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Synthesis, Characterization, and Reactivity of the Highly Unsaturated Silica-Supported Trisiloxy Tantalum: $(\equiv SiO)_3Ta^{(III)}$

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The silica-supported tantalum hydride, $(\equiv SiO)_2Ta^{(III)}H$, is transformed under hydrogen by thermal treatment up to 500 °C into a new well-defined surface species, the trisiloxy tantalum $(\equiv SiO)_3Ta^{(III)}$. The Ta L_{III}-edge EXAFS gives a first coordination sphere of three oxygen atoms at 1.908 Å. The mechanism of formation of $(\equiv SiO)_3Ta^{(III)}$ has been studied by IR: it involves a hydride transfer from tantalum to silicon and a siloxy transfer from silicon to tantalum. This surface reconstruction occurs by opening of the $\equiv Si-O-Si\equiv$ bridge of silica probably in the vicinity of the tantalum hydride. $(\equiv SiO)_3Ta^{(III)}$ reacts with pyridine and PMe_3 to give 1:1 adducts. It also reacts with ethanol and water by an oxidation process to give molecular hydrogen and the surface compounds $(\equiv SiO)_3Ta^{(V)}(OEt)_2$ and $(\equiv SiO)_3Ta^{(V)}(OH)_2$. It still reacts with molecular oxygen to give $(\equiv SiO)_3Ta^{(V)}(=O)$ by an unknown mechanism. Although $(\equiv SiO)_3Ta^{(III)}$ exhibits an extreme electron deficiency and redox properties due to its d^2 configuration, this new surface tantalum species does not show any longer the catalytic properties of the tantalum hydride.

Introduction

We have previously reported that $Ta(-CH_2CMe_3)_3(=CHCMe_3)$, **1**, reacts with the surface hydroxyl groups of a silica (Aerosil 200 m^2/g) to form two different surface species: $(\equiv SiO)Ta(-CH_2CMe_3)_2(=CHCMe_3)$, **2a**, or $(\equiv SiO)_2Ta(-CH_2CMe_3)(=CHCMe_3)$, **2b**, depending on whether the silica was previously dehydroxylated at 700 or 300 °C, respectively.[1a] When silica was treated at 500 °C, a 65/35 mixture of **2a** and **2b** was obtained.[1b] Upon treatment under hydrogen at 150 °C overnight, these two surface complexes or their mixture is transformed into the surface tantalum(III) monohydride $(\equiv SiO)_2TaH$, **3**, which was fully characterized by infrared spectroscopy, EXAFS, elemental analysis, and quantitative chemical reactions.[2] The formation of species **3** is also accompanied by the appearance of silane groups $\equiv SiH$ on the surface, linked to the transformation of species **2a** into the hydride $(\equiv SiO)_2TaH$**, 3**. As already observed with silica-supported Ti,[3a] Zr,[3b−d] and Hf[3e] hydrides, this involves a rearrangement of the silica surface around the tantalum center during which a siloxane bridge in the vicinity of the metal is opened, a second tantalum−oxygen bond is formed, and a hydrogen atom is transferred from a possible tantalum dihydride intermediate to a silicon atom (Scheme 1).[2]

The compound $(\equiv SiO)_2TaH$, **3**, activates at moderate temperature the C−H bond of methane and cycloalkanes to form the corresponding surface tantalum-methyl and tantalum-cycloalkyl derivatives with evolution of 1 equiv of H_2.[2,4] **3** catalyzes the H/D exchange reaction between CH_4 and CD_4.[5] It can also catalyze the hydrogenolysis of C−C bonds of light alkanes such as butane, propane, and even ethane.[6] Interestingly, **3** is a catalyst of the newly discovered reaction of alkane metathesis, which involves the concomitant cleavage and formation of C−C bonds of light acyclic alkanes and produces equimolar amounts of higher and lower homologues.[7] We believe that the exceptional catalytic property of **3** is related to its high electron deficiency (here **3** is formally an eight-electron species (or 12 if one counts the $p_\pi-d_\pi$ back-donation of the two oxygen

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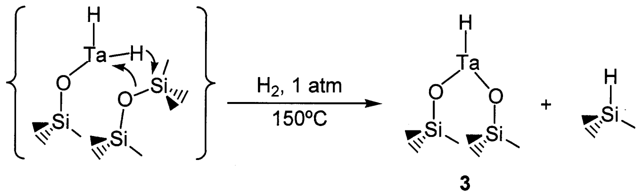
Scheme 1



atoms) with a d^2 configuration) and to the exceptional availability of its d orbitals for H−H, C−H, or C−C coordination and/or metathetical cleavage.[8]

Here we show that $(\equiv SiO)_2TaH$, **3**, can be transformed into a new highly unsaturated silica-supported tantalum species $(\equiv SiO)_3Ta$, **4**, by thermal treatment under hydrogen. **4** was fully characterized by IR and EXAFS. Preliminary results on the reactivity of **4** are given.

Results and Discussion

When the tantalum hydride $(\equiv SiO)_2TaH$, **3**, is heated under hydrogen (760 Torr) by steps of 50 °C from 150 °C to 500 °C, the ν(TaH) bands centered at 1830 cm^{-1} progressively decrease in intensity, whereas the intensity of the ν(SiH) bands at 2215, 2270, and 2300 cm^{-1} increase in parallel (Figure 1). At 500 °C, all the ν(TaH) bands have been replaced by ν(SiH) ones, and the color of the solid has changed from brown to dark brown. Figure 2 shows the quasi linear relationship between the evolution of the ν(TaH) and the ν(SiH) bands. The parallel evolution of the ν(TaH) and ν(SiH) bands suggests that when a $(\equiv SiO)_2Ta{-}H$ species disappears, its hydride should be transferred to form a new silicon hydride and a new tantalum species **4**. Effectively, if the tantalum hydride is first fully exchanged at room temperature with deuterium and then heated under deuterium, the ν(TaD) bands also decrease in intensity and disappear, whereas new bands at 1600, 1625, and 1655 cm^{-1} consistent with ν(SiD) vibration modes increase in parallel. Analysis of the Ta L_{III}-edge EXAFS of species **4** (Table 1, Figure 3) indicates a first coordination sphere of three oxygen atoms at 1.908 Å, consistent with the presence of three σ-bonded surface Si−O groups. The EXAFS derived Ta−O distance compares well with that of the originating complex $(\equiv SiO)_2Ta{-}H$, **3** ($d_{Ta-O} = 1.893$ Å),[2] and with similar single-crystal X-ray distances found in aryloxy or siloxy tantalum complexes: $[Ta(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)_3(H)_2(PMe_2Ph)]$ 1.907(3), 1.912(4), and 1.897(3) Å,[9] $[Ta(OC_6H_3\text{-}2,6\text{-}Cy_2)_2(H)_3(PMe_2Ph)_2]$ 1.901(6) Å,[10] $[Ta(H)_2(OSi^tBu_3)_2]_2$ 1.86(3) Å,[11] $[Ta(OSi^tBu_3)_3]_2(\mu\text{-}C_2)$ 1.878(9) Å.[12] The Fourier transform of the Ta L_{III}-edge EXAFS also contains a number of smaller peaks between 2 and 4.0 Å. Significant fit improvement was observed when additional shells of oxygen (1.07 O at 2.95 Å) and silicon (3.0 Si at 3.364 Å) were included in the refinement; as in the case of silica-supported zirconium hydride,[3b] this fourth oxygen atom could belong to the bulk and interact with tantalum between the three Si−O ligands. The EXAFS as well as the IR results thus provide direct structural evidence for the formation of a new supported tantalum species $(\equiv SiO)_3Ta$, **4**, attached to silica via three σ-bonded Si−O groups.

These results on the structure of the "tripodal" tantalum as well as on the simultaneous formation of the silicon hydride from **3** can also be understood in the way of a rearrangement of the silica surface around the tantalum atom as during the formation of **3** itself. Similarly, this process should involve the transfers of the hydride from tantalum to a silicon atom and of a siloxy group to tantalum. This should involve the opening of a siloxane bridge in the vicinity of the tantalum hydride (Scheme 2).

This process results in the formation of the trisiloxy tantalum $(\equiv SiO)_3Ta$, **4**, a new surface tantalum species bonded to the silica via three oxygen atoms; as a consequence, this new tantalum species does not present any specific IR absorption besides the (Ta−O) bands and becomes practically unobservable by IR spectroscopy. To our knowledge this new Ta species **4** is a rare example of such highly unsaturated surface species, although it has a molecular equivalent known in the literature: the $(Silox)_3Ta$ complex where Silox = ${}^tBu_3SiO$.[13]

4 has been further studied for its chemical reactivity.

When **4** is allowed to react with a vapor of water (18 Torr), the IR self-supported silica disk is discolored from brown to white and 0.95 ± 0.05 equiv of H_2 per Ta is released in the gas phase; a dihydroxytrisiloxy tantalum surface species $(\equiv SiO)_3Ta^{(V)}(OH)_2$, **5**, is expected to form:

$$\underset{\mathbf{4}}{(\equiv SiO)_3Ta} + H_2O \rightarrow \underset{\mathbf{5}}{(\equiv SiO)_3Ta(OH)_2} + H_2$$

Similarly, the complex **4** also reacts with ethanol to release again 0.93 ± 0.05 equiv of H_2 per Ta and form the expected white diethoxytrisiloxy tantalum surface species $(\equiv SiO)_3Ta^{(V)}(OEt)_2$, **6**:

$$\underset{\mathbf{4}}{(\equiv SiO)_3Ta} + EtOH \rightarrow \underset{\mathbf{6}}{(\equiv SiO)_3Ta(OEt)_2} + H_2$$

The ^{13}C CP MAS NMR spectrum of species **6** shows two peaks at 15.2 (CH_3-) and 67.5 ppm ($-CH_2-$), whereas when ethanol is simply physisorbed on silica, it exhibits resonances at 15 ppm (CH_3-) and 58 ppm ($-CH_2-$).

EXAFS spectra of **5** and **6** were also recorded, and the data refinements between the experimental and the theoretical spectra indicated the presence of five oxygen atoms in the vicinity of tantalum around 1.9 Å (Tables 2 and 3). Figure 4 presents a comparison between the Fourier transforms of the experimental EXAFS spectra of the various surface tantalum species $(\equiv SiO)_2Ta^{(III)}{-}H$,[2] $(\equiv SiO)_3Ta^{(III)}$, and $(\equiv SiO)_3Ta^{(V)}(OEt)_2$, which shows clearly the growth of the peak around 1.9 Å following the increasing number of coordinated oxygen atoms.

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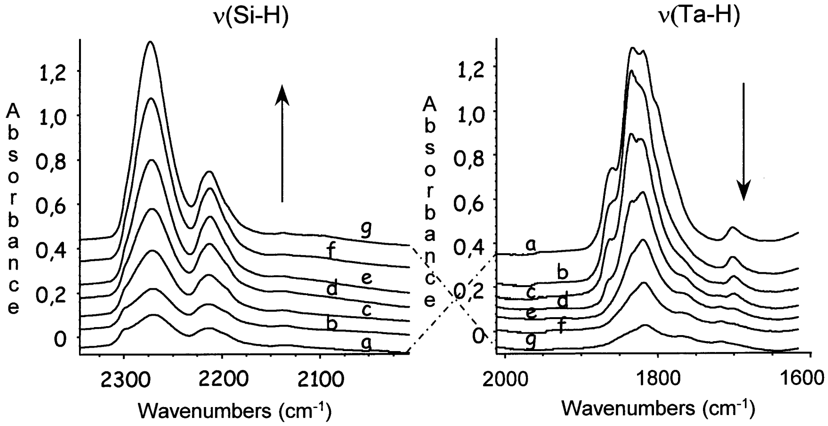

Figure 1. IR spectra of the transformation of the silica-supported tantalum hydride $(\equiv SiO)_2Ta-H$, **3**, into $(\equiv SiO)_3Ta$, **4**, during heating under 650 Torr of hydrogen from 150 (a) to 450 °C (g) by steps of 50 °C (silica spectrum subtracted).

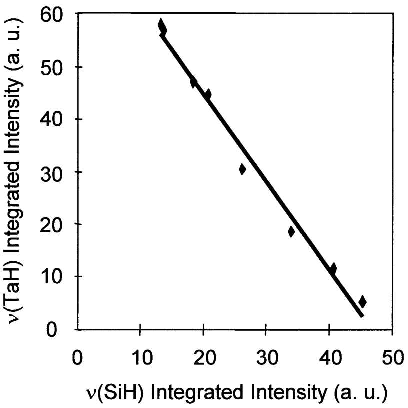

Figure 2. Correlation between the evolution of ν(TaH) and ν(SiH) IR integrated intensities during heating of the silica-supported tantalum hydride $(\equiv SiO)_2Ta-H$, **3**, under 650 Torr of hydrogen from 150 to 450 °C (a.u. arbitrary unit).

Table 1. Ta L_{III}-Edge EXAFS-Derived Structural Parameters for the Trisiloxy-Tantalum Complex $(\equiv SiO)_3Ta$, 4

shell	coordination no.	interatomic distance, Å	$2\sigma^2$,[a] Å^2	ρ-factor[b]
O	3.0	1.908	0.0074	0.058
O′	1.07	2.950	0.0102	
Si	3.0	3.364	0.0375	

[a] σ: Debye–Waller factor. [b] ρ-factor is defined as $\rho = (\sum_k[k^3\chi_{exp}(k) - k^3\chi_{calc}(k)]^2)/(\sum_k[k^3\chi_{exp}(k)]^2)$, where χ_{calc} and χ_{exp} are the calculated and experimental EXAFS and k is the photoelectron wave vector.

The $(\equiv SiO)_3Ta^{(III)}$ species **4** also reacts with the oxygen molecule to fix 0.495 ± 0.01 equiv of O_2 per Ta and form probably the white trisiloxy oxo tantalum species $(\equiv SiO)_3Ta^{(V)}(=O)$, **7**, instead of the expectably unstable peroxo species $(\equiv SiO)_3Ta^{(V)}(\eta_{-2}O-O)$. This behavior is similar to that of the $(Silox)_3Ta^{(III)}$ complex, which also forms the $(Silox)_3Ta^{(V)}(=O)$ species under 1 atm of oxygen.[13] Conversely, $(Silox)_3Ta$ can also fix 1 equiv of H_2, forming $(Silox)_3TaH_2$,[13] whereas $(\equiv SiO)_3Ta$, **4**, apparently cannot.[14]

Similarly to the surface tantalum hydride $(\equiv SiO)_2Ta-H$, **3**,[15] $(\equiv SiO)_3Ta$ species **4** can coordinate one molecule of trimethylphosphine to form a surface complex $(\equiv SiO)_3Ta-PMe_3$, **8**, with no color change. This complex presents ν(CH) and δ(CH) bands at 2975, 2911 and 1437, 1423 cm^{-1}, respectively. The ^{31}P CP MAS NMR spectrum of this complex shows a unique peak at −24 ppm, whereas the trimethylphosphine physisorbed on silica gives a peak at −57 ppm. The ^{13}C CP MAS NMR spectrum shows a peak at 14 ppm corresponding to the $-CH_3$ groups. The elemental analysis gives ratios P/Ta = 1.05 and C/P = 3.16.

The $(\equiv SiO)_3Ta$ species can also coordinate a pyridine molecule to form the dark brown surface complex $(\equiv SiO)_3Ta-Py$, **9**. After desorption of the excess of pyridine from silica at 150 °C for 3 h according to a parallel blank experiment,[16] the IR spectrum of **9** (Figure 5) shows several bands at 1449, 1489, 1576, and 1610 cm^{-1}. The band at 1449 cm^{-1} is characteristic of the pyridine coordinated to a Lewis acidic center, whereas the lack of a band at 1540 cm^{-1} related to the pyridinium ion indicates the absence of Brönsted acidic sites.[17] The ^{15}N CP MAS NMR spectrum of this complex shows a unique peak at −120 ppm, whereas the pyridine physisorbed on silica gives a peak at −97 ppm.[18] The elemental analysis gives ratios N/Ta = 0.92 and C/N = 5.05, consistent with the coordination of one pyridine molecule on each tantalum center. Thus, the coordination of pyridine on the $(\equiv SiO)_3Ta$ species reveals some Lewis acidic properties of the tantalum center.

The transformation of the surface tantalum hydride $(\equiv SiO)_2Ta-H$, **3**, into the new trisiloxy tantalum species $(\equiv SiO)_3Ta$, **4**, leads to a complete modification of its chemical and catalytic properties regarding alkanes. Complex **4** is not able to activate the C−H bond of linear or cyclic alkanes; complex **4** also cannot catalyze the H/D exchange reaction between CH_4 and CD_4. Furthermore, at the difference of complex **3**, it does not catalyze the hydrogenolysis nor the metathesis reactions of alkanes. Although complex **4** remains a d^2 Ta^{III} species just like the surface tantalum hydride $(\equiv SiO)_2Ta-H$, **3**, its

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(14) Complex $(\equiv SiO)_3Ta$, **4**, has been prepared and cooled under hydrogen, and its IR spectrum does not show any ν(Ta−H) bands; at the difference of $(Silox)_3Ta$, which leads to a trans dihydrido complex $(Silox)_3TaH_2$, the strained configuration of $(\equiv SiO)_3Ta$, **4**, on the surface probably forces a cis dihydrido configuration, which may be unstable.

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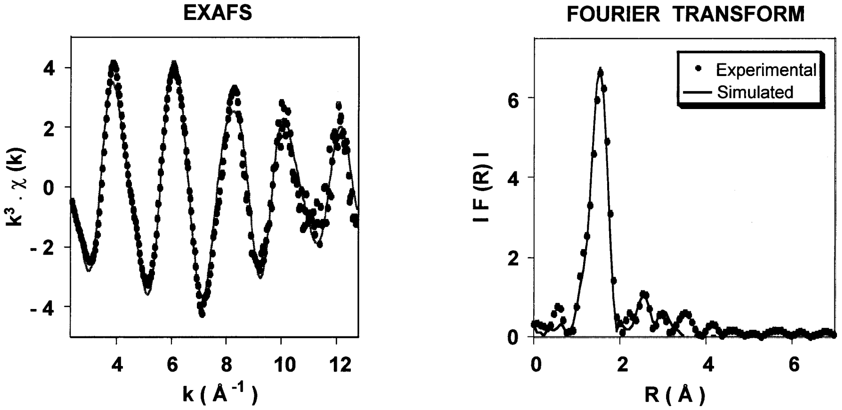

Figure 3. Comparison of experimental (dots) and simulated (line) EXAFS spectra at the tantalum L_{III}-edge of $(\equiv SiO)_3Ta$ (left) and modulus of the Fourier transform (right).

Scheme 2

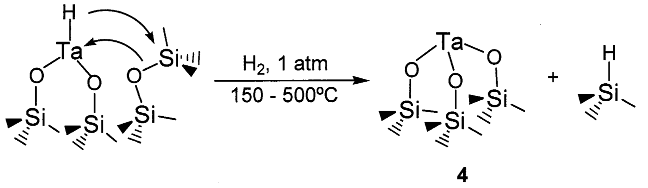

Table 2. Ta L_{III}-Edge EXAFS-Derived Structural Parameters for the Dihydroxy Trisiloxy Tantalum Complex $(\equiv SiO)_3Ta(OH)_2$, 5

shell	coordination no.	interatomic distance, Å	$2\sigma^2$,[a] Å^2	ρ-factor[b]
O	5.0	1.909	0.0113	0.043
O′	1.1	2.840	0.0069	
O″	3.5	3.055	0.0093	
Si	3.0	3.584	0.0148	

[a] σ: Debye–Waller factor. [b] ρ-factor is defined as $\rho = (\sum_k[k^3\chi_{exp}(k) - k^3\chi_{calc}(k)]^2)/(\sum_k [k^3\chi_{exp}(k)]^2)$, where χ_{calc} and χ_{exp} are the calculated and experimental EXAFS and k is the photoelectron wave vector.

Table 3. Ta L_{III}-Edge EXAFS-Derived Structural Parameters for the Diethoxy Trisiloxy Tantalum Complex $(\equiv SiO)_3Ta(OEt)_2$, 6

shell	coordination no.	interatomic distance, Å	$2\sigma^2$,[a] Å^2	ρ-factor[b]
O	5.0	1.905	0.0099	0.052
O′	1.1	2.960	0.0096	
C	2.2	3.132	0.0078	
Si	3.0	3.585	0.0108	

[a] σ: Debye–Waller factor. [b] ρ-factor is defined as $\rho = (\sum_k [k^3\chi_{exp}(k) - k^3\chi_{calc}(k)]^2)/(\sum_k [k^3\chi_{exp}(k)]^2)$, where χ_{calc} and χ_{exp} are the calculated and experimental EXAFS and k is the photoelectron wave vector.

coordination sphere is completely changed; the hydrido ligand is in fact replaced by a siloxy group; this observation may suggest that the above-mentioned reactions involving alkanes require either the Ta–H bond for the activation step or at least three available valencies to take place.

Conclusion

In summary, the new, well-defined silica-supported trisiloxy-tantalum complex $(\equiv SiO)_3Ta$, **4**, has been obtained by the progressive heating of the surface tantalum hydride $(\equiv SiO)_2Ta{-}H$, **3**, under hydrogen up to 500 °C. This new tantalum complex bears no ligand on its top and is undetectable by infrared spectroscopy; it is a rare example of such a highly unsaturated surface complex. At the difference of $(\equiv SiO)_2Ta{-}H$, **3**, complex **4** cannot catalyze the H/D exchange reaction between alkanes, neither the hydrogenolysis of alkanes nor the alkane metathesis reaction.

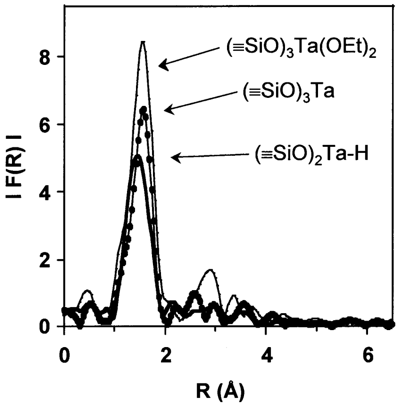

Figure 4. Comparison of experimental EXAFS spectra (modulus of the Fourier transform) at the tantalum L_{III}-edge of $(\equiv SiO)_2TaH$, $(\equiv SiO)_3Ta$, and $(\equiv SiO)_3Ta(OEt)_2$.

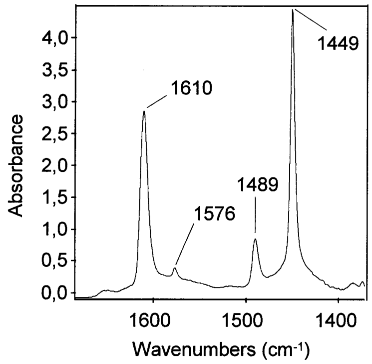

Figure 5. IR spectrum of the pyridine coordinated to the $(\equiv SiO)_3Ta$ species **4** after desorption of the excess at 150 °C for 3 h.

Experimental Section

General Procedures. All procedures were carried out under vacuum or purified argon using break-seal or Schlenk techniques in conjunction to a glovebox. All solvents were rigorously dried prior to use. Liquid reagents were degassed and stored over molecular sieves (4 Å). Gas reagents were purified over a deoxo-catalyst-zeolithes trap during their introduction. Silica (Aerosil Degussa, 200 m^2/g) was treated under vacuum (10^{-5} Torr) at 500 °C for 15 h. For infrared experiments, the silica was pressed into a 17 mm self-supporting disk of 20−50 mg. For other applications, it was compacted by pressing into thick disks, which were then ground in a mortar. **1** was prepared by the method of Schrock.[19] The preparations of **2a**, **2b**,[1] and **3**[2] have been reported previously. Infrared spectra were recorded on a Nicolet FT-IR Magna 550 spectrometer equipped with a cell designed for in-situ preparations under controlled atmosphere.[20] Gas phase analyses of hydrocarbons were performed on a Hewlett-Packard 5890 chromatograph equipped with a flame ionization detector and a Al_2O_3/KCl on a fused silica capillary column (50 m × 0.32 mm). Gas phase analyses of hydrogen were performed on an Intersmat IGC 120 MB chromatograph equipped with a catharometric detector and a filled molecular sieve column (2.50 m × 3.17 mm). Gases were expanded from an 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 Pascher Laboratories in Remagen-Bandorf (Germany). MAS NMR spectra were recorded on a Bruker DSX 300 spectrometer operating at 75.47 MHz for ^{13}C. The probehead was a commercial double-tuned 4 mm double-bearing system from Bruker, allowing spinning frequencies up to 12 kHz. The samples were introduced under the dry nitrogen atmosphere of a glovebox into the rotor made of zirconia, which was then tightly closed.

EXAFS Data Acquisition and Analysis. X-ray absorption spectra were recorded at the Synchrotron Radiation Source at LURE (Paris), with the X-ray beam emitted by the DCI storage ring (operating at 1.85 GeV, with an average current of ca. 300 mA). Samples of complex **4** for EXAFS analysis were prepared in situ, as pressed disks, in a controlled environment and placed in an air-protected cell equipped with Kapton windows. A double-crystal Si(111) monochromator was used, and the flux before and after entering the cells was measured by ionization chambers. The final absorption spectra were obtained by averaging four successive acquisitions recorded at room temperature in the transmission mode, at the tantalum L_{III}-edge, from 9700 to 11 000 eV, with a 2 eV step. EXAFS analysis was performed using software written by Michalowicz.[21] The background absorption was calculated by using a theoretical expression developed by Lengeler and Eisenberger,[22] and the single atomic absorption of the absorber was interpolated by a fifth- or sixth-degree polynomial between ca. 9900 and 11 000 eV. To remove low-frequency contributions from the spectrum, each spectrum was carefully extracted by varying both the degree and first point of the polynomial. The program FEFF-7 was used to calculate theoretical values of amplitudes and phases. Multiple scattering effects were also taken into consideration for **5** and **6**. 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. Selective Fourier-filtering of the EXAFS was used to aid in the identification of the backscatterers giving rise to the peaks occurring between 2 and 4 Å.

Preparation and Reactivity of 4. Typical procedures are described hereafter.

Preparation of 4. After in situ preparation of $(\equiv SiO)_2TaH$, **3** (57 mg, 5.88 wt % Ta), under hydrogen (650 Torr) and evacuation, a new atmosphere of hydrogen (650 Torr) was introduced in the IR cell, which was then heated by steps of 50 °C up to 450 °C.

Reaction of 4 with H_2O or C_2H_5OH. After in situ preparation of **4** (37 mg, 6.08 wt % Ta) and evacuation of the gases, a vapor pressure of H_2O (13 Torr; 25 °C) was introduced in the IR cell. The silica disk turned from dark brown to white. GC analysis indicated the liberation of 0.95 ± 0.05 equiv of hydrogen per Ta.

Similarly, the introduction of a vapor of C_2H_5OH (57 Torr; 25 °C) on a sample of **4** (58 mg, 5.78 wt % Ta) led to the discoloration of the silica disk, the formation of $(\equiv SiO)_3Ta(OEt)_2$, **6**, and the liberation of 0.93 ± 0.05 equiv of hydrogen per Ta. ^{13}C CP MAS NMR of **6**: $\delta = 15.2$ (CH_3-) and 67.5 ppm ($-CH_2-$).

Reaction of 4 with O_2. After preparation of **4** as a powder, 845 mg (5.03 wt % Ta, 234.8 μmol) was transferred to a specific cell in the glovebox; then, a pressure of dry O_2 (176.4 Torr; 25 °C) was introduced in the cell. The silica turned from dark brown to white. The pressure decrease was measured with a Texas Instrument gauge and compared with the theoretical decrease due to simple expansion; the difference between both ($\Delta P = 29.5$ Torr, 116.3 μmol) gave an amount of 0.495 ± 0.01 equiv of O_2 fixed per Ta.

Reaction of 4 with PMe_3. After in situ preparation of **4** (62 mg, 7.63 wt % Ta) and evacuation of the gases, a vapor pressure of PMe_3 (275 Torr; 25 °C) was introduced in the IR cell for 30 min; then the cell was evacuated at 25 °C for 2 h and 30 min. ^{31}P CP MAS NMR: $\delta = -24$ ppm; ^{13}C CP MAS NMR: $\delta = 14$ ppm. Anal.: Ta: 5.67; P: 1.02; C: 1.25; P/Ta = 1.05 and C/P = 3.16.

Reaction of 4 with Pyridine. After in situ preparation of **4** (58 mg, 5.49 wt % Ta) and evacuation of the gases, a vapor pressure of pyridine (21 Torr; 25 °C) was introduced in the IR cell for 30 min; then the cell was evacuated at 150 °C for 3 h. ^{15}N CP MAS NMR: $\delta = -120$ ppm. Anal.: Ta: 5.49; N: 0.39; C: 1.84; N/Ta = 0.92 and C/N = 5.05.

Catalytic Tests with 4. After in situ preparation of **4** and evacuation, the various gaseous reagents were introduced at the desired pressure in the cell, which was heated accordingly.

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Supporting Information Available: Ta L_{III}-edge EXAFS spectra of species **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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