Synthesis, Structures and Reactions of Trimethyltantalum(V) Bis[tri(*tert.*-butyl)silanolate]

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Bis[tri(*tert.*-butyl)silanolato]tantalum(V) trichloride reacts with LiMe to give trimethyl-bis[tri-(*tert.*-butyl)silanolato]tantalum(V), **6**. Its molecular structure shows a trigonal-bipyramidal coordination of the Ta atom with the Me groups in the equatorial plane. Its reaction with catecholborane produces preferably *B*-methyl-catecholborane besides some phenylene-1,2-dioxo-bis(1,3,2-dioxaborolane), **9**, and $H_3B \cdot THF$. Similarly, the reaction of **6** with dimeric 9-borabicyclononane (9-BBN) generates preferable tri(*tert.*-butyl)siloxy-9-BBN (75 %) and Me-9-BBN (25 %). In contrast, cleavage of the Ta–O bonds is the preferred route in the treatment of **6** with $H_3B \cdot THF$. ^{11}B NMR shows the formation of $(tBu_3SiO)_2BH$ and $(tBu_3SiO)_3B$ or $(tBuSiO)_3B_3O_3$. No tantalum hydride could be isolated.

Key words: Trimethyl-bis(tri-*tert.*-butylsilanolato)tantalum, Reaction with Borane Derivatives, Molecular Structure

Introduction

So far only three tetrahydridoborates of tantalum are known. They are depicted in formulae **1** to **3** [1–3]. Tantalum hydrides such as $Cp_2Ta(PMe_3)(\eta^1\text{-}BH_3Si(tBu)_2H$, **1**, are stable only in the presence of triorganylphosphines [2]. As far as we are aware neither (organyloxo)tantalum tetrahydroborates nor (organyloxo)tantalum hydrides are known. We expected that bulky(organyloxo)tantalum(V) groups might yield stable tantalum hydrides of the type $(RO)_2TiH_3$ or $(RO)_3TiH_2$ as well as their corresponding tetrahydroborates. We chose the bulky (tBu_3SiO) group as a suitable RO group for this purpose because tantalum tri-*tert.*-butylates tend to decompose [4].

Results

Synthesis and Reactions

The starting material $[(Me_3C)_3SiO]_2TaCl_3$, **5**, was obtained as colorless crystals in 66 % yield from the reaction of $TaCl_5$ with $(Me_3C)_3SiONa \cdot 2THF$ [5]. Treatment of **5** with LiMe in diethyl ether yielded colorless prisms of $[(Me_3C)_3SiO]_2TaMe_3$, **6**, in 58 % yield (Eq. 1).

We expected that the reaction of **6** with catecholborane in THF would result in an H/Me group exchange as shown in Eq. 2, producing the trihydridotantalum bis(*tert.*-butylsilanolate), **7**. However, the ^{11}B NMR spectra of the reaction mixture showed neither after 45 min nor after 5 d any resonance at about 30 to 20 ppm for a molecule of type $[(Me_3C)_3SiO]_2TaH_{3-n}(BO_2C_6H_4)_n$, in contrast to results with $Cp_2TaH_{3-n}(BO_2C_6H_4)_n$ [6]. ^{11}B NMR signals were observed at 0.5 ppm (q, $^1J(^{11}B^1H)$ = 105 Hz, 9 % relative intensity) for $H_3B \cdot THF$, at 18.3 ppm (s, 4 %) for phenylene-1,2-dioxo-bis(1,3,2-dioxaborolane), **9**, at 25.8 ppm (d, $^1J(^{11}B^1H)$ = 186 Hz, 50 %) for catecholborane, and at 36.2 ppm for *B*-methyl-catecholborane **8** (37 %). The formation of the latter compound demonstrates that an H/Me exchange indeed occurs, but the excess of catecholborane does not add to the Ta species. This fits with the observation [6, 7] that oxo-subsituted tantalum(V) hydride hydridoborates need a stabilization by PR_3 donors. On the other hand, the disproportionation of catecholborane with formation of $H_3B \cdot THF$ and phenylene-1,2-dioxo-bis(1,3,2-dioxaborolane) as shown in Eq. 3 has already been reported in 1993 by Burgess *et al.* [8]. Well defined compounds $[(Me_3C)_3SiO]_2TaMe_{3-n}H_n$ or $[(Me_3C)_3SiO]_2TaH(H_2BO_2C_6H_4)_2$ could neither be detected nor isolated.

In contrast to catecholborane, 9-borabicycloborane $[(HBC_8H_{14})_2$, $(H\text{-}9BBN)_2]$ does not disproportionate and, therefore, we expected a reaction according to

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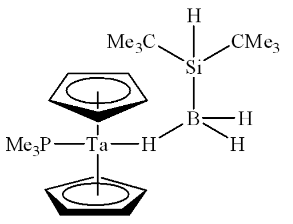

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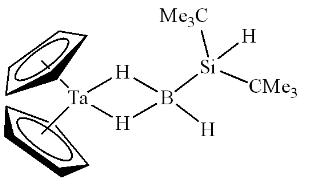

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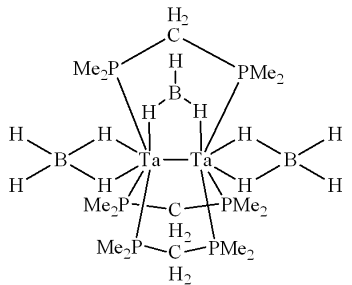

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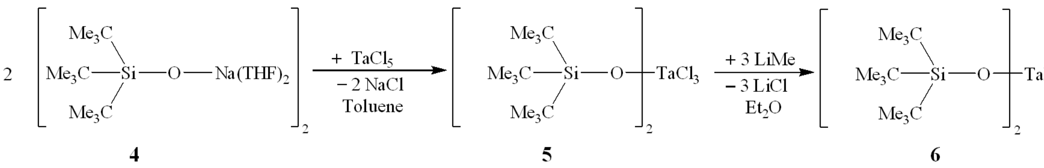

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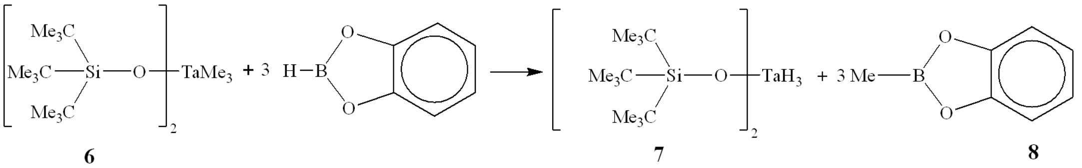

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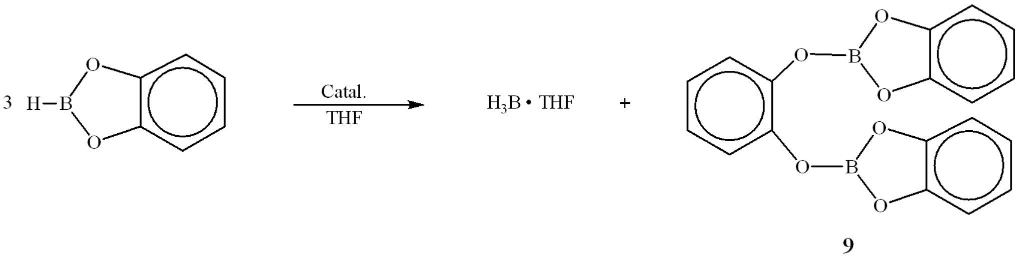


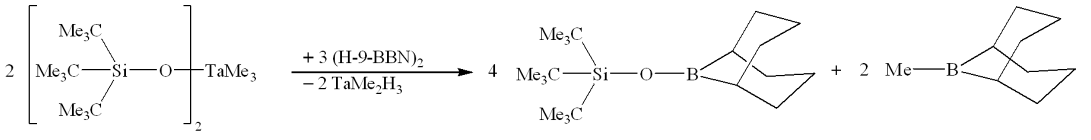
(3)

Eq. 4. However, the ^{11}B NMR spectrum of the Et_2O solution showed after 15 min besides the signal for $(H\text{-}9BBN)_2$ only one other signal at 58.1 ppm which can be assigned to $(Me_3C)_3SiO\text{–}BC_8H_{14}$, **10**. After 6 d there were two ^{11}B resonances with 75 and 25 % relative intensites at 58.4 ppm for $(Me_3C)_3SiO\text{–}BC_8H_{14}$ and at 89.6 ppm for $MeBC_8H_{14}$, **11**. These could result from an attack of H-9BBN on an O atom of **6** and cleavage of the Si–O bond with migration of one H atom to the Ta atom. This suggests that a compound $(Me_3C)_3SiOTaMe(H_2BC_8H_{14})_3$ might be formed, but we could not isolate and characterize any other defined tantalum species.

We finally reacted **6** with $H_3B \cdot THF$ in an NMR experiment expecting the formation of $[(Me_3C)_3SiO]_2\text{-}TaH_{3-n}(BH_4)_n$. This compound should give rise to an ^{11}B NMR signal between -5 and -10 ppm. However, we observed a doublet at 25.5 ppm ($^1J(^{11}B^1H)$ = 185 Hz, 11 %) which we assign to $[(Me_3C)_3SiO]_2BH$ and a singlet at 15.1 ppm (57 %) which is due to either $[(Me_3C)_3SiO]_3B$ or more likely to the boroxine derivative $[(Me_3C)_3SiO\text{–}BO]_3$, because a model calculation showed that $[(Me_3C)_3SiO]_3B$ is quite crowded and, therefore, could be unstable.

Molecular structure of 6

Colorless prisms of compound **6** crystallize in the monoclinic system, space group $P2_1/c$ with $Z = 4$. The molecular structure is shown in Fig. 1. It demonstrates nicely the trigonal-bipyramidal coordination geometry around the Ta atom. Deviations from 90 and 120°, respectively, are less than 1.5°. The O1–Ta1–O2 bond angle is 178.78(9)°, and the Ta–O–Si bond angles are 179.1(1)° and 178.9(1)° for Si1 and Si2, respectively, *i. e.* their O atoms can be considered to be *sp*-hybridized. This results in short Si–O bond lengths



$$2\,[(Me_3C)_3Si{-}O]_2TaMe_3 \xrightarrow[-\,2\,TaMe_2H_3]{+\,3\,(H\text{-}9\text{-}BBN)_2} 4\,(Me_3C)_3Si{-}O{-}B(C_8H_{14}) + 2\,Me{-}B(C_8H_{14})$$

(4)

10 **11**

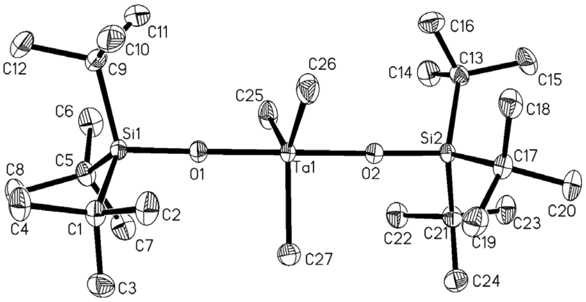


Fig. 1. Molecular structure of $[(Me_3C)_3SiO]_2TaMe_3$, **6**, in the crystal with displacement ellipsoids at the 25 % probability level. Hydrogen atoms are omitted for clarity. Bond lengths (Å) and bond angles (deg): Ta1–O1 1.906(2), Ta1–O2 1.902(2), Ta1–C25 2.158(3), Ta1–C26 2.156(3), Ta1–C27 2.151(3), Si1–O1 1.658(2), Si2–O2 1.660(2), Si1–C1 1.926(3), Si1–C5 1.927(3), Si1–C9 1.931(3), Si2–C113 1.928(3), Si2–C17 1.917(3), Si2–C21 1.933(3); O1–Ta1–O2 178.78(9), Ta1–O1–Si1 179.1(1), Ta1–O2–Si2 178.9(1), O1–Ta1–C25 88.9(1), O1–Ta1–C26 90.6(1), O1–Ta1–C27 89.8(1), O2–Ta1–C25 89.9(1), O2–Ta1–C26 90.4(1), O2–Ta2–C27 90.4(1), C25–Ta1–C26 120.9(2), C25–Ta1–C27 119.9(1), C26–Ta1–C27 119.2(2), O1–Si1–C1 106.1(1), O1–Si1–C5 106.1(1), O1–Si1–C9 107.1(1), O2–Si2–C13 106.2(1), O2–Si2–C17 106.3(1), O2–Si2–C21 106.1(1).

(Si1–O1 = 1.658(2), Si2–O2 = 1.660(2) Å). Normal Si–O bond lengths range from 1.6 to 1.79 Å. The Ta–C bond lengths [Ta1–C27 = 2.152(3), Ta1–C26 = 2.156(3), Ta1–C25 = 2.158(3) Å] and Ta–O bond lengths [Ta1–O1 = 1.906(2), Ta1–O2 1.902(2) Å] fit into the Ta–C bond range of 2.103 to 2.207 Å and the Ta–O range of 1.856 to 1.922 Å found in comparable coordination spheres of $(RO)_2TaR_3$ compounds [8–13].

Discussion and Conclusion

The reaction of $TaCl_5$ with $NaOSi(CMe_3) \cdot THF$ leads in good yield to $(Me_3SiO)_2TaCl_3$ which can be readily converted to the monomeric methyl derivative $[(Me_3C)_3SiO]_2TaMe_3$. Its Ta atom shows an almost perfect trigonal-bipyramidal arrangement of its substituents with the $(Me_3C)_3SiO$ groups in the apical positions. This structural orientation is found for several other $(RO)_3TaR_3$ compounds such as trimethyl(2,6-di*iso*propylphenolato)tantalum [9] or tribenzyl-bis(2,6-dimethylphenolato)tantalum [8]. In contrast, substituted bis(phenolato)tantalum trichlorides such as bis(2,6-*t*$Bu_2C_6H_3O)_2TaCl_3$ [10], (2,6-Ph_2-3,5-$Me_2C_6HO)_2TaCl_3$ [11] and (2,6-Ph_2-3,5-di-*t*Bu_2-$C_6HO)_2TaCl_3$ [12] have strongly distorted trigonal-bipyramidal structures as shown by O–Ta–O bond angles of 104.2°, 105.89°, and 105.61°, respectively, and O–Ta–Cl bond angles of up to 150.4°. Bis(2,6-*i*$Pr_2C_6H_3O)_2TaCl_3$ is dimeric with hexacoordinated Ta atoms [13]. On the other hand penta(organyloxo)tantalum(V) compounds are generally dimeric as shown by penta(4-methylphenolato)tantalum [14], tetra(isopropyloxo)methoxotantalum [15], tetra(*tert.*-butylmethylato)(ethyloxo)tantalum(VI) [16] or pentakis(isopropoxy)tantalum [15]. This demonstrates the structural variety of organyloxo tantalum compounds.

The expectation that the reaction of the trimethyltantalum compound **6** with borane derivatives would be dominated by a hydrogen/methyl group exchange to produce new tantalum hydrides or hydridoorganylborates could not be confirmed. Although this exchange was partly observed, neither $[(Me_3C)_3SiO]_2TaH_nMe_{3-n}$ nor $[(Me_3C)_3SiO]_2TaH_{3-n}(H_2BR_2)_n$ or $[(Me_3C)_3SiO]_2TaH_{3-n}(H_2BH_2)_n$ could be isolated, not even in reactions with $H_3B \cdot THF$. In this case a Ta–O bond cleavage was observed. This demonstrates that the tendency to generate siloxo tantalum hydridoborates is even less pronounced than for organyloxotitanium hydridoborates [17] and -zirconium hydridoborates [18], in contrast to titanocene and zirconocene tetrahydridoborates and dihydridodiorganylborates [18].

Experimental Section

The moisture-sensitive compounds require the handling in a dry nitrogen atmosphere using conventional Schlenk techniques. Only anhydrous solvents were used. NMR spectra were recorded with Jeol EX 400 and Jeol GSX 270 instruments. Bis(tri-*tert.*-butylsilanolato)tantalum(V) trichloride was prepared according to ref. [5].

Table 1. Selected crystallographic data for compound **6**.

Chem. formula	$C_{27}H_{63}O_2Si_2Ta$
M_r	656.90
Crystal size, mm^3	$0.2 \times 0.2 \times 0.2$
Space group	monoclinic, $P2_1/c$
a, Å	14.717(3)
b, Å	13.658(2)
c, Å	17.065(3)
β, deg	105.797(8)
V, Å^3	3301(1)
Z	4
$\rho_{calc.}$, Mg m^{-3}	1.32
μ, mm^{-1}	3.4
$F(000)$, e	1368
T, K	143(2)
Index ranges	$-18 \le h \le 16$, $-16 \le k \le 17$, $-19 \le l \le 19$
$2\theta_{max}$, deg	55.18
Refl. collected	11157
R_{int}	0.0171
Refl. observed (4σ)	4430
No. ref. variables	310
Final $R(4\sigma)$[a]	0.0211
Final $wR2$[b]	0.0469
Weighting scheme x / y[b]	0.00005 / 5.0077
GoF[c]	1.168
Larg. res. peak, e Å^{-3}	0.581

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (xP)^2 + yP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Trimethyl-bis[tri(tert.-butyl)silanolato]tantalum(V), ***6***

$NaOSi(CMe_3)_3 \cdot 2THF$ (9.23 g, 24.1 mmol) was added at -78 °C to $TaCl_5$ (4.32 g, 12.1 mmol). To the stirred mixture 100 mL of precooled toluene was added. The resulting suspension was allowed to warm to room temperature, and stirring was continued for 12 h. Afterwards, the solvent was removed *in vacuo* and the solid residue treated with hexane (100 mL). After filtration the hexane was removed from the filtrate *in vacuo* and the residue treated with diethyl ether (150 mL). The solution that formed was cooled to -78 °C, and an LiMe solution in Et_2O was then added (23.2 mL, 1.56 M). This mixture was stirred for 3 h. After removal of the solvent the remaining solid was treated with hexane (90 mL). Its filtrate was reduced in volume to about 30 mL. Colorless prisms separated at -30 °C within 2 weeks. These were characterized by X-ray structure determination to be compound **6**. Yield: 4.59 g; 58 %.

Reaction of ***6*** *with catecholborane*

Compound **6** (0.85 g, 1.3 mmol) was dissolved in tetrahydrofuran (20 mL) and the solution cooled to 0 °C. Under stirring, a solution of catecholborane (5.42 mmol) in THF (30 mL) was added at 0 °C. After 45 min the clear solution was subjected to ^{11}B NMR spectroscopy. Signals were observed at $\delta^{11}B$ = 0.5 (qint, $^1J(^{11}B^1H)$ = 105 Hz, $H_3B \cdot THF$ 7 %), 18.2 (s, $t\mathrm{Bu}_3SiO\text{–}BO_2C_6H_4$, 9 %), 25.7 (d, $^1J(^{11}B^1H)$ = 186 Hz, $C_6H_4O_2BH$, 74 %), and 36.1 (s, $MeBO_2C_6H_4$, 10 %). After the sample had been left standing for 5 d at ambient temperature the following percentage concentrations changed as listed here: $\delta^{11}B$ = 0.5 (9 %), 18.3 (4 %), 25.8 (50 %), 36.2 (37 %). Ratio of $MeBO_2C_6H_4 : t\mathrm{Bu}_3SiOBO_2C_6H_4 = 9:1$.

Reaction of ***6*** *with 9-borabicyclononane*

Compound **6** (1.08 g, 1.65 mmol) was dissolved in Et_2O (20 mL). To this solution $(H\text{-}9\text{-}BBN)_2$ (6.15 mmol in Et_2O, 30 mL) was added. For the colorless solution ^{11}B NMR spectra were recorded 15 min after mixing: $\delta^{11}B$ = 29.3 (t, $(HBC_8H_{14})_2$, 92 %), 58.1 (s, **6**). – After one week at ambient temperature the following signals were observed: 29.3 [$(HBC_8H_{14})_2$, 67 %], 58.4 (s, **6**, 26 %), 89.7 ppm ($MeBC_8H_{14}$, 7 %).

Reaction of ***6*** *with* $BH_3 \cdot THF$

In an NMR tube about 10 mg of **6** was dissolved in THF (2 mL). Then 5 drops of a $H_3B \cdot THF$ solution was added. The ^{11}B NMR spectrum recorded after 3 h showed the following signals: δ = 0.4 (quart, $^1J(^{11}B^1H)$ = 101 Hz, $H_3B \cdot THF$, 74 %), 15.0 $(t\mathrm{Bu}_3CSiO)_3B$, 15 %), 25.4 (d, $^1J(^{11}B^1H)$ = 185 Hz, $(t\mathrm{Bu}_3SiO)_2BH$, 11%).

Crystal structure determination

A suitable single crystal of **6** was selected from several crystals suspended in perfluoroether oil cooled to -30 °C by a stream of nitrogen gas. The crystal was mounted on a glass fiber with some perfluoroether oil. A Siemens P4 four-circle diffractometer operating with graphite-monochromatized MoK_α radiation and a scintillation counter was used to determine the unit cell parameters and to collect the reflection data. Reflections were recorded on 15 frames each at different settings of ω and ϕ. From these data the dimensions of the unit cell were calculated (programme SAINT [19]). Data collection was performed in the hemisphere mode (programme SMART, [19]). An absorption correction was employed (SADABS [20]). For structure solution and refinement the programs SHELXTL [21] and SHELX-93 [21] were used. Table 1 shows relevant crystallographic data and parameters related to structure solution and refinement of **6**.

CCDC 782144 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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