

A well-defined silica supported W imido alkylidene olefin metathesis catalyst.

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Abstract. The reaction of $[W(=NAr)(=CHtBu)(CH_2tBu)_2]$ ($Ar=2,6-iPrC_6H_3$) (**1**) with a silica partially dehydroxylated at 700°C, $SiO_{2,(700)}$, gives *syn* $[(-SiO)W(=NAr)(=CHtBu)(CH_2tBu)]$ (**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 $[(c-C_5H_9)_7Si_7O_{12}SiOH]$ to give $[(SiO)W(=NAr)(=CHtBu)(CH_2tBu)]$ (**2m**), which shows similar spectroscopic properties. Surface complex **2** is a highly active propene metathesis catalyst, which can achieve 16000 TON within 100 h, with only a slow deactivation.

Keywords. Tungsten Imido Alkylidene complex. Silica. Olefin Metathesis. Surface Organometallic Chemistry. DFT, plane wave periodic calculations.

We report herein the preparation and the characterisation of a well-defined silica supported W-based olefin metathesis catalyst through the reaction of $[W(=NAr)(=CHtBu)(CH_2tBu)_2]$ (**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 either on 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 $[(X)(Y)M(=E)(=CHR)]$ ($M = Mo/W$, $E = NAr$; $M = Re$, $E = CtBu$), the focus has been on the development of symmetrical catalysts ($X = Y = OR'$).⁵ However, it has been recognised recently that activity can be higher if the X and Y ligands are different ($X = CH_2tBu$, $Y = OR'$).⁶⁻¹¹ Additionally, it also has 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 ligands,^{13,14} and therefore it constitutes a perfect entry into un-symmetric catalysts ($X = CH_2tBu$, $Y = OSi\equiv$). 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 alkylidyne metal complexes, $[(Support-O)_xM(_CtBu)X_{3-x}]$ ($X = CH_2tBu$).¹⁸⁻²⁰ Therefore generation of a silica supported well-defined tungstene alkylidene is still a challenge. Schrock et al. have developed an efficient synthesis of $[W(=NAr)(=CHtBu)(CH_2tBu)_2]$ ⁹ (**1**), which constitutes an ideal precursor for the synthesis of such type of catalysts.

When the reaction of a disk of $SiO_{2-(700)}$ with **1**, $[W(=NAr)(=CHtBu)(CH_2tBu)_2]$ ($Ar = 2,6-iPrC_6H_3$), 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 cm^{-1} 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 aryl imido ligand (*vide infra* for further comments). Furthermore, when the reaction is performed on larger quantities of silica in pentane, 0.9 equiv of 2,2-dimethylpropane are liberated per grafted W, which is consistent with the cleavage of about one neopentyl group in **1** and formation of a SiO-M bond as observed for other molecular complexes.¹³ The resulting yellow solid contains 3.5 %_{wt}, 5.2 %_{wt}, 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 $[(-\text{SiO})\text{W}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$ (**2**) {expected elemental analysis : 22C/W and 1N/W}. Moreover, while $\text{SiO}_{2-(700)}$ 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, $[(-\text{SiO})\text{W}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$ has a projected surface area of about 100 \AA^2 , which correspond to a maximum W loading of 5,9 %_{wt}. This shows that even if the OH groups are about 13 \AA 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).

The solid state ^1H 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 (CHMe_2 , CMe_3), the methine (CHMe_2), the aromatic C-H and the alkylidene protons, respectively. The ^{13}C CP/MAS NMR spectrum of **2** (Figure 2b) shows 8 signals tentatively assigned as follows

(Table S1): 22 ($CHMe_2$), 28 ($CHMe_2$), 31 ppm (tBu), 45 ppm ($=CHCMe_3$), 60 (CH_2tBu), 121 (C_{Ar4}), 125 ($C_{Ar3/3'}$), 144 ($C_{Ar2/2'}$) and 151 (C_{Ar1}) ppm (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 ppm and 255 ppm, which confirms that the former signal can be ascribed to the methylene carbon of the neopentyl ligand (CH_2tBu) and the latter to the neopentylidene ligand ($CHtBu$). Furthermore, in the 2D 1H - ^{13}C dipolar HETCOR NMR spectrum (Figures S1),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 the 1H MAS spectrum, appear at 2.6 ppm. Additionally, all corresponding 1H and ^{13}C signals were found in a molecular analogue, $[(c-C_5H_9)_7Si_7O_{12}SiO]W(=NAr)(=CHtBu)(CH_2tBu)$ **2m**, prepared in the reaction between **1** and $[(c-C_5H_9)_7Si_7O_{12}SiOH]$ in benzene (Table S1). In particular the 1H 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 like 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 **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), 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 a neopentylidene and a 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 aryl imido group. In addition, the presence of an O atom at 2.43(1) Å and a Si 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 $(\equiv\text{SiO})\text{W}(=\text{N}-2,6\text{-di-}i\text{Pr}-\text{C}_6\text{H}_3)(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ supported on a cristobalite (110) surface as a model for silica, **2q**,¹⁴ confirm the metal-ligand bond lengths obtained by EXAFS (Table 1 and Figure S3). 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 $\text{M}\cdots\text{O}(\text{Si}\equiv)_2$ 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, $(\equiv\text{SiO})\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$, 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 $\nu_{\text{C}_{\text{ene-H}}}$), 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 a $\text{SiO}_{2-(700)}$, 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 towards 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% conv. in propene). During this reaction, 0.5 equiv. of a roughly 4:1

ratio of 3,3-dimethylbutene and 4,4-dimethyl-2-pentene are 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 (60mg, 3.5%) in a flow reactor at 30 °C using propene (17 mL/min; 62 mol propene/mol W/min). The initial conversion (@6 min) corresponds to a turnover frequency of 8.4 mol propene/mol W/min. Although the catalyst slowly deactivates, the turnover frequency is still 1,8 mol/mol/min after 6000 min (Figure S4); therefore 16000 mol of propene per W have 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 *E* to *Z* 2-butenes ratio 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 either via secondary cross-metathesis (1-butene/propene) or a sub-stoichiometric amount could be formed also via rearrangement of intermediate metallacyclobutanes.

In conclusion, we have prepared and fully characterized the first well-defined monosiloxy alkylidene tungsten surface complex *syn-2*, [(-SiO)W=NAr(CH₂*t*Bu)(=CH*t*Bu)], from the reaction of **1** with SiO₂₋₍₇₀₀₎. Some of the surface species interact with residual silanols, which appear red-shifted by 40 to 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 co-catalyst. Activation of the metal center by supporting organometallic reagents on silica demonstrates the dramatic effect of siloxy substituent,^{10,27,28} and further studies are currently underway to test the scope of this catalyst.

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Table 1. M-X bond distances as measured by EXAFS for **2** and calculated by DFT for **2q**.

Neighbor	# of Neighbors	Distance (Å)	σ^2 (Å ²)	Distance (Å) by DFT
NAr	1	1.734(7)	0.00088(5)	1.775
CH t Bu	1	1.873 ^a	0.00088 ^b	1.891
OSi	1	1.95(3)	0.006(2)	1.935
CH $2t$ Bu	1	2.16(2)	0.00581 ^b	2.162
OSi ₂	1	2.43(1)	0.006(1)	4.285
Si	1	2.96(1)	0.0030(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 to the ipso carbon of the imido group, the tertiary carbon of the alkyl and alkylidene groups. Includes two multiple scattering paths for the ipso carbon, which have the same distance and Debye-Waller factor. ^d Distances for the ipso carbon of the aryl imido, the quaternary carbon of the neopentylidene and neopentyl respectively.

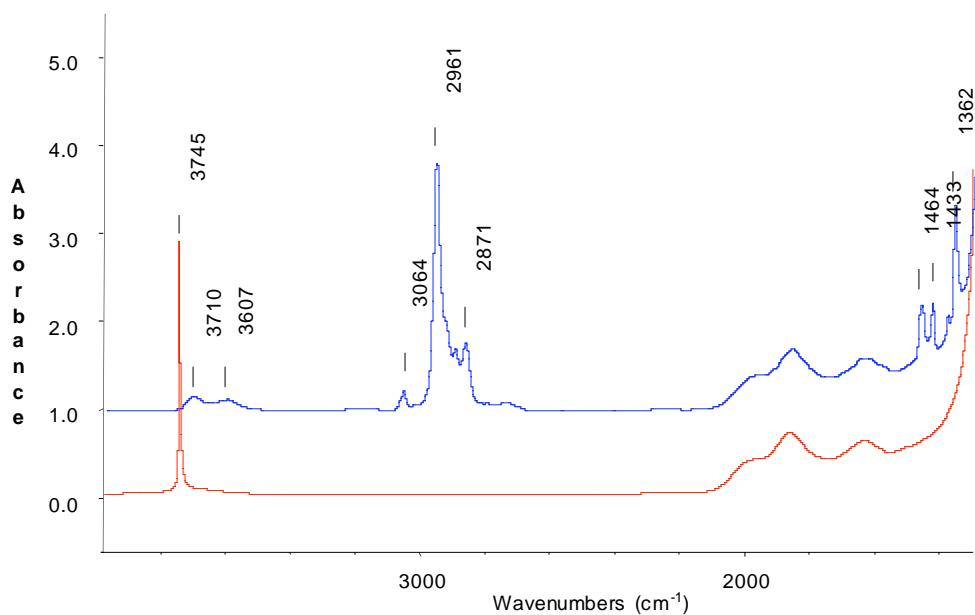


Figure 1. Infrared spectra of the grafting reaction of $[W(=NAr)(=CHtBu)(CH_2tBu)_2]$ ($Ar=2,6-iPrC_6H_3$) onto $SiO_{2-(700)}$ by impregnation method. (a) Silica partially dehydroxylated at 700 °C for 15 h. (b) After impregnation of **(1)** at 25 °C for 3 h followed by washing in pentane and drying under vacuum.

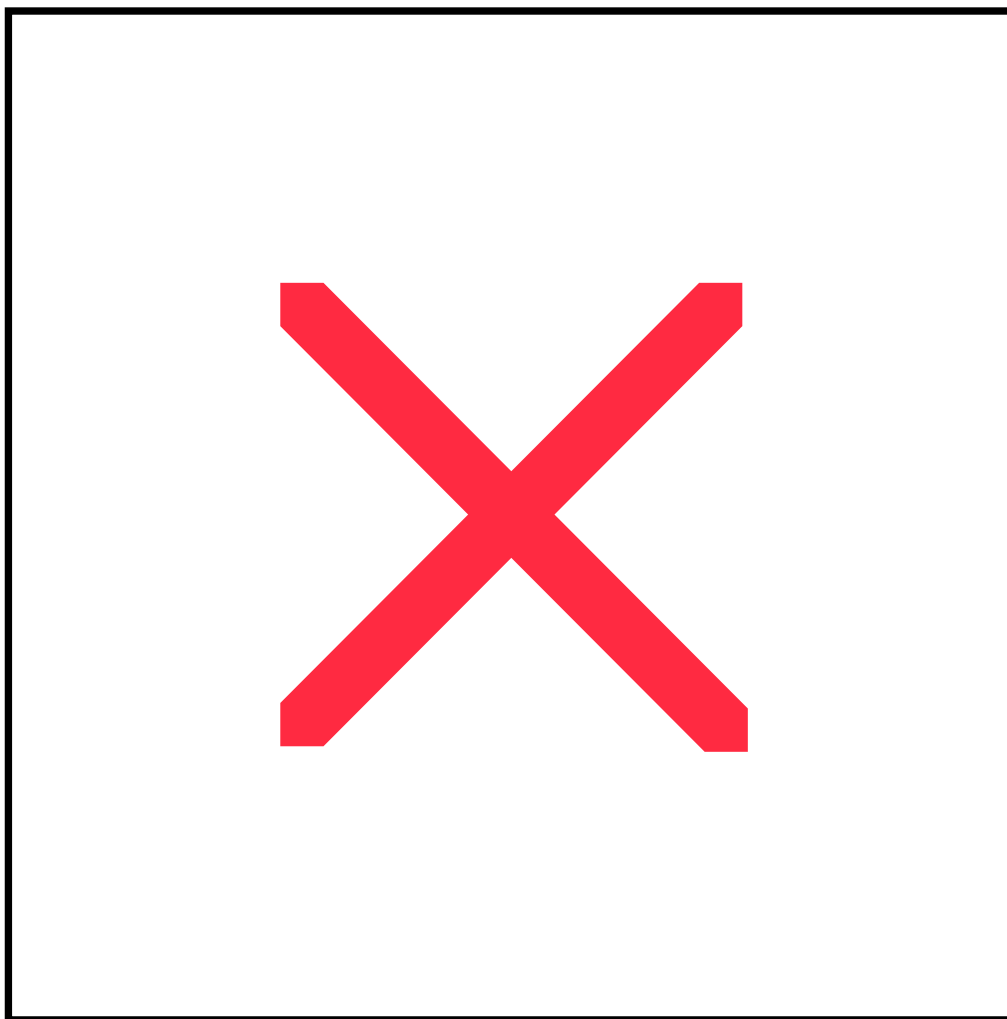
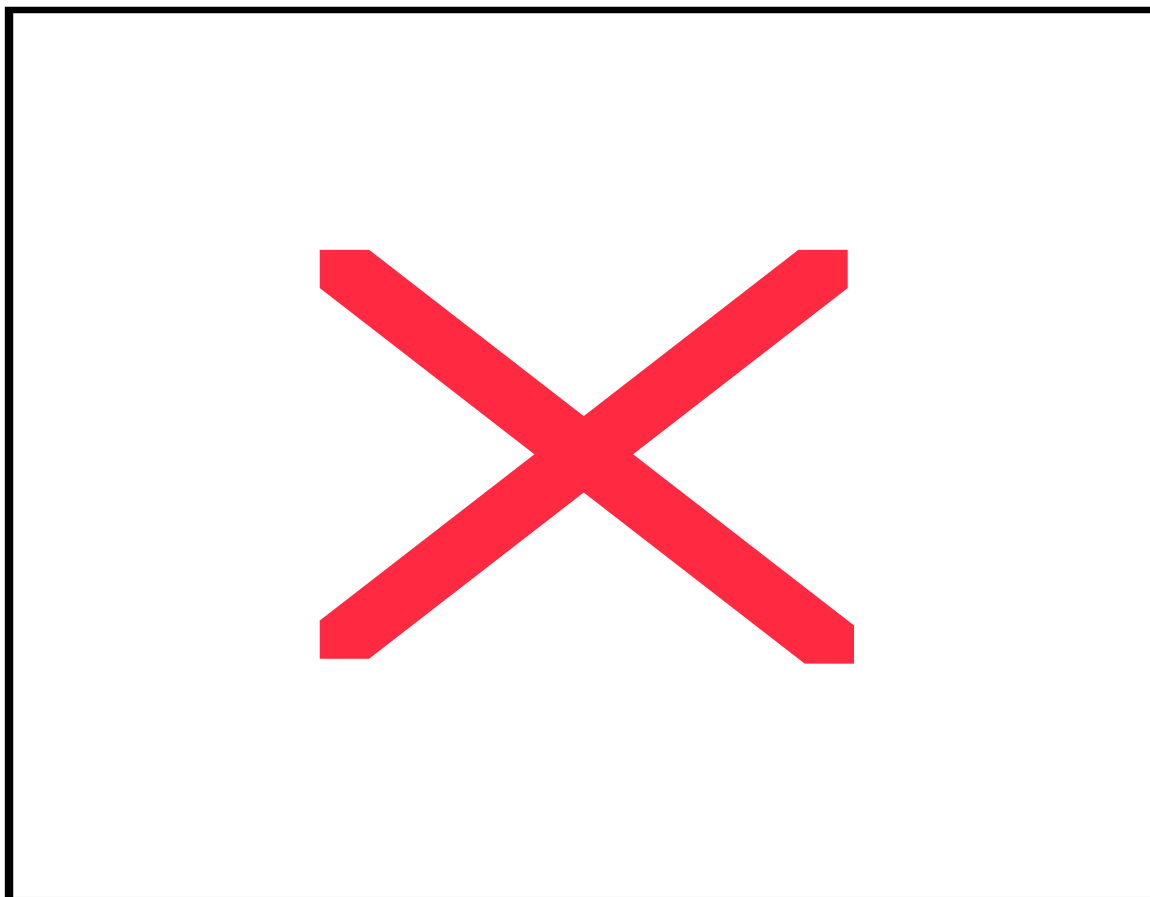
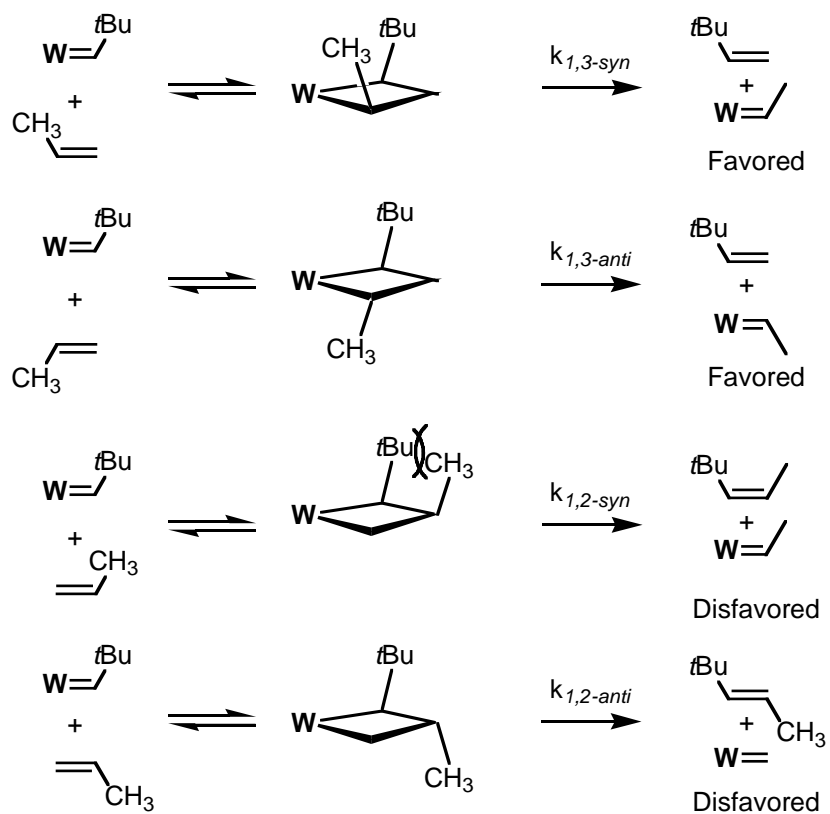


Figure 2. (a) ^1H MAS NMR spectrum of **2**. The spectrum was recorded with 8 scans and a relaxation delay of 2 s. (b) CP/MAS ^{13}C NMR of **2**. The spectrum was recorded with 50000 scans, a relaxation delay of 2 s and a CP contact time of 2 ms. An exponential line broadening of 80 Hz was applied before Fourier transform. (c) ^1H 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 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.



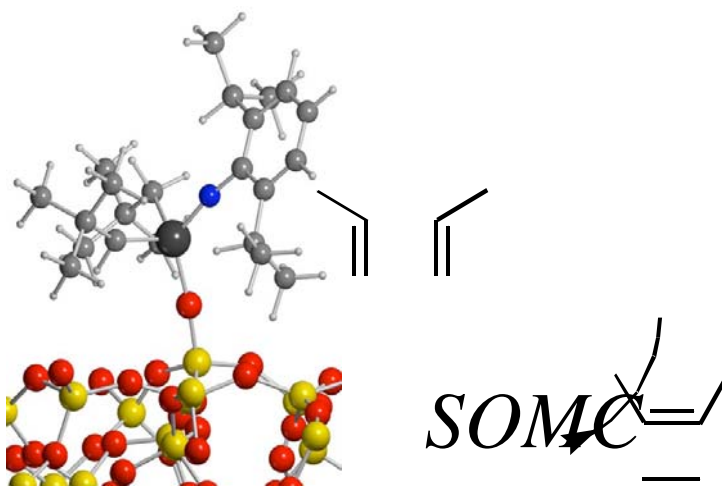
Scheme 1. Reaction of **1** with $\text{SiO}_{2-(700)}$ and a molecular analogue of $\text{SiO}_{2-(700)}$.



Scheme 2. Cross-metathesis of **2** with propene.

TOC.

TOF ~ 8.4 TON/min
Slow deactivation
TON > 16000



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