Mo[N(*t*-Bu)(Ar)]$_3$ Complexes As Catalyst Precursors: In Situ Activation and Application to Metathesis Reactions of Alkynes and Diynes

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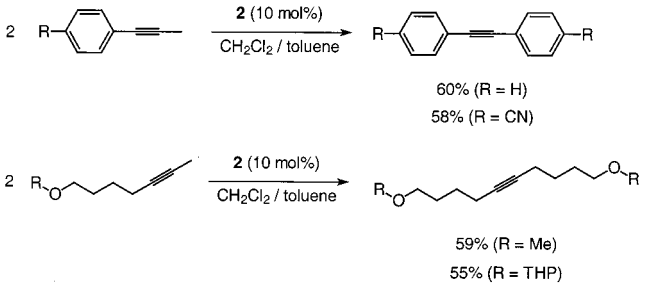
A strongly renewed interest in alkyne metathesis can presently be noticed within the organic as well as the polymer chemists community.[1,2] Schrock-type alkylidyne complexes as well as less defined species prepared in situ e.g. from $Mo(CO)_6$ and phenol additives constitute adequate catalysts for these purposes.[2] In this context we have reported the first synthesis of macrocyclic cycloalkynes via ring-closing metathesis (RCM) of *diyne* substrates catalyzed by $(tBuO)_3W{\equiv}CCMe_3$ (**1**).[3,4] In view of the great preparative potential of this new transformation we have embarked into a systematic study of its scope, as it seems to supplement the well-established RCM reaction of dienes.[5,6]

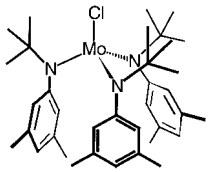
Inspired by publications of Cummins et al. on molybdenum complexes of the general type Mo[N(tBu)(Ar)]$_3$ (**2**),[7,8] which activate the triple bond of molecular nitrogen in a *stoichiometric* fashion, we investigated the reactivity of such compounds toward alkynes. Although **2** (Ar = 3,5-dimethylphenyl) itself does not effect any metathesis event, we noticed a strongly endothermic process upon dissolving complex **2** in CH_2Cl_2; the resulting mixture efficiently *catalyzes* a metathetic coupling of different aliphatic as well as aromatic alkynes (Scheme 1). CH_2Cl_2 can be used as the solvent, but the addition of ≈25 equiv (not optimized) of CH_2Cl_2 per mol of **2** to a solution in toluene turned out to be equally effective.

Activation of complex **2** with CH_2Cl_2 and evaporation of all volatiles affords a very sensitive solid residue that contains different molybdenum species. MS and NMR inspection indicates

Scheme 1



that [(Ar)(tBu)N]$_3$MoCl (**3**)[9] and the *terminal* alkylidyne complex [(Ar)(tBu)N]$_3$Mo≡CH (**4**)[10,11] constitute major components of this



3

mixture. Although we were unable so far to separate the individual compounds by crystallization, authentic **3** can be conveniently obtained by reaction of **2** and Cl_2 in ether solution (eq 1). To the best of our knowledge, this is the first example of a trisamidomolybdenum(IV) chloride reported in the literature. An X-ray analysis of this compound (Figure 1)[9] shows the close packing of the amido ligands on one side of the molecule. Thereby a pocket is formed around the Mo center that seems to shield the central metal quite efficiently. This congested arrangement may explain some of the favorable chemical properties of **3** (vide infra).

$$2\ [(t\text{-Bu})(Ar)N]_3Mo\ (\mathbf{2}) + Cl_2 \xrightarrow{Et_2O} 2\ [(t\text{-Bu})(Ar)N]_3MoCl\ (\mathbf{3}) \quad (1)$$

$$2\ [(t\text{-Bu})(Ar)N]_3Mo\ (\mathbf{2}) + Br_2 \xrightarrow{Et_2O\ /\ hexane} 2\ [(t\text{-Bu})(Ar)N]_3MoBr\ (\mathbf{5}) \quad (2)$$

In view of our previous experiences in ring closing diyne metathesis effected by complex **1**[3] and of the generally accepted mechanism involving metal alkylidyne intermediates,[12] it seemed reasonable to assume that alkylidyne **4** present as a major component in the crude mixture constitutes the catalytically relevant species. Control experiments, however, using either pure **3** or its bromo analogue **5** (eq 2) revealed that these inorganic compounds catalyze alkyne metathesis as efficiently as the "in situ" mixture formed form **2** and CH_2Cl_2 (cf. Table 1). In line with this observation, we noticed that treatment of **2** with halide

(1) For the first alkyne metathesis using a defined alkylidyne catalyst see: Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932.

(2) For a short review see: Bunz, U. H. F.; Kloppenburg, L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 478. For applications see: (b) Weiss, K.; Michel, A.; Auth, E. M.; Bunz, U. H. F.; Mangel, T.; Müllen K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 506. (c) Pschirer, N. G.; Bunz, U. H. F. *Tetrahedron Lett.* **1999**, *40*, 2481. (d) Kloppenburg, L.; Song, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **1998**, *120*, 7973. (e) Mortreux, A.; Blanchard, M. *J. Chem. Soc., Chem. Commun.* **1974**, 786. (f) Villemin, D.; Cadiot, P. *Tetrahedron Lett.* **1982**, *23*, 5139.

(3) Fürstner, A.; Seidel, G. *Angew. Chem.* **1998**, *110*, 1758; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1734.

(4) For the preparation and applications of **1** see: (a) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Reingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (c) Schrock, R. R. *Polyhedron* **1995**, *14*, 3177.

(5) For recent reviews on RCM of alkenes see the following for leading references: (a) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (b) Fürstner, A. *Top. Catal.* **1997**, *4*, 285. (c) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036. (d) Fürstner, A. *Top. Organomet. Chem.* **1998**, *1*, 37.

(6) For recent macrocycle syntheses by RCM from our laboratory see: (a) Fürstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997**, *119*, 9130. (b) Fürstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 95. (c) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315. (d) Fürstner, A.; Koch, D.; Langemann, K.; Leitner, W.; Six, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2466. (e) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792. (f) Fürstner, A.; Müller, T. *J. Org. Chem.* **1998**, *63*, 424. (g) Fürstner, A.; Gastner, T.; Weintritt, H. *J. Org. Chem.* **1999**, *64*, 2361.

(7) Cummins, C. C. *Chem. Commun.* **1998**, 1777. (b) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (c) Laplaza, C. E.; Johnson, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **1996**, *118*, 709. (d) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. *J. Am. Chem. Soc.* **1996**, *118*, 8623.

(8) Preparation: Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 4999.

(9) Compound **3**: MS (70 eV): *m/z* 661 (3, M^+), 604 (24, $M^+ - C_4H_9$), 548 (29, 604 − C_4H_8), 492 (100, 548 − C_4H_8). Crystallographic data: red plates, monoclinic $P2_1$, a = 10.7575(6) Å, b = 11.1362(6) Å, c = 14.8699(8) Å, β = 94.480(2)°, T = 100 K, Z = 2, wR^2 = 0.102, R = 0.055. For further details see the Supporting Information.

(10) Although the NMR analysis of the crude material is hampered by the paramagnetic nature of admixed open-shell molybdenum species, the very characteristic signals of **4** were unequivocally identified, thus corroborating the MS data. Compound **4**: ^{13}C NMR (125 MHz, C_6D_6): δ 287.0 ppm (Mo≡CH), ^{1}H NMR (600 MHz, C_6D_6) δ 5.66 ppm (Mo≡CH); positive cross-peak between these signals in ^{1}H, ^{13}C correlation experiments. MS (70 eV): *m/z* 639 (9, M^+), 582 (30), 526 (34), 470 (12). The admixed paramagnetic species give rise to the following signals in the ^{1}H NMR spectra: δ 23.74 (br), 6.44 (s), 6.35 (s), −1.02 (br), −1.41 (br), −4.95 (br).

(11) Complex **4** has been prepared by Cummins by a different route: Peters, J. C.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1995.

(12) The mechanism via alkylidyne- and metallacyclobutadiene complexes has originally been proposed by: Katz, T. J.; McGinnis, J. *J. Am. Chem. Soc.* **1975**, *97*, 1592. See also ref 1.

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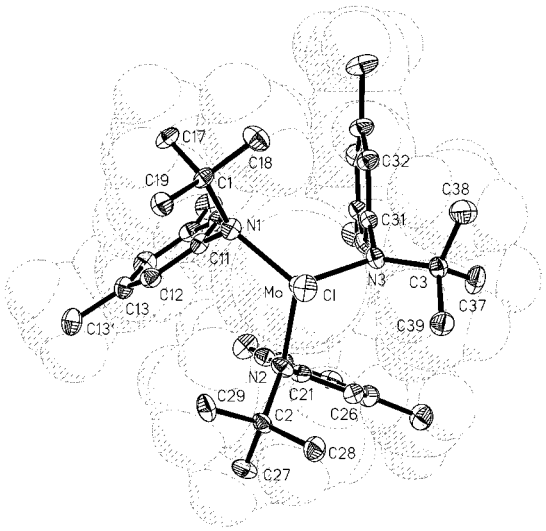
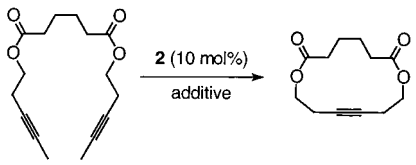


Figure 1. Molecular structure of **3**. Selected bond length (Å) and angles (deg): Mo−N1 1.963(3), Mo−N2 1.963(3), Mo−N3 1.952(3), Mo−Cl 2.350(1), N1−Mo−Cl 97.4(1), N2−Mo−Cl 102.7(1), and N3−Mo−Cl 101.2(1). Note that all three amido groups have planar geometry.

Table 1. Ring Closing Metathesis Effected by Complex **2** Activated in Situ by Different Additives



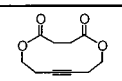
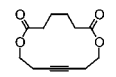
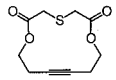
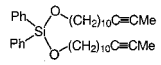
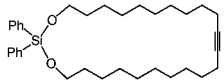
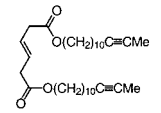
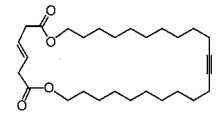
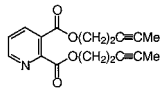
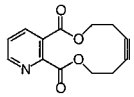
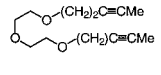
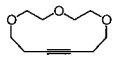
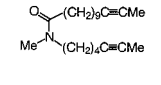
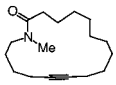
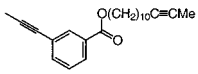
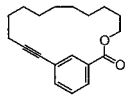
entry	solvent	additive[a]	yield (%)
1	CH_2Cl_2		80
2	toluene	CH_2Cl_2	81
3	$CHCl_3$		82
4	CCl_4		70
5	toluene	CH_2Br_2	84
6	toluene	CH_2I_2	84
7	toluene	$C_6H_5CHCl_2$	78
8	toluene	$C_6H_5CH_2Cl$	81
9	toluene	Me_3SiCl	75
10	toluene	[(Ar)(tBu)N]$_3$MoCl (**3**)[b]	70
11	toluene	[(Ar)(tBu)N]$_3$MoBr (**5**)[c]	79

[a] ≈25 equiv of the respective additive relative to **2** are used. [b] Pure **3** was used as the catalyst instead of **2** + additive. [c] Pure **5** was used as the catalyst instead of **2** + additive.

sources other than CH_2Cl_2 also leads to the generation of active species in solution (Table 1). This raises interesting questions as to how such halide species trigger a catalytic cycle and what intermediates along the ensuing alkyne metathesis pathway may possibly look like.[13]

Although these mechanistic aspects are not yet clear,[14] the catalyst formed in situ as well as pure **3** or **5** are excellent tools from the preparative point of view (Table 2). Not only do they effect the formation of macrocyclic cycloalkynes of different ring sizes, but they also *tolerate functional groups which completely shut down the catalytic activity of the tungsten alkylidyne catalyst **1** previously used*.[2,3] This is true for thioethers (entry 3), basic nitrogen atoms (entry 6), and polyether chains (entry 7). This favorable property is tentatively ascribed to the crowded coordination sphere around the Mo(IV) center in **3** endowed by the bulky amide substituents (cf. Figure 1). The steric shielding attenuates the effective Lewis acidity of the metal center and prevents coordination of potential donor substrates onto the catalytically active template. In contrast to complex **1**, however, catalyst **3** is sensitive toward "acidic" protons such as those of secondary amides, whereas tertiary amides are fully compatible and deliver the corresponding cyclic products in excellent yield (entry 8). Therefore catalysts **1** and **3** are complementary with respect to their tolerance toward certain functional groups. Note, however, that esters, isolated double bonds, and silyl ethers are compatible with both of them.[3]

Table 2. RCM Catalyzed by [(Ar)(tBu)N]$_3$MoCl (**3**) (10 mol %) Generated in Situ from Complex **2** and CH_2Cl_2[a]

Entry	Substrate	Product	Yield (%)
1	[MeC≡C(CH$_2$)$_2$OOC(CH$_2$)]$_2$		91
2	[MeC≡C(CH$_2$)$_2$OOC(CH$_2$)$_2$]$_2$		81
3	S[CH$_2$COO(CH$_2$)$_2$C≡CMe]$_2$		84
4			74
5			82
6			88
7			60
8			72
9			83

[a] All reactions are carried out in toluene at 80 °C for 20−48 h.

Because of the excellent performance of complex **2** in this new field of application, we developed an improved synthesis of the required sterically demanding amine ligand (*t*-Bu)(Ar)NH based on the palladium-catalyzed amination reaction pioneered by Buchwald.[15,16] For details see the Supporting Information.

In short, we believe that compound **2** and its derivatives **3** and **5** are useful and versatile reagents for advanced organic synthesis. Further studies will be disclosed in the near future.

Acknowledgment. Financial support by the MPG, the DFG (Leibniz program), and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: A procedure for ring closing diyne metathesis, large scale preparation of (tBu)(Ar)NH, NMR spectra of all new cycloalkynes, and X-ray structure of compound **3** (PDF). This material is available free of charge via the internet at http://pubs.acs.org.

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(13) It has been suggested that pathways that do not involve metal alkylidyne intermediates may also be operative in alkyne metathesis, cf.: Kaneta, N.; Hirai, T.; Mori, M. *Chem. Lett.* **1995**, 627. (b) Kaneta, N.; Hikichi, K.; Asaka, S.-I.; Uemura, M.; Mori, M. *Chem. Lett.* **1995**, 1055.

(14) Another interesting question concerns the formation of the terminal alkylidyne complex **4** from **2** and CH_2Cl_2.

(15) Wolfe, J. P.; Wagwaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215.

(16) For a related synthesis of similar ligands see: Johnson, A. R.; Cummins, C. C. *Inorg. Synth.* **1998**, *32*, 123.