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## Journal Article

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# W-oxo Adamantylidenes: Stable Molecular Precursors for Efficient Silica-Supported Metathesis Catalysts

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Dedicated to the memory of Prof. *Jack Dunitz*

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Tungsten oxo adamantylidenes (=Ad) are a new class of readily accessible alkylidenes, that opens the possibility to evaluate a broader class of molecular and supported olefin metathesis catalysts. In this context,  $W(O)(=Ad)X_2$ , with  $X$  = pyrrolide and perfluoro-*tert*-butoxide, were grafted on partially dehydroxylated silica, to generate the corresponding silica-supported tungsten oxo adamantylidenes. The high thermal stability of the molecular perfluoro-*tert*-butoxide complex, that exists as a dimer in the solid state, even enables its grafting through sublimation. Evaluation of their catalytic activities toward olefin metathesis using standardized protocols show that these supported species display high activity toward internal and terminal olefins. In particular, avoiding the use of solvent during grafting of the highly electrophilic perfluoro-*tert*-butoxide compounds, that can bind to the  $W$  center, enable to generate significantly more active catalysts.

**Keywords:** adamantylidenes, olefin metathesis, surface chemistry, surface organometallic chemistry, tungsten.

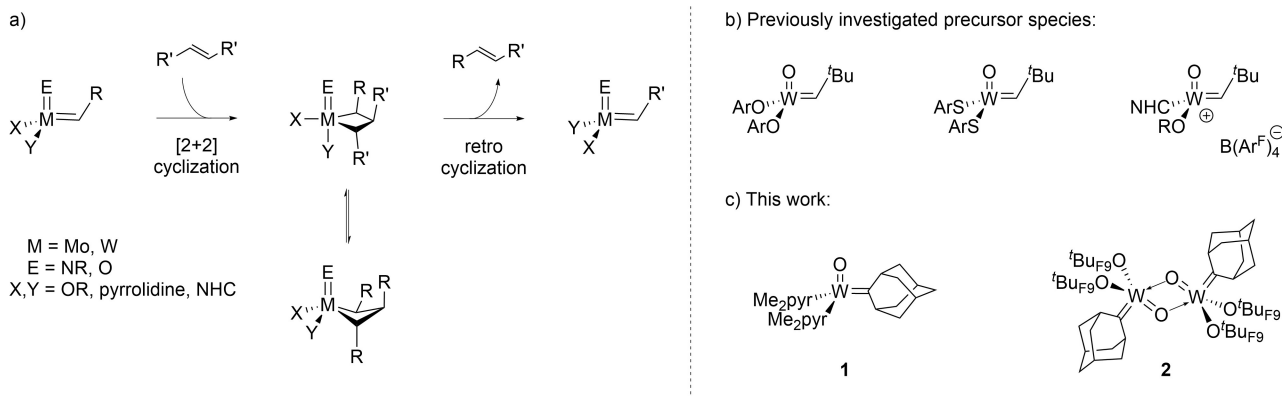
## Introduction

Olefin metathesis is a highly efficient reaction to form olefins from olefins. The versatility and scope of this reaction has led to its significant impact in both academia and industry.<sup>[1–4]</sup> This reaction has been shown to involve metal alkylidene and metallacyclobutane complexes as the two key intermediates.<sup>[5,6]</sup> While [2 + 2] cycloaddition of a  $d^0$  metal alkylidene with an olefin yields a metathesis-active metallacyclobutane with a trigonal bipyramidal (TBP) geometry, the latter can often rearrange readily to generate a metathesis-inactive (off-cycle) metallacyclobutane having a square planar (SP) geometry (*Scheme 1,a*). The overall rate of metathesis therefore, in many instances, depends on the energy difference (energy span)<sup>[7]</sup> between TBP or

SP forms and the transition state associated with either cycloreversion or olefin de-coordination steps. In the case of *Schrock*  $d^0$  metal alkylidenes with the general formula  $(X)(Y)M(=CHR)E$ , where  $M$  is Mo or W,  $E$  is an oxo or imido ligand and  $X$  and  $Y$  are anionic ligands (often alkoxides or pyrrolides), the  $\sigma$ -donation of the  $E$ ,  $X$  and  $Y$  ligands are key for the high activity and stability of metathesis catalysts.<sup>[8–12]</sup> The large number of possible combinations has led to the ongoing search for ligand sets that yield optimum catalytic activity and selectivity.

Detailed investigations of the influence of the ligands on the metal center have shown that the highest activities have been achieved with a combination of strongly donating  $E$  ligands along with weakly donating  $X/Y$  ligands or *vice versa* (weaker donating  $E$  ligands along with at least one stronger donating  $X$  ligand).<sup>[13–18]</sup> This principle also applies for cationic alkylidene compounds,<sup>[19,20]</sup> where the  $\sigma$ -donating mono-anionic  $X$  ligand is replaced by a  $\sigma$ -donating

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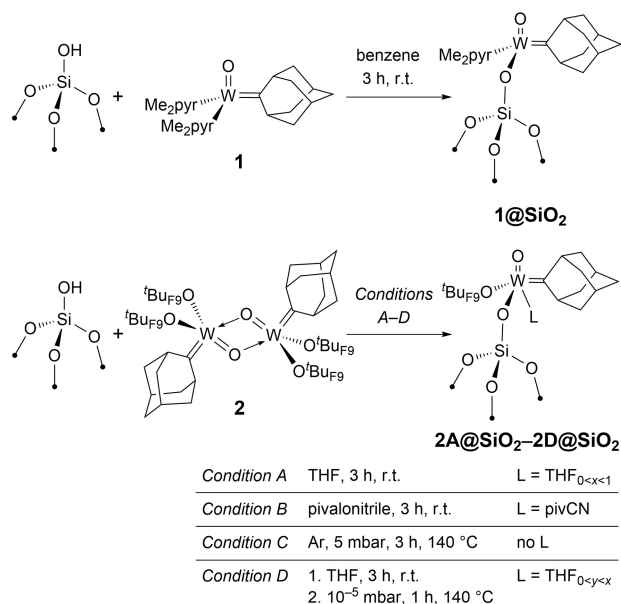
**Scheme 1.** a) *Chauvin* mechanism for olefin metathesis. b) Compounds used in the previous investigation of X/Y Ligand effects for supported W-oxo alkylidenes and c) W-oxo adamantylidenes **1** and **2** used in the present study.

neutral NHC ligand. In addition, it has been shown over the years that grafting these metal complexes on silica yields more active and stable catalysts in many instances.<sup>[21–23]</sup> Most such investigations have been performed on the larger family of imido complexes,<sup>[16,24]</sup> because isolable oxo complexes have been more difficult to prepare (*Scheme 1,b*).<sup>[25–27]</sup> However, recent synthetic developments in molecular chemistry have shown that W oxo adamantylidene complexes can be readily prepared (*Scheme 1,c*), possibly as a consequence of the sterically demanding adamantylidene, which prevents decomposition by homocoupling.<sup>[28]</sup> In this work, we investigate the grafting and reactivity of W-oxo adamantylidenes containing strongly donating X/Y ligands (pyrrolidine) **1** and weakly donating X/Y ligands (-OR<sub>F9</sub>) **2** (*Scheme 1,c*). We show that both species can be grafted to silica, with the activity of the grafted species following the established trends of activity with electron donation from the ligands.

## Results and Discussion

### Preparation and Characterization of Silica Supported Materials

The silica-supported materials were prepared under an inert atmosphere through grafting of the precursor (**1** or **2**) onto partially dehydroxylated silica; protonolysis with surface hydroxides yielded **1@SiO<sub>2</sub>** and **2@SiO<sub>2</sub>**. While the monomeric molecular precursor **1** could be grafted in a non-polar solvent such as benzene, **2** required that a coordinating solvent such as THF or pivalonitrile was used. Since **2** is unusually stable thermally and can be sublimed (*Scheme 2*), we also



**Scheme 2.** Grafting procedures of W-oxo adamantylidenes and resulting surface structures.

explored vapor deposition as an alternative and attractive method of grafting that avoids binding of solvents to the metal.

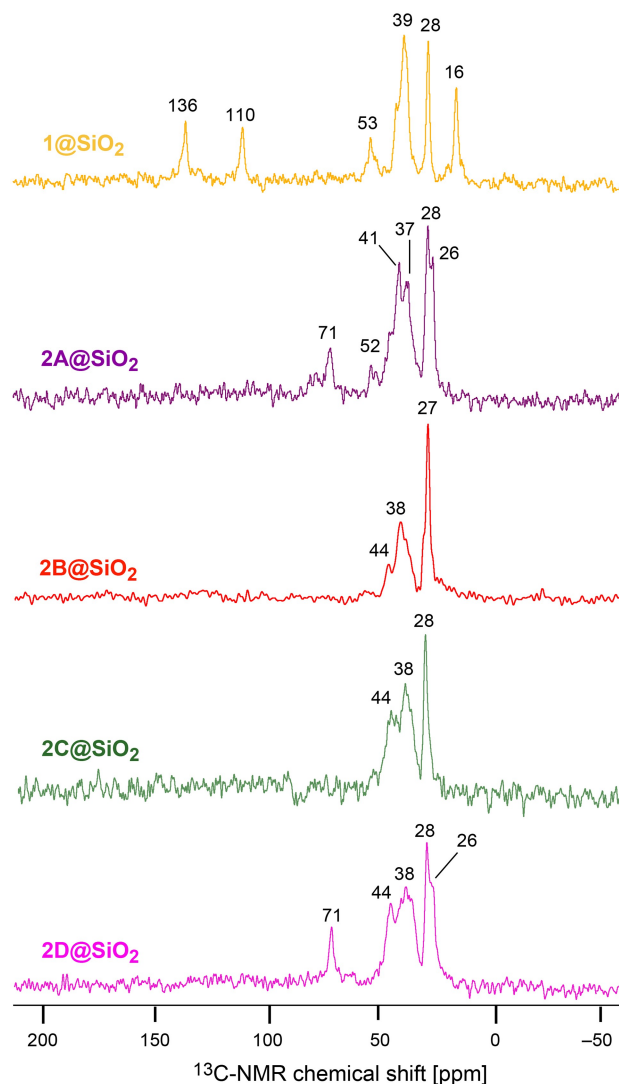
The grafting efficiency was first evaluated by elemental analysis. While the grafting efficiency reached 82% (4.95% wt%, 0.79 W/nm<sup>2</sup>) for **1@SiO<sub>2</sub>**, it was much lower for **2** in THF (40% of the W in solution; **2A@SiO<sub>2</sub>**, 2.41 wt%, 0.38 W/nm<sup>2</sup>), in pivalonitrile (45%; **2B@SiO<sub>2</sub>**, 2.70 wt%, 0.43 W/nm<sup>2</sup>), or through sublimation (56%; **2C@SiO<sub>2</sub>**, 3.37 wt%, 0.54 W/nm<sup>2</sup>). The amount of immobilized W stayed almost constant when **2A@SiO<sub>2</sub>** was treated at 140 °C under high vacuum, with the overall grafting yield of

39% (**2D@SiO<sub>2</sub>**, 2.34 wt%, 0.36 W/nm<sup>2</sup>). All grafted compounds were further analyzed by IR spectroscopy (Figures S1, S4, S7, S10, S13 in the Supporting Information). Typically signals that correspond to C–H stretching vibrations increase, while those for isolated SiOH groups at 3745 cm<sup>-1</sup> correspondingly decrease. However, for materials prepared using **2** as a molecular precursor, we still see a remaining band at 3745 cm<sup>-1</sup>, in addition to red-shifted signals that correspond to OH groups interacting with grafted materials. These observations correlate with the lower grafting efficiency observed by elemental analysis and indicate that some surface OH moieties cannot react with compound **2**.

We ascribe the low reactivity of **2** with surface OH groups to an inaccessibility of some sites due to the steric demands of the adamantylidene ligand combined with the large perfluoroalkoxide ligand. It may also be due to the insufficient Brønsted acidity of SiOH to protonate the electron deficient perfluoro-*tert*-butoxy group.

IR spectra of **1@SiO<sub>2</sub>** and **2A/B@SiO<sub>2</sub>** also show broad absorption bands in the range of 3200–3700 cm<sup>-1</sup>, which are attributed to residual surface OH interacting with the grafted species. In the case of **2A@SiO<sub>2</sub>**, the intensity of the band at 3300 cm<sup>-1</sup> can be reduced through a heat treatment of the material at 140 °C under high vacuum (**2D@SiO<sub>2</sub>**), which suggests that coordinated THF is being removed.

The materials were further analyzed by CP/MAS <sup>13</sup>C-NMR (Figure 1). In the case of **1A@SiO<sub>2</sub>**, we observe two strong signals at 28 ppm and 39 ppm for the adamantylidene group. A third, weaker signal at 53 ppm is attributed to the C-atoms α to the alkylidene carbon of the adamantylidene, which could not be observed itself. The remaining signals are attributed to the pyrrolylide ligand by comparison with corresponding molecular compounds,<sup>[29]</sup> with the methyl carbon signals appearing at 16 ppm and the last two signals at 110 and 136 ppm being ascribed to the α- and β-carbons of the pyrrolyl ligand. For **2A@SiO<sub>2</sub>**, we observe a total of four signals in the adamantylidene region, which can be divided into two pairs, one pair at 26 and 28 ppm and a second at 37 and 41 ppm. This splitting could be due to a significant fraction of the metal centers having THF coordinated. Additionally, we observe a single signal at 71 ppm which we attribute to THF bound to some of the W sites. In the case of **2B@SiO<sub>2</sub>**, the adamantylidene signals are not split, although the first of the two adamantylidene peaks is superimposed with a large signal from the methyl groups of



**Figure 1.** CP/MAS <sup>13</sup>C-NMR spectra of the investigated materials.

pivalonitrile, which suggests that this material also has coordinated solvent molecules. The surface structure of **2B@SiO<sub>2</sub>** appears to be monomeric albeit with coordinated pivalonitrile. Lastly, the NMR spectrum of **2C@SiO<sub>2</sub>** shows isolated signals for the adamantylidene consistent with a monomeric structure. As the preparation of this material does not include coordinating solvent molecules, there is also no L-type ligand to fill the coordination sphere of W.

#### Catalytic Investigation

Metathesis activity was assessed using 1- and (*Z*)-4-nonenes as prototypical substrates. Initial catalytic tests with 1000 equivalents of substrates show that all

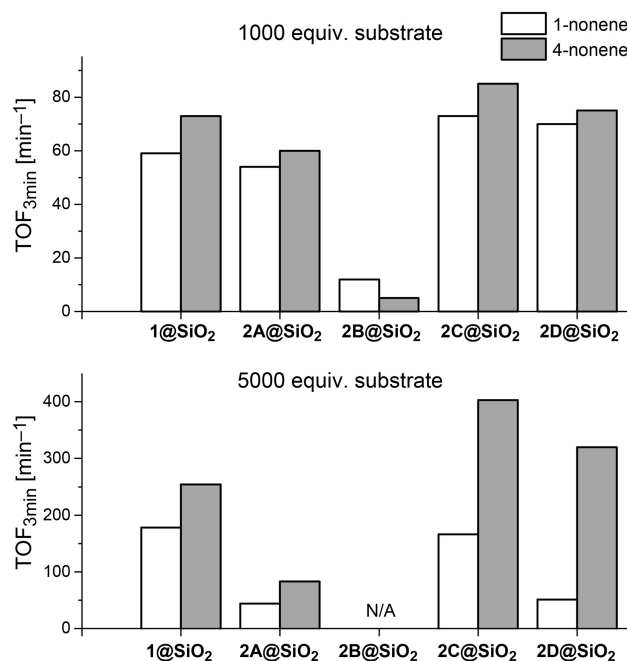
materials efficiently catalyze the metathesis of internal and terminal olefins, with the exception of **2B@SiO<sub>2</sub>** (Figure 2). We attribute this difference to the presence of coordinated pivalonitrile in **2B@SiO<sub>2</sub>**, which (partially) poisons some active sites.

In order to evaluate the catalytic activity (the initial turnover frequency TOF<sub>3min</sub>) of the various materials, we also investigated their catalytic performance with 5000 equivalents of substrates, with the exception of **2B@SiO<sub>2</sub>**. Under these conditions we found that **1@SiO<sub>2</sub>** shows high TOF<sub>3min</sub> for both internal (254 min<sup>-1</sup>) and terminal olefins (178 min<sup>-1</sup>). **2C@SiO<sub>2</sub>** showed a similar performance towards terminal olefins (166 min<sup>-1</sup>), but it clearly showed higher activity towards internal olefins (403 min<sup>-1</sup>), which is consistent with established reactivity trends.<sup>[18]</sup> **2D@SiO<sub>2</sub>** shows reduced activity compared to **2C@SiO<sub>2</sub>**, and it is significantly less efficient for terminal olefins (53 min<sup>-1</sup>) than internal ones (320 min<sup>-1</sup>). Lastly, the material prepared by grafting **2** in THF (**2A@SiO<sub>2</sub>**) showed the lowest activity among the investigated species for both 1- and 4-nonenes, with TOF<sub>3min</sub> of 44 min<sup>-1</sup> and 83 min<sup>-1</sup>, respectively. This trend in activities (**2C@SiO<sub>2</sub>** > **2D@SiO<sub>2</sub>** > **2A@SiO<sub>2</sub>**) correlates with the maximum conversions. Of the investigated catalysts, only **1@SiO<sub>2</sub>** was found to reach equilibrium conversion with 5000 equiv. of 4-nonene within 1 h, in spite of **2D@SiO<sub>2</sub>** showing higher initial TOFs. None of

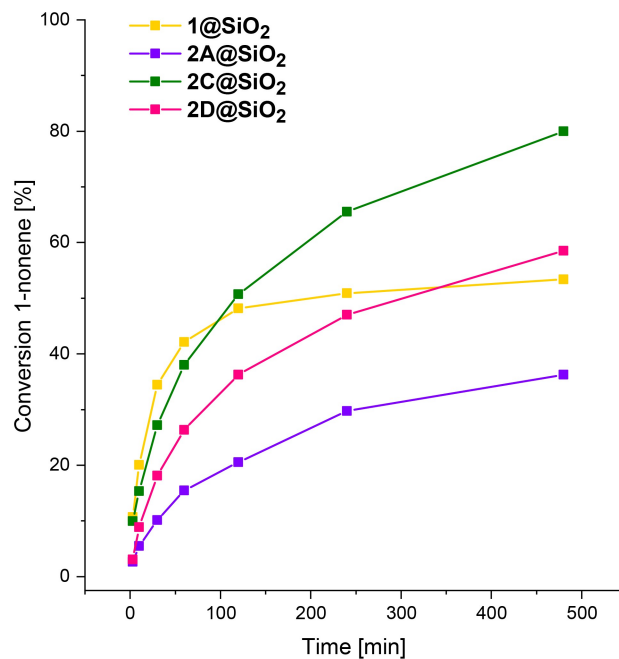
the investigated materials reached equilibrium conversion when 1-nonene was used as a substrate (Figure 3). Treatment of **1@SiO<sub>2</sub>** and **2C@SiO<sub>2</sub>** with ethylene resulted mostly in formation of the corresponding reduced olefin complexes in place of the expected alkylidenes or metallacyclobutanes.<sup>[21]</sup>

Notably, the catalytic efficiency among the materials prepared from **2** correlates inversely with the amount and donor strength of coordinated solvent on the surface sites; **2C@SiO<sub>2</sub>**, which was prepared without any solvent, shows the highest activity and stability. **2A@SiO<sub>2</sub>**, which was prepared in THF, shows significantly lower activity, although activity can be increased through heating under vacuum to remove some of the coordinated solvent. The strongest solvent coordination, and concomitantly the lowest activity, is observed for **2B@SiO<sub>2</sub>**, which was prepared in pivalonitrile.

**1@SiO<sub>2</sub>** shows comparable activity to the most active previously reported neutral W-oxo aryloxides<sup>[25]</sup> in the metathesis of 4-nonene and superior activity for the conversion of 1-nonene. In the case of **2C@SiO<sub>2</sub>**, which contains the more electron withdrawing per-fluoro *tert*-butoxide, we observe higher activity for conversion of both internal and terminal olefins, reaching a level comparable to the highly active cationic tungsten-oxo alkylidenes, albeit with a lower stability.<sup>[30]</sup>



**Figure 2.** TOF<sub>3min</sub> of catalytic materials with 1- and 4-nonenes using 1000 and 5000 equivalents of olefin.



**Figure 3.** Conversion vs. time for catalysis of 1-nonene with 0.02 mol% **1@SiO<sub>2</sub>**, **2A@SiO<sub>2</sub>**, **2C@SiO<sub>2</sub>** and **2D@SiO<sub>2</sub>**.

## Conclusions

This study illustrates that *W* adamantylidene complexes are proficient catalysts in the olefin metathesis when grafted on silica. The activity of these species was found to depend upon the grafting conditions and bound solvents are present or not. The activity is inversely correlated with the donor strength of and the amount of coordinated solvent. Interestingly, there is not as much of a difference in activity between compounds with weakly donating (perfluoro *tert*-butoxy) and strongly donating (pyrrolylide) *X*-type ligands, as previously observed for the molybdenum analogs.<sup>[13]</sup>

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## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Author Contribution Statement

*D. F. N.* contributed to the preparation, characterization and catalytic testing of the materials, as well as the computational analyses. *M. B.* contributed to the preparation of the molecular precursors. *L. L.* contributed to the NMR measurements. *R. R. S.* and *C. C.* designed and led the project. All authors contributed to interpreting the results and writing the manuscript.

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