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The first tantalasilsesquioxanes

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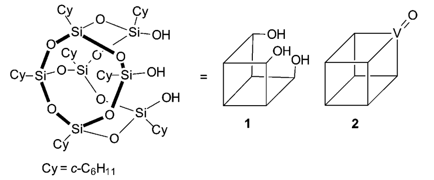
Amide routes starting from either $Ta(NMe_2)_5$ or $(C_2B_9H_{11})Ta(NMe_2)_3$ have been employed to synthesize the first tantalasilsesquioxanes including the "half-sandwich" complex $Cy_7Si_7O_{12}Ta(NMe_2)_2$ (**3**, Cy = *c*-C_6H_{11}), the anionic "sandwich" complex $[H_2NMe_2][Ta(Cy_7Si_7O_{12})_2]$ (**4**) as well as the novel "mixed-sandwich" complex $Cy_7Si_7O_{12}Ta(C_2B_9H_{11})$ (**5**) with the latter being the first example of a carborane/silsesquioxane hybrid compound.

Introduction

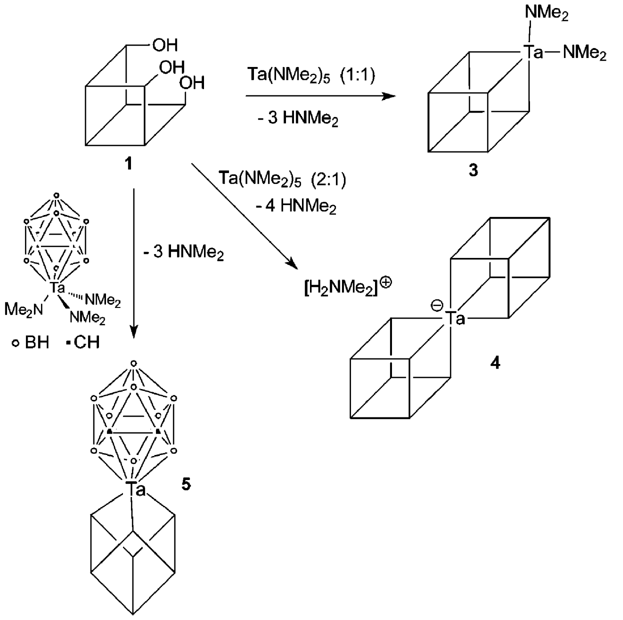
Polyhedral silsesquioxanes are in the focus of current interest in organosilicon chemistry. Their general formula $(RSiO_{1.5})_n$ places them formally between silica (SiO_2) and the silicones $(R_2SiO)_n$. Silsesquioxanes play an important role in catalysis research[1–5] as well as materials science.[6–8] Metal complexes derived from incompletely condensed silsesquioxanes such as **1**[9] (Scheme 1) are generally regarded as "realistic" model compounds for silica-immobilized heterogeneous catalysts, and various early transition metal derivatives (Ti, V, Cr, Mo) are veritable catalysts by themselves.[3] For example, the vanadyl silsesquioxane **2** (Scheme 1) has been reported to be a single-site catalyst for olefin polymerization.[10] Surprisingly, no metallasilsesquioxanes have been described for the heavier Group 5 metals,[11] presumably due to the lack of suitable synthetic procedures. We report here the synthesis of the first tantalum silsesquioxanes *via* a versatile amide route.



Scheme 1

Results and discussion

Commercially available tantalum dimethylamide, $Ta(NMe_2)_5$, was chosen as the key starting material for the development of a salt-free route leading to tantalum silsesquioxane derivatives. Clean protonation and liberation of three equivalents of dimethylamine took place upon reaction of $Ta(NMe_2)_5$ with **1** in a 1 : 1 molar ratio (Scheme 2). The pale yellow "half-sandwich" complex $Cy_7Si_7O_{12}Ta(NMe_2)_2$ (**3**) was isolated in 92% yield. It represents the first example of an amido metallasilsesquioxane derivative. Somewhat surprisingly, similar treatment of $Ta(NMe_2)_5$ with **1** in a 1 : 2 molar ratio did not lead to the formation of the neutral tantalum(V) species $Cy_7Si_7O_{12}Ta[Cy_7Si_7O_{11}(OH)]$ with one Si–OH function remaining intact. Instead, liberation of only four equivalents of dimethylamine occurred and the anionic bis(silsesquioxane) "sandwich" complex $[Ta(Cy_7Si_7O_{12})_2]^-$ was obtained in the form of its colorless dimethylammonium salt **4** (89% yield) (Scheme 2). In the resulting anion the central Ta atom is encapsulated between two silsesquioxane frameworks in a similar manner as in the neutral metal(VI) species $W(Cy_7Si_7O_{12})_2$[12] and $U(Cy_7Si_7O_{12})_2$.[13] We then investigated the possibility of adapting the amide route to more complex systems. Indeed, the amido tantalacarborane species $(C_2B_9H_{11})Ta(NMe_2)_3$[14] was found to react cleanly with one equivalent of **1** to afford the novel "mixed-sandwich" complex $Cy_7Si_7O_{12}Ta(C_2B_9H_{11})$ (**5**) which was isolated in 82% yield as an orange crystalline solid. Compound **5** is the first representative of a novel class of inorganic cage compounds in which a carborane and a silsesquioxane framework are linked through a single metal center. Further examples of such hybrid complexes should be accessible by varying either the central atom or using different carborane and silsesquioxane ligands.



Scheme 2

The compounds **3** and **4** are considerably less reactive towards atmospheric moisture than the parent amide $Ta(NMe_2)_5$. They can be handled in air for short periods of time but should be stored under nitrogen. Even more air-stable is the mixed sandwich complex **5** which shows virtually no change after several days in air. All new compounds are highly thermally stable and freely soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, toluene, THF, and diethyl ether, with the only exception that salt-like **4** has very limited solubility in

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hydrocarbon solvents. Although crystal structure determinations were hampered by severe disorder problems arising from the cyclohexyl substituents, all new compounds were fully characterized by spectroscopic methods and elemental analyses. The ^{1}H NMR spectra of compounds **3**, **4** and **5** show typical signals of the C_6H_{11} groups, and the ^{13}C NMR spectra display a characteristic 3 : 3 : 1 pattern at 25–22 ppm for the *C*H groups, in agreement with the C_{3v} symmetry of the molecules. In $CDCl_3$, both the ^{1}H and the ^{13}C NMR spectra of compound **3** display only a single resonance for the two NMe_2 methyl groups, indicating fast exchange in solution. In the IR spectra all three compounds show a very strong band at 1110–1120 cm^{-1} attributable to the Si–O–Si vibration. For compound **4** we see a strong broad signal at 3440 cm^{-1} which is typical for the N–H absorption. Given the lack of structural data from X-ray diffraction studies, CI mass spectrometry was found to be extremely helpful in unambiguously characterizing the new tantalasilsesquioxanes. In the case of the ionic compound **4** both positive and negative CI measurements have been carried out. While the molecular ion could not be detected, it was possible to observe the anion of **4** by both methods. In the positive mode the anion stabilizes by hydrogen uptake (*m*/*z* 2123) as well as addition of C_2H_5 (*m*/*z* 2151) which is typical for CH_4-CI mass spectrometry. The base peak is a fragment resulting from loss of a cyclohexyl group. In the negative mode the $[Ta(Cy_7Si_7O_{12})_2]^-$ anion is detected with the highest relative intensity. In the case of **5** CH_4-CI mass spectrometry enabled us to detect the molecular ion with its characteristic isotope pattern (maximum at *m*/*z* 1283), thus confirming the presence of a novel inorganic sandwich complex. A high intensity peak at *m*/*z* 981 (maximum) is in agreement with the fragmentation of **5** (elimination of "$Cy_2Si_2O_5$") as all typical peaks originating from the silsesquioxane cage alone have smaller *m*/*z* values.

In summarizing these results, we have identified an amide route as a versatile synthetic pathway to different tantalasilsesquioxanes. Using this simple route three unprecedented types of metallasilsesquioxanes have become easily accessible. Suitable tantalum dimethylamides are readily protonated in the presence of silsesquioxanes bearing Si–OH functional groups to form either "half-sandwich" or "sandwich" complexes depending on the stoichiometry. This salt-free method is likely to work equally well with the corresponding Nb derivatives as well as with other Si–OH functionalized silsesquioxanes. The "mixed-sandwich" complex $Cy_7Si_7O_{12}Ta(C_2B_9H_{11})$ (**5**) is just the first example of an unusual new class of hybrid compounds combining carborane and silsesquioxane chemistry.

Experimental

All reactions were carried out under dinitrogen, either in a glove-box or using conventional Schlenk techniques. Solvents were dried over Na/benzophenone and freshly distilled under nitrogen prior to use. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrometer System 2000. NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer (^{1}H 400 MHz, ^{13}C 101 MHz, ^{29}Si 79.5 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{13}C) or an internal standard (^{1}H, ^{29}Si: TMS = 0 ppm). Elemental analyses were performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS 932 apparatus. Melting and decomposition points were measured on a Electrothermal IA 9100 apparatus. The starting materials **1**,[9] $C_2B_9H_{13}$ [15] and $(C_2B_9H_{11})Ta(NMe_2)_3$ [14] were synthesized according to literature procedures.

Syntheses

$Cy_7Si_7O_{12}Ta(NMe_2)_2$ (3). A solution of **1** (730 mg, 0.75 mmol) in 20 ml THF was slowly added at room temperature to a solution of $Ta(NMe_2)_5$ (300 mg, 0.75 mmol) in 20 ml THF. The reaction mixture was stirred for 24 h and the solvent was removed under reduced pressure to afford the pure product as a pale yellow solid. Yield 885 mg (0.69 mmol, 92%). Mp > 300 °C (dec.). Found (Calc. for $C_{48}H_{95}N_2O_{12}Si_7Ta$): C, 44.70 (44.91); H, 7.78 (7.46); N, 3.02 (3.27)%. ^{1}H NMR (25 °C, $CDCl_3$): δ 2.65 (s, 12H, NMe_2), 1.72 (br m, 35H, CH_2), 1.22 (br m, 35H, CH_2), 0.76 (br m, 7H, CH). ^{13}C{H} NMR (25 °C, $CDCl_3$): δ 43.5 (s, NCH_3), 27.74, 27.60, 27.00, 26.80, 26.61 (s, CH_2), 24.91, 23.35, 23.06 (s, 3 : 3 : 1, CH). MS (CI-CH_4, relative intensity): *m*/*z* 955 (20%), 871 (40%), 811 (100%). IR (KBr disc): 2922s, 2850s, 1110vs cm^{-1}.

$[H_2NMe_2][Ta(Cy_7Si_7O_{12})_2]$ (4). A solution of **1** (1460 mg, 1.50 mmol) in 20 ml THF was slowly added at room temperature to a solution of $Ta(NMe_2)_5$ (300 mg, 0.75 mmol) in 20 ml THF. The reaction mixture was stirred for 24 hours. The solvent was removed under reduced pressure and the residue was washed with cold pentane (2 × 5 ml), leaving a white solid. Yield: 1415 mg (0.66 mol, 89%). Mp > 300 °C. Found (Calc. for $C_{86}H_{162}NO_{24}Si_{14}Ta$): C, 47.51 (47.64); H, 7.53 (7.53); N, 0.69 (0.65)%. ^{1}H NMR (25 °C, $CDCl_3$): δ 3.20 (br, 2H, NH_2), 2.70 (s, 3H, NCH_3), 1.74 (br m, 70H, CH_2), 1.24 (br m, 70H, CH_2), 0.72 (br, m, 14H, CH). ^{13}C{H} NMR (25 °C, $CDCl_3$): δ 35.33 (s, NCH_3), 28.03, 27.63, 27.20, 27.07, 26.96, 26.77 (s, CH_2), 24.85, 23.68, 23.41 (s, 3 : 3 : 1, CH). MS (CI-CH_4, relative intensity): *m*/*z* positive: 2151 (anion + C_2H_5, 1%), 2123 (anion + H, 40%), 2038 (anion + H − C_6H_{11}, 100%); negative: 2121 (anion − H, 100%), 2037 (anion − C_6H_{11}). IR (KBr disc): 3440s br, 2918s, 2848s, 1450s, 1120vs cm^{-1}.

$Cy_7Si_7O_{12}Ta(C_2B_9H_{11})$ (5). A solution of **1** (1460 mg, 1.50 mmol) in 20 ml toluene was slowly added at room temperature to a solution of $(C_2B_9H_{11})Ta(NMe_2)_3$ (675 mg, 1.50 mmol) in 20 ml toluene and the reaction mixture was stirred for 24 h. The solvent was then removed under reduced pressure and the residue was washed with cold pentane (2 × 5 ml), leaving an orange solid. Yield: 1580 mg (1.23 mmol, 82%). Mp > 300 °C (dec.). Found (Calc. for $C_{44}H_{88}B_9O_{12}Si_7Ta$): C, 42.17 (41.16); H, 7.08 (6.91)%. ^{1}H NMR (25 °C, $CDCl_3$): δ 1.90–2.70 (m, 11H, CH, BH), 1.73 (br, 35H, CH_2), 1.23 (br, 35H, CH_2), 0.77 (br, 7H, CH). ^{13}C{H} NMR (25 °C, $CDCl_3$): δ 52.00 (s, carborane-CH), 28.05, 27.71, 27.62, 27.21, 27.08, 27.03, 26.97, 26.77 (s, CH_2), 24.93, 23.70, 23.43 (s, 3 : 3: 1, CH). MS (CI-CH_4, relative intensity): *m*/*z* 1283 (M^+, 1%), 981 (M^+ − 302, 14%), 955 (70%), 871 (100%), 811 (90%). IR (KBr disc): 2920s, 2850s, 1115vs cm^{-1}.

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