N-(2,4,6-Trimethylborazinyl)-substituted Boron, Aluminum and Titanium Compounds*

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The *N*-lithioborazine $LiH_2N_3B_3Me_3$, **1**, reacts with organoboron halides not only to the respective borazinyl organylboranes but also by Me/halogen exchange. $(Me_2N)_2B$-$H_2N_3B_3Me_3$ was obtained from **1** and $(Me_2N)_2BCl$. A new ten-membered B_6N_4 ring system, **5**, results on treatment of $Cl(Me_2N)B$–$B(NMe_2)Cl$ with **1**. The *B*-*N*-borazinyl borazines **6** – **8** can be prepared from **1** and *B*-monohalo borazines. The synthesis of 2,4,6-trimethylborazinyl-aluminum and -titanium compounds is achieved only with mononuclear monohalides of Al(III) and Ti(IV). The 2,4,6-trimethylborazinyl-bis(piperidino)alane **9** and the tris(2,6-diisopropylphenoxo)-2,4,6-trimethylborazinyl-titanium **10** were characterized by X-ray structure analysis.

The distortion of the borazine ring by B and N substitution is discussed. In case of the N-substituted borazines $YH_2N_3B_3Me_3$ the B–N bonds of the YNB_2 units are elongated, *e. g.* for Y = PBr_2 or $(RO)_3Ti$, while N lithiation leads to a shortening of these B–N bond. These changes of bond lengths are also reflected by changes in the B1–N2 and B3–N3 bond lengths which become shorter in the presence of electron-withdrawing groups, but longer in case of Li substitution. Also, the bond angles B1–N2–B2 and B2–N3–B3 are affected by an increase of up to 128°.

Key words: Borazine Derivatives, Diborane(4) Compound, Aminoalane, Titanium Phenoxide, X-Ray Structures

Introduction

The diethyl ether solvate of *N*-lithio-2,4,6-trimethylborazine, **1**, [1] is a reagent which can be used in many ways, as, *e. g.*, for the preparation of trimethylborazinyl substituted phosphanes, arsanes or stibanes [2]. These results suggested that **1** can also be employed to generate *N*-(2,4,6-trimethylborazinyl) derivatives of many more elements, compounds that are of interest for comparison with the corresponding mesityl compounds. We report here on first results involving compounds of boron, aluminum and titanium. A more systematic study is presently conducted.

Results

Reactions of $Me_3B_3N_3H_2Li$ with organoboron halides

Organoboron halides such as Ph_2BBr or $PhBCl_2$ do not react with the borazine $Me_3B_3N_3H_3$ at ambient temperature by substitution at the N atom, even in the presence of triethylamine or piperidine as HX scavengers. At reflux temperature Me/X (X = Cl, Br) exchange can be observed by ^{11}B NMR. However, it is to be expected that the more strongly basic diethyl ether complex of *N*-lithio-2,4,6-trimethylborazine, **1** [1], will react with organoboron halides to give borazinyl-substituted organoboranes as shown in Eq. 1.

$$\underset{\mathbf{1}}{n\,\mathrm{Me_3B_3N_3H_2Li}} + \underset{n\,=\,1,\,2}{\mathrm{R}_{3-n}\mathrm{BX}_n} \longrightarrow \mathrm{R}_{3-n}\mathrm{B(H_2N_3B_3Me_3)}_n + \underset{\mathrm{X\,=\,Cl,\,Br}}{n\,\mathrm{LiX}} \tag{1}$$

Similarly, reaction of **1** with BX_3 (X = F, Cl, Br) may give access to borazinyl-substituted haloboranes and even tris(trimethylborazinyl)borane provided that there is no steric hindrance for the third substitution step. Here we describe only reactions according to Eq. 1. Although most of the studied organoboron halides react with **1**, one observes also Me/halogen exchange. This competing reaction leads to mixtures of products which can be analyzed by ^{11}B NMR or mass spectrometry, but we have been unable to isolate pure products either by distillation or by crystallization.

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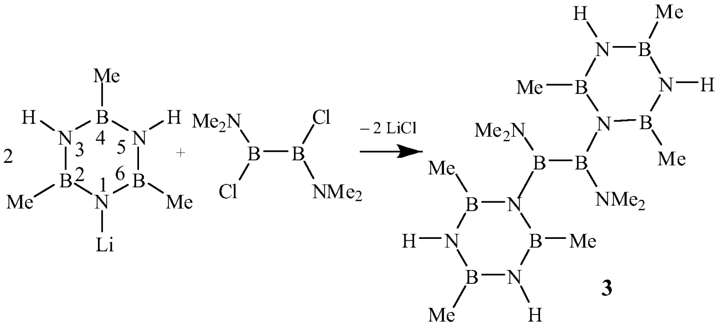
$$\underset{\mathbf{1}}{(Me_2N)_2BCl + LiH_2N_3B_3Me_3} \longrightarrow \underset{\mathbf{2}}{(Me_2N)_2B\text{-}H_2N_3B_3Me_3} + LiCl \qquad (2)$$



Scheme 1.

The 1 : 1 reaction of **1** with Ph_2BBr in toluene led to Ph_2BMe (20 %), $(Me_3B_3N_3H_2)BPh_2$ (60 %) and $Me_{3-x}Br_xB_3N_3H_3$ (20 %). A 1 : 1 mixture of **1** and $PhBCl_2$ in toluene did not react at r. t., but after heating to reflux LiCl was formed and the filtrate showed the presence of MePhBCl (15 %), $(Me_3B_3N_3H_2)B(Cl)Ph$ (20 %), $Me_3B_3N_3H_3$ (45 %), and $Me_{3-x}Cl_xB_3N_3H_3$ (20 %). *t*Bu_2BCl in hexane did not react with **1** even under reflux conditions. On the other hand, a precipitate of LiCl was formed rapidly on mixing **1** in hexane with 9-Cl-9-BBN to give the borazinyl-substituted 9-BBN derivative, but again Cl/Me exchange was also noted with the formation of 9-Me-9-BBN.

Reactions of $Me_3B_3N_3H_2Li$ with dimethylamino-chloroboranes and B-haloborazines

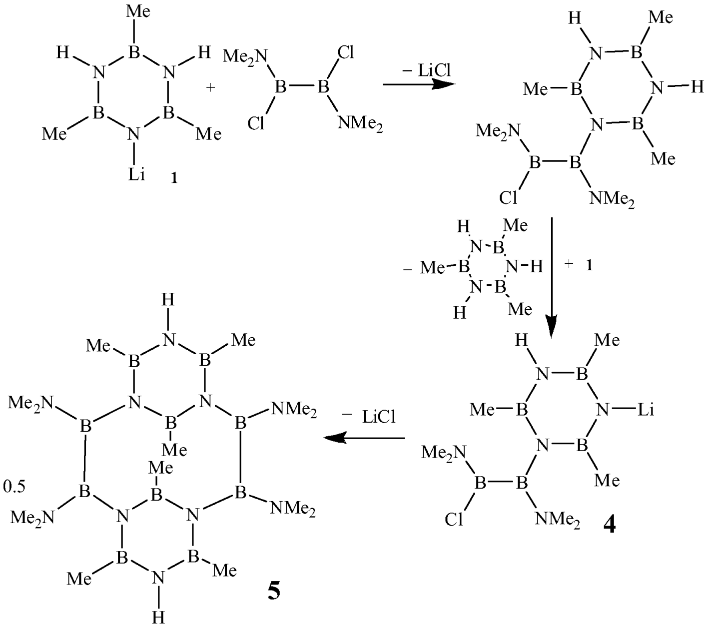
In order to prevent the R/X exchange we studied some reactions of dimethylamino-chloroboranes and B-haloborazines with **1** because LiX elimination is the highly preferred pathway for reactions of LiR compounds with aminoboron halides [3]. Indeed, no Me/NMe_2 exchange was noted for the 1 : 1 reaction of **1** with $(Me_2N)_2BCl$. The reaction proceeded smoothly in hexane as shown in Eq. 2 to yield the solid compound **2** in 80 % yield. **2** was characterized only by NMR and IR spectroscopy and by elemental analysis, because no crystals suitable for X-ray structure analysis could be grown. In contrast to this straightforward result we observed an unexpected reaction when **1** was treated with $Cl(Me_2N)B\text{–}B(NMe_2)Cl$ in a 2 : 1 ratio. We had anticipated that the reaction would take the course as shown in Scheme 1. However, instead of compound **3**, we obtained the ten-membered ring compound **5** (Scheme 2). Its formation is only possible if the lithium borazine becomes additionally metallated (deprotonated) in the course of the reaction. Most likely the first step in this reaction is the generation compound **4**. Its NH proton should be more acidic than the NH groups in compound **1** due to π-bonding with an additional boron atom. And, therefore, one NH proton is liable to react with a further molecule of **1** by deprotonation, generating compound **4**. Two molecules of **4** can then react with formation of the ten-membered ring **5**.

Compound **1** can also be used to synthesize *B,N*-borazinyl-borazines. We used this method to prepare compounds **6**, **7** and **8** according to Scheme 3. Non-optimized yields are in the range from 45 to 70 %.

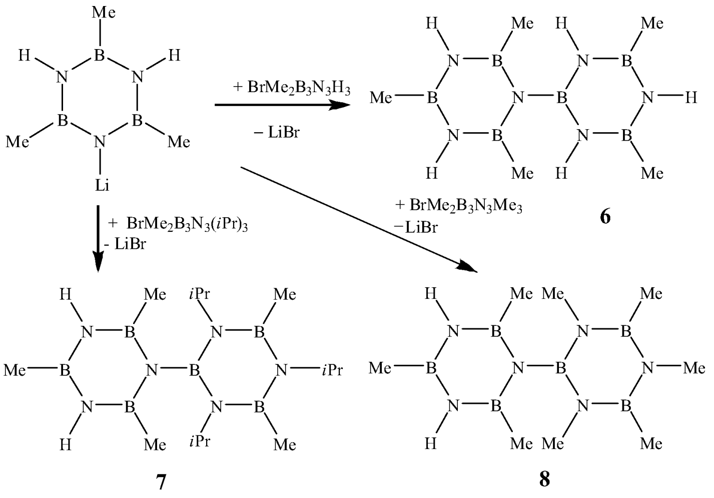
NMR Spectra

Table 1 lists the NMR data of the dimethylamino-borane derivatives **2** and **5** as well as those of the diborazines **6**, **7** and **8**.

The ^{11}B chemical shift for the $B(NMe)_2$ group of **2** is 31.1 ppm. This is 3.4 ppm at lower field compared with $B(NMe_2)_3$ and 1.3 ppm compared with $PhB(NMe_2)_2$ [4]. Although one expects two ^{11}B NMR signals for the B atoms of the borazinyl group only a single broad signal with a maximum at $\delta^{11}B$ = 36.1 ppm is recorded for **5** at ambient temperature showing a small low field shift in comparison with **1** ($\delta^{11}B$ = 35.4 ppm) [1]. However, two ^1H NMR signals are observed for the BMe groups of the ring system. The H atoms of the *p*-BMe group are slightly deshielded compared to the H atoms in *o*-position. Only a single ^1H NMR signal is found for the $B(NMe_2)_2$ group, indicating free rotation about the respective B–N bonds. This was also observed for $PhB(NMe_2)_2$ [4].



Scheme 2.



Scheme 3.

The ten-membered ring compound **5** must be symmetrical as there are only two NMR signals for the B atoms, two for the ring methyl groups and two for the NMe_2 groups. The borazinyl groups are represented by an ^{11}B NMR signal at 35.8 ppm. Its B atoms are slightly better shielded than in compound **2** (Δ = 1.5 ppm). In contrast, the B atoms of the diborane(4) units are significantly deshielded compared with other tetra(amino)diborane(4) compounds whose ^{11}B NMR signals are observed within the range from 34 – 38.5 ppm [5]. This indicates that bonds of the borazinyl nitrogen atoms to the B_2 units have little π-character in contrast to bonds of the Me_2N groups of the diborane(4) unit, because the two ^1H NMR signals for these groups are compatible with hindered rotation about their BN bonds. This makes the two Me groups of each NMe_2 unit non-equivalent.

The pentamethyldiborazine **6** should show four ^{11}B NMR signals. However, only two are observed. The signals at δ = 30.2 and 34.3 ppm are partially overlapping indicating an intensity ratio of 1 : 2. The signal at 34.3 ppm most likely represents BMe groups with two NH neighbors, while the better shielded boron atoms are those with a Me/NH/N environment. There

Table 1. NMR spectroscopic data of compounds **2** and **5** to **8** (δ values in ppm).

Compound	δ^{11}B	δ^{1}H *p*-Me	δ^{1}H *o*-BMe	δ^{1}H *m*-BMe	δ^{1}H NMe	δ^{1}H NH
2	36.1 Borazine 31.1 B(NMe$_2$)$_2$	0.34	0.31		2.51	
5	35.8 Borazine 41.2 B$_2$(NMe$_2$)$_2$	0.39	0.15		2.64, 2.80	
6	30.2, 34.3	0.33 3H	0.35 6H	0.20		4.33 (1H) 4.09 (2H) 4.55 (2H)
7	35.8, 38.1	0.31 pme	1.35CMe$_2$ 4.06 CH	0.38, 1.28, 3.94 sept.		4.53
8	35.8, 38.1	0.27 (6H)	0.26 (6 H)			4.60

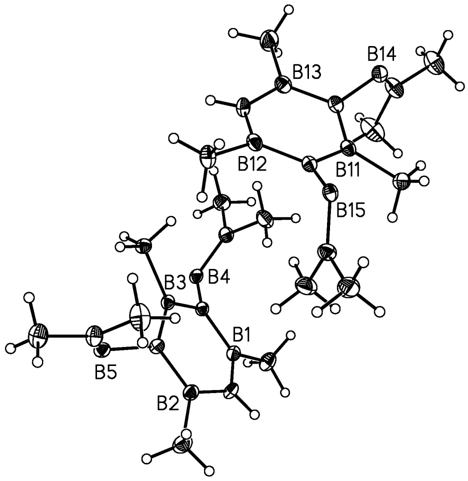


Fig. 1. Atoms in the asymmetric unit of compound **5** (ORTEP).

are three ^{1}H NMR signals for the NH groups in a 2 : 1 : 2 ratio as well as for the protons of the Me groups (δ^{1}H = 0.20, 0.32, 0.34 in a 2 : 1 : 2 ratio). Although ^{13}C resonances for boron-bonded Me groups can often not be detected as a consequence of the quadrupole moment of the boron nuclei, two (instead of three) broad ^{13}C signals were observed at 1.54 and 2.95 ppm.

The *B*-pentamethyl-*N*-triisopropyl-diborazine **7** exhibits also only two ^{11}B NMR signals instead of the expected four. We attribute the signal at 35.8 ppm to the $Me_3B_3N_3H_2$ borazine ring, and the signal at 38.1 ppm to the $Me_2B_3N_3(i\mathrm{Pr})_3$ group. The two non-equivalent Me groups of the $Me_3B_3N_3H_2$ unit are represented by two ^{1}H NMR signals at 0.31 and 0.38 ppm (ratio 1 : 2), while the proton resonance for the BMe groups in the $Me_2B_3N_3(i\mathrm{Pr})_3$ unit is observed at 0.76 ppm. There are two signal pairs for the isopropyl groups (ratio 2 : 1).

The close similarity of compounds **7** and **8** is demonstrated by two ^{11}B NMR signals which show the same chemical shifts. There are three types of BMe groups in **8**. Similar to compound **7**, one observes deshielded BMe protons for the $Me_2B_3N_3Me_3$ unit (δ^{1}H = 0.48 ppm) as compared with the BMe protons of the $Me_3B_3N_3H_2$ group (δ^{1}H = 0.26 and 0.27 ppm). The NH protons are represented by two signals at δ^{1}H = 2.74 and 2.82 (ratio 2 : 1). This shows that the NH proton in *p*-position is deshielded compared with those in the *o*-positions.

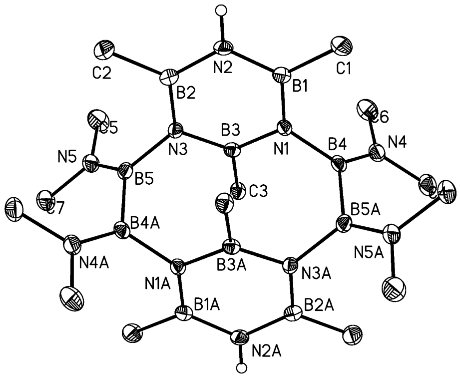


Fig. 2. ORTEP plot of compound **5a**: Selected bond lengths (Å) and bond angles (deg) (see also Table 3). B5-N5 1.395(4), B4-N4 1.402(3), N1-B4 1.494(4), N3-B5 1.508(3), B1–N1 1.439(3), B1–N2 1.426(3), B2–N2 1.424(3), B2–N3 1.441(3), B3–N3 1.444(3), B1–C1 1.575(4), B2-C2 1.572(4), B3-C3 1.590(4), B4–B5A 1.731(4); B3–N1–B4 120.0(2), N1–B4–N4 119.4(2), N1–B4–B5A 114.5(2) 113.6(2), N3–B5–B4A 113.6(2), N4–B4–B5A 125.8(2); torsion angles: N3–B3–N1–B4 −168.5°, N1–B1–N2–B5 −149.8°, N5–B5–B4A–N4A −95.9°, N1–B4–B5A–N3A −119.6°.

*X-Ray structures of compounds **5** and **6***

The new ten-membered BN heterocycle **5** crystallizes in the triclinic system, space group $P\bar{1}$, $Z = 2$. The structure determination revealed two crystallographically independent molecules, with inversion centers being located in the centroids of the ten-membered rings. Fig. 1 shows the atoms in the asymmetric unit, and Fig. 2 one of the two molecules. Charac-

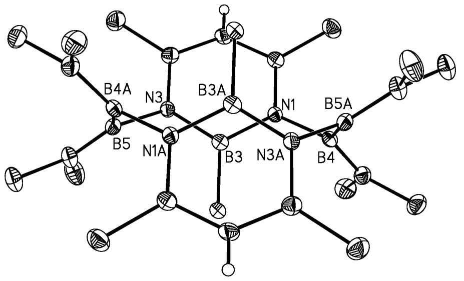


Fig. 3. The puckered ten-membered B_6N_4 ring of compound **5a**.

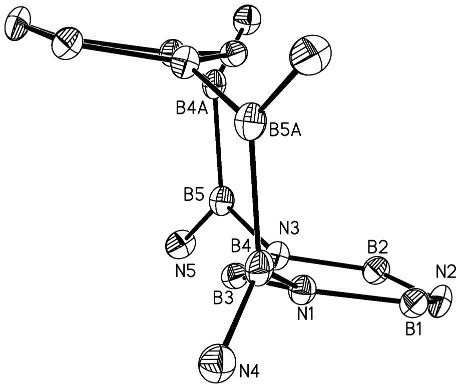


Fig. 4. Side view on molecule **5a**: Interplanar angles (deg): N1B1B2N3/B1N2B2 8.2°, N1B1B2N3/B1N1B3N3 4.3°, N4B4N1/B5AN5AN2A 120.8°.

teristic is the shape of the ten-membered ring built from two NBN units of two borazine rings and the two diborane(4) units (Fig. 3). Due to the inversion center the two borazine units are parallel. The B–N bond lengths within the borazines span a range from 1.426 to 1.444(3) Å. These bond lengths agree nicely with those of other *B*-triorganoborazines [6]. The B–B bond lengths of 1.731(4) Å, are shorter than in B_2(piperidine)$_4$ (d_{B-B} = 1.750(8) Å) [7], but longer than in bis(1,3-dimethyl-1,2,3-diazaborolidines) (1.693(9) Å). [8]. All boron atoms reside in a planar environment, and all N atoms also. Therefore, conditions for BN-π-bonding seem to be excellent. However, the B–N bond lengths are not as short as expected for B–N double bonds as found in monoaminoboranes, because all boron atoms have two nitrogen neighbors. Therefore, the BN bond order could be 1.5 at best. One should, therefore, rather compare the BN bond lengths with those of *e. g.* bis(1,3-dimethyl)-1,3,2-diazaborolidines (1.414(7) Å) [8]. The B–N bonds from the B_2 units to the borazine rings are noticeably longer than those within the borazine rings.

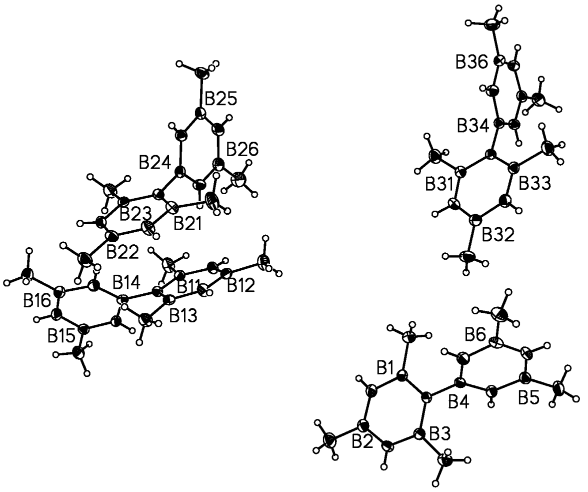


Fig. 5. View on the four independent molecules of compound **6**.

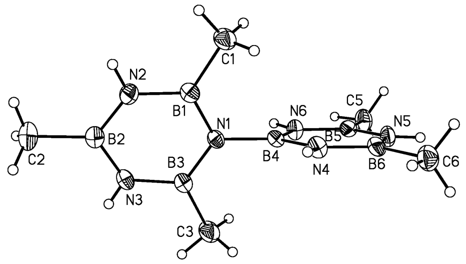


Fig. 6. ORTEP plot of one of the four crystallographically independent molecules of **6** (**6A**). B–C bond lengths (Å): B1-C1 1.571(5), B2-C2 1.571(5), B3-C3 1.575(5), B5-C5 1.566(5), B6–C6 1.573(6) (see also Table 3); interplanar angle N1B1N2B2N3B3/B4N4B5N5B6N6: 69.5°.

These four bonds span a range from 1.49 to 1.51 Å. They represent single bonds between sp^2-type N and B atoms and can be compared with the exocyclic BN bond lengths found in *B*-chloro-B'',B'''bis(-dimethylamino)borazine (d_{BN} = 1.497(3) Å) [9].

Bond angles at atom B1 are rather different. The angle N3–B1–B2A is 114.6(2)° while those of N1–B1–B2A and N3–B1–N1 are 125.7(2)° and 119.7(2)°, respectively. This may be due to the higher BN double bond contribution of the B1–N1 bond. According to Gillespie and Nyholm the space required for a double bond is larger than for a single bond [10].

Fig. 2 shows that the two adjacent $BNMe_2$ units are twisted against each other by 68°. Similar interplanar angles between Me_2N groups at adjacent boron atoms are also observed in dimethylaminotri- and tetraboranes [11]. The interplanar angle between the $Me_2N(4)$ and $Me_2N(N5A)$ groups is 63.9°, and the angle be-

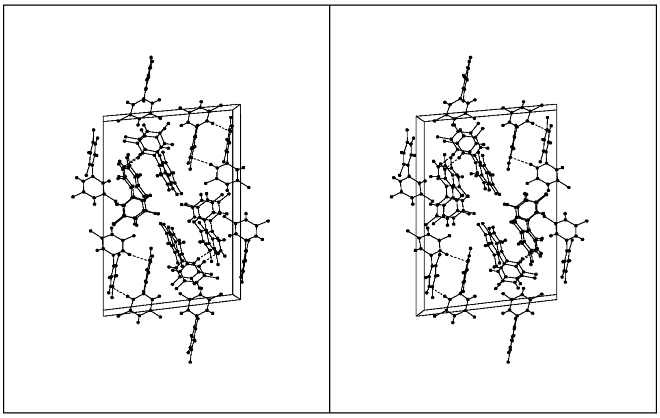


Fig. 7. Stereo view of the unit cell of compound **6** down the crystallographic *a* axis. Note the hydrogen bond interaction N–H–N.

tween the planes B2N2B1 and B5N5B4A is even closer to 90° at 81.2°.

Fig. 4 shows that the borazine rings are *not* planar but are present in the boat conformation. This conformation of the borazine ring is characterized by the interplanar angles N3B3N1/B3N3B1N21 = 6.8° and B3N3B1N2/B2N2B1 = 11.6°.

The B-C bond lengths in compound **5** (1.575(4) Å) correspond with B–C single bonds. Only the B5–C7 bond is longer at 1.590(3)°. This is the bond to the methyl group that "looks" into the ten-membered ring.

Although 1,1′-diborazines, 1,2′-diborazines and 2,2′-diborazines have peen prepared by various methods [12 – 15], as well as some bis(borazinyl)borazines and tris(borazinyl)-borazines [12], none of them has yet been fully characterized by NMR spectroscopic methods and by X-ray crystallography [3]. After having obtained single crystals of pentamethyl-1,2′-diborazinyl, **6**, we determined its structure by X-ray crystallography. The crystals are triclinic, space group $P\bar{1}$. The unit cell contains 8 molecules of **6**, *i. e.*, there are four independent molecules in the asymmetric unit. Fig. 5 shows these four molecules and Fig. 6 molecule **6A**. The N1–B4 bond which connects the two borazinyl units in **6C** is the longest B–N bond within the molecule with 1.492(3) Å. In the molecules **6A**, **6B** and **6D** this B–N bond is shorter: B14–N11 = 1.480(4) Å, B24–N21 = 1.485(3) Å and B34–N31 = 1.484(3) Å. There is a correlation between these B–N bond lengths and the interplanar angles of the two borazine units in each diborazine molecule, which are 69.5° for molecule **6A**, 60.5° for molecule **6B**, 86.6° for molecule **6C**, and 82.3° for molecule **6D**. The BN π-bonding contribution must be zero in the case of **6C**. For similar reasons, the B14–N11 bond length in **6B** should be shorter than in **6D** due the small interplanar angle which may allow some BN π-bonding, but the B–N bond seems to be only slightly shorter than in **6D**. The smaller interplanar angle in **6B** brings the *o*-Me groups closer to the NH groups of the neighboring borazine rings than in any of the other three molecules. This steric effect is most likely the reason that the B–N distances of **6B** and **6D** are equal within standard deviations.

Fig. 7 shows a stereoscopic view on the unit cell of compound **6**. It reveals that the molecules are connected by N–H–N hydrogen bridges.

Bis(tetramethylpiperidino)-N-(2,4,6-trimethylborazinyl)alane and tris[2,6-(diisopropylphenoxo)]-N-(2,4,6-trimethylborazinyl)titanium

1-Lithio-2,4,6-triorganylborazines can be prepared form the respective borazines and alkyllithium compounds [1, 17]. By replacing LiR by triorganoaluminum compounds, borazinyl-substituted organoalanes might become available. However, $Me_3B_3N_3H_3$ did not react with $(AlMe_3)_2$ under reflux conditions in toluene. Moreover, $[(Me_2N)_2AlCl]_2$ did also not react with **1** even in refluxing toluene. The missing reactivity may be due to the dimeric nature of the amino-chloroalane, making the Al center less attractive for nucleophilic substitution. Therefore, we studied the reaction of **1** with the monomeric bis (tetramethyl-piperidino)chloroalane, tmp_2AlCl. In this case we obtained bis(tetramethylpiperidino)-*N*-(2,4,6-trimethylborazinyl)alane, **9**, in 85 % yield. It is formed according to Eq. 3.

Reactions of $TiCl_4$ with **1** in various molar ratios from 1 : 1 to 1 : 4 led to yellow and even colorless suspensions containing insoluble LiCl. The amount of

$$\mathrm{Me_3B_3N_3H_2Li + tmp_2AlCl \longrightarrow \underset{\textbf{9}}{tmp_2Al\text{-}N_3H_2B_3Me_3} + LiCl} \quad (3)$$

$$\mathrm{Me_3B_3N_3H_2Li + ClTi[OC_6H_3(\mathit{i}Pr)_2]_3 \longrightarrow \underset{\textbf{10}}{Me_3B_3N_3H_2\text{-}Ti[OC_6H_3(\mathit{i}Pr)_2]_3} + LiCl} \quad (4)$$

Table 2. NMR spectroscopic data of compounds **9** and **10** (δ values in ppm).

Compound	δ^{11}B	δ^{1}H (*o*-Me)	δ^{1}H (*p*-Me)	δ^{1}NH	δ^{27}Al
9	35.8, 37.7	0.74	0.29	4.55	110.0
10	34.0	0.29	0.19	4.38	–

LiCl formed was in most cases > 90 %. However, attempts to obtain well defined products from toluene solutions at −78 °C were unsuccessful. Mass spectrometric analysis showed the presence of the molecular ions for all members of the series $(\mathrm{Me_3B_3N_3H_2})_n\mathrm{TiCl}_{4-n}$ (n = 1, 2, 3, 4), but no pure compound could be isolated from the mixture by extraction or crystallization.

Also an attempt to prepare $\mathrm{Me_2NTi(H_2N_3B_3Me_3)_3}$ from $\mathrm{Me_2NTiCl_3}$ and **1** failed. As we could prepare the borazinyl-bis-(amino)alane **7** by using a monofunctional aluminum species we treated the bulky tris(2,6-diisopropylphenoxo)titanium chloride with **1**. Indeed, this reaction generated the expected borazinyltitanium compound **10** as shown in Eq. 4. Compound **10** was isolated in 80 % yield.

Spectroscopic characterization

Table 2 lists some relevant NMR spectroscopic data of compounds **9** and **10**.

While compound **9** shows two ^{11}B NMR signals for the borazinyl substituent, compound **10** exhibits only a broad signal ($h_{1/2}$ = 450 Hz). However, in both cases, two ^{1}H NMR signals for the BMe groups were detected. Because the intensity of the proton signals for the Me groups in *ortho*-position is twice that of the *para*-position, assignment of the two ^{1}H NMR signals is unequivocal. From this point of view it is surprising that the shift difference between the BMe protons for compound **9** is 0.35 ppm, but only 0.1 ppm for **10**. The ^{27}Al resonance at 110 ppm lays in the high field range for monomeric bis(tetramethylpiperidino)alanes [18].

X-Ray structures

The crystals of the aluminum compound **9** are monoclinic, space group $C2/c$ with $Z = 4$. Therefore, the molecule must show crystallographic symmetry. Fig. 8 depicts the structure of the molecule. The atoms Al1, N1, B2 and C2 are located on a crystallographic twofold axis. The tricoordinated N atoms of the tmp ligand are of the sp^2 type. They are present in a distorted trigonal planar environment. This arrangement is also found for the Al atom which is surrounded by three N atoms which share a plane with the Al atom. The Al–N bonds to the tmp substituents (1.821(2) Å)

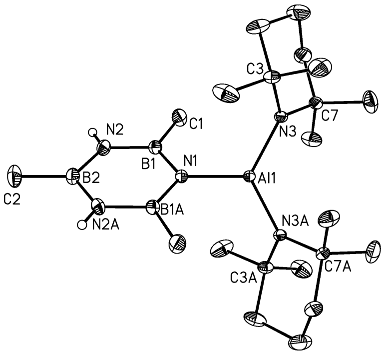


Fig. 8. ORTEP presentation of the molecular structure of compound **9**. Selected bonding parameters (in Å or deg; see also Table 4): Al1-N3 1.821(2), N3-C7 1.496(3), N3-C3 1.499(3), B1-C1 1.577(4), B2-C2 1.581(6); N3–Al1–N3A 124.6(1), N3–Al1–N1 117.69(7), Al1–N3–C3 122.4(2), Al1–N3–C7 121.8(2), C3–N3–C7 115.8(2).

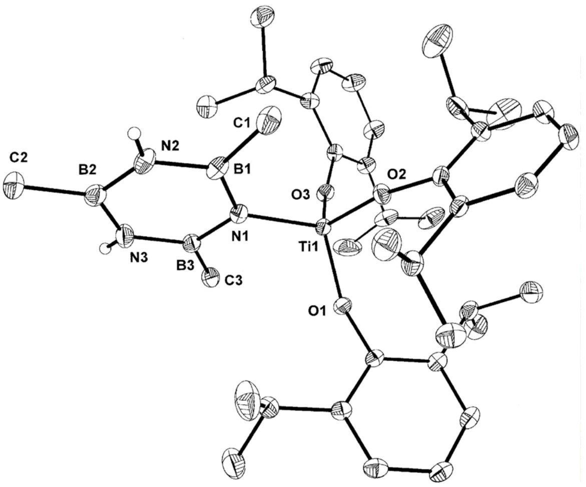


Fig. 9. ORTEP plot of the titanium compound **10**: Selected bond lengths and bond angles (see also Table 4): B1-C1 1.578(6), B2-C2 1.582(6), B3-C3 1.583(6); O1–C4–C9 119.7(3), O1–C4–C5 118.5(3), O2–C16–C17 118.5(3), O2–C16–C21 117.9(4), O3–C28–C29 119.1(3), O3–C28–C33 118.8(3).

Table 3. Selected bond lengths (Å) and bond angles (deg) of compounds **5** and **6**.

	5a	**5b**	**6a**	**6b**	**6c**	**6d**
N1–B1	1.446(3)	1.448(4)	1.443(4)	1.440(4)	1.439(4)	1.439(4)
B1–N2	1.445(3)	1.447(4)	1.432(4)	1.427(4)	1.424(4)	1.429(4)
N2–B2	1.442(3)	1.441(3)	1.419(4)	1.423(4)	1.413(4)	1.428(4)
B2–N3	1.427(4)	1.427(4)	1.418(5)	1.414(4)	1.427(4)	1.426(4)
N3–B3	1.425(4)	1.428(4)	1.431(4)	1.423(4)	1.436(4)	1.430(4)
B3–N1	1.440(3)	1.435(3)	1.441(4)	1.443(4)	1.433(4)	1.437(4)
N1–B4	1.494(4)	1.507(3)	1.481(4)	1.485(4)	1.492(4)	1.484(4)
B4–N4	1.402(3)	1.395(4)	1.409(4)	1.419(4)	1.421(4)	1.421(4)
N4–B5			1.426(4)	1.436(4)	1.427(4)	1.438(4)
B5–N5	1.395(4)	1.399(3)	1.425(5)	1.428(5)	1.417(5)	1.428(5)
N5–B6			1.427(5)	1.428(5)	1.424(5)	1.422(5)
B6–N6			1.426(4)	1.430(5)	1.434(4)	1.439(4)
N6–B4			1.430(49	1.417(4)	1.409(5)	1.417(4)
B4–B5A	1.729(4)	1.727(4)				
B1–N1–B3	119.4(2)	119.7(2)	120.6(2)	119.6(2)	120.7(2)	120.7(2)
B2–N3–B3	124.2(2)	123.6(2)	125.4(3)	125.6(3)	124.1(3)	125.3(3)
N2–B2–N3	117.1(2)	117.2(2)	114.3(3)	1141(3)	114.7(3)	114.4(3)

are somewhat shorter than the Al–N bond to the borazine group (1.844(3) Å). This is probably the effect of a different twisting of these groups. The interplanar angle between the two C_2N units of the tmp substituents is 90.7°. The borazine plane forms an angle of 125.1° with the N1C3C7 plane. These interplanar angles indicate that there is no Al–N π-bonding. The twisting of the tmp groups and the borazine unit is due to steric interactions of the methyl groups. Closest $H\cdots H$ contacts are between 2.3 and 3.1 Å.

The molecular structure of the titanium compound **10** is shown in Fig. 9. This yellow compound crystallizes in the monoclinic system, space group $P2_1/n$, $Z = 4$. Its Ti atom resides in a distorted tetrahedral environment of three oxygen atoms and one nitrogen atom. The O–Ti–O and O–Ti–N bond angles span a range from 104.8(1) to 112.7(1)°. Its Ti–O bond lengths are slightly different, the shortest one is Ti1–O2 (1.760(2) Å), the longest Ti1–O1 (1.801(2) Å), while the Ti1–N1 bond is slightly longer (1.941(3) Å). A look at the C–O distances shows that these bonds are all very short (1.371, 1.372, 1.380(4) Å). This can be understood as the C–O–Ti bond angles are quite open: C4–O1–Ti1 (151.0(2)°), Ti1–O2–C16 (167.7(2)°) and Ti1–O3–C28 (155.4(2)°), *i. e.* the O atoms approach *sp* hybridization.

The introduction of the $(RO)_3Ti$ unit as a substituent at atom N1 of the 2,4,6-trimethylborazine ring affects the symmetry of the B_3N_3 ring significantly. The B–N bonds to atom N1 are rather long (1.460(5) Å). The neighboring bonds, B1-N2 and N3-B3 (1.427(5) and 1.426(5) Å) correspond with B–N bond lengths found in many borazine rings, while the bonds N2-B2 and B2-N3 at 1.419(6) and 1.415(6) are the shortest. This distortion of the ring becomes also apparent by the bond angles. Angle B1–N1–B3 is 118.9(3)°, the N–B–N bond angles on atoms B1 and B3 are 117.3(4) and 117.9(3)°, and at atom B2 even sharper with 113.9(4)°. In contrast, the B1–N2–B2 and the B2–N3–B3 bond angles are 126.1(4) and 126.5(4)°.

The isopropyl groups are bent away from the TiO_3 core, a steric effect to avoid close contacts between their Me groups. In line with this is the observation that the methyl groups Me1 and Me3 of the borazinyl unit are also bent away from the TiO_3 core as shown by the bond angles N1–B1–C1 and N1–B3–C3 (124.6(4) and 123.0(3)°, respectively).

Discussion and Outlook

The value of *N*-lithio-2,4,6-trimethylborazine as a reagent is limited when competing reactions can take place as has been demonstrated for its reactions with organoboron chlorides and bromides. In this case a Me/X exchange occurs besides the substitution. This exchange can, however, be suppressed by using aminoboron chlorides. The formation of compound **2** is achieved because no Me_2N/Me exchange takes place. However, the substitution reaction may take a course different as the expected one as shown for the system **1** and $B_2Cl_2(NMe_2)_2$, where a ten-membered BN ring system, **5**, is generated. This can only be understood if the borazinyl unit is doubly metallated. Because we have so far no evidence that solutions of **1** in ethers or hydrocarbons are unstable with respect to disproportionation into $Me_3B_3N_3H_3$ and $Me_3B_3N_3HLi_2$, the additional deprotonation of **1** must occur during the reaction.

Table 4. Selected bond lengths (Å) and bond angles (deg) for compounds **9** and **10**.

	9	10		9		10
M–N1	1.844(3)	1.941(3)	M–N1–B1	121.0(2)		126.9(2)
N1–B1	1.448(3)	1.460(5)	M1–N1–B3	121.0(2)		113.6(3)
B1–N2	1.441(4)	1.427(5)	B1–N1–B3	117.9(3)	B3=B1a	118.9(3)
N2–B2	1.415(3)	1.419(6)	N1–B1–N2	119.0(3)		117.3(4)
B2–N3		1.415(6)	B1–N2–B2	124.8(3)		126.1(4)
N3–B3		1.426(5)	N2–B2–N3	114.4(4)	N3=N2a	113.9(4)
B3–N1		1.460(5)	B2–N3–B3			125.5(4)
			N3–B3–N1			117.9(4)
			N3–B3–N1			117.9(4)

1 proved to be a useful reagent for the preparation of *B–N*-borazinyl borazines. The introduction of the borazinyl unit into Al and Ti compounds was, so far, only successful with mononuclear monochlorides of Al and Ti.

The introduction of substituents, such as lithium, boron, aluminum, phosphorus, arsenic, antimony or titanium on the trimethylborazine ring leads to a significant distortion of the $Me_3B_3N_3H_2$ unit, and even the ring planarity may be lost. These distortions can readily be seen by comparing the B–N bond lengths of the rings as well as their endocyclic angles [1, 17, 19]. The distance between the metal/non-metal-substituted N atom to its *para* B atom (in most cases N1···B2) may thus be used as a probe for the inductive effect of the substituents at atoms N1 and/or N4. However, as the other B–N bond lengths besides those to N1 are also affected the B2-N1 distance turned out not to be a good reference. Therefore, we restrict our discussion to the N1-B1 and N1–B3 bond lengths and the B1–N1–B3 bond angles. Table 4 lists some of the relevant data.

Table 5 contains preferentially data of unsymmetrically substituted borazines, because the ring B–N bonds in symmetrically substituted borazines differ only marginally. It shows only data for the boron or nitrogen atoms which are unique considering that these borazines either have a mirror plane or a twofold axis, or show no symmetry at all. Standard deviations are usually in the range of 0.003 to 0.005 Å. Bond length differences > 0.01 Å represent significant differences as shown for the substituents $Ti(OR)_3$, $SbCl_2$ or PBr_2. These groups induce a significant bond lengthening, while N-lithio derivatives show N1-B1/3 distances that are significantly shorter than the average B–N bond of borazines (1.43 Å) (Scheme 4, Table 5). This is due to the higher electron density at atom N1 which strengthens BN-π-bonding. It will be of interest to investigate unsymmetrically substituted borazines carrying very strongly electrophilic groups such as CF_3, SO_3CF_3 *etc.* or strongly electropositive groups to further substantiate the present view and to compare their structures with comparable mesityl derivatives.

Experimental Section

All experiments were performed by using the Schlenk techniques with N_2 as the protecting gas.

Solvents were made anhydrous by conventional methods. NMR: Bruker ACP 200 (^1H, ^{11}B, ^{13}C), Jeol GSX 270 (^1H, ^{27}Al). Standards: C_6D_6, $SiMe_4$, 1 M aqueous $Al(NO_3)_3$ solution, $BF_3 \cdot OEt_2$ external. – IR: Nicolet 520 FT; Nujol-Hostaflon mulls. – Siemens P4 diffractometer with area detector and LT2 low temperature device. – MS: Atlas CH 4 (70 eV).

*Reaction of **1** with Ph_2BBr*

To a stirred solution of **1** (570 mg, 2.8 mmol) in toluene (30 mL) was added a solution of Ph_2BBr (620 mg, 2.80 mmol) in toluene (20 mL). A white precipitate was formed rapidly. After stirring over night the solid (LiBr, yield 101 %) was removed by filtration. The solution showed ^{11}B NMR signals at 75.1 (Ph_2BMe, 20 %), 35.3 ($Me_3B_3N_3H_2BPh_2$, 60 %) and 31.3 ppm ($Me_{3-x}Br_xB_3N_3H_3$, 20 %). Attempts to separate the components were unsuccessful.

*Reaction of **1** with $PhBCl_2$*

To a solution of **1** (530 mg, 2.63 mmol) in toluene (30 mL) was added at ambient temperature a solution of $PhBCl_2$ (0.35 mL, 2.63 mmol) in toluene (20 mL). No reaction was observed. Therefore, the mixture was kept at reflux for one day. Then the precipitate (LiCl) was removed by filtration. The filtrate showed ^{11}B NMR signals at 70.1 (MePhBCl, 15 %), 51.6 and 35.6 ($PhClB–N_3H_2B_3Me_3$, 65 %) and 31.4 ppm ($Me_{3-x}Cl_xB_3N_3H_3$, 20 %). – MS: *m/z* = 245 $[Me_3B_3N_3H_2–BPhCl]^+$, 224 $[Me_3B_3N_3H_2–BPhMe]^+$, 143 $[Me_2ClB_3N_3H_3]^+$, 138 $[MePhBCl]^+$.

*Reaction of **1** with tBu_2BCl*

To a stirred solution of $t$$Bu_2BCl$ (520 mg, 2.55 mmol) in hexane (50 mL) was added at ambient temperature a solution of **1** (410 mg, 2.53 mmol) in hexane (10 mL). No reaction was observed at ambient temperature and after keeping the solution at reflux for 3 d.

*Reaction of **1** with 9-chloro-9-borabicyclo [2.2.1]nonane*

To a stirred solution of **1** (280 mg, 1.41 mmol) in toluene/diethyl ether (30/10 mL) was added a solution of 9-Cl-9-BBN (220 mg, 1.41 mmol) in 10 mL of toluene. A white precipitate was formed rapidly. After stirring over night the solid was removed by filtration. The filtrate showed ^{11}B NMR signals at 35.8 (borazine moiety), 72.3 (B atom of 9-BBN) and 88.7 (9-Me-9-BBN). After removal of the solvents a viscous oil remained from which no pure product could be isolated by distillation.

*Reaction of **1** with 2-chloro-1,3-bis(isopropyl)benzo-1,3,2-diazaborolidine*

To a stirred solution of **1** (810 mg, 3.98 mmol) in a mixture of hexane and diethyl ether (30/5 mL) was added a solution of the B-chlorodiazaborolidine (1.12 g, 3.98 mmol) in hexane (10 mL). The solution turned yellow, but no LiCl precipitate was formed. Heating to reflux generated a white precipitate within one h. The mixture was kept boiling for one day. The solid was then removed from the red solution by filtration. ^{11}B NMR signals were observed at δ = 22.8 (borolidine unit), 29.1 (**1**) and 35.4 ppm (trimethylborazine unit). No crystalline material was formed on attempted crystallization from various solvents.

*Bis(dimethylamino)-N-(2,4,6-trimethylborazinyl)borane, **2***

A solution of $(Me_2N)_2BCl$ (530 mg, 3.98 mmol) in hexane (10 mL) was added to a stirred solution of **1** (810 mg, 3.98 mmol) in a mixture of hexane and diethyl ether (30/5 mL). A fine white precipitate was formed. After the addition was complete the suspension was stirred for one day. Then the solid was removed and the volume of the filtrate reduced to 1/4. Storing the solution for one week at −25 °C generated tiny colorless crystals. Recrystallization from toluene, diethyl ether or THF produced no crystals suitable for X-ray structure determination. Yield: 700 mg (80 %). – NMR data (C_6D_6): δ^1H = 0.31 (s, NMe, 6H), 0.34 (s, BMe, 3H), 2.51 (s, NMe, 12H), 4.62 ppm (s, NH, 2H); $\delta^{11}B$ = 31.1, 36.0 ppm (overlapping signals). – IR (nujol, hostaflon, cm^{-1}): ν = 3443 m, 3439 m, 2997 m, 2960 st, 2923 st, 2872 st, 2791 m, 1531 wt, 1466 st, 1456 st, 1409 st, 1388 st, 1361 st, 1261 st, 1228 st, 1145 m, 1128 st, 1101 m, 1066 m, 1020 m, 891 m, 845 w, 804 m, 708 m, 660 w, 402 w, 326 w. – $C_7H_{23}N_5B_4$ (220.51): calcd. C 38.13, H 10.51, N 31.75; found C 39.17, H 10.44, N 30.77.

*1,1′,3,3′-Bis(dimethylamino)diboryl-2,4,6-trimethylborazinyl-2′,4′,6′-trimethylborazine, **5***

To a stirred solution of **1** (1.00 g, 4.93 mmol) in hexane (50 mL) was slowly added at −78 °C a solution of $Cl(Me_2N)B–B(NMe_2)Cl$ (450 mg, 2.46 mmol) in hexane (10 mL). After warming to r. t. and stirring for 2 h a white precipitate had formed. The suspension was kept at reflux over night. Then the solid was removed by filtration. The solution was concentrated to 1/4 of its original volume *in vacuo*. The remaining solution was stored at −25 °C. Single crystals separated within a few days. Yield: 510 mg (45 %), m. p. 142 °C. – NMR (in C_6D_6): δ^1H = 0.15 (s, *p*-BMe, 3H), 0.39 (s, *o*-BMe, 6H), 4.54 (s, NH, 1H), 2.64, 2.80 ppm (s, NMe, 12H); $\delta^{13}C$ = 36.53 ppm (NMe); $\delta^{11}B$ = 35.9, 41.3 ppm (br). – IR (nujol, hostaflon, cm^{-1}): ν = 3440 st, 3000 m, 2955 st, 2922 st, 2872 st, 2856 st, 2793 m, 1474 st, 1408 st, 1346 st, 1325 st, 1298 st, 1273 m, 1183 m, 1145 st, 1112 m, 1093 m, 1075 m, 1063 m, 1046 m, 1016 m, 954 w, 942 w, 891 st, 838 w, 755 w, 709 st, 634 w, 588 w, 580 w, 569 w, 399 w. – $C_{14}H_{44}N_{10}B_{10}$(460.68): calcd. C 36.50, H 9.63, N 30.40; found C 36.12, H 9.81, N 29.96.

*2,4,6-2′,4′-Pentamethyl-B–N-diborazinyl, **6***

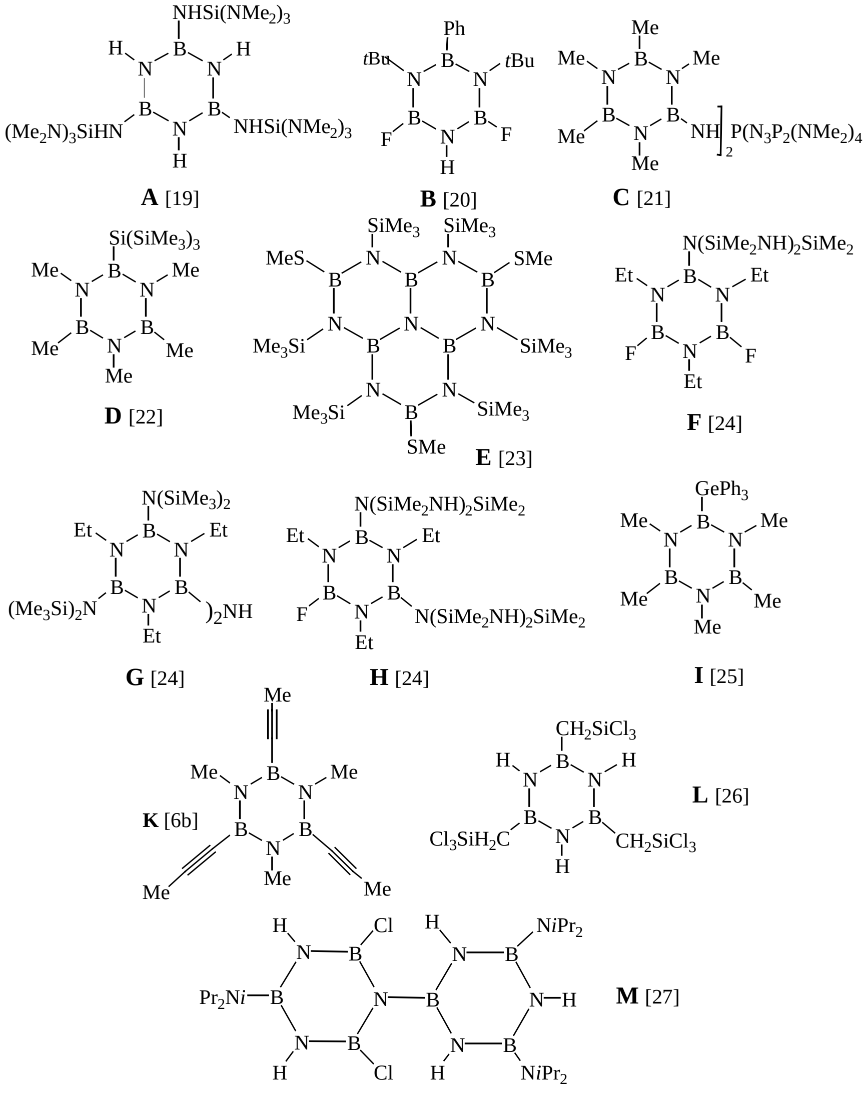
2,4,6-Trimethylborazine (715 mg, 8.16 mmol) dissolved in diethyl ether (20 mL) was treated with LiBu (5.5 mL of a 1.6 M LiBu solution in hexane) at −78 °C, and the solution kept at reflux for 5 h. The turbid solution was dropped into a solution of 2-bromo-4,6-dimethylborazine (1.17 g, 8.1 mmol) in hexane (50 mL) cooled to −78 °C. The mixture was then kept for 5 h at reflux. After removing the resulting solid by filtration the filtrate was stored at −20 °C. This led to the formation of colorless single crystals of **6**. Yield: 835 mg (45 %), m. p. 57 – 58 °C. – NMR (in C_6D_6): δ^1H = 0.20 (s, BMe, 6H), 0.33 (s, BMe, 3H), 0.35 (s, BMe, 6H), 4.09 (s, NH, 3H), 4.55 ppm (s, NH, 2H); $\delta^{13}C$ = 1.54 (Me), 2.95 ppm (Me). – IR (nujol, hostaflon, cm^{-1}): ν = 3442 st, 3422 st, 2950 m, 2908 m, 2866 m, 2397 w, 1806 w, 1670 w, 1647 w, 1586 w, 1482 st, 1459 st, 1300 st, 1208 st, 1198 m, 1183 m, 1670 w, 1647 w, 1586 w, 1483 st, 1459 st, 1333 st, 1314 st, 1300 st, 1208 st, 1198 m, 1183 m, 1156 m, 1127 m, 1120 m, 1080 m, 892 st, 826 w, 806 w, 734 st, 721 st, 703 m, 684 m, 671 m, 578 m, 534 m, 506 m, 460 w, 441 w. – MS: *m/z* (%) = 229 (80) $[M]^+$, 214 (100) $[M–Me]^+$, 199 (90) $[M–2 Me]^+$, 184 (15) $[M–3 Me]^+$, 116 (45) $[MeB_3N_3BNH]^+$, 91 (75) $[MeB_3N_3H]^+$, 82 (10) $[Me_2B_2N_2H_2]^+$, 66 (60) $[Me_2B_2N_2H]^+$, 41 (30) $[MeBNH]^+$.

*2,4,6, 4′,6′-Pentamethyl-1′,3′,5′-triisopropyl-B,N-diborazinyl, **7***

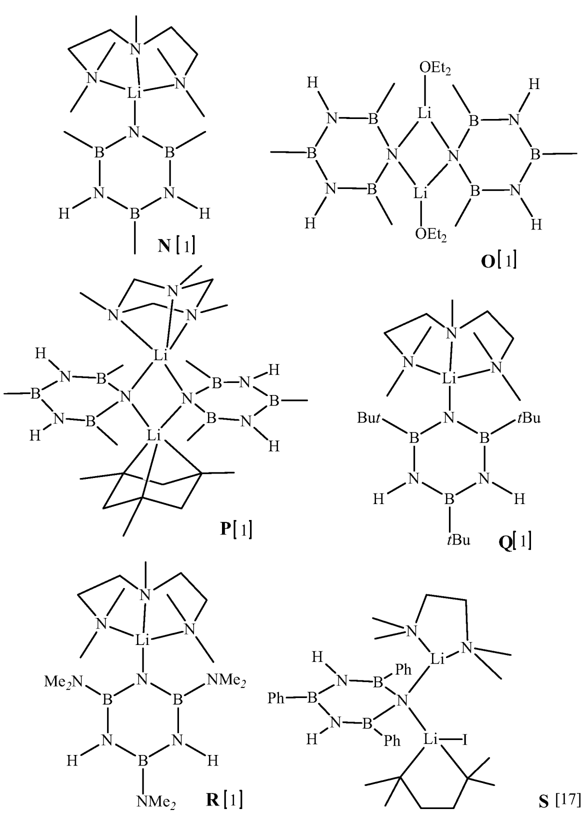
In analogy to **6** a solution of **1** (740 mg, 3.56 mmol) in hexane/diethyl ether (230/10 mL) was dropped into a solution of 2-bromo-4,6-dimethyl-2,3,5-triisopropylborazine (1.14 g, 3.46 mmol) in hexane (10 mL). At r. t. no reaction was observed. After heating for 3 days at reflux, LiBr precipitated and was removed by filtration from the suspension. Crystals separated from the concentrated solution (reduced to 1/4 of its original volume) while it was stored at 5 °C. Yield: 880 mg (70 %), m. p. 173 °C. The crystals turned out to be twins. Crystallization from $CHCl_3$, CH_2Cl_2, or diethyl ether gave no crystals suitable for X-ray crystallography. – NMR (C_6D_6): δ^1H = 0.31 (s, BMe, 3H), 0.38 (s, BMe, 6H), 4.53 (s, NH, 2H), 0.76 (s, BMe, 6H), 1.28 (d, CMe, 12H), 1.35 (d, CMe, 6H), 3.94 (sept., CH, 2H), 4.06 ppm (sept., CH, 1H); $\delta^{13}C$ = 23.5, 23.9 (C*Me*), 46.4,

Table 5. The influence of substituents X on the lengths of the B–N or N–B bonds (Å) and on the respective NBN or BNB bond angles (deg). For the numbering of the compounds see Scheme 4.

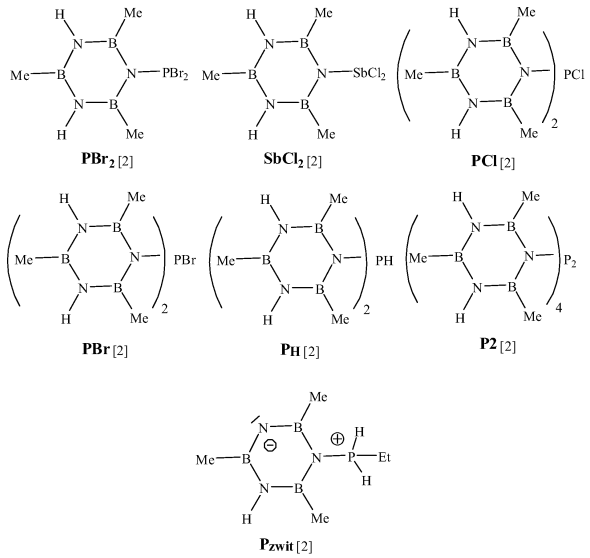
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
B1–N1	1.437	1.449	1.557	1.440	1.435	1.471	1.444	1.439	1.439
B1–N3	1.441	1.449	1.423	1.432	1.450	1.450	1.451	1.440	1.435
N1–B1–N3	115.8	117.1	103.6	115.6	115.64	116.7	115.9	117.0	119.3
	K	**L**	**M**	**N**	**O**	**P**	**Q**	**R**	**S**
N1–B1	1.419	1.424	1.424	1.439	1.417	1.414	1.422	1.411	1.421
N3–B1	1.419	1.423	1.423	1.437	1.415	1.420	1.411	1.413	1.425
N1–B1–N3	117.4	117.65	117.7	124.7	117.4	117.2	118.3	117.1	117.4
	5	**6**	**9**	**10**	**PBr2**	**SbCl2**	**PCl**	**PBr**	**PH**
N1–B1	1.446	1.441	1.448	1.460	1.482	1.470	1.474	1.475	1.452
N1–B3	1.440	1.441	1.448	1.462	1.482	1.465	1.481	1.469	1.464
B1–N1–B3	119.4	120.6	117.1	118.9	119.8	120.9	119.1	120.5	120.4
	PHzwit	**P2**							
N1–B1	1.462	1.44							
N1–B2	1.439	1.49							
B1–N1–B3	121.3	118.0							



Scheme 4. Borazines cited in Table 5.



N [1] **O** [1] **P** [1] **Q** [1] **R** [1] **S** [17]



PBr_2 [2] **$SbCl_2$** [2] **PCl** [2] **PBr** [2] **PH** [2] **P2** [2] **Pzwit** [2]

Scheme 4 (continued). Borazines cited in Table 5.

48.7 ppm (CMe_2); $\delta^{11}B$ = 35.8, 38.1 ppm. – IR (nujol, hostaflon, cm^{-1}): ν = 3475 w, 3437 w, 3026 w, 3004 m, 2961 st, 2875 st, 1561 w, 1470 st, 1440 st, 1419 st, 1360 st, 1334 st, 1319 st, 1302 st, 1254 st, 1242 st, 1205 st, 1184 st, 1161 st, 1135 st, 1120 st, 1025 w, 999 m, 984 m, 962 w, 896 w, 885 m, 855 w, 844 w, 808 w, 764 w. – MS: *m/z* (%) = 355 (10) $[M]^+$, 340 (75) $[M–Me]^+$, 325 (25) $[M–2 Me]^+$, 233 (55) $[Me_2B_3N_3iPr_2]^+$, 218 (20) $[MeB_3N_3iPr_3]^+$, 203 (15) $[B_3N_3iPr_3]^+$, 190 (12) $[Me_2B_3N_3iPr_2]^+$, 147 (15) $[Me_2B_3N_3iPr]^+$, 122 (55) $[Me_3B_3N_3H_2]^+$. – $C_{14}H_{38}N_6B_6$ (355.36): calcd. C 47.32, H 10.78, N 23.65; found C 46.12, H 11.01, N 23.52.

2,4,6,2′,4′,6′,3′,5′-Octamethyl-N,B-diborazinyl, 8

A solution of $BrMe_2B_3N_3Me_3$ (960 mg, 4.19 mmol) in hexane (20 mL) was added to a solution of **1** (850 mg, 4.19 mmol), dissolved in hexane/diethyl ether (20/10 mL). No reaction was observed at ambient temperature. After keeping the mixture at reflux for several hours, a solid had formed which was removed by filtration. 3/4 of the solvents was removed from the filtrate *in vacuo*. The soilid that separated corresponded to a yield of 60 % (680 mg). However, no single crystals could be grown from solutions in CH_2Cl_2, diethyl ether or toluene. – NMR (in C_6D_6): δ^1H = 0.26 (s, BMe, 3H), 0.27 (s, BMe, 6H), 0.49 (s, BMe, 6H), 2.74 (s, NMe, 6H), 2.82 (s, NMe, 3H), 4.60 ppm (s, br, NH, 2 H); $\delta^{11}B$ = 38.1, 35.8 ppm. – IR (nujol, hostaflon, cm^{-1}): ν = 3455 w, 3434 w, 3004 m, 2965 st, 2895 m, 1566 w, 1471 st, 1439 st, 1417 st, 1371 st, 1346 st, 1336 st, 1319 st, 1302 st, 1254 st, 1242 st, 1203 st, 1184 st, 1162 st, 1135 st, 1115 st, 1025 w, 999 m, 984 m, 886 w, 855 w, 844 w, 808 w, 746 w, 704 w, 675 m, 650 w. – MS: *m/z* (%) = 271 (75) $[M]^+$, 256 (100) $[M–Me]^+$, 241 (20) $[M–2 Me]^+$, 226 (20) $[M–3 Me]^+$, 150 (65) $[Me_2B_2N_3M_3]^+$, 121 (45) $[Me_3B_3N_3H_2]^+$.

2,4,6-Trimethylborazinyl-bis(tetramethylpiperidino)alane, 9

To a stirred solution of **1** (0.876 g, 4.29 mmol) in toluene (50 mL) were added 23 mL of a 0.2 M solution of tmp_2AlCl (4.6 mmol). A solid separated after about 15 min. The suspension was then heated to reflux over night and the LiCl precipitate was removed by filtration. The filtrate was reduced in volume to about 1/3. Storing the solution at −25 °C provided colorless crystals of **9**, m. p. 293 °C. Yield: 1.56 g (85 %). – NMR (in C_6D_6): δ^1H = 0.29 (s, BMe, 3H), 0.74 (s, BMe, 6H), 1.39 (t, β-CH_2, 8H), 1.44 (s, Me, 24H), 1.50 (quint, tmp-γ-CH_2), 4.55 ppm (s, NH, 2H); $\delta^{13}C$ = 18.8 (tmp-γ-CH_2), 34.2 (tmp-Me), 39.5 (tmp-β-CH_2), 52.5 ppm (tmp-α-CH_2); $\delta^{27}Al$ = 110 ppm ($h_{1/2}$ = 60 Hz). – IR (nujol, hostaflon, cm^{-1}): ν = 3443 m, 3414 m, 2960 st, 2923 st, 2857 st, 1473 st, 1404 st, 1378 st, 1362 st, 1345 m, 1333 m, 1306 st, 1299 st, 1235 st, 1201 m, 1177 m, 1131 st, 1065 m, 1007 w, 884 m, 977 m, 942 m, 926 w, 897 w, 887 w, 865 w, 798 w, 754 w, 715 m, 654 w, 506 w, 528 w, 500 w. – MS: *m/z* (%) = 429 (25) $[M]^+$, 414 (45) $[M–Me]^+$, 289 (85) $[M–tmp]^+$, 274 (100) $[M–Me–tmp]^+$, 166 (30) $[tmpAl]^+$, 122 (15) $[Me_3B_3N_3H_2]^+$. – $C_{21}H_{47}N_5B_3Al$ (429.05): calcd. C 58.79, H 11.04, N 16.92; found C 56.67, H 10.65, N 16.64.

Table 6. Crystallographic data and data related to structure solution and refinement.

Compound	**5**	**6**	**9**	**10**
Chem. formula	$C_{14}H_{44}B_{10}N_{10}$	$C_{10}H_{20}B_6N_6$	$C_{21}H_{48}AlB_3N_5$	$C_{39}H_{62}B_3N_3O_3Ti$
Form. wght.	460.69	229.13	430.05	702.25
Size [mm]	0.15 × 0.15 × 0.3	0.1 × 0.2 × 0.3	0.10 × 0.20 × 0.2	0.30 × 0.20 × 0.20
Cryst. system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/n$
a, Å	7.8592(6)	7.929(3)	16.5611(5)	11.8290(8)
b, Å	11.9674(9)	16.315(4)	12.9165(4)	28.392(2)
c, Å	16.255(1)	22.668(8)	12.2131(3)	12.6987(8)
α, deg	107.278(2)	84.12(1)	90	90
β, deg	92.094(1)	89.81(1)	94.49	97.653(1)
γ, deg	101.607(1)	78.94(1)	90	90
V, Å^3	1422.4(2)	2862(2)	2604.5(1)	4226.8(5)
Z	2	8	4	4
ρ(calc), Mg m^{-3}	1.076	1.063	1.097	1.102
μ, mm^{-1}	0.063	0.064	0.095	0.239
F(000), e	496	976	948	1512
Index range	$-9 \le h \le 9$ $-15 \le k \le 13$ $-19 \le l \le 22$	$-7 \le h \le 9$ $-15 \le k \le 18$ $-15 \le l \le 26$	$-19 \le h \le 19$ $-15 \le k \le 15$ $-13 \le l \le 12$	$-13 \le h \le 13$ $-31 \le k \le 23$ $-14 \le l \le 14$
2θ, deg	58.12	49.42	49.42	46.52
Temp, K	193(2)	193(2)	193(2)	193(2)
Refl. collect.	8314	6823	6151	18659
Refl. unique	4490	6764	1921	5636
Refl. obs. (4σ)	3147	5510	1729	3529
R_{int}	0.025	0.031	0.021	0.079
No. variables	307	670	149	465
Weighting scheme x/y[a]	0.0603/0.5746	0.017/2.976	0.0948/5.5606	0.0879/1.2253
GOOF	1.124	1.307	1.050	1.012
Final R (4σ)	0.056	0.078	0.062	0.057
Final $wR2$	0.137	0.154	0.168	0.117
$\Delta\rho_{\max}$, e Å^{-3}	0.29	0.35	0.92	0.24

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

*Tris(2,6-diisopropyl-phenoxo)-N-(2,4,6-trimethylborazinyl) titanium, **10***

1 (100 mg, 0.49 mmol) was dissolved in diethyl ether (5 mL). To this solution was added dropwise and with stirring a solution of $(2,6\text{-}i\mathrm{Pr_2C_6H_3O})_3\mathrm{TiCl}$ (300 mg, 0.49 mmol) dissolved in diethyl ether (10 mL). A white precipitate formed rapidly. After stirring for additional 2 h the solid was removed by filtration from the yellow solution. Most of the diethyl ether was then evaporated *in vacuo*, Yellow crystals formed within 3 months from the viscous residue. Yield: 270 mg (80 %); m. p. > 250 °C. – NMR: (in C_6D_6): δ^1H = 0.19 (s, BMe, 3H), 0.29 (s, BMe, 6H), 4.38 (s, NH, 2H), 1.13 (d, CH*Me*$_2$, 36H), 3.69 (sept., C*H*Me$_2$, 6H), 6.87 – 7.15 ppm (m, H arom, 9H); δ^{11}B = 34.0 ppm. – IR (cm^{-1}): ν = 3436 m, 3420 m, 3057 m, 3032 w, 3013 w, 2961 m, 2927 st, 2886 m, 2868 st, 1587 w, 1550 w, 1486 st, 1473 st, 1434 st, 1361 m, 1324 st, 1305 w, 1295 w, 1281 m, 1254 st, 1194 st, 1168 m, 1145 w, 1139 w, 1102 m, 1072 w, 1058 w, 1044 m, 1023 w, 912 st, 880 m, 795 m, 750 m, 721 st, 617 m, 593 w, 574 w, 536 w, 424 m, 388 m, 355 m. – $C_{39}H_{62}O_3N_3B_3Ti$ (701.25): calcd. C 66.80, H 8.91, N 5.99; found C 66.53, H 8.85, N 5.68.

X-Ray structure analysis

Single crystals were placed in precooled perfluoroether oil at −25 °C and a specimen selected under the microscope. It was transferred onto a glass fibre mounted on the goniometer head. The goniometer head was then transferred to the goniometer which was cooled with a stream of gaseous dinitrogen to −80 °C. Five sets of data were collected on 25 frames, each at different settings with ω changed by 0.4°. These reflections were used to calculate the dimensions of the unit cell using the program SMART [28]. Data were collected in the hemisphere mode and reduced with the program SAINT [29]. The programs SHELXTL [30] or SHELXL-97 [31] were used for structure solution and refinement. The molecular structures are depicted with displacement ellipsoids at the 25 % probability level.

CCDC 657260 (**6**), 657261 (**9**), 657262 (**5**) and 657263 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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