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

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The N-lithioborazine LiH2N3B3Me3, 1, reacts with organoboron halides not only to the respective borazinyl organylboranes but also by Me/halogen exchange. (Me2N)2B-H2N3B3Me3 was obtained from 1 and (Me2N)2BCl. A new ten-membered B6N4 ring system, 5, results on treatment of Cl(Me2N)B–B(NMe2)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 YH2N3B3Me3 the B–N bonds of the YNB2 units are elongated, e.g. for Y = PBr2 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 Phenoxyde, 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 trimethylborazine substituted phosphines, 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 Me3B3N3H2Li with organoboron halides

Organoboron halides such as Ph2BBr or PhBCl2 do not react with the borazine Me3B3N3H3 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 11BN M R. 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.

\[ n \text{Me}_3\text{B}_3\text{N}_3\text{H}_2\text{Li} + R_{1n}\text{BX}_n \rightarrow R_{1n}\text{B}(\text{H}_2\text{N}_3\text{B}_3\text{Me}_3)_n + n\text{LiX} \]

Similarly, reaction of 1 with BX3 (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 11B NMR or mass spectrometry, but we have been unable to isolate pure products either by distillation or by crystallization.
The 1:1 reaction of 1 with Ph₂BBr in toluene led to Ph₂BMe (20%), (Me₃B₃N₃H₂)BPh₂ (60%) and Me₃Br, B₃N₃H₃ (20%). A 1:1 mixture of 1 and PhBCl₂ 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%), (Me₃B₃N₃H₂)B(Cl)Ph (20%), Me₃B₃N₃H₃ (45%), and Me₃Cl,B₃N₃H₃ (20%). iBu₂BCl 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 Me₃B₃N₃H₂Li with dimethylaminochloroboranes and B-haloborazines

In order to prevent the R/X exchange we studied some reactions of dimethylaminochloroboranes 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/NMe₂ exchange was noted for the 1:1 reaction of 1 with (Me₃N)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(Me₃N)₂B–B(NMe₂)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 dimethylaminoborane derivatives 2 and 5 as well as those of the diborazines 6, 7 and 8.

The ¹¹B chemical shift for the B(NMe₂) group of 2 is 31.1 ppm. This is 3.4 ppm at lower field compared with B(NMe₂)₃ and 1.3 ppm compared with PhB(NMe₂)₂ [4]. Although one expects two ¹¹B NMR signals for the B atoms of the borazinyl group only a single broad signal with a maximum at δ¹¹B = 36.1 ppm is recorded for 5 at ambient temperature showing a small low field shift in comparison with 1 (δ¹¹B = 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(NMe₂)₂ group, indicating free rotation about the respective B–N bonds. This was also observed for PhB(NMe₂)₂ [4].

\[
\text{(Me₃N)₂BCl + LiH₂N₃B₃Me₃} \rightarrow \text{(Me₃N)₂B-H₂N₃B₃Me₃ + LiCl}
\]
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 NMe₂ groups. The borazinyl groups are represented by an ¹¹B 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 ¹¹B NMR signals are observed within the range from 34 – 38.5 ppm [5]. This indicates that bonds of the borazinyl nitrogen atoms to the B₂ units have little π-character in contrast to bonds of the Me₂N 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 NMe₂ unit non-equivalent.

The pentamethyldiborazine 6 should show four ¹¹B 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).

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ^{11}B</th>
<th>δ^{1}H p-Me</th>
<th>δ^{1}H o-BMe</th>
<th>δ^{1}H m-BMe</th>
<th>δ^{1}H NMe</th>
<th>δ^{1}H NH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>36.1 Borazine</td>
<td>0.34</td>
<td>0.31</td>
<td>2.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>35.8 Borazine</td>
<td>0.39</td>
<td>0.15</td>
<td>2.64, 2.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>30.2, 34.3</td>
<td>0.33 3H</td>
<td>0.35 6H</td>
<td>0.20</td>
<td>4.33 (1H)</td>
<td>4.09 (2H)</td>
</tr>
<tr>
<td>7</td>
<td>35.8, 38.1</td>
<td>0.31 pme</td>
<td>1.35CMe₂</td>
<td>0.38, 1.28,</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>35.8, 38.1</td>
<td>0.27 (6H)</td>
<td>4.06 CH</td>
<td>3.94 sept.</td>
<td>4.60</td>
<td></td>
</tr>
</tbody>
</table>

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

There are three ¹H NMR signals for the NH groups in a 2:1:2 ratio as well as for the protons of the Me groups (δ¹H = 0.20, 0.32, 0.34 in a 2:1:2 ratio). Although ¹³C 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 ¹³C signals were observed at 1.54 and 2.95 ppm.

The B-pentamethyl-N-trisopropyl-diborazine 7 exhibits only two ¹¹B NMR signals instead of the expected four. We attribute the signal at 35.8 ppm to the Me₂B₃N₃H₂ borazine ring, and the signal at 38.1 ppm to the Me₂B₃N₃(iPr)₃ group. The two non-equivalent Me groups of the Me₂B₃N₃H₂ unit are represented by two ¹H NMR signals at 0.31 and 0.38 ppm (ratio 1:2), while the proton resonance for the BMe groups in the Me₂B₃N₃(iPr)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 ¹¹B 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 Me₂B₃N₃Me₃ unit (δ¹H = 0.48 ppm) as compared with the BMe protons of the Me₂B₃N₃H₂ group (δ¹H = 0.26 and 0.27 ppm).

The NH protons are represented by two signals at δ¹H = 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.

X-Ray structures of compounds 5 and 6

The new ten-membered BN heterocycle 5 crystallizes in the triclinic system, space group P1, 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-
The puckered ten-membered \( \text{B}_6\text{N}_4 \) ring of compound \( 5a \).

Fig. 4. Side view on molecule \( 5a \): Interplanar angles (deg): \( \text{N}1\text{B}1\text{N}2\text{B}2 8.2^\circ, \text{N}1\text{B}1\text{N}3\text{B}1\text{B}3\text{N}3 4.3^\circ, \text{N}4\text{B}4\text{N}1\text{B}5\text{N}5\text{N}2\text{A} 120.8^\circ \).

Characteristic is the shape of the ten-membered ring built from two \( \text{NBN} \) 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 \( \text{B}–\text{N} \) 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 \( \text{B} \)-triorganoborazines [6]. The \( \text{B}–\text{B} \) bond lengths of 1.731(4) Å, are shorter than in \( \text{B}_2\text{(piperidine)}_4 \) (\( d_{\text{B}–\text{B}} = 1.750(8) \) 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 \( \text{N} \) atoms also. Therefore, conditions for \( \text{BN}–\pi \)-bonding seem to be excellent. However, the \( \text{B}–\text{N} \) bond lengths are not as short as expected for \( \text{B}–\text{N} \) 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 \( \text{B}–\text{N} \) bonds from the \( \text{B}_2 \) 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): \( \text{B}1–\text{C}1 1.571(5), \text{B}2–\text{C}2 1.571(5), \text{B}3–\text{C}3 1.575(5), \text{B}5–\text{C}5 1.566(5), \text{B}6–\text{C}6 1.573(6) \) (see also Table 3); interplanar angle \( \text{N}1\text{B}1\text{N}2\text{B}2\text{N}3\text{B}3/\text{B}4\text{N}4\text{B}5\text{N}5\text{B}6\text{N}6: 69.5^\circ \).

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

Bond angles at atom \( \text{B}1 \) are rather different. The angle \( \text{N}3–\text{B}1–\text{B}2 \) is 114.6(2)° while those of \( \text{N}1–\text{B}1–\text{B}2 \) and \( \text{N}3–\text{B}1–\text{N}1 \) are 125.7(2)° and 119.7(2)°, respectively. This may be due to the higher BN double bond contribution of the \( \text{B}1–\text{N}1 \) 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 \( \text{BNMe}_2 \) units are twisted against each other by 68°. Similar interplanar angles between \( \text{Me}_2\text{N} \) groups at adjacent boron atoms are also observed in dimethylaminotri- and tetraboranes [11]. The interplanar angle between the \( \text{Me}_2\text{N}(4) \) and \( \text{Me}_2\text{N}((\text{N}5\text{A}) \) groups is 63.9°, and the angle be-
between 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) Å. 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 been 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′-diborazine, 6, we determined its structure by X-ray crystallography. The crystals are triclinic, space group P1. 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 to 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 from the respective borazines and alkyl lithium compounds [1,17]. By replacing LiR by triorganoaluminum compounds, borazinyl-substituted organoalanes might become available. However, Me3B3N3H3 did not react with (AlMe3)2 under reflux conditions in toluene. Moreover, [(Me2N)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)chboroalane, tmp2AlCl. 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 TiCl4 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
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 \((\text{Me}_3\text{B}_3\text{N}_3\text{H}_2)_n\text{TiCl}_{4−n}\) \((n = 1, 2, 3, 4)\), but no pure compound could be isolated from the mixture by extraction or crystallization. Also an attempt to prepare \(\text{Me}_2\text{NTi}(\text{H}_2\text{N}_3\text{B}_3\text{Me}_3)_3\) from \(\text{Me}_2\text{NTiCl}_3\) 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ(^{11}\text{B})</th>
<th>δ(^{1\text{H}}) (o-Me)</th>
<th>δ(^{1\text{H}}) (p-Me)</th>
<th>δ(^{\text{NH}})</th>
<th>δ(^{27}\text{Al})</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>35.8, 37.7</td>
<td>0.74</td>
<td>0.29</td>
<td>4.55</td>
<td>110.0</td>
</tr>
<tr>
<td>10</td>
<td>34.0</td>
<td>0.29</td>
<td>0.19</td>
<td>4.38</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 8. ORTEP presentation of the molecular structure of compound 9. Selected bonding parameters (in Å or deg; see also Table 4): A11–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–A11–N3A 124.6(1), N3–A11–N1 117.69(7), A11–N3–C3 122.4(2), A11–N3–C7 121.8(2), C3–N3–C7 115.8(2).

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 A11, 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)
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 C2N 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···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 P2₁/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 B₃N₃ 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 N2–N3 at 1.419(6) and 1.415(6) Å 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 TiO₃ 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 TiO₃ 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 amino-boron chlorides. The formation of compound 2 is achieved because no Me₂N/Me exchange takes place. However, the substitution reaction may take a course different as the expected one as shown for the system 1 and B₂Cl₂(NMe₂)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 Me₂B₃N₃H₂ and Me₂B₃N₃HLi₂, the additional deprotonation of 1 must occur during the reaction.
strongly electrophilic groups such as CF₃, SO₂CF₂ 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 N₂ as the protecting gas.

Solvents were made anhydrous by conventional methods.
NMR: Bruker ACP 200 (¹H, ¹¹B, ¹³C), Jeol GSX 270 (¹H, 
⁲⁷Al). Standards: C₆D₆, SiMe₄, 1 M aqueous Al(NO₃)₃
solution, BF₃·OEt₂ 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 I with Ph₂Br

To a stirred solution of I (570 mg, 2.8 mmol) in toluene (30 mL) was added a solution of Ph₂Br
(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 ¹¹B NMR signals at 75.1 (Ph₂BMe,
20 %), 51.6 and 35.6 (PhClB–N 3H2B₃Me₃, 6 %) and
31.3 ppm (Me₃–Br,B₃N₃H₂, 20 %). Attempts to separate the
components were unsuccessful.

Reaction of I with PhBCl₂

To a solution of I (530 mg, 2.63 mmol) in toluene (30 mL) was added at ambient temperature a solution of PhBCl₂
(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 filtra-
tion. The filtrate showed ¹¹B NMR signals at 75.1 (Ph₂BMe,
20 %), 51.6 and 35.6 (PhClB–N 3H2B₃Me₃, 65 %) and
31.3 ppm (Me₃–Br,B₃N₃H₂, 20 %). Attempts to separate the
components were unsuccessful.

Reaction of I with tBu₂BCl

To a stirred solution of tBu₂BCl (520 mg, 2.55 mmol) in
hexane (50 mL) was added at ambient temperature a solution of I (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 I with 9-chloro-9-borabicyclo[2.2.1]nonane

To a stirred solution of I (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
¹¹B NMR signals at 35.8 (borazine moiety), 72.3 (B atom

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

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<td>B1–N3</td>
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</table>

I 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 ti-
tanium on the trimethylborazine ring leads to a sig-
nificant distortion of the Me₃B₃N₃H₂ 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 unsymmet-
rically substituted borazines, because the ring B–N
bonds in symmetrically substituted borazines differ
only marginally. It shows only data for the boron or ni-
trogen 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
depicted for the substituents Ti(OR)₃, SbCl₂ or PBr₂.
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
lengths of borazines (1.43 Å) (Scheme 4, Table 5). This is due to
the higher electron density at atom N1 which strengthen-
s BN-π-bonding. It will be of interest to investigate
unsymmetrically substituted borazines carrying very

1

2

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9

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Table 5. Selected bond lengths (Å) and bond angles (deg) for compounds 9 and 10.

<table>
<thead>
<tr>
<th></th>
<th>9</th>
<th>10</th>
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<tbody>
<tr>
<td>M–N1</td>
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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 (1.14 g, 3.98 mmol) in hexane (10 mL). The solution turned yellow, but no LiCl precipitate was formed. Heating to reflux regenerated a white precipitate within one h. The solid was then removed from the red solution by filtration. Recrystallization from toluene, diethyl ether or THF produced no crystals. The suspension was kept at reflux (10 mL). After warming to r. t. and stirring for 2 h a white precipitate was formed. The remaining solution was stored 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 (C₆D₆): δH = 0.31 (s, NMe, 6H), 0.34 (s, BMe, 3H), 2.51 (s, NMe, 12H), 4.62 ppm (s, NH, 2H); δ¹¹B = 31.1, 36.0 ppm (overlapping signals). − IR (nujol, hostaflon, cm⁻¹): ν = 3443 m, 3439 m, 2997 m, 2960 st, 2923 st, 2927 st, 2791 m, 1531 wt, 1467 w, 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. − C₂H₅N₂B₂ (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)diethyl-2,4,6-trimethylborazinyl-2',4'-pentamethylborazine, 2

A solution of (Me₂N)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. Heating to reflux generated a white precipitate within one h. The solid was then removed from the red solution by filtration. Recrystallization from toluene, diethyl ether or THF produced no crystals. The suspension was kept at reflux (10 mL). After warming to r. t. and stirring for 2 h a 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 ¼. 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: 835 mg (45 %), m. p. 57–58 °C. − NMR (in C₆D₆): δH = 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); δ¹¹B = 1.54 (Me), 2.95 ppm (Me). − IR (nujol, hostaflon, cm⁻¹): ν = 3442 st, 3422 st, 2925 m, 2908 m, 2866 m, 2397 w, 1806 w, 1670 w, 1647 w, 1586 w, 1549 st, 1494 st, 1345 m, 1314 st, 1300 st, 1208 st, 1198 m, 1183 m, 1670 w, 1586 w, 1485 st, 1459 m, 1347 m, 1337 m, 1314 st, 1300 st, 1208 st, 1198 m, 1183 m, 1156 m, 1127 m, 1120 m, 1080 m, 892 st, 826 w, 806 m, 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–3 Me⁺], 199 (90) [M–2 Me⁺], 184 (15) [M–3 Me⁺], 116 (45) [MeB₂(N₂)⁺], 91 (75) [MeB₂(N₂)⁺], 82 (10) [Me₂B₂(N₂)⁺], 66 (60) [Me₂B₂(N₂)⁺].

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. A 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: 325 mg (45 %), m. p. 78–80 °C. − NMR (in C₆D₆): δH = 0.15 (s, BMe, 3H), 0.39 (s, BMe, 6H), 4.54 (s, NH, 1H), 2.64, 2.80 ppm (s, NMe, 12H); δ¹¹B = 36.53 ppm (NMe); δ¹¹B = 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. − C₂H₅N₂B₂ (460.68): calcd. C 36.50, H 9.63, N 29.96; found C 36.12, H 9.81, N 29.96.

2,4,6-2',4'-Pentamethyl-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-trisopropylborazine (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 ¼ 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 CHCl₃, CH₂Cl₂, or diethyl ether gave no crystals suitable for X-ray crystallography. − NMR (in C₆D₆): δH = 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); δ¹¹B = 23.5, 23.9 (CMe), 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.

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Scheme 4. Borazines cited in Table 5.
48.7 ppm (CMe₂); δ¹¹B = 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, 886 w, 855 w, 854 w, 808 w, 746 w, 704 w, 675 m, 650 w. – MS: m/z (%) = 355 (10) [M⁺], 340 (75) [M–Me]⁺, 325 (25) [M–2 Me]⁺, 233 (55) [Me₂B₃N₃(iPr)₂]⁺, 218 (20) [Me₂B₃N₃(iPr)₃]⁺, 203 (15) [B₃N₃(iPr)₃]⁺, 190 (12) [Me₂B₃N₃(iPr)₂]⁺, 147 (15) [Me₂B₃N₃(iPr)]⁺, 122 (55) [Me₂B₃N₃H₂]⁺, 110, 108, 104, 102, 99, 98, 96, 94, 92, 90, 88, 86, 84, 82, 80, 78, 76, 74, 72, 70, 68, 66, 64, 62, 60, 58, 56, 54, 52, 50, 48, 46, 44, 42, 40, 38, 36, 34, 32, 30, 28, 26, 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4, 2, 1.

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 tmp₂AlCl (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 1/3. Storing the solution at −25 °C provided colorless crystals of 9, m.p. 293 °C. Yield: 1.56 g (85 %). – NMR (in C₆D₆): δ¹H = 0.29 (s, BMe, 3H), 0.74 (s, BMe, 6H), 1.39 (t, β-CH₂, 8H), 1.44 (s, Me, 24H), 1.50 (quint, tmp-γ-CH₂), 4.55 ppm (s, NH, 2H); δ¹³C = 18.8 (tmp-γ-CH₂), 34.2 (tmp-Me), 39.5 (tmp-β-CH₂), 52.5 ppm (tmp-α-CH₂); δ²⁷Al = 110 ppm (h₁/₂ = 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 w, 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) [Me₂B₃N₃H₂]⁺, 110, 108, 106, 104, 102, 99, 98, 96, 94, 92, 90, 88, 86, 84, 82, 80, 78, 76, 74, 72, 70, 68, 66, 64, 62, 60, 58, 56, 54, 52, 50, 48, 46, 44, 42, 40, 38, 36, 34, 32, 30, 28, 26, 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4, 2, 1.

2,4,6-Trimehtyborazinyl-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 tmp₂AlCl (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 1/3. Storing the solution at −25 °C provided colorless crystals of 9, m.p. 293 °C. Yield: 1.56 g (85 %). – NMR (in C₆D₆): δ¹H = 0.29 (s, BMe, 3H), 0.74 (s, BMe, 6H), 1.39 (t, β-CH₂, 8H), 1.44 (s, Me, 24H), 1.50 (quint, tmp-γ-CH₂), 4.55 ppm (s, NH, 2H); δ¹³C = 18.8 (tmp-γ-CH₂), 34.2 (tmp-Me), 39.5 (tmp-β-CH₂), 52.5 ppm (tmp-α-CH₂); δ²⁷Al = 110 ppm (h₁/₂ = 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 w, 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) [Me₂B₃N₃H₂]⁺, 110, 108, 106, 104, 102, 99, 98, 96, 94, 92, 90, 88, 86, 84, 82, 80, 78, 76, 74, 72, 70, 68, 66, 64, 62, 60, 58, 56, 54, 52, 50, 48, 46, 44, 42, 40, 38, 36, 34, 32, 30, 28, 26, 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4, 2, 1.
B. Gemünd et al. \textit{N-(2,4,6-Trimethylborazinyl)-substituted Boron, Aluminum and Titanium Compounds} 35

Tris(2,6-diisopropyl-phenoxy)-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-\textit{Pr2C6H3O})3TiCl (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 \textit{in vacuo}. Then crystals formed within 3 months from the viscous residue.

Yield: 270 mg (80%); m.p. > 250 °C. – NMR: (in C6D6): \(\delta^1 H = 0.19 \text{ (s, BMe, 3H),} 2.99 \text{ (s, BMe, 6H),} 4.38 \text{ (s, NH, 2H),} 1.13 \text{ (d, CMe}_2\text{, 36H),} 3.69 \text{ (sept., CMe}_2\text{, 6H),} 6.87–7.15 \text{ ppm (m, H arom, 9H);} \delta^{11}B = 34.0 \text{ ppm. – IR (cm}^{-1})): \nu = 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, 1186 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. – C38H62B10N10O3Ti (701.25): calcd. C 66.80, H 8.91, N 5.99; found C 66.53, H 8.85, N 5.68.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Compound} & \textbf{5} & \textbf{6} & \textbf{9} & \textbf{10} \\
\hline
\textbf{Chem. formula} & C10H20B6N6 & C21H25AlB3N5 & C9H21B3N3O3Ti & C21H25AlB3N5Ti \\
\hline
\textbf{Form. wght.} & 56.91 & 91.12 & 0.75 & 1.05 \\
\hline
\textbf{Size [mm]} & 0.15 \times 0.15 \times 0.3 & 0.1 \times 0.2 \times 0.3 & 0.10 \times 0.20 \times 0.2 & 0.30 \times 0.20 \times 0.2 \\
\hline
\textbf{Cryst. system} & triclinic & triclinic & monoclinic & monoclinic \\
\hline
\textbf{Space group} & P1 & P1 & C2/c & P21/n \\
\hline
\textbf{a, Å} & 7.8592(6) & 7.929(3) & 16.5611(5) & 11.8290(8) \\
\textbf{b, Å} & 11.9674(9) & 16.3154(4) & 12.9165(4) & 28.392(2) \\
\textbf{c, Å} & 16.2535(1) & 22.6688(8) & 12.2131(3) & 12.6987(8) \\
\hline
\textbf{\(\sigma\), deg} & 107.278(2) & 84.12(1) & 90 & 90 \\
\textbf{\(\beta\), deg} & 92.094(1) & 89.81(1) & 94.49 & 97.653(1) \\
\textbf{\(\gamma\), deg} & 101.607(1) & 78.94(1) & 90 & 90 \\
\hline
\textbf{V, Å\(^3\)} & 1422.4(2) & 2862(2) & 2604.5(1) & 4226.8(5) \\
\hline
\textbf{Z} & 2 & 8 & 4 & 4 \\
\hline
\textbf{\(\rho\)(calc), Mg m}^{-3} & 1.076 & 1.063 & 1.097 & 1.102 \\
\hline
\textbf{\(\mu\), mm}^{-1} & 0.063 & 0.064 & 0.095 & 0.239 \\
\hline
\textbf{\(F(000), e\)} & 496 & 976 & 948 & 1512 \\
\hline
\textbf{Index range} & \(-9 \leq h \leq 9\) & \(-7 \leq k \leq 9\) & \(-19 \leq h \leq 19\) & \(-13 \leq h \leq 13\) \\
\hline
\textbf{\(\Delta \rho\), deg} & 58.12 & 49.42 & 49.42 & 46.52 \\
\hline
\textbf{Temp, K} & 193(2) & 193(2) & 193(2) & 193(2) \\
\hline
\textbf{Refl. collect.} & 6823 & 4940 & 4940 & 4940 \\
\hline
\textbf{Refl. unique} & 6764 & 4940 & 4940 & 4940 \\
\hline
\textbf{Refl. obs. (4\(\sigma\))} & 3147 & 5510 & 1729 & 3529 \\
\hline
\textbf{R_{int}} & 0.025 & 0.031 & 0.021 & 0.079 \\
\hline
\textbf{No. variables} & 307 & 670 & 149 & 465 \\
\hline
\textbf{Weighting scheme x/\(\sigma^a\))} & 0.0603/0.5746 & 0.0172/2.976 & 0.0948/5.5606 & 0.0879/1.2253 \\
\hline
\textbf{GOOF} & 1.124 & 1.307 & 1.050 & 1.012 \\
\hline
\textbf{Final R (4\(\sigma\))} & 0.056 & 0.078 & 0.062 & 0.057 \\
\hline
\textbf{Final w/R2} & 0.137 & 0.154 & 0.168 & 0.117 \\
\hline
\textbf{\(\Delta\rho_{max}\), e Å\(^{-3}\)} & 0.29 & 0.35 & 0.92 & 0.24 \\
\hline
\end{tabular}
\caption{Crystallographic data and data related to structure solution and refinement.}
\end{table}

\textbf{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 \(\phi\) changed by 0.4°. These reflections were used to calculate the dimensions of the unit cell using the program \textit{SMART} [28]. Data were collected in the hemisphere mode and reduced with the program \textit{SAINT} [29]. The programs \textit{SHELXTL} [30] or \textit{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), 657265 (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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[16] We will report on a larger set of boryl-substituted borazines shortly [9].