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Synthesis, Structure, and Reactions of the First Stable Dimercaptoborane[1]

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*Summary: The first stable dimercaptoborane, TbtB(SH)$_2$ (**1**), was synthesized by the sulfurization of the corresponding overcrowded lithium aryltrihydroborate bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group. Dilithiation of **1** followed by treatment with Cp$_2$TiCl$_2$ resulted in the isolation of a novel metallacycle, 1,3,2,4-dithiaboratitanetane **2**, as stable red crystals. Molecular structures of the novel organoboron compounds **1** and **2** were both determined by X-ray crystallographic analysis.*

In contrast to the extensive studies carried out for heteroatom-containing organoboranes such as aminoboranes, haloboranes, and boronic acid derivatives,[2] the chemistry of organoboranes incorporating sulfur functionalities has been less well investigated in the past though they are also considered to be an important class of organoboron compounds. Meanwhile, we have recently developed a new and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), and reported its high efficiency in the isolation of highly reactive chemical species such as novel cyclic polychalcogenides,[3] highly strained tin-containing small ring compounds,[4] and heavy congeners of ketones (silanethione,[5] germanethione,[6] and germaneselone[7]). Here, we present an application of the Tbt group to the stabilization of unstable sulfur-containing organoboron compounds leading to the first isolation of a stable aryldimercaptoborane, TbtB(SH)$_2$ (**1**), and a novel boron-containing metallacycle, 1,3,2,4-dithiaboratitanetane derivative **2**.

Treatment of Tbt-substituted dimethoxyborane **3**, which was readily prepared by the reaction of TbtLi with trimethyl borate, with excess lithium aluminum hydride in THF resulted in a quantitative formation of the corresponding lithium hydroborate **4**. Pure **4** was isolated as an air- and moisture-sensitive white solid by concentration of the reaction mixture after solvent exchange into hexane, followed by filtration of insoluble materials. The structure of **4** was confirmed by the characteristic signals in ^{11}B NMR [δ −30.7 (q, $^1J_{BH}$ = 74.4 Hz)] and ^{1}H NMR spectra, the latter of which showed not only the signals of the BH protons at δ 0.90 (3H, $^1J_{BH}$ = 74.4 Hz) but also those of three molecules of THF coordinated to lithium. In the IR spectra **4** showed characteristic absorptions at 2080 and 2190

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(1) Dedicated to Prof. Dr. Richard Neidlein of the University of Heidelberg on the occasion of his 65th birthday.

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(4) (a) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1993**, 407. (b) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R. *Organometallics* **1993**, *12*, 2573.

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(7) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem.* **1994**, *106*, 2418; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316.

(8) Eaborn et al. have already reported the X-ray structural analysis of [(THF)$_3$Li(μ-H)$_3$BC(SiMe$_2$Ph)$_3$] together with its spectroscopic data [IR ν_{BH} 2085, 2200 cm^{-1}; ^{11}B NMR(C$_6$D$_6$) δ −30.2, $^1J_{BH}$ 80 Hz]: Eaborn, C.; El-Kheli, M. N. A.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1984**, 1673.

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(10) In the following are shown experimental procedures for the preparation of **1**, **2**, and **5** together with their spectral and analytical data. Since the analytically pure samples of **1** and **5** were obtained by a reprecipitation procedure (addition of ethanol to their hexane solutions), they contained crystalline water the existence of which was evidenced by ^{1}H NMR spectroscopy and elemental analysis (*vide infra*). We have often experienced that Tbt-substituted compounds are liable to include crystalline water.[11] *Preparation of 1:* A mixture of **3** (1.40 g, 2.23 mmol) and LiAlH$_4$ (533 mg, 14.0 mmol) in THF (15 mL) was stirred at room temperature for 7 h. After solvent exchange into hexane, insoluble materials were filtered off with Celite. The filtrate was evaporated to give **1** as a white solid, to which was added 15 mL of THF and elemental sulfur (1.35 g, 5.31 mmol as S$_8$), and the solution was stirred for 30 min. The reaction mixture was treated with aqueous NH$_4$Cl and then extracted with hexane. Concentration of the organic layer gave a pale yellow crude oil, which was subjected to flash column chromatography (SiO$_2$/hexane) followed by HPLC separation to afford **1** (300 mg, 21% from **3**) as white crystals. **1**: mp 184 °C (dec); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.04 (s, 18H), 0.05 (s, 36H), 1.33 (s, 1H), 1.52 (s, 3H, *H*$_2$O), 1.56 (s, 2H), 2.88 (s, 2H), 6.23 (brs, 1H), 6.35 (brs, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.64 (q), 0.90 (q), 1.02 (q), 29.20 (d), 29.67 (d), 30.20 (d), 121.02 (d), 125.45 (d), 133.56 (brs, ipso-arom), 144.07 (s), 144.37 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 67.5; HRMS (70 eV) *m/z* found 628.2950 [M$^+$], calcd for C$_{27}$H$_{61}$BS$_2$Si$_6$ 628.2923. Anal. Calcd for C$_{27}$H$_{61}$BS$_2$Si$_6$·1.5H$_2$O: C, 49.42; H, 9.89; S, 9.77. Found: C, 49.19; H, 9.51; S, 10.43. *Preparation of 2:* To a THF solution (10 mL) of **1** (316 mg, 0.502 mmol) was added *n*-BuLi (1.67 M in hexane, 0.6 mL, 2.0 equiv) at −78 °C. After being stirred for 2 h, to the reaction mixture was added Cp$_2$TiCl$_2$ (182 mg, 0.73 mmol, 1.45 equiv) in portions from a bent tube to give a dark-red solution. Gradual warming to room temperature followed by evaporation of the solvent afforded a reddish brown solid, which was separated by flash column chromatography (SiO$_2$/hexane:CH$_2$Cl$_2$ = 4:1) to give **2** (283 mg, 70%) as red crystals. **2**: mp >300 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.03 (s, 18H), 0.10 (s, 36H), 1.25 (s, 1H), 1.38 (s, 2H), 6.19 (brs, 1H), 6.31 (brs, 1H), 6.39 (s, 10H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.68 (q), 1.05 (q), 1.18 (q), 28.88 (d), 29.30 (d), 29.48 (d), 117.68 (d, Cp), 121.73 (d), 124.00 (brs, ipso-arom), 126.21 (d), 141.11 (s), 146.11 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 47.0; HRMS (FAB) *m/z* found 804.2985 [M$^+$], calcd for C$_{39}$H$_{69}$BS$_2$Si$_6$Ti 804.3029. Anal. Calcd for C$_{37}$H$_{69}$BS$_2$Si$_6$Ti: C, 55.19; H, 8.64; S, 7.96. Found: C, 55.12; H, 8.43; S, 7.88. *Preparation of 5:* To a THF solution (3 mL) of **1** (56.0 mg, 0.089 mmol) was added *n*-BuLi (1.64 M in hexane, 0.11 mL, 2.0 equiv) at −78 °C. After being stirred for 2 h, to the reaction mixture was added methyl iodide (0.10 mL, 1.60 mmol, 18 equiv) by means of a syringe. Gradual warming to room temperature followed by evaporation of the solvent afforded a white solid, which was separated by column chromatography (SiO$_2$/hexane) to give **5** (52.6 mg, 90%) as white crystals. **5**: mp 168.5−170 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.04 (s, 18H), 0.05 (s, 36H), 1.32 (s, 1H), 1.54 (s, 2H, *H*$_2$O), 1.63 (brs, 2H), 2.18 (s, 6H), 6.20 (brs, 1H), 6.36 (brs, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.71 (q), 1.64 (q), 14.13 (q), 28.50 (d), 30.13 (d), 121.49 (d), 126.21 (d), 130.95 (s), 143.50 (s), 145.92 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 67.6; HRMS (EI, 70 eV) *m/z* found 656.3235 [M$^+$], calcd for C$_{29}$H$_{65}$BS$_2$Si$_6$ 656.3236. Anal. Calcd for C$_{29}$H$_{65}$BS$_2$Si$_6$·H$_2$O: C, 51.58; H, 10.00; S, 9.50. Found: C, 51.95; H, 10.14; S, 9.92.

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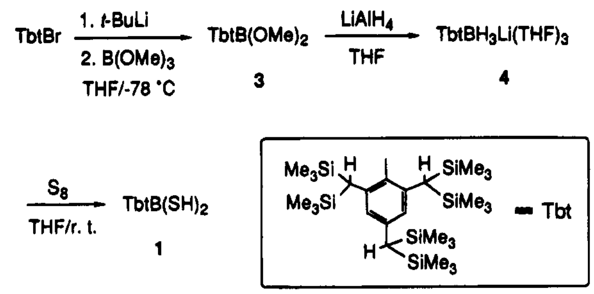
Scheme 1



cm^{-1} which are similar to those given for the crystallographically analyzed lithium alkyltrihydroborate [(THF)$_3$Li(μ-H)$_3$BC(SiMe$_2$Ph)$_3$].[8] An attempt to convert **4** into the corresponding dihydroborane by the reaction with hydrochloric acid or chlorotrimethylsilane[9] failed, while the direct reaction of **4** with elemental sulfur followed by treatment with saturated aqueous NH$_4$Cl resulted in the isolation of the Tbt-substituted dimercaptoborane **1** as white crystals (21% from **3**) after chromatographic separation on silica gel.[10] Compound **1** was found to be quite stable toward air and moisture and showed satisfactory spectral and analytical data, e.g., a singlet signal in the ^{11}B NMR [δ_B(CDCl$_3$) 67.5] attributable to the boron atom connecting two mercapto groups and a singlet signal in the ^{1}H NMR spectrum assignable to the two SH protons (Scheme 1).

The formation of **1** is worthy of note as the first example of a stable dimercaptoborane, and the molecular structure was definitively determined by X-ray crystallographic analysis (Figure 1).[12] Even in the solid state **1** showed no significant intermolecular interaction, and the geometry around the central boron atom was found to be completely trigonal planar. The dihedral angle between the plane defined by C(1)–B(1)–S(1)–S(2) and the aromatic ring plane of the Tbt group is 86.0°, suggesting no essential conjugative interaction of π-electrons on the Tbt group with the dimercaptoboryl group. The B(1)–C(1) bond length [1.53(2) Å] in **1**, however, was somewhat shorter than those of the related monomeric boron–sulfur compounds, TipB(SPh)$_2$ [1.574(8) Å] and Mes$_2$BSPh (1.556 Å).[14]

With the stable dimercaptoborane **1** in hand, we next examined its further molecular transformation via lithiation of the mercapto groups. Thus, treatment of **1** with n-BuLi (2.0 equiv) in THF at −78 °C followed by addition of methyl iodide (2.0 equiv) resulted in the formation of the corresponding bis(methylthio)borane **5** in 90% yield, while the use of bis(cyclopentadienyl)titanium dichloride (1.45 equiv) instead of methyl iodide gave a novel boron-containing titanacycle, 1,3,2,4-dithiaboratitanetane derivative **2** [δ_B(CDCl$_3$) 47.0] (70%), as very stable red crystals.[10,15] X-ray crystallographic analysis of **2** was also performed to reveal that its geometry around the boron atom was not much affected as compared to that of **1** in spite of being embedded in the ring system (Figure 2).[12] The four-membered dithiaboratitanetane ring was found to be almost planar and perpendicular to the aromatic ring of Tbt (dihedral angle 84.4°) as in the case of **1** (Scheme 2).

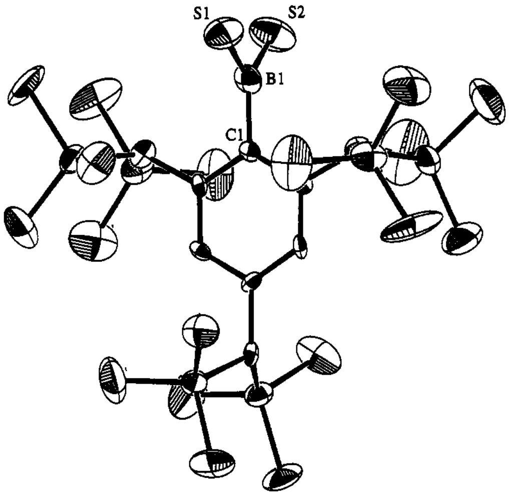


Figure 1. ORTEP drawing of TbtB(SH)$_2$ (**1**) with thermal ellipsoids plotted at 30% probability. The fragment of solvated toluene was omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)–C(1) 1.53(2), B(1)–S(1) 1.80(2), B(1)–S(2) 1.81(2); C(1)–B(1)–S(1) 122(1), C(1)–B(1)–S(2) 121(1), S(1)–B(1)–S(2) 115(1).

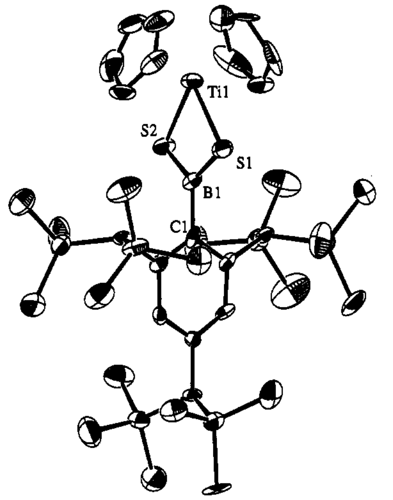


Figure 2. ORTEP drawing of TbtBS$_2$TiCp$_2$ (**2**) with thermal ellipsoids plotted at 30% probability. The fragment of solvated benzene was omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)–C(1) 1.57(3), B(1)–S(1) 1.80(2), B(1)–S(2) 1.84(2), Ti(1)–S(1) 2.422(5), Ti(1)–S(2) 2.409(7); C(1)–B(1)–S(1) 120(1), C(1)–B(1)–S(2) 120(1), S(1)–B(1)–S(2) 118(1), B(1)–S(1)–Ti(1) 80.3(8), B(1)–S(2)–Ti(1) 80.7(6), S(1)–Ti(1)–S(2) 80.5(2).

The successful isolation and noticeable stability of dimercaptoborane **1** and dithiaboratitanetane **2** here

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(11) For example, see: Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351.

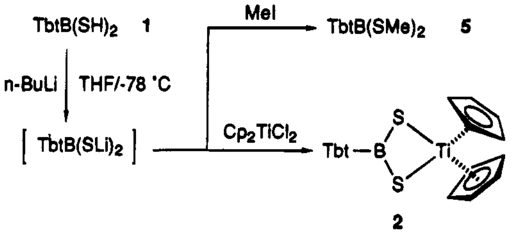
(12) Crystallographic data for **1**: $C_{27}H_{61}BS_2Si_6\cdot 0.5C_7H_8$, $M = 676.3$, monoclinic, space group $C2/c$, $a = 40.605(7)$ Å, $b = 11.14(1)$ Å, $c = 20.270(6)$ Å, $\beta = 104.36(2)°$; $V = 8881(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.011$ g cm^{-3}, $\mu = 2.99$ cm^{-1}, R (R_w) = 0.067 (0.073). Crystallographic data for **2**: $C_{37}H_{69}BS_2Si_6Ti\cdot C_6H_6$, $M = 844.35$, triclinic, space group $P\bar{1}$, $a = 13.378(4)$ Å, $b = 17.720(3)$ Å, $c = 13.039(5)$ Å, $\alpha = 110.38(2)°$, $\beta = 119.21(2)°$, $\gamma = 81.35(2)°$, $V = 2528(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.109$ g cm^{-3}, $\mu = 4.19$ cm^{-1}, R (R_w) = 0.079 (0.095). The intensity data were collected on Rigaku AFC7R (for **1**) and AFC5R (for **2**) diffractometers with Mo Kα radiation ($\lambda = 0.710\,69$ Å, graphite monochromator), and the structures were solved by direct methods with SHELXS-86.[13] All nonhydrogen atoms except for the solvents were refined anisotropically. The final cycles of full-matrix least-squares refinement were based on 1575 (for **1**) and 2378 (for **2**) observed reflections [$I > 4.00\sigma(I)$] and 339 (for **1**) and 431 (for **2**) variable parameters, respectively.

(13) Sheldrick, G. M. SHELXS-86; University of Göttingen: Göttingen, Germany, 1986.

(14) Wehmschulte, R.; Ruhlandt-Senge, K.; Olmstead, M. M.; Petrie, M. A.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1994**, 2113.

(15) An example of a dithiaborametalletane derivative containing two iron tricarbonyl units, Me$_2$NBS$_3$[Fe(CO)$_3$]$_2$, has already been reported. See: Nöth, H.; Schuchardt, U. *Z. Anorg. Allg. Chem.* **1975**, *418*, 97.

Scheme 2



obtained are obviously due to the steric demand of the Tbt group. Since it is well-known that bis(cyclopentadienyl)titanium−chalcogen bonds in some other ring systems have a versatile reactivity toward electrophiles,[16] dithiaboratitanetane **2** is expected to be useful as a stable, overcrowded boron dithiolate unit in the synthesis of new types of highly reactive organoboron compounds. Further investigation on the reactivities of **1** and **2** is currently in progress.

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Supporting Information Available: ORTEP diagrams and tables of crystal data and structural refinement details, positional and thermal parameters, and bond lengths and angles for **1** and **2** (61 pages). Ordering information is given on any current masthead page.

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(16) (a) Albertsen, J.; Steudel, R. *Phosphorus, Sulfur, Silicon* **1992**, *65*, 165. (b) Steudel, R. *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; p 233.