Molybdenum Catalysts

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Alkyne Metathesis with Silica-Supported and Molecular Catalysts at Parts-per-Million Loadings

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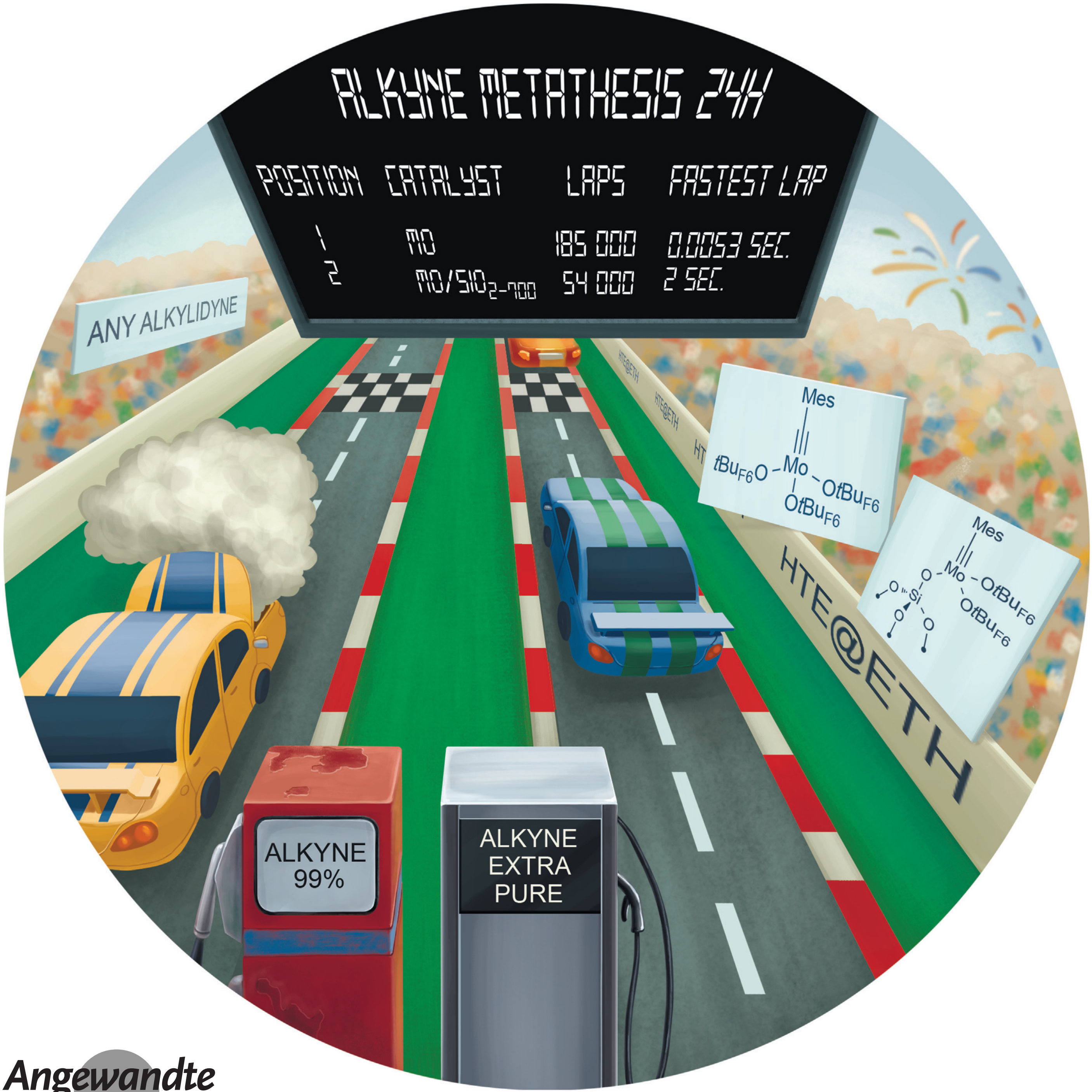
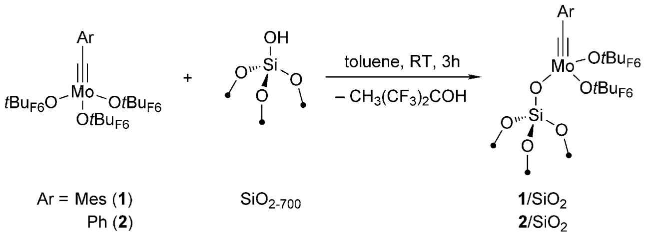


Abstract: *Improvement of the activity, stability, and chemoselectivity of alkyne-metathesis catalysts is necessary before this promising methodology can become a routine method to construct C≡C triple bonds. Herein, we show that grafting of the known molecular catalyst [MesC≡Mo(OtBu$_{F6}$)$_3$] (**1**, Mes = 2,4,6-trimethylphenyl, OtBu$_{F6}$ = hexafluoro-tert-butoxy) onto partially dehydroxylated silica gave a well-defined silica-supported active alkyne-metathesis catalyst [(≡SiO)Mo(≡CMes)(OtBu$_{F6}$)$_2$] (**1**/SiO$_{2\text{-}700}$). Both **1** and **1**/SiO$_{2\text{-}700}$ showed very high activity, selectivity, and stability in the self-metathesis of a variety of carefully purified alkynes, even at parts-per-million catalyst loadings. Remarkably, the lower turnover frequencies observed for **1**/SiO$_{2\text{-}700}$ by comparison to **1** do not prevent the achievement of high turnover numbers. We attribute the lower reactivity of **1**/SiO$_{2\text{-}700}$ to the rigidity of the surface Mo species owing to the strong interaction of the metal site with the silica surface.*

The development of active and practical alkyne-metathesis catalysts has been a burgeoning field of research in the past decade. A number of molybdenum and tungsten alkylidyne complexes of the Schrock type [RC≡MX$_3$] (M = Mo, W)[1] have become available as homogeneous catalysts for the efficient cleavage and formation of C≡C triple bonds.[2] In particular, siloxides,[3] chelating phenoxides,[4] and fluorinated alkoxides[5] have been established as ancillary ligands (X), and the resulting complexes were used for ring-closing alkyne metathesis (RCAM) in natural product synthesis[2c,6] and supramolecular chemistry,[7] ring-opening alkyne metathesis polymerization (ROAMP),[8] and 1,3-diyne metathesis,[9] among other reactions. Nonetheless, alkyne metathesis is currently used much less than olefin metathesis, in part as a result of the narrower substrate scope, higher catalyst loadings, lower reaction rates, faster catalyst deactivation, and undesired side reactions, such as alkyne polymerization. These problems are particularly significant for the metathesis of terminal and aryl alkynes.[10] Therefore, the identification of robust and highly active alkyne-metathesis catalysts remains a formidable challenge.

Surface organometallic chemistry (SOMC) has enabled the site isolation of reactive intermediates on partially dehydroxylated surfaces, thereby suppressing bimolecular pathways for catalyst deactivation.[11] Catalysts with extremely high activity and longevity in alkene metathesis have been synthesized by SOMC.[12] This strategy has also been applied to alkyne-metathesis catalysts. Heterogeneous catalysts that are active for alkyne metathesis have been synthesized by treating partially dehydroxylated silica with molecular alkylidyne species, such as [(tBuC≡)Re(CHtBu)(CH$_2$tBu)$_2$],[13] [(tBuC≡)Mo[N(tBu)(3,5-Me$_2$C$_6$H$_3$)]$_3$],[14] [N≡Mo(OSiMe$_3$)$_2$(N(SiMe$_3$)$_2$)(Py)],[15] and [(tBuC≡)W(OAr)$_2$(CH$_2$tBu)],[16] (Ar = 2,6-iPr$_2$C$_6$H$_3$). In some cases, the activity of supported species was comparable to that of the corresponding molecular catalysts.[13,15] These systems were active in the self-metathesis of internal alkynes. The highest turnover frequencies (TOFs) and turnover numbers (TONs) were 0.24 s^{-1} and 1250, respectively. However, catalyst deactivation was observed at lower catalyst loadings.[11c]

The molybdenum alkylidyne [MesC≡Mo(OtBu$_{F6}$)$_3$] (**1**, Scheme 1) was recently shown to be an active and selective catalyst for the metathesis of a variety of alkynes, including even terminal alkynes.[5b] Herein, we demonstrate that the grafting of **1** onto silica dehydroxylated at 700 °C (SiO$_{2\text{-}700}$) produces a supported catalyst that shows unusually high TONs (up to 54000) and TOFs (up to 2.3 s^{-1}) in alkyne metathesis. Our results also suggest that these catalytic reactions are very sensitive to impurities in the reaction medium. Reactions with molecular catalyst **1** exhibited extremely high TOFs above 188 s^{-1} and TONs up to 185000 with carefully purified alkynes.



Scheme 1. Grafting of **1** onto SiO$_{2\text{-}700}$. Mes = 2,4,6-trimethylphenyl, OtBu$_{F6}$ = hexafluoro-*tert*-butoxy.

The reaction of **1** with SiO$_{2\text{-}700}$ (1.1 equiv with respect to surface ≡SiOH, 0.26 mmol g^{-1}) gave **1**/SiO$_{2\text{-}700}$ (Scheme 1). The material **1**/SiO$_{2\text{-}700}$ contained 0.18 mmol Mo g^{-1}, as well as 18.9 C/Mo, 19.3 H/Mo, and 11.3 F/Mo, respectively, as determined by elemental analysis. After grafting, the solution contained only 0.8 equivalents of tBu$_{F6}$OH per grafted Mo atom, thus indicating that a minor amount of tBu$_{F6}$OH remains adsorbed on the silica surface. The remaining tBu$_{F6}$OH could be removed by treatment in vacuo (10^{-5} mbar) at room temperature for 16 h. The IR spectrum of **1**/SiO$_{2\text{-}700}$ (see Figure S8 in the Supporting Information) confirmed the mass-balance analysis and showed unreacted silanol groups at the silica surface (band at 3747 cm^{-1}).

The ^{1}H magic angle spinning (MAS) NMR spectrum of **1**/SiO$_{2\text{-}700}$ features peaks at $\delta = 2.0, 2.5, 2.9$, and 7.1 ppm that can be assigned to three chemically inequivalent CH$_3$ groups and the aromatic protons (see Figure S9). The ^{19}F MAS NMR spectrum showed a broad feature centered around −84 ppm. This signal can be decomposed into two separate signals at −83.5 and −84.8 ppm attributed to the diastereotopic CF$_3$ groups of the alkoxide ligand (see Figure S10). The alkylidyne signal was absent from the ^{13}C NMR spectrum of **1**/SiO$_{2\text{-}700}$

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(see Figure S11). The lack of an alkylidyne resonance is probably due to its expected large chemical-shift anisotropy (CSA),[17] the absence of nearby hydrogen atoms, and the fact that there is only one alkylidyne carbon atom in the molecule. To confirm that the alkylidyne was present on the surface, we synthesized the previously unknown ^{13}C-enriched molecular complex [Ph^{13}C≡Mo(O*t*Bu$_{F6}$)$_3$] (**2***) and grafted it onto SiO$_{2\text{-}700}$ (see the Supporting Information for the synthetic strategy and characterization of **2*** as well as its precursors).

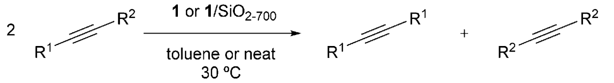
The ^{13}C cross-polarization (CP) MAS NMR spectrum of the labeled supported species **2***/SiO$_{2\text{-}700}$ showed a signal at $\delta_{iso} = 300.9$ ppm with large CSA and axial symmetry ($\Omega = 475.8$ ppm, $\kappa = 0.99$; see Figure S12). This signal is consistent with an alkylidyne carbon atom and similar to that of molecular complex **1** ($\delta_{iso} = 317$ ppm, $\Omega = 502$ ppm, $\kappa = 0.97$ as well as $\delta_{iso} = 321$ ppm, $\Omega = 509$ ppm, $\kappa = 0.98$, associated with two inequivalent sites in the solid state; see Figure S13). All these data suggest that the main structural features of **1** are preserved upon grafting and that **1**/SiO$_{2\text{-}700}$ is the major (> 95 %) Mo surface species.

Quantification of the active sites of **1**/SiO$_{2\text{-}700}$ by the metathesis of diphenylacetylene (33 equiv) showed 88 % formation of the cross-metathesis alkyne product MesC≡CPh, thus indicating a 0.16 mmol g^{-1} concentration of the active alkylidyne sites in **1**/SiO$_{2\text{-}700}$ (see Figure S14). Next, we tested the activity of **1**/SiO$_{2\text{-}700}$ (1.2 mol %) in the self-metathesis of gaseous 2-pentyne (83 equiv, 0.25 atm in 90 mL) at room temperature and found that equilibrium was reached in less than 1 h. Subsequent addition of 2-pentyne gave the same result, showing that no deactivation of the catalyst occurred (see Figure S15). Monitoring of the composition of the gas phase over time enabled us to estimate the initial TOF as 0.3 s^{-1} (with respect to consumed 2-pentyne). Next, we tested **1**/SiO$_{2\text{-}700}$ in the self-metathesis of 4-nonyne (700 equiv, 0.6 M in toluene) and detected conversion into 4-octyne and 5-decyne (TON = 181) in less than 10 min, after which time the catalyst was deactivated (see Figure S16). We hypothesized that rapid catalyst deactivation was caused by trace impurities in the solvent and therefore conducted subsequent tests in carefully purified neat 4-nonyne (see the Supporting Information for the alkyne-purification protocol). Under these conditions, with only a 39 ppm loading in neat 4-nonyne, **1**/SiO$_{2\text{-}700}$ converted 25 600 equivalents to equilibrium in 5 h (see Figure S17). This conversion corresponds to a TON value of 15 800 and an initial TOF of 2.3 s^{-1}, which are remarkably high for a supported alkyne-metathesis catalyst (Table 1; TOF is expressed in conversion × selectivity (mol cat)$^{-1}$ s^{-1}).

The catalyst **1**/SiO$_{2\text{-}700}$ was also active in the self-metathesis of more challenging aryl alkynes. It reacted with 143 000 equivalents of 1-phenyl-1-propyne (0.6 M) to give diphenylacetylene with an initial TOF value of 0.5 s^{-1} and TON = 54 000 (Table 1; see also Figure S18). The only detectable product was diphenylacetylene under these conditions, since the catalytic tests were conducted in the presence of 5 Å molecular sieves, which selectively absorb 2-butyne.[18]

To compare the effect of grafting on the reactivity, we reinvestigated the activity of the molecular complex **1** under our optimized conditions in neat 4-nonyne. Astonishingly, alkylidyne **1** (7.5 ppm) equilibrated 133 500 equivalents of 4-nonyne in less than 5 min. This conversion corresponds to TON = 80 000 and TOF > 178 s^{-1}. Likewise, **1** (4 ppm) converted 1-phenyl-1-propyne (0.6 M, TON = 185 000, 93 % conversion) with an initial TOF value of 188 s^{-1} (Table 1; see also Figure S19). Complex **1** is at least 75 times faster than **1**/SiO$_{2\text{-}700}$ in the metathesis of 4-nonyne and 375 times faster for 1-phenyl-1-propyne metathesis. We tentatively explain this effect by the conformational rigidity of the **1**/SiO$_{2\text{-}700}$ surface species, as shown by the very large chemical-shift anisotropy, closely related to the CSA of the molecular complex. This phenomenon is indicative of conformational rigidity at the Mo sites, probably because of the interaction of the metal center with adjacent siloxane bridges and/or of ancillary ligands with the surface.[19] Such interactions could prevent the necessary distortion of the metal sites to accommodate the incoming alkyne substrate, thereby decreasing the overall reaction rates.[20]

Table 1: Catalytic activity of **1**/SiO$_{2\text{-}700}$ and **1** in the self-metathesis of 4-nonyne and 1-phenyl-1-propyne at 30 °C.



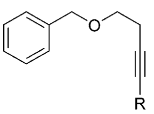
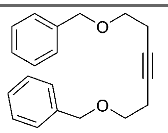
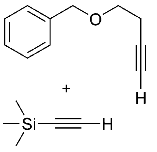
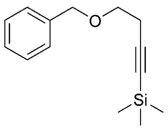
Substrate	Catalyst	Loading [ppm]	TOF$_{5\,min}$[a]	TON[b]
4-nonyne	**1**/SiO$_{2\text{-}700}$	39	2.3	15 800
	1	7.5	> 178	80 000
1-phenyl-1-propyne	**1**/SiO$_{2\text{-}700}$	7	0.5	54 000[c] (38 %)
	1	4	188	185 000 (93 %)

[a] TOF at 5 min, given in s^{-1} with respect to the amount of starting material consumed. [b] Given in parentheses is the conversion when equilibrium was not reached. [c] The reaction was stopped after 70 h, but the catalyst had not yet been deactivated.

We also tested alkynes with more complex structures that had been used previously as model substrates for exploring the activity of **1**,[5b] that is, in the homometathesis of 5-(benzyloxy)-2-pentyne and 4-(benzyloxy)-1-butyne as well as in the alkyne cross-metathesis of 4-(benzyloxy)-1-butyne with Me$_3$SiC≡CH to afford the silylated alkyne 4-(benzyloxy)-1-(trimethylsilyl)butyne. The supported catalyst **1**/SiO$_{2\text{-}700}$ was used for these conversions under reaction conditions more similar to those used in natural product synthesis (Table 2; see also the Supporting Information). Thus, the catalyst loading was increased to 1 mol % molybdenum, and 5 Å molecular sieves were added as 2-butyne or acetylene scavengers to enable full conversion in short reaction times.[5b] Both **1** and **1**/SiO$_{2\text{-}700}$ gave excellent yields for all reactions. However, the reaction rates with the supported catalyst are lower (see Figures S22–24), which is in good agreement with the results described above (Table 1).

In conclusion, we have shown that both complex **1** and the corresponding surface species **1**/SiO$_{2\text{-}700}$ are remarkable catalysts for alkyne metathesis. They show extremely high activity, stability, and functional-group tolerance. The supported catalyst **1**/SiO$_{2\text{-}700}$ is less reactive than the corresponding molecular complex, presumably owing to the rigidity of the surface species, as shown by solid-state NMR spectroscopy. Our results suggest that the alkyne purity is crucial for the

Table 2: Catalytic activity of **1**/$SiO_{2\text{-}700}$ and **1** in the self-metathesis and cross-metathesis of model alkynes in the presence of 5 Å molecular sieves.

Substrate	Product	Catalyst	Conv. [%][d]	Yield [%][e]
		**1**/$SiO_{2\text{-}700}$[a]	97	95
		1[a]	99	97
		1/$SiO_{2\text{-}700}$[b]	90	79
		1[b]	90	88
		**1**/$SiO_{2\text{-}700}$[c]	98	92
		1[c]	100	98

[a] R = Me; reaction conditions: substrate (0.29 mmol) in toluene (1.5 mL, 0.2 M), catalyst (1 mol%), molecular sieves (5 Å; 290 mg). [b] R = H; reaction conditions: substrate (0.125 mmol) in toluene (6 mL, 21 mM), catalyst (1 mol%), molecular sieves (5 Å; 125 mg). [c] Reaction conditions as in [b]. [d] Maximum conversion, as determined by GC. [e] Yield of the isolated product after 1 h.

observed unprecedented catalytic activity and that the purification protocol used in this study may enable significantly higher turnover numbers to be attained with previously reported catalysts. The activity and selectivity of the alkyne-metathesis catalysts reported herein rival those of some of the best olefin-metathesis catalysts.[21] We are currently exploring ways to further increase the catalytic performance of **1** and **1**/$SiO_{2\text{-}700}$.

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Keywords: alkynes · metathesis · molybdenum · NMR spectroscopy · supported catalysts

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