Formation of a Tantalum Siloxane Cage Complex in the Reaction of (η^5-C_5Me_5)$TaMe_4$ with a Silanetriol

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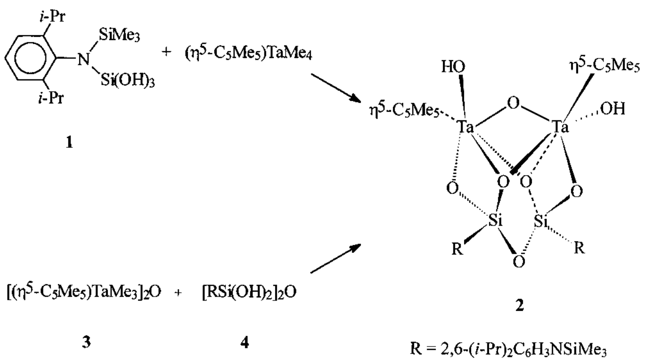
The immobilization of organometallic compounds on solid surfaces such as oxides, zeolites, or metals is a vigorously growing branch of organometallic chemistry. This field is attracting the attention of chemists due to the highly active surface species involved in the heterogeneous catalysis.[1] Furthermore, anchoring catalysts to insoluble materials reduces the loss of catalyst during the catalytic process. A common method used in preparing grafted organometallic complexes involves gas-phase reactions between silica surfaces covered with exposed hydroxyl groups and suitable organometallic precursors. For example, reaction of the trineopentyl(neopentylidene)-tantalum complex [$Ta(CH_2CMe_3)_3({=}CHCMe_3)$] with the silanol groups of partially dehydroxylated silica has been reported to yield surface carbene species.[2] Subsequent treatment of the surface species with hydrogen leads to the formation of a tantalum(III) monohydride. The nature of this species was ascertained by FT-IR and CP-MAS ^{13}C NMR spectrocopy, as well as elemental analyses and chemical reactivity. Moreover, EXAFS studies have been carried out in the case of the Ta(III) monohydride species. However, the exact structure of these surface-bound species, the nature of the bonding, and the mechanism by which the tantalum precursor reacts with the silica surface remain largely unknown. Therefore, obtaining three-dimensional *molecular* model compounds for organometallic complexes supported on the silica surface is of interest in order to identify more exactly the species present on a supported surface and understand the bonding between the metal and oxide surfaces and how these properties are related to catalytic activity.

Herein we report on the reaction of (η^5-C_5Me_5)$TaMe_4$ with the kinetically stable silanetriol **1** which leads to the stepwise formation of unexpected product **2**. Compound **2** was characterized by X-ray crystallography and represents the first example of a tantalum siloxane *cage* complex. Moreover, compound **2** can be thought of as *molecular* model for organometallic tantalum supported on a silica surface. The mechanism of this reaction involves dehydroxylation and condensation reactions, leading to stepwise formation of product **2**. Furthermore, **2** may also be prepared independently by the reaction of the known complexes **3** and **4** which support a mechanism involving a dehydroxylation step (Scheme 1).

Scheme 1



During the addition of (η^5-C_5Me_5)$TaMe_4$ to silanetriol **1**, in ether or toluene at room temperature, small amounts of methane evolution can be observed. At this stage of the reaction only the (μ-oxo)tantalum dimer **3** can be isolated from the reaction mixture and characterized by ^1H NMR, MS, and X-ray analysis.[3] If the reaction mixture is warmed slowly to 130−140 °C, further methane evolution is observed, and upon workup, the corresponding tantalum siloxane complex **2** can be isolated in moderate yield (30%) in analytically pure form. **2** has been characterized by elemental analysis and mass, IR, and NMR spectroscopic measurements, as well as single-crystal X-ray diffraction.

The crystal structure of **2**[4] shows a distorted bicapped cubane, constructed of two tantalum, two silicon, and six oxygen atoms (Figure 1). The Ta_2Si_2 tetranuclear core is surrounded by six bridging oxo ligands: four doubly bridging (μ_2-O) and two triply bridging (μ_3-O) oxygen atoms. The coordination sphere of each tantalum is completed by one terminal hydroxide ligand and one (η^5-C_5Me_5) ligand. The Ta−Ta separation of 3.099(1) Å is significantly longer than those found in Ta−Ta-bonded systems.[5] The coordination sphere of the tantalum atoms is comparable with those found in the related structure [(η^5-C_5Me_5)Ta]$_4$(μ_2-O)$_4$(μ_3-O)$_2$(μ_4-O)(OH)$_2$.[6] Due to their higher coordination number, the bond distances between Ta and the triply-bridged oxygen ligands (2.205(4)−2.342(4) Å) are significantly longer than those for μ_2-oxygen bridges (1.931(4)−1.984(4) Å).

The most intense peaks in the MS spectrum of **2** are observed at 1296 ($M^+ - H_2O$, 40%) and at 1161 ($M^+ - H_2O - C_5Me_5$, 100%). This observation indicates that ligand abstraction takes place, rather than framework decomposition, and is evidence of the remarkable stability of compound **2** in the gas phase. Infrared spectra give two characteristic sharp absorptions in the region 3599−3606 cm^{-1}, assigned to Ta−OH vibrations.[3] ^{1}H

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(4) Crystal data for **2**: $C_{50}H_{84}N_2O_8Si_4Ta_2$, $M_r = 1315.45$; monoclinic, $P2_1/c$, $a = 16.975(2)$ Å, $b = 12.771(1)$ Å, $c = 26.541(3)$ Å, $\beta = 97.91(3)$, $V = 5699.0(10)$ Å^3, $Z = 4$. The R-values are $R1 = 0.0440$ and $wR2 = 0.0981$ (all data).

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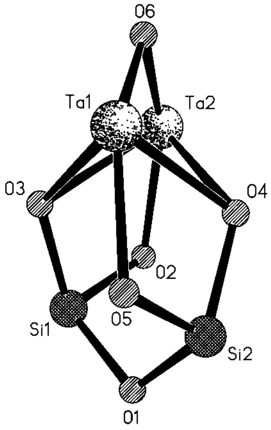

Figure 1. X-ray structure of the core atoms of **2** (all nonbridging ligands omitted for clarity). Selected bond distances (Å): Ta1−O6 1.931(4), Ta2−O6 1.932(4), Ta1−O4 2.205(4), Ta1−O5 1.987, Ta2−O4 2.304(4), Ta2−O2 1.984(4), Si2−O5 1.636(4), Si2−O4 1.673(4), Si2−O1 1.642(4), Si1−O1 1.636(4), Si1−O3 1.668(4), Si1−O2 1.635(4).

and ^{13}C NMR data in solution are consistent with structure of **2** in the solid state.[7]

In order to prove that the reaction between (η^5-C_5Me_5)$TaMe_4$ and **1** takes place stepwise via dehydroxylation processes, an independent synthesis of **2** from [(η^5-C_5Me_5)$TaMe_3$]$_2$O (**3**) and the first dehydration product of silanetriol **4**[8] was performed. Slowly warming a mixture of **3** and **4** in mesitylene as a solvent, followed by heating at 140−150 °C for 2 h and subsequent workup, leads to the formation of **2** in good yield (65%). Spectroscopic and analytical data were found to be identical to those obtained for **2** prepared via (η^5-C_5Me_5)$TaMe_4$ and the silanetriol **1**.

The analogous reaction of (η^5-C_5Me_5)$TaMe_4$ and deuterium-labeled silanetriol **1**, containing Si−OD bonds, gives rise to the deuterium-labeled analog of **2**, where only the terminal hydroxy groups are deuterated. Disappearance of the OH signal in the ^{1}H NMR spectrum and a characteristic shift of Ta−OD frequencies to 2662 and 2654 cm^{-1} in the IR spectrum in comparison to previously found Ta−OH vibrations are observed.[2] These observations are consistent with a mechanism involving dehydroxylation of the silanetriol during the formation of **2**.

A comparable dehydration mechanism was proposed earlier for the reaction of Re_2O_7 and *t*-BuSi$(OH)_3$,[9] which leads to an eight-membered cyclosiloxane framework of composition [*t*-BuSi(O)(OReO$_3$)]$_4$ on which four ReO$_4$ fragments are anchored.

Previous studies have demonstrated the presence of geminal silanols on the silica surface.[10] The results described herein indicate that dehydroxylation reactions with Si$(OH)_n$ groups which give rise to the Ta−O−Ta species should also be considered in the discussions of the mechanisms of surface reactions. Moreover, comparison of the X-ray structural results for **2** and the EXAFS data, found for the surface-bound tantalum(III) monohydride species,[2,11] allows for a more critical appraisal of structural models proposed for surface species.

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Supporting Information Available: Figures showing the X-ray structure of **2** (ORTEP-like plot with 50% probability ellipsoids) and IR spectra of **2** in the regions 4000−400 and 700−250 cm^{-1} (3 pages). An X-ray crystallographic file, in CIF format, for the complex **2** is available on the Internet only. Access and ordering information is given on any current masthead page.

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(7) A solution of RSi$(OH)_3$ (0.88 g, 2.66 mmol) in ether (30 mL) was added dropwise to the solution of (η^5-C_5Me_5)$TaMe_4$ (1.00 g, 2.66 mmol) in ether (30 mL). After addition, the reaction mixture was stirred for 8 h at room temperature. All volatiles were removed *in vacuo*, and residue was dissolved in dry mesitylene (50 mL). The solution was slowly warmed to 120−130 °C and stirred for additional 1 h. After cooling, all volatiles were removed *in vacuo* and residue was treated with *n*-hexane (15 mL). Compound **2** precipitates as pale-yellow microcrystals. Yield: 0.59 g (30%). ^{1}H NMR (CDCl$_3$; ppm): 0−0.1 (m, Si$(CH_3)_3$, 18H); 1.0−1.4 (m, CH$_3$(*i*-Pr), 24H); 1.8−2.1 (m, CH$_3$(η^5-C_5Me_5), 30H); 3.45 (sept, CH(*i*-Pr), 2H); 3.75 (sept, CH(*i*-Pr), 2H); 4.95 (s, OH, 2H); 7.0 (m, arom.H, 6H). ^{13}C NMR (CDCl$_3$; ppm): 2.06 (s, Si$(CH_3)_3$); 2.42 (s, Si$(CH_3)_3$); 10.73 (s, CH$_3$(η^5-C_5Me_5)); 11.15 (s, CH$_3$(η^5-C_5Me_5)). IR (Nujol, KBr, cm^{-1}): υ 3606 w, 3599 w, 1318 w, 1261 m, 1249 m, 1176 m, 1104 w, 1044 w, 987 s, 973 s, 952 s, 934 s, 897 m, 880 m, 839 s, 803 s, 751 w, 722 w, 691 w, 651 w, 631 w, 619 w, 580 w, 560 w, 546 w, 519 w. IR (Nujol, CsI, cm^{-1}): υ 489 w, 458 w, 439 w, 421 m, 359 s, 317 w, 303 w. Anal. Calcd for $C_{50}H_{84}N_2O_8Si_4Ta_2$: C, 45.65; H, 6.44; N, 2.13; Si, 8.54. Found: C, 45.8; H, 6.8; N, 2.1; Si, 9.0.

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(11) EXAFS studies of Ta(III) monohydride surface species indicate a first coordination sphere of Ta of two oxygens at 1.89 Å and presence of a third oxygen at 2.63 Å interacting weakly with Ta. For complex **2**, the coordination sphere of each Ta is composed of two μ_2-O at *ca.* 1.987(4) and 1.931(4) Å and two μ_3-O at *ca.* 2.2 Å.