4274 *Organometallics* **2005,** *24,* 4274−4279

Well-Defined Surface Tungstenocarbyne Complexes through the Reaction of $[W(\equiv CtBu)(CH_2tBu)_3]$ with Silica

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Received February 8, 2005

The molecular complex $[W(\equiv CtBu)(CH_2tBu)_3]$, **1**, reacts with $SiO_{2-(700)}$ to give as major species **2a**, $[(\equiv SiO)W(\equiv CtBu)(CH_2tBu)_2]$, while a bisgrafted surface species **3a**, $[(\equiv SiO)_2W(\equiv CtBu)(CH_2tBu)]$, is obtained on $SiO_{2-(200)}$. As in molecular organometallic chemistry, the alkylalkylidyne tautomeric form is favored. Despite these structural features, these surface organometallic complexes are very active olefin metathesis catalysts, as reported earlier, and it is very likely that the necessary metallocarbene intermediates are generated under the reaction conditions.

Introduction

The reaction of molecular organometallic complexes with partially dehydroxylated silica aims at generating supported catalysts. Early studies focused first on preparing supported metal alkyl complexes for polymerization catalysis.[1−3] An important aspect of this field is to understand the reaction of organometallic complexes with the surface of supports in order to control the coordination sphere of the grafted metal, with the goal to undertake a more rational development of heterogeneous catalysts through structure−activity relationships. This requires a precise definition of the active sites, which is one of the goals of surface organometallic chemistry (SOMC).[4,5] In the past few years, we have shown that the reaction of an organometallic complex with silica partially dehydroxylated at 700 °C ($SiO_{2-(700)}$) yields the replacement of one of the M−C bonds by a M−OSi bond.[6−9] In this way, well-defined monosiloxy surface complexes are obtained, and in these cases silica can be compared to a bulky η^1 ligand.[10] Moreover, by using lower temperatures of pretreatment, e.g., 200 °C, it is possible to increase the number of bonds between the metal and the support, and bisgrafted species can also be selectively obtained as the result of the cleavage of two M−C bonds by surface silanols.[10−13]

In the attempt to generate well-defined metallocarbene surface complexes for olefin metathesis single-site heterogeneous catalysts, it was proposed that metallocarbynes, $[W(\equiv CtBu)X_3]$ with X = CH_2tBu, O*t*Bu, or Cl, could generate metallocarbenes via their protonation with a surface silanol.[14,15] In fact, these materials proved to be highly active olefin metathesis catalysts without the use of activators such as Lewis acids. Later studies showed that they were quite structurally complex and that several metallocarbene species were probably present.[15,16] We have recently investigated the reactivity of $[Mo(\equiv CtBu)(CH_2tBu)_3]$, a metallocarbyne, with $SiO_{2-(700)}$ and showed that the metallocarbyne functionality was preserved after grafting.[6]

Here we have investigated the reactivity of $[W(\equiv CtBu)(CH_2tBu)_3]$[17] with $SiO_{2-(200)}$ and $SiO_{2-(700)}$,

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10.1021/om050086a CCC: $30.25

Table 1. Grafting of 1 on Silica Partially Dehydroxylated at Various Temperatures by Impregnation

entry	support	method[a]	time/h	tBuCH$_3$/W[b]	%$_{wt}$ W[c]	%$_{wt}$ C[d]	C/W ratio	tBuCH$_x$/W[e]
1	$SiO_{2-(200)}$	s	4	1.8	3.4			2.2
2	$SiO_{2-(200)}$	ns	4	1.8	6.4	4.6	11.0	2.1
3	$SiO_{2-(700)}$	s	2		2.2	2.2	15.3	2.8
4	$SiO_{2-(700)}$	s	4	0.9	3.5			3.1
5	$SiO_{2-(700)}$	ns	4	0.9	4.4	4.2	14.5	2.9

[a] The abbreviations s and ns stand for the procedure with or without solvent, respectively. [b] The error in the determination of neopentane evolved is around 10%. [c] The error on W is <5%. [d] The error on the analyses is ±1 amu for C. [e] Upon treatment under H_2, alkanes are formed including 2,2-dimethylpropane, and the number represents the number of alkane in 2,2-dimethylpropane equivalent.

and the two different resulting species have been characterized at the molecular level by using solid-state NMR techniques and both are found to contain the metallocarbyne unit intact.

Results and Discussions

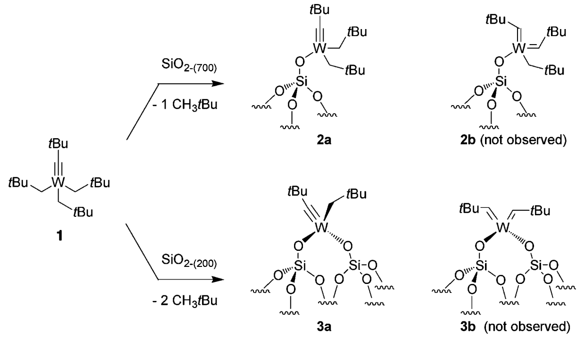
In-Situ IR Study. When an excess of [W(≡CtBu)(CH$_2$$t$Bu)$_3$], **1**, is sublimed at 80 °C on a $SiO_{2-(700)}$ disk, the disk immediately turns pale yellow, and the band attributed to isolated silanol $\nu_{(OH)}$ groups at 3747 cm^{-1} totally disappears from the IR spectrum (see Figure S1 in the Supporting Information). A broad band of very weak intensity appears at lower wavenumbers (3740−3550 cm^{-1}), in agreement with the presence of a small amount of residual silanols (10% with respect to the amount of silanols measured by IR spectroscopy on $SiO_{2-(700)}$). Concomitantly, two groups of bands appear in the 3000−2700 and 1500−1300 cm^{-1} regions, which are assigned to $\nu_{(CH)}$ and $\delta_{(CH)}$ vibrations of perhydrocarbyl ligands (probably bonded to tungsten). When **1** is grafted on a $SiO_{2-(200)}$ disk (see Figure S2 in the Supporting Information), the same phenomena are observed, with the main difference being the presence of a larger amount of remaining silanols (60%, vide infra for further comments), which are probably interacting with perhydrocarbyl ligands (attached to W).

The irreversible disappearance of the free silanols' stretching band, the appearance of $\nu_{(CH)}$ and $\delta_{(CH)}$ bands, and the presence of tBuCH$_3$ in the gas phase are in full agreement with a chemical grafting of W on silica.

Mass Balance Analyses. To establish the mass balance of the reaction of **1** with silica, the reaction was first carried out by impregnation of silica in a pentane solution of **1** (Table 1, entries 1, 3, and 4).

First, note the W loading is relatively low and that increasing reaction time increases the W loading (entries 3 and 4). This is quite different from what has been observed for other perhydrocarbyl metal complexes (Zr, Ta, Mo, and Re), which graft within 30 min to 1 h under similar reaction conditions. In fact, 0.12−0.19 mmol of W/g of silica is grafted while the concentration of silanols is about 0.26 mmol OH/g on $SiO_{2-(700)}$. Similarly, the W loading is relatively low on $SiO_{2-(200)}$ (0.18 mmol of W/g of silica) considering that $SiO_{2-(200)}$ contains 0.86 mmol OH/g,[11] which implies that W loading could be up to 15.2%$_{wt}$ if one considers the grafting of one W per surface OH group (vide infra for further comments).

Scheme 1. Reactivity of 1 with the Surface of a Silica Partially Dehydroxylated at 200 and 700 °C



Changing the grafting method to the reaction of **1** and SiO_2 as a mechanical mixture maintained at 70 °C (Table 1, entries 2 and 5) substantially increases the W loading (solventless impregnation method). First, in the case of $SiO_{2-(700)}$, the W loading can be increased up to 4.4%$_{wt}$ (Table 1, entry 3), which corresponds to 0.24 mmol of W/g of silica. This shows that about 95% of the silanols have been consumed during the grafting process under these conditions, consistent with what has been observed by IR spectroscopy. During this step, 0.9 equiv of tBuCH$_3$ per grafted W is formed, and the solid obtained, **2**, contains around 2.9−3.1 "neopentyl-like" ligands according to elemental analysis and hydrogenolysis. A similar mass balance is also observed when grafting is performed in a pentane solution. All these data are therefore consistent with the formation of a monografted surface complex as a major species, which can be tentatively formulated as [(≡SiO)W(≡CtBu)(CH$_2$$t$Bu)$_2$], **2a**, or [(≡SiO)W(=CHtBu)$_2$(CH$_2$$t$Bu)], **2b** (Scheme 1). Second, in the case of $SiO_{2-(200)}$, this solventless impregnation method also gives a yellow solid, **3**, with a higher W loading, ca. 6.4%$_{wt}$, that is 0.35 mmol of W/g of silica. Note however that 1.8 equiv of tBuCH$_3$/grafted W is formed, which is consistent with the formation of a bisgrafted surface complex as a major species.[18] Conversely, 0.65 (1.8 × 0.35) mmol of OH/g of silica has been consumed, while $SiO_{2-(200)}$ contains 0.86 mmol OH/g, and therefore some OH groups (25%) have not been consumed during this process. This is somewhat different from what we observed by IR spectroscopy (60% remaining silanols assuming a similar extinction coefficient for free silanols and those in interaction), which shows that their extinction coefficients are in fact quite different. Independently of the method of preparation, the 2,2-dimethylpropane evolved during grafting, carbon elemental analysis, and hydrogenolysis of the solid are consistent with a bisgrafted W complex surrounded by an average of 2.1 neopentyl-like ligands. The structure of the major species can be tentatively formulated as [(≡SiO)$_2$W(≡CtBu)(CH$_2$$t$Bu)], **3a**, or [(≡SiO)$_2$W(=CH$t$Bu)$_2$], **3b** (Scheme 1).

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[18] This is different from what has been observed previously in ref 16. Nonetheless, in this reference, Buffon et al. prepared $SiO_{2-(200)}$ in a different way: after a calcination at 450 °C, silica was treated under vacuum at 200 °C. We have found that when calcination is performed at a temperature T higher than that of dehydroxylation, the resulting silica corresponds to a silica dehydroxylated at the temperature T. Therefore the silica used by Buffon et al. corresponds to a silica treated at 450 and not 200 °C; at this temperature, silica contains mainly isolated silanols and generates mainly monosiloxy species (see ref 5).

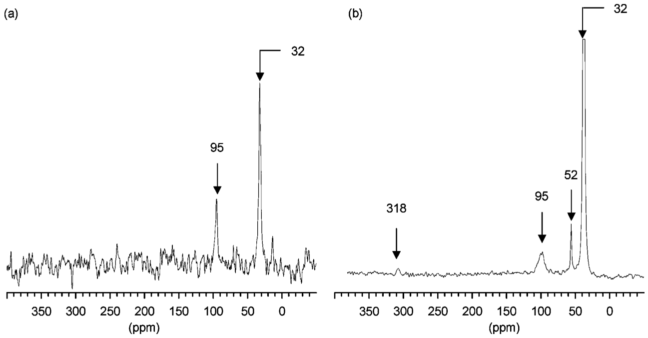

Figure 1. (a) CP/MAS ^{13}C NMR spectrum of **2**. The spectrum was recorded with 70 000 scans, a relaxation delay of 1 s, and a CP contact time of 10 ms. An exponential line broadening of 100 Hz was applied before Fourier transform. (b) CP/MAS ^{13}C NMR of **3**. The spectrum was recorded with 70 000 scans, a relaxation delay of 1 s, and a CP contact time of 10 ms. An exponential line broadening of 100 Hz was applied before Fourier transform.

In conclusion, we note that in molecular chemistry, d$^{0-2}$ bis-alkylidene complexes are rare[19-26] and generally only the alkylalkylidyne tautomeric form is observed. Thus, **2b/3b** would be unexpected, but would explain the olefin metathesis activity of such systems. In contrast, **2a/3a** would be more consistent with molecular chemistry, although olefin metathesis requires metallocarbene intermediates. To determine which molecular structure is present on $SiO_{2-(200)}$ and $SiO_{2-(700)}$, solid-state NMR spectroscopy was performed.

Solid-State NMR Spectroscopy. On one hand, the solid-state ^1H magic angle spinning (MAS) NMR spectrum of **2** displays three barely resolved signals at 1.1, 1.45, and 2.0 ppm (Figure S3a), while there are only two signals, at 32 and 95 ppm, in the solid-state ^{13}C CP/MAS NMR spectrum (Figure 1a). On the other hand, the ^1H MAS spectrum of solid **3** shows a single broad signal centered at 1.1 ppm (Figure S3b), while the ^{13}C CP/MAS spectrum contains four signals at 32, 52, 95, and 318 ppm. In this case, they can be tentatively assigned to $C(\mathbf{C}H_3)_3$, $\mathbf{C}(CH_3)_3$, $(\mathbf{C}H_2t\mathrm{Bu})$, and $(\equiv\mathbf{C}t\mathrm{Bu})$ resonances, respectively (see Table 2 and Figure 1b).

Due to lower loading of W on $SiO_{2-(700)}$ the ^{13}C signal-to-noise ratio of **2** is significantly lower than **3**, preventing the observation of the two other expected signals (vide infra). However, the somewhat narrower lines obtained for the ^1H MAS spectrum of **2**, $SiO_{2-(700)}$, is consistent with a greater mobility of the monosiloxy species **2a/b** (around the W−OSi bond) compared to the bissiloxy species **3a/b** of solid **3** (possibly due to greater dipolar interactions in the latter case).

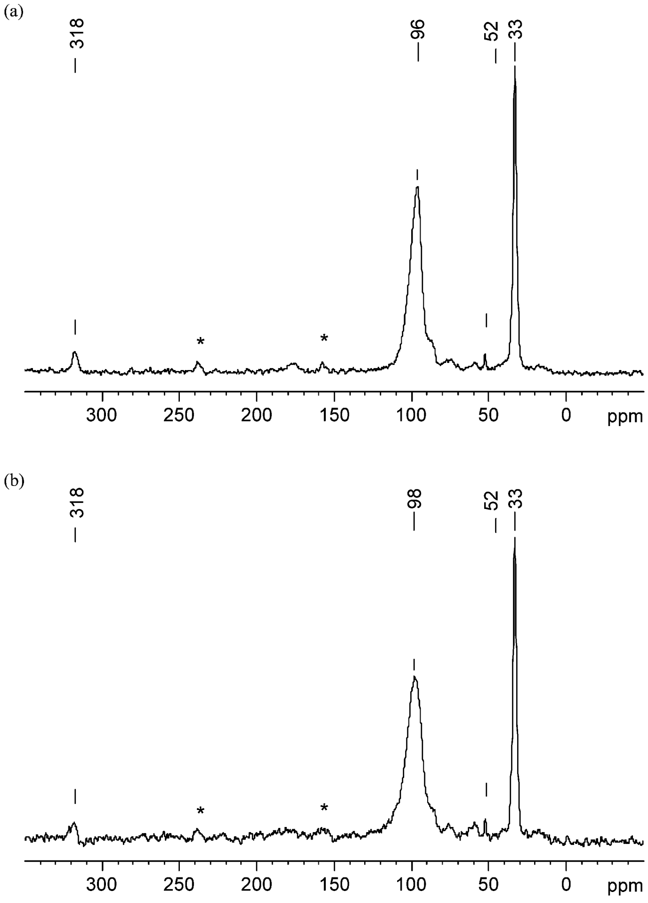

Figure 2. ^{13}C CP/MAS solid-state NMR spectra of solid **2*** (a) and **3*** (b). The spectra were recorded with 2048 scans (a) and 1024 scans (b), a relaxation delay of 1 s, and a CP contact time of 10 ms. An exponential line broadening of 80 Hz was applied before Fourier transform.

To obtain higher quality ^{13}C spectra, the complex **1***, ^{13}C labeled on the carbons attached directly to W, was prepared and grafted on $SiO_{2-(200)}$ and $SiO_{2-(700)}$. While the ^1H MAS spectra of **2*** [**1***/$SiO_{2-(700)}$] and **3*** [**1***/$SiO_{2-(200)}$] are similar to those of **2** and **3**, their ^{13}C CP/MAS spectra are noteworthy: the spectrum of **2*** [**1***/$SiO_{2-(700)}$] now shows an extra signal at 318 ppm (Figure 2a), consistent with a neopentylidyne ligand. The spectrum of **3*** [**1***/$SiO_{2-(200)}$] shows the same signals at 32, 52, 95, and 318 ppm (Figure 2b), as already observed without labeling, but the intensities of those at 95 and 318 ppm dramatically increase, which is consistent with their assignments to the ^{13}C-enriched carbons directly attached to the metal, i.e., the $(W\text{-}\mathbf{C}H_2t\mathrm{Bu})$ and $(\equiv\mathbf{C}t\mathrm{Bu})$, respectively. Note that the signal at 318 ppm is more easily detected when a direct single ^{13}C pulse acquisition is used (see Figure S4 in the Supporting Information), as already observed in the case of $[(\equiv SiO)Re(\equiv Ct\mathrm{Bu})(=CHt\mathrm{Bu})(CH_2t\mathrm{Bu})_2]$.[7] Note that similar features are also obtained for the solid-state NMR of **1** (Figures S5 and S6), which shows the dramatic influence of the chemical shift anisotropy on the carbynic carbons compared to the methylene of the neopentyl ligand.

Moreover, the assignments are confirmed by 2D $^1H-^{13}C$ HETCOR solid-state NMR spectroscopy,[6,9,27] for which short contact times (1 ms) have been chosen in

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Table 2. Chemical Shift Assignments for $[W(\equiv C\mathit{t}Bu)(CH_2\mathit{t}Bu)_3]$, $[(\equiv SiO)W(\equiv C\mathit{t}Bu)(CH_2\mathit{t}Bu)_2]$ (2a) and $[(\equiv SiO)_2W(\equiv C\mathit{t}Bu)(CH_2\mathit{t}Bu)]$ (3a) through the Combined Use of 1D and 2D HETCOR NMR Data

complex	^{1}H NMR, δ/ppm resonances	^{1}H NMR, δ/ppm assignments	^{13}C NMR, δ/ppm resonances	^{13}C NMR, δ/ppm assignments
$[W(\equiv C\mathit{t}Bu)(CH_2\mathit{t}Bu)_3]$	1.2	$\{CH_2C(C\mathbf{H}_3)_3\}$	34	$\{CH_2C(\mathbf{C}H_3)_3)\}$
	1.6	$\{\equiv CC(C\mathbf{H}_3)_3\}$	32	$\{\equiv CC(\mathbf{C}H_3)_3)\}$
			38	$\{CH_2\mathbf{C}(CH_3)_3)\}$
	1.0	$\{C\mathbf{H}_2\mathit{t}Bu\}$	53	$\{\equiv C\mathbf{C}(CH_3)_3)\}$
			103	$\{\mathbf{C}H_2\mathit{t}Bu\}$
			316	$\{\equiv\mathbf{C}\mathit{t}Bu\}$
$[(\equiv SiO)W(\equiv C\mathit{t}Bu)(CH_2\mathit{t}Bu)_2]$	1.1	$\{CH_2C(C\mathbf{H}_3)_3\}$	32	$\{\equiv C(\mathbf{C}H_3)_3)\}$
	1.5	$\{\equiv CC(C\mathbf{H}_3)_3\}$	33	$\{CH_2C(\mathbf{C}H_3)_3)\}$
				$\{CH_2\mathbf{C}(CH_3)_3)\}$
	1.1	$\{C\mathbf{H}_AH_B\mathit{t}Bu\}$	52	$\{\equiv C\mathbf{C}(CH_3)_3)\}$
	2.0	$\{CH_A\mathbf{H}_B\mathit{t}Bu\}$	95	$\{\mathbf{C}H_2\mathit{t}Bu\}$
			318	$\{\equiv\mathbf{C}\mathit{t}Bu\}$
$[(\equiv SiO)_2W(\equiv C\mathit{t}Bu)(CH_2\mathit{t}Bu)]$	1.1	$\{CH_2C(C\mathbf{H}_3)_3\}$	32	$\{\equiv C(\mathbf{C}H_3)_3)\}$
	1.1	$\{\equiv CC(C\mathbf{H}_3)_3\}$	32	$\{CH_2C(\mathbf{C}H_3)_3)\}$
				$\{CH_2\mathbf{C}(CH_3)_3)\}$
	1.1	$\{C\mathbf{H}_AH_B\mathit{t}Bu\}$	52	$\{\equiv C\mathbf{C}(CH_3)_3)\}$
	2.0	$\{CH_A\mathbf{H}_B\mathit{t}Bu\}$	95	$\{\mathbf{C}H_2\mathit{t}Bu\}$
			318	$\{\equiv\mathbf{C}\mathit{t}Bu\}$

order to detect only the protons directly attached to a carbon. Under these conditions, the 2D HETCOR spectrum of **2*** shows three strong correlations between proton and carbon signals (δ ^{1}H; δ ^{13}C): (1.2; 32), (1.1; 95), and (2.0; 95 ppm) (Figure 3). No correlation is observed for the ^{13}C signals at 318 and 52 ppm, consistent with their assignment to quaternary carbons. The correlation at (1.2; 32) can be assigned to the methyls of the two types of *t*Bu groups (traces in Figure 3b). Moreover, the methylene group of the neopentyl ligands ($CH_2\mathit{t}Bu$, 95 ppm) gives two correlations with protons at 1.1 and 2.0 ppm (traces in Figure 3c), which can be assigned to the two diastereotopic protons. In fact, these data are very similar to what has been observed for the corresponding Mo derivatives, $[\equiv SiOMo(\equiv C\mathit{t}Bu)(CH_2\mathit{t}Bu)_2]$[6] or similar W complexes.[21,24,28−31]

The 2D ^{1}H−^{13}C HETCOR NMR spectrum of **3*** recorded with a contact time of 1 ms (Figure S7) also shows three strong correlations: (1.1 ppm, 32 ppm), assigned to the methyl of all the *t*Bu fragments, as well as the two correlations between the methylene carbon signal at 95 ppm ($\mathbf{C}H_2\mathit{t}Bu$) and two protons at 1.1 and 2.0 ppm. As for **2***, no correlation is also observed with the quaternary carbons. In the case of $SiO_{2-(700)}$, we have assigned the two different protons at 1.1 and 2.0 ppm to diastereotopic protons. In the case of $SiO_{2-(200)}$, the presence of two different proton signals also implies that the two protons are not equivalent, which would arise from (i) the heterogeneity of the silica surface (the two siloxy substituents are not equivalent), (ii) the rigidity of the neopentyl ligand (no free motion around the M−C bond because of the surface ligands or the interaction of one of the methylidene proton with the metal center (agostic interaction)),[32] or (iii) the assignment of one of the protons to a different species (Scheme 2). For (iii), residual silanols (25%), observed around 2.0 ppm (typically at 1.8 ppm), could correlate with the carbon at 95 ppm. However, when **1*** is grafted on a deuterated $SiO_{2-(200)}$, no major difference is observed in the ^{1}H spectrum, and the same correlations are observed in its 2D ^{1}H−^{13}C HETCOR solid-state NMR spectrum (Supporting Information, Figure S8). Therefore, the two correlations at 1.1 and 2.0 ppm in the F_1 dimension (^{1}H) with the signal at 95 ppm in the F_2 dimension (^{13}C) correspond indeed to two inequivalent protons.

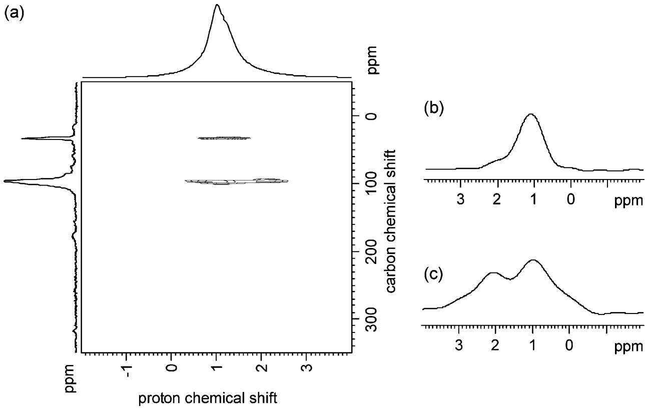
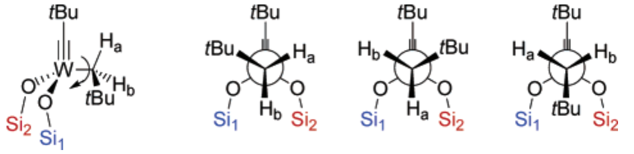


Figure 3. (a) ^{1}H−^{13}C HETCOR spectrum of solid **2***. The spectra were recorded with 4096 scans, a relaxation delay of 1 s, and a CP contact time of 1 ms. An exponential line broadening of 50 Hz was applied before Fourier transform. Traces perpendicular to F2 at (b) 32 ppm and (c) 95 ppm.

Scheme 2



Finally, *J*-resolved 2D solid-state NMR spectroscopy[33−37] has been performed on **2*** and **3*** (Figures 4 and S9 in the Supporting Information). In both cases,

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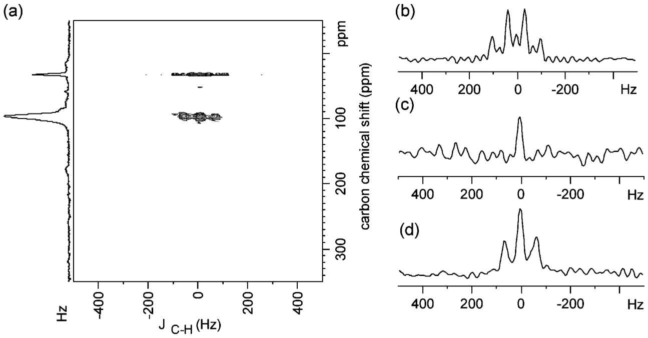
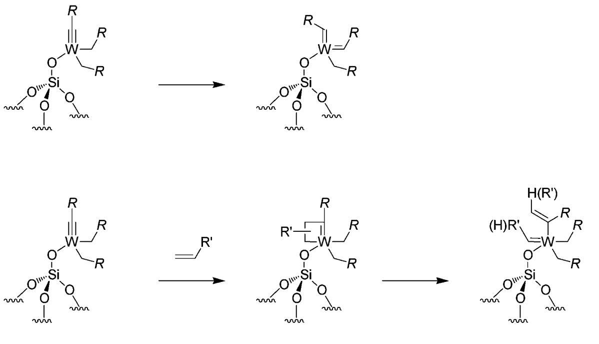


Figure 4. 2D *J*-resolved solid-state NMR spectrum of the solid **2***, 30% ^{13}C enriched at the α positions (*). (a) The spectra were recorded with 2028 scans, a relaxation delay of 1 s, and a CP contact time of 1 ms. Traces extracted along the ω_1 dimension of the 2D *J*-resolved spectrum at different carbon chemical shift frequencies: (b) 32 ppm, (c) 52 ppm, and (d) 95 ppm.

Scheme 3. Possible Formation of the Initiation Carbene Ligands from an Alkylidyne



no signal is detected for the carbynic carbons, because of the low signal-to-noise ratio. For **2*** and **3***, the singlet at 52 ppm is assigned to the quarternary carbon of the *t*Bu group attached to the carbynic carbon, and the quadruplet (*t*Bu, $^1J_{C-H} = 125$ Hz) at 32 ppm is fully consistent with its assignments to the methyl of the *t*Bu groups. The triplet (CH_2tBu, $^1J_{C-H} = 110$ Hz) at 95 ppm is assigned to the methylene carbon of the neopentyl fragment, and the low $^1J_{C-H}$ value for the methylene is indicative of a weak agostic interaction of these protons with the metal center.[32]

Activity in Olefin Metathesis. Moreover, despite the absence of the necessary alkylidene ligands, the metathesis activity is quite high and similar to that observed previously:[15,16] 1600 equiv of propene in the presence of **2** is converted at room temperature into a thermodynamic mixtures of propene, ethylene, and 2-butenes within 180 min (ca. 35% conv in propene). The initial rate after 5 min is 36 TON/min, which is close to that observed previously (15 TON/min). Additionnally, the surface organometallic complex **2** also catalyzes the metathesis of methyl oleate: 100 equiv is converted to the equilibrium mixtures within 200 min with an initial rate of 0.6 TON/min. Therefore, this system can be used as a precursor for olefin metathesis, and the carbene ligand is probably generated in situ either by H-transfer from an alkyl ligand to generate a bis-alkylidene or by direct metathesis of an olefin with an alkylidyne, which generates in turn a propagating ligand (Scheme 3).

Conclusion

According to mass balance analysis, IR, and solid-state NMR spectroscopy techniques, the molecular complex **1** reacts with $SiO_{2-(700)}$ to give **2a**, [($\equiv$SiO)W($\equiv$C*t*Bu)($CH_2tBu)_2$], as the major surface species, while a bisgrafted surface species **3a**, [($\equiv$SiO)$_2$W($\equiv$C*t*Bu)(CH_2tBu)], is obtained on $SiO_{2-(200)}$ (Scheme 1). As in molecular organometallic chemistry, the alkylalkylidyne tautomeric form is favored.

Despite these structural features, these surface organometallic complexes are very active olefin metathesis catalysts, as reported earlier, and it is very likely that the necessary metallocarbene intermediates are generated under the reaction conditions.

Experimental Section

General Procedure. All experiments were carried out under controlled atmosphere, using Schlenk and glovebox techniques for the organometallic synthesis. For the synthesis and treatments of the surface species, reactions were carried out using high-vacuum lines (1.34 Pa) and glovebox techniques. [W($\equiv$C*t*Bu)($CH_2tBu)_3$] was prepared according to the literature procedure.[17] Pentane was distilled on NaK alloy and degassed through freeze−pump−thaw cycles. Infrared spectra were recorded on a Nicolet Magna 550 FT spectrometer equipped with a cell designed for in situ reactions under controlled atmosphere. Elemental analyses were performed at the Service Central d'Analyses of CNRS in Solaize.

^1H MAS and ^{13}C CP-MAS solid-state NMR spectra were recorded on a Bruker DSX-300 spectrometer. For specific studies (see below), ^1H MAS and ^{13}C CP-MAS solid-state NMR spectra were recorded on Bruker Avance-500 spectrometers with a conventional double-resonance 4 mm CP-MAS probe at the Laboratoire de Chimie in Ecole Normale Supérieure de Lyon or at the Laboratoire de Chimie Organometallique 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.

Heteronuclear Correlation Spectroscopy. The two-dimensional heteronuclear correlation experiment was 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[38,39] centered at 60 kHz was applied on protons, while the carbon rf field was matched to obtain optimal signal. The contact time for CP was set to 1 ms. During acquisition, the proton decoupling field strength was set to 83 kHz (TPPM decoupling).[40] A total of 32 t_1 increments with 1024 scans each were collected. The spinning frequency was 10 kHz,

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and the recycle delay was 1 s (total acquisition time of 9 h). Quadrature detection in ω_1 was achieved using the TPPI method.[41]

***J*-Resolved Spectroscopy.** The two-dimensional J-resolved experiment was performed as previously described:[37] after cross-polarization from protons, carbon magnetization evolves during t_1 under proton homonuclear decoupling. Simultaneous 180° carbon and proton pulses are applied in the middle of t_1 to refocus the carbon chemical shift evolution while retaining the modulation by the heteronuclear J_{CH} scalar couplings. A Z-filter is finally applied to allow phase-sensitive detection in ω_1. Proton homonuclear decoupling was performed by using the frequency-switched Lee−Goldburg (FSLG) decoupling sequence.[42,43] Quadrature detection in ω_1 was achieved using the TPPI method.[41] The rotor spinning frequency was 10.2 kHz. The proton rf field strength was set to 83 kHz during t_1 (FSLG decoupling) and acquisition (TPPM decoupling).[40] The lengths of carbon and proton 180° pulses were 7 and 6 μs, respectively. An experimental scaling factor, measured as already described,[44] of 0.52 was found, which gave a corrected spectral width of 2452 Hz in the ω_1 dimension. The recycle delay was 1.3 s, and a total of 80 t_1 increments with 1024 scans each were collected (total acquisition time = 30 h).

Preparation of $SiO_{2-(200)}$ and $SiO_{2-(700)}$. Silica Aerosil from Degussa with a specific area of 200 m^2/g was dehydroxylated directly at 200 °C for 12 h for $SiO_{2-(200)}$ or at 500 °C for 12 h and at 700 °C for 4 h for $SiO_{2-(700)}$ under high vacuum (10^{-5} mmHg). After this treatment, the specific area was about 200 m^2/g and 180 m^2/g with an OH density of 2.5 OH/nm^2 and 0.7 OH/nm^2, respectively for $SiO_{2-(200)}$ and $SiO_{2-(700)}$.

Preparation of 2 by Impregnation in Pentane. General Procedure. A mixture of **1** (115 mg, 0.247 mmol) and $SiO_{2-(700)}$ (0.8 g) in pentane (10 mL) was stirred at 25 °C for 4 h. After filtration, the solid was washed three times with pentane and all volatile compounds were condensed into another reactor (volume known > 6 L) in order to quantify 2,2-dimethylpropane evolved during the grafting. The resulting yellow powder (solid **2**) was dried under vacuum (1.34 Pa).

Synthesis of 3 by Impregnation in Pentane. The same procedure as the one described above was used: **1** (600 mg, 1.25 mmol, 1.2 equiv) and $SiO_{2-(200)}$ (1.8 g), giving 2.1 g of solid **3** (see Tables 1 and 2).

Preparation of Solid 2 by Solventless Impregnation. General Procedure. A mixture of **1** (68 mg, 0.14 mmol, 1.2 equiv) and $SiO_{2-(700)}$ (444 mg) was stirred at 66 °C for 4 h. All volatile compounds were condensed into another reactor (of known volume) in order to quantify 2,2-dimethylpropane evolved during grafting. Analysis of the gas phase by GC on a KCl/Al_2O_3 column indicated the formation of 142 ± 14 μmol of 2,2-dimethylpropane (0.9 ± 0.1 tBuCH$_3$/W). Pentane (10 mL) was introduced into the reactor by distillation, and the solid was washed three times. After evaporation of the solvent, the resulting brown powder was dried under vacuum (1.34 Pa) to yield 498 mg of solid **2** (see Tables 1 and 2).

Preparation of Solid 3 by Solventless Impregnation. The same procedure as the one described above was used: **1** (76.4 mg, 0.16 mmol, 1.2 equiv) and $SiO_{2-(200)}$ (362 mg), giving 410 mg of solid **3** and 142 ± 14 μmol of 2,2-dimethylpropane, that is, 1.8 ± 0.2 tBuCH$_3$/W (see Tables 1 and 2).

Preparation of Solid 2* by Solventless Impregnation. The preparation of **1*** was performed according to the same procedure as that used for **1**, but starting with a 70:30 (or 90:10) mixture of nonlabeled tBuCH$_2$Cl and (99% atom ^{13}C) monolabeled tBuCH$_2$Cl to form tBuCH$_2$MgCl (30% or 10%) labeled as alkylating agents (yield 80−85%, see refs 8, 9 for experimental details).

The ^{13}C-enriched surface compound **2*** was prepared using the same procedure as described above by using **1*** in place of **1**. (See Table 2 for data.)

Preparation of Solid 3* by Solventless Impregnation. The ^{13}C-enriched surface compound **3*** was prepared using the same procedure as described above by using **1*** in place of **1**.

Treatment under H_2 of the Solids (quantification of neopentyl-like ligands). The solid was heated at 150 °C in the presence of a large excess of anhydrous H_2 (77 330 Pa). After 15 h, the gaseous product was quantified by GC (see Table 1).

Metathesis of Propene. The solid **2** (0.0625 mol % W) was contacted with propene (0.600 Bar, 1600 equiv) purified over R3-11 BASF catalyst/MS4A in a reactor at 25 °C. Small aliquots were analyzed by GC over time.

Metathesis of Methyl Oleate. A solution of known concentration of methyl oleate (0.123 M, 100 equiv) in toluene containing octadecane as an internal standard (16 mg, 6.0 μmol) was freshly prepared, degassed with three freeze−pump−thaw cycles, and dried over freshly 3 Å activated molecular sieves. The solid **2** (1.0 mol % W) was placed in a 5 mL batch reactor equipped with a magnetic stirring bar, and the reactor was closed with a cap equipped with a Teflon septum. At $t = 0$, the solution was added at 25 °C under vigorous stirring via a syringe through the septum, and small aliquots were sampled, diluted in pure solvent (0.5 mL), and analyzed by GC.

Acknowledgment. We would like to acknowledge the French Ministry of Research and Education, the Rhône-Alpes district, the CNRS, CPE Lyon, and BP Chemicals for financial support. We are also grateful to Drs. B. M. Maunders and G. J. Sunley from BP Chemicals for helpful discussions.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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