# **ORGANOMETALLICS**

# Facile and Efficient Synthesis of the Surface Tantalum Hydride $(\equiv SiO)_2 Ta^{III}H$ and Tris-Siloxy Tantalum $(\equiv SiO)_3 Ta^{III}$ Starting from Novel Tantalum Surface Species $(\equiv SiO)TaMe_4$ and $(\equiv SiO)_2 TaMe_3$

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**Supporting Information** 

**ABSTRACT:** By grafting of TaMe<sub>5</sub> (1) on the surface of silica partially dehydroxylated at 500 °C (silica<sub>500</sub>), a mixture of ( $\equiv$ SiO)TaMe<sub>4</sub> (**2a**; major, 65 ± 5%) and ( $\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub> (**2b**; minor, 35 ± 5%) was produced, which has been characterized by microanalysis, IR, and SS NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H-<sup>13</sup>C HETCOR, proton double and triple quantum). After grafting, these surface organometallic compounds are more stable than the precursor TaMe<sub>5</sub>. Treatment of **2a,b** with water and H<sub>2</sub> resulted in the formation of methane in amount of 3.6 ± 0.2 and 3.4 ± 0.2 mol/grafted Ta, respectively. **2a,b** react with H<sub>2</sub> (800 mbar) to form ( $\equiv$ SiO)<sub>2</sub>TaH. After ( $\equiv$ SiO)<sub>2</sub>TaH was heated to 500 °C under hydrogen or vacuum, [( $\equiv$ SiO)<sub>3</sub>Ta][ $\equiv$ SiH] was produced, and the structure was confirmed by IR, NMR, and EXAFS. Considering the difficulty of the previous prepare tantalum surface species ( $\equiv$ SiO)<sub>2</sub>TaH is in the formation of the difficulty of the previous prepare tantalum surface species ( $\equiv$ SiO)<sub>2</sub>TaH.



and  $(\equiv SiO)_3Ta$  via the intermediate of the new surface organometallic precursors:  $(\equiv SiO)TaMe_4/(\equiv SiO)_2TaMe_3$ .  $(\equiv SiO)_2TaH$  and  $(\equiv SiO)_3Ta$  exhibit equal reactivities in alkane metathesis and ethylene polymerization in comparison to those in previous reports.

# INTRODUCTION

Immobilization of organometallic complexes on solid supports, such as oxides, zeolites, and metals, allows the preparation of relatively well-defined surface species acting as highly selective heterogeneous catalysts,<sup>1,2</sup> which are commonly regarded as "single site" catalysts. Some extremely unstable species can be isolated effectively by this strategy: for example, immobilized tantalum species on partially dehydroxylated silica (silica<sub>700</sub>), ( $\equiv$ SiO)Ta(=CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>,<sup>3</sup> can leads to supported tantalum hydride ( $\equiv$ SiO)<sub>2</sub>Ta(H)<sub>x</sub> (x = 1-3, depending on preparation conditions) upon hydrogenolysis. The highly electron deficient nature of similar hydride species with M = Ti,<sup>4</sup> Zr,<sup>5</sup> Hf,<sup>6</sup> Ta,<sup>7</sup> W<sup>8</sup> gives rise to unusual catalytic activity: for example, in the low-temperature hydrogenolysis of acyclic alkanes or polyolefins (Ziegler-Natta depolymerization) via C-H and C-C bond activation and cleavage.<sup>9</sup> More interestingly, the supported tantalum hydrides catalyze the metathesis of alkanes in which acyclic alkanes are transformed into their lower and higher homologues.<sup>1,10,11</sup>

In addition,  $(\equiv \text{SiO})_2 \text{Ta}(\text{H})_x$  (x = 1-3) favors activation of the N $\equiv$ N bond in dinitrogen<sup>12-14</sup> and the C-H and C-C bonds in alkanes,<sup>15-20</sup> promoting alkane metathesis, the nonoxidative coupling of methane,<sup>18</sup> and cleavage of alkanes by methane.<sup>10</sup> The surface Ta<sup>III</sup> species ( $\equiv$ SiO)<sub>3</sub>Ta<sup>21,22</sup>

prepared from  $(\equiv SiO)_2 Ta(H)_x$  is active for ethylene polymerization.<sup>23</sup> However, the synthesis of the surface compound ( $\equiv$  SiO)Ta(=CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>, a crucial precursor for the Ta hydrides, is very tedious.<sup>2,24</sup>

We have been inspired by our recent syntheses of various monopodal silica surface complexes that we found to be stable on surfaces:  $(\equiv SiO)TaMe_2Cl_2$ ,<sup>25</sup>  $(\equiv SiO)WMe_5$ ,<sup>26</sup> and  $(\equiv$ SiO)Ta $(\equiv CH_2)Cl_2$ .<sup>27</sup> All of these compounds contain a methyl ligand which, in contrast to the neopentyl or neopentylidene ligand, does not contain  $\beta$ -H or  $\gamma$ -H. Therefore, we considered that the methyl ligand could be another option to develop surface tantalum chemistry. Thus, we decided to prepare the silica-supported ( $\equiv$ SiO)TaMe<sub>4</sub> using TaMe<sub>5</sub> as the starting material. Although this molecular compound is not stable and readily decomposes at room temperature via a multimolecular pathway,<sup>28</sup> we expected that its stability could be improved due to immobilization.

Herein, we report the preparation of novel well-characterized surface tantalum<sup>V</sup> methyl complexes ( $\equiv$ SiO)TaMe<sub>4</sub> (2a) and ( $\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub> (2b) by the reaction of TaMe<sub>5</sub> with silica partially dehydroxylated at 500 °C (silica<sub>500</sub>). These surface

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Scheme 1. Synthesis of (=SiO)TaMe<sub>4</sub>/(=SiO)<sub>2</sub>TaMe<sub>3</sub> (2a,b)



Figure 1. (a) 600 MHz <sup>1</sup>H MAS NMR spectrum of  $(\equiv$ SiO)TaMe<sub>4</sub>/ $(\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub> (2). (b, c) Two-dimensional contour plots of the double (DQ)- and triple-quantum (TQ) proton solid-state NMR correlation spectra of 2. (d) <sup>13</sup>C CP-MAS NMR of 2. (e) Contour plot of the aliphatic region of the <sup>1</sup>H-<sup>13</sup>C HETCOR spectrum of 2.

organotantalum complexes are easily transformed into ( $\equiv$  SiO)<sub>2</sub>TaH and ( $\equiv$ SiO)<sub>3</sub>Ta by controlled hydrogenolysis.

## RESULTS AND DISCUSSION

TaMe<sub>5</sub> was synthesized according to a modified procedure (see NMR in the Supporting Information).<sup>28</sup> An essentially pure pentane solution of TaMe<sub>5</sub> reacted with Aerosil<sub>500</sub> in situ to afford a grayish powder product which was identified as a mixture of ( $\equiv$ SiO)TaMe<sub>4</sub> (2a) and ( $\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub> (2b) (Scheme 1).

Upon adsorption of the pentane solution of TaMe<sub>5</sub>, the characteristic IR bands of the silanol groups at 3747 cm<sup>-1</sup> (sharp) and 3646 cm<sup>-1</sup> (broad) disappear (Figure S2, Supporting Information), a new broad band at 2932 cm<sup>-1</sup> appears which is assigned to the  $\nu$ (C–H) band of the methyl groups, and a band at 1397 cm<sup>-1</sup> belongs to the  $\delta$ (C–H) vibrations of the same ligand. Elemental analysis gives 7.85% Ta, 1.90% C, and 0.48% H with the Ta/C/H ratio = 1.0/(3.6 ± 0.3)/(11.0 ± 1.0) (theoretical ratio for the monopodal species1.0/4.0/12.0), which indicates that 96% of the silanols are consumed and the compound is not a purely monopodal species. The structure of this compound has been further confirmed by NMR spectroscopy<sup>29</sup> and mass balance.

NMR Study. The <sup>1</sup>H-MAS NMR spectrum of 2 displays a main signal at 0.9 ppm, as well as two peaks of weak intensity at 1.9 and 0.0 ppm; these two peaks can be assigned respectively to the small amount of unreacted silanols on the surface (1.90 ppm) and a trace amount of gaseous methane or  $\equiv$ SiMe<sup>25</sup> (0.0 ppm; Figure 1a). In order to get a better signal to noise ratio  $2^*$ (<sup>13</sup>C 97% enriched) was synthesized according to the same protocol starting from <sup>13</sup>CH<sub>3</sub>I. The <sup>13</sup>C CP/MAS NMR spectrum of 2\* displays only one signal at 72 ppm, and <sup>1</sup>H-<sup>13</sup>C HETCOR NMR shows a correlation of the <sup>1</sup>H signal at 0.9 ppm with the <sup>13</sup>C signal at 72 ppm (Figure 1e). Proton double (DQ)- and triple-quantum (TQ) autocorrelation spectra with 22 kHz MAS (Figure 1b,c) support the hypothesis that the signal belongs to the methyl group, as autocorrelation peaks are observed on the diagonal of the 2D DQ and TQ spectrum (0.9 ppm in F2 and 1.8, 2.7 ppm in F1, respectively). However, these NMR results did not show a difference between 2a and 2b.

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With <sup>13</sup>C CP-MAS NMR we observed room-temperature decomposition of **2**, since a broad peak at 50–70 ppm appeared (Figure S3, Supporting Information); GC analysis shows methane as the main product in the gas phase, and more methane is produced upon hydrolysis. As we know, on the surface of silica<sub>500</sub> the concentration of silanol groups is around

Scheme 2. Synthesis of (≡SiO)<sub>2</sub>TaH and (≡SiO)<sub>3</sub>Ta and the Corresponding PMe<sub>3</sub>-Coordinated Compounds



2 OH/nm<sup>2 30</sup> and the silanol groups are close in space (average distance around 7 Å on the basis of calculations), so that **2** possibly decomposed by a surface "bimolecular" pathway. However, in comparison to the case for  $TaMe_5$ , which decomposes readily at room temperature in a few hours, the grafted species are much more stable.

**Hydrolysis of** ( $\equiv$ SiO)TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub>. When 2a,b were treated with water vapor (13 mbar), the solid turned white rapidly and the IR band at 1800 cm<sup>-1</sup> region completely disappeared; methane was found as the main product in the gas phase, and the gas analysis revealed that methane was produced in an amount of 1.52 ± 0.15 mmol/(g of ( $\equiv$ SiO)TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub>) (Ta/C ratio 1.0/(3.6 ± 0.3)), which agrees well with the data from elemental analysis and suggests a ( $\equiv$ SiO)TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>SiO)<sub>2</sub>TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>SiO)<sub>2</sub>TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>SiO)<sub>2</sub>S

Hydrogenolysis of ( $\equiv$ SiO)TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub>. ( $\equiv$ SiO)TaMe<sub>4</sub>/( $\equiv$ SiO)<sub>2</sub>TaMe<sub>3</sub> readily react with H<sub>2</sub> at 80 °C (Scheme 2), after treatment under H<sub>2</sub> for 1 h (500 mbar, 80 °C); the characteristic  $\nu$ (Ta–H) band around 1830 cm<sup>-1</sup> is identical to the IR band of Ta–H previously observed by us,<sup>5</sup> and simultaneously the intensity of the  $\nu$ (C–H) bands at 2900 cm<sup>-1</sup> decreases (Figures S4 and S5, Supporting Information). At 150 °C, the reaction was complete within 3 h. Methane was found as the main product in the gas phase, and gas analysis revealed 1.42 ± 0.2 mmol of methane produced/g of 2 (Ta/C ratio 1.0/(3.4 ± 0.3)), which matches previous results.

**Preparation of** ( $\equiv$ SiO)<sub>2</sub>TaH. When 2a and 2b were treated at 200 °C with hydrogen (800 mbar) for 1 h, followed by evacuation at 10<sup>-5</sup> mbar for another <sup>1</sup>/<sub>2</sub> h, the tantalum hydride was produced, which has the characteristic  $\nu$ (Ta-H) IR band at 1830 cm<sup>-1</sup>, and a new band at 2269 cm<sup>-1</sup> for the Si-H produced in the reaction is also observed. The band at 1830 cm<sup>-1</sup> disappeared after a H<sub>2</sub>-D<sub>2</sub> exchange, at which point a new band  $\nu$ (Ta-D) at ca. 1320 cm<sup>-1</sup> appeared (Figure 2a).

$$[Ta]_{s}H + CH_{3}I \rightarrow [Ta]_{s}I + CH_{4}$$

This compound was identified by  $CH_3I$  titration and methane evolution, as halogenated hydrocarbons are known to exhibit a high reactivity toward early-transition-metal hydrides.<sup>6</sup> The treatment of 3 with  $CH_3I$  vapor (13 mbar; 25 °C) for 10 min resulted in the complete disappearance of its IR band at 1830 cm<sup>-1</sup> and methane evolution to the gas phase. Gas analysis revealed that methane is produced in an amount of  $0.41 \pm 0.04$  mmol/g of 3 (Ta/H =  $0.96 \pm 0.1$ ) (on the basis of the data from elemental analysis). This indicates the presence of



**Figure 2.** (a) IR spectrum of  $(\equiv SiO)_2$ TaH prepared from 2 (green), spectrum after D<sub>2</sub> exchange (purple), and subtraction spectrum (red). (b) IR spectrum of  $(\equiv SiO)_2$ TaH (purple), spectrum after addition of PMe<sub>3</sub> (green), and subtraction spectrum (red).

tantalum monohydride on the silica surface, denoted as ( $\equiv$  SiO)<sub>2</sub>Ta<sup>III</sup>H.

After treatment of  $(\equiv SiO)_2$ TaH with PMe<sub>3</sub> (13 mbar) at room temperature for a few minutes, IR spectra showed that the band for  $\nu$ (Ta-H) at 1830 cm<sup>-1</sup> disappeared and a new peak appeared at 1304 cm<sup>-1</sup> (Figure 2b). The <sup>31</sup>P CP-MAS solid-state NMR spectrum showed a main broad peak at -13.0 ppm for ( $\equiv SiO)_2$ Ta<sup>III</sup>H(PMe<sub>3</sub>) (Figure 3 and Figures S7a and S8a (Supporting Information); a very small peak at 6 ppm may



Figure 3. 1D <sup>31</sup>P CP-MAS NMR spectrum of  $(\equiv SiO)_2 Ta^{III}H(PMe_3)$ .

contribute to a trace amount of  $(\equiv SiO)_2 Ta^V H_3(PMe_3))$ , which coincide with those in a previous report.<sup>31</sup>

Alkane Metathesis with  $(\equiv SiO)_2TaH$  (3). Under the same conditions as reported before, <sup>15-20</sup> we tested the reactivity of  $(\equiv SiO)_2TaH$  as prepared in alkane metathesis in a batch reactor (Table 1). When propane (420 equiv) was

Table 1. Alkane Metathesis with (≡SiO)<sub>2</sub>TaH as Prepared

		product selectivity, %					
alkane <sup>a</sup>	$TON^b$	C1	C2	C3	C4	C5	C6
propane	63 (14.1)	15.4	39.1		36.3	7.8	
butane	79 (17.7)	1.7	13.4	37.2		31.3	10.8

<sup>a</sup>After 120 h of reaction in a batch reactor (Ta/alkane ratio ~420, 150 °C, 0.95 atm). <sup>b</sup>TON is expressed in (mol of alkane transformed)/ (mol of Ta). The values in parentheses are conversions.

brought into contact with 3 at 150 °C in a batch reactor, it was converted mainly into methane (15.4%), ethane (39.1%), butanes (36.3%), and pentanes (7.8%), with a TON of 63 after 120 h (more information can be found in Table S2, Supporting Information). When the reaction was carried out with butane, the TON was found to be 79. These results demonstrate that the tantalum hydride prepared from the TaMe<sub>5</sub> precursor has a reactivity and selectivity toward alkane metathesis equivalent to those previously reported.

**Preparation of** ( $\equiv$ SiO)<sub>3</sub>**Ta.** After vacuum or hydrogen treatment at 200–500 °C (50 °C/h, Scheme 2) for 10 h, ( $\equiv$  SiO)<sub>2</sub>TaH<sub>x</sub> is converted into ( $\equiv$ SiO)<sub>3</sub>Ta<sup>III</sup>. The intensity of IR band of  $\nu$ (Ta-H) at 1830 cm<sup>-1</sup> decreases with time, while the intensity of the  $\nu$ (Si-H) band at 2170 cm<sup>-1</sup> increases (Figures S4 and S6, Supporting Information).<sup>21</sup>

The coordinated complex  $(\equiv SiO)_3 Ta(PMe_3)$  was also synthesized and characterized by NMR. The <sup>13</sup>C NMR spectrum shows a sharp peak at 10 ppm, and the <sup>31</sup>P NMR spectrum shows a main broad peak at -23.2 ppm (Figure 4 and and Figures S7b and S8b (Supporting Information))<sup>23</sup> instead of the peak at -13.0 ppm of  $(\equiv SiO)_2 Ta^{III}H(PMe_3)$ .

Upon the hydrolysis of the complex formed by reacting ( $\equiv$  SiO)<sub>3</sub>Ta with 2-pentyne, *cis*-2-pentene is evolved as the major product at a ratio of 5:1 to *trans*-2-pentene (Scheme 3). This further supports the Ta<sup>III</sup> species on the silica surface by analogy with that found by Wolczanski et al. for Ta-(OSilox)<sub>3</sub>.<sup>23,32</sup>



Figure 4. (a)  ${}^{13}C$  and (b)  ${}^{31}P$  CP-MAS NMR spectra of ( $\equiv$  SiO)<sub>3</sub>Ta<sup>III</sup>(PMe<sub>3</sub>).

Scheme 3. Reaction between  $(\equiv SiO)_3$ Ta and 2-Pentyne



The tantalum  $L_{III}$ -edge EXAFS signal is acquired for the ( $\equiv$ SiO<sub>3</sub>Ta as prepared. As we know 2 is possibly decomposed by a surface "bimolecular" pathway, we analyzed the EXAFS data of 3 with increased k range to identify any possible cluster formed on the surface, since the detection of Ta-Ta contributions with a bond distance ranging from 2.9 to 3.1 Å is best resolved when k values are higher than 10.5 Å<sup>-1</sup> (for a tantalum cluster supported on silica<sup>33</sup>). Thus, the value of k range we used was up to 12.6 Å<sup>-1</sup>, and no contribution attributed to the presence of a Ta-Ta bond could be found, illustrating that the formation of a tantalum cluster is negligible in the preparation of  $(\equiv SiO)_3$ Ta. Analysis results indicate a first coordination sphere consisting of  $2.9 \pm 0.4$  oxygen atoms in the vicinity of tantalum with a Ta–O distance of  $1.88 \pm 0.01$ Å (Figure 5 (bottom), Table 2). This is in agreement with the previously reported formation of a tris-siloxy tantalum complex.<sup>21</sup>

The reactivity of  $(\equiv SiO)_3$ Ta as prepared was tested in ethylene polymerization, under 50 bar of ethylene at 70 °C;



**Figure 5.** Imaginary part of the back Fourier transforms (top) and Fourier transforms (bottom) of the EXAFS  $k^2 \chi(k)$  functions for ( $\equiv$  SiO)<sub>3</sub>Ta<sup>III</sup>. Experimental data are given as open white squares, while the solid red lines are the fit results conducted with a *k* range of 3.4 up to 9.8 Å<sup>-1</sup> and with an *R* range of 1 up to 2.3 Å.

neighboring atom of Ta	no. of atoms	distance (Å)	Debye–Waller factor $(\sigma/\text{\AA})$					
Та-О	$2.9\pm0.4$	$1.88 \pm 0.01$	$0.008 \pm 0.001$					
$^aR$ factor 0.002 ( $\Delta k$ = 3.4–9.8 Å $^{-1}$ ); energy shift $\Delta E_0$ = –1.81 (2) eV; amplitude factor $S_0{}^2$ = 1.04.								

polyethylene was produced with an efficiency of 78 (kg of PE)/ ((mol of Ta) h), which is equal to that in a previously reported case.<sup>23</sup>

### CONCLUSION

These results show a simple and efficient way to prepare surface organometallic compounds of tantalum. The fact that we can obtain identical data in both spectroscopic and catalytic results is a proof of the reliability of surface organometallic chemistry to prepare well-defined surface compounds for catalysis, and we are able to prepare the same surface compound from different precursors.

This study confirms that the unstable metal methyl compounds become more stable in the monomolecular state after grafting on the silica surface, as we already observed with  $(\equiv$ SiO)TaMe<sub>2</sub>Cl<sub>2</sub> and  $(\equiv$ SiO)WMe<sub>5</sub>, and provides a possibility to study the decomposition of the unstable methylmetal compounds.

Finally, the methyl ligand seems to be much more interesting than the neopentyl ligand, due to the relative simplicity of the synthesis and easy characterization; the use of a cheap and commercially available starting material also facilitates the inexpensive and immediate preparation.

# EXPERIMENTAL SECTION

**General Procedures.** All experiments were carried out under an inert atmosphere, using Schlenk and glovebox techniques for the organometallic synthesis. For the synthesis and treatments of the surface species, experiments were carried out using high-vacuum-line  $(10^{-5} \text{ mbar})$  and glovebox techniques. Infrared spectra (transmission) were recorded on a Nicolet Magna 6700 FT spectrometer equipped with a cell under a controlled atmosphere. Elemental analyses were performed at the Mikroanalytisches Labor Pascher in Germany (Table S1, Supporting Information). Liquid NMR spectra were recorded on Bruker Avance 500 spectrometers, and solid state NMR spectra were recorded under MAS on a Bruker Avance 400 instrument. All chemical shifts were given relative to the residual <sup>1</sup>H or <sup>13</sup>C resonance in the deuterated solvents.

**Preparation of Compounds.** *TaMe*<sub>5</sub> (1). Under an argon atmosphere, TaCl<sub>5</sub> (359 mg, 1 mmol) was placed in one compartment of a chilled (-30 °C) double-Schlenk tube with 15 mL of dry pentane; after the mixture was stirred for 5 min, 200 mg of MeLi powder (60% purity based calibration, ca. 5.5 equiv) was added into the suspension in small portions. The reaction mixture was stirred at -20 to -10 °C for 2 h; the suspension became black, and after it stood for a few minutes, it separated into a bright yellow solution and a dark gray precipitate. The solution was filtered into the other compartment of the double Schlenk to give a pure solution of TaMe<sub>5</sub> (0.027 mmol/mL based on gas analysis of methane produced in hydrolysis of a 1 mL solution, yield 41%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ 0.88 (s, 15H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, -10 °C): δ 82.0. <sup>1</sup>H-<sup>13</sup>C COSY: <sup>1</sup>H 0.88 ppm correlated with <sup>13</sup>C 82.0 ppm.

(≡SiO)TaMe₄/(≡SiO)<sub>2</sub>TaMe<sub>3</sub> (2). In a chilled (−30 °C) double-Schlenk tube, silica Aerosil<sub>500</sub> (0.8 g of Aerosil<sub>200</sub> was dehydroxylated at 500 °C for 15 h under 10<sup>-5</sup> mBar vacuum) was placed in one compartiment, followed by chilled TaMe<sub>5</sub> solution produced in the first step from 1 mmol of TaCl<sub>5</sub>. The reaction mixture was stirred at −20 °C for 1 h, and the silica became grayish; after filtration and washing three times with chilled pentane, the product was dried in vacuo for 1 h at −20 °C. Then, it was dried in vacuo (10<sup>-5</sup> mBar) for an additional 1 h to afford a grayish powder. Elemental analysis gave Ta 7.85%, C 1.92%, H 0.48%, Cl <0.1%.

(≡SiO)<sub>2</sub>TaH (3) and (≡SiO)<sub>2</sub>TaH(PMe<sub>3</sub>) (4). 2 (1.0 g) was placed in a 150 mL Schlenk tube and heated to 200 °C under H<sub>2</sub> (800 mbar) for 1 h and under vacuum for another  $^{1}/_{2}$  h to afford a brown powder. Elemental analysis gave 7.97 wt % of tantalum with trace amounts of carbon and hydrogen belonging to the transfer of methyl groups to the silica surface. 3 (100 mg) was placed in a Schlenk flask through a septum, and after evacuation (10<sup>-5</sup> mbar), PMe<sub>3</sub> (10 µL) was added via syringe at room temperature. After standing for 1 h, the excess PMe<sub>3</sub> was removed in vacuo to yield 4 as a black solid. Elemental analysis gave Ta 7.72%, C 2.48%, H 0.56%, P 1.60%.

Alkane Metathesis with **3**. A 100 mg portion of **3** was placed in a 400 mL Schlenk batch reactor, and after evacuation to  $10^{-5}$  mbar, 0.95 atm of dry propane or butane was added. The reactor was heated to 150 °C for 120 h, and the products were analyzed by GC.

 $(\equiv$ SiO)<sub>3</sub>Ta<sup>III</sup> (5) and  $(\equiv$ SiO)<sub>3</sub>Ta<sup>III</sup>(PMe<sub>3</sub>) (6). A 0.5 g portion of 3 was placed in a 100 mL Schlenk tube and heated under vacuum or H<sub>2</sub> (800 mbar) to 500 °C to afford a dark brown powder of 5. Elemental analysis gave 7.70 wt % of tantalum with trace amounts of carbon and hydrogen. 6 was prepared as described for 4. Elemental analysis gave Ta 7.62%, C 2.42%, H 0.57%, P 1.53%. After a pellet of 5 was heated to 120 °C with dry 99.9% D<sub>2</sub> for 2 h, the IR spectrum stayed exactly

the same (Figure S4, Supporting Information); the subtraction spectrum did not show any  $\nu$ (Ta-H) band.

Ethylene Polymerization with 5. 5 (25 mg) and dry toluene (5 mL) were placed in a glass vial equipped with a magnetic stirrer. The glass vial was sealed with a rubber cap under argon. Then the vial was put into an ILS Premex parallel reactor system and stirred at 70 °C, after the reactor was purged with N<sub>2</sub> (99.999%) three times, ethylene (99.95%) was introduced into the system with 50 bar pressure. After the mixture was stirred for 1 h, the reaction was stopped and the reactor was cooled to -5 °C to condense all the volatile components. The liquid products were characterized by GC, and the PE produced was isolated by filtration.

Reaction of 5 with 2-Pentyne. A 100 mg portion of 5 was placed in a Schlenk flask with a septum, and the flask was evacuated to  $10^{-5}$ mbar. Then, 10  $\mu$ L of 2-pentyne was added by syringe. After standing for 1 h at room temperature, 50  $\mu$ L of H<sub>2</sub>O was added. The gas-phase products in the flask were analyzed by GC; 55% of 2-pentyne (corresponds to 1 equiv of the Ta<sup>III</sup> species) was consumed, and *cis*-2pentene and *trans*-2-pentene were found as the products in a ratio of 5:1.

Solid-State Nuclear Magnetic Resonance. All of the solid-state NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 400, 100, and 162 MHz resonance frequencies for  ${}^{1}$ H,  ${}^{13}$ C, and  ${}^{31}$ P respectively, with a conventional double-resonance 4 mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 17 kHz for <sup>1</sup>H and 10 kHz for <sup>13</sup>C and <sup>31</sup>P spectra. NMR chemical shifts are given with respect to TMS or H<sub>3</sub>PO<sub>4</sub> as external references. For CP/MAS <sup>13</sup>C NMR, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a crosspolarization step with a contact time of typically 1 ms, and finally acquisition of the <sup>13</sup>C signal under high-power proton decoupling. The delay between scans was set to 5 s, to allow the complete relaxation of the <sup>1</sup>H nucleus, and the number of scans was 20000 for 1D <sup>13</sup>C NMR. An apodization function (exponential) corresponding to a line broadening of 100 Hz was applied prior to Fourier transformation. For CP/MAS <sup>31</sup>P NMR, 90° pulse on the proton and a crosspolarization step with a contact time of 2 ms were used. The delay between the scans was set to 5 s, no spectral smoothing was employed prior to Fourier transformation, and the number of scans was 15000 for phosphine. For 2D HETCOR multiple-quantum spectra were recorded on a Bruker DSX-600 spectrometer with a conventional double-resonance 3.2 mm CPMAS probe. <sup>1</sup>H-<sup>13</sup>C heteronuclear correlation solid-state NMR was performed according to the following scheme: 90° proton pulse,  $t_1$  evolution period, cross-polarization (CP) to carbon spins, and detection of carbon magnetization under TPPM decoupling.  $^{34,35}$  For the cross-polarization step, a ramped radio frequency (rf) field centered at 75 kHz was applied to the protons, while the carbon rf field was matched to obtain the optimal signal. A total of 32  $t_1$  increments with 2000 scans each were collected. The sample spinning frequency was 10 kHz. Two-dimensional doublequantum (DQ) and triple-quantum (TQ) spectra were recorded with the following scheme:<sup>36</sup> excitation of DQ coherences,  $t_1$  evolution, Z filter, and detection. The spectra were recorded in a rotor synchronized fashion in  $t_1$ ; that is, the  $t_1$  increment was set equal to one rotor period (4.545  $\mu$ s). One cycle of the standard back-to-back (BABA) recoupling sequence was used for the excitation and reconversion period. Quadrature detection in  $w_1$  was achieved using the States-TPPI method. A spinning frequency of 22 kHz was used. The 90° proton pulse length was 2.5  $\mu s$ , while a recycle delay of 5 s was used. A total of 128  $t_1$  increments with 32 scans each were recorded.

**EXAFS Experiments.** All of the manipulations for the sample preparation were done inside a nitrogen-filled glovebox. Finely ground surface organometallic samples were spread uniformly on Scotch tape and folded multiple times to obtain the desired thickness. This sample was then placed inside an airtight commercial cross equipped with Kapton windows. The bottom of the cross was closed with a blank KB flange, centering ring including the O-ring, and hinged clamps. A tray for holding the specimen was then attached to the other blank KB

flange, which was held to the top of the cross. The remaining two sides of the cross were closed with KB flanges with holes where Kapton windows were pasted at the center for X-rays to pass through. X-ray absorption spectra were acquired at the National Synchrotron Light Source (NSLS) (Beamline X-18b), at Brookhaven National Laboratory, Upton, NY, USA, at room temperature at the tantalum L<sub>III</sub> edge, in the transmission mode with a double-crystal Si(111) monochromator. The flux at X18b is  $1 \times 10^{10}$  photons/s at 100 mA and 2.8 GeV, and the usable energy range is 5.8–40 keV. The calibration was done using tantalum foil of 5  $\mu$ m thickness. The spectra were recorded between 9750 and 11000 eV with a 2.0 eV step. The spectra analyzed were the result of the averaging of three such acquisitions, and it was carefully checked that the results obtained were comparable and reliable, since for each sample no evolution could be detected by comparing the spectra between the first and last acquisitions.

XAS data were analyzed using the HORAE package, a graphical interface to the AUTOBK and IFEFFIT code.<sup>37</sup> XANES and EXAFS spectra were obtained after performing standard procedures for preedge subtraction, normalization, polynomial removal, and wave vector conversion. Determination of the energy level  $(E_0)$  was performed at the first inflection point of the edge. For each atomic shell, the following structural parameters were adjusted: coordination number (N), bond length distance (R), and the so-called Debye–Waller factor via the mean-square relative displacement ( $\sigma^2$ ) of the considered bond length. The parameter  $\Delta E_{0}$ , which accounts for the difference between the experimental absorption-edge energy and its estimate made by the code, was also fitted. The amplitude factor  $(S_0^2)$  was fitted to the EXAFS spectrum obtained for the tantalum(V) methoxide (Ta- $(OMe)_5$ ) reference compound, the molecular structure of the compounds being a dimeric molecule with two [TaO<sub>6</sub>] octahedra sharing a common edge.<sup>38</sup>  $S_0^2$  was found to be equal to 1.04 (see the Supporting Information).

#### ASSOCIATED CONTENT

#### Supporting Information

Tables and figures giving IR, NMR, and other characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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In the version of this paper published on February 5, 2014, an incorrect Conflict of Interest statement appeared. In the version that appears as of February 14, 2014, the Conflict of Interest statement has been revised to accurately report on the financial interests of the authors.