Synthesis and Structures of Novel Dithiaboretanes Containing a Group 4, 14, or 15 Element

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Dilithiation of the dimercaptoborane $TbtB(SH)_2$ (**1**), which was synthesized by the sulfurization of the corresponding overcrowded lithium aryltrihydroborate bearing the 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, followed by treatment with electrophiles such as Cp_2TiCl_2, Mes_2GeBr_2, Ph_2SnCl_2, and $TbtSbBr_2$ resulted in the isolation of novel four-membered boracycles, 1,3,2,4-dithiaboratitanetane, 1,3,2,4-dithiagermaboretane, 1,3,2,4-dithiastannaboretane, and 1,3,2,4-dithiastibaboretane as stable crystals, respectively. The introduction of a C, Si, or P atom to the four-membered ring was not successful. The structures of the newly obtained four-membered boracycles were determined by X-ray crystallographic analysis. The four-membered rings are almost planar and perpendicular to the aromatic ring of Tbt group. The geometries around the boron atom in the four-membered ring are found to be almost trigonal planer, and the S−B−S angles in the ring are not much smaller than 90°, indicating that the geometry around the boron and sulfur atoms was not so different from that of **1** in spite of being embedded in the ring system.

Introduction

Although extensive studies have been carried out for boracycles containing carbon, nitrogen, and oxygen atoms,[1] very little is known of the properties of sulfur-containing four-membered boracycles because of their instability toward air and moisture as well as the lack of suitable synthetic methods. Meanwhile, we have recently developed a new and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and reported its high efficiency in the isolation of highly reactive chemical species such as novel cyclic polychalcogenides,[2] highly strained tin-containing small ring compounds,[3] and heavy congeners of ketones (silanethione,[4] germanethione,[5] germaneselone,[6] germanetellone[7]). We thought that the steric protection afforded by the Tbt group would be applicable also to the syntheses of unstable organoboron species and preliminarily reported the synthesis of the first stable dimercaptoborane $TbtB(SH)_2$, **1**, and its successful application to the synthesis of some new four-membered boracycles.[8,9]

Here we present a detailed account of the synthesis of dimercaptoborane **1** and some four- and five-membered boracycles containing a group 4, 14, or 15 element which are prepared from **1**.

Results and Discussion

Synthesis of Dimercaptoborane 1. Although there have been several reports on the synthesis of dialkyl- or diarylmonomecaptoboranes $R_2B(SH)$ (R = Me, *n*-Bu, Ph, etc.)[10] and thioboronic ester derivatives $R'B(SR'')_2$,[11] dimercaptoboranes had not been known until **1** was synthesized by us utilizing kinetic stabilization with a sterically bulky substituent, Tbt group.[8]

Compound **1** was synthesized (Scheme 1) by a procedure slightly modified from that of the preliminary paper. The reaction of lithium hydroborate **3** with elemental sulfur for a shorter time (5 min) followed by treatment with dilute HCl resulted in the isolation of the Tbt-substituted dimercaptoborane **1** as colorless

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⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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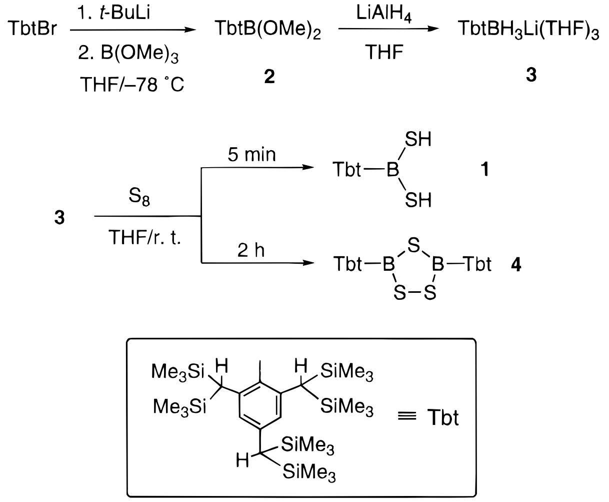
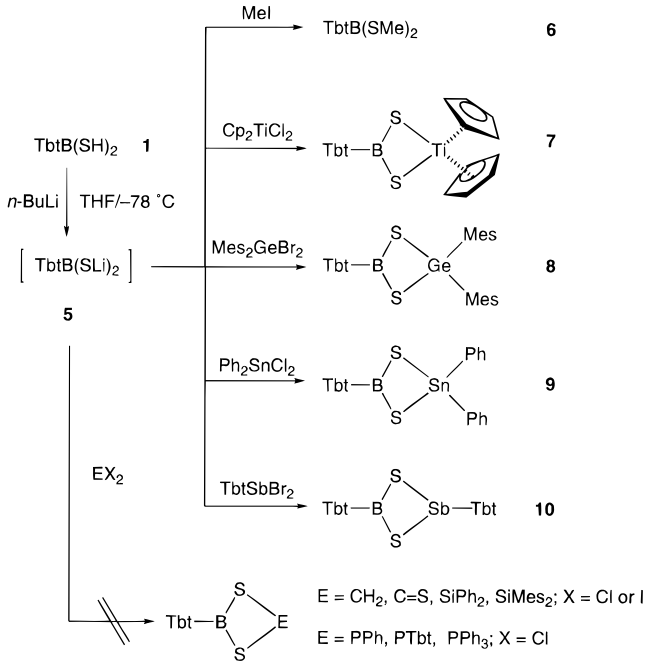
Scheme 1



crystals (46% from **2**) along with boronic acid TbtB(OH)$_2$ (34% from **2**). The use of dilute HCl instead of aqueous NH$_4$Cl described in the preliminary report[8] raised the yield of **1** from 21 to 46%. Furthermore, it was found that the reaction of **3** with elemental sulfur for 2 h (THF, room temperature) gave a 1,2,4,3,5-trithiadiborolane derivative **4** (62%) without the formaton of **1**. 1,2,4-Trithiadiborolanes were previously obtained, for example, by the reaction of diiodoboranes with elemental sulfur.[11d,12a] The successful isolation of **1** suggests that the shorter reaction time retards intermolecular reactions leading to the formation of the 1,2,4,3,5-trithiadiborolane **4**. Compound **1** is quite stable toward air and moisture, and no change was observed for months in the air. It is in sharp contrast with sulfur-containing organoboranes so far known, which are reportedly not only sensitive toward air and moisture but are also thermally unstable. The instability of the sulfur-containing organoboranes is most likely due to its high sensitivity toward hydrolysis and high Lewis acidity, which are diminished in the case of **1** by the presence of the effective bulky substituent, Tbt. The thermal stability of **1** was measured by differential scanning calorimetry (DSC). The heat absorption was observed at 197 °C by comparing with an inert standard of Al$_2$O$_3$. Since thermolysis of **1** in the solid state at ca. 200 °C gave a mixture of unidentified compounds, it is highly probable that the thermal decomposition of **1** occurred at 197 °C.

Syntheses of Dithiametallaboretane Derivatives. Previous reports on sulfur-containing organoboracycles are mostly concerned with 1,2,4,3,5-trithiadiborolane[12] and 1,3,5,2,4,6-trithiatriborane[12c,13] derivatives, and to our knowledge, a 1,3,2,4-dithiadiboretane[12c,14,15] is the sole known example of a sulfur-containing four-membered boracycle. In view of the quantitative formation of bis(methylthio)borane **6** via dilithiodimercaptoborane TbtB(SLi)$_2$ **5**,[8] **1** is expected to be a useful precursor for the synthesis of various sulfur-containing organoboron compounds, e.g., novel sulfur-containing four-membered boracycles. At first, we carried out the introduction of titanium into the four-membered ring. Thus, the reaction of **5** with Cp$_2$TiCl$_2$ afforded 1,3,2,4-dithiaboratitanetane **7** as air- and moisture-stable red crystals in 70% yield.[8,16] The ^{11}B chemical shift of **7** [δ_B(CDCl$_3$) 47.0] was about 20 ppm high-field shifted in comparison with **1**. We think that **7** can also be regarded as a titanocene complex of dithiolateborane. The sulfur atoms of **7** may be much negatively charged than the usual molecules with a RBS$_2$ unit, thus rendering its boron atom more shielded.

Scheme 2



We next attempted to synthesize boracycles containing group 14 elements by treatment of dithiolate **5** with 1.0 equiv of electrophiles containing C, Si, Ge, and Sn. In the reactions with both C and Si electrophiles such as CH$_2$I$_2$, Cl$_2$C=S, Ph$_2$SiCl$_2$, and Mes$_2$SiCl$_2$ however, only a complex mixture was obtained without any formation of the desired four-membered ring compounds (Scheme 2). By contrast, treatment of **5** with 1.0 equiv of Mes$_2$GeBr$_2$ and Ph$_2$SnCl$_2$ gave novel four-membered boracycles **8** (84%) and **9** (97%), respectively, as stable crystals in high yields. Interestingly, a similar trend was also observed in the reaction of **5** with group 15 element electrophiles. Although introduction of the phosphorus atom to a four-membered ring system by the reactions of **5** with PhPCl$_2$, TbtPCl$_2$, and Ph$_3$PCl$_2$ was unsuccessful, the reaction of **5** with TbtSbBr$_2$ gave stable 1,3,2,4-dithiastibaboretane **10**, a new metallacycle, in a high yield (80%) as pale yellow crystals. The fact that the reactions of **5** with an electrophile containing heavier homologues of group 14 (Ge, Sn) and group 15 elements (Sb) can afford the four-membered rings (**8**–**10**), while those of the corresponding lighter coun-

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[15] There has been reported an example of a *S,S*-dialkyl dithiadiboretane derivative as a dimer of alkylthiodialkylborane in the solid state: Köster, R.; Seidel, G.; Boese, R. *Chem. Ber.* **1988**, *121*, 1137.

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

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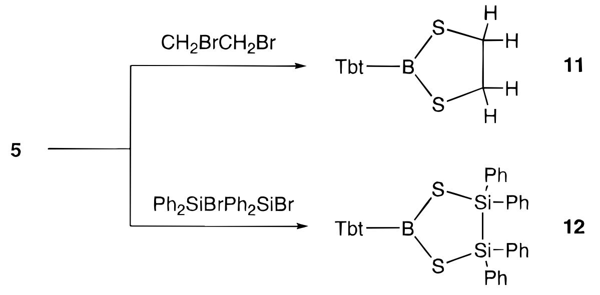
Scheme 3



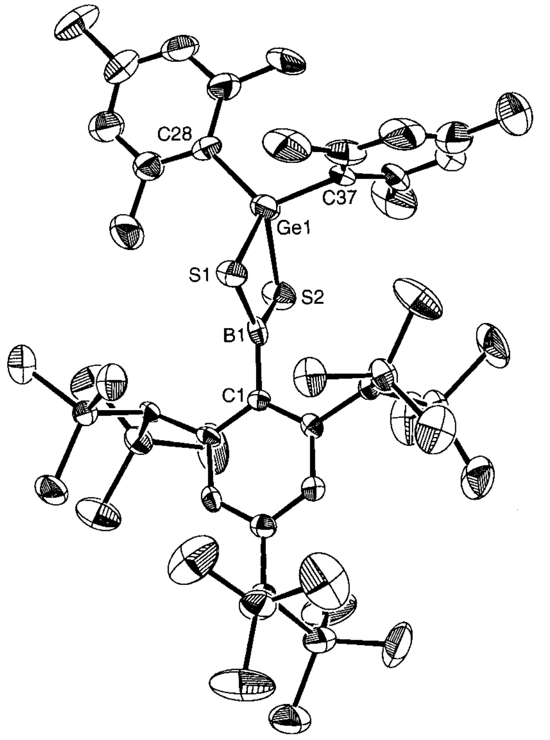


Figure 1. ORTEP drawing of **8** with thermal ellipsoid plots (30% probability).

terparts (C, Si, P) cannot, suggests the importance of the bond length between boron and the electrophilic atom becoming a member of the ring. This interpretation was substantiated by the reactions of **5** (Scheme 3) with 1,2-dibromoethane and 1,2-dibromo-1,1,2,2-tetraphenyldisilane which led to ready formation of five-membered compounds **11** and **12**,[16] respectively. This point will be discussed below in connection with the X-ray crystal structures of **1** and **7**−**9**.

Compounds **8**−**10** were also found to be quite stable toward air and moisture and showed satisfactory spectral and analytical data, e.g., a singlet signal in ^{11}B NMR [δ_B(CDCl$_3$) 70.6, 74.5, and 72.8, respectively] attributable to the boron atom connecting two sulfur atoms.

Structures of Dithiametallaboretane Derivatives. The structures of novel four-membered ring systems **7**−**9** were definitively determined by X-ray crystallographic analysis.[17] The ORTEP drawings of **8** and **9** are shown in Figures 1 and 2, respectively.[18] Crystallographic data and selected bond lengths and angles for **1** and **7**−**9** are summarized in Tables 1 and 2, respectively. In the solid state, **7**−**9** show no significant intermolecular interaction, and the geometries around the central boron atoms in them are completely trigonal planar as in the case of **1**. The dihedral angles between the plane of the four-membered rings and the aromatic ring plane of the Tbt group are 84.4, 89.5, and 87.9°, respectively, suggesting no essential conjugative interaction of π-electrons on the Tbt group with the four-membered rings. The fold angles of the four-membered rings are 5.6° for **7**, 10.9° for **8**, and 3.9° for **9**, indicating that these four-membered dithiametallaboretane rings are almost planar.

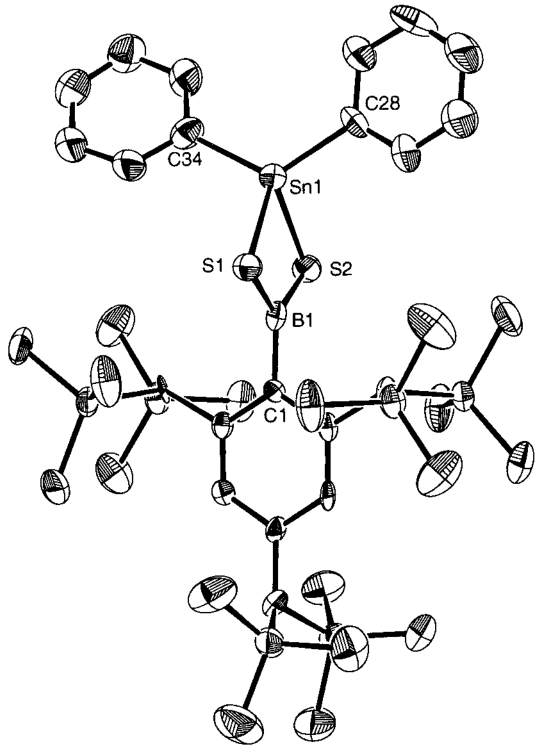


Figure 2. ORTEP drawing of **9** with thermal ellipsoid plots (30% probability).

The S(1)−B(1)−S(2) angles of **7**, **8**, and **9** [118(1), 110.4(4), and 114.7(6)°, respectively] are close to that of the dimercaptoborane **1** [115(1)°]. The B(1)−S(1)−M(1) and B(1)−S(2)−M(1) [M = Ti, Ge, Sn] angles, which are in the range of 80.3(8)°−83.3(4)°, are slightly smaller than 90°. These results indicate that geometries around the boron and sulfur atoms in **7**−**9** are not much different from that of **1** in spite of being embedded in the ring system. That is to say, the strain of the four-membered rings is mainly imposed on the bonds around the titanium, germanium, or tin atom. In the case of these atoms that have bond lengths longer than those for carbon and silicon, the four-membered ring can be formed without much strain, while in the case of carbon and silicon, the corresponding four-membered rings are so strained that an intermolecular reaction is preferred over an intramolecular ring closure. This notion is supported by the successful isolation of the five-membered ring compounds **11** and **12** containing two carbon or silicon atoms, which are undoubtedly less strained than the corresponding four-membered ring compounds. The successful synthesis of the antimony heterocycle **10**, but not the corresponding phosphacycle, can be explained similarly.

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[17] There has been reported only one example of 1,3,4,5,2-dithiadisilaborolane: Nöth, H.; Fussstetter, H.; Pommerening, H.; Taeger, T. *Chem. Ber.* **1980**, *113*, 342.

[18] For the ORTEP drawings of **1** and **7**, see ref 8.

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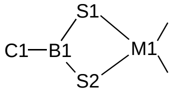
Table 1. Experimental Crystallographic Data for 1 and 7−9

	1	**7**	**8**	**9**
empirical formula	$C_{27}H_{61}BS_2Si_6{\cdot}0.5C_7H_8$	$C_{37}H_{69}BS_2Si_6Ti{\cdot}C_6H_6$	$C_{45}H_{81}BGeS_2Si_6$	$C_{39}H_{69}BS_2Si_6Sn$
fw	676.30	844.35	938.17	900.11
cryst size, mm	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.40 × 0.40 × 0.30
temp, K	296	296	296	296
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
unit cell dimens				
a, Å	40.605(7)	13.378(4)	13.235(5)	12.590(4)
b, Å	11.14(1)	17.720(3)	25.771(4)	23.581(6)
c, Å	20.270(6)	13.039(5)	18.112(4)	9.408(5)
α, deg		110.38(2)		96.89(2)
β, deg	104.36(2)	119.21(2)	110.80(2)	109.09(2)
γ, deg		81.35(2)		75.94(2)
V, Å^3	8881(6)	2528(1)	5575(2)	2557(1)
Z	8	2	4	2
density (calcd), g cm^{-3}	1.011	1.109	1.079	1.169
scan type	$\omega-2\theta$	$\omega-2\theta$	ω	$\omega-2\theta$
no. of obsd reflns	1575 ($I > 4\sigma(I)$)	2378 ($I > 4\sigma(I)$)	3486 ($I > 2\sigma(I)$)	3103 ($I > 3\sigma(I)$)
data to param ratio	4.65	5.52	7.03	7.02
largest diff peak, e Å^{-3}	0.45	0.59	0.31	0.41
largest diff hole, e Å^{-3}	0.33	0.35	0.31	0.51
R, %	6.7	7.9	6.9	5.3
R_w, %	7.3	9.5	3.4	6.0
goodness of fit	1.96	2.07	1.62	1.76

Table 2. Selected Bond Lengths and Angles for 1 and 7−9



	1	**7** (M = Ti)	**8** (M = Ge)	**9** (M = Sn)
	Bond Lengths (Å)			
B(1)−S(1)	1.80(2)	1.80(2)	1.817(8)	1.834(11)
B(1)−S(2)	1.81(2)	1.84(2)	1.817(7)	1.825(11)
B(1)−C(1)	1.53(2)	1.57(3)	1.564(9)	1.533(13)
S(1)−M(1)		2.422(5)	2.260(2)	2.402(3)
S(2)−M(1)		2.409(7)	2.265(2)	2.430(3)
	Bond Angles (deg)			
C(1)−B(1)−S(1)	122(1)	120(1)	123.7(5)	123.0(8)
C(1)−B(1)−S(2)	121(1)	120(1)	125.9(5)	122.3(7)
S(1)−B(1)−S(2)	115(1)	118(1)	110.4(4)	114.7(6)
B(1)−S(1)−M(1)		80.7(6)	83.2(3)	83.3(4)
B(1)−S(2)−M(1)		80.3(8)	83.0(3)	82.7(4)
S(1)−M(1)−S(2)		80.5(2)	82.54(8)	79.22(9)

Conclusion

The successful isolation and noticeable stability of the novel four-membered ring compounds **8**−**10** here obtained are obviously due to the high steric demand of the Tbt group, which increases their stability toward hydrolysis. The synthesis of **7**−**10** from **1** shows that **1** is a very useful precursor for the synthesis of various novel sulfur-containing organoboron compounds. Furthermore, the newly obtained boracycles **7**−**10** are expected to be used for the synthesis of a new type of highly reactive organoboron compound, for example, a boron−sulfur double-bond compound (thioxoborane).[19] Further investigation on the reactivities of **7**−**10** is currently in progress.

Experimental Section

General Procedure. All melting points are uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAI gel 1H+2H columns and LC-908-C60 with JAI gel 1H-40+2H-40 columns (Japan Analytical Industry) with chloroform as solvent. Dry column chromatography (DCC) and wet column chromatography (WCC) were performed with ICN silica DCC 60A and Wakogel C-200, respectively. Flash column chromatography (FCC) was performed with silica gel BW 300 (Fuji Davison Chemical). Preparative thin-layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF254 Art. 7747. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were measured in $CDCl_3$ with a Bruker AM-500, JEOL α-500, or JEOL EX-270 spectrometer using $CHCl_3$ as an internal standard. The ^{11}B NMR (160 or 86.4 MHz) spectra were measured in $CDCl_3$ with a JEOL α-500 or JEOL EX-270 spectrometer using $BF_3{\cdot}OEt_2$ as an external standard. The ^{29}Si NMR (53.0 MHz) spectra were measured in $CDCl_3$ with a JEOL EX-270 spectrometer using tetramethylsilane as an external standard. The ^{119}Sn NMR (100 MHz) spectra were measured in $CDCl_3$ with a JEOL EX-270 spectrometer using tetramethylstannane as an external standard. High-resolution mass spectral data (HRMS) were obtained on a JEOL SX-102 mass spectrometer. Infrared spectra were recorded with a Jasco FT/IR-300E spectrometer. DSC was measured with a Shimadzu DSC-50 differential scanning calorimeter. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]-phenyl}dimethoxyborane (2). To a solution of 1-bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene[20] (TbtBr, 10.7 g, 17.0 mmol) in THF (150 mL) was added *t*-BuLi (1.65 M in pentane, 23 mL, 37 mmol) at −78 °C. After the mixture was stirred for 60 min, $B(OMe)_3$ (9.4 mL, 85 mmol) was added at −78 °C. The solution was stirred for 10 h, during which time it was warmed to room temperature. To this solution was added a saturated aqueous solution of NH_4Cl, and the organic layer was separated. The water layer was extracted with 50 mL of hexane, and the combined organic layer was dried with anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue thus obtained was chromatographed by WCC (SiO_2 with hexane) to afford $TbtB(OMe)_2$ (8.37 g, 79%), which was purified by reprecipitation from CH_2Cl_2 and ethanol. **2**: white crystals, mp 181−185 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.021 (s, 36H), 0.023 (s, 18H), 1.19 (s, 1H),

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[19] Recently, we reported the formation and reactions of an intermediary thioxoborane by the thermolysis of **9**; see ref 9.

[20] Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1987**, 2293.

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1.30 (br s, 2H), 3.56 (s, 6H), 6.19 (br s, 1H), 6.33 (br s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.72 (q), 0.93 (q), 1.02 (q), 29.10 (d), 29.26 (d), 30.15 (d), 51.92 (q), 120.78 (d), 125.37 (d), 129.40 (br s), 142.71 (s), 146.07 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 31.10; HRMS(EI, 70eV) *m/z* calcd for $C_{29}H_{65}BO_2Si_6$ 624.3693, found 624.4072. Anal. Calcd for $C_{29}H_{65}BO_2Si_6 \cdot H_2O$: C, 51.58; H, 10.00. Found: C, 51.95; H, 10.14.[21]

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}dimercaptoborane (1). A mixture of **2** (2.74 g, 4.39 mmol) and LiAlH$_4$ (693 mg, 18.3 mmol) in THF (60 mL) was stirred at room temperature for 12 h. After solvent exchange into hexane, insoluble materials were filtered off with Celite. The filtrate was evaporated to give **3** as a white solid, to which was added 60 mL of THF and elemental sulfur (1.19 g, 4.65 mmol as S$_8$), and the solution was stirred for 15 min. To this solution was added a saturated aqueous solution of HCl, and the organic layer was separated. The water layer was extracted with 50 mL of hexane, and the combined organic layer was dried with anhydrous MgSO$_4$. Concentration of the organic layer gave a pale yellow solid, which was subjected to WCC (SiO$_2$/hexane) followed by GPLC separation to afford **1** (1.28 g, 46% from **2**) as white crystals and boronic acid TbtB(OH)$_2$ (883 mg, 34% from **2**). **1**: mp 197 °C (dec, measured by DSC); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.04 (s, 18H), 0.05 (s, 36H), 1.33 (s, 1H), 1.56 (s, 2H), 2.88 (s, 2H), 6.23 (br s, 1H), 6.35 (br s, 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 (br s, ipso aromatic), 144.07 (s), 144.37 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 67.5; HRMS (EI, 70 eV) *m/z* calcd for $C_{27}H_{61}BS_2Si_6$: 628.2923; found 628.2950. Anal. Calcd for $C_{27}H_{61}BS_2Si_6 \cdot 1.5H_2O$: C, 49.42; H, 9.89; S, 9.77. Found: C, 49.19; H, 9.51; S, 10.43. **3**: white crystals; ^{1}H NMR (270 MHz, CDCl$_3$) δ −0.05 (s, 18H), −0.04 (s, 18H), 0.01 (s, 9H), 0.02 (s, 9H), 0.90 (q, 3H, $^1J_{BH} = 74.4$ Hz), 1.18 (s, 1H), 1.90 (m, 12H), 2.91 (br s, 2H), 3.87 (m, 12H), 6.15 (br s, 1H), 6.22 (br s, 1H); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ −30.7(q, $^1J_{BH} = 74.4$ Hz). IR(CCl$_4$) 2080, 2190 cm^{-1} (B−H). TbtB(OH)$_2$: mp 220−224 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.01 (s, 18H), 0.02 (s, 36H), 1.32 (s, 1H), 1.36 (br s, 2H), 4.11 (s, 2H), 6.23 (br s, 1H), 6.35 (br s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.42 (q), 0.62 (q), 29.96 (d), 30.12 (d), 30.29 (d), 120.70 (d), 125.27 (d), 130.60 (br s, ipso aromatic), 143.55 (s), 145.28 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 31.7; HRMS(70 eV) *m/z* calcd for $C_{27}H_{61}BO_2Si_6$ 596.3380, found 596.3345. Anal. Calcd for $C_{27}H_{61}BO_2Si_6 \cdot 1.5H_2O$: C, 51.96; H, 10.33. Found: C, 52.00; H, 9.84.

Preparation of 3,5-Bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2,4,3,5-trithiadiborolane (4). A mixture of **2** (343 mg, 0.548 mmol) and LiAlH$_4$ (129 mg, 3.40 mmol) in THF (10 mL) was stirred at room temperature for 12 h. After solvent exchange into hexane, insoluble materials were filtered off with Celite. The filtrate was evaporated to give **3** as a white solid, to which was added 10 mL of THF and elemental sulfur (140 mg, 0.548 mmol as S$_8$), and the solution was stirred for 2 h. After solvent exchange into hexane, the solution was removed by decantation to leave **4** as insoluble materials (209 mg, 62% from **2**). The solution, after evaporating of the solvent, was subjected to HPLC separation followed by WCC (SiO$_2$/hexane) to afford TbtB(OH)$_2$ (20.5 mg, 9% from **2**). **4**: mp >300 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.04 (s, 36H), 0.05 (s, 72H), 1.36 (s, 2H), 1.50 (br s, 2H), 1.55 (br s, 2H), 6.29 (br s, 2H), 6.41 (br s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.42 (q), 0.62 (q), 29.96 (d), 30.12 (d), 30.29 (d), 120.70 (d), 125.27 (d), 130.60 (br s, ipso aromatic), 143.55 (s), 145.28 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 69.3; HRMS(FAB) *m/z* calcd for $C_{54}H_{118}B_2S_3Si_{12}$ 1220.5813, found 1220.5784. Anal. Calcd for $C_{54}H_{118}B_2S_3Si_{12} \cdot H_2O$: C, 52.29; H, 9.75; S, 7.75. Found: C, 52.49; H, 10.33; S, 8.13.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}bis(methylthio)borane (6). 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 stirring for 2 h, methyl iodide (0.10 mL, 1.60 mmol, 18 equiv) was added to the reaction mixture 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 **6** (59.0 mg, 100%) as white crystals. **6**: 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), 1.63 (br s, 2H), 2.18 (s, 6H), 6.20 (br s, 1H), 6.36 (br s, 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* calcd for $C_{29}H_{65}BS_2Si_6$ 656.3236, found 656.3235. Anal. Calcd for $C_{29}H_{65}BS_2Si_6 \cdot H_2O$: C, 51.58; H, 10.00; S, 9.50. Found: C, 51.95; H, 10.14; S, 9.92.

Preparation of 4,4-Di-η^5-cyclopentadienyl-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dithiaboratitanetane (7). 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 stirring for 2 h, Cp$_2$TiCl$_2$ (182 mg, 0.73 mmol, 1.45 equiv) was added to the reaction mixture in portions from a bent tube to give a dark red solution. Gradual warming of the solution to room temperature followed by evaporation of the solvent afforded a reddish brown solid, which was separated by FCC (SiO$_2$/hexane:CH$_2$Cl$_2$ = 4:1) to give **7** (283 mg, 70%) as red crystals. **7**: 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 (br s, 1H), 6.31 (br s, 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 (br s, ipso aromatic), 126.21 (d), 141.11 (s), 146.11 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 47.0; HRMS(FAB) *m/z* calcd for $C_{37}H_{69}BS_2Si_6Ti$ 804.3029, found 804.2985. Anal. Calcd for $C_{37}H_{69}BS_2Si_6Ti$: C, 55.19; H, 8.64; S, 7.96. Found: C, 55.12; H, 8.43; S, 7.88.

Preparation of 4-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-2,2-dimesityl-1,3,2,4-dithiagermaboretane (8). To a THF solution (10 mL) of **1** (134 mg, 0.210 mmol) was added *n*-BuLi (1.64 M in hexane, 0.25 mL, 2.0 equiv) at −78 °C. After stirring for 2 h, to the reaction mixture was added Mes$_2$GeBr$_2$[22] (105 mg, 0.22 mmol) in portions from a bent tube to give a colorless solution. Gradual warming to room temperature followed by evaporation of the solvent afforded a white solid, which was separated by WCC (SiO$_2$/hexane) to give **8** (168 mg, 84%). **3**: white crystals; mp 245−248 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ −0.04 (s, 36H), 0.01 (s, 18H), 1.29 (s, 1H), 1.74 (br s, 1H), 1.78 (br s, 1H), 2.27 (s, 6H), 2.58 (s, 12H), 6.17 (br s, 1H), 6.29 (br s, 1H), 6.84 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.58 (q), 0.66 (q), 0.75 (q), 21.02 (q), 23.67 (q), 28.77 (d), 29.32 (d), 30.18 (d), 120.75 (d), 125.28 (d), 129.68 (d), 135.67 (s), 136.46 (s), 140.25 (s), 142.84 (s), 143.31 (s), 144.39 (s), 144.55 (s); ^{11}B NMR (86.4 MHz, CDCl$_3$) δ 70.6; HRMS(FAB) *m/z* calcd for $C_{45}H_{81}BGeS_2Si_6$ 938.3804, found 938.3700. Anal. Calcd for $C_{45}H_{81}BGeS_2Si_6 \cdot H_2O$: C, 56.52; H, 8.74; S, 6.17. Found: C, 56.35; H, 8.33; S, 7.25.

Preparation of 4-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-2,2-diphenyl-1,3,2,4-dithiastannaboretane (9). To a THF solution (15 mL) of **1** (296 mg, 0.470 mmol) was added *n*-BuLi (1.65 M in hexane, 0.57 mL, 2.0 equiv) at −78 °C. After stirring for 2 h, Ph$_2$SnCl$_2$[23] (197 mg, 0.56 mmol) was added to the reaction mixture in portions from a bent tube to give a colorless solution. Gradual warming of the solution to room temperature followed by evaporation of the solvent afforded a white solid, which was separated by WCC (SiO$_2$/CH$_2$Cl$_2$) to give **9** (408 mg, 97%). **9**: white crystals; mp 175

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(21) We have often experienced that Tbt-substituted compounds are liable to form crystals including crystalline water. For example, see: Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351.

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(23) Ph$_2$SnCl$_2$ (Aldrich) was obtained commercially and used as received.

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°C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 18H), 0.10 (s, 36H), 1.34 (s, 1H), 2.03 (br s, 2H), 6.24 (br s, 1H), 6.35 (br s, 1H), 7.55 (m, 6H), 7.90 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.64 (q), 0.85 (q), 29.70 (d), 30.18 (d), 120.64 (d), 124.95 (d), 129.48 (d), 131.18 (d), 136.06 (s), 138.18 (d), 139.52 (s), 143.25 (s), 143.57 (s); ^{11}B NMR (86.4 MHz, $CDCl_3$) δ 74.5; ^{119}Sn NMR (100 MHz, $CDCl_3$) δ −73.97; HRMS(FAB) *m/z* calcd for $C_{39}H_{69}BS_2Si_6Sn$ 900.2571, found: 900.2475. Anal. Calcd for $C_{39}H_{69}BS_2Si_6Sn\cdot0.5H_2O$: C, 51.52; H, 7.76; S, 7.05. Found: C, 51.23; H, 7.77; S, 7.52.

Preparation of 2,4-Bis{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}-1,3,2,4-ditihastibaboretane (10). To a THF solution (5.0 mL) of **1** (44.6 mg, 0.071 mmol) was added *n*-BuLi (1.65 M in hexane, 0.09 mL, 2.0 equiv) at −78 °C. After stirring for 2 h, $TbtSbBr_2$[24] (containing ca. 20% of TbtH, 89.0 mg, 0.085 mmol) was added to the reaction mixture in portions from a bent tube to give a pale yellow solution. Gradual warming of the solution to room temperature followed by evaporation of the solvent afforded a pale yellow solid, which was separated by GPLC to give **10** (73.1 mg, 80% from **1**). **10**: pale yellow crystals; mp 238 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 36H), 0.05 (s, 36H), 0.10 (s, 36H), 1.31 (s, 1H), 1.35 (s, 1H), 1.46(s, 2H), 1.83 (br s, 1H), 1.93 (br s, 1H), 6.20 (br s, 1H), 6.32 (br s, 1H), 6.36 (br s, 1H), 6.49 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.66 (q), 0.71 (q), 0.86 (q), 0.96 (q), 29.34 (d), 29.89 (d), 30.39 (d), 30.45 (d), 32.85 (d), 33.08 (d), 120.75 (d), 122.88 (d), 125.42 (d), 127.57 (d), 138.90 (s), 141.90 (br s), 143.35 (s), 144.41 (s), 144.79 (s) 145.63 (s), 149.61 (s), 149.71 (s); ^{11}B NMR (86.4 MHz, $CDCl_3$) δ 72.8; HRMS(FAB) *m/z* calcd for $C_{54}H_{118}BSbS_2Si_{12}$ 1300.5050, found 1300.5109. Anal. Calcd for $C_{54}H_{118}BSbS_2Si_{12}$: C, 49.84; H, 9.14; S, 4.93. Found: C, 49.93; H, 8.99; S, 5.35.

Preparation of 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]-phenyl}-1,3,2-dithiaborolane (11). To a THF solution (15 mL) of **1** (101 mg, 0.16 mmol) was added *n*-BuLi (1.41 M in hexane, 0.25 mL, 2.0 equiv) at −78 °C. After stirring for 2 h, 1,2-dibromoethane (0.015 mL, 0.17 mmol) was added to the reaction mixture to give a colorless solution. Gradual warming of the solution to room temperature followed by evaporation of the solvent afforded a white solid, which was separated by GPLC followed by PTLC (SiO_2/hexane) to give **11** (35.9 mg, 34%). **11**: white crystals; mp 172−176 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.02 (s, 36H), 0.04 (s, 18H), 1.33 (s, 1H), 1.51 (br s, 2H), 3.34 (s, 4H), 6.23 (br s, 1H), 6.34 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.63 (q), 0.70 (q), 29.60 (d), 29.96 (d), 30.13 (d), 38.39 (t), 120.85 (d), 125.22 (d), 127.17 (s), 143.74 (s), 145.81 (s); ^{11}B NMR (160 MHz, $CDCl_3$) δ 71.1. HRMS(FAB) *m/z* calcd for $C_{29}H_{63}BS_2Si_6$ 654.3080, found 654.3046. Anal. Calcd for $C_{29}H_{63}BS_2Si_6\cdot H_2O$: C, 51.69; H, 9.43; S, 9.52. Found: C, 51.68; H, 9.29; S, 9.62.

Preparation of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]-phenyl}-2,2,3,3-tetraphenyl-1,3,4,5,2-dithiadisilaborolane (12). To a THF solution (15 mL) of **1** (80.0 mg, 0.127 mmol) was added *n*-BuLi (1.67 M in hexane, 0.17 mL, 2.0 equiv) at −78 °C. After stirring for 2 h, 1,2-dibromo-1,1,2,2-tetraphenyldisilane[25] (72.6 mg, 0.139 mmol) was added to the reaction mixture in portions from a bent tube to give a colorless solution. Gradual warming of the solution to room temperature followed by evaporation of the solvent afforded a white solid, which was separated by GPLC to give **12** (24.5 mg, 19%). **12**: white crystals; mp 185−188 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.00 (s, 36H), 0.04 (s, 18H), 1.32 (s, 1H), 1.62 (br s, 1H), 1.66 (br s, 1H), 6.23 (br s, 1H), 6.35 (br s, 1H), 7.10−7.25 (m, 8H), 7.27−7.37 (m, 4H), 7.37−7.48 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.68 (q), 0.95 (q), 1.09 (q), 29.05 (d), 29.63 (d), 30.13 (d), 121.00 (d), 125.47 (d), 128.03 (d), 130.06 (d), 132.43 (s), 134.91 (s), 135.39 (d), 143.32 (s), 144.53 (s); ^{11}B NMR (86.4 MHz, $CDCl_3$) δ 71.0; ^{29}Si NMR (53.0 MHz, $CDCl_3$) δ −5.66, −5.59, −5.39, −5.15, −3.23. HRMS(FAB) *m/z* calcd for $C_{51}H_{79}BS_2Si_8$ 990.3871, found 990.3876. Anal. Calcd for $C_{51}H_{79}BS_2Si_8\cdot H_2O$: C, 60.60; H, 7.88; S, 6.35;. Found: C, 60.80; H, 7.88; S, 5.78.

X-ray Data Collection. Single crystals of **1** and **7** were grown by the slow evaporation of a saturated solution in toluene and in benzene at room temperature, respectively. Single crystals of **8** and **9** were grown by the slow evaporation of a saturated solution in ethanol and chloroform at room temperature. The intensity data were collected on a Rigaku AFC7R diffractometer (for **1**, **8**, and **9**) or a Rigaku AFC5R diffractometer (for **7**) with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The structure of **1** was solved by direct methods with SHELXS-86[26] and refined by the full-matrix least-squares method. The structure of **7** was solved by heavy-atom Patterson methods with PATTY,[27] expanded using Fourier techniques[28] and refined by the full matrix least-squares method. The structures of **8** and **9** were solved by heavy-atom Patterson methods with SAPI91,[29] expanded using Fourier techniques,[30] and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically. The final cycle of the least-squares refinement was based on 1575 (for **1**) and 2378 (for **7**) observed reflections [$I > 4\sigma(I)$] and 339 (for **1**) and 431 (for **7**) variable parameters with R (R_w) = 0.067 (0.073) (for **1**) and 0.079 (0.095) (for **7**). The final cycle of the least-squares refinement was based on 3486 (for **8**) and 3103 (for **9**) observed reflections [$I > 2\sigma(I)$ (for **8**) and $I > 3\sigma(I)$ (for **9**)], and 496 (for **8**) and 442 (for **9**)) variable parameters with R (R_w) = 0.069 (0.034) (for **8**) and 0.053 (0.060) (for **9**). The crystal data for these molecules are summarized in Table 1.

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Supporting Information Available: Tables listing atomic coordinates, temperature factors, bond lengths and angles, torsion angles, and figures of packing diagrams for **1** and **7**−**9** (134 pages). Ordering information is given on any current masthead page.

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