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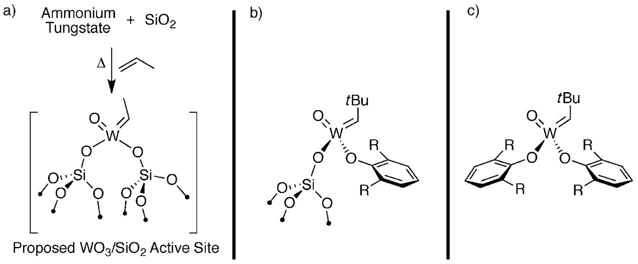
Supported Catalysts

Bulky Aryloxide Ligand Stabilizes a Heterogeneous Metathesis Catalyst**

Matthew P. Conley, William P. Forrest, Victor Mougel, Christophe Copéret, and Richard R. Schrock**

Abstract: *The reaction of [W(=O)(=CHCMe$_2$Ph)(dAdPO)$_2$], containing bulky 2,6-diadamantyl aryloxide ligands, with partially dehydroxylated silica selectively yields a well-defined silica-supported alkylidene complex, [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)]. This fully characterized material is a very active and stable alkene metathesis catalyst, thus allowing loadings as low as 50 ppm in the metathesis of internal alkenes. [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)] also efficiently catalyzes the homocoupling of terminal alkenes, with turnover numbers exceeding 75 000 when ethylene is constantly removed to avoid the formation of the less reactive square-based pyramidal metallacycle resting state.*

The synthesis and design of metal alkylidene complexes over the past 40 years led to highly active alkene metathesis catalysts which established metathesis as a proven method in organic and polymer syntheses.[1] In contrast, the classical heterogeneous metathesis catalysts, oxide-supported MOx (MOx = metal oxide; M = Mo, W and Re), are still restricted to a narrow substrate class, suffer from low activity and/or stability,[2] and require high operating temperatures (typically above 150 °C for Mo and 400 °C for W). One exception is Re_2O_7/Al_2O_3.[3] These catalysts are generally prepared by the dispersion of metal salts onto an oxide support followed by high-temperature calcination. The catalytically active alkylidene species is generated in situ under reaction conditions at the high operating temperatures required for Mo and W. The working active sites have never been observed for these systems, but are commonly assumed to be an oxo alkylidene species, as shown in Scheme 1 a for the WO_3/SiO_2 catalysts.[4] Though the active sites are unknown, the WO_3/SiO_2 catalyst emerged as an effective alkene metathesis catalyst for the production of propene by the ethenolysis of 2-butenes.[5]



Scheme 1. Proposed active sites in WO_3/SiO_2 (a) and the corresponding well-defined surface (b) and molecular species (c).

From a molecular perspective, preparation of W-oxo alkylidenes was also a challenge. Osborn and co-workers described a [W(=O)(CH$_2t$Bu)$_3$X] (X = Cl, Br, OR) which lacks alkylidenes and does not have metathesis activity in the absence of cocatalysts.[6] Supporting [W(=O)(CH$_2t$Bu)$_3$X] or [W(=O)(CH$_2t$Bu)$_4$] on silica gives metathesis-active materials, though only at elevated temperatures, and a supported alkylidene was not observed.[7] The first four-coordinate W-oxo alkylidene complexes only recently became available through the introduction of 2,6-disubstituted aryloxide ligands (Scheme 1 c), and show catalytic activity in solution at 22 °C.[8]

By immobilizing molecular metathesis catalysts onto partially dehydroxylated silica supports[9] we recently reported the formation of the supported W-oxo alkylidene [(≡SiO)W(=O)(=CHtBu)(OHMT)] (Scheme 1 b; R = mesityl, OHMT = 2,6-dimesitylphenoxide), which has higher activity than the molecular catalyst under the same reaction conditions (TOF = 300 versus 3 min^{-1}).[10] Although [(≡SiO)W(=O)(=CHtBu)(OHMT)] had catalytic activity higher than that of other well-defined silica-supported imido complexes,[11] this catalyst was contaminated with approximately 20 % of the unreactive [(≡SiO)W(=O)(CH$_2t$Bu)(OHMT)] species, which forms during grafting by protonation of the alkylidene. In addition, this material also showed signs of deactivation at low catalyst loading. Herein we report that incorporation of the very bulky bis(2,6-diadamantyl-4-methylphenoxide) (dAdPO)[12] ligand gives the selective formation of [(≡SiO)W(=O)(=CHCMe$_2$R)(dAdPO)], a highly active and stable catalyst which operates at loadings as low as 50 ppm for internal alkene metathesis and gives exceptionally high turnover in the homocoupling of terminal alkene (> 75 000).

Reacting [(dAdPO)$_2$W(=O)(=CHCMe$_2$Ph)] (**1a**) with silica partially dehydroxylated at 700 °C ([SiO$_{2\text{-}700}$])[13] results in 0.071 mmol of dAdPOH released per gram of silica during

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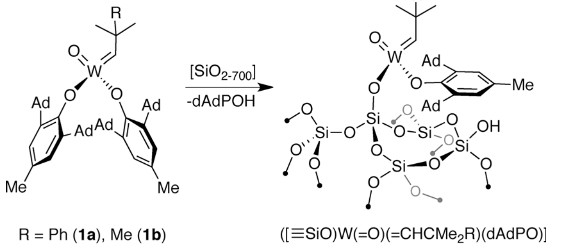
grafting and a solid with 1.37 wt % W (0.074 mmol W g^{-1}), thus indicating that roughly 27 % of the surface silanols reacted to generate the corresponding monografted species. The tungsten loading is slightly lower than we obtained for [(≡SiO)W(=O)(=CH*t*Bu)(OHMT)], probably because of the larger dAdPO ligand, which is consistent with the much larger buried volume of the dAdPO ligand (36.8 %) compared to HMTO (24.3 %; see Table S1 in the Supporting Information).[14] The infrared spectrum of this material contains a band at 3624 cm^{-1}, thus indicating that some surface silanols are interacting with the aromatic ligand,[11b] and that there is also a significant fraction of unreacted isolated silanols, thereby suggesting that the rather bulky [(dAdPO)$_2$W(=O)(=CHCMe$_2$Ph)] complex cannot access some surface silanols.[15] Carbon elemental analysis shows the presence of 3.45 wt %, which corresponds to 39 ± 1 C/W, which is in very close agreement with the expected value (37 C/W) for the selective formation of [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)] (**2a**) as shown in Scheme 2. These data are in contrast with those of the the corresponding HMTO system.



Scheme 2. Selective formation of **2a** by grafting **1a** on silica partially dehydroxylated at 700 °C.

The ^{1}H magic angle spinning (MAS) NMR spectrum of [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)] contains signals at $\delta = 1.9$ ppm, which are assigned to the adamantyl fragments and the methyl groups of the neophylidene, and at $\delta = 7.1$ ppm, which represents the phenyl group of the dAdPO and neophylidene ligands. The spectrum also contains a broad resonance centered at $\delta = 9.1$ ppm, which is assigned to the alkylidene proton and is in good agreement with the NMR spectrum of **1a** in solution. The ^{13}C cross polarization magic angle spinning (CPMAS) NMR spectrum of [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)] contains signals at $\delta = 19$, 30, 36, 42, 126, and 140 ppm from the dAdPO ligand and neophylidene groups. The alkylidene signal was not observed, and is typical of supported alkylidenes at natural abundance. We prepared the corresponding ^{13}C-labeled neopentylidene equivalent [W(=O)(=C*H*t*Bu)(dAdPO)$_2$] (**1b***), with 50 % ^{13}C enrichment at the alkylidene carbon atom, and grafted this compound onto [SiO$_{2\text{-}700}$]. Similar to the grafting of **1**, about 24 % of the surface silanols react under grafting conditions as determined from mass balance analysis. The ^{1}H MAS NMR spectrum of [(≡SiO)W(=O)(=C*H*t*Bu)(dAdPO)] (**2b***) is similar to that of [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)], though in this case the *tert*-butyl neopentylidene resonance is separated from the adamantyl signals at $\delta = 1.9$ and appears at 1.1 ppm. The ^{13}C CPMAS spectrum of [(≡SiO)W(=O)(=C*H*t*Bu)(dAdPO)] contains signals for the dAdPO ligand at similar chemical shifts as for [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)], and also contains the characteristic alkylidene signal at $\delta = 260$ ppm. In addition, small amounts of [(≡SiO)W(=O)(C*H$_2$*t*Bu)(dAdPO)$_2$] are formed as evidenced by the presence of a signal at $\delta = 68$ ppm, and presumably results from addition of the silanol onto the smaller neopentylidene ligand. The ^{1}H–^{13}C HETCOR spectrum[16] of [(≡SiO)W(=O)(=C*H*t*Bu)(dAdPO)] is shown in Figure 1 and contains a crosspeak at $\delta = 9.3$ ppm which correlates with the alkylidene signal. These results are in excellent agreement with the solution data of **1b***.

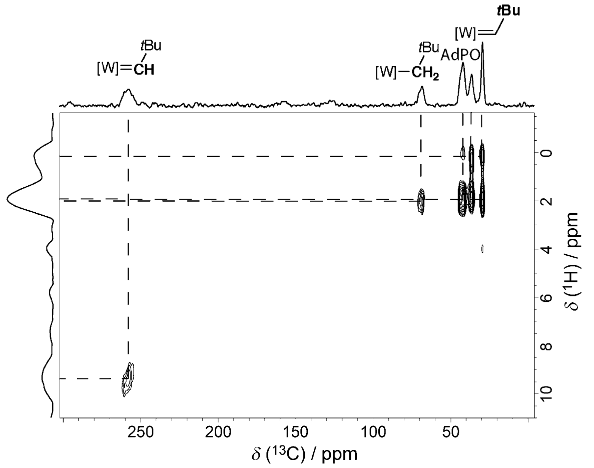


Figure 1. Two-dimensional ^{1}H–^{13}C HETCOR spectrum of **2b** recorded with a CP contact time of 600 μs. Other experimental details are given in the Supporting Information. The one-dimensional ^{13}C CPMAS spectrum is shown above the two-dimensional plots together with the assignment of the resonances.

We evaluated the catalytic activity of [(≡SiO)W(=O)(=CHMe$_2$Ph)(dAdPO)] (**2a**) in *cis*-4-nonene metathesis at 30 °C (Table 1): **2a** converts 5000 equivalents of *cis*-4-nonene into 80:20 *E*/*Z* mixtures of 4-octenes and 5-decenes in 10 minutes. At lower catalyst loading (0.005 mol %, 50 ppm), the substrate is fully converted in 5 hours, and the initial turnover frequency (TOF) is about 350 min^{-1}. Under these reaction conditions the molecular **1a** shows less than 1 % conversion of

Table 1: Catalytic data for [(≡SiO)W(=O)(=CHCMe$_2$Ph)(dAdPO)].

Substrate	mol %	TOF[b]	Time to equilibrium conversion
cis-4-nonene	0.02	325 (22 %)	10 min
cis-4-nonene	0.005	356 (5 %)	5 h
ethyl oleate	0.05	133 (15 %)	ca. 6 h
1-nonene[a]	0.1	5 (2 %)	42 % conversion after 24 h

[a] Run in a flow reactor. [b] Turnover frequency (TOF) at 3 min, given in min^{-1} with the corresponding conversions given in brackets. [c] Productive turnover numbers.

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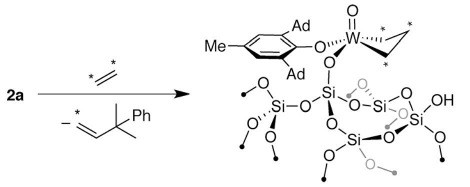
cis-4-nonene after 24 hours, probably because of the presence of two bulky dAdPO ligands.[12] Replacing one of them by the locally small surface siloxy ligand (with 20.6 % buried volume using 111 β-cristobalite as a model)[11c] dramatically increases the reactivity of the metal alkylidene, and the catalyst stability is increased through surface-site isolation.[17] We also found that ethyl oleate, a substrate incompatible with classical heterogeneous catalysts is fully converted to equilibrium in less than 6 hours with an initial TOF of 133 min^{-1} with 0.05 mol % catalyst. The initial TOF values obtained with **2a** are slightly higher than observed for the corresponding HMTO analogue, probably because of the cleaner grafting of **1a** on the silica surface. In addition, **2a** is less prone to deactivation, as illustrated by the much shorter equilibration time measured for *cis*-4-nonene metathesis (10 min versus 60 min for $[(\equiv \text{SiO})\text{W}(=\text{O})(=\text{CH}t\text{Bu})(\text{OHMT})]$).

In sharp contrast, 1-nonene gave sluggish results with only 42 % conversion after 24 hours and a low initial TOF of 5 min^{-1} even with significantly higher catalyst loading (0.1 mol %). We reasoned that this stark difference in activity between internal and terminal alkenes was due to ethylene build-up in the reaction mixture, thus leading to stable metallacyclobutanes and/or irreversible deactivation.[12] To test this hypothesis, we generated the stable metallacycle $[(\equiv \text{SiO})\text{W}(=\text{O})(^*\text{CH}_2{}^*\text{CH}_2{}^*\text{CH}_2)(\text{dAdPO})]$ (**3**) by reacting **2a** with excess bis(^{13}C-labeled) ethylene (10 equiv/W) and it resulted in the release 0.9 equivalents of mono-^{13}C-labelled 3-methyl-3-phenyl-1-butene per tungsten (Scheme 3). The resulting solid shows the expected signal in the ^{13}C CPMAS spectrum and the ^{1}H-^{13}C HETCOR for the formation of the surface square-pyramidyl (SP) metallacycle ($\mathbf{3}_{\text{SP}}$). The formation of the SP metallacycle is also consistent with DFT calculations which indicate this isomer is generally more stable than the trigonal bipyramidyl (TBP) metallacycle, particularly for tungsten oxo species.[18]



$([\equiv \text{SiO})\text{W}(=\text{O})(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dAdPO})]$ (**3**)

Scheme 3. Formation of the parent metallacyclobutane **3** by reaction of **2a** with ^{13}C-labeled ethylene. * = ^{13}C.

Reacting **3** with *cis*-4-nonene (0.02 %) under the optimized reaction conditions resulted in full conversion of the substrate after an induction period and a significantly reduced initial TOF (17 min^{-1} versus 325 min^{-1} for **2a**). These results are consistent with metathesis inhibition (reversible deactivation) by ethylene through the formation of the stable and less reactive unsubstituted metallacycle intermediate. Since terminal alkene homocoupling results in significant ethylene build-up in the reaction mixture we conducted this reaction with a reactor that allowed removal of ethylene during the reaction (see the Supporting Information for details). Briefly, a frit was loaded with the supported catalyst and connected to a flask containing 1-hexene. The alkene was refluxed at 65 °C under a slow flow of argon and distilled over the catalyst bed which allowed the liquid to pass through the catalyst bed and the frit, and ethylene to be vented. Under these reaction conditions, we loaded this reactor with 1-hexene several times over 70 hours and obtained 76 300 turnovers. This finding illustrates the stability of the catalyst under conditions that allow for the removal of ethylene, which is known to deactivate some metathesis catalysts.[19]

Overall, we described the synthesis and the characterization of a well-defined silica-supported W-oxo-based metathesis catalysts incorporating the bulkier dAdPO ligand. This ligand improves the stability of the catalyst, thus allowing a decrease in catalyst loading, down to 50 ppm. This heterogeneous catalyst is also compatible with alkenes bearing an ester functionality, that is, ethyl oleate, in contrast to the classical tungsten catalysts. The high stability of this system allows the efficient homocoupling of terminal alkenes which are a challenging substrate class because it yields ethylene as a co-product, which tends to deactivate—reversibly or not—metathesis catalysts. In this case, ethylene forms a very stable unsubstituted metallacyclobutane which is not prone to cycloreversion, hence lower metathesis rates and reduced catalyst performance can be overcome by continuous ethylene venting under flow conditions, thus allowing very high turnover numbers (> 75 000) to be reached. This study shows that combining a very bulky molecular ligand (here AdPO) and a small surface siloxy group provides an optimal ligand set to achieve both high reactivity and stability. We are exploring this concept to design more efficient heterogeneous catalysts.

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Supported Catalysts

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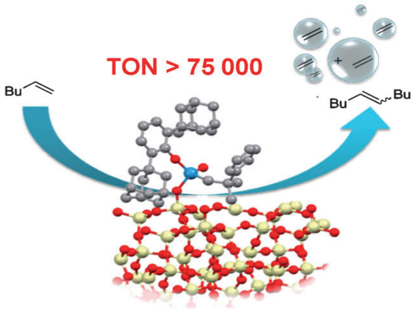
Bulky Aryloxide Ligand Stabilizes
a Heterogeneous Metathesis Catalyst



Like a rock: Grafting a W-oxo alkylidene, containing bulky adamantyl-substituted phenoxy ligands, onto partially dehydroxylated silica generates a very active and stable metathesis catalyst. This large ligand allows efficient terminal alkene homocoupling with a turnover number (TON) exceeding 75 000.