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A Highly Active, Heterogeneous Catalyst for Alkyne Metathesis**

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Highly active alkyne-metathesis catalysts have been realized by exchanging the amide ligands on molybdenum(VI) alkylidyne trisamide complexes **1** with simple phenols,[1,2] such as 4-nitrophenol, or by use of chlorotrisamide Mo(IV) complexes.[3] In spite of this practical utility, these catalysts can become deactivated over time, apparently through a bimolecular dimerization pathway.[4] The polymerization of 2-butyne, the metathesis by-product obtained from propynyl substrates,[1a,b] is another interfering reaction which occurs when the catalytic reaction is preformed at room temperature. Herein, we describe a heterogeneous, alkyne-metathesis catalyst that avoids the use of phenolic ligands. The supported catalyst exhibits very high activity at room temperature while showing exceptional selectivity for catalyzing alkyne metathesis rather than alkyne polymerization, even on a preparative scale.

We investigated the coordination of the molybdenum center to amorphous silica to avoid bimolecular decomposition with minimal changes to the electronic structure of the catalyst. The similarity of the pK_a values of the phenolic hydroxy and silanol groups was the basis for this choice.[5,6] Mortreux et al. have pioneered similar, although less well-defined, approaches by impregnating $[Mo(CO)_6]$ on silica.[2e,7a] Alumina- and titania-supported molybdenum species have also been reported.[7] However, none of these previous systems were particularly efficient; all required high temperatures (160–350 °C) to obtain turn-over frequencies (TOFs) of several turnovers per hour.[7,8] Utilization of organic silanols as cocatalysts with molybdenum hexacarbonyl for alkyne metathesis were somewhat successful, yet high catalyst

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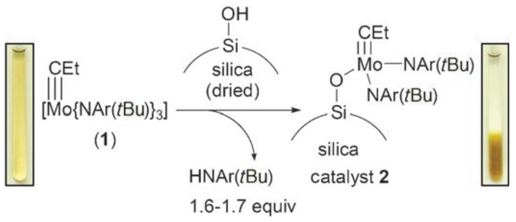
loading and temperatures above 150 °C were again required.[8a,9] Basset and co-workers reported the impregnation of silica surfaces with well-defined molybdenum, tungsten, and rhenium alkylidyne complexes for olefin metathesis.[10] It was suggested that α-hydrogen elimination was responsible for metal-carbene formation and thus, possibly, for deactivation of possible alkyne metathesis.[9e] Only the silica-supported rhenium catalyst $[(SiO)Re(C{-}tBu)({=}CH{-}tBu)(CH_2Bu)]$ has been mentioned briefly as a well-defined precursor for heterogeneous alkyne metathesis.[10d]

In a typical procedure, a solution of precursor **1** in toluene is added to a suspension of silica[11] with an approximately equimolar ratio of silanols and molybdenum. After stirring for one minute at room temperature, the honey-brown color of the solution transfers onto the silica (Scheme 1). The amount of residual molybdenum in the washings was determined to be 0.7 % of the starting material, thus indicating > 99 % of **1** reacted with the silica. Based on the characterization data described below, the resulting structure is consistent with catalyst **2** shown in Scheme 1.



Scheme 1. Reaction of Mo precursor **1** with a silica surface. The images show the capture of **1** from solution onto silica to produce an active catalyst.

Elemental analysis of the impregnated silica indicated that the surface contained 1.56 ± 0.04 wt. % molybdenum and 4.2 ± 0.6 wt. % carbon, thus suggesting that the average Mo/aniline ratio on the surface was approximately 1:1.35 (Scheme 1). This ratio was independently verified by measuring the quantity of aniline released and collected in the washings. Further evidence for the formation of **2** was obtained from IR spectroscopy. The SiO–H stretching band at 3747 cm^{-1} observed in unmodified silica was absent in the spectrum of **2**, thus indicating consumption of the surface silanols groups. Bands at 3020, 1592, and 1460 cm^{-1} in the spectrum of **2** indicate the presence of a substituted aromatic moiety, and the bands at 2971–2871 and 1390–1361 cm^{-1} indicate the existence of an aliphatic moiety (see the Supporting Information).

To further confirm the immobilization of the complex onto the silica surface, X-ray photoelectron spectra of catalyst **2** were obtained and compared to the X-ray photoelectron spectra of the crystalline precursor **1**. A 1.4-eV shift in the peak that corresponds to the Mo 3d electrons is evident for **2** (Figure 1), which is consistent with a significant change in the coordination sphere of the molybdenum center (Figure 1). Similar trends have been observed for other high-oxidation state Mo species when ligands are changed by the introduction of more electron-withdrawing groups.[12] This shift suggests the reduction of electron density around the Mo center, a likely result of an exchange between an amide and an oxide ligand. A similar increase of 1.2 eV in the N 1s binding energy is also evident (see the Supporting Information). This energy change is consistent with amido ligands bound to a more Lewis acidic Mo center (e.g., a Mo center bound to an oxide ligand).

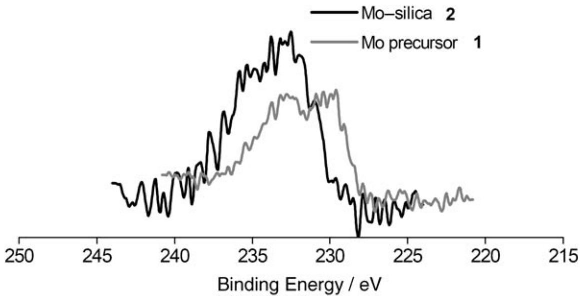


Figure 1. X-ray photoelectron spectroscopy data for the peak that corresponds to the Mo 3d electrons of crystalline precursor **1** and the supported catalyst **2**.

To prove the existence of the carbyne[12] on the silica surface of **2**, we measured the ^{13}C-MAS NMR spectrum at natural abundance (Figure 2). A peak at $\delta = 330$ ppm corresponding to a typical chemical shift for Mo≡C in the liquid phase[14] and other silica-impregnated molybdenum alkylidyne complexes is evident.[15] Resonances at 100–145 ppm and 0–40 ppm are consistent with aromatic and aliphatic carbon atoms on the surface, respectively.

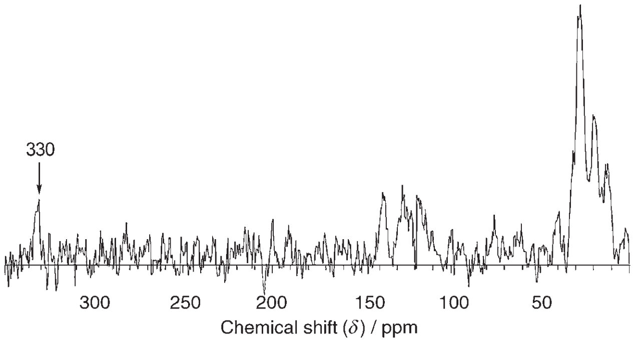
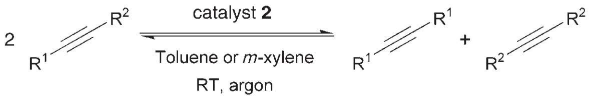


Figure 2. ^{13}C-MAS NMR spectrum of **2**.

Alkyne-metathesis reactions [Eq. (1)] were performed differently to test the metathesis activity of **2**. In a typical experiment, **2** was preweighed into an NMR tube and the substrate was introduced in a solution of [D$_8$]toluene. In experiments testing the recycling capability of the silica support, a suspension of **2** was centrifuged, the solvent decanted, and the silica was rinsed once with [D$_8$]toluene before the addition of the next batch of substrate.



(1)

Alkyne-metathesis experiments with catalyst **2** are summarized in Table 1. The scope of metathesis activity was probed with 2-propynylthiophene (**3**), 1-phenyl-1-butyne (**4**), 1-phenyl-1-propyne (**5**), 3-butynyl methyl benzoate (**6**), 3-propynyl methyl benzoate (**7**), 3-heptyne (**8**), 3-hexyne (**9**), and 3-octyne (**10**), and four different catalyst loadings were tested. Half-lives at room temperature of less than 1 h were generally observed, even with as little as a catalyst loading of 0.8 mol% (based on Mo). Table 2 shows $k_{2,\mathrm{obs}}$ and TOF values from the alkyne homodimerization reactions of **4**–**7**, 4-(1-butynyl)anisole (**11**), and 4-(1-propynyl)anisole (**12**) [Eq. (2)]. The steric and electronic trends seen in Tables 1 and 2 parallel those observed for the analogous **1**/phenol system.[1,2] More significantly, high catalytic activity is achieved for **2**, even though its molybdenum alkylidyne moieties likely contain a mixture of nitrogen- and oxygen-containing ligands.

Table 1: Values of $t_{1/2}$ for metathesis reactions[a] of **3**–**10**.

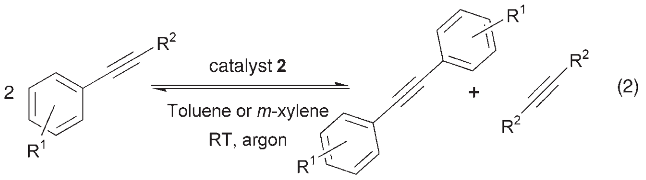
Entry	Substrate	R¹	R²	Catalyst loading [mol%][b]	$t_{1/2}$ [min][c]
1	**3**	2-thiophenyl	Me	4.0	<10[d]
2	**4**	Ph	Et	0.8	<5[e]
3				0.4	<8[f]
4				0.2	11[g]
5	**5**	Ph	Me	0.2	20[g]
6	**6**	3-methyl benzoate	Et	4.0	<5[d]
7				0.8	<10[e]
8				0.4	40[f]
9	**7**	3-methyl benzoate	Me	0.2	14[g]
10	**8**[h]	Et	*n*Pr	0.8	<5[e]
11	**9** **10**[h]	Et *n*Pr	Et *n*Pr	0.8	<5[e]

[a] Conditions: 24 °C, [D$_8$]toluene (600 μL). [b] Load of **2** relative to substrate. [c] $t_{1/2}$ = time for the reaction to proceed to half of the final equilibrium concentrations. [d] Substrate amount = 62.5 μmol. [e] Substrate amount = 62.5 μmol. [f] Substrate amount = 125 μmol. [g] Substrate amount = 250 μmol. [h] Carried out in *m*-xylene (600 μL).

Table 2: Values of $k_{2,\mathrm{obs}}$ and TOF for the homodimerization of **4**–**7**, **11**, and **12**.[a]

Entry	Substrate	R¹	R²	$k_{2,\mathrm{obs}}$ [$\mathrm{M^{-1}\,min^{-1}}$]	TOF [$\mathrm{mol_p\,mol_c^{-1}\,s^{-1}}$]
1	**11**	MeO	Et	0.24	0.31
2	**12**	MeO	Me	0.058	0.087
3	**4**	H	Et	0.19	0.33
4	**5**	H	Me	0.031	0.051
5	**6**	*m*-MeO$_2$C	Et	0.068	0.13
6	**7**	*m*-MeO$_2$C	Me	0.023	0.046

[a] The alkyne substrate (167 μmol) was added to a NMR tube containing **2** (0.30 mol%) in [D$_8$]toluene (600 μL).



No oligomerization of the alkyne substrates or the products was observed by ^{1}H NMR spectroscopic analysis for all the reactions, even after several days. A mass balance higher than 93% was established with an internal standard. The fact that **2** was able to metathesize propynyl derivatives, including the unprecedented homodimerization of 2-propynyl thiophene,[3c,d] demonstrates the success of the heterogeneous approach in constricting the coordination sphere around the molybdenum center. Good metathesis activity with **2** is observed under conditions that were impossible in the past because of problems with polymerization. Recyclability was tested with **3** as the substrate and an initial catalyst loading of 4.0 mol% of **2**. Cycles 1–3 produced conversions of 45, 52, and 32%, respectively, thus suggesting the recyclability of the catalyst. The activity with **4** as the substrate at a catalyst loading of 0.2 mol% was measured to monitor the stability of solid **2**. The catalytic activity of **2** stored at room temperature in an argon-filled dry box remained relatively unchanged for at least two weeks.

We tested the homodimerization of 1-phenyl-1-propyne at room temperature under vacuum-driven conditions to demonstrate the applicability of this system for preparative synthesis. The yield of the isolated and purified homodimer on a 7.5-mmol scale was 88%.

A series of experiments was preformed to confirm catalysis takes place on the support rather than in solution. First, we confirmed that a solution of precursor **1** is catalytically inactive at room temperature. Second, filtrates obtained from suspensions of catalyst **2** exhibit no residual metathesis activity. Similarly, when a substrate suspended with **2** is removed before reaching equilibrium, metathesis activity ceases. Finally, activity resumes as soon as the filtrate is combined with recovered **2**.

We have developed a readily accessible heterogeneous system that exhibits high catalytic activity and good stability, probably because bimolecular deactivation is prevented.[1a,b] The catalyst can be utilized with a loading of less than 1% at room temperature. Several other benefits of the catalytic system have also been found. The system is resistant to alkyne polymerization, which is problematic for similar homogeneous catalysts.[1a,b] Catalyst **2** is recyclable, shows activity over at least three cycles, and has unprecedented metathesis activity for the homodimerization of 2-propynylthiophene, a substrate unable to undergo metathesis with any other known catalyst system.[16] The study of ring-closing alkyne-metathesis[2a,17] activity and other types of metal oxides in this catalyst system are under way. Our results for these studies will be reported elsewhere.

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