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A Mo(VI) Alkylidyne Complex with Polyhedral Oligomeric Silsesquioxane Ligands: Homogeneous Analogue of a Silica-Supported Alkyne Metathesis Catalyst

Hyeon Mo Cho, Haim Weissman, Scott R. Wilson, and Jeffrey S. Moore*

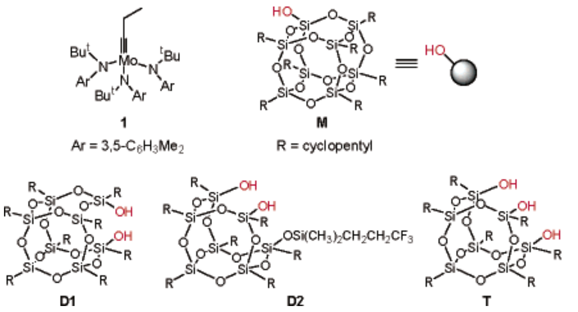
School of Chemical Sciences, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

Received July 17, 2006; E-mail: jsmoore@uiuc.edu

We recently reported[1] a phenol-free, silica-supported molybdenum catalyst for alkyne metathesis that was easily formed by mixing a molybdenum(VI) trisamide alkylidyne[2] and fumed silica. This heterogeneous catalyst exhibited high activity at ambient temperature and selectively catalyzed alkyne metathesis over alkyne polymerization. These features prompted us to investigate homogeneous analogues based on incompletely condensed POSS (polyhedral oligomeric silsesquioxane) ligands. POSS has previously been shown to function as an effective homogeneous mimic of the surface silanols on amorphous silica.[3] Here we report various silsesquioxane-bound catalysts whose reactivity ranges from promoting only alkyne metathesis to catalysts that exhibit metathesis activity and undesired alkyne polymerization. An X-ray structure of a five-coordinate amidodisiloxymolybdenum(VI) alkylidyne complex whose reactivity mirrors that of the silica-supported Mo catalyst is also described.

For our initial studies, alkyne metathesis was carried out using a mixture of **1** and various silsesquioxanes (Chart 1) in the presence of an excess amount of phenylpropyne (**2**). The mixture of **1** and monosilanol **M** successfully metathesized propyne **2**; complete mass balance was observed by ^{1}H NMR spectroscopy using mesitylene as an internal standard, indicating that no oligomerization[4] of **2** or the alkyne products occurred (Table 1). The mixture of **1** and **M** is stable in solution for more than 3 days. The POSS **M** catalyst exhibits characteristic reactivities of the fumed silica-supported Mo catalyst, such as high activity, good stability in solution, and the absence of alkyne polymerization.

Chart 1

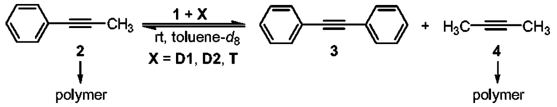


To extend the analogy to vicinal silanols also believed to be on silica surfaces, diol silsesquioxanes **D1** and **D2** and triol silsesquioxane **T** were mixed with **1**. Alkyne metathesis activity of these catalytic mixtures with **2** is summarized in Table 1. In contrast to **M**, catalysts from these ligands polymerized both **2** and **4** in addition to showing the expected metathesis activity. The polymerization rate (based on the loss of alkyne) was highest with POSS ligand **D2**. Only 12% of **2** remained after 18.5 h (entry 7).

Table 1. Values of $t_{1/2}$, Mass Balance, and TOF for Reactions of **2** with **1** and Various POSS Ligands[a]

entry	catalyst[b]	$t_{1/2}$ (h)	mass balance[c]	TOF[d]
1	**1** + **M** (1)	5	100 (156 h)	0.0054
2	**1** + **M** (2)	2	100 (59 h)	0.010
3	**1** + **M** (3)	<0.3	100 (204 h)	0.057
4	**1** + **D1** (1)	0.8	77 (60 h)	0.020
5	**1** + **D1** (3)	0.6	74 (37 h)	0.036
6	**1** + **M** (1) + **D1** (1)	<0.2	78 (107 h)	0.067
7	**1** + **D2** (1)	2	68 (18 h)	0.014
8	**1** + **T** (1)	3	88 (70 h)	0.0025
9	**5**·HN(Ar)(^{t}Bu)	2	100 (12 h)	0.010

[a] Conditions: 1.0 mol % of **1**, 0.27 M of **2**, 600 μL of toluene-d_8, rt. [b] POSS equivalents relative to Mo are in parentheses. [c] Mass balance was determined by summation of aryl ^{1}H NMR signals due to **2** and **3** relative to mesitylene. Monitoring times are given in parentheses. [d] Turnover frequency: mol$_p$·mol$_c$$^{-1}$·s^{-1}.



The reactivities of the various POSS-based catalysts were compared to those of heterogeneous catalysts derived from silicas dried at 400, 200, and 140 °C. It is known that, as silica is dehydrated above 400 °C, silanols become isolated.[5] Silica treated at 400 °C under dry oxygen and subsequently exposed to **1** gave a metathesis catalyst that did not promote alkyne polymerization.[1,6] Silicas treated at 200 and 140 °C and subsequently treated with **1** exhibited both butyne polymerization as well as alkyne metathesis catalytic activity. We suggest that isolated silanols on amorphous silica serve as the effective supporters for alkyne metathesis and vicinal silanols cause alkyne polymerization as well as alkyne metathesis, by analogy to the behavior of **1** with ligands **D** and **T**.[7]

To characterize the structure of the POSS **M** alkylidyne catalyst, a mixture of **1** with 1 equiv of **M** in pentane was prepared and analyzed by FD MS. The main species identified from the molecular ion had a composition consistent with amidodisiloxymolybdenum(VI) alkylidyne complex **5** [$C_{85}H_{149}MoNO_{26}Si_{16}$ 2146.6 (calcd), 2146.4 (found)]. Also, ^{1}H NMR of the solution showed resonances of unreacted **1** and resonances assigned to **5**·HN(Ar)(^{t}Bu). A mixture of **1** and 1 equiv of **M** in hexane gave crystals suitable for X-ray structure determination. Single crystal analysis of **5**·HN(Ar)(^{t}Bu) showed an amido ligand [Mo-N(1): 2.021(12) Å],[2d,e,8] an aniline ligand [Mo−N(2): 2.315(15) Å],[8] and two siloxy ligands trans-coordinated to a Mo(VI) alkylidyne (Figure 1). A characteristic Mo−C(13) triple bond distance of 1.735(9) Å is in accord with the observed ^{13}C NMR chemical shift of 315 ppm for the carbyne carbon.[2c,d] When crystals of **5**·HN(Ar)(^{t}Bu) were dissolved in toluene-d_8, ^{1}H NMR signals of the amido ligand and of aniline were distinguishable. On the basis of the crystal structure, a dative bond apparently forms between HN(Ar)(^{t}Bu) and Mo(VI),[9] resulting in a distorted square pyramidal structure in which the aniline ligand blocks[10] the COO face approached by alkyne substrates, implicating

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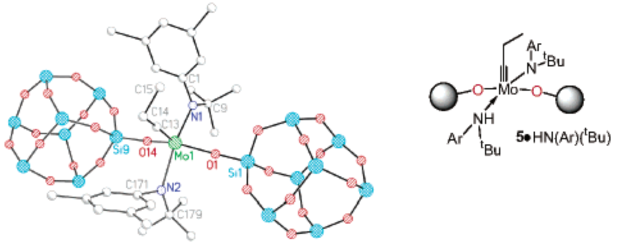


Figure 1. SHELXTL plot of **5**·HN(Ar)(^{t}Bu), showing 35% probability ellipsoids for non-H atoms. Cyclopentyl ligands, H atoms, and disordered positions were omitted for clarity. The sum of the angles of N(1)−Mo−O(1), N(1)−Mo−O(14), N(2)−Mo−O(1), and N(2)−Mo−O(14) is 357(3)°.

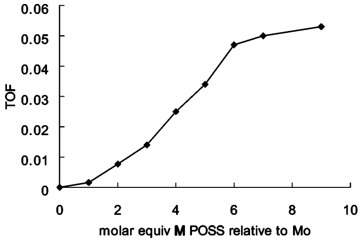
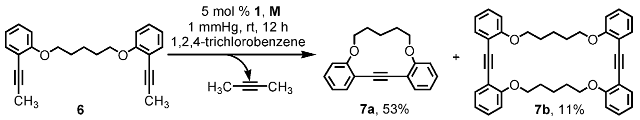
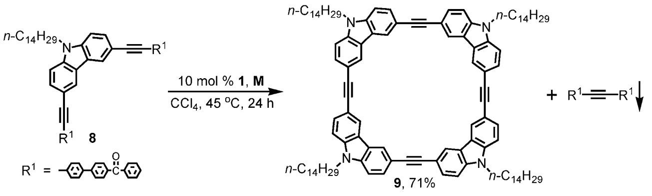


Figure 2. Alkyne metathesis rate (TOF) dependence on the equivalent of **M**. Conditions: 20 μL of **2**, 700 μL of toluene-d_8, rt. TOF = mol$_p$·mol$_c$$^{-1}$·s^{-1}.

the role of HN(Ar)(^{t}Bu) in retarding alkyne metathesis. The most likely mechanism for metathesis with **5**·HN(Ar)(^{t}Bu) involves initial dissociation of the labile aniline ligand. Incidentally, the pentacoordinated complex **5**·HN(Ar)(^{t}Bu) is metathesis active (entry 9) with a rate similar to **1** + **M** (2 equiv) and is selective for metathesis similar to **1** + silica (dried at 400 °C).

To further investigate the function of **M** as an activator for **1**, the reaction rates for alkyne metathesis of **2** were measured using 0.50 mol % of **1** and variable quantities of **M**. Interestingly, TOF values were observed to increase sharply as the equivalent of M increased (Figure 2). This result is contrary to the expectation that 3 equiv of **M** would fully activate complex **1** by substituting the three amide ligands.[2c,4c] One possibility is that association of the third silanolate ligand is competitive with amide binding. Alternatively, excess **M** might associate with the aniline byproduct, decreasing its interaction with the molybdenum center. For example, excess **M** could associate with HN(Ar)(^{t}Bu) through hydrogen bonding.[11]





The POSS **M** catalyst was applied to RCAM[2e] (ring closing alkyne metathesis) and cyclooligomerization reactions.[12] RCAM of diyne[13] **6** with **1** and **M** gave a mixture of monomeric macrocycle **7a** and dimeric macrocycle **7b** under vacuum-driven conditions. We also applied **1** + **M** to the cyclooligomerization of arylene ethynylenes, a reaction that requires highly active and robust catalysts. Tetrameric macrocycle **9** was obtained in high isolated yield via alkyne metathesis of substrate **8** using **1** and **M** under precipitation-driven conditions.[12] These preparatory scale reactions demonstrate the high activity and durability of the POSS **M** catalyst.

In conclusion, POSS ligands successfully activate precatalyst **1** for alkyne polymerization and alkyne metathesis. Pentacoordinated complex **5**·HN(Ar)(^{t}Bu) has activity analogous to that of the silica-supported Mo complex. The bulky POSS **M** ligand stabilizes the monomeric Mo alkylidyne complex and shows no unwanted alkyne polymerization. In contrast, the multidentate POSS ligands **D** and **T** with **1** were accompanied by considerable alkyne polymerization as well as alkyne metathesis. Aniline coordination and the reactivity of Mo(VI) complexes with multidentate POSS ligands give insight into the active species that are involved in alkyne polymerization and alkyne metathesis.

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Supporting Information Available: Experimental details, characterization data, and X-ray data for **5**·HN(Ar)(^{t}Bu). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) We saw 1.6−1.7 equiv of free aniline by NMR when we added silica treated at 400 °C to complex **1**.[1] The monosiloxy complex is likely to be present, but we cannot fully account for the observed additional 0.6−0.7 equiv of free aniline without considering additional ligand displacement.

(7) Why catalysts from **D** and **T** cause polymerization while **M** does not remains open to speculation. The bite angle for bidentate or tridentate ligands is certainly smaller than the coordination angle by monodentate ligands. As a result, the space opposite of the chelating ligand, where the alkyne substrate approaches, is expanded. In this scenario, the alkyne substrate might insert repeatedly into the Mo−C bond to give polymers.

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(10) Similarly, Schrock suggested that a two-electron donor could block metathesis by binding strongly to the metal to give a five-coordinated species. See: Schrock, R. R. *Polyhedron* **1995**, *14*, 3177.

(11) To investigate the interaction between HN(Ar)(^{t}Bu) and **M**, ^{1}H NMR signals of HN(Ar)(^{t}Bu) at variable equivalents of **M** in the absence of **1** were monitored in toluene-d_8 at room temperature. The ^{1}H NMR signals in the aromatic region of HN(Ar)(^{t}Bu) shifted to higher frequency, while those of ^{t}Bu shifted to lower frequency as the amount of **M** increased. However, the $\Delta\delta$ is too small for a reliable determination of the association constant (less than 0.01 ppm). The same trends were found in the mixture of **1** and **M** as the amount of **M** increased from 1 to 6 equiv. The proton resonances of the Ar and ^{t}Bu groups changed from 6.300 to 6.319 ppm and from 1.177 to 1.170 ppm, respectively. This fact partially supports the idea that the additional 3 equiv of **M** in the solution weaken the interaction between Mo and aniline.

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