A Well-Defined, Silica-Supported Tungsten Imido Alkylidene Olefin Metathesis Catalyst

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*Summary: The reaction of [W(═NAr)(═CHtBu)(CH$_2$tBu)$_2$] (**1**; Ar = 2,6-iPrC$_6$H$_3$) with a silica partially dehydroxylated at 700 °C, SiO$_{2-(700)}$, gives syn-[(≡SiO)W(═NAr)(═CHtBu)(CH$_2$tBu)] (**2**) as a major surface species, which was fully characterized by mass balance analysis, IR, NMR, EXAFS, and DFT periodic calculations. Similarly, complex **1** reacts with [(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$-SiOH] to give [(SiO)W(═NAr)(═CHtBu)(CH$_2$tBu)] (**2m**), which shows similar spectroscopic properties. Surface complex **2** is a highly active propene metathesis catalyst, which can achieve a TON of 16 000 within 100 h, with only a slow deactivation.*

We report herein the preparation and the characterization of a well-defined, silica-supported, W-based olefin metathesis catalyst through the reaction of [W(═NAr)(═CH*t*Bu)(CH$_2$*t*Bu)$_2$] (**1**) with a silica partially dehydroxylated at 700 °C (SiO$_{2-(700)}$).

Finding more efficient and more robust olefin metathesis catalysts is still a challenge today. Homogeneous catalysts are based on either d^0 (Mo, W, and Re)[1−3] or d^4 (Ru) transition-metal complexes.[4] In the case of d^0 complexes of the type [(X)-(Y)M(≡E)(═CHR)] (M = Mo, W, E = NAr; M = Re, E = C*t*Bu), the focus has been on the development of symmetrical catalysts (X = Y = OR′).[5] However, it has been recognized recently that the activity can be higher if the X and Y ligands are different (X = CH$_2$*t*Bu, Y = OR′).[6−11] Additionally, it has also been shown that a major pathway of deactivation for homogeneous olefin metathesis catalysts is dimerization of active species.[12] Thus, generating isolated active sites through grafting is a potential approach to more stable and active catalysts.[11] In surface organometallic chemistry, silica partially dehydroxylated at 700 °C can be considered to be a large siloxy ligand,[13,14] and therefore it constitutes a perfect entry into asymmetric catalysts (X = CH$_2$*t*Bu, Y = OSi≡). One strategy has been to use alkylidyne molecular complexes such as [M(≡CCMe$_3$)X$_3$] as a route to these systems through protonation of the alkylidyne ligand, [(≡SiO)M(═CHCMe$_3$)X$_3$].[15] While the resulting species can be highly active olefin metathesis catalysts,[16,17] they are in fact well-defined metal alkylidyne complexes, [(Support-O)$_x$M(≡C*t*Bu)X$_{3-x}$] (X = CH$_2$*t*Bu).[18−20] Therefore, generation of a silica-supported, well-defined tungsten alkylidene is still a challenge. Schrock et al. have developed an efficient synthesis of [W(═NAr)(═CH*t*Bu)(CH$_2$*t*Bu)$_2$][9] (**1**), which constitutes an ideal precursor for the synthesis of such a type of catalyst.

When the reaction of a disk of SiO$_{2-(700)}$ with **1**, [W(═NAr)-(═CH*t*Bu)(CH$_2$*t*Bu)$_2$] (Ar = 2,6-*i*PrC$_6$H$_3$), in pentane is monitored by IR spectroscopy, we observe that the band attributed to isolated silanol ν_{OH} groups at 3745 cm^{-1} totally disappears from the IR spectrum (Figure 1). Concomitantly, two groups of bands appear in the 3000−2700 and 1500−1300 cm^{-1} regions, which are assigned to ν_{CH} and δ_{CH} vibrations of perhydrocarbyl ligands, respectively. Moreover, two broad bands also appear at 3710 and 3607 cm^{-1}. While the former is typical of residual surface hydroxyls in interaction with perhydrocarbyl groups,[21] the latter is attributed to the interaction of other hydroxyls with the arylimido ligand (vide infra for further

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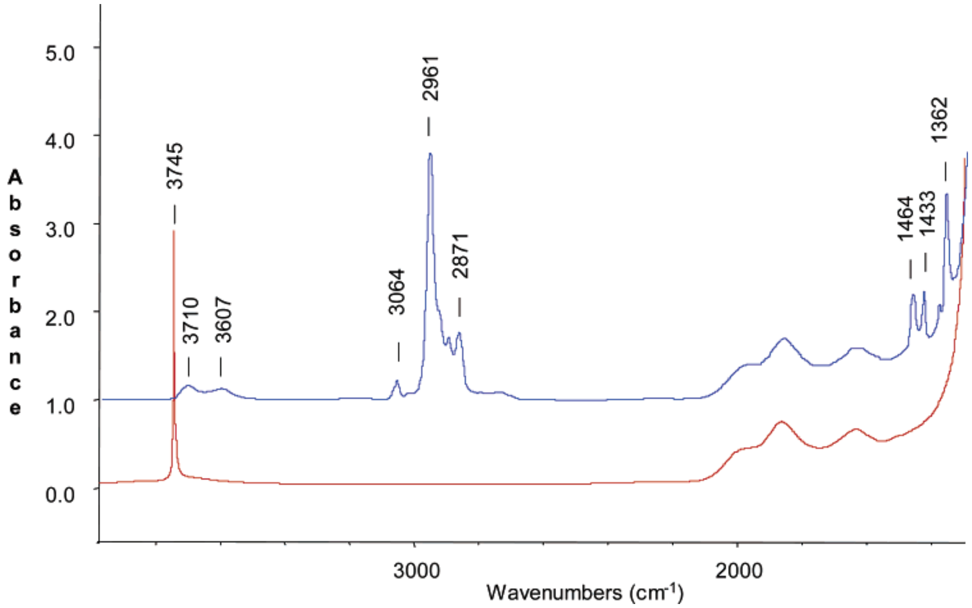

Figure 1. Infrared spectra of the grafting reaction of $[W({=}NAr)({=}CH\textit{t}Bu)(CH_2\textit{t}Bu)_2]$ (Ar = 2,6-iPrC$_6$H$_3$) onto $SiO_{2-(700)}$ by impregnation methods: (a, red line) silica partially dehydroxylated at 700 °C for 15 h; (b, blue line) the sample in (a) after impregnation of **1** at 25 °C for 3 h followed by washing in pentane and drying under vacuum.

comments). Furthermore, when the reaction is performed on larger quantities of silica in pentane, 0.9 equiv of 2,2-dimethylpropane is liberated per grafted W, which is consistent with the cleavage of about one neopentyl group in **1** and formation of an SiO−M bond, as observed for other molecular complexes.[13] The resulting yellow solid contains 3.5, 5.2, and 0.29 wt % of W, C, and N, respectively, which corresponds to 22.4 C/W and 1.1 N/W. These data are also consistent with the removal of one neopentyl group per grafted W and formation of a monografted surface complex as a major species, which can be tentatively formulated as $[(\equiv SiO)W({=}NAr)({=}CH\textit{t}Bu)(CH_2\textit{t}Bu)]$ (**2**) (expected elemental analysis: 22 C/W and 1 N/W). Moreover, while $SiO_{2-(700)}$ contains 0.26 mmol of OH/g, the W elemental analysis shows that only 0.19 mmol of OH/g of silica has been consumed (73%). This is consistent with the presence of residual silanols, as observed in the IR spectrum (vide supra). Note that the grafted organometallic fragment $[(\equiv SiO)W({=}NAr)({=}CH\textit{t}Bu)(CH_2\textit{t}Bu)]$ has a projected surface area of about 100 Å^2, which correspond to a maximum W loading of 5.9 wt %. This shows that even if the OH groups are about 13 Å apart, they are not uniformly distributed and the large organometallic fragment probably prevents the access of **1** to some residual silanols (OH in interaction by IR spectroscopy).

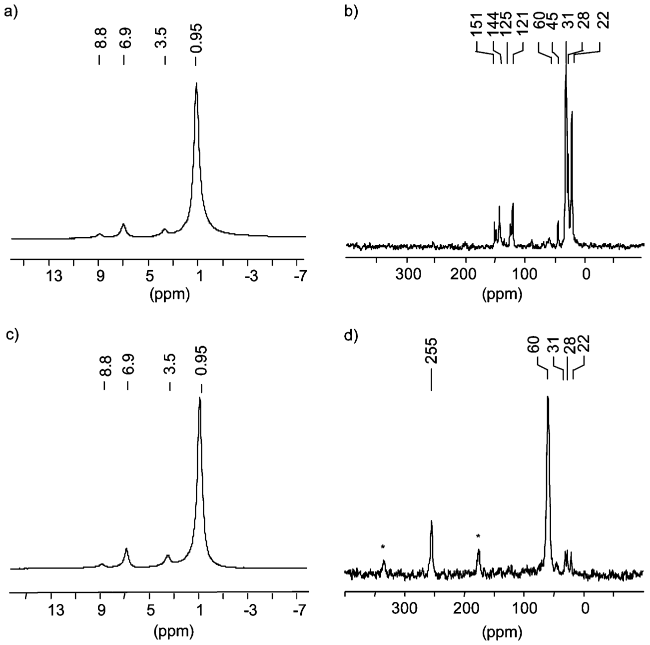

Figure 2. (a) ^{1}H MAS NMR spectrum of **2**. The spectrum was recorded with 8 scans and a relaxation delay of 2 s. (b) CP/MAS ^{13}C NMR spectrum of **2**. The spectrum was recorded with 50 000 scans, a relaxation delay of 2 s, and a CP contact time of 2 ms. An exponential line broadening of 80 Hz was applied before Fourier transform. (c) ^{1}H MAS NMR spectrum of **2***. The spectrum was recorded with 8 scans and a relaxation delay of 2 s. (d) CP/MAS ^{13}C NMR spectrum of **2***. The spectrum was recorded with 200 scans, a relaxation delay of 2 s, and a CP contact time of 2 ms. An exponential line broadening of 80 Hz was applied before Fourier transform.

The solid-state ^{1}H MAS NMR spectrum of **2** displays four resolved signals at 0.95, 3.5, 6.9, and 8.8 ppm (Figure 2a), which can be attributed tentatively to the methyl ($CH\textit{Me}_2$, $C\textit{Me}_3$), the methine ($C\textit{H}Me_2$), the aromatic C−H, and the alkylidene protons, respectively. The ^{13}C CP/MAS NMR spectrum of **2** (Figure 2b) shows eight signals tentatively assigned as follows (Table S1, Supporting Information): 22 ($CH\textit{Me}_2$), 28 ($\textit{C}HMe_2$), 31 (tBu), 45 ($=CH\textit{C}Me_3$), 60 ($\textit{C}H_2\textit{t}Bu$), 121 ($C_{Ar4}$), 125 ($C_{Ar3/3'}$), 144 ($C_{Ar2/2'}$), and 151 ppm ($C_{Ar1}$) (Scheme 1). Note, however, the low intensity of the signal at 60 ppm and the absence of an alkylidene signal. Using **2***, prepared by the reaction of **1*** (100% ^{13}C labeled on the carbons directly attached to W) with $SiO_{2-(700)}$, the ^{13}C CP/MAS spectrum displays two intense signals at 60 and 255 ppm, which confirms that the former signal can be ascribed to the methylene carbon of the neopentyl ligand ($\textit{C}H_2\textit{t}Bu$) and the latter to the neopentylidene ligand ($\textit{C}H\textit{t}Bu$). Furthermore, in the 2D ^{1}H−^{13}C dipolar HETCOR NMR spectrum (Figure S1, Supporting Information),[18] one correlation (δ_H in F$_1$; δ_C in F$_2$) at (8.8; 255) confirms their respective attribution to the H and C of the alkylidene ligand, and one at (2.6; 60) shows that the methylene protons, not observable in

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Scheme 1. Reaction of 1 with SiO_2−$_{(700)}$ and a Molecular Analogue of SiO_2−$_{(700)}$

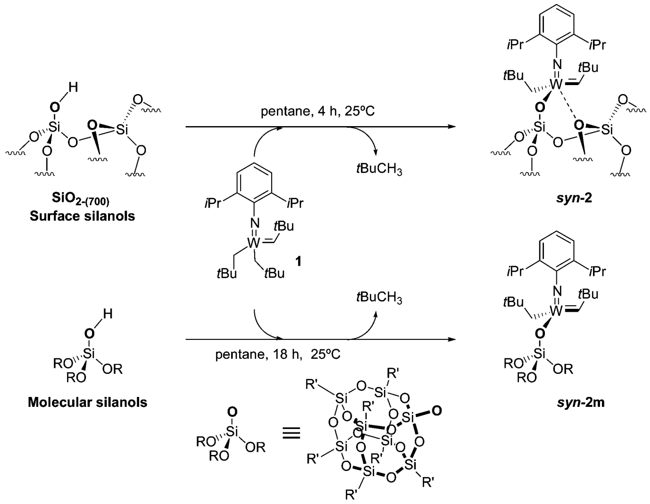

Table 1. M−X Bond Distances As Measured by EXAFS for 2 and Calculated by DFT for 2q

neighbor	no. of neighbors	dist (Å)	σ^2 (Å^2)	dist (Å) by DFT
*N*Ar	1	1.734(7)	0.000 88(5)	1.775
*C*H*t*Bu	1	1.873[a]	0.000 88[b]	1.891
*O*Si	1	1.95(3)	0.006(2)	1.935
*C*H$_2$*t*Bu	1	2.16(2)	0.005 81[b]	2.162
O*Si*$_2$	1	2.43(1)	0.006(1)	4.285
Si	1	2.96(1)	0.003 0(6)	3.554
C[c]	3	3.18(1)	0.002(1)	3.152, 3.258, 3.282[d]

[a] Constrained to move with the first shell. [b] σ^2 constrained to equal that of the preceding shell. [c] $S_0^2 = 1$, $\Delta E_0 = 2(1)$ eV. Distances are given to the ipso carbon of the imido group and the tertiary carbon of the alkyl and alkylidene groups, including two multiple scattering paths for the ipso carbon, which have the same distances and Debye−Waller factors. [d] Distances for the ipso carbon of the aryl imido and the quaternary carbons of the neopentylidene and neopentyl groups, respectively.

the ^{1}H MAS spectrum, appear at 2.6 ppm. Additionally, all corresponding ^{1}H and ^{13}C signals were found in a molecular analogue, [(c-C_5H_9)$_7$$Si_7O_{12}$SiO)W(=NAr)(=CH*t*Bu)($CH_2$*t*Bu)] (**2m**), prepared in the reaction between **1** and [(*c*-C_5H_9)$_7$$Si_7O_{12}$-SiOH] in benzene (Table S1). In particular, the ^{1}H and ^{13}C chemical shifts of the alkylidene H and C appear at 9.28 ppm (J_{C-H} = 107 Hz) and 256.9 ppm, respectively. The low J_{C-H} coupling constant indicates that **2m** is present as the syn isomer, as is the case for **1**. The methylene carbon signals appear at 58.9 ppm, and the corresponding diastereotopic proton signals of the neopentyl ligand appear as two distinct signals at 2.22 and 2.74 ppm, in contrast to the case for **2**, for which the signal appears as a large broad peak, probably because of the presence of dipolar interactions (even under MAS). Overall, the data obtained for **2m** show that **2** is probably formed as the *syn* isomer. The structural assignment for **2** is also supported by the EXAFS data (Table 1; Figure S2, Supporting Information), which are in agreement with a W atom bound to one nitrogen at 1.734(7) Å, a bond length consistent with an imido ligand,[12] two carbons at 1.873 and 2.16(2) Å, consistent with neopentylidene and neopentyl ligands, respectively,[5] and one oxygen at 1.95(3) Å, consistent with a siloxy substituent. The EXAFS data are further improved by including three carbons at 3.18(1) Å, assigned to the two quaternary carbons of the neopentyl and neopentylidene ligands in addition to the ipso carbon of the arylimido group. In addition, the presence of an O atom at 2.43(1) Å and a Si atom at 2.96(1) Å suggests the presence of a siloxane bridge close to the W center.[7,22] DFT periodic calculations using VASP[23,24] on (≡SiO)W(=N-2,6-*i*Pr_2-C_6H_3)(=CH*t*Bu)(CH_2*t*Bu) supported on a cristobalite (110) surface as a model for silica, **2q,**[14] confirm the metal−ligand bond lengths obtained by EXAFS (Table 1; Figure S3, Supporting Information). Moreover, they show that the surface complex has the usual pseudo-tetrahedral syn structure, the anti isomer lying 5.7 kcal mol^{-1} above.[5,25] The main difference between the calculated and experimental structures is the absence of a M···O(Si≡)$_2$ secondary interaction represented by relative short M−O and M−Si distances. Nonetheless, this interaction, already observed experimentally in the isoelectronic silica-supported Re complex (≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH_2*t*Bu), is probably only marginally stabilizing, as shown recently through DFT calculations,[14] and could be due to the inhomogeneity of the amorphous silica surface, not represented in the cristobalite model. More importantly, calculations show that residual surface OH groups are able to interact with all ligands surrounding W through H bonding (isopropyl, neopentylidene, imido, and aromatic rings). These interactions result in a decrease of ν_{OH} by 50−190 cm^{-1}, without affecting the electronic structure of the metal fragment (same geometry and ν_{Cene-H}), the larger red shift being associated with the interaction of the OH with the aromatic C−C double bonds. As there is an average of one OH every 13 Å on $SiO_{2-(700)}$, the two observed shifts (37 and 140 cm^{-1}) most likely correspond to residual OH groups interacting with functionalities remote from W, which are the alkyl C−H and aromatic C=C bonds of the *t*Bu and imido ligands. All data point toward the formation of *syn*-**2**.

Addition of 600 equiv of propene to *syn*-**2** at room temperature gives within 150 min the thermodynamic mixture of propene, ethylene, and 2-butenes along with small amounts of 1-butene (0.17%) (ca. 35% conversion in propene). During this reaction, 0.5 equiv of a roughly 4:1 ratio of 3,3-dimethylbutene and 4,4-dimethyl-2-pentene is obtained, which indicates that initiation takes place via cross-metathesis, as in well-defined systems. Moreover, this ratio is consistent with formation of cross-metathesis products through a pathway involving reaction intermediates in which the interaction between the alkyl substituents is minimized, as already proposed (Scheme 2).[26] We have also tested the catalyst (60 mg, 3.5%) in a flow reactor at 30 °C using propene (17 mL/min; 62 mol of propene/((mol of W) min)). The initial conversion (at 6 min) corresponds to a turnover frequency of 8.4 mol of propene·((mol of W)·min)$^{-1}$. Although the catalyst slowly deactivates, the turnover frequency is still 1.8 mol·(mol·min)$^{-1}$ after 6000 min (Figure S4, Supporting Information); therefore, 16 000 mol of propene per W has been transformed through metathesis. After the conversion reaches a pseudo-plateau (after ca. 1400 min), the selectivities are nearly constant: ethylene (49.3%), (*E*)-2-butene (28.9%), and (*Z*)-2-butene (21.2%) along with small amounts of 1-butene (0.3%) and 2-pentenes (0.4%). The ratio of (*E*)- to (*Z*)-2-butene is 1.3, which is close to the statistical distribution of 2-butenes, and thus, no information on the active site can be obtained.[26] 1-Butene and 2-pentenes are probably formed via secondary

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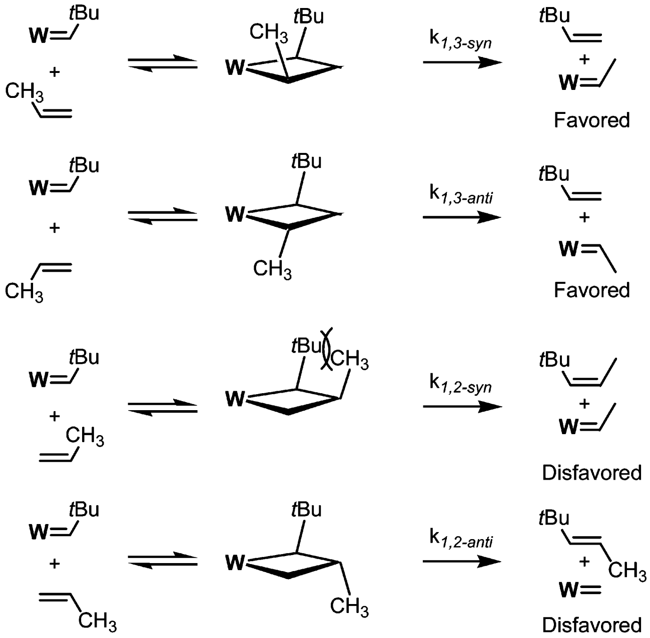
Scheme 2. Cross-Metathesis of 2 with Propene



cross-metathesis (1-butene/propene), or a substoichiometric amount could also be formed via rearrangement of intermediate metallacyclobutanes.

In conclusion, we have prepared and fully characterized the first well-defined monosiloxy alkylidene tungsten surface complex, $[(\equiv SiO)W{=}NAr(CH_2tBu)({=}CHtBu)]$ (*syn*-**2**), from the reaction of **1** with $SiO_{2-(700)}$. Some of the surface species interact with residual silanols, which appear red-shifted by 40−140 cm^{-1}. This system behaves like a well-defined single-site catalyst, as evidenced by a clean initiation process through cross-metathesis and good performance in propene metathesis without the need of cocatalyst. Activation of the metal center by supporting organometallic reagents on silica demonstrates the dramatic effect of the siloxy substituent,[10,27,28] and further studies are currently underway to test the scope of this catalyst.

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Supporting Information Available: Text giving details of the experimental procedures, a table giving chemical shift assignments for **2m** and **2**, and figures giving the $^1H-^{13}C$ HETCOR spectrum of **2***, the EXAFS spectrum of **2**, optimized structures of $(\equiv SiO)W({=}N\text{-}2,6\text{-}iPr_2\text{-}C_6H_3)({=}CHtBu)(CH_2tBu)$, and a plot of the catalytic activity of **2** in the metathesis of propene. This material is available free of charge via the Internet at http://pubs.acs.org.

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