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Synthesis, Characterization, and Reactivity, in the C−H Bond Activation of Cycloalkanes, of a Silica-Supported Tantalum(III) Monohydride Complex: $(\equiv SiO)_2Ta^{III}-H$

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Contribution from the Laboratoire de Chimie Organométallique de Surface, UMR CNRS-CPE 9986, 43, Bd du 11 Novembre 1918, 69616 Villeurbanne Cédex, France, and Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, U.K.

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Abstract: Reaction of $Ta[CH_2C(CH_3)_3]_3[=CHC(CH_3)_3]$ (**1**) with a silica dehydroxylated at 500 °C has been previously reported to produce a mixture of $\equiv SiOTa[CH_2C(CH_3)_3]_2[=CHC(CH_3)_3]$ (**2a**) and $(\equiv SiO)_2Ta[CH_2C(CH_3)_3][=CHC(CH_3)_3]$ (**2b**). Treatment of these two surface organometallic complexes under 1 atm of hydrogen up to 200 °C leads to the formation of a surface tantalum(III) monohydride: $(\equiv SiO)_2Ta^{III}H$ (**3**) as a major product and surface Si−H groups. **3** has been characterized in the following way: it reversibly exchanges with deuterium to give the corresponding [Ta]−D species; **3** reacts with CH_3I to give methane; **3** reacts quantitatively with di(*tert*-butyl)ketone to form the corresponding tantalum di(*tert*-butyl)methoxide; **3** reacts with D_2O to give a mixture of HD and D_2 (2 ± 0.2 mol equiv per tantalum); and **3** activates the C−H bond of cycloalkanes (C_5 to C_8) at room temperature to form the corresponding surface tantalum(III) monoalkyls $(\equiv SiO)_2Ta$-alkyl, with liberation of 1 ± 0.1 equiv of hydrogen. The surface tantalum-alkyls are transformed under oxygen into the corresponding $(\equiv SiO)_2Ta^{V}(=O)(O\text{-alkyl})$. Quantitative determinations on the last three reactions are consistent with the formulation of **3** as a bis(siloxy)-tantalum(III) monohydride $(\equiv SiO)_2Ta^{III}H$ as the major surface species. Ta L_{III}-edge EXAFS studies of **3** confirm that two σ-bonded surface Si−O groups are attached to tantalum (Ta−O 1.89 Å). However, additional evidence is provided for a third surface oxygen (most probably siloxane) interacting weakly with the tantalum center (Ta···O 2.63 Å). A mechanism for the simultaneous formation of $(\equiv SiO)_2Ta^{III}H$ **3** and Si−H groups from **2a** is proposed, which involves a hydride transfer from tantalum to a neighbor silicon atom and the transfer of an oxygen from the same silicon atom to the more oxophilic tantalum.

1. Introduction

One of the objectives of surface organometallic chemistry is to immobilize organometallic complexes on solid surfaces such as oxides, zeolites, or metals in order to prepare relatively well-defined surface species acting as highly selective heterogeneous catalysts.[1] Grafting organometallic complexes on oxides isolates the "active sites" and prevents possible deactivation via dimerization of reactive intermediates. For example, it is possible to stabilize on oxide surfaces some transition metal hydrides (e.g., $(\equiv SiO)_3M^{IV}H$, (M = Zr, Hf) which can be extremely electron deficient and give rise to unusual catalytic activity such as the low temperature hydrogenolysis of acyclic alkanes of low molecular weight, via the activation of both their C−H and C−C bonds.[2]

In this way, we have recently reported that the reaction of the trisneopentyl(neopentylidene)tantalum complex $Ta[CH_2C(CH_3)_3]_3[=CHC(CH_3)_3]^3$ (**1**) with the silanol groups of a silica previously dehydroxylated at 500 °C (silica 500) leads to the formation of two surface carbene species: $\equiv SiOTa[CH_2C(CH_3)_3]_2[=CHC(CH_3)_3]$ (**2a**) (65 ± 5%) and $(\equiv SiO)_2Ta[CH_2C(CH_3)_3][=CHC(CH_3)_3]$ (**2b**) (35 ± 5%), with liberation of neopentane. These two grafted complexes have been characterized by elemental analysis, chemical reactivity with D_2O and acetone (Wittig-type reaction) and by FT-IR and CP-MAS ^{13}C NMR spectroscopies.[4]

We wish to report here that **2a**,**b** can be transformed under hydrogen into a silica-supported tantalum hydride complex $[Ta]_sH$ (**3**) which proved to be able to activate the C−H bond of light alkanes such as cyclooctane and methane to form the corresponding tantalum-alkyls;[5] we report here the characterization of this surface tantalum complex as a predominant tantalum(III) monohydride species: $(\equiv SiO)_2Ta^{III}H$ (**3**).

2. Results and Discussion

2.1. Preparation of a Silica-Supported Tantalum Monohydride $[Ta]_sH$ (3). The preparation of $\equiv SiOTa[CH_2C(CH_3)_3]_2[=CHC(CH_3)_3]$ (**2a**) and $(\equiv SiO)_2Ta[CH_2C(CH_3)_3][=CHC(CH_3)_3]$ (**2b**) by reaction of $Ta[CH_2C(CH_3)_3]_3$-

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S0002-7863(95)03524-4 CCC: $12.00

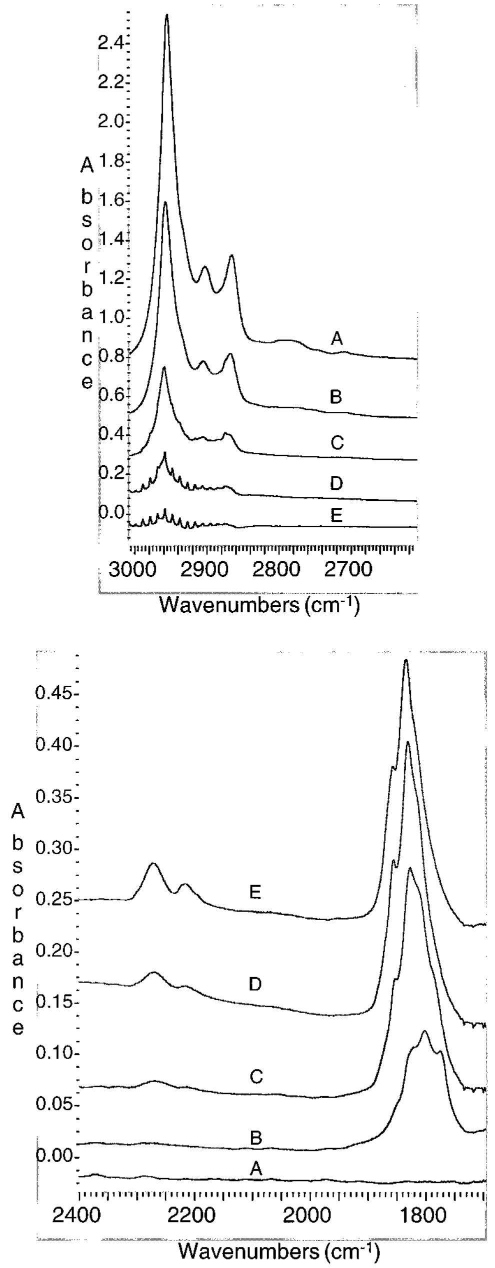

Figure 1. Evoluation of the IR spectra of the silica-supported tantalum surface species, during the preparation of the $[Ta]_sH$ species **3** from **2a** and **2b** (silica spectrum subtracted); (a) spectrum of **2a** and **2b** under vacuum; (b) (a) after 15 h at 25 °C under 1 atm of H_2; (c) (b) after heating 2 h at 90 °C; (d) (c) after further heating 2 h at 150 °C; (e) (d) after further heating 2 h at 200 °C.

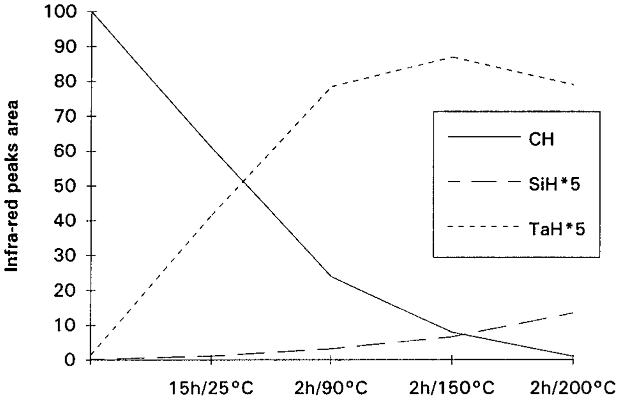

Figure 2. Evolution of the IR bands area of CH, TaH, and SiH surface groups (streching modes) during heating for the preparaton of the $[Ta]_sH$ species **3** from **2a** and **2b** (the scale of bands TaH and SiH have been adjusted by a factor of 5).

$[{=}CHC(CH_3)_3]$[3] (**1**) with the silanol groups of a silica previously dehydroxylated at 500 °C (silica 500) has already been described in detail.[4] It is a reproducible synthesis provided the reaction is carried out with great care in order to avoid possible contamination with traces of oxygen and/or moisture and provided the temperature of sublimation of **1** is lower than ca. 90 °C, the temperature at which it starts to decompose.

When silica discs of **2a**,**b** are treated under 1 atm of hydrogen at 25 °C, the IR bands in the range 2700−3000 cm^{-1} ν(C−H) and 1300−1500 cm^{-1} δ(C−H) corresponding to the neopentyl or neopentylidene groups progressively decrease in intensity (Figure 1a) and a set of new bands of lower intensity appears in the 1800 cm^{-1} region which will be further assigned to ν(Ta−H) vibration modes (Figure 1b). Simultaneously, neopentane is evolved in the gas phase. When the sample is further heated stepwise to 200 °C, the intensity of the ν(C−H) bands decreases faster, and those in the 1800 cm^{-1} region increase with a slight shift toward higher wavenumbers; other bands of smaller intensity already attributed to surface silanes[6] (ν(Si−H)) also appear at 2215, 2270 cm^{-1} with a shoulder at 2300 cm^{-1} and increase in intensity with the temperature of preparation. After 2 h at 200 °C, the ν(C−H) and δ(C−H) bands have almost completely disappeared, those around 1800 cm^{-1} have passed through maxima and present a strong broad absorption centered at 1830 cm^{-1} and two shoulders at 1815 and 1855 cm^{-1}, whereas the ν(Si−H) bands have increased continuously in intensity (Figure 2).

At this stage, the silica disc has darkened from yellow to brown. GC analysis of the gas phase in the IR cell shows the presence of neopentane as well as methane, ethane, propane, and isobutane resulting either from a partial hydrogenolysis of the neopentyl or neopentylidene ligands or more likely from the hydrogenolysis of the neopentane released during the hydrogenolysis of these hydrocarbonyl ligands.[7] The species producing IR bands in the 1800 cm^{-1} region will be further characterized mainly as a silica supported tantalum(III) monohydride: $(\equiv SiO)_2Ta^{III}H$ (**3**). Another common preparation procedure of the surface species **3** can be achieved by heating **2a**,**b** under hydrogen, directly at 150 °C overnight (15 h), then at 200 °C for 2 h.

2.2. Characterization and Reactivity of the Surface Tantalum Hydride $[Ta]_sH$ (3) and of the Surface Silicon Hydride $[Si]_sH$.

2.2.1. Exchange Reaction with D_2. When **3** is treated with deuterium (40 Torr, 25 °C), the IR bands in the 1800 cm^{-1} region are replaced within a few minutes by a new band at 1318 cm^{-1}, in the limit of the frequency window allowed by silica, which is consistent with the higher expected ν(Ta−D) vibration mode (expected values: 1315, 1297, 1287 cm^{-1}). This band disappears and the initial ν(Ta−H) bands are restored after evacuation and refilling with hydrogen (400 Torr); this demonstrates the possibility of a reversible H/D exchange process at 25 °C on **3** and supports the nature of a tantalum hydride. In contrast, the ν(Si−H) bands are not modified and present the same frequency and intensity during

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(6) This assignment is consisent with the vibration frequencies of various silanes: (a) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1992; p 175, or molecular analogues as $SiH(OR)_3$ (νSiH = 2238 cm^{-1}). (b) King, S. A.; Schwartz, J. *Inorg. Chem.* **1991**, *30*, 3771−4. Similar IR bands have been observed during the preparation of silica-supported zirconium hydride. (c) Reference 2b and 2d.

(7) The catalytic hydrogenolysis of neopentane and lower alkanes in the presence of a silica-supported zirconium hydride has been reported and a mechanism involving α-alkyl-transfer in the zirconium-alkyl intermediate was proposed: ref 2c.

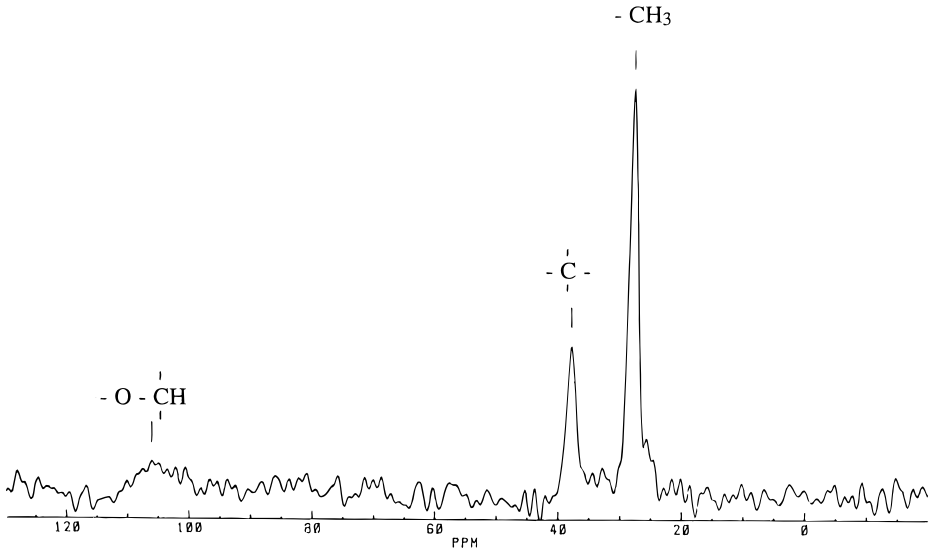


Figure 3. CP MAS ^{13}C NMR spectrum of the di(*tert*-butyl)methoxy−tantalum complex resulting from the reaction of **3** with di(*tert*-butyl)ketone.

the exchange experiments in agreement with the low capacity of exchange of silanes with D_2.

2.2.2. Reaction with CH_3I. Halogenated hydrocarbons are known to exhibit a high reactivity with early transition metal hydrides.[8−10] When **3** is treated with a vapor of CH_3I (400 Torr; 25 °C), the silica disc rapidly turns from brown to white; simultaneously, the IR bands in the 1800 cm^{-1} region completely disappear, and methane is evolved in the gas phase; no modification of the bands at 2215, 2270, and 2300 cm^{-1} is observed in agreement with the lack of reactivity of Si−H groups with halogenated hydrocarbons in the absence of catalyst;[11] this result is consistent with the following equation (eq 1)

$$[Ta]_sH + CH_3I \rightarrow [Ta]_sI + CH_4 \quad (1)$$

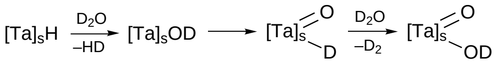
2.2.3. Reaction with $(t\text{-}Bu)_2CO$. When **3** is treated with a vapor of di(*tert*-butyl)ketone, the IR bands in the 1800 cm^{-1} region completely disappear, and ν(C−H) bands appear at 2876, 2915 and 2963 cm^{-1} corresponding to *tert*-butyl groups; the insertion of the C═O bond of the ketone into the Ta−H bond is assumed to occur according to (eq 2)[6b]

$$[Ta]_sH + (t\text{-}Bu)_2CO \rightarrow [Ta]_sOCH(t\text{-}Bu)_2 \quad (2)$$

Further treatment with acetic acid of the resulting solid liberates the expected di(*tert*-butyl)methyl acetate (GC/MS analysis) and confirms the presence of the alkoxide depicted in reaction 2. The CP MAS ^{13}C NMR spectrum of the alkoxy−tantalum complex shows signals at 27.6 ppm ($OCH(C(\mathit{C}H_3)_3)_2$), 37.8 ppm ($OCH(\mathit{C}(CH_3)_3)_2$), and 106 ppm ($O\mathit{C}H(C(CH_3)_3)_2$) (Figure 3). Conversely, the ν(Si−H) bands are not modified by the presence of the ketone in agreement with the lack of reactivity of molecular silanes with ketone in the absence of catalyst.[12]

The elemental analysis of another preparation of the alkoxy−tantalum compound, after adequate desorption (10^{-4} Torr, 150 °C, 4 h) of the excess ketone physisorbed on silica, controlled by a blank experiment, revealed 9.03 C per Ta (expected value: 9 C per Ta for $[Ta]_sOCH(t\text{-}Bu)_2$); this shows that exactly 1 mol of ketone per Ta has reacted with the surface tantalum hydride; the result of this quantitative reaction indicates the presence of an average of one hydride per Ta.

2.2.4. Reaction with D_2O. When **3** is treated with a vapor of D_2O it turns white rapidly, and the IR bands in the 1800 cm^{-1} region completely disappear; a 1/1 mixture of HD-D_2 (MS analysis) is evolved in the gas phase.[13] The formation of a deuteroxy-tantalum species and the evolution of HD are first expected during this reaction; α-hydrogen abstraction on a hydroxy intermediate has been proposed in molecular chemistry during the stoichiometric hydrolysis of $Cp^*_2Ta(H)({=}CH_2)$ affording the oxo-hydrido tantalum complex $Cp^*_2Ta(H)({=}O)$;[14,15] similar evolution on the silica surface would enable further reaction of an oxo-deuteride complex with D_2O to produce another equivalent of D_2 (eq 3)


(3)

$$[Ta]_sH \xrightarrow[-HD]{D_2O} [Ta]_sOD \longrightarrow [Ta]_s({=}O)(D) \xrightarrow[-D_2]{D_2O} [Ta]_s({=}O)(OD) \quad (3)$$

The presence of a mixture of HD/D_2 in comparable amount in the gas phase indicates that such a process is plausible. Thus the hydrolysis of each tantalum hydride can lead to the liberation of 2 equiv of hydrogen. The results of this experiment are again consistent with the presence of one hydride per Ta.

2.2.5. Reaction with Cyclic Saturated Hydrocarbons. Complex **3** reacts at room temperature with cyclic saturated hydrocarbons (C_5 to C_8 introduced as gases) via C−H bond activation to form the corresponding surface tantalum-alkyls with liberation of 1 ± 0.1 equiv of hydrogen;[5] complete reaction is reached by smooth heating to 50−80 °C. A CP MAS ^{13}C NMR spectrum could be obtained in the case of cycloheptyl tantalum complex (Figure 4) which presents signals at 24.3,

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(13) The SiH groups do not react with pure water (see ref 19). IR spectroscopy shows that D_2O can reversibly H-bond to the SiH surface species but do not react with them: the SiH bands at 2215, 2270, and 2300 cm^{-1} come together in a unique broad band of same area.

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(15) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, LeRoy; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82−5.

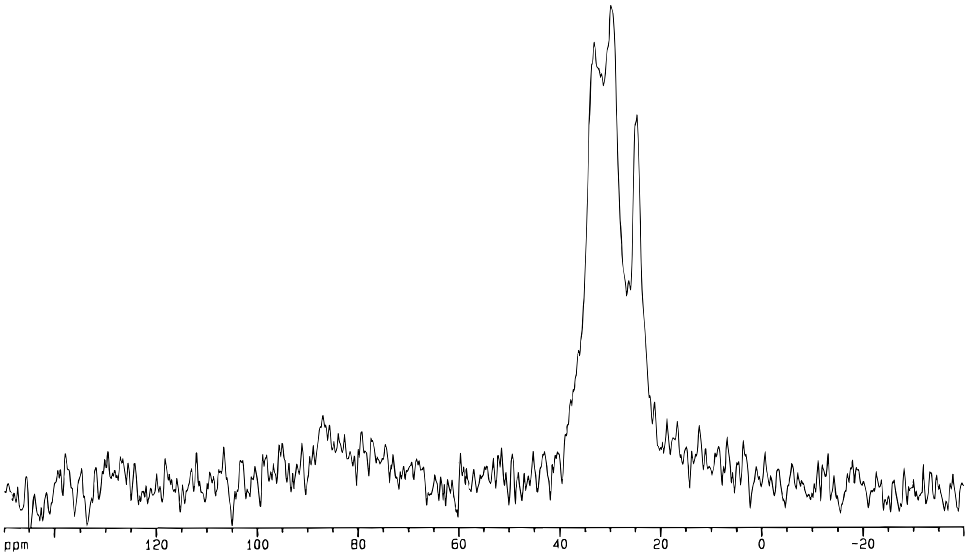
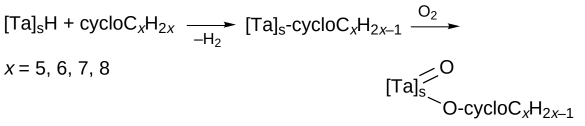


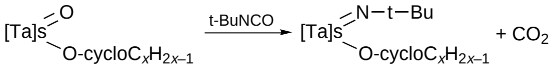
Figure 4. CP MAS ^{13}C NMR spectrum of the cycloheptyl−tantalum complex resulting from the reaction of **3** with cycloheptane.

29.5, 33.2 ppm ($-CH_2-$) and 86.9 ppm ($Ta-CH<$). After evacuation of the excess hydrocarbon, further treatment of these complexes with dry oxygen leads to the formation of air-stable oxo-alkoxy tantalum surface complexes without loss of any alkyl fragment (eq 4):



$$[Ta]_sH + \text{cycloC}_xH_{2x} \xrightarrow[-H_2]{} [Ta]_s\text{-cycloC}_xH_{2x-1} \xrightarrow{O_2} [Ta]_s(=O)(O\text{-cycloC}_xH_{2x-1}) \qquad x = 5, 6, 7, 8 \tag{4}$$

The intermediacy of a peroxo-alkyl complex is assumed in this transformation by analogy with results of molecular chemistry.[16] The volumetric determination of the oxygen consumed indicates that this reaction requires 1 ± 0.15 equiv of O_2 per Ta. The presence of an oxo ligand is further demonstrated by its reactivity with *tert*-butyl isocyanate affording the evolution of CO_2 and the formation of an expected surface imido−tantalum complex[17] (elemental analysis: 0.97 N per Ta) (eq 5).



$$[Ta]_s(=O)(O\text{-cycloC}_xH_{2x-1}) \xrightarrow{\text{t-BuNCO}} [Ta]_s(=N-t-Bu)(O\text{-cycloC}_xH_{2x-1}) + CO_2 \tag{5}$$

The elemental analysis of the various oxo-alkoxy complexes derived from the experiments of cycloalkane activation leads to the following cycloalkoxy/Ta stoichiometries (Table 1). All these results are again consistent with a stoichiometry of one hydride per Ta.

Table 1. Analytical Data Corresponding to the Activation of Cycloalkanes on the $[Ta]_sH$ Species, Followed by Treatment under O_2

cyclopentyloxy/ Ta	cyclohexyloxy/ Ta	cycloheptyloxy/ Ta	cyclooctyloxy/ Ta
0.97	0.85	1.05	0.99

2.2.6. Titration of the $[Si]_sH$ Groups. The Si−H groups do not react with pure water but can be hydrolyzed under conditions of alkaline catalysis;[18,19] after previous hydrolysis of the $[Ta]_sH$ species, the addition of KOH/H_2O liberates 0.63 equiv of hydrogen per Ta; this indicates the presence of ca. 0.63 Si−H groups per grafted Ta.

2.3. Formulation of the Silica-Supported Tantalum Hydride 3. All the reactions previously described with D_2, CH_3I, di(*tert*-butyl)ketone, and D_2O, indicate that **3**, which presents a main IR band at 1830 cm^{-1}, plus two shoulders at 1815 and 1855 cm^{-1}, is a tantalum hydride. Quantitative titration of hydrogen evolved from the reactions of **3** with D_2O or cyclic hydrocarbons as well as elemental analysis of the products formed by reaction with di(*tert*-butyl)ketone or cyclic hydrocarbons is consistent with an average stoichiometry of one hydride per Ta. However, the IR spectrum of the $[Ta]_sH$ species **3** presents two shoulders besides the main band; this indicates that the main band should correspond to a tantalum monohydride species, but the two shoulders may suggest the presence of a small amount of a tantalum dihydride (symmetrical and antisymmetrical vibration modes). Nevertheless, according to the high sensitivity of the IR technics, the tantalum monohydride should be strongly predominant.

The next logical question about **3** concerns the number of surface oxygen atoms σ-bonded to tantalum, which according to the presence of one hydride per tantalum will govern its formal oxidation state. As already observed, the tantalum hydride reacts in a stoichiometric manner with cycloalkanes to give the corresponding tantalum-monocycloalkyls plus 1 equiv of H_2. These tantalum-cycloalkyls react further with 1 equiv of oxygen to give an oxo-alkoxy tantalum complex which is plausibly a Ta(V) species given that tantalum is extremely oxophilic and its higher oxidation state is +5.[20] It is therefore

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(16) Van Asselt, A.; Trimmer, M. S.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 8254−5.

(17) The conversion of metal-oxo ligand into metal-imido ligand by reaction with aryl or alkyl isocyanate reagents is of current interest: (a) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley: New York, 1988 and references therein. (b) Kolomnikov, I. S.; Koreshkov, Yu. D.; Lobeeva, T. S.; Volpin, M. E. *J. Chem. Soc., Chem. Commun.* **1970**, 1432−3. This conversion is well documented in the case of tungsten. (c) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Ewitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262−75. (d) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483−91. The conversion is well documented in the case of rhenium. (e) Nielson, A. J. *Inorg. Synth.* **1986**, *24*, 194−96. (f) Scott, S. L.; Basset, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 12069−70 and references therein. In the case of group V metals, the catalytic transformation of phenyl isocyanate to *N,N′*-diphenylcarbodiimide involving the reversible conversion of vanadium oxo and imido complexes, has been reported. (g) Birdwhistell, K. R.; Boucher, T.; Ensminger, M.; Harris, S.; Johnson, M.; Toporek, S. *Organometallics* **1993**, *12*, 1023−5.

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(19) Allinger, N. L.; Cava, M. P.; de Jongh, D. C.; Johnson, C. R.; Lebel, N. A.; Stevens, C. L. *Chimie Organique*; McGraw Hill: Paris, 1983; p 896.

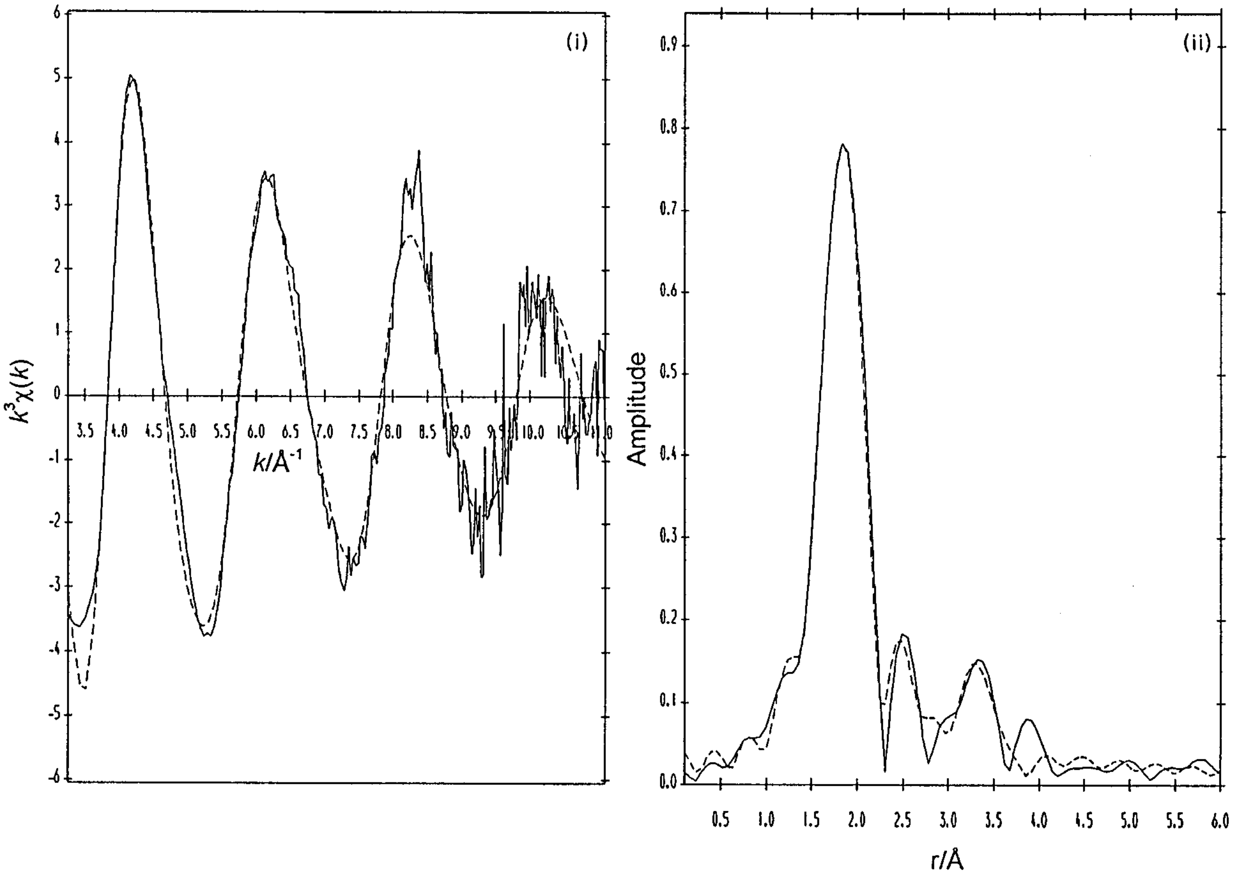

Figure 5. Ta L$_{\mathrm{III}}$-edge k^3-weighted EXAFS (i) and Fourier transform (ii) phase-shift corrected for oxygen of silica-supported tantalum hydride species **3**.

suggested, according to eq 4 that the tantalum-cycloalkyl is a tantalum(III) species. During the C−H bond activation of cycloalkanes on **3**, 1 equiv of hydrogen is evolved, and consequently the oxidation state of the metal is not modified (in eq 4 the hydrido ligand is simply replaced by a cycloalkyl ligand). Then the oxidation state of the [Ta]$_s$H species should be the same as that of the tantalum-cycloalkyls, that is +3. The assumption of an oxidation state of +3 for the [Ta]$_s$H species is also consistent with the evolution of 2 equiv of the 1/1 HD−D$_2$ mixture during its reaction with D$_2$O; the final species being an oxo-deuteroxy tantalum(V) complex (see eq 3). In the presence of one hydride on each tantalum, the resultant oxidation state of +3 is achieved by the coordination of two surface Si−O groups σ-bonded to the metal. Under these conditions, the formulation of the [Ta]$_s$H species **3** could be ($\equiv$SiO)$_2$Ta$^{\mathrm{III}}$H. A second possibility is that a third surface oxygen is behaving as a neutral ligand and interacting weakly with the tantalum center in order to fulfill the high oxophilicity of the metal and increase the number of electrons in its coordination sphere. EXAFS studies of **3** were thus performed to attempt to identify the exact structure of the tantalum hydride on the surface.

2.4. EXAFS Studies of Silica-Supported Tantalum Hydride 3. Analysis of the Ta L$_{\mathrm{III}}$-edge EXAFS of species **3** [See Experimental Section.] (Figure 5, Table 2) gave a first coordination sphere of *ca.* two oxygens at 1.89 Å, consistent with the presence of two σ-bonded surface Si−O groups. The EXAFS-derived Ta−O distance compares well with single crystal X-ray Ta−O distances found in siloxy, aryloxy, and hydride complexes of tantalum: [Ta(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$Cl(H)$_2$(PMe$_2$Ph)$_2$] 1.899(5) and 1.900(5) Å;[21] [Ta(OC$_6$H$_3$-2,6-^{i}Pr$_2$)$_3$(H)$_2$(PMe$_2$Ph)] 1.907(3), 1.912(4), and 1.897(3) Å;[22] [(^{t}Bu$_3$SiO)$_2$Ta(H)$_2$]$_2$ 1.86(3) Å;[23] [(^{t}Bu$_3$SiO)$_3$Ta]$_2$(μ-C$_2$) 1.878(9) Å;[24] and [(TpO)$_2$TaNp$_3$] (where TpO = 9-oxytriptycene) 1.86(1) and 1.880(8) Å.[25] The Fourier transform of the Ta L$_{\mathrm{III}}$-edge EXAFS also contains a number of smaller peaks between 2.5 and 4.0 Å. Significant decreases in the *R*-factor were observed when additional shells of *ca.* one oxygen at 2.63 Å and two silicons at 3.39 Å were included in the refinement. The inclusion of a fourth shell of silicon at 3.99 Å also gave a slight improvement in the fit but this shell was not considered statistically significant. The presence of an oxygen shell at 2.63 Å does indeed suggest that a third

Table 2. Ta L$_{\mathrm{III}}$-Edge EXAFS-Derived Structural Parameters[a] for Silica-Supported Tantalum Hydride Species **3**

shell	coordination no.	interatomic distance, Å	$2\sigma^2$,[b] Å^2	*R*-factor, %
O	2.3(1)	1.893(3)	0.0093(4)	25.4
O	0.7(1)	2.629(9)	0.0068(23)	
Si	1.7(3)	3.391(11)	0.0293(58)	

[a] EF = −8.85 eV and AFAC = 0.88. [b] Debye−Waller factor. σ = root mean square internuclear separation. [c] *R*-factor is defined as $(\int|\chi^{\mathrm{T}}-\chi^{\mathrm{E}}|k^3\mathrm{d}k/\int|\chi^{\mathrm{E}}|k^3\mathrm{d}k) \times 100$ %, where χ^{T} and χ^{E} are the theoretical and experimental EXAFS and k is the photoelectron wave vector. The values given in parentheses represent the statistical errors generated in EXCURVE; for details of true error estimation see the Experimental Section.

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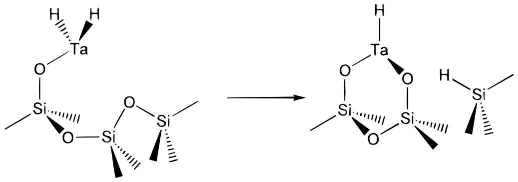
Scheme 1

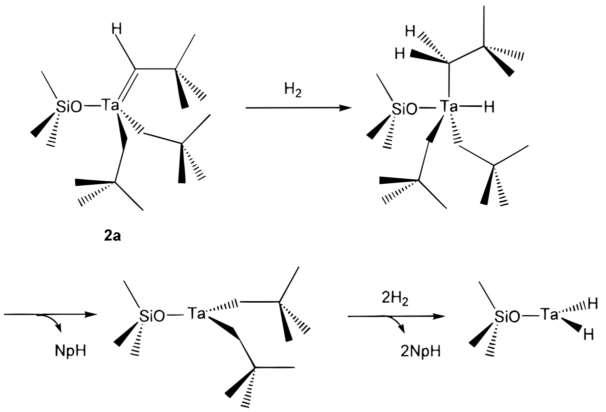


surface oxygen atom is interacting weakly with the tantalum. Such long range interactions have been detected using EXAFS in silica-supported zirconium systems.[26] The Ta···Si distance of 3.39 Å is not unreasonable for Ta bound via oxygens to two adjacent silicons: taking the EXAFS Ta−O distance of 1.89 Å and assuming a Si−O distance of around 1.7 Å,[23,24] the Ta−O−Si angle can be calculated as 142° with an estimated error of 5−10°. This angle is much smaller than the Ta−O−Si angles found in the siloxy complexes $[(^t\mathrm{Bu_3SiO})_2\mathrm{Ta(H)_2}]_2$ and $[(^t\mathrm{Bu_3SiO})_3\mathrm{Ta}]_2(\mu\text{-}\mathrm{C_2})$, which are typically 170−175°, but is not unexpected if one takes into account the surface constraints imposed upon the tantalum. The EXAFS results thus provide direct structural evidence for the presence of the supported tantalum hydride species **3** attached to silica via two adjacent σ-bonded surface Si−O groups, with a third surface oxygen (most probably siloxane) providing a weak interaction with the Ta center.

Considering that in the original neopentyl, neopentylidene complexes **2a** and **2b** tantalum is bonded to silica by one or two oxygens, respectively, one must assume that a siloxy ligand has been transferred to tantalum during the transformation of $\equiv\mathrm{SiOTa[CH_2C(CH_3)_3]_2[{=}CHC(CH_3)_3]}$ (**2a**) into **3**, in order to obtain the bis(siloxy) configuration. This hypothesis will now be examined and take consistence in view of the possible mechanism of formation of the Si−H groups.

2.5. Proposition of a Mechanism of Formation of the Si−H Groups. During the transformation of 65% of $\equiv\mathrm{SiOTa[CH_2C(CH_3)_3]_2[{=}CHC(CH_3)_3]}$ (**2a**) and 35% of $(\equiv\mathrm{SiO})_2\mathrm{Ta[CH_2C(CH_3)_3][{=}CHC(CH_3)_3]}$ (**2b**) into tantalum hydride, 65% of $\equiv\mathrm{SiOTaH_2}$ and 35% of $(\equiv\mathrm{SiO})_2\mathrm{TaH}$ could be expected instead of the only latter one. Then 0.65 H per Ta is lacking on the one hand, whereas 0.63 SiH per Ta has appeared on the silica surface, on the other hand; this observation suggests that a hydride transfer has occurred from tantalum to silicon during which a new Ta−O bond should also form; such a process may involve neighboring siloxane bridges which are known to form during the thermal dehydroxylation of silica;[27,28] the following scheme can then be proposed (Scheme 1). The siloxane bridges should react and the silica surface reorganize until most of the intermediate tantalum dihydride has been transformed into monohydride. The configuration of this monohydride should make improbable a further interaction with other siloxane bridges. The three bands assigned to Si−H groups probably correspond to a mixture of a geminal silicon dihydride (2215 and 2300 cm^{-1}) and a monohydride (2270 cm^{-1}); the silicon dihydride can originate from the transfer of hydride from two tantalum centers adjacent to the same doubly-bridged silicon atom.

Scheme 2



2a

2.6. Proposition of a Mechanism of Formation of 3. The substitution of neopentyl and neopentylidene groups by hydride in complexes **2a** and **2b** proceeds at as low a temperature as 25 °C in contrast to $\equiv\mathrm{SiOZrNp_3}$ for which heating to 70 °C at least is required.[6d] The presence of a neopentylidene ligand in **2a** and **2b** probably favors the process; the addition of a hydrogen molecule on this ligand can first be assumed, affording hydrido-neopentyl-tantalum(V) species; after the first elimination of neopentane, repeated elimination of neopentane in the presence of hydrogen would lead to the complete replacement of neopentyl ligands by the hydride (Scheme 2).[29] A similar mechanism can be assumed in the case of **2b**. The various hydrido-neopentyl-tantalum intermediates would correspond to the variation in the ν(Ta−H) wavenumbers observed in Figure 1b during the preparation of **3**; the consecutive reaction of the expected tantalum dihydride intermediate with siloxane bridges would explain the evolution by a maximum of the Ta−H bands area versus temperature in Figure 2. The general evolution of the surface tantalum species can then be summarized as follows (Scheme 3). Several types of hydroxyl groups on the silica surface can be involved: isolated OH groups with neighboring siloxane bridges would lead to $\equiv\mathrm{SiOTa[CH_2CH_3)_3]_2[{=}CHC(CH_3)_3]}$ (**2a**) and then under hydrogen to the formation of $(\equiv\mathrm{SiO})_2\mathrm{TaH}$ and Si−H groups (species **3a**), via the intermediacy of a tantalum dihydride $\equiv\mathrm{SiOTaH_2}$ and a hydride transfer; double OH groups including vicinal and geminal types would afford the direct formation of tantalum species bonded to the surface by two oxygen atoms: $(\equiv\mathrm{SiO})_2\mathrm{Ta[CH_2C(CH_3)_3][{=}CHC(CH_3)_3]}$ (**2b**) and then under hydrogen to $(\equiv\mathrm{SiO})_2\mathrm{TaH}$ alone (species **3b**). The weak interaction of tantalum with a third siloxane oxygen atom would then occur, due to the high electronic and coordinative unsaturation of the metal.

3. Conclusions

The reaction of $\equiv\mathrm{SiO\text{-}Ta[CH_2C(CH_3)_3]_2[{=}CHC(CH_3)_3]}$ (**2a**) and $(\equiv\mathrm{SiO})_2\mathrm{Ta[CH_2C(CH_3)_3][{=}CHC(CH_3)_3]}$ (**2b**) with hydrogen up to 200 °C affords the predominant formation of a surface tantalum(III) monohydride $(\equiv\mathrm{SiO})_2\mathrm{Ta^{III}H}$ (**3**) and of Si−H groups. A weak interaction from a third surface oxygen (most probably siloxane) has however also been identified from the Ta $\mathrm{L_{III}}$-edge EXAFS of **3**. The supported tantalum hydride shows a reactivity comparable to that of early transition metal

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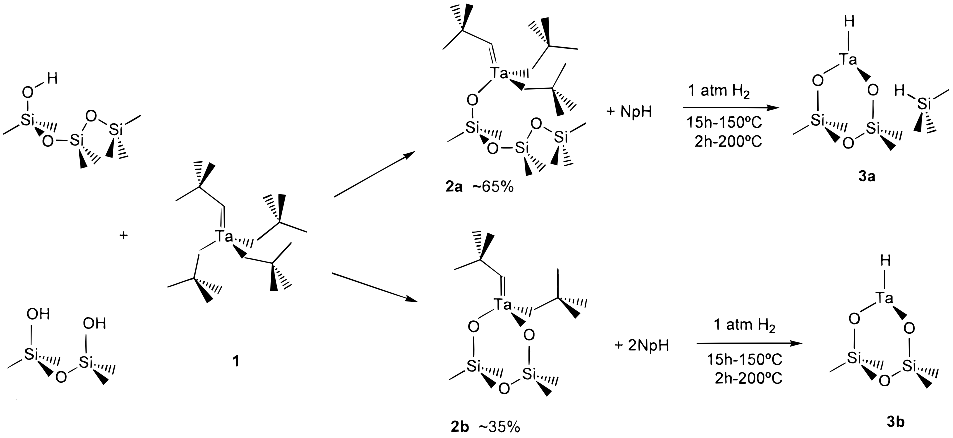
(29) The substitution of neopentyl groups by hydride may proceed via a four-centered intermediate and σ-bond metathesis as it was proposed for alkyl exchange reaction on early transition metal complexes. (a) Reference 9. (b) Raba, H.; Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327−33. (c) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502−9. However, in the case of tantalum, an oxidative addition-reductive elimination process must also be considered in view of the proposition in the literature. (d) Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* **1989**, *111*, 8049−51. (e) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701−7. (f) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648−55.

Scheme 3



hydrides. Quantitative determinations of the tantalum hydride and of the Si−H groups support a mechanism in which a hydride is transferred from the expected tantalum(III) dihydride ≡SiO-TaH$_2$ originating from **2a** to a neighboring siloxane bridge; this transfer affords the formation of the Si−H groups and the bonding of a second Si−O group to Ta.

Experimental Section

General Methods. All manipulations and reactions are conducted in the absence of solvent under strict inert atmosphere or vacuum conditions since surface tantalum complexes are extremely air and water sensitive. Sealed tube reactors are used throughout. Infrared spectra were recorded on a Nicolet FT-IR Magna 550 spectrometer equipped with a cell designed for in situ preparations under controlled atmosphere, using a self-supported silica disc.[30] Gas phase analysis of hydrocarbons was performed on a Intersmat IGC 121 FL chromatograph equipped with a flame ionization detector and a Al$_2$O$_3$/KCl on fused silica column (50 m × 0.32 mm). Gas phase analysis of hydrogen was performed on a Intersmat IGC 20 MB chromatograph equipped with a thermal conductivity detector and a filled molecular sieve column (2.50 m × 3.17 mm). Gases were expanded from IR cell into a small lock chamber connected to the vacuum line and fitted with a rubber septum; air was admitted to this chamber to atmospheric pressure just before GC analysis. Elemental analyses were performed by the Central Analysis Service of the CNRS at Solaize. Mass spectra were recorded on a quadrupole analyzer (Supravac VG) connected to a vacuum system able to maintain a residual pressure of 10^{-10} Torr.

Silica (Degussa, 200 m^2/g) was treated under vacuum (10^{-5} mmHg) at 500 °C for 15 h. Silica thus treated [silica 500] has been determined to have surface hydroxyl concentration of 2 OH/nm^2 as determined by the titration with LaAlH$_4$.[31] The liquid reagents were degassed and stored over molecular sieves (4 Å). D$_2$O (Aldrich) was degassed and stored under vacuum. **1** was prepared by the method of Schrock.[3] The preparation of **2a** and **2b** has been reported previously.[4]

MAS−NMR Spectroscopy. MAS−NMR spectra were recorded on a BRUKER MSL-300 spectrometer operating at 75.47 MHz for ^{13}C. The probehead was a commercial double-tuned 7 mm double-bearing system from BRUKER allowing spinning frequencies up to 4 kHz. The samples were introduced in the rotor made of zirconia under a dry nitrogen atmosphere in a glovebox and tightly closed. Boil-off nitrogen was used for both bearing and driving the rotors. For ^{13}C NMR, a typical cross polarization sequence was used: 90° rotation of the ^{1}H magnetization (impulsion length 6.2 ms), then contact between carbon and proton during $T_c = 5$ ms, and finally recording of the spectrum under high power decoupling. The delay between each scan was fixed to 5 s, to allow for the complete relaxation of the ^{1}H nuclei. Chemical shifts are given with respect to TMS by using adamantane as an external reference ($\delta = 37.7$ ppm for the highest chemical shift).

Preparation of Silica-Supported Tantalum Hydride Species [Ta]$_s$H (3). Complexes **2a** and **2b** were treated under 1 atm of hydrogen at 150 °C overnight (15 h) and then at 200 °C for 2 h; the gas phase was evacuated (15 min; 10^{-5} Torr) before further studies.

H/D Exchange Reaction on 3. Complex **3** was prepared in situ, in the IR cell; 40 Torr of D$_2$ were introduced, and the H/D exchange reaction was monitored by IR spectrometry at 25 °C. After 2 h the cell was evacuated and refilled with 400 Torr of H$_2$.

Reaction of 3 with CH$_3$I. After in situ preparation of **3** and evacuation of the gases, a vapor pressure of CH$_3$I (400 Torr; 25 °C) was introduced in the IR cell. The silica disc turned immediately from brown to white. The methane evolved was analyzed by GC.

Reaction of 3 with (t-Bu)$_2$CO. A vapor pressure of (t-Bu)$_2$CO was introduced at 25 °C in the IR cell where complex **3** has been prepared. The silica disc turned white immediately. After 1 h at 25 °C, the cell was evacuated at 25 °C and then at 150 °C for 4 h to remove any physisorbed ketone. Further introduction of acetic acid vapor at 25 °C afforded the liberation of di(*tert*-butyl)methyl acetate which was analyzed by GC/MS. Elemental analysis for Ta and C was performed on an other preparation of the di(*tert*-butyl)methoxy−tantalum surface complex: Ta, 3.94%; C, 2.36%.

Reaction of 3 with D$_2$O and Titration of the [Si]$_s$H Groups. A vapor pressure of D$_2$O was introduced at 25 °C in the IR cell where complex **3** had been prepared. The silica disk turned white immediately. The hydrogen evolved was quantified by GC (89.6 μmol of HD + D$_2$ for 47.9 μmol of Ta, that is (HD + D$_2$)/Ta 1.87) and by pressure measurement (99.4 μmol of HD + D$_2$ for 47.9 μmol of Ta, that is (HD + D$_2$)/Ta = 2.075) after trapping the D$_2$O pressure in liquid nitrogen. The HD/D$_2$ ratio was approached by direct introduction of the gas phase in the MS spectrometer via a capillary tube and monitoring of the peaks m/e = 2, 3, and 4: whereas HD and D$_2$ has not exactly the same response, the peaks 3 and 4 were comparable in height and largely higher than peak 2. The cell was evacuated again, and the aqueous solution of KOH was poured on the silica disk. Again, the hydrogen evolved was quantified by GC (29.46 μmol of H$_2$ for 47.9 μmol of Ta, that is H$_2$/Ta = 0.615) and by pressure measurement (30.65 μmol of H$_2$ for 47.9 μmol of Ta, that is H$_2$/Ta = 0.64) after trapping the D$_2$O pressure in liquid nitrogen.

Reaction of 3 with Cyclic Hydrocarbons (C$_5$ to C$_8$). A vapor pressure of the selected hydrocarbon was introduced at 25 °C in the IR cell where complex **3** has been prepared. The TaH bands decreased when the CH bands increased; after 1 h at 25 °C the reaction with cyclooctane was quantitative, whereas a smooth heating at 50−80 °C was applied for the other hydrocarbons. The hydrogen evolved was quantified in the case of cycloheptane, affording 1.04 equiv of H$_2$ per Ta. After evacuation of the cell, 200 Torr of O$_2$ was introduced, the consumption of which was determined by the pressure decrease (0.85 O$_2$ per Ta for cyclohexane; 1.12 O$_2$ per Ta for cycloheptane). Elemental analysis of the alkoxy-oxo-tantalum complexes was as follows: cyclooctane: Ta, 5.29%, C, 2.78%; cycloheptane: Ta, 6.25%, C, 3.05%; cyclohexane: Ta, 2.25%, C, 0.76%; cyclopentane: Ta, 4.35%, C, 1.4%.

EXAFS Data Acquisition and Analysis. X-ray absorption spectra were recorded at the Synchrotron Radiation Source at LURE, with the

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[31] Silica characteristics are provided by DEGUSSA (technical note).

X-ray beam emitted by the DCI storage ring (operating at 1.85 GeV, with an average current of *ca*. 300 mA) using a Ge(400) double crystal monochromator. Samples of the silica-supported tantalum hydride species **3** for EXAFS analysis were prepared *in situ* (as pressed discs) in a controlled environment, dual-purpose IR-EXAFS cell fitted with perpendicularly oriented CaF_2 and Kapton windows. Spectra were acquired at room temperature in transmission. The background subtracted-EXAFS was obtained using the program PAXAS.[32] A polynomial of order 2 was used in the pre-edge background subtraction and the post-edge background was subtracted using coupled polynomials of order 8 in order to remove low frequency contributions from the spectrum. Spherical wave curve fitting analyses, by least squares refinement of non-Fourier filtered EXAFS, were carried out in EXCURVE,[33] using Von-Barth ground state potentials and Hedin-Lundqvist exchange potentials. Fits were optimized by considering both k^1 and k^3 weightings of the EXAFS since the latter emphasizes the higher shells, whereas the former favors near shells of light scatterers. No significant differences were observed for refinements carried out using the two weightings: k^1-weighted EXAFS refined as 2.2 Ta−O at 1.89 Å, 0.7 Ta···O at 2.66 Å, and 1.8 Ta···Si at 3.29 Å. The k^3-weighted parameters are presented in Table 2. Selective Fourier-filtering of the EXAFS was used to aid in the identification of the backscatterers giving rise to the smaller peaks occuring between 2.5 and 4 Å. The accuracy of bonded and nonbonded interatomic distances is considered to be 1.4% an 1.6%, respectively.[34] Precision on first shell coordination numbers is estimated to be *ca*. 5−10% and, for nonbonded shells, between 10 and 20%. The statistical validity of shells was assessed by published means,[35] and the numbers of independent parameters used in the fits fall within the guideline, $N_{pts} = 2(k_{max} - k_{min})(R_{max} - R_{min})/\pi$ (ref 36).

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