Synthesis and Structures of some Trisorganylstannyl Boranes and Triorganylstannyl Borates [1]

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Abstract. New stannylboranes were prepared from tetramethylpiperidino dichloroborane or B-bromo-pentamethylborazine with lithium triorganylstannides $LiSnR_3$. Only double stannylation was possible with $tmpBCl_2$ and $LiSnMe_3$, while $tmpBCl(SnPh_3)$ was obtained by employing $LiSnPh_3$. This chloride reacted with $LiGePh_3$ to the stannyl germyl borane $tmpB(GePh_3)(SnPh_3)$. On the other hand, $PhMeNBCl_2$ and an excess of $LiSnMe_3$ gave the borate $Li[B(NMePh)(SnMe_3)_3]$, which was isolated as a solvate with 4 molecules of THF. The compound is present in the solid state as a solvent separated ion pair. The borate $Li(H_3BSnMe_3) \cdot 2\,THF$ is dimeric in the solid state. Dimerization occurs via two single Li–H–B bridges and a Li–H(B)–Li bridge. The B–Sn bonds in the borates are practically of the same lengths as those in the boranes. In solution all BH bonds of this trihydridoborate are equivalent.

Keywords: Boron; Tin; Stannyl boranes; NMR spectroscopy; Crystal structures

Synthese und Strukturen einiger Triorganylstannylborane und Triorganylstannylborate

Inhaltsübersicht. Neue Stannylborane wurden aus Tetramethylpiperidino-dichlorboran oder B-Bromopentamethylborazin mit Lithium-Triorganylstanniden $LiSnR_3$ hergestellt. Doppelte Stannylierung war nur mit $tmpBCl_2$ und $LiSnMe_3$ möglich, während $tmpBCl(SnPh_3)$ mit $LiSnPh_3$ zugänglich war. Dieses Chlorid reagierte mit $LiGePh_3$ zu dem Stannyl-Germyl-Boran $tmpB(GePh_3)(SnPh_3)$. Andererseits ergab die Reaktion von $PhMeNBCl_2$ mit überschüssigem $LiSnMe_3$ das Borat $Li[B(NMePh)(SnMe_3)_3]$, das als Solvat mit vier Molekülen THF isoliert wurde. Die Verbindung liegt im festen Zustand als Salz vor. Das Borat $Li(H_3BSnMe_3) \cdot 2\,THF$ ist im festen Zustand dimer. Die Dimerisierung erfolgt über zwei Li–H–B- und eine Li–H(B)–Li-Brücke. Die B–Sn-Bindungen in den Boraten sind praktisch genauso lang wie in den Boranen. In Lösung sind alle B–H-Bindungen des Trihydridoborats äquivalent.

Introduction

In spite of their favorable synthetic potential [2], stannylboranes have been rather poorly investigated so far, especially concerning their molecular structures. Although stannylboranes are known since 1964 [3] the first structurally characterized stannylborane was 1,2-bis[(diisopropylamino-trimethylstannyl)boryl]ethene which was described by *Siebert* et al. in 1994 [4]. It was obtained from lithium trimethylstannide and 1,2-bis(diisopropylamino-chloro-boryl)ethene. Recently, we described the molecular structures of several bis(amino)stannylboranes [5] as well those of stannyl-diboranes(4) and stannyl-triboranes(5) [6]. In this context we observed an unusual shortening of the B–Sn distance with increasing coordination number at the boron atom. In attempts to check this observation we decided to study the molecular structures of additional stannylboranes and stannylborates by X-ray crystallography in order to obtain more molecular parameters for comparison.

Results and Discussion

The most straightforward pathway for building B–Sn bonds are salt elimination reactions between boron halides and alkali metal organylstannides. As the latter compounds have to be prepared in ether as solvents particularly in THF [7] only boron compounds can be employed, which will not induce ether cleavage reactions, at least not at low temperatures. In order to prevent ether cleavage we used mainly boron compounds of low Lewis acidity, e. g. aminoboron chlorides. For a successful synthesis not only the appropriate boron compound had to be selected but also the proper alkali metal triorganylstannide. Thus,

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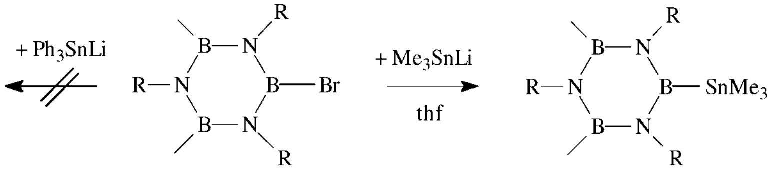
Me_3SnLi was found to be much more reactive than Ph_3SnLi. For example the reaction of the bromo-borazines **1a** and **1b** [8] yielded the stannyl-borazines **2a** and **2b**, whereas no reaction occurred with Ph_3SnLi (s. Equ. (1)).

The different reactivity of Ph_3SnLi compared to Me_3SnLi becomes also apparent in their reactions with $tmpBCl_2$ (tmp = 2,2,6,6-tetramethylpiperidino group) [9]. When Me_3SnLi was used the bisstannyl compound **3** was formed as a single product [10]. Attempts to synthesize the monostannyl derivative $tmpB(Cl)SnMe_3$ failed. Even by slowly adding Me_3SnLi to an excess of $tmpBCl_2$ at low temperatures, **3** is the only product. In contrast, the preparation of the triphenylstannyl-substituted borane **4** was easily achieved regardless of the reaction conditions. We obtained **4** even when we added $tmpBCl_2$ to Ph_3SnLi at ambient temperature. The stannylborane **4** bears a reactive halide substituent and is, therefore, itself a suitable starting material for preparing still other stannylboranes. For example, the reaction of **4** with Ph_3GeLi allows the synthesis of the stannyl-germyl-substituted borane **5**. This compound is the first borane, which carries two different heavier elements of the 14th-main group. On the other hand, the analogous reaction of **4** with Ph_3SnLi failed to generate $tmpB(SnPh_3)_2$. This result provides evidence that steric factors play an important role in these substitution reactions.

Compounds **4** and **5** were isolated as single crystals. Their molecular structures could be determined by X-ray structure analysis. Compound **3** was obtained as a crystalline material too, but the crystals were not suitable for an X-ray structure analysis.

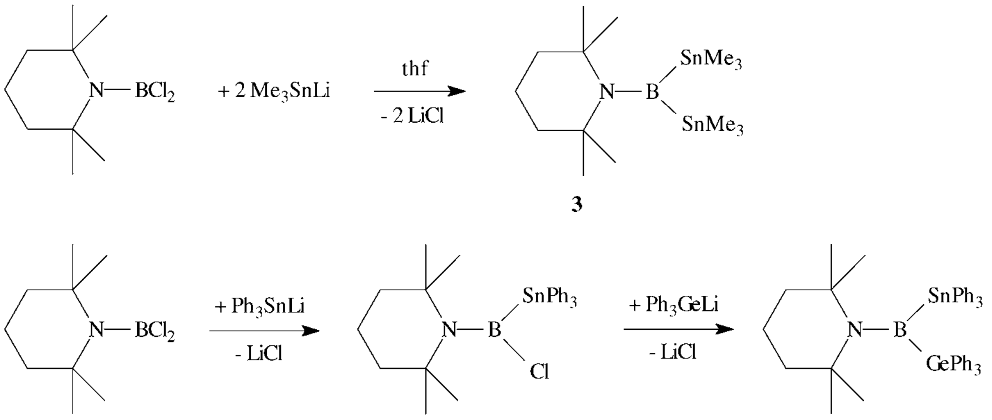
The higher reactivity of Me_3SnLi was further demonstrated by the reaction of Me_3SnLi with the sterically less crowded aminoborane $Ph(Me)NBCl_2$ [11]. This time, not only the expected double substitution by a stannyl group occurred, but even a third equivalent of Me_3SnLi was added and the borate $Li[Ph(Me)NB(SnMe_3)_3]$, **6**, generated. Compounds si-



1a R = Me
1b R = Isp

2a R = Me
2b R = Isp

(1)

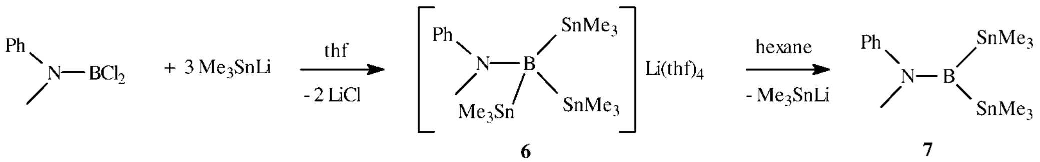


3

4

5

(2)



6

7

$$Me_3SnLi + BH_3{*}thf \xrightarrow[-78^{\circ}C]{thf} \xrightarrow{hexane} \underset{\mathbf{8}}{Li(thf)_2(H_3B\text{-}SnMe_3)} \xrightarrow[-LiBr]{+CatBBr} CatBH + \underset{\mathbf{9}}{"Me_3SnBH_2"}$$

(3)

milar to **6** are scarce. That closest to **6** are the alkali metal triorganylamidoborates $M(R_3BNR'_2)$ ($NR'_2 = NH_2$, NHEt) [12]. Only few other monoalkylaminoborates have been reported to our knowledge [13] while dialkylamino and particularly pyrazolylborates are well investigated [14]. The latter are much more stable than the tris(stannylamino)borate **6**. Decomposition was observed on redissolving **6** in hexane as well as on gentle heating. Among other compounds, the bis(stannyl)aminoborane **7** was generated. Obviously, one Me_3Sn group is bound rather weakly to the boron moiety (s. Equ. (2), (3)).

A stannylborate which decomposes on gentle warming is $Li(H_3BSnMe_3)$ which is readily formed in the reaction of Me_3SnLi with BH_3*THF [15]. As no X-ray structure of this borate is known, we reproduced the synthesis. However, we isolated the compound as the bis-THF adduct [16] and not as the reported mono-THF adduct [15]. The trihydridoborate **8** was crystallized from hexane, and completely characterized. To investigate, whether the Me_3Sn group of **8** or its hydrides are more reactive we treated **8** with bromocatecholatoborane CatBBr (Cat = catecholate^{2-}). Only the formation of CatBH was observed but no $CatBSnMe_3$. On the other hand we found no evidence in the ^{11}B NMR spectrum for the formation of a trimethylstannyl borane **9**. This compound may decompose with formation of trimethylstannane and a polyboron hydride. Because we did not record the ^{119}Sn NMR spectrum we have no evidence for the presence of Me_3SnH in the solution. Thus, the borate **8** can be regarded as a hydride-transfer agent. As **8** is highly reactive and soluble in hexane one can imagine that **8** may find applications in organic synthesis.

NMR and IR Spectra

The ^{11}B NMR spectra of the two borazines **2a** and **2b** are practically identical. For both compounds two sets of signals in a 2 : 1 ratio were found [**2a**: $\delta^{11}B = 37.4$, 2 B), 44.7 (d, $^1J_{B,Sn} = 950$ Hz, 1 B), **2b**: $\delta^{11}B = 37.8$ (2 B), 44.7 (d, $^1J_{B,Sn} = 960$ Hz)]. The resonances of the boron atoms attached to the Me_3Sn-groups appear as doublets due to B, Sn coupling, and this proves the presence of B–Sn bonds. These boron nuclei are significantly deshielded compared with the boron atoms in hexaorganylborazines ($\delta = 35.8$ for $(MeBNMe)_3$ and 36.0 for $(MeBNiPr)_3$ [17], even more than the analogous Ph_3Ge-substitued borazines [18], where signals at $\delta^{11}B = 39.3$ (R = Me) and $\delta^{11}B = 41.4$ (R = iPr) were found.

Due to the low symmetry of the aminoboranes **4** and **5**, we were unable to determine the $^1J_{BSn}$ coupling constants for these compounds neither from the ^{11}B NMR spectrum nor from the ^{119}Sn NMR spectrum. Nevertheless, the observed ^{11}B NMR chemical shifts [**4**: $\delta^{11}B = 50.1$, **5**: $\delta^{11}B = 70.0$] are consistent with the proposed structures. Once again these resonances are at lower field compared with analogous silicon and germanium compounds [18]. For the bis(stannyl)-borane **3**, a ^{11}B NMR signal at $\delta = 68.4$ and a ^{119}Sn NMR signal at $\delta = -146$ was found. The ^{11}B NMR signal is deshielded with respect to amino-diorganyl boranes [16]. The symmetry of compound **3** allowed the determination of the $^1J_{BSn}$ coupling constant [$^1J_{BSn} = 650$ Hz]. The NMR data for compound **7** are very similar to those of **3**: the ^{11}B signal appears at $\delta = 71.6$ (d, $^1J_{BSn} = 650$ Hz).

Of special interest are the NMR data for the tris-(stannyl)borate **6**. Its ^{11}B NMR shows a quartet at $\delta^{11}B = -13.1$ (d, $^1J_{BSn} = 580$ Hz). The ^{119}Sn NMR signal appears as a 1 : 1 : 1 : 1 quartet at $\delta^{119}Sn = -42$ ($^1J_{BSn} = 580$ Hz). The value of the coupling-constant is smaller than observed for those of stannylboranes with tricoordinated boron atoms. This can be explained by a decreased s-orbital participation of the B–Sn bonds. Informative is also the ^{13}C NMR spectrum: the C atoms of the Me_3Sn-groups not only show $^1J_{CSn}$-coupling (250 Hz), but also that the nine methyl groups attached to the three tin atoms are chemically equivalent. For the PhN group five different signals were found in the ^1H and the ^{13}C NMR spectra indicating hindered rotation about the N–C(Ph) bond. This is caused by a strong π-interaction between the N atom and the Ph group.

The ^{11}B NMR spectrum of compound **8** [$\delta^{11}B = 42.0$] is almost identical to the monosilyl and monogermyl trihydridoborates $Li(Me_3EBH_3)$ [15]. The observed coupling patterns and coupling constants – doublet of quartet with $^1J_{BSn} = 598$ Hz and $^1J_{BH} = 84$ Hz – correspond fairly well with previous data [19]. In solution, all hydrogen atoms bound to the boron atom are magnetically and chemically equivalent, in spite of the fact that this is not the case in the solid state (v. i.). The IR spectrum of **8** shows two strong BH_3 stretching bands at 2293 (vst) and 2267 (vst) cm^{-1} for the antisymmetric and the symmetric stretching BH_3 vibrations. The IR spectrum, therefore, is consistent with local C_{3V} symmetry for the Me_3SnBH_3 anion.

Molecular Structures in the Solid State

The structures of compound **4** and **5** are both influenced by the presence of the bulky tmp ligand (Figures 1 and 2). To meet with the steric requirements in these compounds, the tmp ligands are twisted about the BN bonds. This results in interplanar angles of 22.4° (**4**) and 33.5° (**5**) for the planes C_2N/BClSn and C_2N/BGeSn, respectively. The B–N distances in **4** and **5** are of equal lengths [**4**: 1.387(4) Å and **5**: 1.387(5) Å]. They are rather short in spite of the non-coplanar orientation of the boron and the nitrogen bonding planes. Therefore, the B–N bonds have still considerable double bond character. The steric demand of the tmp group can also be derived from the wide bond angles found at the boron atoms: [**5**: N(1)–B(1)–Ge(1) = 129.8(3), N(1)–B(1)–Sn(1) = 124.9(3) and Ge(1)–B(1)–Sn(1) = 105.3(2)]. Especially the small Ge–B–Sn angle is striking. The smaller N–B–Sn bond angle compared with the wider N–B–Ge bond angle is indicative for the greater steric effect of the triphenylgermyl group which is due to the shorter metal boron distance compared to the Sn–B bond. To cope with the space available and in order to minimize the steric interactions between the substituent the phenyls of the Ph_3Ge-group and the Ph_3Sn-group are arranged in a type of staggered conformation (see

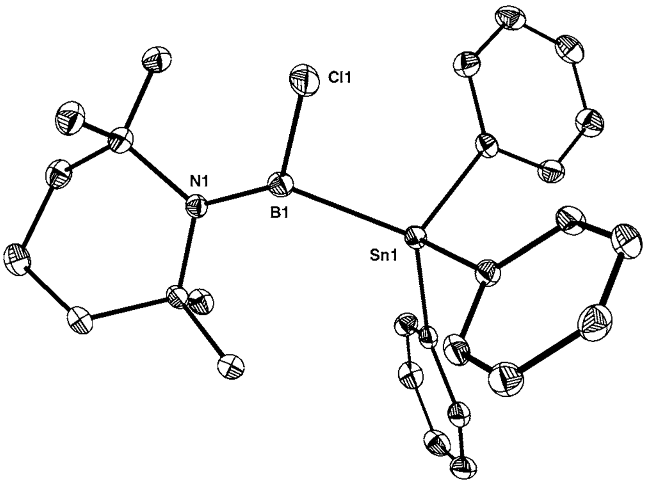


Fig. 1 Molecular structure of **4** in the crystal; thermal ellipsoids are shown on a 25% probability level. Hydrogen atoms are omitted for clarity. Selected atom distances/Å and bond angles/°:

Sn1–B1 2.277(4), Cl1–B1 1.834(3), N1–B1 1.387(4), N1–B1–Cl1 121.4(2), N1–B1–Sn1 136.9(2), Cl1–B1–Sn1 101.7(2).

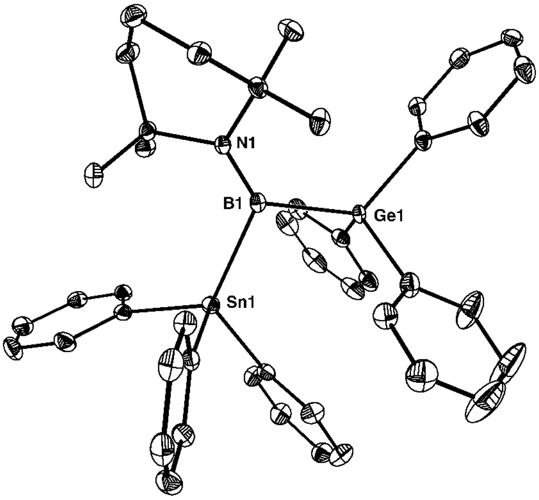


Fig. 2 Molecular structure of **5** in the crystal; thermal ellipsoids are shown at a 25% probability level. Hydrogen atoms are omitted for clarity. Selected atom distances/Å and bond angles/°:

Sn1–B1 2.316(5), Ge1–B1 2.143(4), N1–B1 1.387(5), C10–Sn1–C22 102.1(1), C10–Sn1–C16 100.7(2), C22–Sn1–C16 103.8(2), C10–C34–Ge1–C28 102.8(2), C40–Ge1–B1 111.4(2), C34–Ge1–B1 99.5(2), C28–Ge1–B1 124.4(2), N1–B1–Ge1 129.8(3), N1–B1–Sn1 124.9(3), Ge1–B1–Sn1 105.3(2).

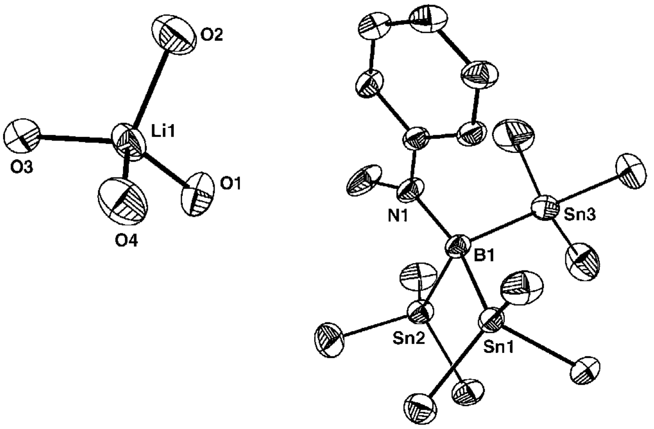


Fig. 3 Molecular structure of **6** in the crystal; thermal ellipsoids are shown at a 25% probability level. The carbon atoms of the THF molecules and all hydrogen atoms are omitted for clarity. Selected atom distances/Å and bond angles/°:

Sn1–B1 2.289(7), Sn2–B1 2.296(6), Sn3–B1 2.291(8), N1–B1 1.545(8), N1–C1 1.442 (7), N1–C2 1.379(7), Sn1–B1–Sn2 100.8(3), Sn1–B1–Sn3 107.6(3), Sn2–B1–Sn3 104.9(3), N1–B1–Sn1 121.8(5), N1–B1–Sn2 111.6(4), N1–B1–Sn3 108.7(4), C1–N1–C3 114.3(5), C1–N1–B1 120.2(5), C1–N1–B2 124.6(5).

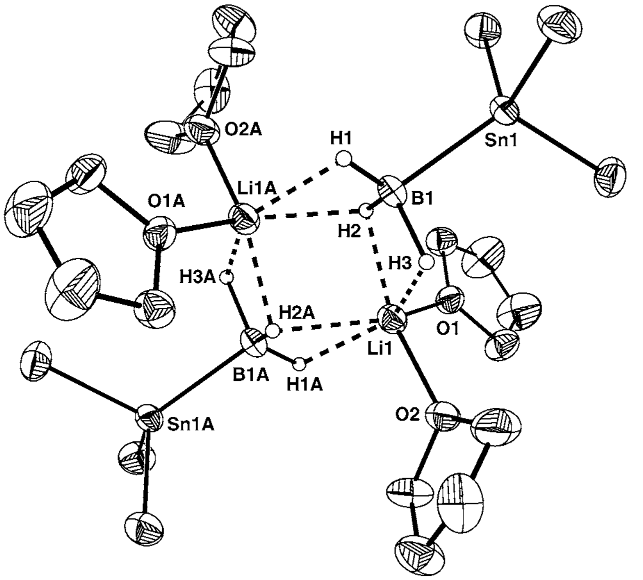


Fig. 4 Molecular structure of **8** in the crystal; thermal ellipsoids are shown at a 25% probabilty level. One of the two independent molecules is depicted. All hydrogen atoms attached to carbon atoms are omitted for clarity. Selected atom distances/Å and bond angles/°:

Sn1–B1 2.254(6), Sn2–B2 2.246(5), B1–H1 1.15(2), B1–H2 1.13(3), B1–H3 1.32(3), B1–Li1 2.46(1), Li1–O2 1.93(1). Land the Li1–O2 1.92(1), Sn1–B1–Li1 125.3(3).

Table 1 Crystallographic data and data referring to data collection and refinement

Compound	**4**	**5**	**6**	**8**
Chem. formula	$C_{45}H_{48}BGeNSn$	$C_{27}H_{33}BClNSn$	$C_{32}H_{59}BLiNO_4Sn_3$	$C_{30}H_{78}B_2Li_2O_6Sn_2$
Form. wght.	804.93	536.49	895.62	807.80
Cryst. size/mm	0.20×0.20×0.30	0.05×0.20×0.20	0.30×0.30×0.30	0.20×0.20×0.30
Cryst. system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	P2(1)/c	P2(1)/n	P2(1)/n
a/Å	10.6028(3)	8.68180(10)	18.3180(13)	16.5711(13)
b/Å	12.7814(3)	15.8320(2)	12.8073(10)	12.4142(9)
c/Å	15.4537(4)	18.8794(2)	18.5683(13)	17.4044(13)
α/°	90.790(1)	90.00	90.00	90.00
β/°	90.504(1)	96.63	101.197(2)	108.443(1)
γ/°	110.120(1)	90.00	90.00	90.00
V/Å^3	1966.07(9)	2577.62(5)	4273.3(5)	3396.5(4)
Z	2	4	4	4
ρ(calcd.)/Mg/m^3	1.360	1.382	1.392	1.580
µ/mm^{-1}	1.431	1.109	1.769	1.511
F(000)	824	1096	1792	1688
Index range	$-13 \le h \le 13$	$-10 \le h \le 10$	$-23 \le h \le 23$	$-21 \le h \le 21$
	$-17 \le k \le 12$	$-18 \le k \le 18$	$-15 \le k \le 16$	$-15 \le k \le 15$
	$-19 \le l \le 19$	$-22 \le l \le 18$	$-23 \le l \le 23$	$-22 \le l \le 22$
2θ/°	58.22	49.42	57.64	58.54
Temp/K	193	193	183(2)	183
Refl. collected	11151	12129	24371	19140
Refl. unique	6039	3998	7484	6675
Refl. observed (4 s)	5320	3349	5294	4889
R (int.)	0.0153	0.0249	0.0312	0.0756
No. variables	446	284	408	301
Weighting scheme[a)] x/y	0.0615/4.0935	0.0130/2.2452	0.081/3.989	0.065/4.304
GOOF	1.006	1.096	1.029	1.133
Final R (4σ)	0.0355	0.0281	0.0463	0.0495
Final wR2	0.1002	0.0529	0.1264	0.1421
Larg. res. peak/e/Å^3	1.168	0.355	0.920	0.846

[a)] $w^{-1} = s^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$

figure 2). The Sn–B-bond in **4** is 2.277(4) Å long and increases to 2.316(5) Å in **5**. These values correspond well with those determined by *Siebert* et al. [4] for alkyl substituted amino(stannyl)boranes [2.27(2) Å–2.323(7) Å]. The shorter B–Sn bond lengths in **4** can be explained by the inductive effect of the Cl atom to which a steric relief may contribute. Compound **5** shares three space demanding groups around its boron atom. The B–Ge distance in **5** comprises a fairly long B–Ge bond [2.143(4) Å] similar to the B–Ge-bond length found for tmpB(GePh$_3$)$_2$ [18].

The tristannylborate **6** which was isolated as [Li(THF)]$_4$ [(Me$_3$Sn)$_3$BNMePh] is present as a solvent separated ion pair (see figure 3). The Li cation is almost perfectly surrounded tetrahedrally by the oxygen atoms of the THF molecules. Its structures fits with those reported in the literature [20]. More interesting is the anionic part. The boron atom resides in a slightly distorted tetrahedral environment. The Sn–B–Sn bond angles show an average value of 104.4(3)°, whereas the average N–B–Sn angle is 114.0(3)°. This indicates, that the methylanilino ligand demands more space than the trimethylstannyl groups, a result of the comparably short B–N bond. The B–Sn bond is on average 2.293(6) Å long. In spite of the tetracoordination of the boron atom and the presence of three trimethylstannyl groups the Sn–B bonds in **6** are not longer than those found for **4** and **5** with its tricoordinated boron atoms. The B–N bond length (B1–N1 = 1.545(8) Å) is consistent with a B–N single bond to a tetracoordinated boron atom. The missing π-interaction between the boron and the nitrogen atom is compensated by a strong π-interaction between the N and the ipso-C atom of the phenyl group. This can be readily seen from the short N1–C2 bond length (1.379(7) Å) as well as from the almost planar coordination at the N atom (angle sum = 359.1°).

The stannyltrihydridoborate **8** is dimeric in the solid state as two molecules are connected via Li–H–B-bridges (Fig. 4). Two independent molecules were found in the unit cell. However, the structural parameter of the two molecules are not distinctively different. Therefore, only one molecule will be described here. The BH$_3$ groups show a $2\mu_1{}^1,\mu_1{}^2$-coordination, e. g. two hydrogen bridges to two different Li ions and one H atom bridging to two Li atoms. This coordination type is also realized for the analogous germanium compound [Li(py)$_2$(H$_3$BGePh$_3$)]$_2$ [18]. Consistent with the coordination type of the BH$_3$ group the B–Li distance is short with 2.46(1) Å and the Li–B–Sn angle quite open with 125.3(3)°. The Li atoms are hexacoordinated by two oxygen atoms and by four hydrogen atoms. The hydrogen atoms attached to the boron atom were located in the Fourier map. Due to the high electron density at the Sn atom, the determination of these hydrogen positions is not very accurate.

The B–H and Li–H bond distances have, therefore, rather large standard deviations. The B–Sn bond lengths in **8** were determined as 2.254(6) Å and 2.244(6) Å, respectively. These B–Sn bonds are significantly different and shorter than those of **4** and **5**. Therefore, this is another example that bonds of the boron atom to electropositive elements such as tin tend to shrink in length when the coordination number increases [21].

Experimental

General: All experimental manipulations were conducted in an dry atmosphere of dinitrogen or argon employing standard Schlenk and vacuum line techniques. Solvents were dried by conventional methods. Starting materials were prepared by literature methods. – NMR: Jeol 270 and 400 as well as Bruker 200 spectrometers [standards: TMS (^{1}H, ^{13}C), external $BF_3{*}OEt_2$ (^{11}B), external $SnMe_4$(^{119}Sn)] – X-ray structure determination: Siemens P4.

*B-(trimethylstannyl)-pentamethyl-borazine (**2a**):* A stirred solution of Me_3SnLi [22] (6.4 mmol) in THF was cooled to 0 °C and slowly treated with a solution of B-bromo-pentamethylborazine [8b] (1.4 g, 6.1 mmol) dissolved in ether (25 ml). After stirring for 1 h at ambient temperature, all volatile components were removed in vacuo and the solid residue was treated with hexane (60 ml). The hexane solution was then decanted. Analysis by ^{11}B NMR spectroscopy revealed the presence of **2a** as the sole product. Attempts of crystallization did not afford analytically pure samples as **2a** decomposes slowly, and only oily samples were obtained. Decomposition of **2a** produces hexamethylborazine ($\delta^{11}B = 35.5$ ($h_{1/2} = 190$ Hz) [16]) within a few days.

2a: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.34$ (d, $^2J_{HSn} = 48.8$ Hz, 9 H, $Sn(C\mathbf{H}_3)_3$), 0.39 (s, 6 H, $BC\mathbf{H}_3$), 2.70 (s, 3 H, $NC\mathbf{H}_3$), 2.89 (s, 6 H, $NC\mathbf{H}_3$) – ^{13}C NMR (100 MHz, C_6D_6): $\delta = -8.4$ (m, $Sn(\mathbf{C}H_3)_3$), –0.5 (broad, $B\mathbf{C}H_3$), 34.2 ($N\mathbf{C}H_3$), 39.2 ($N\mathbf{C}H_3$) – ^{11}B NMR (64 MHz, hexane): $\delta = 37.4$ ($h_{1/2} = 160$ Hz, 2 B), 44.7 (d, $^1J_{B,\,Sn} = 950$ Hz, $h_{1/2} = 165$ Hz, 1 B) – ^{119}Sn NMR (149 MHz, C_6D_6): $\delta = -153.1$ (q, $J_{B,\,Sn} = 950$ Hz).

*B-(trimethylstannyl)-B′,B″-dimethyl-N,N′,N″-triisopropyl-borazine (**2b**):* 10.0 mmol of Me_3SnLi were prepared in ~40 ml of THF. The stirred solution was cooled to –78 °C and slowly treated with a solution of B-bromo-B′,B″-dimethyl-N,N′,N″-triisisopropyl-borazine [8c] (3.0 g, 9.5 mmol) in ether (25 ml). After stirring for 1 h at ambient temperature, all volatile components were removed in vacuo. The solid residue was treated with hexane (60 ml) and the suspension filtered. The filtrate was cooled to 5 °C. Within 5 months 1.2 g (31%) of **2b** separated as colorless prisms, mp.: 20 °C. $C_{14}H_{36}B_3N_3Sn$ (399.2), calcd.: C 42.29, H 9.13, N 10.57, found: C 43.08, H 9.33, N 10.86%.

^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.34$ (d, $^2J_{HSn} = 42.3$ Hz, 9 H, $Sn(C\mathbf{H}_3)_3$), 0.72 (s, 6 H, $BC\mathbf{H}_3$), 1.24 (d, 6 H, $^3J_{HH} = 7.0$ Hz, $CH(C\mathbf{H}_3)_2$), 1.30 (d, $^3J_{HH} = 7.1$ Hz, 12 H, $CH(C\mathbf{H}_3)_2$), 3.95 (m, $^3J_{HH} = 7.0$ Hz, 1 H, $C\mathbf{H}(CH_3)_2$), 4.10 (m, $^3J_{HH} = 7.1$ Hz, 2 H, $C\mathbf{H}(CH_3)_2$) – ^{13}C NMR (100 MHz, C_6D_6): $\delta = -7.7$ (m, $Sn(\mathbf{C}H_3)_3$), 5.0 (broad, $B\mathbf{C}$), 23.3 ($CH(\mathbf{C}H_3)_2$), 23.7 ($CH(\mathbf{C}H_3)_2$), 47.2 ($\mathbf{C}H(CH_3)_2$), 54.8 ($\mathbf{C}H(CH_3)_2$) – ^{11}B NMR (64 MHz, hexane): $\delta = 37.8$ ($h_{1/2} = 235$ Hz, 2 B), 44.7 (d, $^1J_{BSn} = 960$ Hz, $h_{1/2} = 260$ Hz, 1 B) – ^{119}Sn NMR (149 MHz, C_6D_6): –153.6 (q, $^1J_{BSn} = 960$ Hz).

Reaction of triphenylstannyl lithium with B-bromo-pentamethylborazine: Ph_3SnLi [23] (1.2 mmol) was prepared in 50 ml of THF. The solution was cooled to –78 °C and slowly treated with a solution of B-bromo-pentamethylborazine (0.28 g, 1.2 mmol) in hexane (50 ml). Then the solution was allowed to attain ambient temperature. Its ^{11}B NMR spectrum revealed only the presence of the starting borazine ($\delta^{11}B = 31.9$ (1 B, $h_{1/2} = 180$ Hz), $\delta^{11}B = 37.4$ (2 B, $h_{1/2} = 130$ Hz)). After stirring for 24 h at 40 °C the spectrum showed no changes.

*Bis(trimethylstannyl)-(2,2,6,6-tetramethylpiperidino)borane, (**3**)* [10]*:* A stirred solution of Me_3SnLi (42.2. mmol) in THF was cooled to –78 °C and slowly treated with a solution of dichloro(2,2,6,6-tetramethylpiperidino)borane [9] (0.28 g, 1.2 mmol) in hexane (50 ml). After stirring for 1 h at ambient temperature, all volatile components were removed in vacuo, and the solid residue was then treated with 60 ml of hexane. Insoluble products were removed by decantation. Cooling the solution to –30 °C afforded 5.8 g (64%) of **3** as yellow crystals; mp.: 105 °C. $C_{15}H_{36}NBSn_2$ (478.65), calcd.: C 37.64, H 7.58, N 2.93, found.: C 37.19, H 7.43, N 2.82%.

^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.37$ (d, $^2J_{HSn} = 40.0$ Hz, 18 H, $Sn(C\mathbf{H}_3)_3$), 1.26 (s, 12 H, $C(C\mathbf{H}_3)_2$), 1.46 (s, 6 H, $CCH_2C\mathbf{H}_2$ and $CC\mathbf{H}_2$) – ^{13}C NMR (100 MHz, C_6D_6): $\delta = -5.5$ (m, $^1J_{C117Sn} = 216.8$, $^1J_{C119Sn} = 227.3$ Hz, $^3J_{CSn} = 15.6$ Hz, $Sn(\mathbf{C}H_3)_3$), 14.1 ($CH_2\mathbf{C}H_2CH_2$), 33.9($\mathbf{C}(CH_3)_2$), 35.2 ($C(\mathbf{C}H_3)_2$), 59.7 ($\mathbf{C}(CH_3)_2$) – ^{11}B NMR (64 MHz, C_6D_6): $\delta = 68.4$ (d, 1.3 d, $^1J_{BSn} = 650$ Hz, $h_{1/2} = 250$ Hz) – ^{119}Sn NMR (149 MHz, C_6D_6): –146 (q, $^1J_{BSn} = 650$ Hz).

*Chloro(triphenylstannyl)(2,2,6,6-tetramethylpiperidino)borane (**4**):* A stirred solution of Ph_3SnLi (2.6 mmol) in THF was cooled to 0 °C and slowly treated with dichloro(2,2,6,6-tetramethylpiperidino)borane (0.29 g, 1.3 mmol) dissolved in hexane (20 ml). After stirring for 1 h at ambient temperature, all volatile components were removed in vacuo. The solid residue was treated with hexane (40 ml) and the suspension filtered. The filtrate was then reduced in volume to 20 ml and kept at –78 °C. Within 5 days 0.42 g (60%) of **4** were obtained as colorless prisms, mp.: 184 °C. $C_{27}H_{33}NClBSn$ (537.14), calcd.: C 60.44, H 6.20, N 2.61, Cl 6.61, found: C 59.94, H 6.35, N 2.36, Cl 6.73.

^{1}H NMR (270 MHz, C_6D_6): $\delta = 1.31$ (s, 6 H, $CC\mathbf{H}_2$ and $CCH_2C\mathbf{H}_2$), 1.40 (s, 12 H, $C\mathbf{H}_3$), 7.08–7.22 (m, 9 H, m-Ph–**H** and p-Ph–**H**), 7.86 (m, 6 H, o-Ph–**H**) – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.0$ ($CCH_2\mathbf{C}H_2$), 33.0 ($\mathbf{C}H_3$), 35.5 ($C\mathbf{C}H_2$), 58.3 ($\mathbf{C}(CH_3)_2$), 128.4, 136.2, 138.0, 142,4 (**C**-arom) – ^{11}B NMR (64 MHz, C_6D_6): $\delta = 50.1$ ($h_{1/2} = 480$ Hz) – ^{119}Sn NMR (149 MHz, C_6D_6): no signal observed.

*Triphenylgermyl(triphenylstannyl)(2,2,6,6-tetramethylpiperidino)borane (**5**):* 1.3 mmol of Ph_3GeLi [23] were prepared freshly in app. 50 ml of diethyl ether. The solution was cooled to 0 °C and slowly treated with a solution of 0.50 g (1.3 mmol) **4**. After stirring for 5 h at ambient temperature, all volatile components were removed in vacuo, the solid residue was treated with 50 ml of toluene and filtered. The solution was then reduced in volume to 20 ml and layered with 20 ml of hexane. This afforded 0.82 g (72%) **5** as colorless crystals; map.: 189 °C. $C_{45}H_{48}NBSnGe$ (804.9), calcd.: C 67.14, H 6.01, N 1.74, found: C 64.25, H 5.37, N 1.25%.

^{1}H NMR (400 MHz, C_7D_8, –40 °C): $\delta = 1.25$ (s, 6 H, $C\mathbf{H}_3$), 1.33 (m, 4 H, $CC\mathbf{H}_2$), 1.39 (m, 2 H, $CCH_2C\mathbf{H}_2$), 1.50 (s, 6 H, $C\mathbf{H}_3$), 6.99 (s, broad, 2 H, pH-**H**), 7.07 (m, broad, 9 H, pH-**H**), 7.10 (m, broad, 5 H, pH-**H**), 7.14 (s, broad, 2 H, pH-**H**), 7.41 (m, broad, 4 H, pH-**H**), 7.41 (m, broad, 4 H, pH-**H**), 7.54 (m, broad, 6 H, pH-**H**), 7.65 (m, broad, 2 H, pH-**H**) – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 13.9$ ($CCH_2\mathbf{C}H_2$), 31.8 ($C\mathbf{C}H_2$), 33.8 (broad, $\mathbf{C}H_3$), 35.9 ($C\mathbf{C}H_2CH_2$), 60.7 (broad, $\mathbf{C}(CH_3)_2$), 127.2, 128.2, 128.–128.9 (m), 135.2–138.0 (m), 142.2, 143.0, 145.7 (all **C**-aroma.) – ^{11}B NMR (64 MHz, C_6D_6): $\delta = 70.0$ ($h_{1/2} = 500$ Hz).

*Lithium(tetrakis-tetrahydrofuran)(tris-trimethylstannyl)-[N-(methyl)anilino]borate (**6**):* A stirred solution of Me_3SnLi (21.1 mmol) in THF was cooled to –70 °C and a solution of dichloro(N-methylanilino) borane [11] (1.2 g, 6.2 mmol) in hexane (25 ml) was rapidly added. The resulting solution showed only a single ^{11}B resonance at –13.2 ppm (d, $^1J_{BSn} = 580$ Hz). After stirring for 1 h at ambient temperature, all volatile components were removed in vacuo. The black oily residue was extracted twice with 50 ml of diethyl ether. Then the filtrates were unified. The yellow solution was then cooled to –78 °C. Colorless prisms of **6** separated within two days. Yield: 2.9 g (52%) of **6**. The crystals decomposed within a few hours at ambient temperature. They are also not stable in the presence of noncoordinating solvents. Therefore, attempts to recrystallize **6** from hexane failed. After several hours a hexane solution showed no longer the signal for **6** in its ^{11}B NMR-spectrum but signals at $\delta^{11}B = 71.6$ (d, $^1J_{BSn} = 650$ Hz, $h_{1/2} = 150$ Hz) and 30.0 ($h_{1/2} = 150$ Hz), for non-identified decomposition products. Two days later only a signal at 30 ppm remained. In ether solution, however, **6** remains rather stable. $C_{32}H_{67}NBLiO_4Sn_3$ (907.2), calcd.: C 42.53, H 7.47, N 1.55, found: C 38.52, H 6.20, 1.98%. (The large errors are due to decomposition during the handling of the compound).

^1H NMR (400 MHz, C_6D_6, Et_2O): $\delta = 0.43$ (d, $^2J_{SnH} = 32.3$ Hz, 27 H, $Sn(C\mathbf{H}_3)_3$), 2.52 (m, 16 H, $OCH_2C\mathbf{H}_2$), 3.75 (broad, 3 H, $NC\mathbf{H}_3$), 4.36 (m, 16 H, $OC\mathbf{H}_2CH_2$), 6.82 (m, 1 H, Ph–**H**), 7.50 (m, 2 H, Ph–**H**), 7.67 (m, 1 H, Ph–**H**), 7.81 (m, 1 H, Ph–**H**) – ^{13}C NMR (100 MHz, C_6D_6): $\delta = -10.6$ (m, $^1J_{CSn} = 250$ Hz, $^3J_{CSn} = 59$ Hz, $Sn(\mathbf{C}H_3)_3$), 26.0 ($OCH_2\mathbf{C}H_2$), 45.9 (broad, $N\mathbf{C}H_3$), 68.6 ($O\mathbf{C}H_2$), 111.6, (**C**–Ph), 115.9 (broad, **C**–Ph) 122.5, 122.8, 127.4, 128.9 (all **C**-arom.) – ^{11}B NMR (64 MHz, C_6D_6): $\delta = -13.1$ (d, $^1J_{BSn} = 580$ Hz, $h_{1/2} = 30$ Hz) – ^{119}Sn NMR (149 MHz, C_6D_6): $\delta = -42$ ($^1J_{BSn} = 580$ Hz).

Bis(tetrahydrofuran)lithium trimethylstannyltrihydridoborate, **8** was prepared according to literature [15]. The crystals that separated from the THF solution at –20 °C were removed from the solution and covered at –40 °C with perfluoroether oil. NMR data were obtained for the THF solution and correspond fairly well with those reported.

*Reaction between **8** and catecholatobromoborane:* Catecholbromoborane (0.32 g, 1.6 mmol) was dissolved in 20 ml of toluene and the stirred solution treated slowly with a solution of **8** (0.52 g, 1.6 mmol) in hexane (20 ml). Immediately the formation of a colorless precipitate (LiBr) was observed. After filtration the filtrate was cooled to –30 °C. This caused the precipitation of catecholatoborane as a crystalline material ($\delta^{11}B = 27.9$ (d, $^1J_{BH} = 129$ Hz, $h_{1/2} = 240$ Hz)). No other product could be isolated or characterized.

X-Ray-structure-determinations

Single crystals were covered with perfluoropolyether oil, suitable specimens were selected and mounted on the tip of a glass fiber, placed on the goniometer head of the diffractometer, and cooled to 193 K under a flow of N_2. Preliminary dimensions of the unit cells were calculated from the reflections on 15 frames each at four different χ and ψ settings by changing ψ by 0.3° per frame. Data collection was performed in the hemisphere mode of the SMART program [25] at 193 K by collecting a total of 1264 frames. For data reduction the program SAINT [26] was used. For absorption correction the program SADABS was used [27]. The structures were solved by direct or Patterson methods using SHELX97 [28] programs for structure solution and refinement. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the refinement by applying a riding model. The hydrogen atoms attached to the boron were found by difference Fourier map and were refined freely. Relevant data are presented in table 1. Additional information on the structure solution are deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 155709–155712. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CN2 1EZ, U.K. [Fax: (int,) # +44-12 23/3 36-0 33; E-mail: deposit@ccdc.cam.uk]

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