

Articles

Synthesis, Characterization, and Properties of Silica-Supported Trimethylphosphine Disiloxy Tantalum Hydride, $(\equiv\text{SiO})_2\text{TaH}(\text{PMe}_3)$

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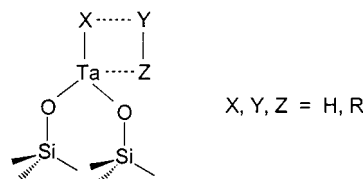
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The silica-supported tantalum hydride $(\equiv\text{SiO})_2\text{TaH}$ reacts with PMe_3 to form a new well-defined surface species, the trimethylphosphine disiloxy tantalum hydride $(\equiv\text{SiO})_2\text{TaH}(\text{PMe}_3)$. The Ta L_{III}-edge EXAFS gives a first coordination sphere of ca. two oxygen atoms at 1.955 Å and one phosphorus atom at 2.615 Å. The presence of the phosphine on the metal center cancels the catalytic activity of the tantalum hydride toward metathesis of acyclic alkanes but affords the oligomerization of ethylene into 1-butene and higher oligomers.

Introduction

We have previously reported that $\text{Ta}(-\text{CH}_2\text{CMe}_3)_3$ ($=\text{CHCMe}_3$) (**1**) reacts with the surface hydroxyl groups of a silica (Aerosil 200 m²/g) to form two different surface species, $(\equiv\text{SiO})\text{Ta}(-\text{CH}_2\text{CMe}_3)_2(=\text{CHCMe}_3)$ (**2a**) and $(\equiv\text{SiO})_2\text{Ta}(-\text{CH}_2\text{CMe}_3)(=\text{CHCMe}_3)$ (**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 are transformed into the surface tantalum(III) monohydride $(\equiv\text{SiO})_2\text{TaH}$ (**3**), which was fully characterized by infrared spectroscopy, EXAFS, elemental analysis, and quantitative chemical reactions.² The complex $(\equiv\text{SiO})_2\text{TaH}$ (**3**) proves capable of activating, at moderate temperature, the C–H bond of methane and cycloalkanes to form the corresponding surface tantalum–alkyl species with evolution of 1 equiv of H₂.^{2,3} Complex **3** can also catalyze the H/D exchange reaction between CH₄ and CD₄.⁴ The catalytic hydrogenolysis of C–C bonds of light alkanes such as butane, propane, and even ethane can be

performed in the presence of $(\equiv\text{SiO})_2\text{TaH}$.⁵ Interestingly, **3** also catalyzes the new reaction of alkane metathesis, which occurs by the concomitant cleavage and formation of C–C bonds of light acyclic alkanes and produces an equimolar amount of higher and lower homologues.⁶ So far all these reactions involve σ -bond metathesis processes with four-center intermediates:⁷



We believe that the exceptional catalytic properties of **3** are related to the high electron deficiency of this immobilized complex (here **3** is finally an 8-electron species (or 12 if one counts the p_π – d_π back-donation of the two oxygen 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 reactions. It was therefore interesting to check whether the coordination of an external 2-electron ligand such as PMe_3 would occur and to what extent it would modify the catalytic properties of $(\equiv\text{SiO})_2\text{TaH}$ (**3**). We report here the synthesis, characterization, and preliminary results on the properties of $(\equiv\text{SiO})_2\text{TaH}(\text{PMe}_3)$ (**4**).

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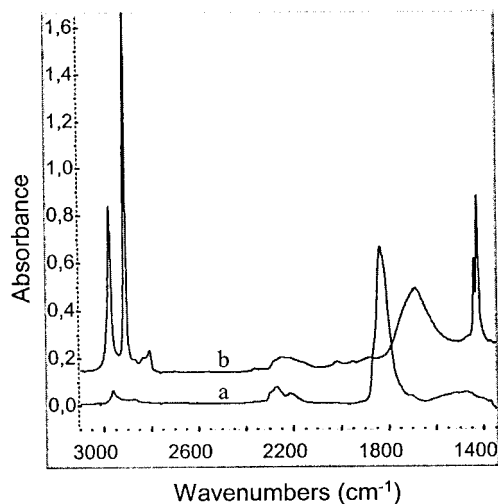


Figure 1. IR spectra of the products of the reaction of trimethylphosphine with the silica-supported tantalum hydride: (a) $(\equiv\text{SiO})_2\text{TaH}$; (b) $(\equiv\text{SiO})_2\text{TaH}(\text{PMe}_3)$ (silica spectrum subtracted).

Results and Discussion

When the tantalum hydride $(\equiv\text{SiO})_2\text{TaH}$ is treated at room temperature with trimethylphosphine ($\text{PMe}_3/\text{Ta} \approx 4$), the $\nu(\text{Ta}-\text{H})$ bands centered at 1830 cm^{-1} are shifted to 1687 cm^{-1} ; the bands due to trimethylphosphine also appear at 2975 , 2911 ($\nu(\text{CH})$) and 1437 , 1423 cm^{-1} ($\delta(\text{CH})$), respectively (Figure 1). These $\nu(\text{CH})$ and $\delta(\text{CH})$ bands resist a prolonged desorption under high vacuum at $25\text{ }^\circ\text{C}$, whereas a blank experiment indicates that the trimethylphosphine does not remain physisorbed on the silica surface under similar conditions; these results suggest that the trimethylphosphine has been coordinated to the tantalum center to form a new silica-supported tantalum species: the trimethylphosphine disiloxy tantalum hydride $(\equiv\text{SiO})_2\text{TaH}(\text{PMe}_3)$ (**4**), the characterization of which will be described now. The IR bands at 1687 cm^{-1} disappear under D_2 (400 Torr) at room temperature and reappear quantitatively under H_2 , which confirms that these bands still correspond to hydride species (the strong absorbance of silica below 1300 cm^{-1} does not allow the observation of the corresponding $\nu(\text{TaD})$ bands). The ^{31}P CP MAS NMR spectrum of **4** presents a unique peak at $\delta -8$ ppm, whereas PMe_3 physisorbed on silica gives a peak at $\delta -57$ ppm; The ^{13}C CP MAS NMR spectrum of **4** gives a signal at $\delta 12$ ppm corresponding to the methyl groups of the phosphine. The elemental analysis of **4** gives 2.96 ± 0.10 equiv of C per Ta and 0.98 ± 0.10 equiv of P per Ta. All these results prove consistent with the coordination of one phosphine to the tantalum center. Analysis of the Ta L_{III}-edge EXAFS of the new Ta species **4** (Table 1; Figure 2) gave a first coordination sphere of ca. two oxygen atoms at 1.955 \AA and one phosphorus atom at 2.615 \AA , consistent with the presence of two σ -bonded surface Si-O groups and one π -coordinated phosphine. The fit was slightly improved by considering a third shell of silicon (1.5 Si at 3.282 \AA). The EXAFS-derived Ta-P distance compares well with similar single-crystal X-ray distances found in phosphine tantalum complexes: $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_4]$, $2.633(6)$, $2.567(5)$, $2.559(5)$, and $2.628(6)\text{ \AA}$;^{8a} $[\text{Ta}(\mu\text{-Cl})\text{Cl}_2(\text{PMe}_3)_2]_2$, $2.666(4)$ and

Table 1. Ta L_{III}-Edge EXAFS-Derived Structural Parameters for the Trimethylphosphine Bis Siloxy Tantalum Hydride Species: $(\equiv\text{SiO})_2\text{TaH}(\text{PMe}_3)$ **4**.

shell	coord no.	interatomic dist, \AA	$2\sigma^2, \text{\AA}^2$	ρ factor ^b
O	2.05	1.955	0.009	0.04
P	1.0	2.615	0.013	
Si	1.5	3.282	0.028	

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

$2.598(4)\text{ \AA}$;^{8b} $[\text{Ta}(\text{OC}_6\text{H}_3\text{-2,6-Cy}_2)_2(\text{H})_3(\text{PMe}_2\text{Ph})_2]$, $2.615(3)\text{ \AA}$.⁹ Interestingly, the presence of the phosphine on the tantalum center in **4** seems to bring some lengthening of the Ta-O bonds compared to $(\equiv\text{SiO})_2\text{TaH}$ (**3**) ($d_{\text{Ta-O}} = 1.893\text{ \AA}$)² or to aryloxy and siloxy tantalum complexes: $[\text{Ta}(\text{OC}_6\text{H}_3\text{-2,6-Cy}_2)_2(\text{H})_3(\text{PMe}_2\text{Ph})_2]$, $1.901(6)\text{ \AA}$;⁹ $[\text{Ta}(\text{H})_2(\text{OSi}^t\text{Bu}_3)_2]_2$, $1.86(3)\text{ \AA}$;^{10a} $[\text{Ta}(\text{OSi}^t\text{Bu}_3)_3]_2(\mu\text{-C}_2)$, $1.878(9)\text{ \AA}$.^{10b} The EXAFS results thus provide direct structural evidence of the coordination of one phosphine molecule to the silica-supported tantalum hydride to form the trimethylphosphine disiloxy tantalum hydride species $(\equiv\text{SiO})_2\text{TaH}(\text{PMe}_3)$ (**4**). Unlike some Ta-PMe₃ complexes, no intramolecular C-H bond activation on the methyl groups occurs which would lead to cyclometalation; indeed, no hydrogen evolution is observed during the coordination of the phosphine and the ^{13}C CP MAS NMR spectrum shows only one peak.¹¹

The presence of a strongly basic phosphine ligand such as PMe_3 on the tantalum brings a deep modification in its catalytic properties. In contrast to $(\equiv\text{SiO})_2\text{TaH}$ (**3**), complex **4** is not able to activate the C-H bonds of alkanes; it cannot catalyze the H/D exchange reaction between CH_4 and CD_4 , the hydrogenolysis of light acyclic alkanes, or the alkane metathesis reaction. These results suggest that the phosphine either strongly decreases the electrophilic properties of the Ta-H or coordinates with some orbital such as the one used for C-H or C-C bond activation. Since the two free electrons in the tantalum hydride structure may be involved in the above-mentioned catalytic reactions, they can no longer play their usual role.

However, the presence of the trimethylphosphine does not inhibit the reaction of the tantalum hydride with *n*-butyl bromide, which leads to the liberation of 1 ± 0.05 equiv of butane per Ta. Furthermore, complex **4** can achieve at $25\text{ }^\circ\text{C}$ the insertion of one ethylene molecule into its Ta-H bond to form the corresponding surface tantalum ethyl complex $(\equiv\text{SiO})_2\text{Ta}(\text{Et})(\text{PMe}_3)$ (**5**)

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(11) The formation of $\text{Ta}(\eta^2\text{-CHPMe}_2)(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)_3$ and $\text{Ta}(\eta^2\text{-CHPMe}_2)\text{Cl}(\text{PMe}_3)_4$ from the reaction of TaCl_5 with sodium sand in liquid PMe_3 was reported (Green, M. L. H.; Hare, P. M.; Bandy, J. A. *J. Organomet. Chem.* **1987**, *330*, 61), whereas that of $\text{Cp}^*\text{Ta}(\eta^2\text{-CHPMe}_2)(\text{H})_2(\text{PMe}_3)$ resulted from the same reduction with Cp^*TaCl_4 (Gibson, V. C.; Kee, T. P.; Carter, S. T.; Sanner, R. D.; Clegg, W. J. *Organomet. Chem.* **1991**, *418*, 197).

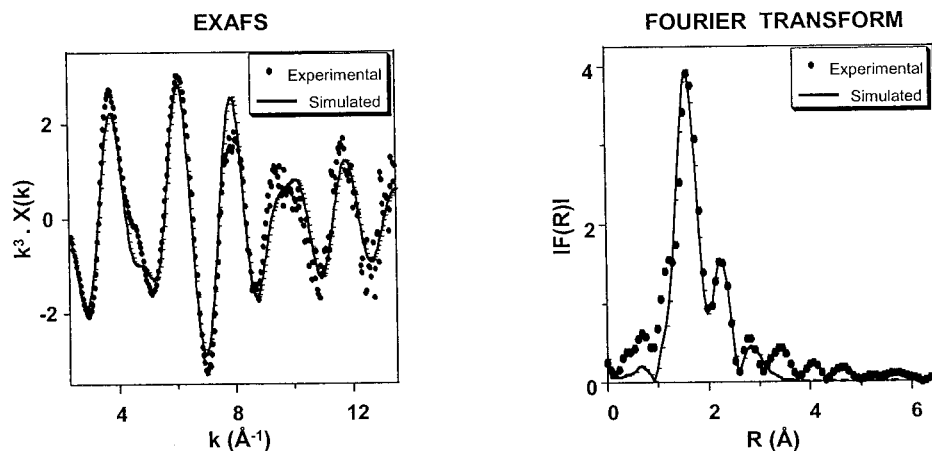
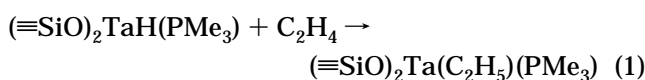


Figure 2. Comparison of experimental (dots) and simulated (line) EXAFS spectra at the tantalum L_{III} edge of (≡SiO)₂-TaH(PMe₃) (left) and modulus of the Fourier transform (right).

(eq 1).¹²



The hydrolysis of species **5** released 1 ± 0.1 equiv of C₂H₆ per Ta. Usually, the migratory insertion of an olefin into a M–H bond requires the previous coordination of the C=C double bond to the metal before the migration of the hydride; it is also assumed to involve a four-center intermediate similar to that of the reverse process of β-hydride elimination¹³ or to the β-H agostic structure.¹⁴ The formation of (≡SiO)₂Ta(Et)(PMe₃) (**5**) by insertion of ethylene into the Ta–H bond of **4** suggests that the phosphine does not block all coordination sites, whereas conversely C–H bond activation of ethane or generally σ-bond metathesis processes appear inhibited.

Furthermore, when a pressure of ethylene (340 Torr) is introduced on species **4** in a static reactor, a catalytic reaction takes place at 90 °C which leads to the dimerization of ethylene into 1-butene. When the contact time is increased, 1-butene isomerizes into *cis*- and *trans*-2-butenes and all butenes react further with ethylene to give hexenes and higher oligomers. A total turnover number of 160, based on ethylene conversion, was reached within 38 h.

In summary, the new well-defined surface organometallic species (≡SiO)₂TaH(PMe₃) (**4**) has been obtained through the coordination of PMe₃ to the silica-supported tantalum hydride **3**. Species **4** does not possess the catalytic properties of **3** with regard to the transformation of alkanes, but it can insert the ethylene molecule into its Ta–H bond at 25 °C and further oligomerize this olefin at 90 °C.

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-zeolite trap during their introduction. Silica (Aerosil Degussa, 200 m²/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.¹⁵ The preparations of **2a**, **b**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.¹⁶ Gas-phase analyses of hydrocarbons were performed on a Hewlett-Packard 5890 chromatograph equipped with a flame ionization detector and a Al₂O₃/KCl on fused silica capillary column (50 m × 0.32 mm). Gas-phase analyses of hydrogen were performed on an Intermat 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 Pascher Laboratories, Remagen-Bandorf, Germany. MAS NMR spectra were recorded on a Bruker DSX 300 spectrometer operating at 75.47 MHz for ¹³C. 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 a 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 three 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 following the single-scattering theory using software written by Michalowicz.¹⁷ The background

(12) The ¹³C CP MAS NMR spectrum of (≡SiO)₂TaEt(PMe₃) shows two broad peaks at 14 (–CH₃) and 60 ppm (–CH₂–).

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absorption was calculated by using a theoretical expression developed by Lengeler and Eisenberger,¹⁸ 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. 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 2.5 and 4 Å.

Preparation of 4. After in situ preparation of ($\equiv\text{SiO}$)₂TaH (**3**) (50 mg, 5.8 wt % Ta) under hydrogen and evacuation, a 4-fold excess of PMe₃ was introduced in the IR cell and the mixture was allowed to react at 25 °C.

H/D Exchange Reaction on 4. After in situ preparation of complex **4** in the IR cell and evacuation, 400 Torr of D₂ 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 H₂.

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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.

Reaction of 4 with C₄H₉Br. After in situ preparation of **4** and evacuation of the gases, a vapor pressure of C₄H₉Br (400 Torr; 25 °C) was introduced in the IR cell. The silica disk turned from brown to white. GC analysis indicated the liberation of 1 ± 0.05 equiv of butane per Ta.

Reaction of 4 with C₂H₄. After in situ preparation of **4** and evacuation, 2 equiv of C₂H₄ was introduced in the IR cell, which was then evacuated after 15 min. The ¹³C CP MAS NMR spectrum of the ($\equiv\text{SiO}$)₂Ta(Et)(PMe₃) species **5** obtained from di-¹³C-labeled ethylene presents a thin peak at 12 ppm and a broad peak at 50 ppm, whereas the ³¹P CP MAS NMR spectrum still shows one peak at -8 ppm. The hydrolysis of species **5** released 1 ± 0.1 equiv of C₂H₆ per Ta.

For the catalytic test, 340 Torr of ethylene was introduced in contact with **4** (85 mg, 6 wt % Ta), the reactor was heated to 90 °C, and the reaction was monitored by GC.

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