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Facile Synthesis of Trialkoxymolybdenum(VI) Alkylidyne Complexes for Alkyne Metathesis

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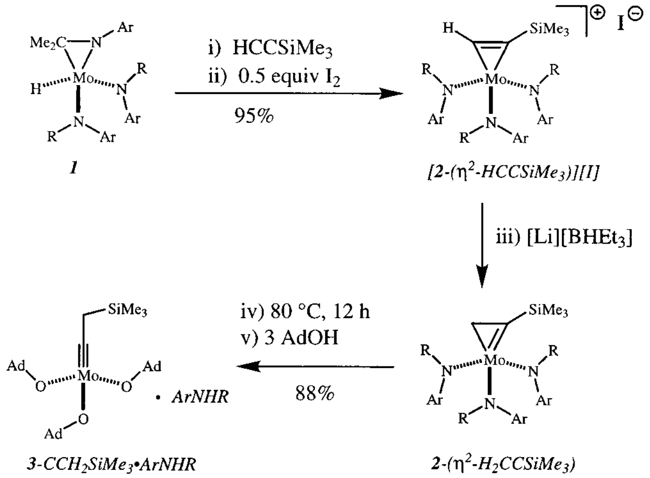
Summary: New molybdenum(VI) alkylidyne complexes $(Ar[^iPr]N)_3MoCCH_2SiMe_3$ *(Ar* $=$ *3,5-*$C_6H_3Me_2$*) and* $(^1AdO)_3MoCR$ *(R* $=$ *Me, Et,* CH_2SiMe_3*) were obtained in high yield and in multigram quantities starting from a known metallaaziridine−hydride complex. The synthetic protocol involves treatment with* Me_3SiCCH*, heating, and ligand exchange via alcoholysis;* $(^1AdO)_3MoCCH_2SiMe_3$ *is an active catalyst for alkyne metathesis at room temperature.*

Prototypical among well-defined catalysts for the alkyne metathesis reaction are the trialkoxytungsten(VI) alkylidyne complexes of Schrock, as typified by $(^tBuO)_3WC^tBu$.[1−4] Such tungsten catalysts have been employed recently for the synthesis of large organic rings.[5−7] Molybdenum analogues are expected to be more tolerant to a heteroatom functionality in the alkyne substrate than are the tungsten-based systems,[8] and they may be expected also to exhibit different rate profiles. Interest in molybdenum catalysts for alkyne metathesis has been evinced recently by the use of the three-coordinate molybdenum(III) complex $Mo(N[^tBu]Ar)_3$ (Ar = 3,5-$C_6H_3Me_2$) or its monohalo derivatives as catalyst precursors.[8] Trialkoxymolybdenum(VI) alkylidyne complexes, including the prototype $(^tBuO)_3MoC^tBu$, are known, but they have been subjected to little scrutiny as catalysts due to drawbacks inherent in the existing synthesis.[9] This report is concerned with a new and facile synthesis of the desired molybdenum(VI) alkylidyne complexes, as well as some initial observations regarding their alkyne metathesis chemistry.

An intriguing synthesis of molybdenum carbyne complexes supported by cyclopentadienyl or indenyl and phosphite coligands was described by Green and coworkers,[10−13] in a report serving as inspiration for the organometallic synthesis reported herein and depicted in Scheme 1. Templeton's studies of η^2-vinyl compounds also provide precedent.[14−20]

Scheme 1



The metallaaziridine−hydride complex $Mo(H)(\eta^2\text{-}Me_2CNAr)(N[^iPr]Ar)_2$ (**1**) is known to serve as a source of the three-coordinate molybdenum(III) complex $Mo(N[^iPr]Ar)_3$ (**2**), a fragment capable of binding alkynes and other unsaturated substrates in an η^2 manner.[21] Accordingly, treatment of **1** in hexane with (trimethylsilyl)acetylene (excess, 2 equiv) produced a color change to green. Rather than isolating the paramagnetic green alkyne complex, it was converted in situ by treatment with iodine (0.5 equiv of I_2 based on Mo) to the diamagnetic yellow salt [**2**-(η^2-$HCCSiMe_3$)][I], which was isolated by filtration in 95% yield. An alternative, and equally high-yielding, preparation of the salt [**2**-(η^2-$HCCSiMe_3$)][I] involves treatment of **1** with 0.5 equiv of I_2 to produce **2**-I in situ, followed by addition of 5 equiv of (trimethylsilyl)acetylene. Characteristic ^{13}C NMR signals are observed at δ 188.6 and 174.2 ppm

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($CDCl_3$, 25 °C), signifying the η^2-bound acetylene moiety in the cationic component of [**2**-(η^2-$HCCSiMe_3$)][I].

Conversion to an η^2-vinyl derivative was accomplished by treatment of [**2**-(η^2-$HCCSiMe_3$)][I] with [Li][$BHEt_3$] in THF solution. The reaction mixture thereupon adopted a dark yellow color. Removal of solvent and extraction with pentane, followed by filtration to effect salt removal, provided a yellow solid in 94% yield characterized as the neutral vinyl derivative **2**-(η^2-$H_2CCSiMe_3$) after removal of volatiles from the filtrate. The diamagnetic η^2-vinyl complex obtained in this way was of high purity according to NMR spectroscopic analysis, characteristic signals being a singlet in the ^1H NMR spectrum at δ 3.33 ppm integrating to 2 H, and a ^{13}C signal at δ 287.1 ppm. These values compare well with those for Green's crystallographically characterized complex Ind([MeO]$_3$P)$_2$Mo(η^2-$H_2CCSiMe_3$).[12] The complex **2**-(η^2-$H_2CCSiMe_3$) also was subjected to scrutiny by X-ray crystallography, pertinent metrical parameters being the Mo−CH_2 bond distance of 2.151(9) Å, the Mo−$CSiMe_3$ bond distance of 1.899(8) Å, and the H_2C−$CSiMe_3$ bond distance of 1.412(12) Å.[22]

Heating a toluene solution of **2**-(η^2-$H_2CCSiMe_3$) to 80 °C for 12 h induced isomerization to its alkylidyne counterpart, **2**-CCH_2SiMe_3, the isomerization being thought to involve trimethylsilyl migration.[12] Characteristic of the alkylidyne functional group is the α-carbon resonance at δ 302.0 ppm in the molecule's ^{13}C NMR spectrum. Because of the oily nature of dark brown **2**-CCH_2SiMe_3 and considering the quantitative nature of the isomerization reaction producing it, **2**-CCH_2SiMe_3 was used without purification.

Alcoholysis is a characteristic reaction of the amidometal functional group,[23-28] and in the present case treatment of **2**-CCH_2SiMe_3 with 3 equiv of 1-adamantanol or 2-methyl-2-propanol[29] was found to provide a highly crystalline and easily purified trialkoxymolybdenum(VI) alkylidyne complex in 88% yield. Crystals of the product (^{1}AdO)$_3$MoCCH_2SiMe_3 (**3**-CCH_2SiMe_3) were determined by NMR spectroscopy in benzene-d_6 solution and by single-crystal X-ray crystallography to retain 1 equiv of the free aniline ligand, HN(^{i}Pr)Ar, which does not interact with the Mo center. The X-ray crystal structure of **3**-CCH_2SiMe_3·HN(^{i}Pr)Ar (Figure 1) evinced a characteristic Mo−C triple bond distance of 1.754(6) Å, in accord with the observed ^{13}C NMR chemical shift of 289.0 ppm for the molecule's α-carbon.

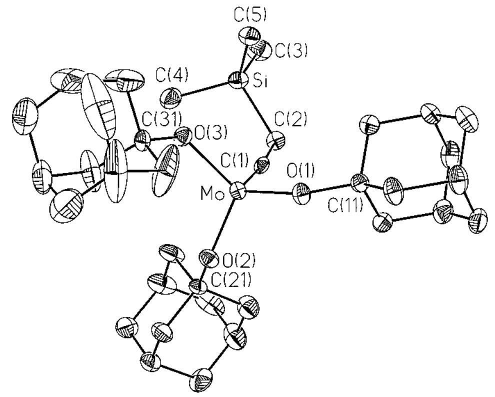
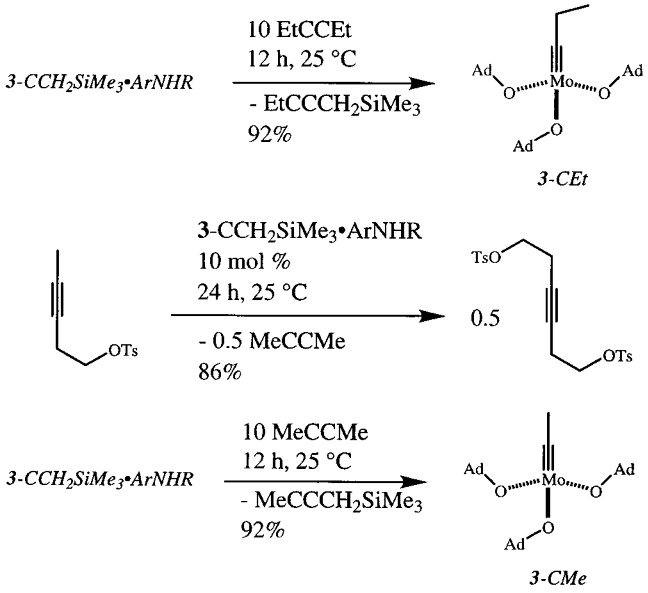


Figure 1. Thermal ellipsoid plot (35% probability) of (^{1}AdO)$_3$MoCCH_2SiMe_3, with HN(^{i}Pr)Ar of crystallization omitted for clarity. Selected distances (Å) and angles (deg): Mo−C(1), 1.754(6); C(1)−C(2), 1.456(8); Mo−O(1), 1.914(4); Mo−O(2), 1.885(4); Mo−O(3), 1.916(4); C(2)−C(1)−Mo, 173.2(5); C(1)−Mo−O(1), 106.0(2); C(1)−Mo−O(2), 107.2; C(1)−Mo−O(3), 97.1(2). Dihedral angles (deg): C(1)−Mo−O(1)−C(11), −4.81(0.52); C(1)−Mo−O(2)−C(21), −9.01(0.52); C(1)−Mo−O(3)−C(31), 174.55(0.40).

Scheme 2



Motivation for the alcoholysis reaction stems from the observation that the amido−alkylidyne **2**-CCH_2SiMe_3 is unreactive toward 10 equiv of 3-hexyne even under coaxing conditions (toluene solution, 80 °C, 24 h), whereas the trialkoxy−alkylidyne **3**-CCH_2SiMe_3 is active for alkyne metathesis under mild conditions. Accordingly, treatment of **3**-CCH_2SiMe_3·HN(^{i}Pr)Ar in ethereal solution with 10 equiv of 3-hexyne led to partial precipitation of the propylidyne derivative, **3**-CEt. The latter was isolated as an analytically pure white solid in 92% yield via a protocol involving solvent removal and washing with cold pentane (Scheme 2). Recrystallization (ether, −35 °C) provided crystals of propylidyne **3**-CEt suitable for an X-ray diffraction study, permitting determination of the Mo−C bond distance (1.743(4) Å) for the pseudotetrahedral complex (Figure 2; ∠C−Mo−O = 106.98(8)°), which exhibits crystallographic mirror symmetry. NMR data for **3**-CEt feature an α-carbon signal at δ 288.8 ppm, the complex evincing 3-fold symmetry as judged by the observation of a single 1-adamantoxide ligand environment.

Further underscoring the alkyne methathesis capability of trialkoxymolybdenum(VI) alkylidyne complexes is the preparation of the nonvolatile alkyne RCCR (R = CH_2CH_2OTs; Scheme 2) in 86% yield from the

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(22) See the Supporting Information.

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(29) Because of the oily nature of (^{t}BuO)$_3$MoCCH_2SiMe_3, we cannot separate this complex from HN[^{i}Pr]Ar. This trialkoxymolybdenum alkylidyne complex was characterized by ^1H and ^{13}C NMR, an α-carbon signal being observed at δ 276.0 ppm.

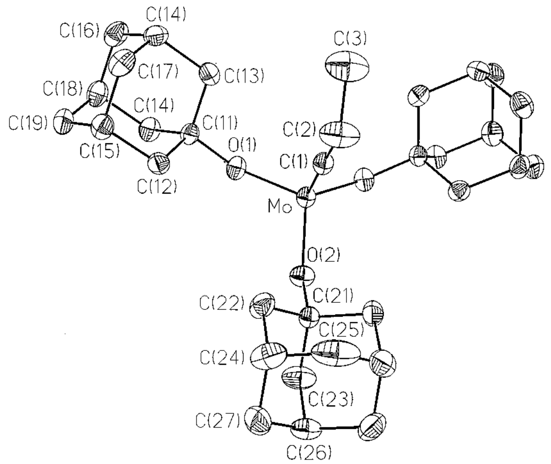

Figure 2. Thermal ellipsoid plot (35% probability) of $(^1\text{AdO})_3\text{MoCEt}$. Selected distances (Å) and angles (deg): Mo−C(1), 1.743(4); C(1)−C(2), 1.488(6); Mo−O(1), 1.889(2); Mo−O(2), 1.886(3); C(2)−C(1)−Mo, 177.4(3); C(1)−Mo−O(1), 106.98(8); C(1)−Mo−O(2), 105.2(2). Dihedral angles (deg): C(1)−Mo−O(1)−C(11), −11.48(0.28); C(1)−Mo−O(2)−C(21), 0.

precursor alkyne MeCCR, with 2-butyne as the volatile side product. The reaction was conducted in toluene solvent (25 °C, 24 h) using 10 mol % of **3**-$\text{CCH}_2\text{SiMe}_3{\cdot}\text{HN}(^i\text{Pr})\text{Ar}$ as the catalyst, with occasional outgassing to remove 2-butyne. Purification of the alkyne product R′CCR′ was accomplished via a procedure involving removal of volatile material and washing of the residue with cold pentane. The ethylidyne complex **3**-CMe formed in the course of this catalytic reaction was observed spectroscopically to be in the filtrate. **3**-CMe was obtained independently as colorless crystals in 92% yield by treatment of **3**-$\text{CCH}_2\text{SiMe}_3{\cdot}\text{HN}(^i\text{Pr})\text{Ar}$ in ethereal solution with 10 equiv of 2-butyne. Identified with ethylidyne **3**-CMe is a singlet in its ^{1}H NMR spectrum at δ 2.89 ppm and an α-carbon resonance in its ^{13}C NMR spectrum at δ 281.1 ppm.

Because starting complex **1** is based upon the trivial amine *N*-isopropyl-3,5-dimethylaniline and consequently is prepared routinely in batches of ca. 22 g, the highly efficient chemistry described herein makes trialkoxymolybdenum(VI) alkylidyne complexes now readily accessible for applications in alkyne metathesis.

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Supporting Information Available: Text giving synthetic, spectroscopic, and analytical data for all new compounds and tables giving crystal data, atomic coordinates, structure solution and refinement details, bond lengths and angles, and anistropic thermal parameters for **2**-(η^2-$\text{H}_2\text{CCSiMe}_3$), **3**-$\text{CCH}_2\text{SiMe}_3{\cdot}\text{HN}(^i\text{Pr})\text{Ar}$, and **3**-CEt. This material is available free of charge via the Internet at http://pubs.acs.org.

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