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A Well-Defined Silica-Supported Tungsten Oxo Alkylidene Is a Highly Active Alkene Metathesis Catalyst

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S *Supporting Information*

ABSTRACT: Grafting (ArO)$_2$W(═O)(═CHtBu) (ArO = 2,6-mesitylphenoxide) on partially dehydroxylated silica forms mostly [($\equiv$SiO)W(═O)(═CHtBu)(OAr)] along with minor amounts of [($\equiv$SiO)W(═O)(CH$_2$tBu)(OAr)$_2$] (20%), both fully characterized by elemental analysis and IR and NMR spectroscopies. The well-defined oxo alkylidene surface complex [($\equiv$SiO)W(═O)(═CHtBu)OAr] is among the most active heterogeneous metathesis catalysts reported to date in the self-metathesis of *cis*-4-nonene and ethyl oleate, in sharp contrast to the classical heterogeneous catalysts based on WO$_3$/SiO$_2$.

Alkene metathesis has had a significant impact in the petrochemical and polymer industries and it has also now become a robust synthetic method in organic synthesis.[1,2] A particularly relevant industrial catalyst is WO$_3$/SiO$_2$, typically prepared by incipient wetness impregnation of ammonium tungstate on silica followed by calcination at ~550 °C. This catalyst operates at elevated temperatures (300−400 °C) and has a small concentration of active sites, commonly described as W-oxo alkylidenes (Figure 1a).[3] This has led to major research efforts in preparing molecular equivalents. Osborn prepared a series of oxo alkyl precursors in the 1980s in the hope of generating well-defined oxo alkylidene.[4,5] Such compounds have been supported on silica, but they operate at relatively high reaction temperatures (150 °C), and the nature of the active species is not clear.[6] The first molecularly defined active oxo alkylidenes have been uncovered only recently, and show room temperature activity in alkene metathesis (Figure 1b).[7,8]

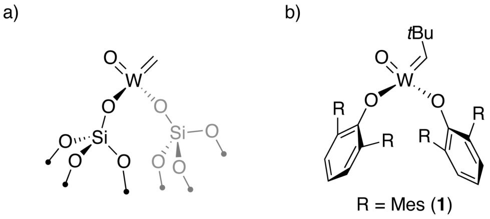


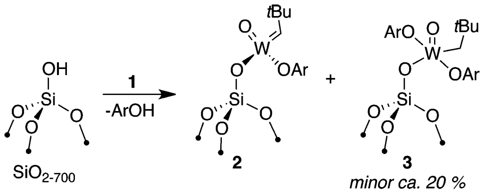
Figure 1. (a) Proposed active site on the WO$_3$/SiO$_2$ metathesis catalyst; (b) one example of a well-defined molecular tungsten oxo alkylidene complex.

We have shown that well-defined heterogeneous metathesis catalysts are accessible by the controlled introduction of molecular alkylidene complexes onto dehydroxylated silica supports, providing Re alkylidyne,[9] as well as Mo and W imido alkylidene surface species.[10−14] Here, we describe the preparation and the characterization of a well-defined silica-supported W oxo alkylidene complex, which displays unprecedented high catalytic activity at room temperature in alkene metathesis.

The reaction of (ArO)$_2$W(═O)(═CHtBu) (**1**, ArO = 2,6-mesitylphenoxide) with SiO$_{2\text{-}700}$ (0.26 mmol SiOH g^{-1}) was monitored by infrared spectroscopy. The ν_{OH} associated with the silanols on the silica surface (3747 cm^{-1}) decreases upon contact with **1**, though free silanols persist (~60%). From quantitative mass balance analysis of recovered ArOH we can infer that ~40% of the silanols present in silica react with **1**. In addition to the IR absorption for free silanol in the infrared spectrum, this material contains a ν_{OH} at 3586 cm^{-1} associated with surface silanols interacting with nearby aromatic residues,[10] and ν_{CH} and δ_{CH} bands from the organic residues in **1@SiO$_{2\text{-}700}$**. The elemental analysis of **1@SiO$_{2\text{-}700}$** give 1.71%$_{\mathrm{wt}}$ W (0.09 mmol·g^{-1}) and 4.38%$_{\mathrm{wt}}$ C corresponding to 39 C per W, slightly higher than the expected 29 C per W. This result is consistent with the presence of [($\equiv$SiO)W(═O)(═CHtBu)(OAr)] (**2**) along with small amounts of [($\equiv$SiO)W(═O)(CH$_2$tBu)(OAr)$_2$] (**3**, 20%) on the silica surface, as shown in Scheme 1.

In addition to signals associated with the *t*Bu and OAr ligands, the solid-state ^{1}H NMR spectrum (Figure S4,

Scheme 1. Grafting 1 on [SiO$_{2\text{-}700}$] Yielding [($\equiv$SiO)W(═O)(═CHCMe$_3$)(OAr)] (2) and Small Amounts of [($\equiv$SiO)W(═O)(CH$_2$CMe$_3$)(OAr)$_2$] (3)



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Supporting Information [SI]) displays a shoulder at 7.6 ppm, tentatively assigned to the metal alkylidene proton by comparison of C_6D_6 solutions containing the molecular precursor **1**. The ^{13}C cross-polarization magic angle spinning (CP-MAS) spectrum also contains the expected signals for the ArO fragment and the *t*Bu unit of the alkylidene, though the resonance of the alkylidene carbon is not observed in this spectrum. The missing alkylidene signal in the solid state NMR spectrum is a common feature in silica-grafted materials because of the small number of sites and large chemical shift anisotropy, making carbon-13 labeling necessary for a direct evidence of this ligand.

We synthesized ^{13}C-labeled analogue of **1** with 15% isotopic enrichment at the alkylidene carbon (**1***). Grafting **1*** on $SiO_{2\text{-}700}$ gives **1*@SiO$_{2\text{-}700}$** with identical IR properties, and mass balance again infers that ~40% of the silanols on the surface react with **1a***. The ^{13}C CPMAS spectrum (Figures 2 and S4SI) contains signals associated with the ArO ligand at 139 and 130 ppm (respectively assigned to the tertiary and secondary carbons from the aryloxy ligand) as well as at 21 ppm for the methyl groups. The *t*Bu methyl groups appear at 34 ppm, with the closely overlapping tertiary carbon from the *t*Bu group at 36 ppm. In addition, the spectrum contains a resonance at 260 ppm that is assigned to the alkylidene carbon of [(≡SiO)W(=O)(=C*HtBu)(OAr)] (**2***). To confirm this assignment we performed ^{1}H−^{13}C two-dimensional (2D) heteronuclear correlation (HETCOR) experiments that showed a strong correlation between the alkylidene carbon resonance and the proton resonance at 7.6 ppm (Figure 2). These results unambiguously confirm the presence of the alkylidene ligand in **1@SiO$_{2\text{-}700}$**. The relatively broad ^{13}C resonance at 85 ppm that correlates with proton chemical shifts at ~1.5 ppm clearly establishes the identity of the second species as [(≡SiO)W(=O)(*CH_2tBu)$(OAr)_2$] (**3***), which arises from addition of the silanol to the alkylidene carbon.

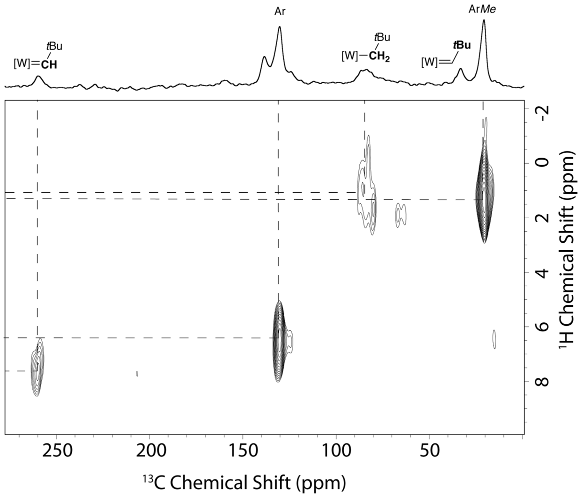

Figure 2. Two-dimensional ^{1}H−^{13}C HETCOR spectrum of **1*@SiO$_2$** recorded with a CP contact time of 200 μs. Other experimental details are given in the SI. The one-dimensional carbon-13 CPMAS spectrum is shown above the 2D plots together with the assignment of the resonances.

Table 1. Catalytic Activity of Complex 1@SiO$_{2\text{-}700}$ in Toluene at 30°C

substrate[a]	mol %	TOF[a]	time to equilibrium conversion[b]
cis-4-nonene	0.1	170[c]	3 min (500)
cis-4-nonene	0.02	280 (17%)	<60 min (2500)
1-nonene	0.1	13 (4%)	66% after 8 h (660)
ethyl oleate	0.2	44 (29%)	<3 h (250)
ethyl oleate	0.05	143 (19%)	46% after 4 h (920)

[a] TOF at 3 min, given in min^{-1} with the corresponding conversions given in brackets. [b] TON given in parentheses. [c] Calculated at full conversion.

The catalytic activities of the [(≡SiO)W(=O)(=CHtBu)(OAr)] in the self-metathesis of *cis*-4-nonene, 1-nonene, and ethyl oleate as prototypical substrates were investigated (Table 1). [(≡SiO)W(=O)(=CHtBu)(OAr)] displays very high activity in alkene metathesis at 30 °C for all three substrates (Table 1, see the SI for details). With 0.1 mol % **1@SiO$_2$**, *cis*-4-nonene is equilibrated to *cis/trans* mixtures of 4-octene and 5-decene in less than 3 min, and the catalyst can be recovered and recycled five times without significant loss of activity. Note that the corresponding W imido [(≡SiO)W(=NAr)(=CHtBu)(2,5-diMePy)][14] has a much lower activity (TOF = 4 min^{-1}) and stability (deactivation after 40%) under the same reaction conditions. **1@SiO$_{2\text{-}700}$** is also 1 order of magnitude more active than one of the best silica-supported Mo catalysts [(≡SiO)Mo(NAr)(=CHtBu)(OtBu$_{F6}$)] under the same conditions (TOF = 46; equilibrium conversion reached in 30 min).[14] At lower loadings of [(≡SiO)W(=O)(=CHtBu)(OAr)] (0.02 mol %) *cis*-4-nonene was converted to 4-octenes and 5-decenes with an initial turnover frequency (TOF) of 280 min^{-1}. This value is significantly higher than for the molecular complex **1** (TOF at 3 min = 5 min^{-1}; 35% conversion after 24 h). The higher activity of **1@SiO$_2$** is probably due to the substitution of one aryloxy group by a smaller siloxy ligand. The high activity and stability of **1@SiO$_{2\text{-}700}$** allowed us to decrease catalyst loading to 50 ppm in *cis*-4-nonene metathesis with full conversion (TON ~10000) in less than 4 h at 30 °C. Under the same reaction conditions, 1-nonene reacts more slowly than internal alkenes, as previously observed with molecular complexes,[7] probably as a result of ethylene buildup in the reaction mixture and the formation of stable metallocyclobutane intermediates. In contrast, ethyl oleate, an alkene containing an ester, is converted with a fast TOF of 44 min^{-1} and reaches equilibrium in less than 3 h with 0.5 mol % catalyst. Decreasing the loading to 0.02 mol % leads to an increase of the TOF to 143 min^{-1}. These results are noteworthy considering that the classical WO_3/SiO_2 catalyst operates only at high temperatures and is not compatible for functionalized alkenes.

In conclusion, [(≡SiO)W(=O)(=C*HtBu)(OAr)], a well-defined silica-supported tungsten oxo alkylidene surface complex, prepared by Surface Organometallic Chemistry, displays unprecedented activity at room temperature in the metathesis of alkenes. In sharp contrast to the industrial catalysts based on WO_3/SiO_2, [(≡SiO)W(=O)(=C*HtBu)(OAr)] tolerates oleic acid esters. These results show that the low activity and the lack of compatibility with functional groups of the industrial catalyst is not intrinsic to silica-supported W catalysts or to oxo alkylidene surface species, but probably is a consequence of the high temperatures employed to generate the small number of active sites in the classical, ill-defined systems. We will continue to explore new ways of generating highly active W-based heterogeneous (silica-supported) alkene metathesis catalysts.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional NMR data, and catalytic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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