

Understanding the reactivity of $[W=NAr(CH_2tBu)_2(=CHtBu)]$ (Ar = 2,6-*i*PrC₆H₃) with silica partially dehydroxylated at low temperatures through a combined use of molecular and surface organometallic chemistry

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Abstract

Reaction of $[W=NAr(CH_2tBu)_2(=CHtBu)]$ (Ar = 2,6-*i*PrC₆H₃) with silica partially dehydroxylated at 200 °C does not lead only to the expected bisgrafted $[(=SiO)_2W=NAr(=CHtBu)]$ species, but also surface reaction intermediates such as $[(=SiO)_2W=NAr(CH_2tBu)_2]$. All these species were characterized by infrared spectroscopy, 1D and 2D solid state NMR, elemental analysis and molecular models obtained by using silsesquioxanes. While a mixture of several surface species, the resulting material displays high activity in the olefin metathesis.

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1. Introduction

Heterogeneous catalysts have been central in industrial chemistry, but the development of better catalysts is often hindered by the presence of different active species or by their low concentration. One possible approach to improve heterogeneous catalysts is to generate single-site species through a molecular approach to surface science, also called surface organometallic chemistry (SOMC) [1]. This can be achieved by grafting organometallic compounds with oxides surfaces under controlled low temperature reaction con-

ditions in order to generate tunable well-defined catalyst precursors having uniform chemical environment.

One of the applications of SOMC has been the preparation of olefin metathesis catalysts, which rely on generating well-defined alkylidene complexes. One strategy consisted in grafting alkylidyne molecular precursors such as $[W(=CtBu)(CH_2tBu)_3]$ on partially dehydroxylated silica in order to obtain well-defined monosiloxy alkylidene W complexes such as $[(=SiO)W(=CHtBu)(CH_2tBu)_3]$ by protonation of the alkylidyne ligand with a surface hydroxyl. However, even if the resulting material is a very active olefin metathesis catalyst [2,3], it has been recently shown that these species are in fact well-defined W alkylidyne complexes [4]. Using a silica partially dehydroxylated at 700 °C (SiO₂₋₍₇₀₀₎), it is possible to selectively generate

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$[(\equiv\text{SiO})\text{W}(\equiv\text{C}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$, while $[(\equiv\text{SiO})_2\text{W}(\equiv\text{C}t\text{Bu})(\text{CH}_2t\text{Bu})]$ is the major species when $\text{SiO}_{2-(200)}$ is used. Alternatively, we have recently shown that the alkyl alkylidene complex $[\text{W}=\text{NAr}(\equiv\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ ($\text{Ar} = 2,6\text{-}i\text{PrC}_6\text{H}_3$) (**1**) [5] reacts with $\text{SiO}_{2-(700)}$ to give a well-defined monosiloxy tungsten imido alkylidene complex, $[(\equiv\text{SiO})\text{W}(\equiv\text{NAr})(\text{CH}_2t\text{Bu})(\equiv\text{CH}t\text{Bu})]$ (**2**), which is a highly active olefin metathesis catalyst [6].

Recent theoretical studies [7] have shown that the reactivity of d^0 olefin metathesis catalysts is strongly affected by the presence of one or two alkoxy or siloxy substituents. We have therefore investigated the preparation of $[(\equiv\text{SiO})_2\text{W}(\equiv\text{NAr})(\equiv\text{CH}t\text{Bu})]$ by grafting **1** on $\text{SiO}_{2-(200)}$, a support which is typically used to obtain bisgrafted species [8,9]. We have also studied the reactivity of **1** with molecular mono- and bisilanol silsesquioxanes derivatives, given their molecular resemblances with surface siloxy species [10], and their capacity to provide molecular insight in surface organometallic chemistry [11]. Finally, we have compared the reactivity of the molecular and surface complexes obtained as olefin metathesis catalysts.

2. Experimental

All experiments were conducted under strict inert atmosphere or vacuum. *cis*-2-Pentene was purchased from Aldrich (98% isomeric purity), distilled over CaH_2 and degassed before use. The complex **1** was prepared according to the literature procedure [12]. The complex **1**^{*} was prepared using the same literature procedure as **1** using $^{13}\text{C}_2$ labeled neopentyl magnesium chloride. $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}]$ (Aldrich) was heated at 40 °C for 12 h at 10^{-5} Torr before use. $[(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{11}(\text{OH})_2]$ (Aldrich) was degassed for 12 h at 10^{-5} Torr before use. Infrared spectra were recorded on a Nicolet FT-IR Magna 550 spectrometer equipped with a cell designed for in situ preparations under controlled atmosphere. For specific studies (see below), ^1H MAS and ^{13}C CP-MAS solid state NMR spectra were recorded on a Bruker Avance-500 spectrometer with a conventional double resonance 4 mm CP-MAS probe at the Laboratoire de Chimie Organométallique de Surface in Ecole Supérieure de Chimie Physique Electronique de Lyon. The samples were introduced under Ar in a zirconia rotor, which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz unless otherwise specified. Chemical shifts were given with respect to TMS as external reference for ^1H and ^{13}C NMR. Elemental analyses were performed at the Service Central d'Analyses of CNRS in Solaize and at the SLSEO University of Bourgogne of Dijon. GC analyses were performed using a gas chromatograph "HP 5890", equipped with a flame ionization detector (FID) and a $\text{KCl}/\text{Al}_2\text{O}_3$ on fused silica column (50 m \times 0.32 mm).

2.1. Heteronuclear correlation spectroscopy

Two-dimensional heteronuclear correlation experiments were performed according to the following scheme: 90°

proton pulse, t_1 evolution period, cross-polarization (CP) to carbon spins, detection of carbon magnetization. For the CP step, a ramp radio-frequency (RF) field centered at 60 kHz was applied on protons while the carbon RF field was matched to obtain optimal signal. During acquisition, the proton decoupling field strength was set to 83 kHz. A total of 32 t_1 increments with 512 scans each were collected. The spinning frequency was 10 kHz and the recycle delay was 2 s (total acquisition time of 9 h).

2.2. Preparation of silica partially dehydroxylated at 200 °C ($\text{SiO}_{2-(200)}$)

The oxide support used in these studies was a silica Aerosil 200 from Degussa. Aerosil 200 is a non-porous flame silica, in the form of regular particles of an average diameter of 150 Å and free of halides impurities with a surface area of $200 \pm 4 \text{ m}^2/\text{g}$. It was dehydroxylated under vacuum (10^{-5} mbar) at 200 °C for a minimum of 15 h leading to $\text{SiO}_{2-(200)}$.

2.3. Monitoring the reaction of **1** with $\text{SiO}_{2-(200)}$ by IR spectroscopy

A 30 mg self-supporting disk pressed under 2 kg/cm² was introduced in a IR cell equipped with CaF_2 windows, and it was then treated under vacuum at 200 °C for 15 h. After recording the infrared spectrum, the disk was immersed in a solution of **1** (30 mg, 0.052 mmol) in pentane (12 mL) for 3 h, washed 3 times in pentane, and finally dried under vacuum for 30 min. The IR spectrum was then recorded.

2.4. Reaction of **1** with $\text{SiO}_{2-(200)}$ by impregnation in pentane. Representative procedure

A mixture of **1** (168 mg, 0.294 mmol) and $\text{SiO}_{2-(200)}$ (0.75 g) in pentane (12 mL) was stirred at 25 °C for 4 h. After filtration, the solid was washed 3 times with pentane, and all volatile compounds were condensed into another reactor. The resulting yellow powder solid (0.70 g) was dried under vacuum (10^{-5} Torr).

2.5. Reaction of **1**^{*} with $\text{SiO}_{2-(200)}$ by impregnation in pentane

The same procedure was used for grafting **1**^{*} as described above for **1**.

2.6. Reaction of **1** with $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}]$ (1:1 ratio). Synthesis of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO}][\text{W}(\equiv\text{NAr})(\equiv\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$ (**2**_{mol})

A C_6D_6 solution of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}]$ (75 mg, 81 μmol , 0.46 mL of solvent) was added to a C_6D_6 frozen solution of **1** (47 mg, 82 μmol , in 0.50 mL). The NMR tube was sealed and thawed just prior to introduction in the

NMR spectrometer. Since the first spectrum (taken within 2 min of thawing and mixing) the resulting orange solution showed complete conversion to the final product $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO}][\text{W}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$, alongside 2,2-dimethylpropane (0.66 mmol, 0.8 mol/mol W by ^1H NMR integration). The volatiles were removed from the solution and the orange solid was used for homogeneous catalytic runs.

2.7. Reaction of **1 with $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}]$ (1:2 ratio). Synthesis of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO}]_2[\text{W}(=\text{NAr})(\text{CH}_2t\text{Bu})_2]$ (**3_{mol-A}**)**

In a procedure similar to the one described above for the synthesis of **2_{mol}**, a solution of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}]$ in C_6D_6 (144 mg, 156 μmol , in 0.72 mL) was added to a frozen C_6D_6 solution of **1** (45 mg, 79 μmol , in 0.35 mL). Initially, a mixture of **2_{mol}**, 2,2-dimethylpropane, and unreacted starting silanol was observed. The solution slowly evolved to the complete conversion to the final product $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO}]_2[\text{W}(=\text{NAr})(\text{CH}_2t\text{Bu})_2]$. The reaction appeared complete after several hours.

2.8. Reaction of **1 with $[(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{11}(\text{OH})_2]$ (1:1 ratio). Synthesis of $[(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{11}\text{O}_2][\text{W}(=\text{NAr})(\text{CH}_2t\text{Bu})_2]$ (**3_{mol-B}**)**

In a procedure similar to the ones described above, a C_6D_6 solution of $[(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{11}(\text{OH})_2]$ (75 mg, 76 μmol , in 0.4 mL) was added to a frozen C_6D_6 solution of **1** (43 mg, 75 μmol , in 0.4 mL). The orange solution slowly lightened with concomitant 2,2-dimethylpropane release in solution, to yield the final yellow product $[(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{11}\text{O}_2][\text{W}(=\text{NAr})(\text{CH}_2t\text{Bu})_2]$ (**3_{mol-B}**). The reaction appeared complete after 24 h. After removal of the

volatiles under vacuum and addition of fresh solvent, the presence of unaltered **3_{mol-B}** was observed. Anal. Calc. for $\text{C}_{62}\text{H}_{111}\text{NO}_{13}\text{Si}_8\text{W}$: C, 48.39; H, 7.38; N, 0.69; Si, 15.88. Found: C, 48.87; H, 7.05; N, 0.99; Si, 16.48%.

2.9. Thermal treatment of $[(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{11}\text{O}_2][\text{W}(=\text{NAr})(\text{CH}_2t\text{Bu})_2]$ (3_{mol-B}**)**

The C_6D_6 solution of **3_{mol-A}** (75 μmol , 0.6 mL) was heated at 60°C. Within 3 h, clean transformation (30% conversion) to **4_{mol}** and concomitant release of 2,2-dimethylpropane in solution were observed. Overnight heating lead to full conversion.

2.10. Thermal treatment of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO}]_2[\text{W}(=\text{NAr})(\text{CH}_2t\text{Bu})_2]$ (3_{mol-A}**)**

The C_6D_6 solution of **3_{mol-A}** (78 μmol , 1 mL) was heated at 60 °C. Within the first 3 h no transformation to carbenic products could be detected, later and under higher temperatures some decomposition to unidentified products was observed still with no carbenic intermediates.

2.11. Propene metathesis (batch reactor)

In a batch reactor of known volume, **2** was introduced in a glove box. After evacuation of Argon, dry propene (600 equiv.) was added. To monitor the reaction, aliquots were expanded in a small volume, brought to atmospheric pressure and analyzed by GC.

2.12. cis-2-Pentene metathesis

In a typical reaction, 100 equiv. of a solution 0.5 M of cis-2-pentene in chlorobenzene was added to the catalyst,

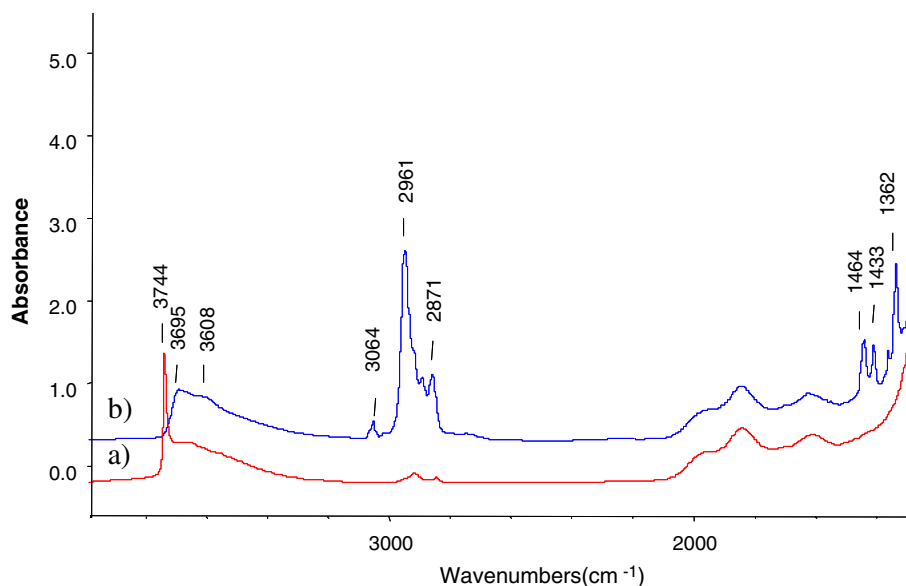


Fig. 1. Infrared spectra of the grafting reaction of **1** onto $\text{SiO}_2\text{-(200)}$. (a) Silica dehydroxylated at 200 °C for 15 h. (b) After impregnation of **1** at 25 °C for 3 h.

and the reaction mixture was heated at 50 °C. The reaction was monitored periodically by GC analysis.

3. Results and discussion

The infrared spectrum of $\text{SiO}_2\text{-(200)}$ shows a sharp band at 3744 cm^{-1} and a broad absorption at $3500\text{--}3700\text{ cm}^{-1}$ attributed to isolated and H-bonded silanols, respectively (Fig. 1a). After reaction with $[\text{W}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ ($\text{Ar} = 2,6\text{-}i\text{PrC}_6\text{H}_3$) (**1**), the band of isolated silanols has completely disappeared, while new bands, assigned to $\nu(\text{C-H})$ and $\delta(\text{C-H})$ vibrations, appear in the $3000\text{--}2700$ and $1500\text{--}1300\text{ cm}^{-1}$ regions. A detailed analysis of the $\nu(\text{O-H})$ region shows that two new bands appeared at 3695 and 3608 cm^{-1} . The former one is typical of residual surface hydroxyls in interaction with perhydrocarbyl groups while the latter can be attributed to hydroxyl groups in interaction with the aryl imido ligand either through the nitrogen atom or the aromatic ring [6].

Chemical analysis of the solid prepared by impregnation gives $3.2\%_{\text{wt}}$ of W, which corresponds to 0.18 mmol W/g , while $\text{SiO}_2\text{-(200)}$ contained 0.86 mmol of OH/g . During

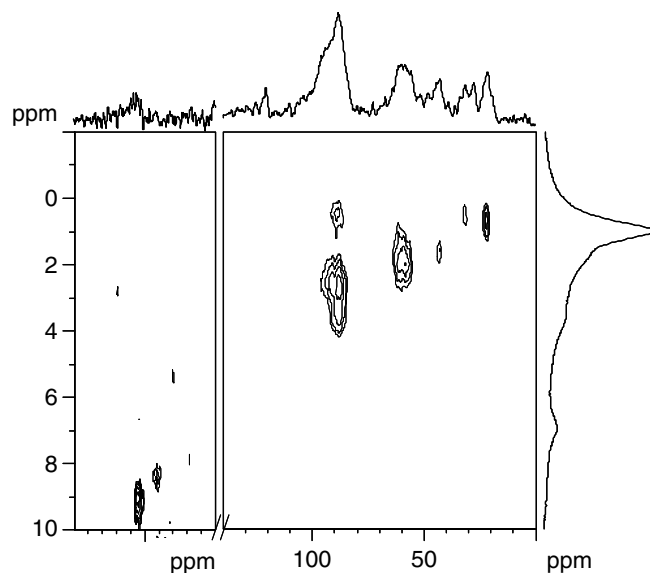


Fig. 3. $^1\text{H}\text{--}^{13}\text{C}$ HETCOR spectrum of solid **2***. The spectra were recorded with 1024 scans, a relaxation delay of 1 s and a CP contact time of 1 ms. An exponential line broadening of 50 Hz was applied before Fourier transform.

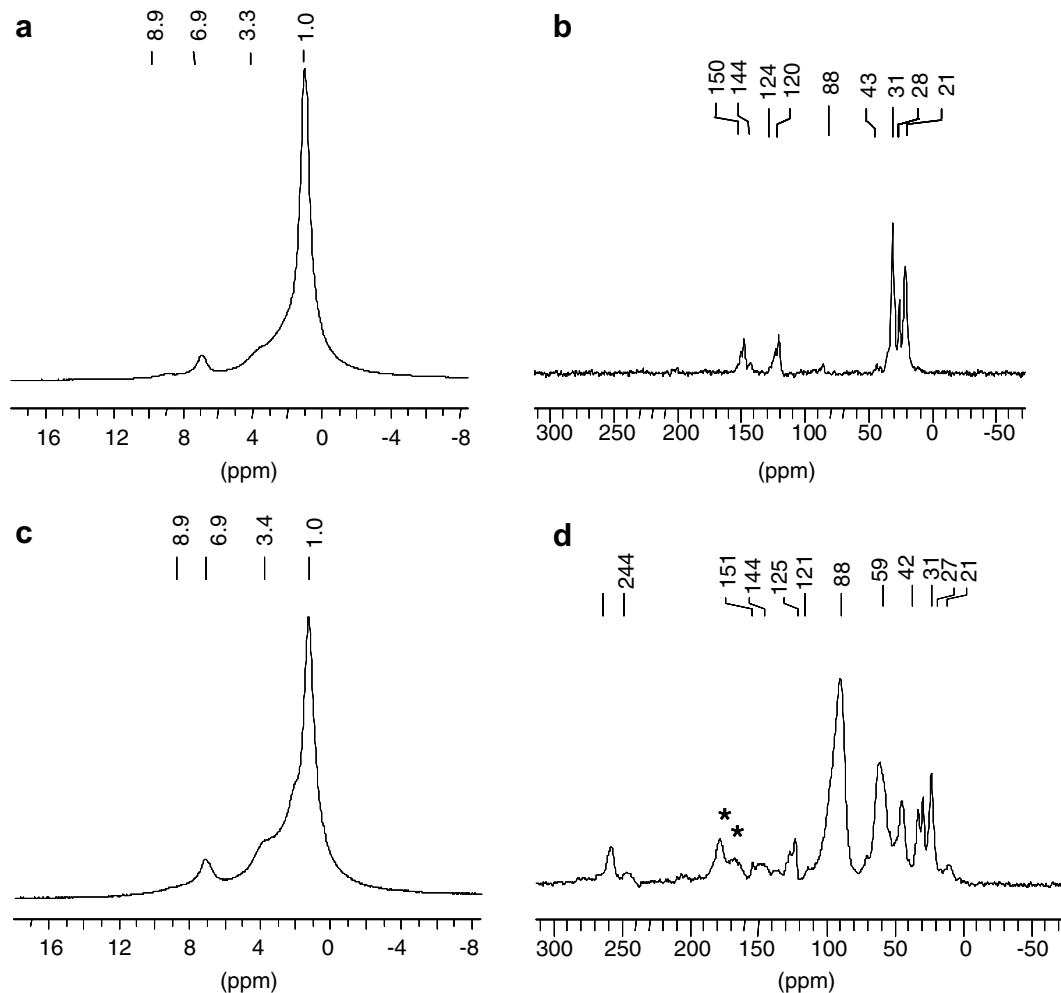
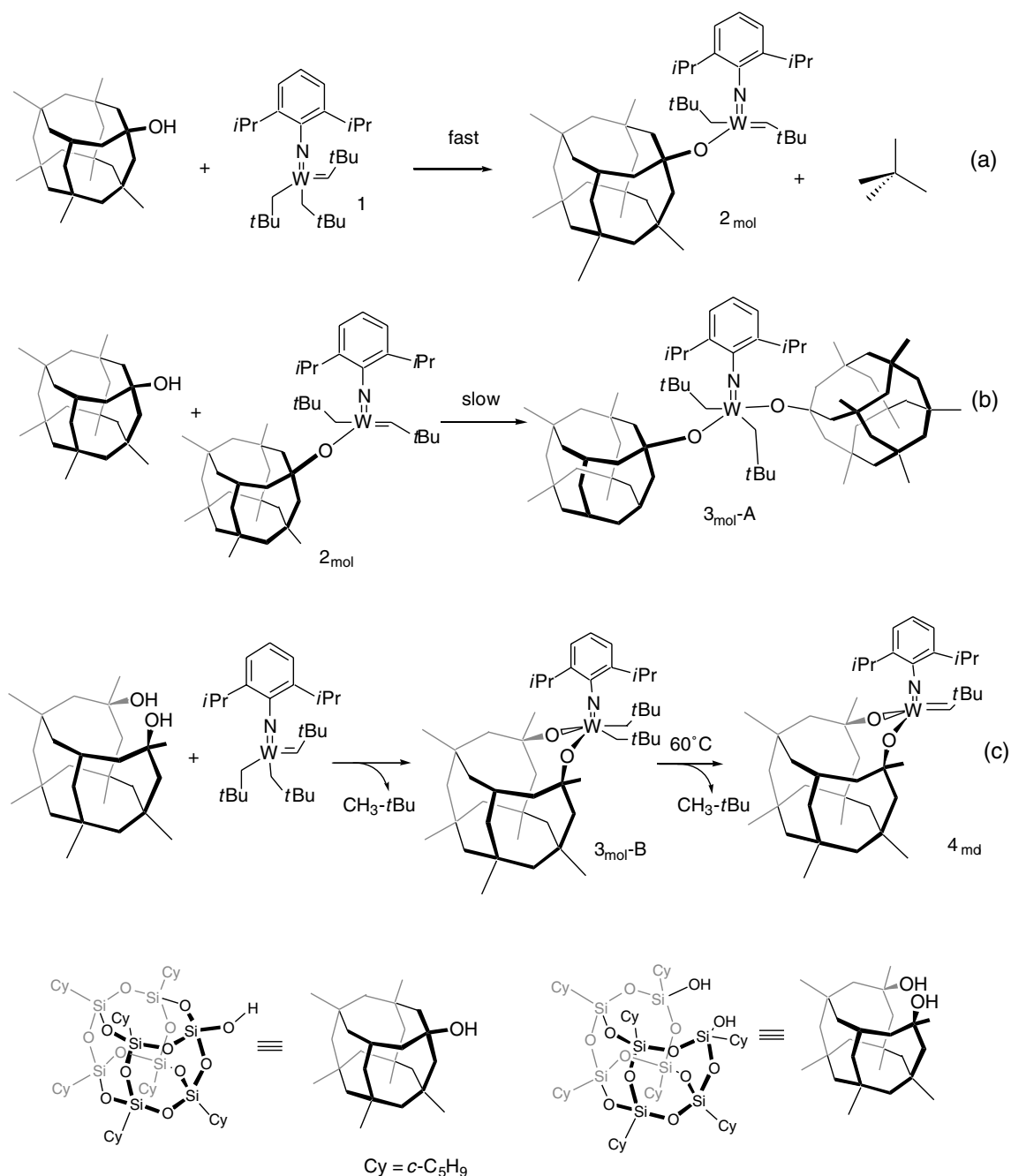


Fig. 2. ^1H MAS NMR (a and c) and ^{13}C CP-MAS NMR of the reaction products of **1** and **1*** with $\text{SiO}_2\text{-(200)}$, respectively.

grafting reaction, 1.5 ± 0.1 equiv. of 2,2-dimethylpropane is evolved per grafted W, which corresponds to 0.27 mmol OH consumed/g of silica and shows that most hydroxyl groups did not react during grafting. These data are consistent with what has been observed by infrared spectroscopy. Moreover, it also shows that on $\text{SiO}_2(200)$ neither the monosiloxy species nor the bisiloxy species are selectively formed, for which 1.0 and 2.0 equiv. of 2,2-dimethylpropane evolved/W and OH consumed/W are expected, respectively. This value corresponds to ca. one W per 2 nm^2 a value which is quite the same than that obtained on silica dehydroxylated at 700°C and corresponds to less

than a monolayer on the surface (the surface projection of the complex on the surface is ca. 1 nm^2). From chemical analysis ($\text{N} = 0.22 \text{ wt}\%$, $\text{C} = 3.7 \text{ wt}\%$, $\text{N}/\text{W} = 0.8$), is the N/W ratio still one, and therefore the aryl imido ligand probably remains intact in the coordination sphere of W, which is further supported by the absence of $[\text{W}]\text{-NH-Ar}$ species (expected at 3290 cm^{-1}) in the infrared spectra of the grafted material.

The solid state ^1H MAS NMR spectrum of $[\mathbf{1}/\text{SiO}_2(200)]$ displays mainly a strong signal at ca. 1.0 ppm with a shoulder around 3.5 ppm (relatively broad) and a small resonance at 7 ppm (Fig. 2). A more detailed examination of



Scheme 1. Reactions of **1** with silsesquioxane silanols.

the spectrum shows also the presence of a very small signal at 9 ppm. All these signals were already observed on [1/SiO₂₋₍₇₀₀₎], and they were attributed to the methyl, the methine of the *i*Pr ligand, the aromatic and the alkylidene proton of the monosiloxy complex *syn-2*, [(≡SiO)W(=NAr)-(CH₂*t*Bu)(=CH*t*Bu)]. Additionally, the peak at 1 ppm has a large shoulder slightly downfield, and it probably corresponds to residual silanols usual observed at 1.8 ppm and further downfield (down to 4 ppm). A similar spectrum is obtained for SiO₂₋₍₂₀₀₎ reacted with **1*** (100% ¹³C labeled on the carbons directly attached to W).

The ¹³C CP/MAS NMR spectrum of [1/SiO₂₋₍₂₀₀₎] (Fig. 2b) shows two sets of signals in the 20–40 and 120–150 ppm ranges, which can be attributed to the aliphatic and aromatic carbon atoms of the grafted species. In order to obtain higher quality ¹³C NMR spectra, the complex [W=NAr(¹³CH₂*t*Bu)₂(=CH*t*Bu)] (**1***), 100% ¹³C labeled on the carbon α to the metal center was prepared, grafted on SiO₂₋₍₂₀₀₎ [1*/SiO₂₋₍₂₀₀₎] and a ¹³C CP/MAS spectrum was recorded (Fig. 2d). In addition to the already observed signals for [1/SiO₂₋₍₂₀₀₎], new peaks have appeared: two signals at 256 and 244 ppm, which are characteristic of alkylidene ligands, and three signals at 88, 59 and 42 ppm. While the peak at 256 and 59 ppm were already observed for [1*/SiO₂₋₍₇₀₀₎] and attributed to the carbons of the methine of the neopentylidene and the methylene of the neopentyl ligand of *syn-2*, [(≡SiO)W(=NAr)(CH₂*t*Bu)(=CH*t*Bu)], respectively, the peaks at 244, 88 and

42 ppm, more difficult to assign, require 2D ¹H–¹³C HETCOR experiment and comparison with molecular analogues (vide infra). Based on the 2D ¹H–¹³C HETCOR experiment (Fig. 3), the two alkylidene carbon atoms at 256 and 244 ppm correlate to two different protons at 8.8 and 8.2 ppm, respectively, and they are attributed to two different W = CHR species, the correlation at 256 and 8.8 ppm being probably associated to *syn-2*, [(≡SiO)W(=NAr)(CH₂*t*Bu)(=CH*t*Bu)]. The signal at 88 ppm shows one strong and one weak correlation with protons at 2.5 ppm and 0.7 ppm, respectively, this at 59 ppm one correlation with a proton at 2.6 ppm and this at 42 ppm one weak correlation with a proton at 2 ppm. While the correlation at 59 (C) and 2.6 (H) ppm can also be attributed to *syn-2*, [(≡SiO)W(=NAr)(CH₂*t*Bu)(=CH*t*Bu)], the other ones speak for the presence of at least two other surface species such as possibly the expected bisiloxy surface species **3**, [(≡SiO)₂W(=NAr)(=CH*t*Bu)] because another typical alkylidene signal at 244 ppm appears in the NMR spectrum.

In order to obtain more information about the possible surface species, which have been formed on SiO₂₋₍₂₀₀₎, we have then studied the reaction of **1** with a series of molecular analogues of surface silanols, respectively, monosilanol silsesquioxane species [(C₅H₉)₇Si₇O₁₂-SiOH] and *cis-endo* disilanol silsesquioxane species [(C₅H₉)₈Si₈O₁₁(OH)₂]. Scheme 1 represents all compounds which were prepared while Table 1 gives their ¹H and ¹³C NMR data.

Table 1

¹H and ¹³C NMR chemical shift assignments for [(≡SiO₂)W(=NAr)(=CH*t*Bu)(CH₂*t*Bu)] (**2**), [(Si_{POSS}-O)W(=NAr)(=CH*t*Bu)(CH₂*t*Bu)] (**2_{mol}**), [(Si_{POSS}-O)₂W(=NAr)(CH₂*t*Bu)₂] (**3_{mol-A}**), [(Si_{POSS}-O₂)W(=NAr)(=CH*t*Bu)(CH₂*t*Bu)] (**3_{mol-B}**) and [(Si_{POSS}-O₂)W=NAr(=CHCMe₃)] (**4_{mol}**) in C₆D₆ (Si_{POSS}-O = [(*c*-C₅H₉)₇Si₇O₁₂SiO]; Si_{POSS}-O₂ = [(*c*-C₅H₉)₈Si₈O₁₁(O-)₂]), and the surface reaction product of **1** with SiO₂₋₍₂₀₀₎ (**4**)

	Assignments	2	2_{mol}	3_{mol-A}	3_{mol-B}	4	4_{mol}
¹ H NMR, δ (ppm)	{=CHC(CH ₃) ₃ }	8.8	9.28 ^a	–	–	8.9	8.41 ^b
	{=CHC(CH ₃) ₃ }	0.95	1.27	–	–	1.0	1.30
	2,6- <i>i</i> PrC ₆ H ₃	6.9	7.18–6.96	7.17–6.97	7.11–6.92	6.9	7.10–6.98
	{CH(CH ₃) ₂ }	3.5	3.80	3.98	3.96	3.3	3.69
	{CH(CH ₃) ₂ }	0.95	1.15	1.41	1.30	1.0	1.23
	{CH ₂ C(CH ₃) ₃ }	2.6	2.74, 2.22	2.47, – ^d	2.81, 2.06 ^d	–	–
	{CH ₂ C(CH ₃) ₃ }	0.95	1.23	1.27	1.24	1.0	–
	(<i>c</i> -CH(CH ₂) ₄)	–	1.86–1.20	1.89–1.25	1.88–1.29	–	1.95–1.35
	(<i>c</i> -CH(CH ₂) ₄)	–	1.11	1.12	1.12	–	1.12
	¹³ C NMR, δ (ppm)	{=CHC(CH ₃) ₃ }	255	256.99 ^a	–	–	256–244
{=CHC(CH ₃) ₃ }		31	35.06	–	–	31	35.54
{=CHC(CH ₃) ₃ }		45	45.69	–	–	42	44.89
2,6- <i>i</i> PrC ₆ H ₃		151–121	152.2–122.9	151–123.6	151.0–123.6	151–121	151.0–122.7
{CH(CH ₃) ₂ }		28	29.10	27.4	28.6	27	29.20
{CH(CH ₃) ₂ }		22	23.6, 23.9	25.6	25.5	21	23.5
{CH ₂ C(CH ₃) ₃ }		60	58.85	–	–	60	–
{CH ₂ C(CH ₃) ₃ } ^c		–	–	92.3	93.2	88	–
{CH ₂ C(CH ₃) ₃ }		31	34.04	34.81	34.04	31	–
{CH ₂ C(CH ₃) ₃ }		–	37.5	37.12	37.5	–	–
(<i>c</i> -CH(CH ₂) ₄)		–	28.0–27.1	28.3–27.3	28.4–27.6	–	29.0–27.1
(<i>c</i> -CH(CH ₂) ₄)		–	22.71, 22.66, 22.63	22.72, 22.66, 22.56	24.1–22.9	–	22.1–24.0

^a J_{C-H} = 106.5 Hz.

^b J_{C-H} = 117.0 Hz.

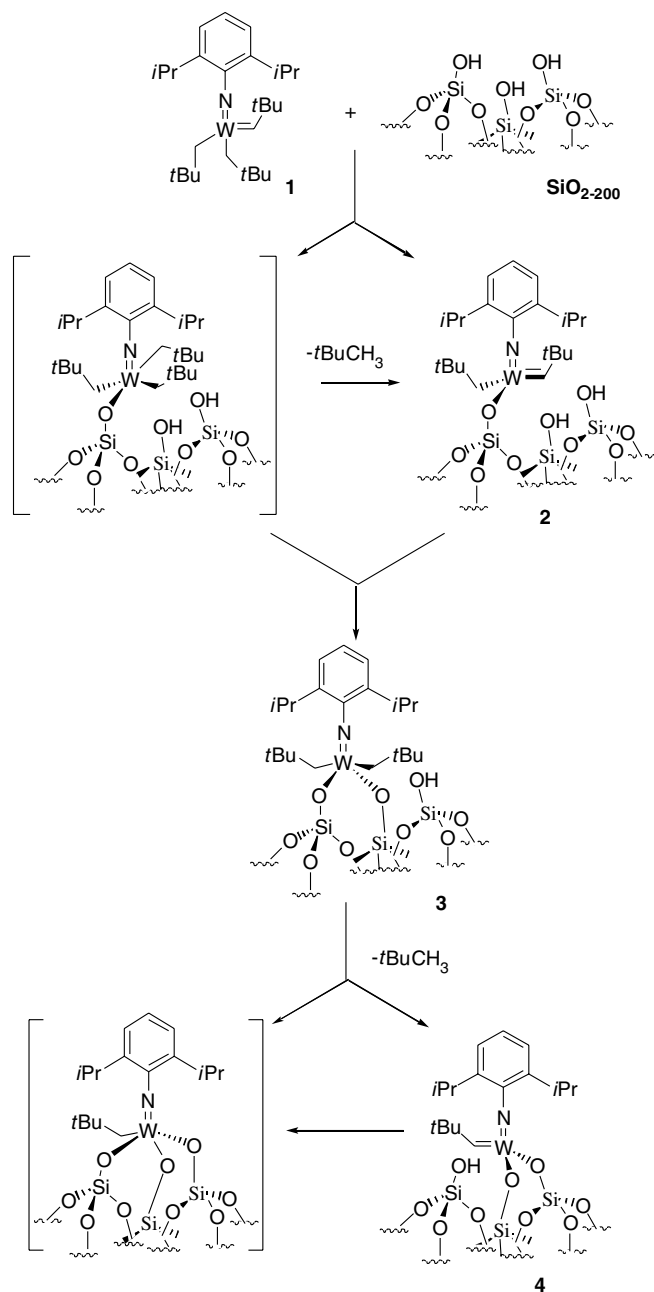
^c Chemical shift of the bisneopentyl.

^d Broad signal with high-field diastereotopic resonance hidden under δ(*c*-C₅H₉) resonances at room temperature; for **3_{mol-B}** both resonances have been resolved at 6°C as doublets (J = 15 Hz).

First, we have already shown that the molecular model of the monosiloxy surface species **2**, $[(C_5H_9)_7Si_7O_{12}-SiO]-W(=NAr)(=CHtBu)(CH_2tBu)$ (**2_{mol}**), could be obtained selectively and rapidly by reaction of **1** with 1 equiv. of $(C_5H_9)_7Si_7O_{12}-SiOH$ in benzene at room temperature (reaction a, Scheme 1) [6]. Its NMR data are quite comparable to those of the surface complex *syn*-**2**: 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 methylene carbon signal is located at 58.9 ppm, the corresponding diastereotopic proton signals of the neopentyl ligand appearing as two distinct signals at 2.22 and 2.74 ppm. These data point towards the presence of **2** upon reacting **1** with $SiO_{2-(200)}$.

In presence of 2 equiv. of this silsesquioxane, compound $[(C_5H_9)_7Si_7O_{12}-SiO]_2W(=NAr)(CH_2tBu)_2$ (**3_{mol-A}**) is selectively formed. The reaction occurs via the rapid formation of **2_{mol}** with release of one neopentyl ligand/W, and the successive slower reaction of the second silanol equivalent, by addition of the silanol across the W–alkylidene double bond (see reaction b, Scheme 1) In complex **3_{mol-A}**, the two silsesquioxane ligands are presumably in *trans* position as previously observed for other organometallic complexes [11]. When heated, the bisalkyl species **3_{mol-A}** does not evolve to a carbenic species, in contrast with what had observed for a similar tetraalkyl monosiloxy Ta(V) species [13]. In order to model the reaction of **1** with vicinal endo silanols present at the surface of $SiO_{2-(200)}$, the reaction of **1** with 1 equiv. of *cis-endo* ($c-C_5H_9$) $_8Si_8O_{11}(OH)_2$ was studied. After 24 h, the *cis*-bisalkyl complex $[(c-C_5H_9)_8Si_8O_{11}O_2][W(=NAr)(CH_2tBu)_2]$ (**3_{mol-B}**) is formed (reaction c, Scheme 1); its ^{13}C NMR spectrum is quite comparable to that of the *trans* isomer, the most interesting feature being the signal of the methylene group at 93.2 ppm. Under mild heating (60 °C), this species releases 2,2-dimethylpropane and **4_{mol}** $[(C_5H_9)_7Si_7O_{12}-SiO]_2W(=NAr)(=CHtBu)$ (whose alkylidene carbon appear at 237.5 ppm, and 8.41 ppm in ^{13}C and 1H NMR, respectively) is formed.

We can then reasonably conclude from these data that the reaction of **1** with $SiO_{2-(200)}$ leads to at least three surface species are present: the monosiloxy- and bisiloxy carbenes, **2** and **4**, as well as the bisneopentyl complex **3**. A possible mechanism of formation of these species is depicted in Scheme 2. In a first step **1** reacts with a silanol group by a succession of addition of hydroxyl on the W=C bond and elimination of neopentane reactions, leading to **2**. The complex **2** and the corresponding trisneopentyl intermediate can further react with another silanol group, leading to the digrafted bis-neopentyl complex **3** on the surface. By elimination of 2,2-dimethylpropane, the neopentylidene complex **4** is obtained. A third reaction with a silanol group could also occur, leading to a trigrafted neopentyl species on the surface. We have no evidence for such a complex from our data but previous studies on the reactivity of other transition metal complexes have shown that it can occur [14].



Scheme 2. Possible W(VI) structures for the W-surface species on $SiO_{2-(200)}$.

All catalysts were tested in the metathesis reaction of *Z*-2-pentene and also with propene for supported catalysts. Table 2 gives values of the initial turnover frequencies for all species and of the time needed to reach thermodynamic equilibrium.

The catalysts can be divided in two groups, depending on their initial activity: compounds **1** and **3_{mol-B}** are only slightly active, and a long time is needed to reach the thermodynamic equilibrium, while **2**, **4** and their corresponding molecular analogues are very active. Because **3_{mol-B}** does not contain the necessary propagating alkylidene group, it is not surprising that the reaction is slow. Comparison of the catalytic activities of **1**, **2** and **1/SiO₂₋₍₂₀₀₎** shows a

Table 2
Olefin metathesis activity for **1**, **2**, **2**_{mol}, **3**_{mol-B}, **4**_{mol} and **1**/SiO₂₋₍₂₀₀₎

Olefin	1		1 /SiO ₂₋₍₇₀₀₎ (2)		2 _{mol}		3 _{mol-B}		4 _{mol}		1 /SiO ₂₋₍₂₀₀₎	
	<i>t</i> (min) ^c	TOF	<i>t</i> (min)	TOF	<i>t</i> (min)	TOF	<i>t</i> (min)	TOF	<i>t</i> (min)	TOF	<i>t</i> (min)	TOF
<i>cis</i> -2-Pentene ^a	1200	0.45 ^d	1	52.2 ^d	1	46.2 ^d	80	0.6 ^d	1	48 ^d	1	45 ^d
Propene ^b	–	–	150	33 ^e	–	–	–	–	–	–	600	15.3 ^e

All reactions are carried out under Ar atmosphere and monitored by gas chromatography.

^a Experimental conditions: 1% W, 50 °C, 0.5 M solution of *Z*-2-pentene in chlorobenzene.

^b Substrate/catalyst ratio = 600.

^c Time to reach the thermodynamic equilibrium (around 50% conversion for *Z*-2-pentene and 34% conversion for propene).

^d Determined after 1 min (min⁻¹).

^e Determined after 5 min (min⁻¹).

dramatic effect of the substitution of an alkyl group by at least one siloxy ligand on the catalytic activity [15]. As **1**/SiO₂₋₍₂₀₀₎ is a mixture of surface complexes, it is difficult to understand what is the most active species (mono- versus bisgrafted). However, the molecular models **2**_{mol} and **4**_{mol} have similar activities, which shows that having one or two siloxy ligands probably leads to catalysts of similar activities. The small difference between **1**/SiO₂₋₍₇₀₀₎, containing mainly **2**, and **1**/SiO₂₋₍₂₀₀₎ is probably due to the presence of inactive species such as **3** in the latter.

4. Conclusion

We have shown that the grafting reaction of **1**[W(=NAr)(=CH*t*Bu)(CH₂*t*Bu)₂] (Ar = 2,6-*i*PrC₆H₃) on silica dehydroxylated at 200 °C does not lead to the selective formation of the bisgrafted species **4**, but to a mixture of mono- (**2**) and bisgrafted (**4**) alkylidenes along with a bisgrafted dineopentyl complex (**3**) as confirmed by the synthesis of molecular analogues using silsesquioxanes, which has allowed the attribution of the different NMR signals associated with these types of species. The formation of these species can be rationalized by step by step addition of hydroxyl groups on the W=C bond and eliminations of neopentane. All neopentylidene species, except **1**, are highly active olefin metathesis catalysts.

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