RC≡CR and volatile 2-butyne, which can be removed by evaporation (b.p. = 27 °C) or adsorption on molecular sieves (MS 5 Å)[3,4] to drive these equilibrium reactions to completion.[5] In contrast, terminal alkyne metathesis (TAM) has rarely been achieved,[2c,6] since many high-oxidation-state, Schrock-type alkylidyne complexes are known to degrade in the presence of terminal alkyne substrates. For most cases, it was suggested that deactivation occurs through deprotonation of intermediate metallacyclobutadiene species with formation of "deprotiometallacycles" (DMCs),[7,8] which can be stabilized and made isolable by addition of donor (Don) molecules (Scheme 1).[9] These DMCs can be regarded as containing

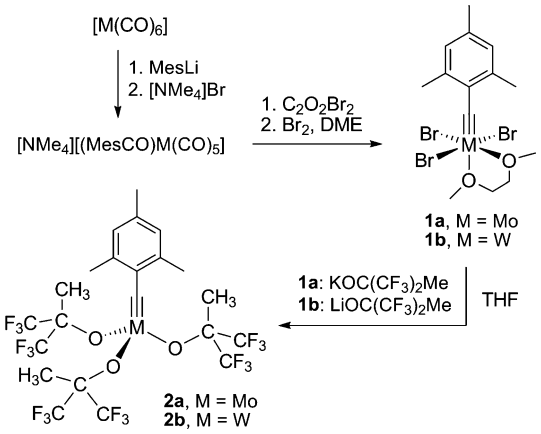


Scheme 1. Formation of deprotiometallacyclobutadienes (DMCs).

a chelating alkynylalkylidene ligand, and it was proposed that such carbene complexes are responsible for the observed high activity towards the polymerization of terminal alkynes.[8b,10] In addition, dimerization of methylidyne complexes [HC≡MX_3] and formation of dimetallatetrahedrane species [X_3M-(μ-C_2H_2)MX_3] should be considered as an alternative deactivation path.[2c,8a,11]

The only known examples in which TAM was promoted by homogeneous tungsten catalysts were reported by Mortreux and co-workers; the neopentylidyne complex [Me_3C-C≡W(O*t*Bu)$_3$] was able to catalyze the metathesis of various aliphatic alkynes such as 1-pentyne, 1-hexyne, and 1-heptyne in diethyl ether, although only little metathesis activity and competing polymerization was observed.[8a] For 1-heptyne, the metathesis yield could be enhanced by addition of quinuclidine as an external ligand, and up to 80 % conversion to 6-dodecyne was observed within 1 min at 80 °C and 4 mol % catalyst loading.[12] Furthermore, a bimetallic complex containing a hemilabile alkoxy ether ligand [W_2-(MMPO)$_6$] (MMPO = 1-methoxy-2-methyl-2-propanolato) gave similar results for the metathesis of 1-heptyne.[13]

We are not aware of any other reports on TAM and wish to present herein the first catalyst capable of promoting not only the efficient metathesis of a wide variety of terminal alkynes, but also the unprecedented terminal ring-closing alkyne metathesis (TRAM) of α,ω-diacetylenes. The novel catalyst was discovered during our attempts to enhance the stability of our catalyst series, which consists of molybdenum and tungsten benzylidyne complexes with imidazolin-2-iminato,[14] phosphoraneiminato,[15] and silanolate[16] ligands. Therefore, we aimed at the preparation of the corresponding 2,4,6-trimethylbenzylidyne complexes in a similar manner from [$Mo(CO)_6$] and [$W(CO)_6$].[14a] Addition of mesityllithium (MesLi) to solutions of [$M(CO)_6$] in diethyl ether, followed by an aqueous solution of NMe_4Br, afforded the stable acyl complexes [NMe_4][(MesCO)M(CO)$_5$] (Scheme 2).



Scheme 2. Synthesis of 2,4,6-trimethylbenzylidyne complexes.

Treatment with oxalyl bromide in CH_2Cl_2 at low temperature (−90 °C) gave the intermediate Fischer carbyne complexes *trans*-[MesC≡M(CO)$_4$Br],[17] which can be directly reacted with bromine and DME at −90 °C to produce the tribromides [MesC≡MBr_3(dme)] **1a** and **1b**[18] as orange or yellow crystalline solids in about 80 % overall yield. The molecular structures of **1a** and **1b** were determined by X-ray diffraction analyses (see the Supporting Information), clearly confirming the expected distorted octahedral geometries with a meridional arrangement of the bromine atoms.

[*] Dipl.-Chem. B. Haberlag, Dr. M. Freytag, Dr. C. G. Daniliuc, Prof. Dr. P. G. Jones, Prof. Dr. M. Tamm
Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
E-mail: m.tamm@tu-bs.de
Homepage: http://www.tu-braunschweig.de/iaac

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207772.

The reaction of the Mo complex **1a** with $KOC(CF_3)_2Me$ in THF for 12 h resulted in the formation of the solvent-free complex $[MesC{\equiv}Mo\{OC(CF_3)_2Me\}_3]$ (**2a**) after evaporation and crystallization from pentane. Related dme-free complexes of the type $[RC{\equiv}Mo\{OC(CF_3)_2Me\}_3]$ (R = Me, Et, *i*Pr, *t*Bu) had already been isolated by Schrock by sublimation of the dme-containing precursors under high vacuum (10^{-2} μm Hg) and at higher temperature or from the alkyne metathesis reaction between the neopentylidyne complex $[Me_3C{-}C{\equiv}Mo\{OC(CF_3)_2Me\}_3]$ and RC≡CR (R = Me, Et, *i*Pr).[7b] Similar tungsten complexes were only isolated as dme adducts,[19] which is in line with our observation that the preparation of the corresponding unsolvated tungsten complex **2b** turned out to be more difficult. After treatment of **1b** with $LiOC(CF_3)_2Me$ in THF, evaporation afforded the etherate **2b** $(thf)_x$ with varying amounts of coordinated THF (x = 0.5–1), and the solvent-free complex **2b** could only be obtained after repeated crystallization from hexamethyldisiloxane (HMDS) at −35 °C, albeit in moderate yield (35 %).

The ^{13}C NMR spectra (in C_6D_6) of the Mo and W complexes **2** show characteristic low-field resonances at 317.6 (**2a**) and 293.7 ppm (**2b**) for the alkylidyne carbon atoms, which fall in the range reported for related complexes.[7b,19] Both structures were also confirmed by X-ray diffraction analysis (yellow single crystals were isolated at −35 °C from pentane and HMDS solution, respectively), revealing the formation of monomeric complexes with slightly distorted tetrahedral geometries. Since the structure of **2b** suffered from disorder of two CF_3 groups (see the Supporting Information), only the molecular structure of **2a** will be discussed below (Figure 1). As expected, a short Mo≡C1 bond of 1.7438(16) Å together with an almost linear Mo-C1-C2 axis of 177.40(13)° is observed, which is in good agreement with the values reported for the molybdenum alkylidyne complex $[EtC{\equiv}Mo(OAd)_3]$ (Ad = adamantyl, 1.743(3) Å, 177.4(3)°).[20]

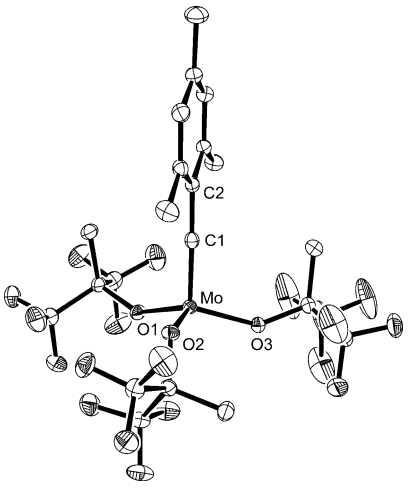


Figure 1. ORTEP diagram of **2a** (ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Mo–C1 1.7438(16), Mo–O1 1.8946(11), Mo–O2 1.9243(11), Mo–O3 1.8963(11); O1-Mo-O2 115.11(5), O1-Mo-O3 117.45(5), O2-Mo-O3 113.21(5),C1-Mo-O1 104.83(6), C1-Mo-O2 97.13(6), C1-Mo-O3 106.04(6), Mo-C1-C2 177.40(13).

To investigate the potential of **2a** and **2b** as alkyne metathesis catalysts, we first performed the homodimerization of the test substrate 3-pentynyl benzyl ether (**3**), employing the molecular-sieve method to adsorb 2-butyne.[3] Thus, toluene solutions (200 mM) of **3** (0.5 mmol), **2a**/**2b** (1 mol %), and molecular sieves (MS 5 Å) were stirred for 60 min. Surprisingly, full conversion to **4** was only observed for the molybdenum catalyst **2a**, whereas the tungsten congener **2b** proved completely inactive, which we tentatively ascribe to the high electrophilicity of the latter species as already indicated by the difficulty of solvent removal.

Therefore, all subsequent experiments were performed exclusively with **2a**. Additionally, the conversion of **3** (R = Me) into **4** was monitored by gas chromatography (GC) in the presence of **2a** (1 mol %), and the resulting conversion versus time diagram is shown in Figure 2. Within one minute, 93 % of the dimer had formed, and the reaction was complete within

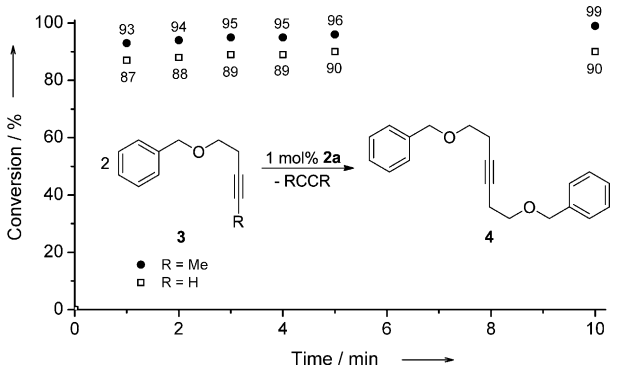


Figure 2. Conversion versus time diagram for the metathesis of the benzyl ethers **3** (R = Me: 0.5 mmol; R = H: 0.25 mmol) in toluene (R = Me: 2.5 mL; R = H: 12 mL) catalyzed by 1 mol % of **2a** in the presence of molecular sieves 5 Å. The conversion was monitored by GC using *n*-decane as an internal standard.

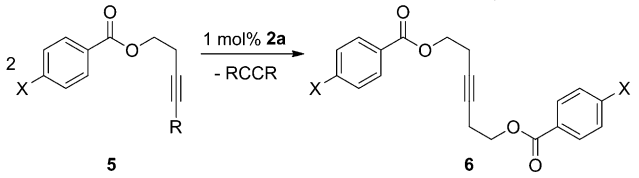
ten minutes. Thus, the initial turnover frequency (TOF) of 93 min^{-1} exceeds even that of highly active phosphoraniminato complexes (TOF = 45 min^{-1}), established under identical conditions.[15] After workup, **4** was isolated as a colorless oil in 98 % yield.

Since we routinely check new catalyst systems for their potential to catalyze the metathesis of terminal alkynes, **2a** was tested with respect to metathesis of the corresponding 3-butynyl ether **3** (R = H). Much to our surprise, rapid conversion to **4** was also observed with optimum results obtained when the reaction was performed at significantly higher dilution (21 mM). Despite the lower substrate and catalyst concentration, 87 % conversion was achieved within one minute, confirming the outstanding catalyst performance in the early stage of the reaction. After 10 min, 90 % conversion was determined, and workup afforded **4** in the same yield (Figure 2).

Similar results were obtained for the metathesis of the functionalized 3-pentynyl (R = Me) and 3-butynyl (R = H) benzoic esters **5** bearing various substituents in the 4-position of the phenyl ring (**5a**, X = Cl; **5b**, X = OMe; **5c**, X = SMe). In a typical experiment, the substrate **5** was dissolved in

toluene and stirred at room temperature in the presence of **2a** (1 mol%) and molecular sieves (5 Å)[21] under the conditions given in Table 1. After 30 or 60 min, the reaction mixture was filtered through a short pad of alumina, and the solvent was

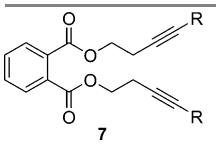
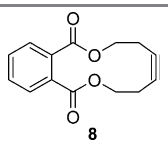
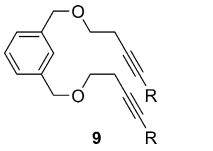
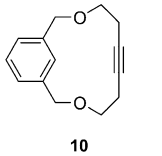
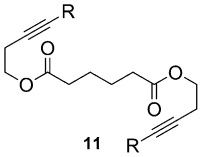
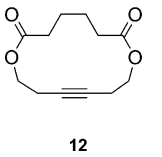
Table 1: Homodimerization of internal and terminal alkynes.



Compound	X	Yield [%] R = Me[a]	R = H[b]
a	Cl	96	96
b	OMe	95	92
c	SMe	91[c]	89

[a] Substrate (0.5 mmol), catalyst **2a** (1 mol%), toluene (2.5 mL), MS 5 Å (500 mg), 25 °C, 30 min. [b] Substrate (0.25 mmol), catalyst **2a** (1 mol%), toluene (12 mL), MS 5 Å (250 mg), 25 °C, 60 min. [c] Substrate (0.5 mmol), catalyst **2a** (1 mol%), toluene (2.5 mL), MS 5 Å (500 mg), 25 °C, 60 min.

Table 2: Ring-closing metathesis of internal and terminal alkynes.

Substrate	Product	Yield [%] R = Me	R = H
		99[a]	95[b]
7	8		
		98[a]	96[c]
9	10		
		96[a]	88[c]
11	12		

[a] Substrate (0.5 mmol), catalyst **2a** (2 mol%), toluene (21 mM, 24 mL), MS 5 Å (1 g), 25 °C, 1 h. [b] Substrate (0.25 mmol), catalyst **2a** (2 mol%), toluene (21 mM, 12 mL), MS 5 Å (500 mg), 2 h. [c] Substrate (0.25 mmol), catalyst **2a** (2 mol%), toluene (4.5 mM, 56 mL), MS 5 Å (500 mg), 2 h.

evaporated to afford the pure diesters (**6a–c**) in very good yields (89–96%). These results indicate a functional-group tolerance similar to that of imidazolin-2-iminato and silanolate complexes, as established by our group.[14,16] However, the metathesis of a related isonicotinic acid pentynyl ester was not successful, indicating that catalyst **2a** might not be compatible with strongly coordinating groups such as the pyridine functionality.

It should emphasized that the metathesis reactions employing terminal alkynes were again performed at significantly higher dilution (21 mM); under these conditions no undesired polymerization product was observed. However, when the reaction was conducted at the concentration used for the internal alkynes (200 mM), the diesters **6** were isolated in lower yield (by approximately 10%), which might be ascribed to side reactions such as polymerization. In this context, it is important to note that the metathesis of phenylacetylene was not successfully catalyzed by **2a**, and polymer formation was immediately observed after addition of the catalyst to the substrate solution. The isolated red solid was identified as poly(phenylacetylene).[22]

Encouraged by the results described above for the homodimerization of internal and terminal alkynes, we also attempted ring-closing alkyne metathesis (RCAM) for the α,ω-diynes **7**, **9**, and **11** bearing either two 3-pentynyl (R = Me) or two 3-butynyl (R = H) groups (Table 2). The reactions were performed in toluene solution (21 mM or 4.5 mM) with a catalyst loading of 2 mol% in the presence of molecular sieves for adsorption of 2-butyne or acetylene. After the reaction mixture had been stirred for 1 h (R = Me) or 2 h (R = H), workup afforded in all cases the cycloalkynes **8**, **10**, and **12** in excellent yields, with the terminal alkynes leading to only slightly lower yields of isolated products. To the best of our knowledge this is the first time that TRAM has been accomplished; the formation of a cycloalkyne in 25% yield by ring-closure of the mixed terminal/internal diyne $HC{\equiv}C(CH_2)_3O(CH_2)_2C{\equiv}CC_3H_7$ in the presence of $[Me_3CC{\equiv}W(O\mathit{t}Bu)_3]\cdot$quinuclidine represents the only other related example.[12]

The discovery that the mesityl-substituted alkylidyne complex $[MesC{\equiv}Mo\{OC(CF_3)_2Me\}_3]$ (**2a**) catalyzes the metathesis of both internal and terminal alkynes efficiently appears to be long overdue, since the closely related neopentylidyne complexes $[Me_3CC{\equiv}Mo\{OC(CF_3)_2Me\}_3(dme)]$ and its dme-free congener $[Me_3CC{\equiv}Mo\{OC(CF_3)_2Me\}_3]$ had been described in the 1980s by Schrock and co-workers, with the latter complex representing "one of the best acetylene metathesis catalysts containing molybdenum"[7b] that had been prepared by that group. The advance presented here relies on the introduction of the mesityl group, which significantly facilitates the isolation of the solvent-free complex **2a**, and its activity in internal alkyne metathesis might have been predictable in view of the earlier work.[7]

We assume that its additionally discovered exceptional activity in terminal alkyne metathesis (TAM) is based on the following factors: 1) The absence of coordinating solvents such as dme or thf results in a highly active metal species with tetrahedral coordination; its rate of alkyne metathesis is significantly faster than its rate of deactivation, for example, by formation of deprotiometallacyclobutadienes (DMC, Scheme 1). The latter reaction is hindered in the case of **2a**, since it was clearly demonstrated that alcohol elimination and DMC formation are favored in the presence of donor ligands.[7,9] 2) The relatively low basicity of the hexafluoro-*tert*-butanolato, $OC(CF_3)_2Me$, ligands can also be expected to disfavor DMC formation in contrast to the reactivity observed for complexes containing more basic alkoxides or silanolates such as $OCMe_3$ or $OSiPh_3$.[8,9] 3) Performing TAM reactions at higher dilution seems to be of critical importance,

since polymerization and/or intermolecular deactivation processes are suppressed. In this context, it should be noted again that the metathesis of terminal aromatic alkynes is still not possible, since rapid polymerization of phenylacetylene in the presence of catalytic amounts of **2a** was observed. Despite this limitation, we feel that a promising catalyst system is now available for a wider application of TAM in organic synthesis. Moreover, **2a** and related species might also be considered as promising catalysts for nitrile–alkyne cross-metathesis (NACM) in view of the encouraging results that were obtained by use of related Mo and W alkylidyne species.[23]

Received: September 26, 2012
Published online: November 14, 2012

Keywords: alkyne metathesis · alkynes · molybdenum complexes · ring-closing metathesis · tungsten complexes

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