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Practical New Silyloxy-Based Alkyne Metathesis Catalysts with Optimized Activity and Selectivity Profiles

Johannes Heppekausen, Robert Stade, Richard Goddard, and Alois Fürstner*

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

Received June 2, 2010; E-mail: fuerstner@kofo.mpg.de

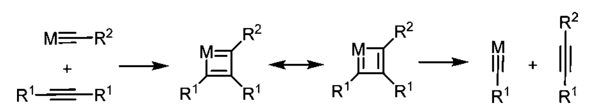
Abstract: Triphenylsilanolate ligands were found to impart excellent reactivity and outstanding functional group tolerance on molybdenum alkylidyne complexes, which catalyze alkyne metathesis reactions of all sorts. The active species either can be obtained in high yield by adaptation of the established synthesis routes leading to Schrock alkylidynes or can be generated in situ from the molybdenum nitride complex **11**, which itself is readily accessible in large quantity from inexpensive sodium molybdate. Complexation of the active silanolate complexes **12** and **24** with 1,10-phenanthroline affords complexes **15** and **25**, respectively, which are stable in air for extended periods of time. Although these phenathroline adducts are per se unreactive vis-à-vis alkynes, catalytic activity is conveniently restored upon exposure to $MnCl_2$. Therefore, the practitioner has the choice of different alkyne metathesis (pre)catalysts, which are easy to handle yet broadly applicable and exceedingly tolerant. A host of representative inter- as well as intramolecular alkyne metathesis reactions, including applications to a considerable number of bioactive and, in part, labile natural products, shows the remarkable scope of these new tools. Moreover, it was found that the addition of molecular sieves (5 Å ≥ 4 Å ≫ 3 Å) to the reaction mixture significantly improves the chemical yields while simultaneously increasing the reaction rates. This benefit is ascribed to effective binding of 2-butyne, which is released as the common byproduct in reactions of alkynes bearing a methyl end-cap. Thus, alkyne metatheses can now be performed at ambient temperature with neither the need to apply vacuum to drive the conversion nor recourse to tailor-made substrates. The structures of representative examples of this new generation of alkyne metathesis catalysts in the solid state were determined by X-ray analysis.

Introduction

A major reason for the overwhelming success of olefin metathesis is the ready availability of catalysts that combine high activity with a good to excellent tolerance toward functional groups other than alkenes.[1,2] As some of these key catalysts are modular, well accessible, and easy to handle, this transformation was rapidly embraced by the synthetic community and has profoundly changed the way contemporary organic and polymer chemistry are practiced.[3]

Compared to the omnipresence of alkene metathesis, the related metathesis of alkynes is much less commonly used.[4,5] Initially described as early as 1968,[6] the principle underlying this scrambling process was swiftly discerned[7] and experimentally proven (Scheme 1).[8,9] The active catalysts were shown to be Schrock alkylidyne complexes,[10] which either can be generated in situ or, preferentially, are administered to the reaction mixtures as structurally well-defined, preformed species. Despite this excellent background knowledge, it was only after a considerable lag period[11] that the potential of alkyne metathesis

Scheme 1. Basic Mechanism of Alkyne Metathesis Catalyzed by Metal Alkylidynes



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was recognized and explored.[12,13] The fact that nonterminal alkynes are required as the substrates may be one reason for the smaller impact compared with olefin metathesis,[14,15] yet a growing number of applications in the recent literature to natural product synthesis,[4] coordination chemistry,[16] and material science[17,18] show that this inherent drawback can be (partly) compensated for or even turned to advantage by the excellent selectivity of alkyne metathesis, as well as by the possibility of further elaborating the acetylenic products primarily formed in a diverse fashion by a host of different postmetathetic transformations.[19−24]

Alkyne metathesis was originally discovered using a heterogeneous catalyst composed of tungsten oxide on silica which was operative only at 200−450 °C.[6,25] Shortly thereafter, Mortreux and co-workers showed that homogeneous mixtures comprising $Mo(CO)_6$ and resorcinol (or other phenols) in high-boiling solvents are active at more manageable temperatures (ca. 130−160 °C).[26] Despite many rounds of optimization of the molybdenum source, the phenol additive, the solvent, and the reaction conditions, this simple and cheap system has not reached the level of activity and selectivity that better-defined (pre)catalysts can offer.[27−29] It was the advent of well-defined d^0-alkylidyne complexes of tungsten,[8,30,31] molybdenum,[32,33] and rhenium[34,35] that set new standards in the field. Among them,

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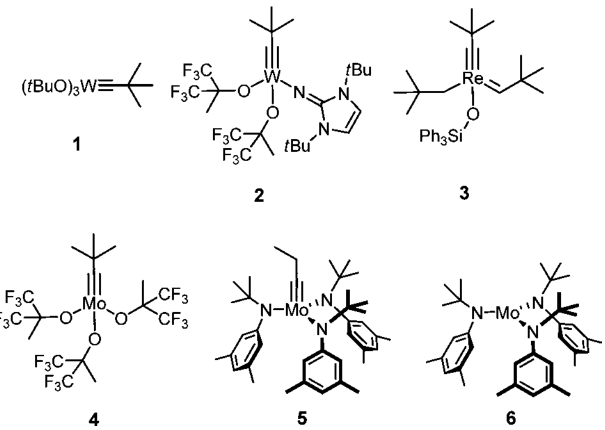
the tungsten neopentylidyne complex **1** found the broadest use and is now commercially available.[8,30]



Early on, this catalyst was shown to induce certain alkyne metathesis reactions, even at ambient temperature, within minutes. **1** turned out to be compatible with surprisingly many functional groups, although donor sites such as basic nitrogen, divalent sulfur, polyether fragments, or various heterocycles block its activity, presumably by coordination to the fairly Lewis acidic tungsten center.[12,13] Moreover, carbonyl groups may react with **1** and analogues in a Wittig-like manner.[36] Subsequent variations of the ligand sphere, as represented, for example, in complex **2**, allowed the activity to be improved even further.[31] The related molybdenum alkylidynes are generally considered to be less reactive but may exhibit an increased functional group tolerance. This fact is usually explained by the lower Lewis acidity of Mo(6+) compared to W(6+), though the chosen set of ancillary ligands must be taken into consideration.[32] Catalytically active and highly tolerant molybdenum species can also be prepared in situ by reacting the now also commercial trisamido complex **6** with CH_2Cl_2 or other *gem*-dihalides.[37−39] Their remarkable selectivity profile is evident from many applications right through to the total synthesis of structurally complex and, in part, labile target molecules, including epothilone A and C,[38,40] the latrunculins,[41] prostaglandin E_2 1,15-lactone,[42] cruentaren A,[43] amphidinolide V,[22a,b] sophorolipid lactone,[44] and myxovirescin.[45−47]

These successes notwithstanding, all available catalysts—except for Mortreux's in situ recipe and its variants—suffer from high sensitivity toward oxygen, moisture, and, in the case of complex **6**,[48] even molecular nitrogen. The necessary expert knowledge in handling such compounds may be another reason why alkyne metathesis has not yet become more popular. Convinced by the power of this transformation, however, our group is committed to change this situation by developing catalysts that retain the excellent selectivity of complexes such as **1**−**6** while being significantly more user-friendly. Ideally, the next generation of alkyne metathesis catalysts should be applicable to complex and polysubstituted targets while being cheap, easy to make, and air stable. In a recent Communication we described a first step toward this goal;[49] outlined below, we present a full account of our work in this area, which led to a set of new catalysts that meet these stringent criteria very well.

Results and Discussion

Molybenum Nitrido Complexes with Ancillary Silanolate Ligands. Inspiration for the development of novel user-friendly yet effective alkyne metathesis catalysts was provided by Johnson and co-workers, who reported that certain nitride complexes of molybdenum and tungsten endowed with fluorinated alkoxide ligands react with sacrificial alkynes to generate metal alkylidynes in situ (Scheme 2).[50] However, the preparation of **7** as a prototype precursor complex requires the use of azides as well as the handling of air-sensitive intermediates.

In an attempt to find a more convenient entry point, we investigated if the same intermediate **8** could be generated by alcoholysis of the much more accessible precursor **11**[51] with hexafluoro-*tert*-butanol (**14**). Even though the mixture of **11** and

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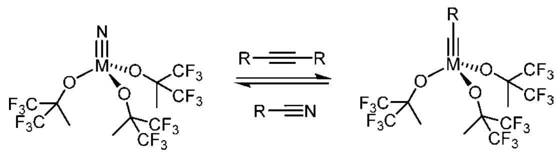
(50) (a) Geyer, A. M.; Wiedner, E. S.; Gary, J. B.; Gdula, R. L.; Kuhlmann, N. C.; Johnson, M. J. A.; Dunietz, B. D.; Kampf, J. W. *J. Am. Chem. Soc.* **2008**, *130*, 8984. (b) Gdula, R. L.; Johnson, M. J. A. *J. Am. Chem. Soc.* **2006**, *128*, 9614.
(51) Chiu, H.-T.; Chuang, S.-H.; Lee, G.-H.; Peng, S.-M. *Adv. Mater.* **1998**, *10*, 1475.

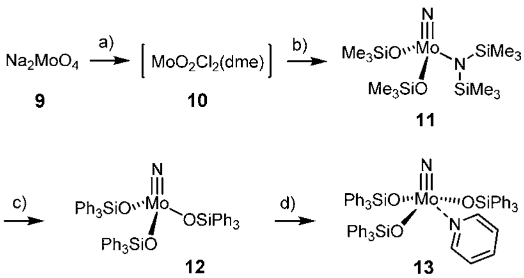
Scheme 2. Metal Nitride/Metal Alkylidyne Interconversion as an Alternative Concept for the in Situ Generation of Alkyne Metathesis Catalysts[a]



7 8 (M = Mo, W)

[a] Cf. ref 50.

Scheme 3. Preparation of a New Metathesis Precatalyst That Is Air-Stable for Limited Periods of Time[a]

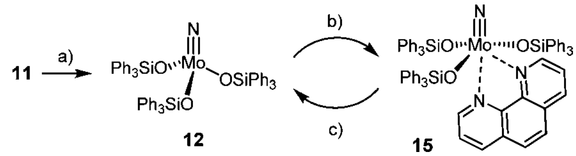


[a] Conditions: (a) TMSCl, 1,2-dimethoxyethane (DME), reflux; (b) LiHMDS, hexane, 64% (over both steps); (c) Ph_3SiOH (3 equiv), toluene, 80 °C; (d) pyridine (5 equiv), 81% (over both steps). Cf. ref 49.

14 was devoid of any appreciable catalytic activity, we were pleased to observe that the use of triphenylsilanol resulted in a catalytically active mixture.[49,52,53] Complex **12** was readily identified as the active component (Scheme 3). Although **12** itself is hydrolytically labile and needs to be handled under an inert atmosphere, the corresponding pyridine adduct **13** turned out to be sufficiently stable to be weighed in air (Scheme 3).[49] At temperatures around 80 °C, however, solutions of this adduct in toluene exhibit appreciable catalytic activity, most likely by slow decomplexation of the pyridine. The fact that the presence of the N-heterocyclic ligand does not quench the catalytic activity of the molybdenum core may explain why this particular precatalyst, which has recently been made commercially available, was found compatible with many other polar groups (ester, ketone, amide, carbamate, sulfonate, nitro, ether, thioether, silyl ether, alkene, acetal, glycoside, thiazole, pyridine, thiophene, etc.); only epoxides, aldehydes, and acid chlorides were found to react stoichiometrically with the nitride function of **12** and hence consume the catalyst.[49,54,55]

Although **13** combines favorable chemical attributes with a reasonable stability, it will eventually hydrolyze and hence must still be stored under an inert atmosphere. In an attempt to find an even more robust alternative, several ligands other than pyridine were tested. During this screening process, it was found

Scheme 4[a]



[a] Reactions and conditions: (a) Ph_3SiOH (3 equiv), toluene; (b) 1,10-phenanthroline, 82%; (c) $MnCl_2$, toluene, 80−100 °C.

that carefully dried 1,10-phenanthroline leads to the nicely crystalline complex **15**, which seems to be indefinitely stable on the benchtop without any precautions whatsoever (Scheme 4).[56] However, judging from the lack of catalytic activity in the metathesis of 1-phenyl-1-propyne as the model reaction, the bidentate ligand does not seem to come off the metal template to any noticeable extent at temperatures below 110 °C.

Gratifyingly, though, the catalytic activity can be restored upon treatment of **15** with metal salts that are able to form stable complexes with phenanthroline, including $MnCl_2$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $CuCl_2$, $ZnCl_2$, $MgCl_2$, and $NiCl_2$ (see the Supporting Information). Among them, $MnCl_2$ is preferred for practical reasons, because this salt is cheap, benign, nontoxic, readily available, hardly Lewis acidic, and nonhygroscopic; hence, commercial samples can be used as such without further drying. The activation of complex **15** with $MnCl_2$ can be performed either prior to the addition of the substrate or in its presence. As expected, the combination of **15**/$MnCl_2$ shows roughly the same activity and selectivity profile as the pyridine complex **13**, since both systems are thought to release an identical active fragment, i.e., complex **12**. Tables 1−3 provide a detailed survey of the performance of the **15**/$MnCl_2$ system in a host of inter- and intramolecular alkyne metathesis reactions (see below).

In view of its impressive scope and unparalleled stability, complex **15** is considered a highly practical yet broadly applicable precatalyst for alkyne metathesis. Although its reactivity after treatment with $MnCl_2$ or related salts is clearly lower than that of preformed Schrock alkylidynes such as **1**−**5** or the powerful precursor complex **6**, the handling of **15** is trivial and the functional group tolerance uncompromised, rivaling or even surpassing that of **1**−**6**; *note that storage on the benchtop in air is totally inconceivable for* ***1***−***6*** *or any other structurally defined alkyne metathesis catalyst known to date*, and even the pyridine adduct **13** will eventually degrade in moist air. An optimized synthesis (see experimental details in the Supporting Information) allows multigram amounts of **15** to be prepared from inexpensive Na_2MoO_4.

The reason why even the only weakly Lewis acidic $MnCl_2$ is capable of pulling the phenanthroline ligand off the Mo(6+) template may be found in the structure of complex **15** in the solid state. As can be seen from Figure 1, the strongly distorted octahedral coordination geometry brings the bulky Ph_3SiO- groups in a *mer* arrangement. The N(1)≡Mo−N(3) angle of

(52) For alkyne metathesis catalysts modified by different silanols, see: (a) Cho, H. M.; Weissman, H.; Wilson, S. R.; Moore, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 14742. (b) Villemin, D.; Héroux, M.; Blot, V. *Tetrahedron Lett.* **2001**, *42*, 3701.

(53) For alkyne metathesis catalysts grafted onto silica, see: (a) Coutelier, O.; Gauvin, R. M.; Nowogrocki, G.; Trébosc, J.; Delevoye, L.; Mortreux, A. *Eur. J. Inorg. Chem.* **2007**, 5541. (b) Cho, H. M.; Weissman, H.; Moore, J. S. *J. Org. Chem.* **2008**, *73*, 4256. (c) Chabanas, M.; Baudouin, A.; Copéret, C.; Basset, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 2062. (d) Weissman, H.; Plunkett, K. N.; Moore, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 585. (e) Gauvin, R. M.; Coutelier, O.; Berrier, E.; Mortreux, A.; Delevoye, L.; Paul, J.-F.; Mamède, A.-S.; Payen, E. *Dalton Trans.* **2007**, 3127. (f) Merle, N.; Taoufik, M.; Nayer, M.; Baudouin, A.; Le Roux, E.; Gauvin, R. M.; Lefebvre, F.; Thivolle-Cazat, J.; Basset, J. M. *J. Organomet. Chem.* **2008**, *693*, 1733.

(54) For a recent application of complex **13** in alkaloid total synthesis, see: Smith, B. J.; Sulikowski, G. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 1599.

(55) For the acylation chemistry of terminal metal nitrides, see the following for leading references: (a) Curley, J. J.; Sceats, E. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 14036. (b) Clough, C. R.; Greco, J. B.; Figueroa, J. S.; Diaconescu, P. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 7742. (c) Figueroa, J. S.; Piro, N. A.; Clough, C. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 940. (d) Sarkar, S.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 16128. and literature cited therein.

(56) A year-old batch shows unchanged appearance and catalytic activity.

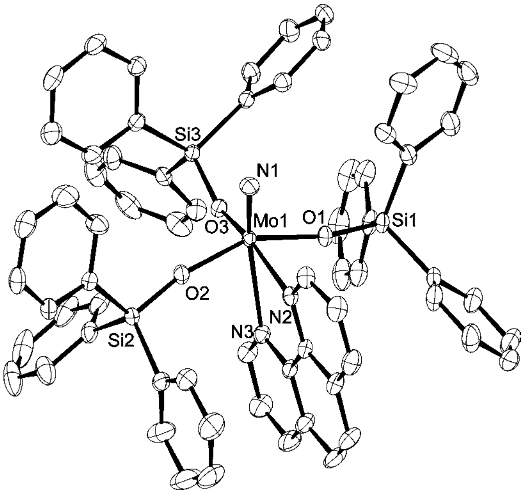


Figure 1. Structure of Mo(≡N)($OSiPh_3$)$_3$(phen) (**15**) in the solid state (N1−Mo1−N2 = 91.2(1)°). Disordered solute toluene is omitted for clarity; phen = 1,10-phenanthroline.

160.24(7)° deviates significantly from 180° and the Mo atom lies 0.33(1) Å above the plane defined by N(2), O(1), O(2) and O(3). Importantly, the Mo−N(3) distance of 2.512(2) Å is much larger than the distance from the metal to the phenanthroline nitrogen atom in the equatorial plane (Mo−N(2) 2.292(2) Å). The fact that the second N-atom of the chelate ligand obviously binds very weakly may explain why **12**, even in the presence of excess pyridine, affords only the monoadduct **13** (Scheme 3). Two of the three Mo−O−Si angles are surprisingly obtuse (Mo−O(1)-Si(1) 165.26(8)°, Mo−O(2)-Si(2) 168.04(8)°, Mo−O(3)-Si(1) 145.78(8)°), which likely reduces the congestion in the periphery. The Mo≡N(1) bond (1.659(2) Å) is slightly longer than that observed in the pyridine adduct **13** (1.653(2) Å)[49] and near the longer end of reported Mo≡N distances (1.563−1.688 Å,[57] with the exception of one outlier of 1.786 Å).[58]

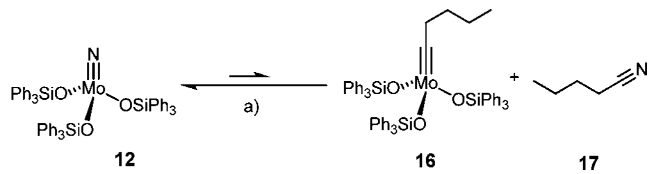
Molybdenum Alkylidyne Complexes with Ancillary Silanolate Ligands. As already mentioned, inspiration for the development of the novel silanolate complexes presented here was the work of Johnson et al., who showed that certain metal nitride species can convert into the corresponding alkylidyne complexes on reaction with a nonterminal alkyne (Scheme 2).[50] An analogous metathetic exchange process is believed to account for the catalytic activity exhibited by nitrides **12**, **13**, and **15**. Yet, on NMR inspection of a mixture comprising (Ph_3SiO)$_3$Mo≡N (**12**)[59] and 5-decyne (2 equiv) in toluene-d_8, we were not able to detect appreciable amounts of valeronitrile (**17**), which must form in a quantity equal to that of the presumed alkylidyne complex **16** (Scheme 5). Only after prolonged heating of the mixture in a sealed tube (100 °C, 6 d) were small amounts of **17** discernible, in addition to massive polymerization of the mixture (see the Supporting Information).

(57) (a) Chisholm, M. H.; Davidson, E. R.; Pink, M.; Quinlan, K. B. *Inorg. Chem.* **2002**, *41*, 3437. (b) Ritleng, V.; Yandulov, D. V.; Weare, W. W.; Schrock, R. R.; Hock, A. S.; Davis, W. M. *J. Am. Chem. Soc.* **2004**, *126*, 6150.

(58) Dilworth, J. R.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *Inorg. Chem. Acta* **1983**, *71*, 21.

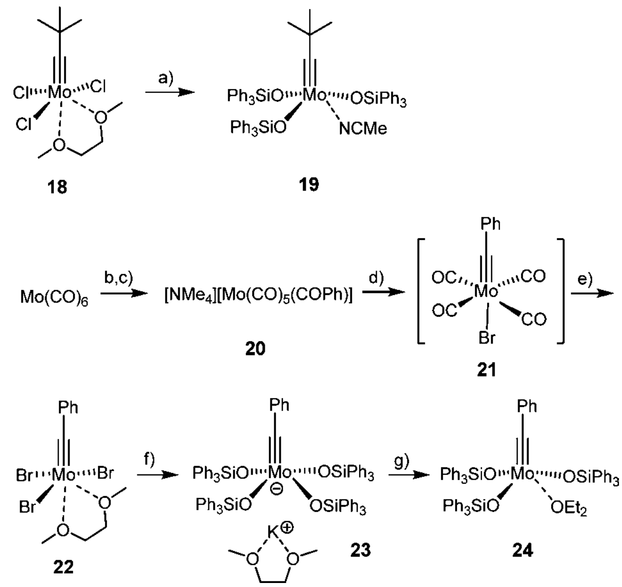
(59) This experiment was deliberately performed with **12** generated in situ from **11** and Ph_3SiOH, as such a solution is free of any N-donor ligand that might retard the metathetic nitride/alkylidyne interconversion by complexation to the metal center.

Scheme 5 [a]



[a] Reagents and conditions: (a) 5-decyne, toluene-d_8, 100 °C, cf. text.

Scheme 6 [a]



[a] Reagents and conditions: (a) Ph_3SiOLi (3 equiv), Et_2O, −40 °C → rt, then MeCN, 85%; (b) PhLi, Et_2O, reflux; (c) NMe_4Br, H_2O, 52% (over both steps); (d) oxalyl bromide, CH_2Cl_2, −78 °C → −15 °C; (e) Br_2, 1,2-dimethoxyethane (dme, 5 equiv), CH_2Cl_2, −78 °C → rt, 88% (over both steps); (f) Ph_3SiOK (4 equiv), toluene; (g) Et_2O, 92%.

The striking inefficiency of the crucial nitride → alkylidyne exchange compared with the excellent catalytic performance of **15** in our preparative experiments (Tables 1−3) implies that the small amounts of alkylidynes, such as **16**, formed in the mixture must be superbly active. We sought to clarify this aspect by preparing the hitherto unknown molybdenum alkylidynes of the general structure (Ph_3SiO)$_3$Mo≡CR and derivatives thereof. This goal was readily attained by adaptation of the established entry routes to related d^0-alkylidynes (Scheme 6). Specifically, the desired neopentylidyne complex **19**·MeCN was obtained by ligand exchange of the corresponding trichloride **18**, which, in turn, was prepared according to the route previously reported by the Schrock group.[32] Much more efficient overall was the synthesis of the corresponding benzylidyne analogue **24**·Et_2O, which was formed analogously from cheap $Mo(CO)_6$ via the known building block **22**.[60,61] As described in the Supporting Information, **24**·Et_2O can be obtained in only three operations, as the intermediates **21** and **23** need not be isolated.

(60) (a) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Fischer, E. O.; Maasböl, A. Ger. Offen. DE 1214233, 1966; *Chem. Abstr.* **1966**, *65*, 12474.

(61) (c) Mayr, A.; McDermott, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 548. (d) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallic* **1987**, *6*, 925.

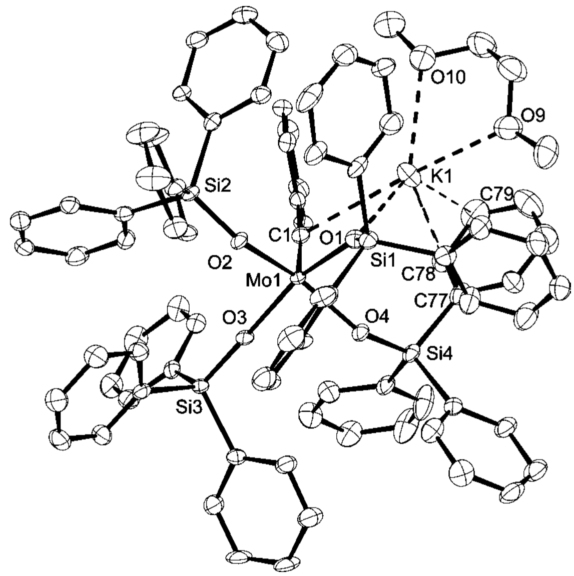


Figure 2. Structure of the ate-complex $[(Ph_3SiO)_4Mo{\equiv}CPh]^-$ $[K^+{\cdot}(dme)]$ (**23**) in the solid state. Only one of the two independent molecules in the unit cell is depicted for clarity; dme =1,2-dimethoxyethane.

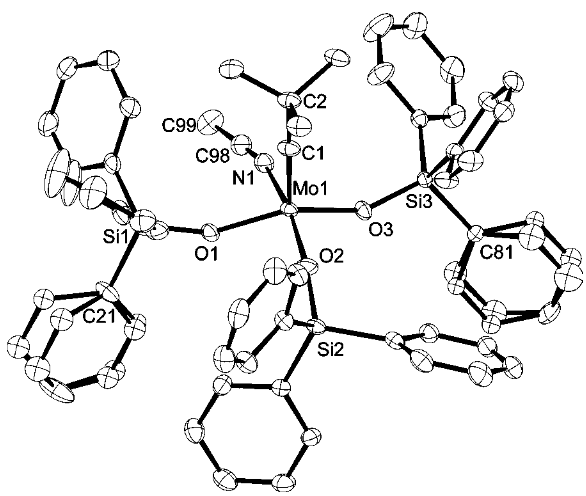


Figure 3. Structure of the complex $Mo({\equiv}CtBu)(OSiPh_3)_3(MeCN)$ (**19**·MeCN) in the solid state (C1−Mo1−N1 94.4(1)°). Two of the phenyl groups (at C21 and C81) are disordered over two positions.

Interestingly, we noticed that the primary product formed during the ligand-exchange process of **22**[62] and Ph_3SiOK was the ate-complex **23**, in which four rather than three silanolates are covalently bound to the molybdenum center (Figure 2).[63] This may be taken as an indication for the poor donor capacity of the silanolates, which allows the molybdenum to retain an appreciable Lewis acidity, which is essential for high activity in alkyne metathesis.[32] Even though the Ph_3SiO unit seems very bulky, the complex accommodates four of them in a square pyramidal environment about the metal center, with the alkylidyne forming the apex and the silanolates the basal plane. The bond angles of the individual Si−O−Mo units differ quite significantly from each other and can be almost linear (Mo(1)−O(3)−Si(3) 177.8(3)°; Mo(1)−O(2)−Si(2) 151.8(2)°; Mo(1)−O(4)−Si(4) 149.0(3)°). This suggests that the Si−O−Mo groups serve as hinges which, through facile bending, allow for optimal use of the available space in the periphery. The potassium cation escorts the molybdate core by binding to the fourth silanolate oxygen, which is more pyramidalized than the other oxygen atoms in order to make its lone pairs accessible for binding to the cation (Mo(1)−O(1)−Si(1) 134.5°). The Mo≡C distances of the two independent molecules of **23** at 1.747(6) and 1.756(5) Å are slightly longer than the equivalent distance of the corresponding neutral analogue **19**·MeCN (1.741(2) Å; see below).

(62) Complex **22** was prepared according to ref 60. A detailed procedure is described in the Supporting Information.

(63) This ate-complex crystallizes from the reaction mixture even if only 3 equiv of Ph_3SiOK is added to complex **22**.

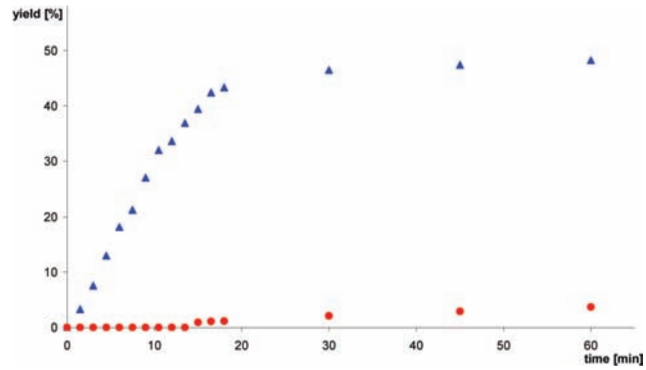


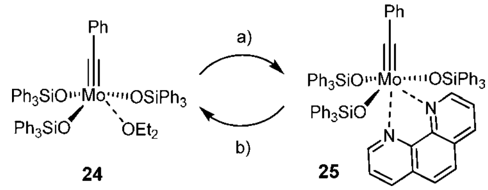
Figure 4. Metathetic conversion of 1-phenyl-1-propyne to tolane catalyzed by 1 mol % of either $Mo({\equiv}CPh)(OSiPh_3)_3(Et_2O)$ (**24**· Et_2O) (blue triangles) or $(tBuO)_3W{\equiv}CtBu$ (**1**) (red circles) in toluene at ambient temperature and ambient pressure. The yields were determined by GC using biphenyl as an internal standard.

Workup of the crude mixtures by evaporation of the solvent and trituration of the residues with MeCN or Et_2O delivered the neutral alkylidyne complexes **19** and **24**, respectively, in the form of the corresponding adducts. Their NMR data were in excellent agreement with the proposed structures. The constitution of **19**·MeCN was unambiguously confirmed by crystal structure analysis (Figure 3), which revealed a distorted square pyramidal coordination geometry about the Mo center. The Mo≡C(1) bond length of 1.741(2) Å is slightly shorter than in the ate-complex **23**. Interestingly, the acetonitrile ligand does not bind in a strictly linear fashion, as evident from the Mo−N(1)−C(98) angle of only 166.31(15)°; moreover, the C≡N triple bond is extended to 1.145(3) Å as a result of the coordination to the high-valent metal center (reference bond length for RC≡N, 1.136 Å).[64] However, no spontaneous metathesis takes place between the ligated nitrile and the alkylidyne unit as a consequence of the still largely end-on rather than side-on coordination mode of the C≡N triple bond.

As expected for prototype Schrock alkylidynes, the acetonitrile and ether adducts of **19** and **24** are both air- and moisture-sensitive. Even though they do not provide any advantage over other alkylidynes in terms of handling, they turned out to be exquisitely active alkyne metathesis catalysts which are operative at low loadings and distinguished by an outstanding selectivity profile. Whereas the preparative details are outlined in a later section of this paper, the plot for the conversion of 1-phenyl-1-propyne to tolane catalyzed by **24**·Et_2O against the rate recorded for the classical tungsten neopentylidyne $(tBuO)_3W{\equiv}CCMe_3$ (**1**), which defines the standard in the field, clearly demonstrates the extraordinary performance of the novel catalyst (Figure 4). Specifically,

(64) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Scheme 7 [a]



[a] Reagents and conditions: (a) 1,10-phenanthroline, toluene/Et_2O, 81%; (b) $MnCl_2$, toluene, 80 °C.

the equilibrium is reached after 25 min at ambient temperature; at this point, complex **1** gave less than 5% conversion. Although molybdenum alkylidynes are generally considered less active than their tungsten counterparts,[31,32,65] these data show that the triphenylsilanolate ligands impart a truly remarkable activity onto the operative molybdenum alkylidyne unit, rendering **24**·Et_2O one of the most active metathesis catalysts known to date. This, in turn, corroborates the view that even small amounts of $(Ph_3SiO)_3Mo{\equiv}CR$ generated in situ from $(Ph_3SiO)_3Mo{\equiv}N{\cdot}L$ (L = pyridine, phenanthroline) and an appropriate alkyne can account for the excellent results obtained with such robust precatalyst systems. Actually, we currently believe that nitride complexes of the type $(Ph_3SiO)_3Mo{\equiv}N{\cdot}L$ act as a reservoir, from which tiny amounts of active alkylidyne species are constantly released during the reaction. This may explain why solutions of **13** and **15** retain catalytic activity at 80 °C over the course of days,[49] whereas all known metal alkylidynes degrade when kept under such forcing conditions for prolonged periods of time.

In an attempt to transfer the stabilizing effect of 1,10-phenanthroline from the metal nitride to the metal alkylidyne series, the crude reaction mixture formed upon ligand exchange of $Br_3Mo{\equiv}CPh{\cdot}dme$ (**22**) with Ph_3SiOK was added to a solution of carefully dried 1,10-phenanthroline in toluene. The desired adduct **25** could be isolated from this mixture in good yield (Scheme 7). Its structure, as determined by X-ray crystallography (Figure 5), closely resembles the structure of the isolobal nitride complex **15**. Once again, a strongly distorted coordination geometry about the metal center is observed, characterized by a significant deviation of the C(1)≡Mo···N(1) axis (168.34(11)°) from linearity. The Mo···N bond lengths are again very uneven (2.244(2) versus 2.408(2) Å), with the distance to the apical nitrogen being much longer. The alkylidyne bond length Mo≡C(1) (1.761(3) Å) exceeds those in the corresponding square pyramidal nitrile adduct **19**·MeCN (1.7410(17) Å) and the ate-complex **23** (1.747(6)/1.756(5) Å).

Importantly, the 1,10-phenanthroline ligand stabilizes this particular Schrock alkylidyne to the extent that complex **25** is stable in air for hours;[66,67] however, complex **25** per se does not react with 1-phenyl-1-propyne to any appreciable extent under conditions in which the corresponding ether adduct **24**·Et_2O leads to very fast conversions. Gratifyingly, though, addition of commercial $MnCl_2$ (1 equiv relative to **25**) and heating of the reaction mixture for 30 min to about 80 °C restores an outstanding performance; the resulting catalyst solution containing complex **24** is then active even at ambient temperature. The ligand swap from molybdenum to manganese can easily be monitored by precipitation of $MnCl_2{\cdot}$phen and was confirmed by mass spectrometry. Within experimental error, the resulting solutions are largely equipotent to those containing authentic **24**·Et_2O (see Tables 1−3 for details) and are able to metathesize most alkyne substrates within unprecedentedly short periods of time. Likewise, the functional group tolerance is extraordinary (see below). Therefore, we conclude that complex **25** is an excellent compromise between the desirable activity, selectivity, and practicality aspects associated with alkyne metathesis.

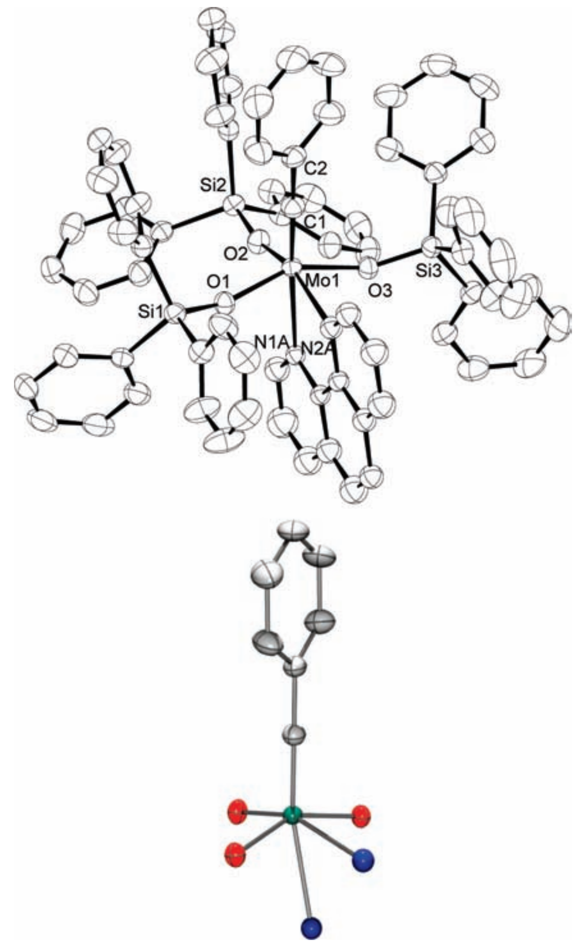


Figure 5. Top: Structure of Mo(≡CPh)$(OSiPh_3)_3$(phen) (**25**) in the solid state. The 1,10-phenanthroline ligand is disordered over two positions in the ligand plane (one conformation shown). Bottom: Core of the complex showing the distorted coordination geometry about the Mo center (green); O, red; N, blue.

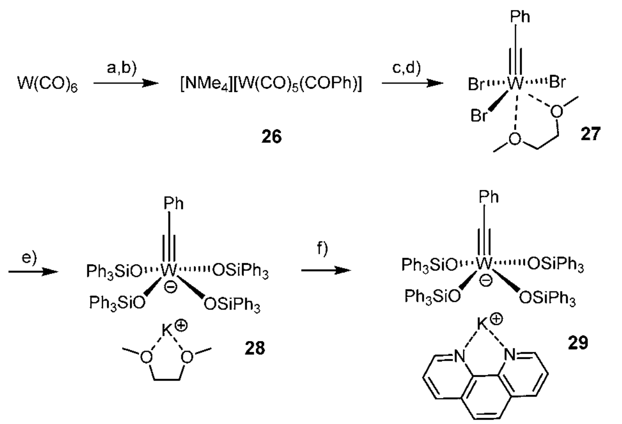
The user may hence choose among (i) the air-sensitive Mo(≡CPh)$(OSiPh_3)_3(Et_2O)$ (**24**·Et_2O), which is superbly active and selective; (ii) the phenanthroline adduct **25** thereof, which, after activation with $MnCl_2$, is similarly potent but can be handled in air, even though it still needs to be stored under argon; and (iii) the totally air-stable nitride complex **15**, which is exceptionally user-friendly. The preexisting alkylidyne unit present in **24** and **25** ensures that these complexes are active under notably mild conditions even at very low loadings (see

(65) For a computational study, see: Zhu, J.; Jia, G.; Lin, Z. *Organometallics* **2006**, *25*, 1812.

(66) Crystalline samples of **25** seem partly intact after several days in air.

(67) (a) Addition of hydrotris(3,5-dimethyl-1-pyrazolyl)borate to (dme)$Cl_3W{\equiv}CPh$ leads to an air-stable but catalytically inactive Schrock alkylidyne; see: Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066. (b) An analogous complex derived from (dme)$Br_3W{\equiv}CPh$ was described as moderately air-stable but sensitive to moisture; see: Jeffery, J. C.; McCleverty, J. A.; Mortimer, M. D.; Ward, M. D. *Polyhedron* **1994**, *13*, 353.

Scheme 8[a]



[a] Reagents and conditions: (a) PhLi, Et_2O, reflux; (b) NMe_4Br, H_2O, 55% (over both steps); (c) oxalyl bromide, CH_2Cl_2, −78 °C → −15 °C; (d) Br_2, 1,2-dimethoxyethane (dme, 5 equiv), CH_2Cl_2, −78 °C → rt, 85% (over both steps); (e) Ph_3SiOK (4 equiv), toluene; (f) 1,10-phenanthroline, toluene, 79%.

below), whereas nitride **15** first needs to be converted into an operative alkylidyne in situ, a process that mandates higher loadings of the precatalyst and heating of the mixture to about 80 °C. Whatever precatalyst one might prefer, however, all systems are available in quantity from cheap and commercially available starting materials, lead to excellent preparative results, and compare favorably with all established alkyne metathesis catalysts (see below). Complex **25** is much more stable and practical than any other catalytically active Schrock alkylidyne known to date. Therefore, we believe that these systems, collectively, represent a significant step forward in our quest for truly user-friendly yet generally applicable alkyne metathesis catalysts.

Tris(triphenylsilyloxy)tungsten Alkylidyne Complexes. To study the generality of the concept, the corresponding tungsten alkylidynes endowed with triphenylsilanolate ancillary ligands were targeted. To this end, the known benzylidyne tribromide complex **27**[60,61] was subjected to ligand exchange with Ph_3SiOK in toluene, which furnished the corresponding ate-complex **28** (Scheme 8). In contrast to its molybdenum analogue **23**, however, treatment with 1,10-phenanthroline in toluene did not afford a neutral adduct but merely replaced the dme ligated to the potassium counterion to give the surprisingly robust ate-complex **29**. X-ray diffraction proved that the phenanthroline ligand binds to the potassium escort rather than the tungsten center (Figure 6). Overall, the structure of **29** in the solid state resembles the molybdenum counterpart **23**, featuring again three obviously flexible metal−O−Si moieties, which manage the bulk in the periphery by appropriate bending. The W≡C(1) bond length (1.758(2) Å) is identical within the error limits to the corresponding bond length in the molybdenum species **23** (1.747(6)/1.756(5) Å).

The corresponding neutral tungsten alkylidyne species could not, so far, be generated upon trituration of **28** or **29** with Et_2O nor on reaction with TMSCl. Not unexpectedly, the catalytic activity of these stable ate complexes themselves is marginal. Even though 1-phenyl-1-propyne slowly gets consumed, only small amounts of tolane (≤25%) were detected. As polymerization seems to prevail, this particular complex is not relevant in the present context; its reaction behavior as well as further attempts to secure neutral tungsten alkylidynes of the general type $[(Ph_3SiO)_3W{\equiv}CR]\cdot L$ are subject of a separate investigation.

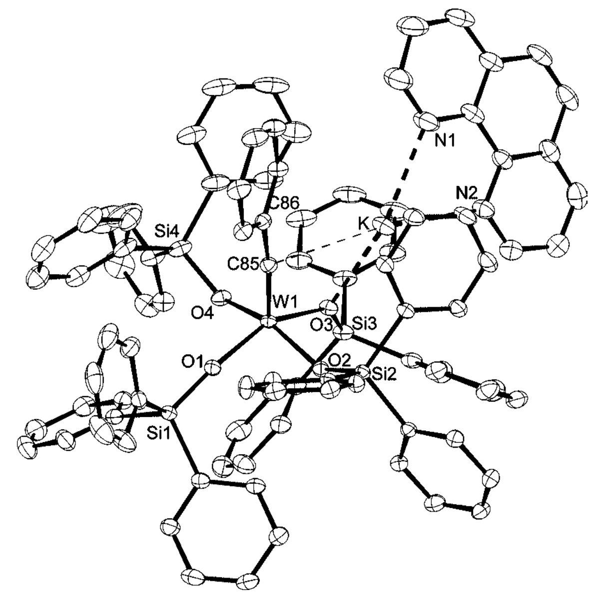


Figure 6. Structure of the ate-complex $[(Ph_3SiO)_4W{\equiv}CPh]^-$ $[K^+\cdot(phen)]$ (**29**) in the solid state.

Scheme 9. Formation of 2-Butyne as a Generic Byproduct in the Reaction of Alkynes End-Capped with a Methyl Group, As Exemplified by the Conversion of 1-Phenyl-1-propyne to Tolane

$$2\ \text{Ph}-\text{C}{\equiv}\text{C}-\text{Me} \xrightleftharpoons{\text{catalyst}} \text{Ph}-\text{C}{\equiv}\text{C}-\text{Ph} + \text{2-butyne}$$

Beneficial Effect of 5 Å Molecular Sieves on Alkyne Metathesis. A priori, the metathetic scrambling of a pair of alkynes leads to an equilibrium, which needs to be shifted to one side in order to make the reaction preparatively useful. If one of the products is an alkyne of low molecular weight (2-butyne, 3-hexyne, etc.), this goal is usually accomplished by driving this compound out of the mixture.

Therefore, alkynes with capping methyl substituents are the most common substrates, and the reactions are usually per-

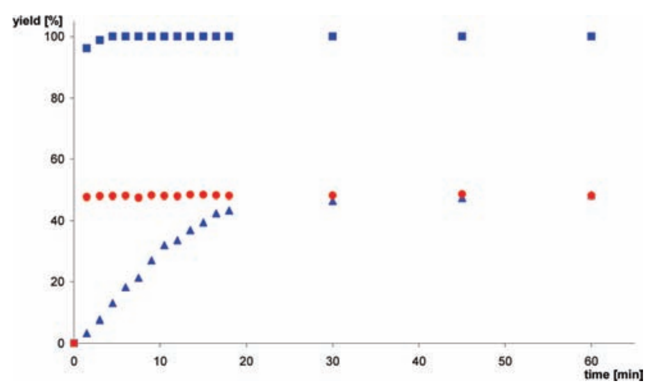


Figure 7. Metathesis of 1-phenyl-1-propyne catalyzed by $Mo({\equiv}CPh)(OSiPh_3)_3(Et_2O)$ (**24**$\cdot Et_2O$, 1 mol %) in toluene in the absence (blue triangles) or in the presence (blue squares) of powdered MS 5 Å at ambient temperature. Comparison with the plot obtained upon pretreatment of the catalyst with MS 5 Å, which was removed prior to the addition of the substrate (red circles). The yields were measured by GC against biphenyl as internal standard.

(68) (a) Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 12796. (b) Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 11863. (c) Zhang, W.; Brombosz, S. M.; Mendoza, J. L.; Moore, J. S. *J. Org. Chem.* **2005**, *70*, 10198.

formed at elevated temperatures and/or by applying gentle vacuum (Scheme 9). However, the solubility of 2-butyne in hydrocarbon solvents is non-negligible, and the use of reduced pressure may lead to undesirable changes in the concentration of the mixture, as the solvent will eventually also distill off. Moreover, 2-butyne may be consumed by certain alkyne metathesis catalysts in a competitive polymerization process.[39a] To avoid such problems, Moore and co-workers have developed a "precipitation-driven" setup for alkyne metathesis;[68] though highly productive, this approach requires tailor-made starting materials and is less favorable from the viewpoint of atom economy.

Since catalysts of increased activity, such as **24**·Et_2O, allow the reaction to be performed at ambient temperature, the problem of possible 2-butyne (bp = 27 °C) accumulation in solution becomes more pressing. This is evident from Figure 7, which shows that the metathesis of 1-phenyl-1-propyne effected by **24**·Et_2O (1 mol %) in toluene is fast but levels off at about 50% conversion after 20 min when carried out at ambient temperature and atmospheric pressure (blue triangles).

We reasoned that 2-butyne might also be removed from the mixture with the aid of an appropriate molecular sieve (MS).[69] Since activated MS 5 Å is capable of adsorbing C4 hydrocarbons,[70] the reaction was repeated in the presence of 2 mg of MS 5 Å per μmol of released 2-butyne.[71] The corresponding plot (blue squares) in Figure 7 shows the dramatic effect of this additive on the reaction rate as well as the conversion, which is essentially complete within 5 min under otherwise identical conditions. This outcome cannot be explained by simple removal of moisture from the mixture, as the equilibrium is not affected by adventitious water. This notion is corroborated by the fact that MS 3 Å has no significant effect on the reaction, even though it is known to bind water effectively; MS 4 Å is slightly less efficient than MS 5 Å, which is the preferred additive (see Supporting Information).

The data in Figure 7 also show that added MS 5 Å not only improves the conversion but also significantly accelerates the reaction rate. This effect became particularly evident when a solution of **24**·Et_2O in toluene was stirred in the presence of powdered MS 5 Å for 30 min and the molecular sieves were then removed from the mixture prior to the addition of the substrate. In this case, the equilibrium is reached in <5 min (Figure 7, red circles), which is much faster than the reaction without this "preactivation". It is believed that the MS 5 Å helps liberate the required free coordination site at molybdenum by absorbing the only weakly bound diethyl ether ligand.[72,73]

In any case, this simple measure of adding powdered MS 5 Å to the reaction mixture turned out to be general and was applied to all preparative experiments compiled in Tables 1−3, unless stated otherwise.[75] Consequently, we recommend the use of MS 5 Å in future alkyne metathesis reactions independent of the chosen catalyst and hope that this convenient setup will make the preparation of tailor-made substrates largely unnecessary.

Survey of the Preparative Scope of the New Alkyne Metathesis Catalysts. With a set of new (pre)catalysts and an optimized procedure for alkyne metathesis at hand, we were committed to explore the scope of this methodology in detail. To this end, a representative set of alkyne homometathesis, alkyne cross-metathesis (ACM),[74] and ring-closing alkyne metathesis (RCAM) reactions was investigated, as well as a prototype cyclooligomerization. Even though not all substrates were tested with all available catalysts, care was taken to accumulate a sufficiently large data set for direct comparison. Furthermore, particular attention was paid to investigating the compatibility of the novel catalysts with polar functional groups, since this aspect is key for future applications in advanced organic synthesis and material science.

The results compiled in Tables 1−3 deserve further comment. With very few exceptions, complexes **15**, **24**·Et_2O, and **25** behaved similarly well, giving good to excellent results with a diverse set of functionalized substrates. Although it may not be surprising that the isolated yields tended to be highest when the preformed alkylidyne **24**·Et_2O was employed, the very stable molybdenum nitride **15** also performed remarkably well. The price to be paid for the use of this fully air stable precatalyst, however, is a larger loading (generally 10 mol %), a higher reaction temperature (usually 80 °C),[75] and longer reaction times.

As expected, the data compiled in the tables also show that the alkylidyne complex **24**·Et_2O and the much more robust phenanthroline adduct **25** thereof, after activation with $MnCl_2$, by and large lead to the same preparative results, although slightly higher loadings were applied in the latter case. However, it is emphasized that the catalyst loading has not been optimized for each entry reported here. In view of the spectacular reactivity of **24** (see Figure 7), we are optimistic that loadings well below the 1−2 mol % generally used during this investigation can be reached by proper adjustment of the reaction parameters, in particular since the half-life of **24**·Et_2O in toluene-d_8 was found to be ~30 h at ambient temperature (see Supporting Information). In fact, a single experiment, in which 1-phenyl-1-propyne was exposed to only 0.1 mol % of **24**·Et_2O and the usual loading of MS 5 Å, reached 95% conversion (GC) after 2 h reaction time. Likewise, the same model substrate was quantitatively converted to tolane within ≤20 min by 1 mol % of complex **24**·Et_2O, even at −10 °C. To the best of our knowledge, this is the lowest temperature at which an alkyne metathesis has so far been successfully performed, but it does not seem to mark the lower limit for our new catalyst.

The compatibility of the new catalysts with various functional groups is outstanding. Esters, ethers, various silyl ethers,

(69) Alkyne metathesis reactions using Mortreux-type catalyst mixtures have previously been run in the presence of MS 4 Å in order to remove traces of moisture. However, it was reported later that carefully dried solvents make the addition of MS 4 Å unnecessary. No effect of this additive on the conversion was noticed; see: (a) Huc, V.; Weihofen, R.; Martin-Jimenez, I.; Oulié, P.; Lepetit, C.; Lavigne, G.; Chauvin, R. *New J. Chem.* **2003**, *27*, 1412. (b) Maraval, V.; Lepetit, C.; Caminade, A.-M.; Majoral, J.-P.; Chauvin, R. *Tetrahedron Lett.* **2006**, *47*, 2155.

(70) MS 5 Å is slightly more effective than MS 4 Å, whereas the use of MS 3 Å has little effect, if any. Since MS 3 Å, however, is an efficient trap for water, this comparison shows that the observed rate acceleration and the improved yields are not caused by ensuring a rigorously dry medium.

(71) As expected, powdered MS 5 Å is more effective than the use of pellets, and about 2 mg/μmol butyne turned out to be optimal.

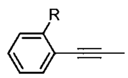
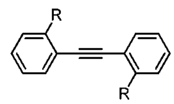
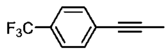
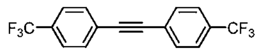
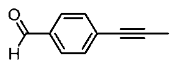
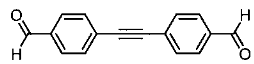
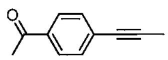
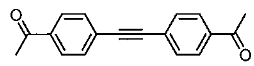
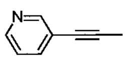
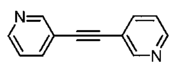
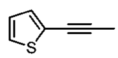
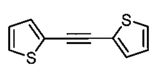
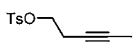
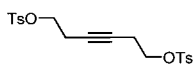
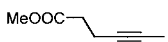
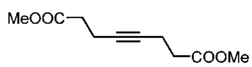
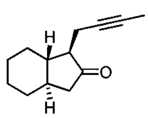
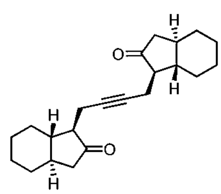
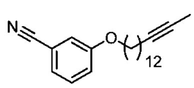
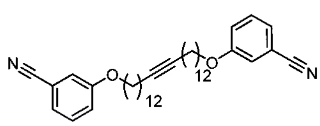
(72) Control experiments, in which the metathesis of 1-phenyl-1-propyne was carried out in Et_2O, THF, or CH_2Cl_2 as the reaction medium, did not go to complete conversion, even in the presence of molecular sieves. Reactions in THF were much slower than those in the other solvents investigated.

(73) Notably, the metathesis of 1-phenyl-1-propyne induced by the molybdate complex **23** (1 mol%) in toluene in the presence of MS 5 Å proceeded with the same rate as that induced by **24**·Et_2O/MS 5 Å.

(74) Fürstner, A.; Mathes, C. *Org. Lett.* **2001**, *3*, 221.

(75) As the reactions with complex **15** have to be performed at higher temperature, addition of molecular sieves is usually not necessary and sometimes even disadvantageous due to possible side reactions at this temperature.

Table 1. Intermolecular Alkyne Metathesis Reactions in the Presence of 5 Å Molecular Sieves

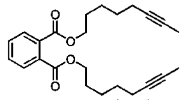
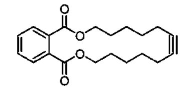
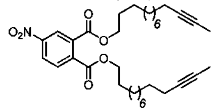
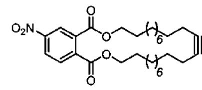
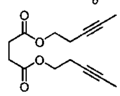
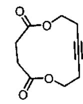
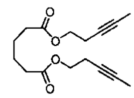
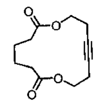
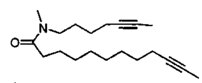
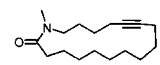
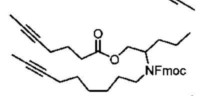
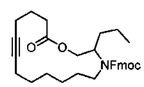
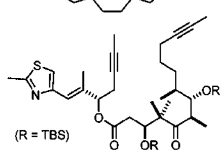
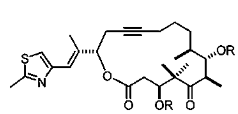
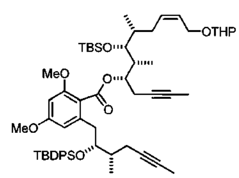
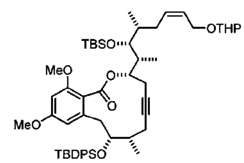
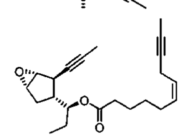
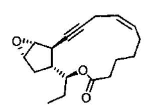
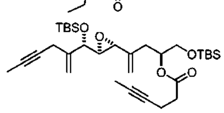
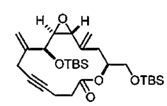
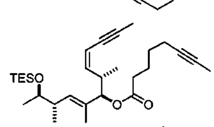
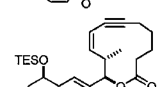
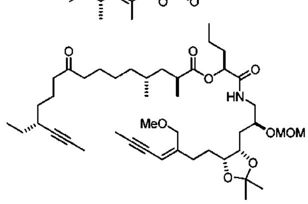
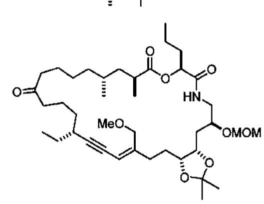
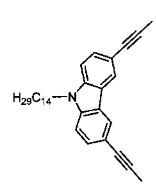
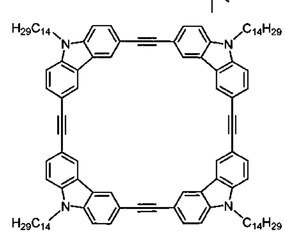
Entry	Substrate	Product		**15**[a]	**24**·Et_2O[b]	**25**[c]
1			R = H	99%	99%	99%
2			R = OMe	96%	97%	97%
3			R = SMe	87%	98%[d]	96%[d]
4			R = COOMe	72%[e]	95%	97%
5				94%	93%	95%
6				NR	NR	NR
7				< 40%[e,f]	84%	84%
8				76%[e]	90%[d]	88%[d]
9				86%	88%	87%
10				95%	92%	92%
11				85%	89%	91%
12					92%	88%
13				81%	87%	89%

[a] **15** (10 mol %), $MnCl_2$ (10 mol %), MS 5 Å, toluene, 80 °C, 30 min, then addition of the substrate and reaction at 80 °C unless stated otherwise. [b] **24**·Et_2O, (2 mol %), toluene, ambient temperature, MS 5 Å. [c] **25** (5 mol %), $MnCl_2$ (5 mol %), toluene, 80 °C, 30 min; then addition of the substrate and MS 5 Å, and reaction at ambient temperature. [d] At 50 °C. [e] At 100 °C. [f] Cf. text; NR = no reaction.

thioethers, sulfonates, amides, carbamates, ketones, acetals, epoxides (see below), nitro groups, and trifluoromethyl groups are generally well tolerated, even if they are oriented toward the reacting alkyne (Table 2, entry 12). Likewise, a nitrile was also found at least kinetically stable in the presence of all three novel molybdenum silanolate complexes, despite being a possible substrate for metathesis (Table 1, entry 13). Moreover, compounds containing various types of aromatic heterocycles (pyridine, thiophene, thiazole, carbazole) known to interfere with the activity of the classical tungsten alkylidyne **1**[13,38] were metathesized without problems. Chiral centers next to enolizable carbonyl groups were not racemized. An elimination-prone primary tosylate (Table 1, entry 10) as well as an acid- and base-sensitive aldol substructure (Table 2, entries 7) also remained intact. Although the orthogonal character of alkene and alkyne metathesis has previously been recognized,[24] the rigorous distinction of the catalysts between the π-systems of alkynes and olefins is noteworthy: olefins are inert, independent of whether they are mono-, di-, or trisubstuted, terminal, internal, or conjugated to a carbonyl group. Likewise, only the acetylene motif of a 1,3-enyne will undergo productive metathesis (Table 2, entries 11 and 12, and Table 3, entry 2), and even highly base- and acid-sensitive skipped 1,4-enynes posed no problems whatsoever (Table 2, entries 9 and 10).

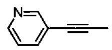
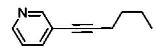
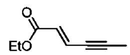
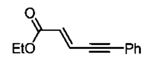
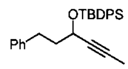
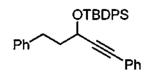
This excellent profile is particularly evident from a host of applications to compounds bearing more than one polar group (Table 2). We have largely relied upon substrates previously used in this laboratory for the total synthesis of bioactive natural products, including homoepilachnene (entry 6)[13] and epothilone C (entry 7).[38,40] The product shown in entry 10 leads to *ent*-amphidinolide V;[22a,b] this example is particularly noteworthy, as it contains reactive vinylepoxide, hydroxyepoxide, allylic ether, and skipped enyne motifs packed in a dense array, in addition to an ester and a silyl ether group. Entry 12 shows

Table 2. Intramolecular Alkyne Metathesis Reactions

Entry	Substrate	Product	15[a]	24·Et_2O[b]	25[c]
1			70%	97%	94%
2				85%	
3			91%	73%	78%
4			85%	92%	90%
5			67%	72%	
6				90%	
7				91%	
8				82%[d]	
9				90%[e]	
10				81%	
11				84%[e]	
12				79%	
13			83%	82%	81%

[a] **15** (10 mol %), $MnCl_2$ (10 mol %), toluene, 80 °C, 30 min, then addition of the substrate and reaction at 80 °C unless stated otherwise; no MS added, cf. ref 75. [b] **24**·Et_2O (2 mol %), toluene, ambient temperature, MS 5 Å. [c] **25** (5 mol %), $MnCl_2$ (5 mol %), toluene, 80 °C, 30 min, then addition of the substrate and MS 5 Å and reaction at ambient temperature. [d] At 80 °C. [e] With 4−5 mol % of catalyst.

Table 3. Alkyne Cross-Metathesis Reactions

Entry	Substrates		Product	15[a]	24·Et$_2$O[b]	25[c]
1		5-decyne		76%	65%	72%
2		tolane		50%	65%	62%
3		tolane		*d*	62%	61%

[a] **15** (10 mol %), $MnCl_2$ (10 mol %), MS 5 Å, toluene, 80 °C, 30 min, then addition of the substrate and reaction at 100 °C unless stated otherwise. [b] **24**·Et_2O (2 mol %), toluene, ambient temperature, MS 5 Å. [c] **25** (5 mol %), $MnCl_2$ (5 mol %), toluene, 80 °C, 30 min, then addition of the substrate and MS 5 Å and reaction at ambient temperature. [d] Only low conversion.

another highly adorned case, in which a ketone, ester, amide, two different acetals, a chelation-prone ether, seven chiral centers, and a 1,3-enyne entity are present; this particular product was instrumental for our synthesis of the antibiotic myxovirescin.[45] Equally instructive is entry 8, which shows the key intermediate en route to the highly cytotoxic F-ATPase inhibitor cruentaren A.[43] Whereas attempted ring closure of this densely substituted diyne substrate with the aid of the tungsten alkylidyne **1** resulted only in the cleavage of the −OTHP group due to the Lewis acidity of this complex, **24**·Et_2O afforded the 12-membered cycloalkyne in excellent yield. These applications are complemented by two additional examples from an ongoing synthesis project in this laboratory, which will be reported in separate publications in due time.[76] They are included in Table 2 to further illustrate the exceptional power of the new alkylidyne complex **24**·Et_2O in forming even particularly fragile (entry 9) as well as fairly strained compounds (entry 11). It is of note that the product displayed in entry 9 could not be made at all with the tungsten alkylidyne **1**, whereas complex **6** gave variable results and required high loadings (20−40 mol %), most likely due to competing side reactions with the very reactive oxirane ring of this particular compound. Apparently, the Mo center in **24**·Et_2O is not sufficiently Lewis acidic to cause any damage, and the silanolates do not engage in epoxide opening due to their low nucleophilicity. From the preparative viewpoint, it is also important to note that the RCAM reactions displayed in Table 2 were performed on scales ranging from a few milligrams to several grams of product (see the Supporting Information).

Another relevant case is the cyclooligomerization of the bis-propynylated carbazole derivative depicted in Table 2, entry 13. The resulting macrocycle is of interest in material science and was previously best prepared by "precipitation-driven" alkyne metathesis in trichlorobenzene that required, however, a specially designed starting material and a highly sensitive complex of type **5** (81%,[68] 61%,[77]). We were pleased to see that the new procedure, benefitting from the ability of MS 5 Å to drive the conversion of a propynylated substrate to completion at ambient temperature, was at least equally productive, independent of which of the newly prepared catalysts was chosen (81−83%).

Only a few limitations of the new molybdenum complexes have so far been encountered. As noticed previously for the pyridine adduct **13**,[49] epoxides do react with the catalysts and nitride species and hence destroy the activity of complexes **13** and **15**. Importantly, however, these reactive groups seem to be tolerated by the preformed alkylidyne **24**·Et_2O (Table 2, entries 9 and 10). Whether this compatibility is due to the fact that **24**·Et_2O reacts at ambient temperature, whereas **13** and **15** need heating, remains to be studied. Likewise, ketones posed no problem with catalysts **24**·Et_2O and **25** (Table 1, entries 7 and 12; Table 2, entry 12) but seem to interfere with the nitride complex **15**. Although the product of intermolecular metathesis of the acetophenone derivative shown in Table 1, entry 7, was detected (<40%), full conversion could not be reached in this particular case. Aldehydes, in contrast, seem to mark the limit of the current methodology. Attempts to metathesize a propynylated benzaldehyde derivative were unsuccessful because the catalysts quickly got destroyed (Table 1, entry 6). Ongoing work in this laboratory studies the stoichiometric reaction behavior of these complexes in more detail.

Conclusions

Although alkyne metathesis may never reach the breadth of alkene metathesis because of a smaller substrate base, the potential of this transformation is nevertheless significant, as witnessed by a rapidly increasing number of applications to sophisticated targets. To fully explore its scope, however, it is mandatory to make the required catalysts more readily available and user-friendly. To this end, we present a new generation of alkyne metathesis (pre)catalysts that are optimized for activity on the one hand and practicality on the other. Specifically, the readily available Schrock alkylidyne complex **24**·Et_2O constitutes one of the most active catalysts known to date, but retains an outstanding tolerance for functional groups. The only weakly donating triphenylsilanolate ligands impart a well-balanced level of Lewis acidity onto the d^0-molybdenum center, which is required for high catalytic activity yet is not high enough to endanger polar substituents. At the same time, the sheer size of the Ph_3Si residues prevents more than one alkyne from binding to the metal center and hence disfavors competing polymerization pathways while likely facilitating the cycloreversion of the metallacyclobutadiene intermediates. In contrast to the previously used alkoxides or fluorinated alkoxides, the bulk of the Ph_3SiO− unit seems more "flexible", as bending of the Mo−O−Si angle is facile. "Stretching" of this hinge provides the necessary space about the molybdenum and, as a consequence, prevents substrate-binding from becoming a limiting factor.

Although **24**·Et_2O itself is air- and moisture-sensitive, the corresponding phenanthroline adduct **25** is stable in air for hours.

(76) Hickmann, V.; Alcarazo, M.; Fürstner, A. *J. Am. Chem. Soc.* **2010**, in press (doi: 10.1021/ja104796a).
(77) Zhang, W.; Cho, H. M.; Moore, J. S. *Org. Synth.* **2007**, *84*, 177.

While solutions of this complex in toluene are inactive per se, reaction of **25** with $MnCl_2$ releases **24** into the solution by a ligand swap and thereby restores superb performance. The combination **25**/$MnCl_2$ is therefore considered a practical entry point into all kinds of alkyne metathesis reactions.

Even more facile is the manipulation of the corresponding phenanthroline nitrido complex **15**, which seems indefinitely stable on the benchtop. **15** is accessible in multigram quantities from inexpensive starting materials. It is again by phenanthroline transfer to $MnCl_2$ that an active template is released from this precatalyst, which needs, however, yet to undergo an exchange of nitride for alkylidyne to become active. Although this process requires heating to about 80 °C, the combination **15**/$MnCl_2$ performed very well in a representative number of inter- and intramolecular alkyne metathesis reactions.

Finally, we report that the addition of 5 Å molecular sieves exerts a pronounced effect on the reaction rate as well as on the conversion in metathesis reactions of alkynes bearing a methyl end-cap. This beneficial influence is ascribed to the removal of 2-butyne from the mixture by absorption into the pores. This operationally simple measure drives the conversion, allows the reactions to be conducted at ambient temperature and atmospheric pressure, and makes the use of designer substrates unnecessary.

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Supporting Information Available: Experimental section including spectroscopic data of all compounds, further information about the structure of the complexes in the solid state, and additional screening data. This material is available free of charge via the Internet at http://pubs.acs.org.

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