# Synthesis of Boron-Halogenated Diborylamines and Diborylhydrazines by Cleavage of Stannazanes

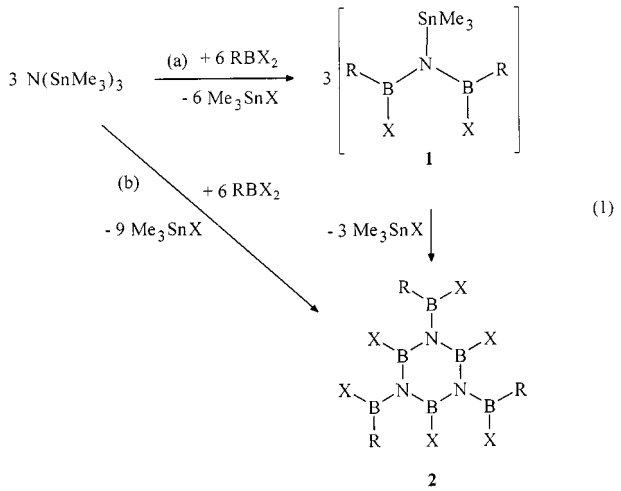
**Stefan Diemer,[a] Heinrich Nöth,*[a] and Wolfgang Storch*[a]**

**Keywords:** Diborylamines / Diborylhydrazines / Bis(organohaloboryl)amines / Bis(organohaloboryl)hydrazines / Structure elucidation

The diborylamines R′–N(BRX)$_2$ (**3**; X = Cl, Br) are obtained by stannazane cleavage of distannylorganylamines R′–N(SnMe$_3$)$_2$ (**4**) with alkyldihaloboranes RBX$_2$ in a 1:2 molar ratio. The presence of the sterically demanding substituents R and R′ also causes carbon–tin bond cleavage, resulting in low yields of **3**. However, carbon–tin bond cleavage can be suppressed by the use of bis(dimethylchlorostannyl)-organylamines **5** as the nitrogen source for the synthesis of diborylamines. This results in almost quantitative yields of the compounds **3**. Treatment of the distannylhydrazines R$_2$N–N(SnMe$_3$)$_2$ (**7**) with RBX$_2$ in a 1:2 molar ratio leads to the formation of *N*,*N*-bis(alkylhaloboryl)hydrazines **8** under mild conditions and in good yield. The molecular structures of **3** and **8** were determined by multinuclear magnetic resonance spectra in solution as well as by X-ray structure analysis in the case of **8d**. A typical structural feature of **8d** is the intramolecular BN adduct formation. Support for the constitutions of compounds **8c** comes from MS fragmentation patterns as well as from IR spectra.

## Introduction

The synthetic potential of aminostannanes, distannylamines as well as tristannylamines, is due to the easy Sn−N cleavage reactions involving Lewis acids.[1] Diborylamines functionally substituted at the boron atoms of the type Me$_3$SnN(BXR)$_2$ (**1**), obtained by the reaction of (Me$_3$Sn)$_3$N with organyldihaloboranes, are labile for X = Cl, Br. The compounds decompose to borylated borazines **2** by further stannazane bond cleavage[2] according to Equation (1).




(1)

Recently, thermally stable examples of **1,** afforded by replacement of the Me$_3$Sn group by the sterically more demanding *t*Bu group, have been reported.[3] Bis(haloboryl)-amines R′−N(BRX)$_2$ (**3**) with small organyl groups R′ attached to the nitrogen atom, and bulky groups R attached to the boron atoms, are up to this date unknown. Only a few examples of asymmetrically substituted diborylamines with different alkyl groups R and X = Cl at the boron atoms have already been described.[4] Boron-functional diborylamines are, however, useful precursors for the synthesis of B-, N- and Sn-containing heterocycles.[5][6] Two different routes for the synthesis of diborylamines of type **3** have been established in recent years. One route involves the electrophilic addition of dihaloorganoboranes to iminoboranes[6] or to aminoiminoboranes.[7] The other route uses the stannazane bond cleavage of distannylamines with dihaloorganoboranes under kinetically controlled conditions. This route represents a rather convenient method for the synthesis of diborylamines of type **3,** which are not accessible by other routes.[3] Compounds **3** containing electron-withdrawing substituents R′ attached to the nitrogen atoms are hardly known. In particular this concerns *N*,*N*-diborylhydrazines containing the hydrazine moiety, obtained by formal replacement of the R′ group for the R″$_2$N group in diborylamines of type **3**.

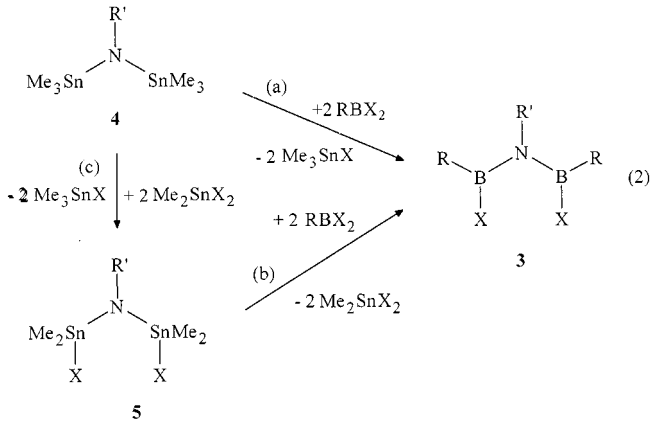
Here we report on the synthesis of boron-halogenated diborylamines and -hydrazines by stannazane cleavage reactions and the spectroscopic properties as well as some structural features.

## Bis(organylhaloboryl)organylamines

A series of diborylamines of type **3** (R′ = alkyl) have been reported using bis(trimethylstannyl)organylamines **4** as starting materials according to Equation 2a.[3] However, the synthesis of **3** with sterically more demanding groups R, for example R = *t*Bu, failed, due to the kinetically hindered approach of the organyldihaloborane to the Lewis-basic nitrogen center of **4** (see Formula 2). Therefore, cleavage of carbon−tin bonds predominates over the cleavage of the

[a] Institute of Inorganic Chemistry,
Ludwig-Maximilians-Universität München,
Butenandtstraße 7−13, Haus D, D-81377 München, Germany

  1434−1948/99/1010−1765 $ 17.50+.50/0 




| 3/4/5 | a | b | c | d | e | f | g | h | i | k | l | m | n | o | p | q |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R | *t*Bu | *t*Bu | Me | Ph | *t*Bu | *t*Bu | *t*Bu | Me | Me | Me | Me | Me | *i*Pr | *t*Bu | Me | Me |
| R′ | Me | Me | Ph | Ph | Ph | Ph | *t*Bu | *t*Bu | Mes | Dipp | $Me_3Si$ | $Me_3Si$ | $Me_3Si$ | $Me_3Si$ | $Me_3Si$ | Mes |
| X | Cl | Br | Br | Cl | Cl | Br | Cl | Br | Br | Br | Cl | Br | Br | Cl | Cl/Br | Me |
| Equation | 2b | 2a/b | 2a | 2b | 2b | 2c/2b | 2b | 2a/2b | – | – | 2b | 2a | 2a | 2b | 2b | 2c,b |

nitrogen−tin bonds even under mild conditions. However, Sn−N cleavage is favoured again by treatment of the distannylamines $R'-N(SnMe_3)_2$ (**4**) with small organoboronhalides: For example reaction of **4** (R′ = *t*Bu) with $RBX_2$ compounds containing the sterically less demanding methyl group yields the diborylamine **3h**.[3] However, the Sn−N bond cleavage of **4** proceeds under mild conditions with $MeBBr_2$, and even with *i*PrBBr$_2$, yielding **3m**[8] and **3n**, in the case of R′ = $Me_3Si$. However, isolation of the *N*-phenyldiborylamines **3c** and **3d** failed, because they decompose rapidly to the respective borazines and organodihaloboranes (see Equation 1b) on removing the solvent from the reaction mixtures. **3f** could also not be isolated, because the stannylaminoborane, *t*BuBrB−NPh−$SnMe_3$, detected by NMR as an intermediate, decomposes more rapidly with formation of a borazine (see Equation 1) prior to a second Sn−N bond cleavage. In addition, there is a competitive reaction due to the carbon−tin bond cleavage. Obviously, the low basicity of the anilino nitrogen atom prevents the attack of another alkylboron dihalide at the N centre. However, when *N*-methyldistannylamine (**4a**) is used, the Sn−N bond cleavage is favored even when it is treated with *t*BuBBr$_2$. The product obtained is **3b** according to Equation 2a. In this case the ratio of Sn−N to Sn−C bond cleavage is 4:1, estimated on the basis of the $^{11}$B-NMR spectrum of the reaction mixture. Contrary to these findings the distannylamines **4i** and **4k,** bearing sterically demanding groups R′, react even with $MeBBr_2$ quantitatively to give $Me_2BBr$ and the bis(bromostannyl)amines **5i** and **5k,** respectively,[9] according to Equation 3.

$$\underset{\textbf{4i,4k}}{R'-N(SnMe_3)_2} \xrightarrow[-\ 2\ Me_2BBr]{+\ 2\ MeBBr_2} \underset{\textbf{5i, 5k}}{R'-N(SnMe_2Br)_2} \qquad (3)$$

Performing the same reaction with **5i**, with the sterically less demanding mesityl group as substituent R′ yields the

$$\underset{\textbf{5i}}{Mes-N(SnMe_2Br)_2} \xrightarrow[-\ 2\ Me_2SnBr_2]{+\ 2\ Me_2BBr} \underset{\textbf{3q}}{Mes-N(BMe_2)_2} \qquad (4)$$

products according to Equation 3 in the first step, but does not prevent further attack of $Me_2BBr$ to immediately form the diborylamine **3q** at room temp. according to Equation 4.

In summary, when distannylamines, $R'-N(SnMe_3)_2$ (**4**) are used as starting materials for the synthesis of *B*-halogen-substituted diborylamines according to Equation 2a, Sn−C bond cleavage reactions can only be suppressed partially. However, almost quantitative Sn−N bond cleavage occurs when distannylamines **5** of type $RN(SnMe_2X)_2$ are treated with organoboron dihalides according to Equation 2b.

Therefore, the whole series of halogenoboron diborylamines **3a**−**3q** can be prepared using a procedure according to Equation 2b, except for **3i** and **3k**. No reaction occurs on treatment of the distannylamines **5i** and **5k** with $MeBBr_2$ even under reflux conditions for several hours. As mentioned above, the steric demands of the mesityl- and the 2,6-diisopropylphenyl group attached to the nitrogen atom of the distannazanes **5i** and **5k** prevents the attack of $RBHal_2$ at the N atom, but not at the Sn atom of the $Me_3Sn$ moiety. Consequently, **5i** and **5k** even react with the strong Lewis acid $BCl_3$ with formation of the distannazanes $RN(SnMe_2Cl)_2$ by tin−carbon bond cleavage.[9]

Sterically demanding groups R attached to the boron atoms in $RBX_2$ also hinder the stannazane cleavage reactions, even if the distannylamine bears a sterically less demanding group R′ at the nitrogen atom. Therefore only one of the Sn−N bonds of **5a** is cleaved by treatment with an excess of $MesBCl_2$ after a period of 2 d in boiling $CHCl_3$ according to Equation 5.

Purification of the stannylaminoborane **6a** by distillation or recrystallisation failed due to slow decomposition at

$$[Me\text{-}N(SnMe_2Cl)_2]_2 \xrightarrow[-\,Me_2SnCl_2\ -\,2\,MesBCl_2]{+\,4\,MesBCl_2} 2\ Mes(Cl)B\text{—}NMe\text{—}SnMe_2Cl \qquad (5)$$

**(5a)$_2$** **6a**

room temp., as indicated by $^{11}$B-NMR spectroscopy. However, the presence of stannylaminoboranes **6** as intermediates en route to diborylamines is shown not only by NMR spectroscopy, but also by the reaction of the distannylamine $PhN(SnMe_2Cl)_2$ (**5d**) with $MesBCl_2$ in a 1:1 molar ratio according to Equation 6b. The stannylaminoborane **6d**, which could not be isolated, subsequently reacts with $MeBBr_2$ in a 1:1 molar ratio with the formation of the asymmetrically substituted diborylamine **3r** according to Equation 6c.

$$PhN(SnMe_3)_2 \xrightarrow[-\,2\,Me_3SnCl]{+\,2\,Me_2SnCl_2} PhN(SnMe_2Cl)_2 \qquad (6a)$$

**4c** **5d**

$$\mathbf{5d} \xrightarrow[-\,Me_2SnCl_2]{+\,MesBCl_2} \mathbf{6d} \qquad (6b)$$

$$\mathbf{6d} \xrightarrow[-\,Me_2SnBr_2]{+\,MeBBr_2} \mathbf{3r} \qquad (6c)$$

Surprisingly, the diborylamine **3r** can be distilled in vacuo and heated to 90°C without decomposition. In general, the synthesis of a variety of diborylamines of type **3** follows the route shown in the Equations 2c and 2b, and described step by step for **3r** (Equations. 6a–c). The derivatives **3e** and **3f**, which are also not accessible following the route according to Equation 2a, are obtained in good yield using the "one-pot reaction" described in Equations 6a–c. The progress of the reactions described by Equations 2c and 2b, leading to the formation of **3e**, has been monitored by $^{11}$B-NMR as a function of time during a period of 145 h; the result is shown in Figure 1. A typical feature of this reaction is the exchange of a bromine atom of *t*BuBBr$_2$ against a chlorine atom of the distannazane **5d** in the initial step. After warming the reaction mixture from −50°C to ambient temp. over a period of 2.5 h the cleavage of the first tin–nitrogen bond of **5d** is completed with formation of the stannylaminoborane PhN(B*t*BuCl)SnMe$_2$Cl. As shown in Figure 1 even after 4 d no further reaction occurs with another equiv. of the alkylhaloborane at room temp.

However, the second Sn–N bond cleavage starts if the reaction mixture is maintained at reflux, and after 2 h the respective diborylamine **3e** is found. It can be isolated (b.p. 50°C/high vac) in good yield, decomposing to yield only trace amounts of the borazine (PhNB*t*Bu)$_3$ under these conditions. Nevertheless, the Cl/Br exchange proceeds selectively as well as quantitatively. This reaction can be used as a convenient method to introduce B–Cl bonds in functionally substituted diborylamines starting with bromoboranes.

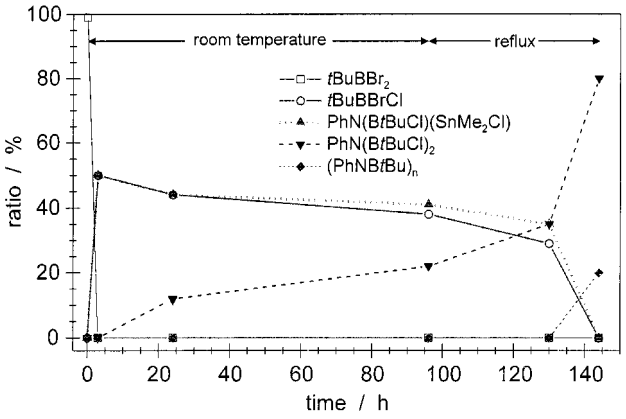



Figure 1. Reaction of $PhN(SnMe_2Cl)_2$ (**5d**) with *t*BuBBr$_2$ in a 1:2 molar ratio monitored by $^{11}$B NMR over a period of 145 h

## *N*,*N*-Bis(organylhaloboryl)-*N*′,*N*′-diorganylhydrazines

A variety of cyclic 1,1-diborylhydrazines[10] as well as few examples of noncyclic derivatives[11] are already known. Their chemical properties and structural features, for example the donor property of the diorganylamino group of the hydrazine moiety,[11b] are scarcely investigated. However, functionally boron-substituted diborylhydrazines, are hitherto unknown, although they might be attractive reagents in preparative chemistry. Moreover, they may offer information about structure and bonding, and for that reason we looked for a convenient access to this class of compounds.

The synthesis of *N*,*N*-diorganyl-*N*′,*N*′-dihaloborylhydrazines is achieved under mild conditions by allowing distannylhydrazines **7** to react with $RBX_2$ in a 1:2 molar ratio according to Equation 7.

$$R'_2N\text{—}N(SnMe_3)_2 \xrightarrow[-\,2\,Me_3SnX]{+\,2\,RBX_2} R'_2N\text{—}N(BRX)_2 \qquad (7)$$

**7** **8**

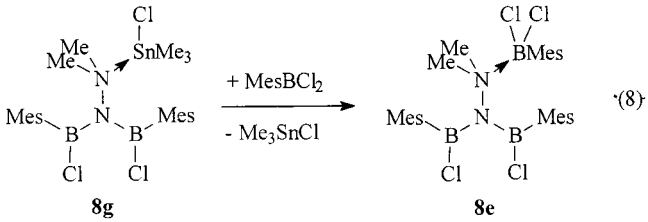
| | **7a** | **7b** |
|---|---|---|
| R' | Me | Ph |

| | **8a** | **8b** | **8c** | **8d** | **8e** | **8f** |
|---|---|---|---|---|---|---|
| R | Me | *i*Pr | *t*Bu | Mes | Me | *t*Bu |
| R' | Me | Me | Me | Me | Ph | Ph |
| X | Br | Br | Br | Cl | Br | Br |

Contrary to the Sn–C bond-cleavage reaction occurring with the formation of the diborylamines **3** according to Equation 2a, no such bond cleavage reaction has been observed in case of the distannylhydrazines. The basicity of the tin atoms bearing a nitrogen atom in compounds **7** is obviously high compared to the distannylamines **4**, presumably due to the α-effect of the nitrogen atom of the adjacent $R_2N$ group.[12] Subsequently, the Sn–N bond cleavage proceeds quantitatively according to Equation 7, even in the presence of sterically demanding groups R attached to the boron atoms of $RBX_2$.

The treatment of the distannylhydrazines **7a** or **7b** with $MeBBr_2$ according to Equation 7 produces only a colorless solid, insoluble in polar and nonpolar solvents, after removal of the volatile components. The $^{11}B$- and the $^{119}Sn$-NMR spectra recorded from the reaction mixture before removal of the volatile components, however, indicate the formation of the diborylhydrazines **8a** and **8e**. In contrast, the reaction of $RBX_2$ with bulkier groups R = *i*Pr, *t*Bu, and Mes proceeds slowly with formation of **8b**−**d**. Surprisingly, these compounds show two $^{11}B$-NMR signals pointing to the presence of tri- and tetracoordinated boron atoms (see Table 2). The remarkable structural difference between the diborylhydrazines **8** when compared to the diborylamines **3** is the formation of an intramolecular Lewis acid/base adduct, featuring a three-membered $B_2N$ ring unit (see below). The presence of monomeric molecular units is also confirmed by a molecular-mass determination of compounds **8** in solution.

Treatment of the *N*,*N*-diphenyl-*N*′,*N*′-distannylhydrazines **7** with $MeBBr_2$ or $tBuBBr_2$ yields the corresponding diborylhydrazines, which, however, could be detected only in solution. A variety of signals are found in the $^{11}B$-NMR spectrum of the reaction mixture [$^{11}B$ NMR: ( = 50.2 (**8f** uncertain), 30.3, 22.5, 2.6].[9] The isolation of **8e** and **8f** from the insoluble residue failed, presumably due to the formation of polymeric species by intermolecular B←N interaction, or adduct formation of the $R_2N$ group of **8** with $Me_3SnX$. The latter can be excluded by controlling the reaction conditions, especially the concentration of the starting materials in the reaction mixture. For example, the diborylhydrazine **8d** formes an adduct only with $Me_3SnCl$ (**8g**) when the concentration of the distannylhydrazine **7a** exceeds 0.13 mol/L in a dichloromethane solution, and the addition time of $MesBCl_2$ is shorter than 60 min (see Experimental Section). In this case the tin halide is only released from **8g** by substitution with an excess of $MesBCl_2$, forming **8h** according to Equation 8.




**8g** **8e** (8)

## NMR Spectra

### Diborylamines

Selected $^1H$-, $^{11}B$-, $^{13}C$-, and $^{14}N$-NMR data of the *B*-halogen substituted diborylamines **3** and triborylamines are listed in Table 1, and of halogenated diborylhydrazines **8** in Table 2. Both tables also contain NMR data of some other compounds for comparison. For additional data see the Experimental Section.

The shielding of the $^{11}B$ and $^{14}N$ nuclei are in accordance with a trigonal-planar environment of both atoms in the diborylamines of type **3**. They are also in agreement with the data of known diborylamines.[3][6] However, compared to aminohaloboranes, for example $Me_2N-B(Me)Cl$ ($^{11}B$ NMR: δ = 38.5),[13] the $^{11}B$ nuclei of the diborylamines are deshielded by 10−15 ppm, as there is only one pair of electrons at the N atom to be shared by two boron atoms in (pp) π-bonding. Additional deshielding results from the torsion between the planes of the boron and the nitrogen atoms due to the bulky substituents R and R′ attached to these atoms. This causes an additional decrease of the (BN) π-interaction. In contrast to the $^{11}B$-NMR data of asymmetrically substituted diborylamines of the type $RN(BR'X)(BR''X)$[6] with two different $^{11}B$-NMR signals (see Table 1; **3p**), there is only one signal detected for the two boron nuclei in **3r**. Therefore, the degree of distortion around the BN axis of both of the boryl groups in type **3** compounds, due to sterically induced crowding, is approximately of the same order, featuring a geometry shown in Figure 2c. The structure of a "borylated aminoborane" **b** (see Figure 2) assumed for compounds of type **3p** as well as a planar diborylamine framework **a** (see Figure 2) can be excluded.

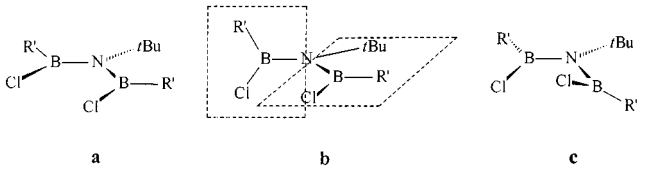



Figure 2. Alternative stereoisomers of diborylamines of type **3**

It is well known that in compounds RR′BX, the exchange of a chlorine for a bromine atom[14] results in a significant deshielding of the boron nucleus. This influence is also detected in the diborylamines of type **3**. Electron-withdrawing substituents (for example R′ = Ph) or sterically demanding groups attached to the nitrogen atom (for example R′ = $SiMe_3$, causing a larger torsion angle between the boron and nitrogen planes) also exhibit a significant downfield shift of the $^{11}B$ resonance. However, introduction of a third boryl group ($R_2B$) at the nitrogen atom leads to a larger deshielding of the boron nuclei of ca. 8 ppm, due to the π-acceptor quality of this group. **3t** (see Table 1) represents one of the rare examples of an asymmetrically substituted triborylamine.[15]

The π-acceptor function of the different boryl groups in diborylamines of type **3** is shown by the deshielding of the central nitrogen nucleus. Our NMR study confirms, that a deshielding of the nitrogen nuclei is accompanied by better shielding of the boron nuclei, owing to (BN)π interaction and vice versa. The larger sensitivity of the nitrogen nucleus to changes in (BN)π interaction is demonstrated by comparison of the $\delta^{14}N$ data for the diborylamines **3l**−**3m** as well as that of **3o**−**3n**. Replacement of a chlorine by a bromine atom leads to a significant downfield shift of about 15−16 ppm ($^{14}N$), as a consequence of less (BX) π-bonding in the B−Br bond. Moreover, the influence of the sterically

Table 1. $^{11}$B-, $^{14}$N-, $^{1}$H- and $^{13}$C-NMR data of diborylamines and related compounds

| Compound | No. | $\delta^{11}$B (ppm) | $h_{1/2}$ [Hz] | $\delta^{14}$N (ppm) | $h_{1/2}$ [Hz] | $^{1}$H NMR (δ) *ECH* | BC*H* | BCC*H* | $^{13}$C NMR (δ) E*C* | B*C* | BC*C* | Remark |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Me−N(B*t*BuCl)$_2$ | **3a** | 49.9 | 154 | −268 | 178 | 2.90 | – | 1.08 | 33.16 | 25 | 28.31 | [a] |
| Me−N(B*t*BuBr)$_2$ | **3b** | 48.0 | 174 | −259 | 197 | 2.88 | – | 1.09 | 33.95 | 26 | 28.48 | [a] |
| *t*Bu−N(B*t*BuCl)$_2$ | **3g** | 45.5 | | −226 | | – | – | 1.11 | 55.13 | 27 | 30.32 | [a,b] |
| Ph−N(BMeBr)$_2$ | **3s** | 51.0 | 161 | | | – | 1.2 | – | | | | [c] |
| Ph−N(B*t*BuCl)$_2$ | **3e** | 50.6 | 253 | −234 | 506 | – | – | 1.01 | 141.47 | 26 | 28.65 | [a] |
| Ph−N(B*t*BuBr)$_2$ | **3f** | 49.3 | 300 | −228 | 488 | – | – | 0.98 | 141.39 | 27 | 29.24 | [a] |
| Ph−N(BPhCl)$_2$ | **3d** | 46.9 | 385 | | | – | – | | | | | [c] |
| Ph−N(B$^1$MeCl)−B$^2$MesCl | **3r** | 50.2 | 600 | not measured | | – | 0.91 | – | 146.54 | 10 (B$^1$) | 136.78 | [a,d] |
| Me$_3$Si−N(BMeCl)$_2$ | **3l** | 50.3 | 128 | −234 | 84 | 0.30 | 0.86 | – | 1.80 | 12 | – | [e1,f] |
| Me$_3$Si−N(BMeBr)$_2$ | **3m** | 49.8 | 248 | −219 | | 0.35 | 1.09 | – | | | – | [e2,g] |
| Me$_3$Si−N(B*i*PrCl)$_2$ | | 52.2 | | −239 | | 0.18 | 1.03 | 0.97 | 1.78 | 24.2 | | [e3,h] |
| Me$_3$Si−N(B*i*PrBr)$_2$ | **3n** | 52.2 | 321 | −230 | 109 | 0.33 | 1.33 | 1.05 | 1.89 | 25.8 | 19.12 | [e4,h] |
| Me$_3$Si−N(B*t*BuCl)$_2$ | **3o** | 53.8 | 218 | −246 | 271 | 0.39 | – | 1.02 | 4.41 | 34.3 | 28.87 | [e5,g,i] |
| *t*Bu−N(B$^1$EtCl)− | B$^1$ | 63.6 | | not measured | | – | 1.1 m | – | – | 9.0 | 29.2q | [i] |
| (B$^2$*t*Bu Cl) (**3s**) | B$^2$ | 40.4 | | | | | – | 1.45 | 55.7 | | | |
| Me$_2$B$^1$−N(B$^2$MeBr)$_2$ | B$^1$ | 68.4 | | −204 | | – | 1.1 | – | – | | | [h] |
| | B$^2$ | 47.1 | | | | | – | 0.97 | | | | |
| *i*Pr$_2$B$^1$−N(B$^2$*i*PrCl)$_2$ | B$^1$B$^2$ | 72.5 | | −213 | | – | 1.1 m | 1.1 m | – | 24.22 | 19.41 | [h] |
| | | 47.5 | | | | | 1.0 m | 1.0 m | | 2.4 | 9.2 | |
| Me$_2$B$^1$−N(B$^2$*t*BuCl)$_2$ | B$^1$ | 62.6 | 276 | −206 | 180 | – | 0.71 | – | – | 14 | – | |
| (**3t**) | B$^2$ | 56.6 | 291 | | | | – | 1.06 | | 12 | 28.51 | |

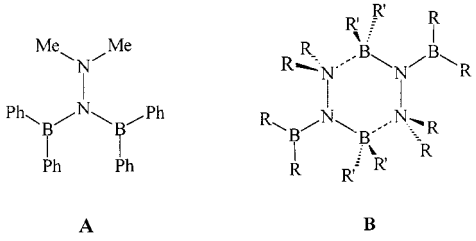
[a] E = N. – [b] Data from ref.[43]; $^{1}$H/$^{11}$B values are largely consistent with the data of Paetzold et al.[6] – [c] Recorded as a sample of the reaction mixture ($CH_2Cl_2$); isolation failed. – [d] $^{11}$B signal accompanied by a high-field shoulder at δ ≈ 48 (B$^1$ or B$^2$); assignment not possible. – [e1] E = Si; $^{29}$Si NMR: δ = 6.46; [e2] not measured; [e3] 4.6; [e4] 5.61; [e5] 7.56. – [f] $^{11}$B-, $^{14}$N- and $^{1}$H-NMR data in agreement with ref.[44] – [g] Data from ref.[45] and references there. – [h] Data from ref.[3] – [i] $^{11}$B, $^{1}$H and $^{13}$C values largely consistent with those of Paetzold et al.[6]

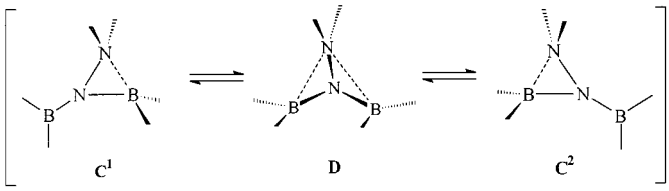
demanding groups R′ on the torsion angle between the nitrogen and the boron planes is demonstrated by a significant deshielding of the nitrogen nuclei as demonstrated by the compound pairs **3n/3o** (ΔN: +12 ppm) and **3m/3n** (ΔN: +11 ppm).

The $^{1}$H- and $^{13}$C-NMR data also are in accordance with the suggested structures, particularly the monomeric molecular geometry of the species of type **3**. The $^{13}$C-NMR signals of the carbon atoms directly linked to the boron atoms can only be detected by cooling the sample between −20°C to −40°C. At ambient temp. the signals vanish due to quadrupolar relaxation of the second kind.[16] The $^{13}$C resonances of carbon atoms adjacent to the boron atoms are hardly affected by changes of the shielding at the boron nuclei owing to smaller changes of the polarity of the B−C σ-bonds.

## Diborylhydrazines

There is some information available about the structures of fully alkylated *N,N*-diborylhydrazines from NMR data. In particular, the nonassociated nature ($^{11}$B NMR: δ = 42.0) of compounds of type **A** (Scheme 1) with tricoordinated boron atoms[11] is ascertained. Replacement of both the $Ph_2B$ groups by $Me_2B$ groups in **A** results in only one broad $^{11}$B-NMR signal at δ = 23.[17] This shift suggests a weak B−N coordinate bond and points to a fluxional behavior of the boryl groups as delineated in the sequence **C**$^1$/**D**/**C**$^2$ (Scheme 1). The molecular-mass determination ascertains the presence of a monomeric unit. These data indicate an equilibrium between the intramolecular adducts **C**$^1$ and **C**$^2$, with rapid migration of the $Me_2N$ group. Therefore, only one high-field $^{11}$B signal appears, according to the nonclassical constitution **D**, representing the transition state between the two resonance hybrids **C**$^1$ and **C**$^2$. Asymmetrically substituted diborylhydrazines show two $^{11}$B resonances ($^{11}$B NMR: δ = 0.7, 43.5), which point to a cyclodimeric structure of type **B**, (Scheme 1), featuring a six-membered ring.[17]




Scheme 1. Structural features of *N,N*-diborylhydrazines

The $^{11}$B-NMR and the $^{14}$N-NMR spectra of the boron-halogen substituted diborylhydrazines **8b**, **8c** and **8d** show one signal for a tricoordinated and one signal for a tetraco-

Table 2. $^{11}$B-, $^{14}$N-, $^{1}$H- and $^{13}$C-NMR data of diborylhydrazines and related compounds

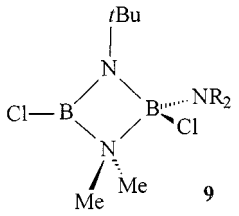
| $R_2N-N(BR'X)(BR''Y)$ | | | | | No. | $^{11}$B NMR | $^{14}$N NMR | $^{13}$C NMR(δ) | | $^{1}$H NMR (δ) | | Structure[a] | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R | R′ | R″ | X | Y | | δ | δ | B(C)*C* | N*C* | B(C)*Me* | N*me* | | |
| Me | *i*Pr | *i*Pr | Br | Br | **8b** | 2.1<br>38.9 | −276<br>−305 | 19.36 | 46.8 | 0.97 | 3.09 | **C** | [b,c] |
| Me | *t*Bu | *t*Bu | Br | Br | **8c** | 2.0<br>40.3 | −263<br>−328 | 29.99<br>30.15 | 46.57<br>51.06 | 1.01<br>1.04 | 3.13<br>3.27 | **C** | [b−d] |
| Me | Mes | Mes | Cl | Cl | **8d** | 0.7<br>38.6 | not measured<br>not measured | | 45.83 | − | 3.12 | **C** | [b] |
| Ph | Me | Me | Br | Br | **8e** | (48.9)<br>−2.4<br>40.0 | | | | | – | **A**<br>**B** or **C** | [b,e] |
| Ph | *t*Bu | *t*Bu | Br | Br | **8f** | 50.2 | | | | 0.80 | – | **A** | [e] |
| Me | Ph | Ph | Ph | Ph | **8g** | 42 | | | | | 2.50 | **A** | [f] |
| Me | Ph | Me | Ph | Me | **8h** | 0.7<br>43.5 | | 4.55<br>143.4 | 46.7 | 0.60 | 2.60 | **B** | [g] |
| Me | Me | Me | Me | Me | **8i** | 23.0 | −196<br>−323 | 6.8 | 38.5 | 0.15 | 2.70 | **C** or **D** | [c,g] |

[a] See Scheme 1. − [b] δ$^{11}$B data: high field: endocyclic B atom; low field: exocyclic B atom. − [c] δ$^{14}$N data: high field: diorganylamino group; low field: diborylamino group. − [d] Pairs of signals for the alkyl groups: *t*Bu: endo- and exocyclic; $NMe_2$: above and below the ring plane. − [e] Not isolated; **8e**: mixture of products, composed of the adduct **B** or **C** and the monomer **A** (δ$^{11}$B in parenthesis) and the borazine. − [f] Data from ref.[11] − [g] Data from ref.[17]

ordinated boron atom. These data are in accordance with both, a dimeric unit **B**, or with a monomeric species **C**, featuring an intramolecular adduct. Molecular-mass determination in solution and subsequently the X-ray structure determination of **8d** (see below) confirm the monomeric structure, derived from type **C**.

The tetracoordinated boron nuclei of compounds **8b−e** are better shielded than those in dimeric aminohaloboranes, for example $[EtClB-NMe_2]_2$ ($^{11}$B NMR: δ = 10.2), or in amineborane adducts, $Ph_2(Cl)B-NMe_3$ ($^{11}$B NMR: δ = 10.9),[14] or in the BN heterocycle **9** ($^{11}$B NMR: δ = 10.8). It is suggested that this indicates higher electron density at the boron nuclei due to the higher basicity of the hydrazine nitrogen atom of the $Me_2N$ group compared to the aminoborane nitrogen atom. Therefore, the deformation of the bond angles in the cycloadduct, featuring a three-membered ring, have no significant influence on the shielding of the boron nuclei. The $^{11}$B-NMR data of the exocyclic tricoordinated boron atoms of the diborylhydrazines are in good agreement with those of aminohaloboranes, for example *t*BuClB−$NMe_2$ ($^{11}$B NMR: δ = 40.5),[14] *t*BuClB−NHMes ($^{11}$B NMR: δ = 40.9),[45] indicating marked (BN) π-interaction between the exocyclic boryl group and the central nitrogen atom. A typical diborylamine $^{11}$B-NMR shift of 10 ppm downfield compared to the respective aminoboranes (see above), can be measured for the diborylhydrazine **8f** ($^{11}$B NMR: δ = 50.2). Obviously, the weak basicity of the $Ph_2N$ nitrogen atom, owing to the π-acceptor function of the phenyl substituents as well as their sterical demand, prevents the formation of an intramolecular adduct.

The $^{14}$N-NMR data of the diborylhydrazines **8b** and **8c** confirm the proposed structures. From other derivatives no signal could be detected. Two signals are observed, one of these at high field in the range of "ammonia" nitrogen nuclei, and the other one in the range of "aminoborane" nitrogen nuclei. These values and the $^{11}$B-NMR data are in good accordance with those measured for asymetrically substituted diborylamines, featuring four-membered rings with formation of an intramolecular BN adduct,[7] as depicted in **9**.




**9**

Additional information about the structural features is provided by $^{1}$H- and $^{13}$C-NMR data. As expected, two groups of signals for the methyl groups above and below the plane of the three-membered ring, as well as for the endo- and exocyclic organyl groups attached to the boron atoms, are observed in the NMR spectra of **8b**, **8c** and **8d**. Those of **8b** and **8d** only show a broadening of the $^{1}$H- and $^{13}$C-NMR signals at room temp., but the doubling of the signals of **8c** is visible even at ambient temperatures.

## Mass Spectra

The diborylamines **3** as well as the diborylhydrazines **8** have been studied by mass spectrometry. Fragments with an abundance larger than 2% are listed in the Experimental Section. The fragmentations of **3b**, **3r** and **8b**, which are characteristic for both classes of compounds are summarized in Schemes 2−4. Measured isotope patterns correspond to the calculated ones.

Characteristic for the ionization by electron impact is the low intensity of the molecular ions of the species containing the B−N−B unit, which show the weak stabilization of the

positive charge of the radical cation in the molecular framework. Contrary to these findings the ionization of the diborylamine **3r** and the diborylhydrazine **8d** leads to the formation of the molecular ion as the base peak, certainly due to the better stabilization of the positive charge by delocalization into the π-system of the aromatic rings attached to the boron atoms. Therefore, these molecules show very few secondary fragments. Concerning the fragmentation pattern, the ionization proceeds preferentially at the central nitrogen atom. This is true also for the fragmentation of the diborylhydrazines, although the first ionization energy of the dimethylamino group is approximately 1 eV lower than that of the diborylamine fragment according to the photoelectron spectrum of $Me_2N-N(BMe_2)_2$.[17]

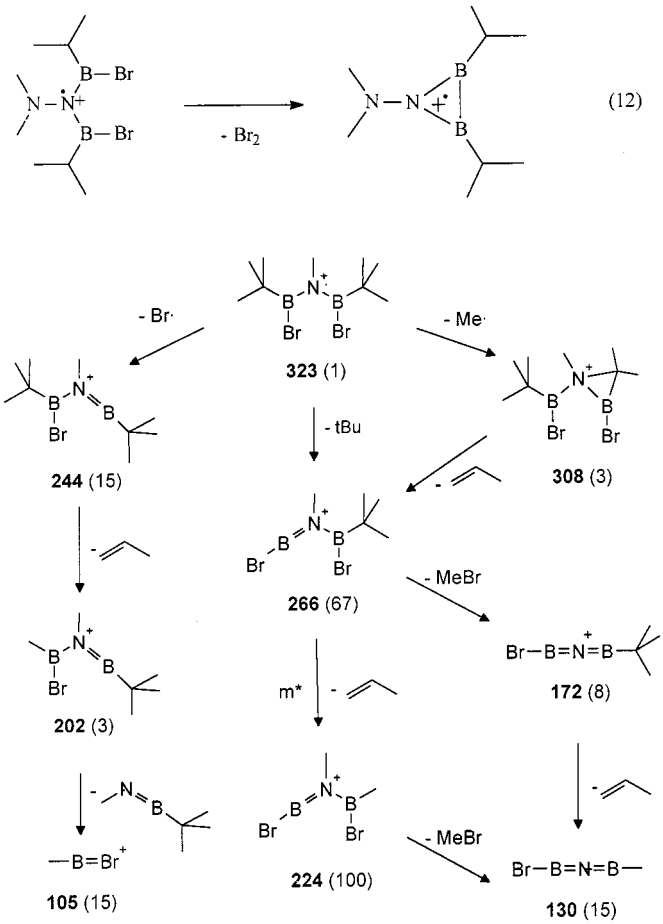
The predominant primary fragmentation is that of α-elimination, demonstrated by the appearence of nitrenium cations $Y-B=N^+R-BR'X$ (Y = alkyl, aryl, hal) in high intensity (see Scheme 2, fragment ion 244; Scheme 3, fragment ion 198). It proceeds by elimination of a substituent in α-position to the ionized centre by homolytic bond cleavage, with the sequence Mes ≈ *t*Bu > *i*Pr > Br > Cl ≈ Me. The ease of α-bond cleavage depends on the stability of the eliminated radical as well as the resulting cation. The mesityl group elimination, however, is facilitated due to the steric relief of the parent ion.

Another important primary fragmentation via neutral particles like $R_2BX$ or $RBX_2$ can be detected in the mass spectra of **3r** (Scheme 2), **3e**, **8c** and **8d**, all of them showing the molecular ion as the 100% peak.

Characteristic fragments found are bis(boranediyl)iminium ions of the type $[X-B=N=B-Y]^+$; they appear at the end of a fragmentation path with remarkable intensity (Scheme 2). The appropriate ions in the mass spectra of the diborylhydrazines bear the even more stabilizing $Me_2N$ group. Therefore, the fragment *m*/*z* 159 and 95 (Scheme 4), for example, appear as 100 and 41% peaks, respectively.

A McLafferty-type rearrangement with the elimination of propene or isobutene, denoted as "McL" in the fragmentation schemes, can be observed in the fragmentations of **3t**, **8a** and **8b** (see Schemes 2 and 4).

The mass spectra of the diborylhydrazines show no fragment ions with masses larger than the monomeric molecular units. This lends support to the formation of an intramolecular adduct as deduced from NMR data and shown in Figure **C** (Scheme 1). Therefore, all nitrenium ions with an amino group attached to the boron atom may also be drawn as a cyclic fragment ion according to the structure of type **C**. Additionally, the fragmentation patterns of the diborylhydrazines exhibit radical cations of remarkable intensity with an azadiboriridine structure. These fragments are formed by α-elimination of halogen molecules from the parent molecular cation according to Equation 12. The appearance of the azadiboriridine ring unit as a relatively stable radical cation gives rise to the assumption that the heterocycle is not only stable as a species in the exited state, but also as molecular unit in the ground state. Therefore, reactions were performed to obtain heterocycles with the hydrazine moiety, depicted in Equation12, by use of the well-known procedure of the reductive B−B bond formation.

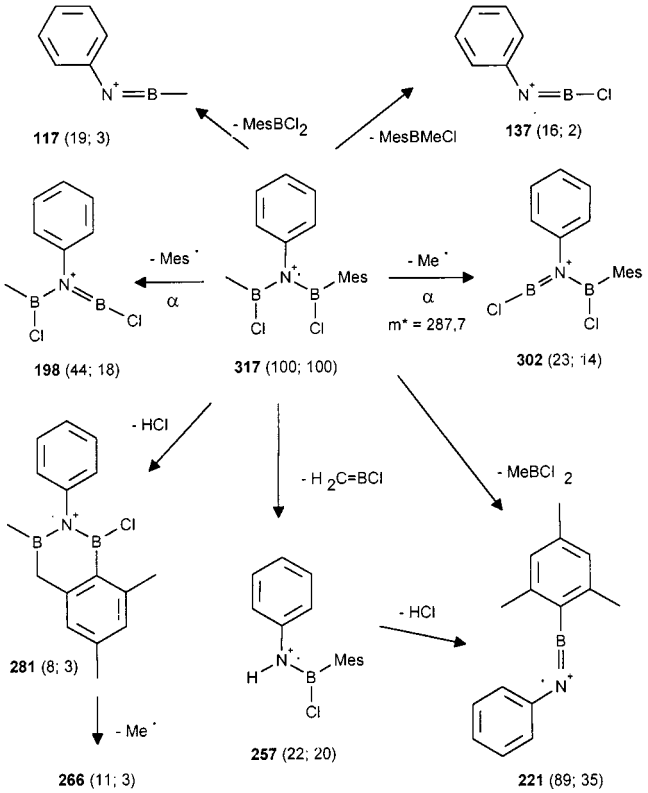



Scheme 2. Fragmentation of the diborylamine **3b**

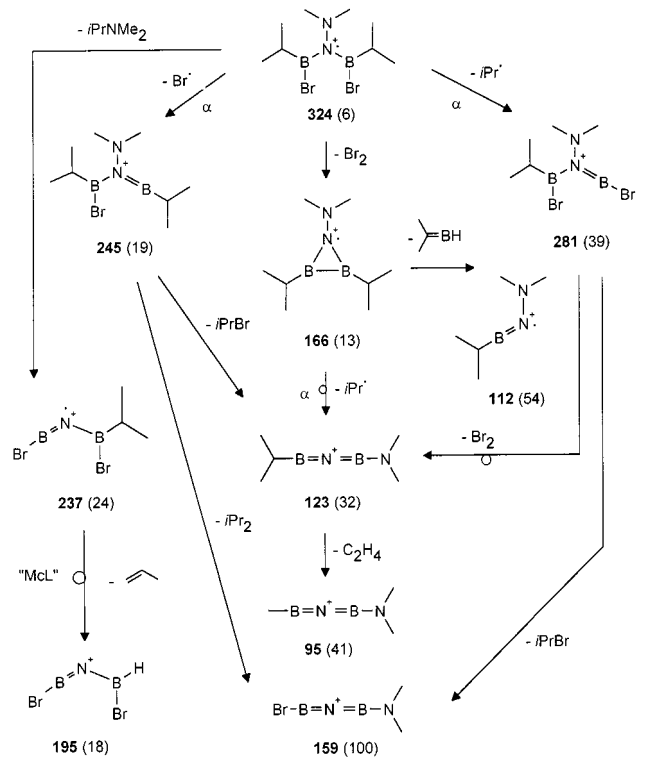
## Molecular Structures

The characteristic structural features of the halogenated *N*,*N*-diborylhydrazines, found in solution, are confirmed by the molecular structure of **8d** (Figure 3), determined in the solid-state by X-ray crystallography. Selected bonding parameters are listed in the caption of Figure 3. Compound **8d** crystallizes in the orthorhombic space group $Pca2_1$, $Z = 4$, and serves as a model for the proposed intramolecular donor-acceptor complex **C** (Scheme 1). The endocyclic B1−N1 length of 1.484(5) Å is in the range of a single ($sp^2-sp^2$) bond length, the exocyclic B2−N1 length [1.381(5) Å] is, however, consistent with a B−N bond order of > 1.5 of a double bond. Moreover, the small torsion angle N2−N1−B2−Cl2 of 3.4° allows effective (BN) π-interaction between the exocyclic boryl group and the N1 atom of the three-membered ring. The molecular geometry of **8d** in the solid state is fully compatible with the NMR data. Thus, the structure of this compound in the solid and in solution do not differ.

The extremely enlarged B1−N1−B2 angle of 163.3(9)° compared to the appropriate N2−N1−B2 angle of




Scheme 3. Fragmentation of the diborylamine **3r**




Scheme 4. Fragmentation of the diborylhydrazine **8b**

129.4(3)° should be noted. This asymmetrical framework can only be rationalized by a steric repulsion between the two mesityl groups. Although the bond angles in the three-membered ring are small, resulting in a weak overlap of the σ-bond orbitals, the B1−N2 length between the tetracoordinated nitrogen atom and boron atom is remarkably short. It is of the same size as that in the borylated hydrazine **10** ($d_{(BN)}$: 1.626 Å).[18] However, the respective B−N bond of the four-membered cycloadduct **11** ($d_{(BN)}$: 1.713 Å)[19] is 0.10 Å longer, probably due to the sterically more demanding tetramethylpiperidino group compared to the $Me_2N$ group. Therefore, steric repulsion of the mesityl groups in **8d** causes the opposite effect and may be responsible for the short B1−N2 bond. As a consequence of the different hybridization of the boron atoms the B1−Cl1 bond is 0.05 Å longer than the B2−Cl2 bond.

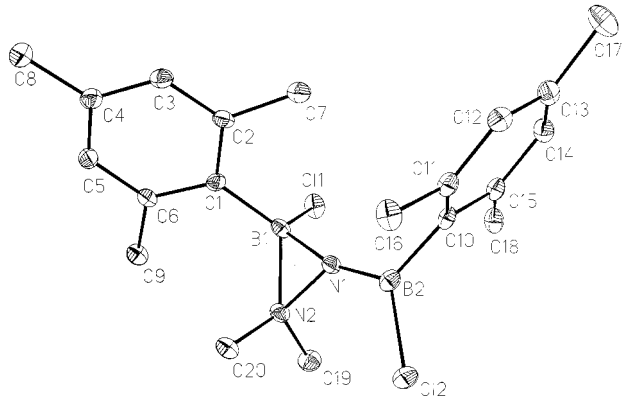
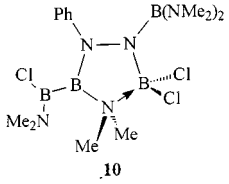
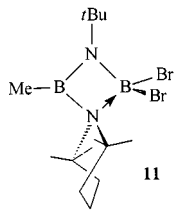



Figure 3. Molecular structure of $Me_2N-N(BMesCl)_2$) (**8d**) in ORTEP-type description; thermal ellipsoids represent a 25% probability; hydrogen atoms are not shown for the sake of clarity; selected bond lengths [Å] (esds are given in parentheses as units in the last digit): B1−N1 1.484(5), B1−N2 1.624(5), B2−N1 1.381(5), N1−N2 1.474(4), B1−Cl1 1.843(4), B2−Cl2 1.796(5), B1−C1 1.575(6), B2−C10 1.562(6), C1−C2 1.423(5), C1−C6 1.432(5), C10−C11 1.405(5), C10−C15 1.412(5); selected bond angles [°]: B1−N1−B2 163.3(9), B1−N1−N2 66.6(2), B2−N1−N2 129.4(3), N1−B2−Cl2 119.5(3), N1−B2−C10 121.8(3), C10−B2−Cl2 118.7(3), N1−B1−C1 124.0(3), N1−B1−Cl1 115.7(3); torsion angle [°]: N2−N1−B2−Cl2 3.4




**10**




**11**

## Experimental Section

**General:** All manipulations were performed in dry nitrogen. Glassware was dried prior to use by heating in vacuo. − NMR: Bruker AC P200 ($^{11}B$, $^{14}N$), Jeol GSX 270 ($^{119}Sn$) or Jeol EX 400 ($^{1}H$, $^{13}C$) instrument; standards: TMS (internal, $^{1}H$, $^{13}C$), $BF_3{\cdot}OEt_2$ (external, $^{11}B$), $NaNO_3$ (aqueous solution, external, $^{14}N$), tetramethyltin (external, $^{119}Sn$). When the coupling constant is stated as $^{n}J^{119(117)}Sn^{m}X$ = ..., (...), the value in parentheses describes the coupling of the X nucleus with the $^{117}Sn$ isotopomer. The notation $^{n}J(^{119/117}Sn^{m}X)$ represents the coupling of both isotopomers with X, when the coupling cannot be resolved. A questionmark after a formula or a number means assignment is uncertain. The solvent-

dependent NMR data of the alkylhalostannanes, detected in the reaction mixtures, are quoted here and compared with ref. values. If no deviation is detected, the data are not mentioned again in the procedures. – $^1$H NMR ($CH_2Cl_2$): δ = 0.67 [$Me_3SnCl$, $^2J(^{119}Sn^1H)$ = 58.5 Hz], 0.79 [$Me_3SnBr$, $^2J(^{119}Sn^1H)$ = 57.8 Hz], 1.21 [$Me_2SnCl_2$, $^2J(^{119}Sn^1H)$ = 68.5 Hz], 1.40 [$Me_2SnBr_2$, $^2J(^{119}Sn^1H)$ = 65.5 Hz]. – $^1$H NMR(ref. values in $CCl_4$): δ = 0.61[20] [$Me_3SnCl$, $^2J$ ($^{119}Sn^1H$) = 58.1 Hz[20]], 0.73[20] [$Me_3SnBr$, $^2J(^{119}Sn^1H)$ = 57.8 Hz[20]], 1.15[20] [$Me_2SnCl_2$, $^2J(^{119}Sn^1H)$ = 68.2 Hz[21]], 1.33[20] [$Me_2SnBr_2$, $^2J(^{119}Sn^1H)$ = 66.7 Hz[20]]. – $^1$H NMR (Tol): δ = 0.27 (!)[45] ($Me_3SnCl$), 0.52 (!) ($Me_2SnCl_2$[45]), 0.52 (!) ($Me_2SnBr_2$[45]). – IR spectra: Nujol-Hostaflon mulls between CsI plates with a Nicolet SZDX FT-IR spectrometer, data are quoted in $cm^{-1}$; selected characteristic vibrations are given only. – MS: Varian CH7 instrument with electron impact ionisation at 70 eV, data are given in the sequence: *m*/*z* (%, assignment). The masses found refer to the isotopes $^1$H, $^{12}$C, $^{11}$B, $^{14}$N, $^{35}$Cl, $^{120}$Sn. – Elemental analyses: performed at the Microanalytical laboratory of the institute. When marked with * the elemental analysis by combustion suffers from a) the deviation from the calculated values due to the formation of boron carbide and boron oxide melt, and b) difficulties in handling of the samples because of spontaneous inflammability or hydrolysis. – X-ray: Siemens P4 four-circle diffractometer; Mo-$K_\alpha$ radiation, graphite monochromator; single crystals were mounted under argon using glass capillaries. Crystal data were determined and intensity data recorded at 213 K; program X-scan, structure solution by Patterson method and refinement using the SHELX-PLUS PC version package; final refinement was performed using the SHELX-93 programs.[22] All atoms except hydrogen atoms are described with anisotropic temp. factors, all hydrogen positions were geometrically placed [*d*(CH) = 0.96 Å] and included in the refinement by using the riding model and fixed $U_i$. Details of the crystal structure determination is available on request from the Cambridge Crystallographic Data Center (CCDC) on quoting the depository number CSD-112146, the names of the authors, and the journal citation.

**Starting Materials:** $N(SnMe_3)_3$[23] was prepared in a modified procedure[15] from $NaNH_2/NH_3/OEt_2/Me_3SnCl$, $(Me_2SnCl)_3N$,[24] $Me_2SnCl_2$,[25] Me–N($SnMe_3$)$_2$,[26] Ph–N($SnMe_3$)$_2$[26], Mes–N($SnMe_3$)$_2$,[9] Dipp–N($SnMe_3$)$_2$,[9] $Me_3Si$–N($SnMe_3$)$_2$,[27] *t*Bu–N($SnMe_2Cl$)$_2$,[9] $Me_3Si$–N($SnMe_2Cl$)$_2$,[9][43] Dipp–N($SnMe_2Cl$)$_2$,[9] $Me_2N$–N($SnMe_3$)$_2$,[28] $N_2(SnMe_3)_4$,[29] $Me_2B$–N($SnMe_3$)$_2$,[30] $MeBBr_2$ and $Et_2BCl$,[31] $Me_2BBr$,[32] *i*$PrBCl_2$,[33] *t*$BuBBr_2$,[34] $MesBBr_2$.[35]

**General Procedure I. – Reaction of Bis(trimethylstannyl)amines with Dihaloorganylboranes $RBX_2$ with Sterically Less Demanding Groups R and Bis(trimethylstannyl)hydrazines with Dihaloorganylboranes:** A solution of the distannylamine $RN(SnMe_3)_2$ in $CH_2Cl_2$ was slowly added (≥ 60 min) to a stirred solution of the dihaloorganylborane $RBX_2$ in $CH_2Cl_2$ at −65°C to −75°C. After allowing the mixture to slowly attain ambient temp., stirring was continued for 12 h at 25°C. A sample of the reaction mixture, checked by $^1$H and $^{11}$B NMR, confirmed quantitative reactions, or in some cases methylation, of the boron atoms. After removal of the solvent at 25°C/12 Torr, the most volatile component was removed either by fractional distillation of the residue using a 10-cm Vigreux column ($Me_3SnBr$, b.p. ca. 30°C/$10^{-2}$ Torr or 53–55°C/12 Torr), or by sublimation ($Me_3SnCl$, subl.p. 25°C/$10^{-3}$ Torr). The removal of $Me_3SnCl$ (or $Me_2SnCl_2$) was completed by repeated dissolution of the residue in $CH_2Cl_2$, followed by removal of the solvent, and repeated sublimation. Finally, the diborylamine was obtained as the next volatile fraction.

**General Procedure II. – Reactions of Bis(halodimethylstannyl)amines with Dihaloorganoboranes $RBX_2$ with Sterically More Demanding Groups R = *t*Bu, Mes:** The bis(halodimethylstannyl)amine $RN(SnMe_2X)_2$ (X = Cl or Br), dissolved in $CH_2Cl_2$, was slowly added (≥ 60 min) at −60 to −50°C, whilst stirring, to a solution of the dihaloorganoborane $RBX_2$ in $CH_2Cl_2$. The mixture was then allowed to slowly attain ambient temp. and the stirring was continued for 12 h at 25°C. A sample was then checked by $^1$H and $^{11}$B NMR which confirmed an almost quantitative reaction. After stripping off the solvent at 25°C/12 Torr, the residue was dissolved in petroleum ether (ca. half of the volume of the previous solvent). The dimethyltin dihalide, which is only sparingly soluble in petroleum ether, crystallized after a period of 4–6 h at −30°C and was then removed by filtration. After removal of the solvent from the filtrate at 25°C/12 Torr the colorless residue, solidifying at ambient temp., was washed with petroleum ether (2 ×) and purified by fractional distillation in vacuo using a 10-cm Vigreux column. If the residue of the reaction mixture is a mobile oil, the $Me_2SnX_2$ compounds were removed by continually maintaining the product at 25°C/$10^{-6}$ Torr. The alkylhalostannanes $Me_3SnX$ and $Me_2SnX_2$ (X = Cl, Br), formed by stannazane bond cleavage according to procedure I or II, were identified by their $^1$H-NMR spectra. Deviations and quantities are given below. The reaction proceeds with Cl/Br exchange, when X equals chlorine in $RN(SnMe_2X)_2$ and bromine in $RBX_2$.

**Bis(bromo-*tert*-butylboryl)methylamine (3b). – Procedure I:** Bis(trimethylstannyl)methylamine (**4a**) (5.40 g, 7.1 mmol), dissolved in 10 mL of $CH_2Cl_2$, was added to a solution of *t*$BuBBr_2$ (3.20 g, 13.9 mmol) in 20 mL of $CH_2Cl_2$ over 90 min. – $^{11}$B NMR (reaction mixture): δ = 48.3 [**3b**, shoulder MeN($SnMe_2Br$)(BMeBr)?], 80.9 [*t*Bu(Me)BBr]; ratio: 8:2. – B.p. 35–38°C/$10^{-3}$ Torr. – Yield: 1.0 g of **3b** (43%); colorless crystals. – M.p. ca. 30°C. – $^1$H- and $^{11}$B-NMR data correspond to another sample of **3b**, prepared according to procedure II (see below).

**Attempt to Prepare Bis(bromomethylboryl)phenylamine (3c) from 4c and $MeBBr_2$ (Molar Ratio 1:2). – Procedure I:** $PhN(SnMe_3)_2$ (**4c**) (5.40 g, 12.8 mmol), dissolved in 20 mL of $CH_2Cl_2$, was added over 30 min to a solution of $MeBBr_2$ (4.80 g, 25.9 mmol) in 20 mL of $CH_2Cl_2$. – $^{11}$B NMR (reaction mixture): δ = 51.5 [$PhN(BBrMe)_2$ (**3c**)], 78.7 ($Me_2BBr$), 62.1 ($MeBBr_2$), 39.8 [$PhN(SnMe_3)(BMeBr)$], 32.3 ($Ph–N=B–Me)_3$; ratio: 10.5:1.5:0.6:1.5:0.7; after 16 h stirring: 12.5:1.5:0:0:0.6 [NMR data of **3c**: $^1$H NMR: δ = 1.2 (s, 6 H, B*Me*), 6.9–7.5 (m, 5 H, $C_6H_5$); $^{11}$B NMR: δ = 51.0]. During removal of the volatile components at 25°C/13 Torr the $^{11}$B-NMR signal of **3c** became weaker and disappeared after the residue was kept at room temp. for 1 d ($^{11}$B NMR: δ = 62.1, 32.3).

**Attempt to Prepare Bis(chlorophenylboryl)phenylamine (3d) by Reaction of 4c with $PhBCl_2$ (Molar Ratio 1:2). – Procedure I:** $PhN(SnMe_3)_2$ (**4c**) (4.70 g, 11.3 mmol), dissolved in 25 mL of $CH_2Cl_2$, was added dropwise over 30 min to a solution of $PhBCl_2$ (3.50 g, 22.2 mmol) in 15 mL of $CH_2Cl_2$. – $^{11}$B NMR (ca. 17 h stirring): δ = 55.0 ($PhBCl_2$), 47 [Ph–N($BPhCl)_2$ (**3d**)], 37.2 [Ph–N(BPhCl)($SnMe_3$)?], signal ratio: 1:0.1:1, after 12 d the ratio had changed to 0.5:9.1:0.4. The solvent and most of the $Me_3SnCl$ was removed at 25°C/12 Torr. – $^1$H NMR (residue, $CH_2Cl_2$): δ = 0.65 ($Me_3SnCl$), 7.30–7.68 (m, $C_6H_5$, **3d**). – $^{11}$B NMR (residue, $CH_2Cl_2$): d = 46.9 (**3d**). – While $Me_3SnCl$ was sublimed from the residue at ambient temp./$10^{-3}$ Torr, the diborylamine **3d** decomposed slowly with formation of $(Ph–N=B–Ph)_3$ and $PhBCl_2$, the latter two were also detectable in the cold trap ($^{11}$B NMR: δ = 34 and 55). The borazine $(Ph–N=B–Ph)_3$,[36] separated from a petroleum ether solution of the residue and kept at room temp. for 2 d (0.52 g, 26%), was recrystallized from decane (15 mL), m.p.

124°C. – $^1$H NMR ($CDCl_3$): δ = 6.71–6.87 (m, 5 H, $C_6H_5$), 6.91–7.49 (5 H, $C_6H_5$). – $^{11}$B NMR ($CH_2Cl_2$): δ = 34.2. – MS: 537 (100, $M^+$), 460 (17, $M^+$ – Ph), 383 (5.2, $M^+$ – 2 Ph), 358 [39, $(Ph–N{\equiv}B–Ph)_2^+$], 230 (12, $460^{2+}$), 179 (80, $Ph–N{\equiv}B–Ph^+$). – IR: $\tilde{\nu}$ = 3074 $cm^{-1}$ (w), 3055 (w), 3026 (w), 3011 (w), 1599 (m), 1492 (m), 1438 (m), 1384 (s, ν(BN); for comparison ν(BN) = 1368 $cm^{-1}$[37]), 1369 (vs), 696 (s). – $C_{36}H_{30}B_3N_3$ (537.1)*: calcd. C 80.51, H 5.63, N 7.82; found C 72.18, H 5.65, N 5.91.

**Reaction of Bis(trimethylstannyl)phenylamine (4c) with *t*BuBBr$_2$ (Molar Ratio 1:2), Attempt to Prepare Bis(bromo-*tert*-butylboryl)-phenylamine (3f), NMR-Scale reaction. – Procedure I:**. A solution of *t*BuBBr$_2$ (0.37 g, 1.6 mmol), dissolved in 2 mL of $CH_2Cl_2$, was added dropwise to a solution of bis(trimethylstannyl)phenylamine (**4c**) (0.33 g, 0.8 mmol) in 1 mL of $CH_2Cl_2$ within 15 min at −78°C. – $^{11}$B NMR (mixture after a period of ca. 3 d stirring at ambient temp.): δ = 80.5 [*t*Bu(Me)BBr], 66.2 (*t*BuBBr$_2$), 43.1 [PhN(B*t*BuBr)(SnMe$_3$)], signal ratio: 3:4:2. – $^1$H NMR: δ = 7.1 (PhN), 1.14 (*t*BuBBr$_2$), 1.03 [*t*Bu(Me)BBr], 0.96 [N(B*t*BuBr)], 0.74 ($Me_3SnBr$), 0.53 ($NSnMe_3$).

**Attempt to Prepare Bis(bromomethylboryl)-2,6-diisopropylphenylamine (3k) from 4k and MeBBr$_2$** (Molar Ratio 1:2), NMR-Scale reaction. – Procedure I: A solution of Dipp-N(SnMe$_3$)$_2$ (**4k**) (0.28 g, 0.56 mmol), dissolved in 1 mL of $CH_2Cl_2$, was added dropwise to a solution of $MeBBr_2$ (0.21 g, 1.1 mmol) in 1 mL of $CH_2Cl_2$ over a period of 30 min at −78°C. – $^{11}$B NMR (mixture after ca. 1 d stirring at ambient temp.): δ = 79.1 ($Me_2BBr$). – $^1$H NMR: δ = 0.79 [Sn*Me*$_2$Br, Dipp-N(SnMe$_2$Br)$_2$ (**5k**)], 1.05 (*Me*$_2$BBr), 1.15 (*Me*$_2$CH, **5k**), 3.64 ($Me_2CH$). – d$^1$H- and d$^{11}$B-NMR data correspond to an authentic sample of **5k**, prepared according to ref.[9] After 14 d stirring at room temp., no intensity change of the NMR signals in the reaction mixture was detected.

**Bis(dimethylboryl)mesitylamine (3q). – Procedure II:** MesN(SnMe$_3$)$_2$ (**4i**) (10.70 g, 23.5 mmol), dissolved in 25 mL of $CH_2Cl_2$, was added to a solution of $MeBBr_2$ (9.15 g, 49.3 mmol) in 10 mL of $CH_2Cl_2$ within 1 h at −50°C. – $^1$H NMR (reaction mixture, $CH_2Cl_2$): δ = 0.78 [N(Sn*Me*$_2$Br)$_2$ of **5i**, $^2J$ ($^{119}$Sn$^1$H) = 63.0]. – $^{119}$Sn NMR: δ = 77.8 [$^2J$($^{119}$Sn$^{117}$Sn) = 135 Hz (**5i**)]. – $^{11}$B NMR: δ = 78.5 ($h_{1/2}$ = 325 Hz, $Me_2BBr$). – After 2 d stirring at room temp. and a workup according to procedure II, the distillation yielded 4.1 g of **3q** (81%), b.p. ca. 50°C/$10^{-6}$ Torr, as a colorless liquid. – $^1$H NMR ($CDCl_3$): δ = 0.43 (s, br., 12 H, B*Me*$_2$), 1.93 (s, 6 H, *o*-*Me*–Ph), 2.25 (s, 3 H, *p*-*Me*–Ph), 6.85 (s, 2 H, $C_6H_2Me_3$). – $^{13}$C NMR: δ = 10.38 (br., $BMe_2$), 19.03 (*o*-*Me*–Ph), 20.84 (*p*-*Me*–Ph), 128.79 (*m*-C), 132.59 (*o*-C), 133.62 (*p*-C), 146.48 (*i*-C). – $^{11}$B NMR: δ = 58.1 ($h_{1/2}$ = 229 Hz). – $^{14}$N NMR: δ = −210 ($h_{1/2}$ = 371 Hz). – MS: 215 (52, M·$^+$), 200 (100, $M^+$ – Me, m*), 185 (6, $M^+$ – $C_2H_5$), 160 (31, $M^+$ – $H_2C$=BMe), etc. – IR [nujol/hostaflone]: $\tilde{\nu}$ = 1314 $cm^{-1}$ [s, $\nu_{as}(B_2N)$,[39] 1251 [s, $\nu_s(B_2N)_s$?], 1263 [s, ν(CN)?], 1000 [w, $\nu_{as}$(BC)], 900 [w, $\nu_s(CB_2)$]. – $C_{13}H_{23}B_2N$ (215.0): calcd. C 72.64, H 10.79, N 6.52; found C 72.29, H 10.78, N 6.41. – Filtration of the residue, insoluble in petroleum ether, yielded $Me_2SnBr_2$ (14.6 g, 96%). – $^1$H NMR ($CH_2Cl_2$: δ = 1.42 [*Me*$_2$SnBr$_2$, $^2J$($^{119}$Sn$^1$H = 65.5].[23]

**Bis(bromomethylboryl)trimethylsilylamine (3m).**[38] **– Procedure I:** A solution of $MeBBr_2$ (13.6 g, 73.1 mmol) in 40 mL of $CH_2Cl_2$ was added dropwise to **4l** (15.2 g, 36.5 mmol), dissolved in 50 mL of $CH_2Cl_2$, over 60 min at −75°C. – $^1$H NMR (ambient temp.): δ = 0.35 ($Me_3Si$), 0.74 ($Me_3SnBr$), 1.09 (MeB). – $^{11}$B NMR: δ = 49.8. – Yield: 6 g of **3m** (55%), b.p. 71–75°C/13 Torr, colorless liquid. – $^1$H NMR: δ = 0.35 ($Me_3Si$), 1.1 (MeB). – $^{11}$B NMR: δ = 49.5. – $^{14}$N NMR: δ = −220. Consistent with the ref. values.[38]

**Bis(bromoisopropylboryl)trimethylsilylamine (3n). – Procedure I:** Bis(trimethylstannyl)trimethylsilylamine (**4l**) (22.8 g, 55 mmol), dissolved in 60 mL of $CH_2Cl_2$, was added over 60 min at ca. −78°C, to a solution of *i*PrBBr$_2$ (23.8 g, 111 mmol) in 50 mL of $CH_2Cl_2$. – $^{11}$B NMR (mixture at ambient temp.): δ = 52.2 (**3n**). – Yield: 15.6 g of **3n** (80%) as a colorless liquid, b.p. 59–65°C/5·$10^{-2}$ Torr. – $^1$H NMR ($CDCl_3$): δ = 0.33 (s, 9 H, $Me_3Si$), 1.05 [d, 12 H, BCH*Me*$_2$, $^3J$($^1$H$^1$H) = 5.9 Hz], 1.33 (m, 2 H, BC*H*Me$_2$). – $^{13}$C NMR: δ = 1.89 [$SiMe_3$, $^1J$($^{29}$Si$^{13}$C) = 59 Hz], 19.12 (BCH*Me*$_2$), 25.8 (br., B*C*HMe$_2$). – $^{11}$B NMR: δ = 52.2 ($h_{1/2}$: 321 Hz). – $^{14}$N NMR: δ = −230 ($h_{1/2}$: 109 Hz). – $^{29}$Si NMR: δ = 5.6. – MS: 355 (12, $M^+$), 340 (18, $M^+$ – Me), 276 (65, $M^+$ – Br), etc. – $C_9H_{23}B_2Br_2NSi$ (354.8): calcd. C 30.47, H 6.53, N 3.95; found C 30.66, H 6.66, N 3.89.

**Bis(*tert*-butylchloroboryl)trimethylsilylamine (3o).**[6a] **– Procedure II:** To a solution of *t*BuBBr$_2$ (30.6 g, 135 mmol) in 90 mL of $CH_2Cl_2$ was added bis(chlorodimethylstannyl)trimethylsilylamine (**5l**) (30.6 g, 67.2 mmol), dissolved in 50 mL of $CH_2Cl_2$, within 60 min at ca. −78°C. – $^{11}$B NMR (mixture at ambient temp): δ = 54.2 (**3o**). – Yield: 13.6 g of **3o** (69%) as a colorless liquid, b.p. 65–66°C/$10^{-1}$ Torr (or 45–49°C/5·$10^{-3}$ Torr). – $^1$H NMR ($CDCl_3$): δ = 0.39 (s, 9 H, $Me_3Si$), 1.02 (s, 18 H, BC*Me*$_3$). – $^{13}$C NMR: δ = 4.41 [$SiMe_3$, $^1J$($^{29}$Si$^{13}$C) = 59.5 Hz], 28.87 (BC*Me*$_3$), 34.31(B*C*Me$_3$). – $^{11}$B NMR: δ = 53.82 ($h_{1/2}$: 218 Hz). – $^{14}$N NMR: δ = −246 ($h_{1/2}$: 271 Hz). – $^{29}$Si NMR ($C_6D_6$): δ = 7.56. – MS: 293 (22, $M^+$), 278 (19, $M^+$ – Me), 258 (11, $M^+$ – Cl), etc. – $C_9H_{23}B_2Cl_2NSi$ (294.0): calcd. C 44.95, H 9.26, N 4.76; found C 45.12, H 9.18, N 4.86.

**Bis(*tert*-butylchloroboryl)methylamine (3a). – Procedure II:** [MeN(SnMe$_2$Cl)$_2$]$_2$ [(**5a**)$_2$] (11.8 g, 14.9 mmol), dissolved in 70 mL of $CH_2Cl_2$, was added to a solution of *t*BuBBr$_2$ (13.8 g, 59.6 mmol) in 80 mL of $CH_2Cl_2$ within 2.5 h at −60 to −50°C. A precipitate formed which redissolved. After removal of $Me_2SnBrCl$ [15 g, 95%,$^1$H NMR($CH_2Cl_2$): δ = 1.32; $^{119}$Sn NMR: δ = 114.1] by crystallization and removal of the solvent at 25°C/12 Torr, compound **3a** (4.1 g, 58%) was obtained by distillation at 29–30°C/$10^{-6}$ Torr as a colorless liquid. – $^1$H NMR ($CDCl_3$): δ = 1.08 (s, 18 H, BC*Me*$_3$), 2.90 (s, 3 H, *Me*N). – $^{13}$C NMR: δ = 25 (br., B*C*Me$_3$), 28.31 (BC*Me*$_3$), 33.16 (N*Me*). – $^{11}$B NMR: δ = 50.0 ($h_{1/2}$ = 147 Hz). – $^{14}$N NMR: δ = −268 ($h_{1/2}$ = 178 Hz). – MS: 235 (< 1, $M^+$), 220 (3, $M^+$ – Me), 200 (3, $M^+$ – Cl), 178 (49, $M^+$ – *t*Bu), 162 (6, $178^+$ – $CH_4$, or $220^+$ – *t*BuH), 158 (< 1, $200^+$ – $H_2C$=CHMe), 142 (3, $158^+$ – $CH_4$), 136 (100, $178^+$ – $H_2C$=CHMe), 61 (10, $136^+$ – MeNBCl). – IR: $\tilde{\nu}$ = 1362 $cm^{-1}$ [vr, $\nu_{as}(B_2N)$[39]], 1283 [s, ν(CN)], 1215 [s, $\nu_s(B_2N)$], 1072 [ν(BC)], 908 [vr, ν(BCl)]. – $C_9H_{21}B_2Cl_2N$ (235.8): calcd. C 45.84, H 8.98, N 94; found C 45.31, H 8.42, N 5.59.

**Bis(bromo-*tert*-butylboryl)methylamine (3b). – Procedure II:** [MeN(SnMe$_2$Br)$_2$]$_2$ [(**5b**)$_2$] (5.8 g, 6.0 mmol) was added to a solution of *t*BuBBr$_2$ (5.4 g, 23.8 mmol) in 20 mL of $CH_2Cl_2$, dissolved in 70 mL of $CH_2Cl_2$, over 1.5 h at −55 to −50°C; a violent reaction with temporary formation of a solid occurred. **3b** (2.50 g, 64%) was obtained by condensation at 25–28°C/$10^{-6}$ Torr into a cooled trap (−78°C); colorless crystals (m.p. ca. 30°C). – $^1$H NMR ($CDCl_3$): δ = 1.09 (s, 18 H, BC*Me*$_3$), 2.88 (s, 3 H *Me*N). – $^{13}$C NMR: δ = 26 (br., B*C*Me$_3$), 28.48 (BC*Me*$_3$), 33.95 (N*Me*). – $^{11}$B NMR: δ = 48.0 ($h_{1/2}$ = 174 Hz). – $^{14}$N NMR: δ = −259 ($h_{1/2} \approx$ 197 Hz). – MS: 323 (ca. 1, M·$^+$), 308 (3, $M^+$ – Me), 266 (67, $M^+$ – *t*Bu), 250 (2, $308^+$ – *t*BuH), 244 (15, $M^+$ – Br), 224 (100, $266^+$ – $H_2C$=CHMe), 202 (3, $244^+$ – $H_2C$=CHMe), 186 (9, $202^+$ – $CH_4$), 172 (8, *t*BuBNBBr$^+$), 160 (14, $202^+$ – $H_2C$=CHMe), 130 (15, MeBNBBr$^+$), 105 (15, $MeBBr^+$), 92 (3, $186^+$ – MeBr); – IR: $\tilde{\nu}$ =

1365 [s, $\nu_{as}(B_2N)$[39]] 1277 [m, ν(CN)], 1210 [s, $\nu_s(B_2N)$], 1068 [m, ν(BC)], 883 [vr, ν(BBr)]. − $C_9H_{21}B_2Br_2N$ (324.7): calcd. C 33.29, H 6.52, N 4.31; found C 33.05, H 6.83, N 4.97.

***tert*-Butylbis(chloro-*tert*-butylboryl)amine (3g).**[6] **− Procedure II:** **t**BuN$(SnMe_2Cl)_2$ (**5a**) (3.50 g, 8.0 mmol), dissolved in 10 mL of $CH_2Cl_2$, was added to a solution of *t*BuB$Br_2$ (3.60 g, 16 mmol) in 10 mL of $CH_2Cl_2$ over 0.5 h at −30°C. Yield: 2.16 g of **3g** (97%), as a colorless liquid, b.p. 42°C/$10^{-2}$ Torr. − $^1$H NMR ($CDCl_3$): δ = 1.11 (s, 18 H, BC*Me*$_3$), 1.28 (s, 9 H, NC*Me*$_3$). − $^{13}$C NMR: δ = 27 (br., B*C*Me$_3$), 30.32 (BC*Me*$_3$), 33.24 (NC*Me*$_3$), 55.1 (N*C*Me$_3$). − $^{11}$B NMR: δ = 45.5 ($h_{1/2}$ = 179 Hz). − $^{14}$N NMR: δ = −226 ($h_{1/2} \approx$ 215 Hz). − MS: 275 (ca. 1, $M^{\cdot+}$), 260 (7, $M^+$ − Me), 240 (3, $M^+$ − Cl), 218 (33, $M^+$ − *t*Bu), 176 (100, $218^+$ − $H_2C$=CHMe), 61 (12, MeBCl). − IR: $\tilde{\nu}$ = 1344 $cm^{-1}$ [s, $\nu_{as}(B_2N)$], 1269 [s, ν(CN)], 1190 [s, $\nu_s(B_2N)$], 1108 [m, ν(BC)], 903 [s, ν(BCl)]. − $C_{12}H_{27}B_2Cl_2N$ (277.9): calcd. C 51.87, H 9.79, N 5.04; found C 52.90, H 10.10, N 5.39.

**Bis(bromomethylboryl)-*tert*-butylamine (3h).**[3] **− Procedure I:** **t**BuN$(SnMe_3)_2$ (**4g**) (26.8 g, 67.2 mmol) dissolved in 25 mL of $CH_2Cl_2$ was added dropwise to a solution of $MeBBr_2$ (25.0 g, 135 mmol) in 25 mL of $CH_2Cl_2$ at −78°C. Yield: 16.1 g of **3h** (85%), as a colorless liquid, b.p. 35°C/$10^{-1}$ Torr. − $^1$H NMR($CDCl_3$): δ = 1.18 (s, 6 H, B*Me*), 1.44 (s, 9 H, NC*Me*$_3$). − $^{11}$B NMR: δ = 47.5 ($h_{1/2}$ = 190 Hz). − $^{14}$N NMR: δ = −212, ($h_{1/2} \approx$ 230 Hz). − $C_6H_{15}B_2Br_2N$ (282.6): calcd. C 25.50, H 5.35, B 7.65, Br 56.54, N 4.96; found C 24.44, H 5.23, B 7.38, Br 55.28, N 4.70. − The NMR data are identical with ref. values.[3]

**Attempt to Prepare Bis(chloromesitylboryl)methylamine (3t) from Bis(bromodimethylstannyl)methylamine (5b)$_2$ and MesBCl$_2$ (Molar Ratio 1:4):** A suspension of (**5b**)$_2$ (2.6 g, 2.7 mmol) in 50 mL of $CH_2Cl_2$ was added to a solution of $MesBCl_2$ (2.15 g, 10.7 mmol) in 30 mL of $CH_2Cl_2$ within 1.25 h at −78°C. NMR data of the mixture after 7 d stirring at ambient temp. indicated the formation of the intermediate stannylaminoborane {$^{11}$B NMR ($CH_2Cl_2$): δ = 38.3 [Me−N(BMesCl) ($SnMe_2Br$) (?)], 60.4 [$MesBCl_2$, ref.: 61.4 ($C_6D_6$);[40] 61.1 ($CD_2Cl_2$)[40]]}. After keeping for 24 h in boiling $CH_2Cl_2$ and an additional 20 h in boiling $CHCl_3$, no change of signal intensities could be detected in an NMR sample of the reaction mixture. $Me_2Sn(Cl)Br$ ($^1$H NMR: δ = 1.32; $^{119}$Sn NMR: δ = 114.1) was removed by crystallization from petroleum ether and the solvent at 25°C/12 Torr. Fractional distillation of the residue gave: (i) $MesBCl_2$ (0.24 g, ca. 85%), b.p. 50°C/$10^{-5}$ Torr [$^{11}$B NMR ($CH_2Cl_2$): δ = 60.4]; (ii) 0.66 g of a highly viscous liquid, b.p. 80°C/$10^{-5}$ Torr; $^{11}$B NMR ($CH_2Cl_2$/$CDCl_3$): δ = 37.8; $^1$H NMR: δ = 1.29 [$SnMe_2$, $^2J(^{117(119)}Sn^1H)$ = 65.2 (68.4) Hz], 2.25 (*o*,*p*-*Me*$_3C_6H_2$−B), 6.81 (*m*-H, Mes); $^{14}$N NMR: δ = −282 ($h_{1/2}$ = 473 Hz); (iii) residue: yellow solid. − $^{11}$B NMR ($CH_2Cl_2$): δ = 38.8, 47 (sh, ?). The purification by crystallization from $CH_2Cl_2$, toluene, or petroleum ether failed according to $^1$H- and $^{11}$B-NMR data.

**Bis(*tert*-butylchloroboryl)phenylamine (3e):**[45] A suspension of $Me_2SnCl_2$ (10.1 g, 46.1 mmol) in 40 mL of $CH_2Cl_2$ was treated with $PhN(SnMe_3)_2$ (**4c**), dissolved in 30 mL of $CH_2Cl_2$, while stirring at room temp. This mixture was added dropwise, while stirring, to *t*B$uBBr_2$ (10.5 g, 46.0 mmol), dissolved in 50 mL of $CH_2Cl_2$, within 1.5 h at −50°C. After allowing the reaction mixture to attain ambient temp. within 1.5 h, the progress of the reaction was controlled by NMR (see Figure 1) during a period of 96 h stirring at room temp. followed by a period of 48 h under reflux. $^1$H- and $^{11}$B-NMR data of the mixture as a function of time, given in the sequence time [h]; d$^{11}$B NMR [ppm], ratio [%]; d$^1$H NMR [ppm]: Measurement 1: 0; 67.5 (*t*B$uBBr_2$); 100; 0.63 ($Me_3SnCl$), 0.78 ($PhN(SnMe_2Cl)_2$). Measurement 2: ca. 3; 40.4 [PhN(B*t*BuCl)$SnMe_2Cl$], 50; 63.5 (*t*BuBClBr), 50; 0.72 ($Me_3SnBr$), 0.78 [$PhN(SnMe_2Cl)_2$], 1.33 ($Me_2SnClBr$); [$^1$H-NMR signal of $Me_3SnCl$ and $PhN(SnMe_2Br)_2$ disappeared]. Measurement 3: 24; 42.1 [PhN(B*t*BuCl)$SnMe_2Cl$], 44; 50.4 [PhN(B*t*BuCl)$_2$], 12; 64.0 (*t*BuBClBr), 44; 0.72 ($Me_3SnBr$), 1.34 ($Me_2SnClBr$), ($^1$H-NMR signal of **4c** vanished completely). Measurement 4: 96; 41.2 [PhN(B*t*BuCl)$SnMe_2Cl$], 41; 49.9 [PhN(B*t*BuCl)$_2$], 22; 64.0 (*t*BuBClBr), 38; 0.73 ($Me_3SnBr$), 1.35 ($Me_2SnClBr$). Measurement 5: 96 (25°C) + 34 (reflux); 43.3 [PhN(B*t*BuCl)$SnMe_2Cl$], 35; 50.0 [PhN(B*t*BuCl)$_2$], 35; 63.7 (*t*BuBClBr), 29. Measurement 6: 96 (25°C) + 48 (reflux); 50.1 [PhN(B*t*BuCl)$_2$], ca. 80; 38.9 [$(PhNBtBu)_n$?], ca. 20. − After the solvent was removed at 25°C/12 Torr and $Me_3SnBr$ as well as $Me_2SnClBr$ (d$^1$H = 1.35) was condensed into a trap at −78°C, fractional distillation of the residue yielded 3.8 g (55%) of **3e** as a colorless liquid; b.p. 48−51°C/$10^{-5}$ Torr. − $^1$H NMR ($CDCl_3$): δ = 1.01 (s, 18 H, BC*Me*$_3$), 7.32 (m, 5 H, $C_6H_5$). − d$^{13}$C: 26 (br., B*C*Me$_3$, detected after Gauß transformation only), 28.65 (BC*Me*$_3$), 127.03 (*p*-C), 29.02 (*o*-C), 129.02 (*m*-C), 141.47 (*i*-C). − $^{11}$B NMR: δ = 50.6 ($h_{1/2}$ = 253 Hz). − $^{14}$N NMR: δ = −234 ($h_{1/2}$ = 506 Hz). − MS [% (70 eV, 15 eV), assignment]: 236 (11, 7, $M^+$ − *t*Bu), 194 (69, 89, $M^+$ − *t*BuBCl), 180 (18, 16, $236^+$ − $C_4H_8$), 152 (14, 11, $194^+$ − $C_3H_6$). 143 (2, 7, $PhN{\equiv}BC_3H_5^+$), 138 (100, 100, $194^+$ − $C_4H_8$), 137 (40, $M^+$ − $tBu_2BCl$), 103 (22, 14, $PhN{\equiv}BH^+$), 77 (40, 2, $Ph^+$). − IR: $\tilde{\nu}$ = 1365 $cm^{-1}$ [s, $\nu_{as}(B_2N)$[42]], 1278 [s, ν(CN)], 1197 [s, $\nu_s(B_2N)$], 1104 [s, ν(BC)], 907 [s, ν(BCl)]. − $C_{14}H_{23}B_2Cl_2N$ (297.9): calcd. C 56.45, H 7.78, N 4.70; found C 54.08, H 7.52, N 4.60.

**Bis(bromo-*tert*-butylboryl)phenylamine (3f):** A suspension of $Me_2SnBr_2$ (16.10 g, 52.1 mmol) in 40 mL of $CH_2Cl_2$ was treated with $PhN(SnMe_3)_2$ (**4c**) (10.90 g, 26.0 mmol), dissolved in 40 mL of $CH_2Cl_2$, while stirring at room temp. This reaction mixture was added dropwise, while stirring, to *t*B$uBBr_2$ (11.9 g, 52.1 mmol), dissolved in 40 mL of $CH_2Cl_2$, within 130 min at −68 to −40°C. After allowing the reaction mixture to attain ambient temp., the solvent was removed at 25°C/12 Torr, $Me_3SnBr$ as well as $Me_2SnBr_2$ was condensed into a trap at −78°C over a period of 4 d, the fractional distillation of the viscous residue yielded 7.0 g (69%) of **3f** as colorless liquid, b.p. 69−77°C/$10^{-5}$ Torr. − $^1$H NMR ($CDCl_3$): δ = 0.98 (s, 18 H, BC*Me*$_3$), 7.30 (m, 5 H, $C_6H_5$). − $^{13}$C NMR: δ = 27 (br., B*C*Me$_3$, detected after Gauß transformation only), 29.24 (BC*Me*$_3$), 127.7 (*p*-C), 129.34 (*o*-C), 129.38 (*m*-C), 141.93 (*i*-C). − $^{11}$B NMR: δ = 49.3 ($h_{1/2}$ = 300 Hz). − $^{14}$N NMR: δ = −228 ($h_{1/2}$ = 488 Hz). − MS: *m*/*z* [% (70 eV, 15 eV), assignment]: 385 (< 1, 3, $M^+$), 328 (32, 66, $M^+$ − *t*Bu), 305 (12, 29, $M^+$ − HBr), 286 (17, 13, $328^+$ − $C_3H_6$),. 263 (12, 29, $305^+$ − $C_3H_6$), 248 (39, 46, $305^+$ − *t*Bu), 239 (26, 61, $385^+$ − $C_4H_8BBr$), 183 (100, 100, $239^+$ − $H_2C$=$CMe_2$), 168 (10, 2, $248^+$ − HBr), 128 (17, 0, PhBNBMe), 103 (18, 1, $PhN{\equiv}BH^+$). − IR: $\tilde{\nu}$ = 1359 [s, $\nu_{as}(B_2N)$[42]], 1270 [s, ν(CN)], 1191 [s, $\nu_s(B_2N)$], 1097 [s, ν(BC)], 884 [vr, ν(BBr)]. − $C_{14}H_{23}B_2Br_2N$ (386.8): calcd. C 43.48, H 5.99, N 3.62; found C 44.02, H 5.99, N 3.77.

**Attempt to Prepare Bis(chloromesitylboryl)phenylamine (3u) from Bis(chlorodimethylstannyl)phenylamine (5d) and MesBCl$_2$ (Molar Ratio 1:2):** A suspension of $Me_2SnCl_2$ (5.8 g, 26.4 mmol) in 20 mL of $CH_2Cl_2$ was treated with $PhN(SnMe_3)_2$ (**4c**) (5.54 g, 13.2 mmol), dissolved in 20 mL of $CH_2Cl_2$, while stirring at room temp. This mixture was added dropwise to a stirred solution of $MesBCl_2$ (5.31 g, 26.4 mmol) in 30 mL of $CH_2Cl_2$ over 110 min at −68 to −40°C. After the reaction mixture had attained ambient temp., it was kept for 2 d at reflux {$^{11}$B NMR ($CH_2Cl_2$): δ = 38.9 [PhN(BMesCl)$SnMe_2Cl$], 59.8 ($MesBCl_2$), ratio: ca. 1:1. − $^1$H NMR: δ = 1.26 ($SnMe_2Cl$), 1.22 ($Me_2SnCl_2$), 0.66 ($Me_3SnCl$), ratio: 1:1:2}. After removal of the solvent at 25°C/12 Torr, the residue

was dissolved in 70 mL of toluene and kept at reflux for another 7 h. No change of signal intensities could be detected in the NMR spectra. After another 7 h at reflux, the solution contained a 1:2 mixture of the diborylamine **3u** ($^{11}$B NMR: δ = 48.1), the stannylaminoborane ($^{11}$B NMR: δ = 38.5) and (PhN≡BMes)$_2$ ($^{11}$B NMR: δ = 40), presumed as the decomposition product. The separation of these products either by fractional crystallization or by fractional sublimation failed. − $^1$H NMR [$CH_2Cl_2$, enriched PhN(BMesCl)SnMe$_2$Cl]: δ = 1.29 [s, 6 H, Sn*Me*$_2$Cl, $^2J(^{117(119)}Sn^1H)$ = 66.5 (69) Hz], 2.29 (s, 3 H, *p*-Me), 2.42 (s, 3 H, *o*-Me), 2.93 (s, 3 H, *o*-Me), 5.58−7.30 (m, 7 H, $C_6H_x$ of Ph and Mes). − $^{11}$B NMR: δ = 39.5 ($h_{1/2}$ = 406 Hz).

**Attempt to Prepare Bis(chloromethylboryl)mesitylamine (3v) from 4i and $BCl_3$ (Molar Ratio 1:2):** $BCl_3$ (3.5 g, 30 mmol) was condensed into a solution of MesN(SnMe$_3$)$_2$ (**4i**) (7.0 g, 15 mmol) in 40 mL of $CH_2Cl_2$, cooled to −50°C. After allowing the solution to attain ambient temp., it was stirred for 17 h at room temp. [$^{11}$B NMR: δ = 61.4 (MeBCl$_2$), 75.9 (Me$_2$BCl), ratio: 10:0.5]. The $^1$H- and $^{119}$Sn-NMR spectra indicated the quantitative formation of MesN(SnMe$_2$Cl)$_2$ (**5i**); the signals are identical with those of an authentic sample of **5i**[9]. Although the reaction mixture was kept under reflux for additional 9 h using a dry ice condensor there was no indication ($^{11}$B-NMR control) of a further reaction.

**(*tert*-Butylchloroboryl)mesitylamine by Reaction of (Bromodimethylstannyl)(*tert*-butylchloroboryl)mesitylamine with $H_2O$ (Molar Ratio 1:1):** After purification of **5i**, obtained according to the procedure (for **3v**) described above, by removal of the volatile components at 25°C/12 Torr and dissolution of the residue in 30 mL of toluene, it was treated dropwise while stirring with a solution of *t*BuBBr$_2$ (6.8 g, 30 mmol) in 15 mL of toluene at −60 to −50°C. NMR data of the reaction mixture after allowing to attain ambient temp. − $^{11}$B NMR: δ = 66.1 (*t*BuBBr$_2$), 64.6 (*t*BuBBrCl), 62.5 *t*BuBCl$_2$. − The NMR control after additional 36 h under reflux indicated the formation of ca. 50% of MesN(B*t*BuCl)SnMe$_2$Br ($^{11}$B NMR: δ = 42.8). After hydrolysis with $H_2O$ (30 µL, 1.7 mmol) and keeping the reaction mixture under reflux for72 h, the solvents were removed in vacuo and MesNHB*t*BuCl (1.5 g, 42%) was sublimed at 43−45°C/$10^{-6}$ Torr as colorless crystals, subl. p. 42°C. − NMR data of MesNHB*t*BuCl in $CDCl_3$: $^1$H NMR: δ = 1.13 (s, 9 H, BC*Me*$_3$), 2.18 (s, 6 H, *o*-Me), 2.29 (s, 3 H, *p*-Me), 5.44 (m, 1 H, N*H*), 6.91 (s, 2 H, *m*-H). − $^{13}$C NMR: δ = 18.52 (*o*-Me), 20.90 (*p*-Me), 27.72 (BC*Me*$_3$), 128.70 (*m*-C), 134.49 (*o*-C), 135.49 (*p*-C), 135.57 (*i*-C). − $^{11}$B NMR: δ = 40.9 ($h_{1/2}$ = 267 Hz). − $^{14}$N NMR: δ = −270 ($h_{1/2}$ = 590 Hz). − MS: 237 (100, M$^+$), 222 (11, M$^+$ − Me), 181 (49, M$^+$ − $C_4H_8$, m*), 180 (55, M$^+$ − *t*Bu), 179 (100, M$^+$ − *t*BuH or 181$^+$ − $H_2$, MesNBCl), 145 (16, MesNBH). − IR: $\tilde{\nu}$ = 3356 cm$^{-1}$ (s, NH), 3040 (w), 3020 (w), 3026 (w), 2942 (vs), 2863 (s), 1608 (m), 1489 (s). 1459 (s), 1442 (s), 1400 (m), 1377 (s), 1359 (s), 1280 (m, vs BN), 1250 (s), 961 (vs, νBCl), 854 (s), 651 (s), 603 (s). − $C_{13}H_{21}BClN$ (237.6)*: calcd. C 65.72, H 8.91, N 5.90; found C 64.94, H 9.13, N 5.69.

**Bromomethylboryl(chloromethylboryl)(trimethylsilyl)amine (3p):** Me$_3$SiN(SnMe$_2$Cl)$_2$ (**5l**) (5.2 g, 11.4 mmol), dissolved in 70 mL of $CH_2Cl_2$, was added dropwise to a solution of MeBBr$_2$ (4.25 g, 22.9 mmol) in 15 mL of $CH_2Cl_2$ within 1.5 h at −55 to −50°C. The workup was according to Procedure I; the distillation of the residue yielded **3p** (1.55 g, 65%) at 59−61°C/12 Torr as a colorless liquid. − $^1$H NMR ($CDCl_3$): δ = 0.30 (s, 9 H, Si*Me*$_3$), 0.89 (br. s, 6 H, B*Me*X). − $^{13}$C NMR: δ = 1.80 [q, $^1J(^{13}C^1H)$ = 119.4 Hz, Si*Me*$_3$], 12 [q, v. br., $^1J(^{13}C^1H)$ = 120 Hz, B*Me*Cl]. − $^{11}$B NMR: δ = 50.3 ($h_{1/2}$ = 128 Hz). − $^{14}$N NMR: δ = −234 ($h_{1/2}$ = 84 Hz). − $^{29}$Si NMR: δ = 6.46 (recorded at 218 K). − $C_5H_{15}B_2BrClNSi$ (253.0)*: calcd. C 23.72, H 5.98, N 5.53; found C 22.98, H 5.77, N 5.01; C/H/N ratio: calcd. 5:15:1; found 5.31:15.9:1.

**Bis(*tert*-butylchloroboryl)(dimethylboryl)amine (3t).[9] − Procedure II:** a) A solution of *t*BuBBr$_2$ (10.85 g, 47.4 mmol) in 50 mL of $CH_2Cl_2$ was added dropwise to Me$_2$BN(SnMe$_2$Cl)$_2$ (10.0 g, 23.6 mmol), dissolved in 50 mL of $CH_2Cl_2$, within 90 min at −70°C. The distillation yielded **3t** (2.20 g, 40%), b.p. 28−38°C/$10^{-6}$ Torr, as a colorless liquid. The NMR data are identical with those of an authentic sample of **3t** described below. − $C_{10}H_{24}B_3Cl_2N$ (261.65)*: calcd. C 45.91, H 9.25, Cl 27.10, N 5.35; found C 48.55, H 9.20, Cl 26.70, N 5.28.

b) Me$_2$BBr (5.6 g, 46.1 mmol), dissolved in 25 mL of $CH_2Cl_2$, was added dropwise to a solution of N(SnMe$_3$)$_3$ (23.30 g, 46.1 mmol) in 35 mL of $CH_2Cl_2$ while stirring for 2 h at −78 to −60°C. After allowing the mixture to attain ambient temp. and 1 h of stirring at room temp., the $^1$H- and $^{11}$B-NMR spectra recorded from a sample of the reaction mixture indicated quantitative formation of Me$_2$BN(SnMe$_3$)$_2$ (**4r**) and Me$_3$SnBr. − $^1$H NMR ($CH_2Cl_2$): δ = 0.30 [s, 18 H, Sn*Me*$_3$, **4r**, $^2J(^{117(119)}Sn^1H)$ = 53 (56) Hz], 0.33 (s, 6 H, B*Me*$_2$), 0.76 (9 H, *Me*$_3$SnBr). − $^{11}$B NMR: δ = 52.4 ($h_{1/2}$ = 157 Hz); ref.:[3][42] $^1$H NMR: δ = 0.26 [s, 18 H, Sn*Me*$_3$, **4r**, $^2J(^{119}Sn^1H)$ = 55 Hz], 0.30 (s, 6 H, B*Me*$_2$). − $^{11}$B NMR: δ = 53.4 ($h_{1/2}$ = 230 Hz). − This mixture was added dropwise over 45 min to a solution of Me$_2$SnCl$_2$ (20.3 g, 92.2 mmol) in 150 mL of $CH_2Cl_2$ at room temp. The quantitative formation of Me$_2$BN(SnMe$_2$Cl)$_2$ (**5r**) and Me$_3$SnCl was checked by NMR ($CH_2Cl_2$). − $^1$H NMR: δ = 0.45 (s, 6 H, B*Me*$_2$), 0.64 (18 H, *Me*$_3$SnCl), 0.76 (9 H, *Me*$_3$SnBr), 0.93 [s, 12 H, Sn*Me*$_2$Cl, $^2J(^{117(119)}$ Sn$^1$ H) = 63(66) Hz]. − $^{11}$B NMR: δ = 53.6 ($h_{1/2}$ = 224 Hz). − After removal of ca. 130 mL of $CH_2Cl_2$, the reaction mixture was added dropwise over 90 min to a solution of *t*BuBBr$_2$ (20.91 g, 91.8 mmol) in 50 mL of $CH_2Cl_2$ at −78°C. After allowing it to attain ambient temp., 4 d stirring at room temp., removal of the solvent at 25°C/12 Torr and the major part of the volatile components (Me$_3$SnCl, Me$_3$SnBr) at 25°C/$10^{-3}$ Torr, Me$_2$SnBr$_2$ was separated from the solid residue by crystallization at −30°C from 50 mL of petroleum ether according to procedure II. After removal of the solvent of the filtrate at 0°C/12 Torr and sublimation of small amounts of alkylhalostannanes at 0°C/$10^{-3}$ Torr, distillation yielded Me$_2$BN(B*t*BuCl)$_2$ (**3w**) [6.04 g, 50% based on N(SnMe$_3$)$_3$] as colorless liquid, extremly sensitive to moisture and oxygen, b.p. 43−45°C/$10^{-3}$ Torr. − $^1$H NMR ($CDCl_3$): δ = 0.71 (s, 6 H, B*Me*$_2$), 1.06 (s, 18 H, BC*Me*$_3$Cl). − $^{13}$C NMR: δ = 12 (br., B*C*Me$_3$Cl), 14 (br., B*Me*$_2$), 28.51 (BC*Me*$_3$Cl). − $^{11}$B NMR ($CDCl_3$): δ = 56.6 (2 B, *Bt*BuCl, $h_{1/2}$ = 291 Hz), 62.6 (1 B, B*Me*$_2$, $h_{1/2}$ = 276 Hz). − $^{14}$N NMR: δ = −206 ($h_{1/2}$ = 179 Hz). − MS: *m/z* [% (70 eV), assignment]: 261 (1, M$^+$), 246 (2, M$^+$ − Me), 226 (1, M$^+$ − Cl), 162 (59, 204$^+$ − Me$_2$BH), 150 (40, 226$^+$ − Me$_2$BCl: *t*BuBNB*t*Bu), 148 (39, 204$^+$ − BMe$_3$), 128 (34, 204$^+$ − ClBMe$_2$), 122 (29, 204$^+$ − H$_2$C=B*t*Bu), 108 (81, 246$^+$ − *t*BuBCl$_2$: *t*BuBNBMe), 86 (87, 204$^+$ − *t*BuMeBCl), 66 (100, MeBNBMe). − IR: $\tilde{\nu}$ = 1313 cm$^{-1}$ [s, $\nu_{as}$(B$_3$N)], 1216 [s, $\nu_s$(B$_3$N)], 946 [s, ν(BCl)], further frequences not assigned. − $C_{10}H_{24}B_3Cl_2N$ (261.7): calcd. C 45.91, H 9.25, N 5.35; found C 45.86, H 9.48, N 5.68.

**(Chloromesitylboryl)(chloromethylboryl)phenylamine (3r):** A solution of Me$_2$SnCl$_2$ (6.6 g, 30.0 mmol) in 30 mL of $CH_2Cl_2$ was treated with PhN(SnMe$_3$)$_2$ (**4c**) (6.31 g, 15.0 mmol), dissolved in 20 mL of $CH_2Cl_2$, and the mixture was then added dropwise over 90 min at −50°C, while stirring, to MesBCl$_2$ (3.0 g, 15.0 mmol), dissolved in 20 mL of $CH_2Cl_2$. − NMR data (after 16 h,$CH_2Cl_2$): $^{11}$B NMR: δ = 38.5 [PhN(BMesCl)SnMe$_2$Cl (**6b**)]. − $^1$H NMR: δ = 1.28 (SnMe$_2$Cl), 1.24 (Me$_2$SnCl$_2$), 0.69 (Me$_3$SnCl), ratio: 1:1:2.

– After cooling the reaction mixture to −50°C again, a solution of $MeBBr_2$ (2.8 g, 15.0 mmol) in 30 mL of $CH_2Cl_2$ was added over a period of 90 min. After 2 d stirring at room temp., the solvent was removed at 25°C/12 Torr and the organotin halides ($Me_3SnCl$, $Me_2SnCl_2$, $Me_2SnClBr$) at 25°C/$10^{-6}$ Torr. Traces of $Me_2SnClBr$ were sublimed at 25−55°C/$10^{-6}$ Torr and the diborylamine **3r** (1.53 g, 32%) distilled at 87−88°C/$10^{-6}$ Torr solidifying to colorless crystals. – $^1$H NMR ($CDCl_3$): δ = 0.88 (br. s, 3 H, B*Me*), 2.66 (s, 3 H, *p*-Me), 2.75 (s, 6 H, *o*-Me), 7.21 (s, 2 H, *m*-H, Mes), 7.44 (m, 2 H, *m*-H, Ph), 7.67 (m, 1 H, *p*-H, Ph), 7.77 (m, 2 H, *o*-H, Ph). – $^{13}$C NMR: δ = 10 (br., B*Me*), 21.22 (*p*-Me), 21.89 (*o*-Me), 119.60 (*p*-C, Ph), 126.39 (*o*-C, Mes), 127.67 (*o*-C, Ph), 127.83 (*m*-C, Mes), 128.95 (*m*-C, Ph), 136.78 (*p*-C, Mes), 137 (v br., *i*-C, B-*Mes*), 146.54 (*i*-C, N−*Ph*). – $^{11}$B NMR: δ = 50.2 (assym., shoulder at ca. 50, *B*Me and *B*Mes, $h_{1/2}$ = 572 Hz). – MS: *m*/*z* [% (70 eV, 20 eV), assignment]: 317 (100, 100, $M^+$), 302 (23, 14, $M^+$ − Me, m* = 287.7), 281 (8, 3, $M^+$ − HCl), 266 (11, 3, $281^+$ − Me), 257 (22, 20, $M^+$ − $H_2C$=BCl), 221 (89, 35, $M^+$ − $MesBCl_2$: MesBNPh), 198 (44, 16, $M^+$ − Mes), 137 [16, 2, $M^+$ − Mes(Me)BCl], 117 (19, 3, $M^+$ − $MesBCl_2$). – IR: ṽ = 1368 [vr, $(B_2N)_{as}$], 1289 (s, CN), 1261 (s, CN), 1203 [s, $(B_2N)_s$], 1113 (m, BC), 1029 (m, BC), 956 (m, BCl), 878 (s, BCl). – $C_{16}H_{19}B_2Cl_2N$ (317.86)*: calcd. C 60.46, H 6.03, N 4.10; found C 61.64, H 6.33, N 4.60.

**Reaction of 1,1-Dimethyl-2,2-bis(trimethylstannyl)hydrazine (7a) with $MeBBr_2$** (Molar Ratio 1:2). – Attempt to prepare 1,1-Dimethyl-2,2-bis(bromomethylboryl)hydrazine (**8a**). – Procedure I: **7a** (4.9 g, 12.8 mmol), dissolved in 15 mL of $CH_2Cl_2$, was added dropwise within 80 min to a solution of $MeBBr_2$ (4.6 g, 25 mmol) in 5 mL of $CH_2Cl_2$ at −70 to −40°C. – NMR data (after 16 h stirring at ambient temp.): $^1$H NMR: δ = 0.76 ($Me_3SnBr$). – $^{11}$B NMR: δ = 45 [$MeBrB(Me_3Sn)NNMe_2$?], 37, 18 (ratio: ca. 1:1:10), additional signals of very low intensity at δ = 9, −1, −4, −25. No evidence for the formation of $Me_2N-N(BMeBr)_2$ (**8a**) was detected by NMR. – After removal of the volatile components at 25°C/13 Torr and distillation of $Me_3SnBr$ (5 g, 83%) at 25−55°C/$10^{-2}$ Torr, a yellow/brown, viscous residue remained, which was fairly insoluble in petroleum ether and benzene. No pure product could be isolated by crystallization, neither from these solvents nor from $CH_2Cl_2$.

**2,2-Bis(bromoisopropylboryl)-1,1-dimethylhydrazine (8b). – Procedure I: 7a** (4.90 g, 12.8 mmol), dissolved in 15 mL of $CH_2Cl_2$, was added dropwise within 150 min to a solution of *i*$PrBBr_2$ (7.90 g, 36.8 mmol) in 40 mL of $CH_2Cl_2$ at −78 to −70°C. The workup was carried out after 20 h of stirring at room temp. After removal of the solvent (25°C/13 Torr) and $Me_3SnBr$ (34°C/$10^{-3}$ Torr), the distillation of the remaining oil yielded 2.46 g of **8b** (41%) as colorless, viscous liquid, b.p. 82−86°C/$10^{-3}$ Torr. Redistillation at 40−41°C/$10^{-5}$ Torr yielded 1.4 g of pure **8b** (23%) and a residue. – $^{11}$B NMR ($CDCl_3$): d = 36.6 [$(Me_2NN{\equiv}BiPr)_3$?]. – **8b** is spontaneously inflammable in contact with air and turns dark brown when stored at room temp. – $^1$H NMR ($CDCl_3$): δ = 0.97 (m, not resolved, 14 H, *iPr*B), 3.09 (s, br., not resolved, 6 H, $Me_2N$). – $^{13}$C NMR: δ = 13 (br., B*C*H$Me_2$), 19.36 (br., BCH*Me*$_2$), 46.84 (br., N*Me*$_2$). – d$^{11}$B: 2.1 ($B_{endo}$, 1 B, $h_{1/2}$ = 265 Hz), 38.9 (1 B, $B_{exo}$, $h_{1/2}$ = 433 Hz). – $^{14}$N NMR: δ = −276 (1 N, *N*$B_2$, $h_{1/2} \approx$ 625 Hz), −305 (*N*$Me_2$, 1 N, $h_{1/2} \approx$ 625 Hz); $h_{1/2}$ is a crude estimate. – MS: 324 (6, $M^+$), 281 (39, $M^+$ &NDASH; *i*Pr), 245 (19, $M^+$ − Br), 237 (24, $M^+$ &NDASH; *i*$PrNMe_2$), 195 (18, 237 − $H_2C$=CH−$CH_3$), 166 (13, $M^+$ − $Br_2$), 159 (100, $BrBNBNMe_2^+$), 130 (17, $BrBNBMe^+$), 123 (32, $166^+$ − *i*$Pr_2$), 116 (14, $BrBNBH^+$), 112 (54, *i*$PrBNNMe_2$), 95 (41, $MeBNBNMe_2^+$). – IR (selected vibrations): ṽ = 1362 cm$^{-1}$ [s, $\nu_{as}(B_2N)$, for comparison (BN) = 1368 cm$^{-1}$[42]] 1308 [m, ν(CN)], 1197 [m, $\nu_s(B_2N)$], 1058 [s, ν(BC)], 819 (s) and 743 [s, ν(BBr)], 658 [s, ν(N→B)]. – $C_8H_{20}B_2Br_2N_2$ (325.7)*: calcd. C 29.50, H 6.19, N 8.60; found C 32.35, H 6.69, N 9.48; C/H(N ratio calcd. 8:20:2; found 8:19.7:2.

**2,2-Bis(bromo-*tert*-butylboryl)-1,1-dimethylhydrazine (8c). – Procedure I: 7a** (15.60 g, 40.4 mmol), dissolved in 60 mL of $CH_2Cl_2$, was added within 3 h to a solution of *t*$BuBBr_2$ (18.40 g, 80.7 mmol) in 50 mL of $CH_2Cl_2$ at −78°C. After 17 h stirring at room temp., removal of the solvent and $Me_3SnBr$, the liquid residue was purified twice by distillation. Yield: 8.4 g of **8c** (58%) as a colorless, viscous liquid, b.p. 63−66°C/$10^{-5}$ Torr. The liquid is spontaneously inflammable in contact with air and moisture. In a second experiment **8c** crystallized after distillation, m.p. 36−41°C. – $^1$H NMR ($CDCl_3$): δ = 1.01 (s, 18 H, *tBu*$B_{endo}$), 1.04 (s, 18 H, *tBu*$B_{exo}$), 3.13 (s, 3 H, *Me*$_A$Me$_B$N), 3.27 (s, 3 H, Me$_A$*Me*$_B$N). – $^{13}$C NMR: δ = 27.99 ($B_{exo}$C*Me*$_3$), 30.15 ($B_{endo}$C*Me*$_3$), 46.57 (N*Me*$_A$Me$_B$), 51.06 (NMe$_A$*Me*$_B$). – $^{11}$B NMR: δ 2.0 (1 B, $B_{endo}$, $h_{1/2}$ = 96 Hz), 40.3 (1 B, $B_{exo}$, $h_{1/2}$ = 193 Hz) (for B*C*Me$_3$ signal not found). – $^{14}$N NMR: δ = −263 (1 N, *N*$B_2$, $h_{1/2} \approx$ 499 Hz), −328 (1 N, *N*$Me_2$, $h_{1/2} \approx$ 403 Hz). – MS (70 eV, 20 eV): 352 (2, 6, $M^+$), 337 (5, 2, $M^+$ − Me), 295 (56, 100, $M^+$ − *t*Bu), 273 (38, 48, $M^+$ − Br), 239 (100, 78, $295^+$ − $H_2C$=$CMe_2$), 217 (26, 8, $273^+$ − $H_2C$=$CMe_2$), 194 (8, $M^+$ − $Br_2$), 179 (6, $194^+$ − Me), 175 (14, $217^+$ − $H_2C$=CH−$CH_3$), 159 (78, $273^+$ − *t*Bu−*t*Bu), 137 (19, *t*$BuBNBNMe_2^+$), 130 (38, $BrBNBMe^+$), 126, (30, 54, *t*$BuBNNMe_2^+$), 116 (74, $BrBNBH^+$), 111 (22, *t*$BuBNNMe^+$), 95 (28, $MeBNBNMe_2^+$), 66 (21, $MeBNBMe^+$). – IR: ṽ = 1361 cm$^{-1}$ [s, $\nu_{as}(B_2N)$], 1265 [s, ν(CN)], 1201 [s, $\nu_s(B_2N)$], 1058 [s, ν(BC)], 851 (s) and 764 [s, ν(BBr)], 651 [s, (N→B)]. – $C_{10}H_{24}B_2Br_2N_2$ (353.76)*: calcd. C 33.95, H 6.84, N 7.92; found C 35.25, H 7.31, N 8.74; C/H(N ratio calcd. 10:24:2; found 9.7:23.2:2.0; mol. mass: found 358.9 (cryoscopically in cyclohexane).

**2,2-Bis(chloromesitylboryl)-1,1-dimethylhydrazine (8d). – Procedure I:** a) **7a** (1.7 g, 4.4 mmol), dissolved in 20 mL of $CH_2Cl_2$, was added within 1 h to a solution of $MesBCl_2$ (1.8 g, 9.1 mmol) in 15 mL of $CH_2Cl_2$ at −70 to −60°C. The work up was carried out after 20 h of stirring at room temp. $^1$H- and $^{11}$B-NMR spectra of the reaction mixture gave no evidence for the formation of the adduct **8d**. After removal of the solvents and sublimation of $Me_3SnCl$, the residue of crude **8d** was purified by crystallization from $CH_2Cl_2$. Yield: 0.97 g of **8d** (57%) as a colorless powder, m.p. 136°C, decomp. Single crystals suitable for X-ray structure determination were obtained by recrystallization from $CH_2Cl_2$ at −18°C. – $^1$H NMR ($CDCl_3$): δ = 2.23 (m, 18 H, *o*-Me−Ph, *p*-Me−Ph), 3.12 (br. s, 6 H, N*Me*$_2$), 6.78 (br. s, 4 H, *m*-H−Ph). – d$^{13}$C: 21.13 (*p*-Me−Ph), 29.69 (*o*-Me−Ph), 45.83 (N*Me*$_2$), 126.9 ($C_6H_2Me_3$), 127.6 ($C_6H_2Me_3$), 127.7 (br.), 138 (br, *i*-$C_A$), 139.5 (br.), 140 (br., *i*-$C_B$). – $^{11}$B NMR: δ = 0.7 (1 B, $B_{endo}$, $h_{1/2}$ = 482 Hz), 38.6 (1 B, $B_{exo}$, $h_{1/2}$ = 573 Hz). – MS: 388 (100, M·$^+$), 373 (1, $M^+$ − Me), 353 (23, $M^+$ − Cl), 345 (15, $M^+$ − $H_2C$=NMe), 344 (20, $345^+$ − H), 343 (21, $345^+$ − $H_2$), 318 (8, $M^{+\cdot}$ − 2 Cl), 309 (10, $344^+$ − HCl), 274 (16, $MesBNBMes^+$), 269 (75, $M^+$ − Mes), 225 (35, $M^+$ − $MesNMe_2$ ), 224 (39, $225^+$ − H), 223 (18, $M^+$ − ClBMes), 190, (27, $MesBNBCl^+$), 189 (14, $225^+$ − HCl), 188 (77, $MesBNNMe_2^+$), 187 (15, $223^+$ − HCl), 144 (24, $344^+$ − $MesBCl_2$); – IR: ṽ = 1357 cm$^{-1}$ [s, $\nu_{as}(B_2N)$], 1260 [s, ν(CN)], 1225 [s, $\nu_s(B_2N)$], 1050 [s, ν(BC)], 932 (s) and 859 [s, ν(BBr)], 664 [s, (N→B)]. – $C_{20}H_{28}B_2Cl_2N_2$ (389.0)*: calcd. C 61.76, H 7.26, N 7.20; found C 59.69, H 7.58, N 7.36; mol. mass: found 377 (cryoscopically in cyclohexane). – X-ray structure analysis data of **8d**: Formula $C_{20}H_{28}B_2Cl_2N_2$; $M_r$ = 388.96; colourless prism; size 0.3 × 0.2 × 0.1 mm, orthorhombic; space group *Pca*2(1), *a* = 12. 3263(1), *b* = 12.6905(2), *c* = 13.7050(1) Å, *V* = 2143.83(4) Å$^3$, *Z* = 4, $\rho_{calcd.}$ = 1.205 g cm$^{-3}$; μ(Mo-$K_\alpha$) = 0.309 mm$^{-1}$, *F*(000) = 824. – Data

collection: 11736 reflections in $-15 \le h \le 15$, $-16 \le k \le 9$, $-16 \le l \le 16$, measured in the range $4.60° \le 2\theta \le 58.22°$; 3751 independent reflections; $R_{int} = 0.0492$, 2456 reflections with $F_o > 4\sigma(F_o)$, semi-empirical absorption correction, 243 variables, $R = 0.0376$, $wR^2 = 0.0845$, largest difference peak: 0.178 e/Å$^3$.

b) A solution of $MesBCl_2$ (2.5 g, 12.5 mmol) in 15 mL of $CH_2Cl_2$ was added to a solution of **7a** (2.5 g, 6.4 mmol) in 15 mL of $CH_2Cl_2$ over a period of 60 min at −70 to −60°C. NMR data after a period of 16 h stirring at ambient temp.: $^1$H NMR: δ = 0.67 [s, 9 H, $Me_3$SnCl, $^2J(^{117(119)}Sn^1H)$ = 56.2 (58.6) Hz], 0.69 [s, 9 H, $Me_3$SnCl, $^2J(^{117(119)}Sn^1H)$ = 55.2 (57.6) Hz, $^3J(^{117(119)}Sn^1H)$ = 35.2 (38.6) Hz?], 2.31 [s, br., 6 H, N$Me_2$, $^3J(^{117(119)}Sn^1H)$ = 36.8 Hz], 2.57 (s, 6 H, *p*-$Me$−Ph), 2.93 (s, 12 H, *o*-Me), 6.81 (br. s, 4 H, *m*-H−Ph). − $^{11}$B NMR: δ = 39.6 ($h_{1/2}$ = 393 Hz). − The workup was according to Procedure I after a period of 17 h. The residue, obtained after removal of the volatile components at 25 to 40°C/12−$10^{-5}$ Torr, was dissolved in $CH_2Cl_2$ and checked by $^1$H- and $^{11}$B-NMR spectroscopy. The spectra are identical with those of the reaction mixture, but the signal of the noncoordinated $Me_3SnCl$ had disappeared. The latter was detected in the trap. The $^1$H-NMR signal for $Me_3SnCl$, forming an adduct with **8d**, was found at δ = 0.70 [$^2J(^{117(119)}Sn^1H)$ = 57.6 Hz]. − Sn−N bond-cleavage experiment: The NMR sample of the residue, dissolved in 5 mL of $CH_2Cl_2$, was checked by NMR after addition of a drop of $MesBCl_2$: $^{11}$B NMR: δ = 39.1 [assignment: $Me_2N-N(BMesCl)_2 \cdot Me_3SnCl$], −0.7 [$Me_2N-N(BMesCl)_2 \cdot MesBCl_2$], ratio: 3:2. − $^1$H NMR: δ = 0.72 and 0.74 ($Me_3SnCl$·coordinated and $Me_3SnCl$ in solution). With additional $MesBCl_2$ the signal at δ = 39.1 ($^{11}$B NMR) lost intensity and the signal at δ = −0.7 gained intensity; the excess of $MesBCl_2$ led to the following NMR data of the reaction mixture: $^{11}$B NMR: δ = 59.5 ($MesBCl_2$), 36.6 and −0.9 [assignment: $Me_2N-N(BMesCl)_2 \cdot MesBCl_2$]. − $^1$H NMR: δ = 0.81 [sharp signal,·dissolved $Me_3SnCl$, $^2J(^{117(119)}Sn^1H)$ = 56.6 (59.1)]. A mixture of unidentifiable products resulted when keeping the residue at room temp. for a few hours or by heating in vacuo up to 100°C/$10^{-5}$ Torr in order to remove $Me_3SnCl$ coordinated to the $Me_2N$ group.

**Attempt to Prepare 2,2-Bis(bromomethylboryl)-1,1-diphenylhydrazine (8e) by Reaction of 7b with $MeBBr_2$ (Molar Ratio 1:2): 7b** (5.34 g, 10.5 mmol), dissolved in 15 mL of $CH_2Cl_2$, was added over 60 min to a solution of $MeBBr_2$ (4.6 g, 24.8 mmol) in 15 mL of $CH_2Cl_2$ at −75 to −65°C. NMR data after 16 h stirring at ambient temp.: $^1$H NMR: δ = 0.77 [s, 9 H, $Me_3$SnBr]. − $^{11}$B NMR: δ = 34.5 [$(Ph_2NN{=}BMe)_3$?], 40.0/−2.4 [signal ratio: ca. 1:1, **8e** (intramolecular BN adduct formation?)], 48.9 [$Ph_2N-N(BMeBr)_2$ (**8e**) noncyclic compound?]. − The workup was carried out according to Procedure I after 17 h of stirring. The residue obtained after removal of the volatile components was dissolved in $CH_2Cl_2$ and checked by $^1$H- and $^{11}$B-NMR spectroscopy. The predominant signal among others in the $^{11}$B-NMR spectrum was that at δ = 34.5 [$(Ph_2NN{=}BMe)_3$?]; after 12 h, additional signals (δ = 28.8, 31.9) could be detected in the solution. Attempts to separate the products failed even by fractional recrystallization from toluene at various temperatures. The only volatile compound obtained was $Me_3SnBr$.

## Acknowledgments

We gratefully acknowledge the support of this research by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Chemetall GmbH. We also thank Mrs. C. Neumann for support of the synthetic work, Mrs. D. Ewald for recording the mass spectra and Mr. T. Seifert for the X-ray structure determination.

[1] A. Appel, C. Kober, C. Neumann, H. Nöth, M. Schmidt and W. Storch, *Chem. Ber.* **1996**, *129*, 175−189 and refs. therein.
[2] H. Nöth, P. Otto, W. Storch, *Chem. Ber.* **1985**, *118*, 3020−3031.
[3] H. Nöth, P. Otto, W. Storch, *Chem. Ber.* **1986**, *119*, 2517−2530.
[4] P. Paetzold, C. v. Plotho, G. Schmid, R. Schrader, D. Bougeard, U. Pfeiffer, R. Gleiter, W. Schäfer, *Chem. Ber.* **1984**, *117*, 1089−1095.
[5] W. Storch, reported at the *VII. Int. Meeting on Boron Chemistry*, Torun, Poland, **1990**.
[6] [6a] R. Boese, B. Kröckert, P. Paetzold, *Chem. Ber.* **1987**, *120*, 1913−1915. − [6b] P. Paetzold, B. Redenz-Stormanns, R. Boese, *Chem. Ber.* **1991**, *124*, 2435−2441.
[7] H. Nöth, S. Weber, *Z. Naturforsch.* **1983**, *38b*, 1460−1465; F. Dirschl, E. Hanecker, H. Nöth, W. Rattay, W. Wagner, *Z. Naturforsch.* **1986**, *41b*, 32−37.
[8] The diborylamine **3m** has also been obtained in low yield via Si−N cleavage but under comparatively drastic conditions: K. Barlos, H. Christl, H. Nöth, *Liebigs Ann. Chem.* **1976**, 2272−2283.
[9] S. Diemer, H. Nöth, K.Polborn, W. Storch, *Chem. Ber.* **1992**, *125*, 389−400 (details on reactions according to Equation 3)
[10] [10a] D. Nölle, H. Nöth, *Angew. Chem.* **1971**, *83*, 112−113. − [10b] D. Nölle, H. Nöth, W. Winterstein, *Z. Anorg. Allg. Chem.* **1974**, *406*, 235−250. − [10c] K. Niedenzu, B. K. Christmas, *Z. Anorg. Allg. Chem.* **1978**, *439*, 103−111. − [10d] P. C. Bharara, H. Nöth, *Z. Naturforsch.* **1979**, *34b*, 1352−1357. − [10e] W.Pieper, D. Schmitz, P. Paetzold, *Chem. Ber.* **1981**, *114*, 3801−3812. − [10f] A. Meller, M. Armbrecht, *Chem. Ber.* **1986**, *119*, 1−8.
[11] [11a] H. Nöth, W. Regnet, H. Rihl, R. Standfest, *Chem. Ber.* **1971**, *104*, 722−733. − [11b] H. Fußstetter, H. Nöth, *Liebigs Ann. Chem.* **1981**, 633−641.
[12] J. March, *Advanced Organic Chemistry*, 3rd edition, John Wiley & Sons Inc., New York, Chichester, Brisbane, Toronto, Singapore, **1985**, p. 310 and refs. cited therein.
[13] H. Nöth, H. Vahrenkamp, *Chem. Ber.* **1967**, *100*, 3353−3358.
[14] H. Nöth, B. Wrackmeyer, *NMR Spectrocopy on Boron Compounds, Basic Principles and Progress* (Eds.: F. Diehl, E. Fluck, P. Kosfeld), Springer Verlag, Berlin, Heidelberg, New York, **1978**.
[15] P. Otto, Ph. D. Thesis, University of Munich, **1986**.
[16] [16a] D. T. Pegg, D. M. Doddrell, W. M. Brooks, M. R. Bendall, *J. Magn. Reson.* **1981**, *44*, 32−36. − [16b] D. T. Pegg, D. M. Doddrell, M. R. Bendall, *J. Chem. Phys.* **1982**, *77*, 2745−2751.
[17] H. Fußstetter, H. Nöth, *Liebigs Ann. Chem.* **1981**, 633−641.
[18] H. Hommer, Ph. D. Thesis, University of Munich, **1994**.
[19] H. Nöth, S. Weber, *Z. Naturforsch.* **1983**, *38b*, 1460−1465.
[20] V. S. Petrosyan, *NMR Spectra and Structures of Organotin Compounds, Progress in NMR Spectroscopy*, **1977**, *11*, 115−148.
[21] B. Wrackmeyer, *Annual Rep. NMR Spectrosc.* **1985**, *16*, 73−186.
[22] G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, **1993**.
[23] K. Sisido, S. Kozima, *J. Org. Chem.* **1964**, *29*, 907−909.
[24] C. Kober, J. Kroner, W. Storch, *Angew. Chem.* **1993**, *105*, 1693−1695; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1608−1610.
[25] [25a] W. P. Neumann, *Die organische Chemie des Zinns*, Ferdinand Enke Verlag, Stuttgart, **1967**. − [25b] M. Pereyre, J.-P. Quintarr, A. Rahm, *Tin in Organic Synthesis*, Butterworth & Co. Ltd., London, Boston, **1987** and refs. cited therein.
[26] K. Jones, M. F. Lappert, *J. Chem. Soc.* **1965**, 1944−1951.
[27] H. W. Roesky, H. Wietzer, *Chem. Ber.* **1974**, *107*, 3186−3190.
[28] N. Wiberg, M. Veith, *Chem. Ber.* **1971**, *104*, 3191−3203.
[29] N. Wiberg, M. Veith, *Chem. Ber.* **1971**, *104*, 3176−3190.
[30] W. Storch, H. Nöth, *Chem. Ber.* **1977**, *110*, 1636−1642.
[31] W. Hansen, P. Paetzold, *Z. Anorg. Allg. Chem.* **1966**, *345*, 79−86.
[32] H. Nöth, P. Fritz, *Z. Anorg. Allg. Chem.* **1963**, *322*, 297−309.
[33] From $i$Pr$_3$B and $BCl_3$ catalysed with BH3·THF: see R. Köster, M. A. Grassberger, *Liebigs Ann. Chem.* **1968**, *719*, 169−172.
[34] Modified procedure, from 2-*t*Bu-1,3,2-dithiaborolane and $Br_2$ in $CH_2Cl_2$, see H. Prigge, Ph. D. Thesis, University of Munich, **1983**.
[35] W. Hansen, P. Paetzold, *Z. Anorg. Allg. Chem.* **1966**, *345*, 79−86.

[36] S. J. Groszos, S. F. Stafiej, *J. Am. Chem. Soc.* **1958**, *80*, 1357−1360.
[37] I. Haiduc, *The Chemistry of Inorganic Ring Systems*, Wiley Interscience, London, New York, Sydney, Toronto **1970**, part 1, p. 124−273.
[38] K. Barlos, H. Christl, H. Nöth, *Lieb. Ann. Chem.* **1976**, 2272−2278.
[39] For comparison $\nu_{as}(B_2N)$ = 1310−40 $cm^{-1}$: H. Vahrenkamp, Ph. D. Thesis, University of Munich, **1967**.
[40] D. Kaufmann, *Chem. Ber.* **1987**, *120*, 901−905.
[41] G. Linti, Ph. D. Thesis, University of Munich, **1990**.
[42] W. Storch, H. Nöth, *Chem. Ber.* **1977**, *110*, 1636−1642. H. Nöth, P. Otto, W. Storch, *Chem. Ber.* **1986**, *119*, 2517−2530.
[43] M. Kaufmann, Staatsexamensarbeit, Universität München, **1988**.
[44] K. Barlos, Ph. D. Thesis, University of Munich, **1977**.
[45] S. Diemer, Ph. D. Thesis, University of Munich, **1993**.

Received November 14, 1998
[I98404]