

Synthesis and Structures of Two New Types of Boronium Salts^[‡]Ulrike Braun^[a] and Heinrich Nöth^{*[a]}**Keywords:** Boronium Cations / Transamination / X-ray structures

Transamination of di(pyrid-2-yl)amine (**1**) with B(NMe₂)₃ leads to the isomeric heterocyclic bis(dimethylamino)boryl compound **4** and not to bis(dimethylamino)di(pyrid-2-yl)aminoborane (**2**). B(NMe₂)₃ reacts with aniline (1:2 ratio) to yield a 1:1 mixture of B(NHPh)₃ and (Me₂N)₂BNHPh. Transamination of this mixture with **1** yields the anilindimethylamino analogue of **4** (compound **7**). Compound **4** reacts with CHCl₃ to generate the boronium salt **5** by the abstraction of HCl

from CHCl₃ and addition of HCl to one of the dimethylamino groups. Compound **5** crystallizes with 4 molecules of CHCl₃. Compound **4** is attacked by AlCl₃ in toluene to give a mixture of unidentified products from which the tetrachloroaluminate of a new type of spirocyclic diboronium cation, **8**, was isolated and characterized by X-ray crystallography. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The cationic chemistry of boron started in 1955.^[1] At that time, there was a lively discussion on the structure of the so-called diammoniate of diborane B₂H₆·2NH₃. Two structures were favored, [NH₄][H₃B–NH₂–BH₃]^[1] and [H₂B(NH₃)₂][BH₄]^[2] The classical papers by Parry and Shore^[2–7] revealed that the latter structure is correct. Since then, many cations with tri- and di-coordinated boron atoms have been characterized in addition to those with tetra-coordinated boron atoms. A recent review summarizes the present status in this field.^[8] The interest in gaseous cations, such as BF₂⁺ or BMe₂⁺, as reagents has also grown.^[9] In spite of these advances, the cationic chemistry of boron, over the last decade, is still a somewhat neglected part of boron chemistry.

Here we present a study that was actually not directed towards the synthesis of new boron cations, but that resulted from reactions aimed at the preparation of aminoboranes suitable for *N*-lithiation.^[10]

Transamination of B(NMe₂)₃ with Di(pyrid-2-yl)amine and Formation of a New Type of Heterocyclic Boronium Salt

N-lithiation of tris(pyridylamino)borane leads to an interesting cluster structure.^[10] For this reason, the unknown bis(phenylamino)di(pyrid-2-yl)aminoborane (**3**) appeared as a potential candidate for *N*-lithiation. We tried to achieve its synthesis in a two step reaction as shown in

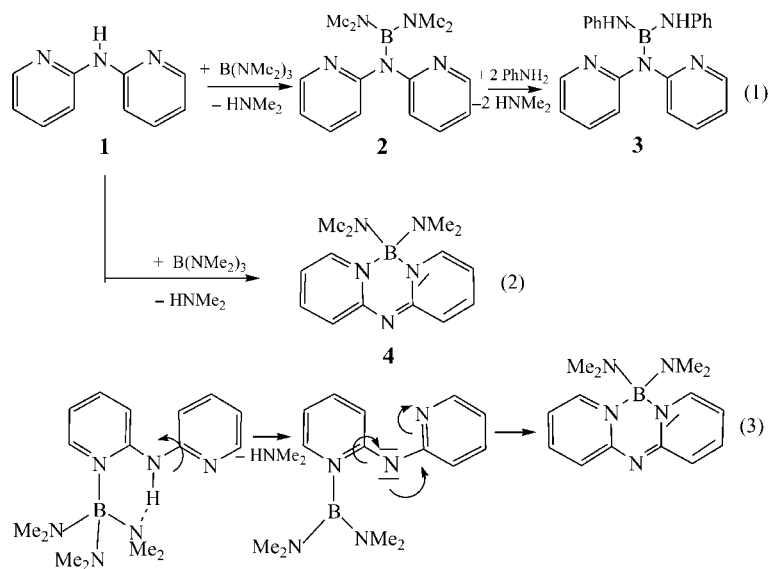
Equation (1). The transamination of di(pyrid-2-yl)amine (**1**) with tris(dimethylamino)borane was expected to yield bis(dimethylamino)di(pyrid-2-yl)aminoborane (**2**), which on further transamination with aniline should have given the target compound **3**.

However, the ¹¹B NMR spectrum definitely excludes the formation of **2**. The solution obtained shows intense yellow fluorescence and a sharp ¹¹B NMR signal at 5.0 ppm in its spectrum, which is typical for a tetra-coordinated boron atom. The elemental analysis corresponds with the composition expected for **2**. However, in the ¹H NMR spectrum, no signal for an NH proton is observed, and all NMR spectroscopic data are in accord with the structure of **4**, as shown in Equation (2). The position of attack of the boron atom of B(NMe₂)₃ is at one of the pyridine N atoms of **1** and not at the NH nitrogen atom, as shown in Equation (3). Elimination of Me₂NH is expected to be favored because of the formation of an N–H···N hydrogen bridge bond. Rotation about the N–C bond of the non-coordinated pyridyl unit allows the formation of a six-membered ring.

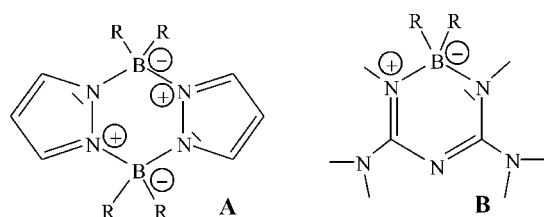
The hydrogen atoms on the *o*-positions of the pyridine rings of **4** give rise to an ¹H NMR signal at 7.64 ppm, and the carbon atoms at the *o*-positions to a ¹³C NMR signal at 138.4 ppm. These nuclei are better shielded than those in **1** (8.23 and 147.6 ppm). This can be compared with the corresponding ¹H and ¹³C NMR signals for pyridine (8.59 and 149.8 ppm) and pyridine *N*-oxide (8.36 and 138.5 ppm), which carries, like **4**, a formal positive charge at the N atom.^[11] In addition, the ¹H resonance for the dimethylamino groups of **4** are found at slightly higher field (δ = 2.36 ppm) relative to those of B(NMe₂)₃ (δ = 2.48 ppm). The coordination mode in compound **4** is similar to that in pyrazaboles **A**^[12] or in the boron biguanidine complexes **B**.^[13] The structures of pyrazaboles have been extensively investigated,^[14–16] although no species is yet known in

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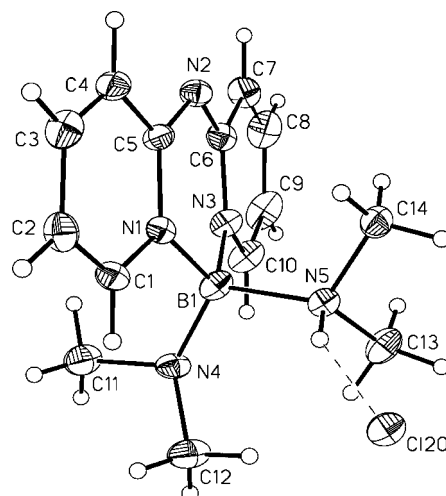


which the boron atoms of the pyrazaboles carry two exocyclic amino groups at the boron atoms; however, CNDO calculations on a *N,N'*-dimethylethylenediamino species have been performed.^[17]



In order to prove the structure of compound **4**, we attempted to obtain single crystals of this compound; but, only polycrystalline material separated from various solvents. Single crystals, however, did form from a 1:1 mixture of chloroform and pentane at -78°C . The X-ray structure determination of a monoclinic crystal (space group $P2_1/n$, $Z = 4$) shows that the investigated species is not compound **4**, but rather its hydrochloride. The crystals have the composition $\text{C}_{14}\text{H}_{20}\text{BN}_5\cdot\text{HCl}\cdot 4\text{CHCl}_3$. The molecular structure of **4·HCl** (**5**) is depicted in Figure 1.

Its $\text{N}_3\text{C}_2\text{B}$ ring adopts a tub-shape conformation. Atoms C6, C5, and N1 lay almost in a plane (interplanar angle $\text{C6-C5-N1/N1-N3-C6} = 1.1^\circ$). The N3-B1-N1 plane forms an interplanar angle of 18.3° with the C6-C5-N3-N1 plane and 7.7° with the C6-N2-C5 plane. The N2 atom sits only $0.095\text{ \AA}$ above the N3-B1-N1 plane. Therefore, it is incorporated into the π -system of the heterocycle. This is also shown by the presence of short C–N bonds. The annulated six-membered rings are bent backwards from the central ring. Their interplanar angles with the C6-C5-N3-N1 plane is 13.4° . The two endocyclic B–N bonds, B1-N1 and B1-N3 , have the same lengths, while the two exocyclic B–N bonds are different [$\text{B1-N4} = 1.453(9)\text{ \AA}$ and $\text{B1-N5} = 1.636(8)\text{ \AA}$]. The N4 atom has an almost planar environment ($\Sigma = 354.4^\circ$), in contrast to the tetra-coordinated N5 atom with its significantly longer B–N bond. Bond angles



most of the positive charge is located at the tetra-coordinated N5 atom. Its H1 atom forms a hydrogen bond to the chloride ion as shown by the bond lengths of 0.98 Å for N5–H1 and 2.307 Å for H1...Cl20. This H...Cl distance is shorter than the NH...Cl bond in 2,2,4,4-tetramethylpiperidinium chloride [2.232(5) Å].^[18] The N5–H1–Cl2 bond angle is 154.0°.

Figure 2 represents a stereoplot of the unit cell of compound **5** that shows that the chloroform molecules fill the spaces between the atoms of the boronium salt. The H atom of the chloroform molecules interact either with the chloride ions or with *p*-N atoms of the heterocycles.

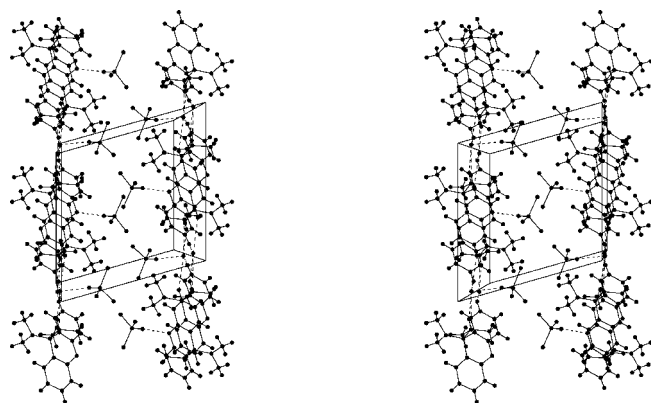
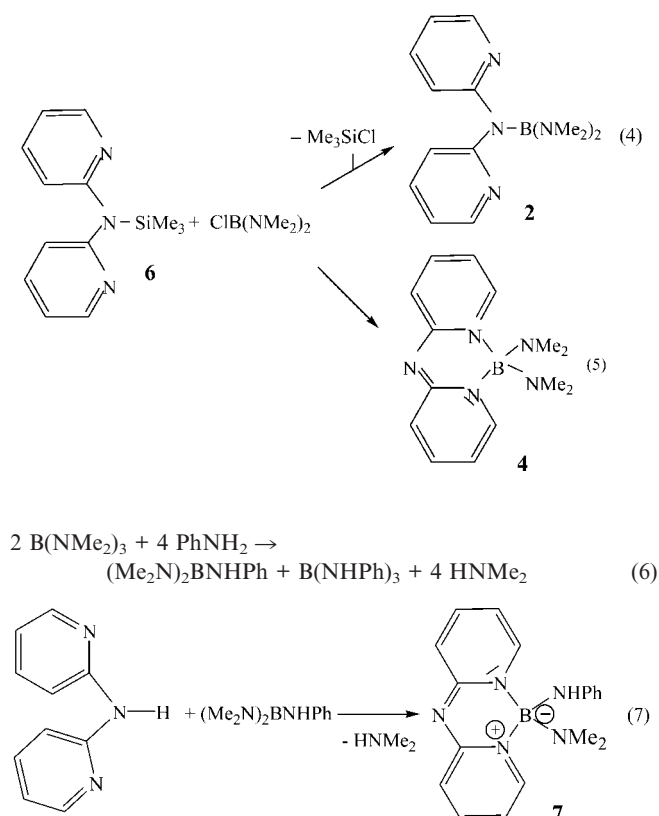


Figure 2. Stereoplot of the unit cell of compound **5**·(CHCl₃)₄. View down the *b* axis. The chloroform molecules are “lined” up between two strands of **5** molecules.

It is obvious that HCl is necessary to form **5**, and chloroform is the HCl source. It is known that strong bases can be protonated by CHCl₃, with subsequent removal of HCl to form dichlorocarbene as an intermediate. Compound **4** possesses a high proton affinity as was already demonstrated for the ready synthesis of the related 2,2'-dipyridylbis(dimethylamino)boronium salt.^[19]

A possible alternative synthesis for compound **2** is shown in Equation (4). The components, **6** and ClB(NMe₂)₂, react readily with the formation of chlorotrimethylsilane, but again the product is **4** [Equation (5)]. This shows that the chlorobis(dimethylamino)borane attacks also at a pyridine nitrogen atom of **1**. Another possible route is to first synthesize dianilinodimethylaminoborane followed by transamination with **1**. However, treatment of B(NMe₂)₃ with 2 mol of aniline resulted in a 1:1 mixture of B(NHPh)₃ and (Me₂N)₂BNHPh as shown in Equation (6). Two ¹¹B NMR signals at δ = 24.9 and 23.6 ppm of equal intensity are observed in the solution. The latter signal is assigned to B(NHPh)₃^[10] and the former to bis(dimethylamino)organylaminoborane.^[20] Treatment of the mixture of B(NHPh)₃ and (Me₂N)₂BNHPh with **1** produced a solution with resonances in the ¹¹B NMR spectrum at 23.7 and 2.0 ppm (*h*_{1/2} = 83 Hz). Obviously, B(NHPh)₃ remained untouched, while (Me₂N)₂BNHPh reacted with the di(pyrid-2-yl)amine with elimination of Me₂NH and formation of **7** [see Equa-

tion (7)]. B(NHPh)₃ precipitated from the concentrated solution, and it was possible to isolate compound **7** from the red-brown fluorescent filtrate. Compound **7** was characterized by NMR spectroscopy and elemental analysis.



The Formation of a Spirocyclic Diboronium Cation as Its Tetrachloroaluminate

While the HCl adduct of **4** is a boronium salt with a tetra-coordinated boron atom, compound **4** may also be the source for a boronium cation with a tri-coordinated boron atom. The first boronium salts with tri-coordinated boron atoms were reported in 1962.^[21] In this case, the pyridine adduct of Ph₂BCl was treated with AgClO₄ to generate (pyBPh₂)ClO₄. It was also reported later^[22] that the abstraction of a chloride ion from Ph₂BCl by AlCl₃ would produce the di-coordinated boron cation BPh₂⁺. But because all these reactions were performed in solvents like nitromethane or ethylmethyl ketone, it is more likely that adducts with the solvents were formed. None of these cations could be isolated as salts. Their existence was, therefore, disputed.^[22,23] Today, sterically and electronically stabilized cations of boron are readily accessible.^[9] In particular, suitable anion acceptors have been widely used for hydride or halide abstraction from base adducts L·BY₂X (X = H, Hal; Y = organyl, OR, NR₂).^[24–26] Compound **4** could form a cation with a tri-coordinated boron atom because this cation should be stabilized by electron delocalization as shown in formula **C**.

To generate this cation we treated **4** with AlCl_3 in a 1:1 ratio in toluene. No reaction occurs at ambient temperature, but after keeping the mixture at reflux, a yellow-green precipitate and a yellow solution forms. The ^{11}B NMR spectrum of the solution shows an intense signal at 26.5 ppm and a very weak multiplet around 0.7 ppm. The intense signal indicates the presence of a triaminoborane^[27] or a triaminoborane cation.^[28] The ^{27}Al NMR spectrum of the solution shows signals at 68.0 and 31.9 ppm (broad) as well as a group of signals with peaks at 80.4, 92.2, and 104.4 ppm. The sharp signal at 104.4 ppm arises from AlCl_4^- .^[29] The others are indicative of a mixture of $\text{AlCl}_{4-n}(\text{NMe}_2)_n^-$ anions. Signals in the range 80–108 ppm have been observed for these anions.^[30,31] Most likely, the first anion formed is $\text{AlCl}_3\text{NMe}_2^-$, followed by redistribution of the substituents, a well-known phenomenon in the chemistry of mixed tetrahaloaluminate anions.^[32]

The yellow solid that remains after evaporation of toluene from the filtrate was almost insoluble in all common solvents, and this was also observed for the precipitate. Only CH_2Cl_2 proved to be a suitable solvent. The spectrum of the dissolved part of the precipitate shows a ^{27}Al NMR signal at $\delta = 106.4$ ppm ($h_{1/2} = 25$ Hz), which is typical for AlCl_4^- , and a broad weak signal around 26.8 ppm, which is due to a hexacoordinate Al species. ^{11}B NMR signals were observed at 1.1 and 0.36 ppm and also at 26.5 ppm. These data show that the reaction between **4** and AlCl_3 is rather complex.

Fortunately, yellow single crystals could be obtained from a CH_2Cl_2 solution at -20°C . They are monoclinic and crystallize in the space group $P2_1/c$ with $Z = 4$. The X-ray structure determination shows the presence of a new kind of spiroheterocyclic molecular cation **8** containing two tetra-coordinated boron atoms and one tri-coordinated boron atom. It crystallizes as a bis(tetrachloroaluminate) with the composition $[\mathbf{8}][\text{AlCl}_4]_2(\text{CH}_2\text{Cl}_2)_2$ (Figure 3 shows the atoms in the asymmetric unit).

The central part of the molecule is a naphthalene-like $\text{B}_3\text{N}_5\text{C}_2$ ring with formal positive charges that reside preferably on the four pyridine nitrogen atoms N1, N3, N9 and N11, while the boron atoms B1 and B2 are formally negatively charged. The ring B–N bond lengths in the tricyclic rings are comparatively long and range from 1.542(7) to 1.569(7) Å. On the other hand, the B1–N5 and B2–N7 bonds are shorter (1.472 and 1.467 Å). The bonds B1–N4 and B2–N8 [1.610(8) and 1.603(8) Å] to the di(pyrid-2-yl)-amino group are much longer despite the fact that these two N atoms are tri-coordinate. By taking the B–N bond lengths as a criterion, these two bonds have to be considered as coordinative B–N bonds.

A tub-shaped conformation is observed for the central ring of the two heteroanthracene groups. The C5–N1–N3 plane is almost coplanar with the N3–C6–C5 plane (1.3°), and the interplanar angle of the C5–C6–N1–N3 plane to the N3–B1–N1 plane is 19.9° , but 29.6° to the C6–N3–C10 plane. Analogous interplanar angles between C25–C26–N9–N11 and N9–B2–N11 or C25–N11–C21 are 11.7° and 5.7° , respectively. N2–C6–C7–C8 and N10–C25–C24–C23 tor-

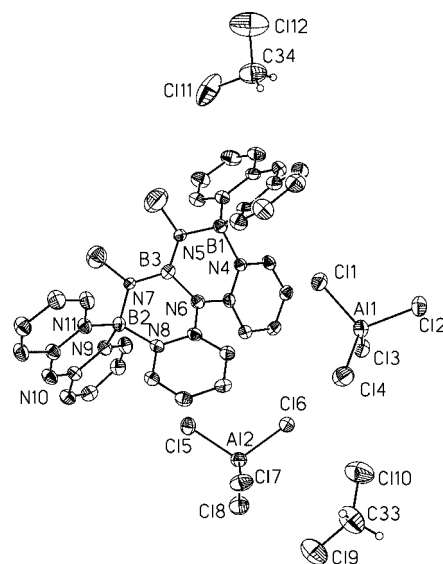
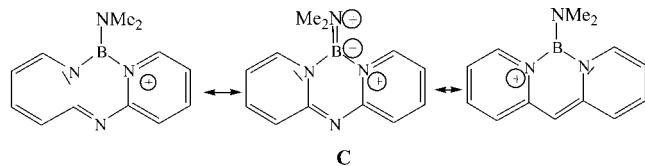


Figure 3. ORTEP plot of the contents of the asymmetric unit in the cell of $\mathbf{8}(\text{AlCl}_4)_2 \cdot 2\text{CH}_2\text{Cl}_2$. Hydrogen atoms of cation **8** are omitted for clarity. Selected bond lengths [Å]: N1–B1 1.561(7), N3–B1 1.543(8), N4–B1 1.610(8), N8–B2 1.603(8), N5–B3 1.382(7), N5–B1 1.472(7), N6–B3 1.455(7), N7–B3 1.401(7), N5–C31 1.495(9). Selected bond angles [$^\circ$]: N1–B1–N5 111.4(5), N5–B1–N4 114.3(5), N3–B1–N1 106.8(5), N5–B1–N4 108.1(5), N3–B1–N4 108.9(4), N1–B1–N4 107.0(4), N5–B3–N7 126.7(5), N7–B3–N6 116.5(5), N4–C15–N6 115.8(5), N8–C16–C6 116.3(5), C15–N6–B3 120.5(4), C15–N6–C16 118.7(4), C16–N6–B3 120.7(4), C11–N3–B1 120.3(4), C11–N3–C15 117.5(4), C15–N4–B1 122.1(4).

sion angles are 3.5° and 1.1° . The central B3 atom is present in a trigonal-planar environment ($\Sigma = 360.1^\circ$) with a wide N5–B3–N7 bond angle of $126.7(5)^\circ$. This open angle is a steric consequence of the interaction between the two NMe groups, because the B3–N5–C31 plane is twisted against the B3–N5–B1 plane by 27.8° but is almost coplanar with the B3–N7–C32 plane. The B3–N5 and B3–N7 bond lengths are 1.382(7) and 1.401(7) Å. This is in the typical range for B–N π -bonding. A significantly longer B–N bond with less double bond character is observed for B3–N6 with a length of 1.455(7) Å. Although the C15–N6–C16 bond angle is $118.7(4)^\circ$, this plane is twisted against the N5–B3–N7 plane by 31.3° . The respective N_2B planes N5–B1–N4 and N7–B2–N8 stand almost perpendicular to the C31–N5–B3 and B3–N7–C32 planes (94.3° and 97.3° , respectively), while the N7–B2–N8 plane forms an interplanar angle with the N5–B1–N4 plane of only 3.5° . The semichair conformation of the central two six-membered rings is typical of what is usually observed.

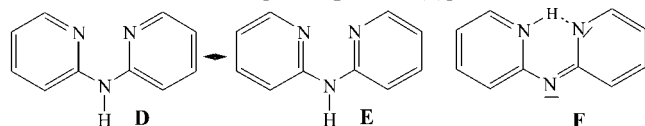
In spite of the NMR spectroscopic data, the route from **4** to **8** remains speculative because not all of the ^{27}Al NMR signals could be unequivocally assigned. For instance, the signal at 68 ppm might result from $\text{AlCl}_3 \cdot 2\text{NMe}_3$ (71 ppm),^[30] but it seems unlikely that AlCl_3 would first form $\text{AlCl}_3 \cdot \text{NMe}_3$ during its attack on **4**, which then must attack a second molecule of **4** in order to form $\text{AlCl}_3 \cdot 2\text{NMe}_3$. It is more likely that AlCl_3 removes a Me_2N group by BN cleavage to form a cation of type **C**, which then attacks another molecule of **4**. Too little information

can be extracted from the NMR spectroscopic data to suggest a route from **4** to **8**. However, it should be noted that **8** contains a di(pyrid-2-yl)amino group. This suggests that isomer **2** is generated during the process.

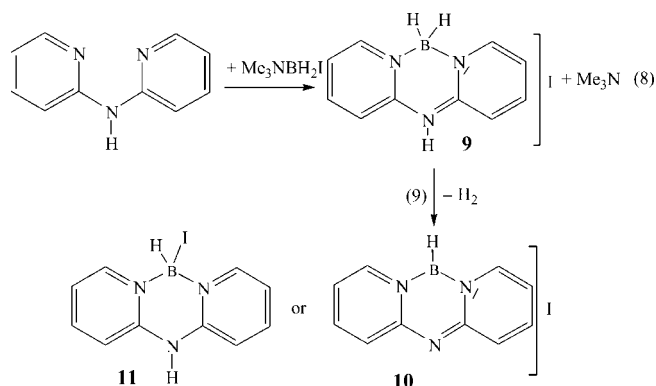


Discussion

Transamination of 2-aminopyridine with $B(NMe_2)_3$ led to 2-aminopyridine(dimethylamino)boranes $(pyNH)_nB(NMe_2)_{3-n}$ ^[10] amongst which $B(HNpy)_3$ is most readily isolated. In contrast, di(pyrid-2-yl)amine (**1**) reacts in a different manner. This is due to the different basicity of the NH_2/NH groups as well as to the sterically more shielded NH group. In addition, the driving force for the formation of **4** is not only a consequence of steric factors, but also because of greater electron delocalization, as shown by the formulae **D/E**. In principle, **1** might exist in two forms, **D/E** and **F**. The structure of the isomer **D/E** is said to remain intact on reaction with $Me_3N \cdot BH_2I$, which generates the boronium iodide **9** [see Equation (8)].



Since the proton of **1** can be readily removed in strong basic solutions,^[33] it is surprising that compound **9** is stable. One would expect that this compound would readily lose hydrogen gas, as shown in Equation (9), with formation of a tri-coordinate borenium salt **10** or the intramolecular iodoborane dipyr-2-yl complex **11**.



Although we have only studied the transamination of $B(NMe_2)_3$ with **1** in a 1:1 ratio, it would be interesting to also perform the transamination reaction with 2 and 3 mol of this amine in order to see whether the 1:3 transamination product $B(Npy'_2)_3$ contains structural elements in analogy to those in **4** or whether it is a "normal" triaminoborane $B(Npy'_2)_3$. In this context, one should note that cation **8** contains a di(pyrid-2-yl)amino group, an indication that isomers **2** and **4** may interconvert.

The transamination of $B(NMe_2)_3$ with aniline leads to a mixture of $(Me_2N)_2BNHPh$ and $B(NHPh)_3$. This is in accord with earlier observations,^[34] although it has been reported that $(Me_2N)_2BNHPh$ and $Me_2NB(NHPh)_2$ can be prepared by transamination.^[35] We did not find any ^{11}B NMR evidence for the formation of the latter compound.

The removal of a Me_2N anion from compound **4** by $AlCl_3$ leads finally to the heterocyclic boronium dication in the salt $[8][AlCl_4]_2$ (Figure 4). As far as we know, this is the first example of a diboronium cation and the second example^[25] in which a cationic boron species has been generated from a triaminoborane. Particularly surprising is the fact that, in the course of this reaction, the dimethylamino groups are transformed by loss of a methyl group into NMe

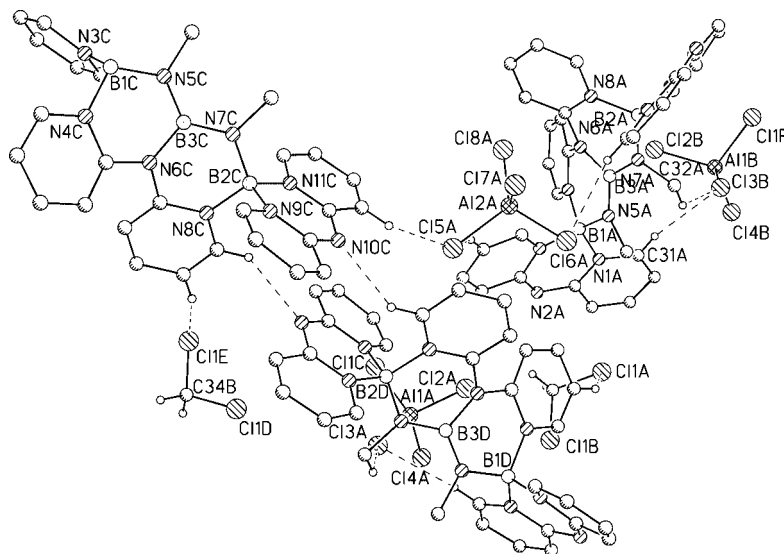


Figure 4. Section representing three cations of **8**, three $AlCl_4$ anions, and two CH_2Cl_2 molecules. $Cl \cdots HC$ distances are in the order of 2.7(0.2) Å, and CHN distances in the order of 2.1 Å. Only relevant H atoms are shown.

units. As far as we know, this N–C bond cleavage is rather unusual, although this step must occur in order to reasonably explain the formation of **8**. Obviously, aminoboron halides are better suited^[8] to generate borenium cations than triaminoborane systems. However, there is no doubt that this result opens up new aspects for the chemistry of cationic boron compounds. Reactions that take unexpected routes are certainly more interesting than those that occur along a “normal” route, and this example shows that BN chemistry still offers surprises.

Experimental Section

All experiments have been performed under anhydrous conditions using N₂ or Ar as protective gases. All compounds were freshly crystallized or distilled. Solvents were dried by conventional methods. NMR spectroscopy: Bruker ACP-200 and Jeol EX 400. Standards for ¹¹B, ¹⁴N and ²⁷Al: external BF₃·OEt₂, nitromethane, and 1 M AlCl₃ in water, respectively. UV/Vis Spectroscopy: Varian Cray 60 CONC spectrometer. Elemental analysis: microanalytical laboratory of the department. X-ray structure determinations: Bruker P4 four circle diffractometer equipped with an area detector and a LT2 cooling device; Mo-K_α radiation, graphite monochromator. Thermal ellipsoids are represented at a 25% probability level.

Compound 4: To a stirred solution of **1** (1.59 g, 9.3 mmol) in toluene (40 mL) was added tris(dimethylamino)borane (1.6 mL, 9.3 mmol). After heating to reflux for 20 h, a bright yellow fluorescing solution formed, which presented an ¹¹B NMR signal at 4.7 ppm (*h*_{1/2} = 57 Hz). The solvent was removed, and a yellow powder of **4** remained. Yield: 2.3 g (91%). C₁₄H₂₀BN₅ (269.22): calcd. C 63.46, H 7.48, N 26.02; found C 61.87, H 7.53, N 25.92. ¹H NMR (270 MHz, C₆D₆): δ = 2.36 (N–Me)₂ ppm. ¹³C NMR (100 MHz): δ = 39.5 (N–Me)₂ ppm, as well as the resonances listed for **5**. ¹¹B NMR (64 MHz): δ = 4.7 (*h*_{1/2} = 57 Hz) ppm.

Compound 5: The yellow solid that remained after evaporation of the solvent from **4** was dissolved in CHCl₃ (30 mL). After 10 d, addition of pentane (20 mL) to the top of the solution led to the formation of only a few very small crystals in two days. A few days later, the homogeneous solution was cooled to –78 °C. Yellow fluorescing crystals of **5**·(CHCl₃)₄ separated. On drying the crystals in vacuo, they turned turbid as they lost weight. Yield: 2.19 g (83%). M.p. 180 °C. C₁₄H₂₁BClN₅ (305.62): calcd. C 55.02, H 6.93, N 22.92, Cl 11.60; found C 54.12, H 6.88, N 21.75, Cl 10.74. ¹H NMR (400 MHz, C₆D₆): δ = 2.54 (s, 6 H, HN–Me), 5.47 (br. s, 1 H, N–H), 6.06 [td, ³J(¹H¹H) = 6.6 Hz, ⁴J(¹H¹H) = 1.2 Hz, 2 H, C2–H], 6.81 [td, ³J(¹H¹H) = 8.3 Hz, ⁴J(¹H¹H) = 3.1 Hz, 2 H, C3–H], 7.06 [br. d, ³J(¹H¹H) = 8.7 Hz, 2 H, C4–H], 7.64 [dd, ³J(¹H¹H) = 6.4, ⁴J(¹H¹H) = 1.7 Hz, 2 H, C1–H] ppm. ¹³C NMR (100 MHz): δ = 48.7 (N–Me₂), 111.7 (py-C2), 121.9 (py-C4), 131.8 (py-C3), 138.4 (py-C1), 156.5 (py-C5) ppm. ¹¹B NMR (64 MHz): δ = 5.0 ppm. ¹⁴N NMR (28.9 MHz): δ = –92.5 (py-N), –203.8 (N–H), –356.2 (N–Me₂, HN–Me₂) ppm. UV/Vis (toluene): λ_{max} = 320, 393 cm^{–1}.

Compound 7: A mixture of B(NMe₂)₃ (3.45 mL, 20 mmol) and aniline (3.65 mL, 40 mmol) in toluene (150 mL) was kept at reflux for 20 h. After cooling the solution, ¹¹B NMR signals (1:1 intensity) at 24.9 ppm for (Me₂N)₂BNHPh^[10] and at 23.6 ppm for B(NHPh)₃ were observed in the spectrum.^[6] **1** (3.42 g, 20 mmol) was added to the reaction mixture, which was kept at reflux for another 20 h. The ¹¹B NMR spectrum showed a signal for B(NHPh)₃ in addition to one at 2.0 ppm. On cooling the mixture

to –20 °C, most of the B(NHPh)₃ separated as a solid, which was removed by filtration. The filtrate exhibited red brown fluorescence. It was then reduced in volume to 20 mL. At –50 °C, only a few additional crystals of B(NHPh)₃ separated, which were removed by filtration. All the volatile material from the filtrate was then evaporated under vacuum to leave behind a light brown powder of **7**. C₁₈H₂₀BN₅ (317.18): calcd. C 68.10, H 6.35, N 22.07; found C 68.29, H 5.22, N 22.20. ¹H NMR (400 MHz, C₆D₆): δ¹ = 2.11 (N–Me₂), 2.82 (br., N–H), 6.42, 6.70, 6.72, 6.96, 7.63, 7.97 (Ar–H, Ph–H) ppm. ¹¹B NMR (64 MHz, toluene): δ = 2.0 ppm (*h*_{1/2} = 83 Hz).

Di(pyrid-2-yl)aminotrimethylsilane (6): To a solution of **1** (1.712 g, 10.1 mmol) in toluene (80 mL) was added a solution of *n*BuLi (6.4 mmol, 1.56 M, 10 mmol) at –78 °C. A precipitate of (py')₂NLi formed immediately. At room temperature, the suspension was treated with Me₃SiCl (1.3 mL, 10 mmol). After stirring for 2 h, the insoluble material (LiCl) was removed by filtration, and the filtrate reduced in volume to about 15 mL. White needles of **6** separated over a week by keeping the solution at 0 °C. Yield: 1.97 g (81%). C₁₃H₁₇N₃Si (243.59): calcd. C 64.17, H 6.99, N 17.28; found C 66.18, H 7.06, N 17.88. ¹H NMR (400 MHz, C₆D₆): δ = 0.44 (s, 9 H, Si–Me₃), 6.38 [br. d, ³J(¹H¹H) = 8.5 Hz, 2 H, py-C3–H], 6.48 [ddd, ³J(¹H¹H) = 6.5 Hz, ³J(¹H¹H) = 5.6 Hz, ⁴J(¹H¹H) = 1.3 Hz, 2 H, py-C5–H], 7.02 [ddd, ³J(¹H¹H) = 7.0 Hz, ⁴J(¹H¹H) = 1.1 Hz, 2 H, py-C4–H], 8.27 [dd, br, ³J(¹H¹H) = 5.4 Hz, ⁴J(¹H¹H) = 2.1 Hz, 2 H, py-C6–H] ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 1.3 (Si–Me₃), 116.9 (py-C5), 117.7 (py-C3), 137.6 (py-C4), 149.0 (py-C6), 160.0 (py-C2) ppm. ²⁹Si NMR (80 MHz, C₆D₆): δ = 6.8 ppm. ¹⁴N NMR (28.9 MHz, toluene): δ = –85.9 (py-N), –266.6 (N–Si) ppm.

Reaction of 6 with Chlorobis(dimethylamino)borane: A solution of **6** (2.44 g, 10 mmol) in toluene (40 mL) was cooled to 0 °C. (Me₂N)₂-BCl (1.35 mL, 10 mmol) in toluene (20 mL) was then added. After stirring the solution for several hours and warming to ambient temperature, a single ¹¹B NMR signal at 4.7 ppm was observed in the spectrum, which shows a quantitative conversion to **4**. All other NMR spectroscopic data were identical to those found for **4**. Yield: 2.6 g of **4** (97%).

Diboronumbis(tetrachloroaluminate) 8(AlCl₄)₂: To a solution of **4** (2.05 g, 7.6 mmol) in toluene (70 mL) was added AlCl₃ powder (1.00 g, 7.6 mmol). The suspension was stirred for 1 d. The ¹¹B NMR spectrum shows that no reaction had occurred. The mixture was then kept at reflux for 20 h. During this period, a green-yellow precipitate formed. The yellow solution presented a ¹¹B NMR signal at δ = 26.5 ppm (70%) and a multiplet at 0.7 ppm (≈30%). Two signals were observed in the ²⁷Al NMR spectrum at 80.4 and 68 ppm, in addition to overlapping bands in the range 92–104 ppm. After filtration, the solid material was dried and treated with CH₂Cl₂. Only part of the material dissolved. The concentrated solution was then cooled to –20 °C. Fairly large yellow-orange crystals with an octahedral shape formed over a few days. As revealed by the X-ray structure determination, the crystals have the composition **8**(AlCl₄)₂·2CH₂Cl₂. Yield: not determined. M.p. 200 °C. C₃₄H₃₄Al₂B₃Cl₁₂N₁₁ (1108.51): calcd. C 36.81, H 3.07, N 13.90, Cl 38.38; found C 36.00, H 2.78, N 12.84, Cl 37.89. ¹H NMR (400 MHz, CH₂Cl₂/C₆D₆): δ = 2.13 (s, C–Me) ppm. ¹³C NMR (100 MHz, CH₂Cl₂/C₆D₆): δ = 21.2 (N–Me) ppm. ¹¹B NMR (64 MHz): δ = 2.0, –26.5 ppm. ²⁷Al NMR: δ = 106.4 (AlCl₄[–], *h*_{1/2} = 20 Hz) ppm.

X-ray Structure Determinations: Single crystals were suspended in perfluoro ether oil, and a suitable crystal was selected, fixed on a glass fibre and mounted on the goniometer head flushed with nitrogen gas cooled to –80 °C. The unit cell was determined from the reflections recorded on 5 sets of 15 different exposures each. Data

collection was performed in the hemisphere mode. Data were reduced with the program SMART.^[36] For the structure solution, the SHELXTL program system^[37] was used. Hydrogen atoms bound to N atoms were taken from the Fourier maps as well as those in CH₂Cl₂ and CHCl₃. All other hydrogen atoms were placed in calculated positions. Crystallographic data and structural parameters are summarized in Table 1. CCDC-626869 and -626870 contains 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.

Table 1. Crystallographic data and structure refinement parameters.

Compound	5·4CHCl ₃	8(AlCl ₄) ₂ ·2CH ₂ Cl ₂
Chemical formula	C ₁₈ H ₂₅ BCl ₁₃ N ₅	C ₃₄ H ₃₄ Al ₂ B ₃ Cl ₁₂ N ₁₁
Formula weight	783.09	1108.51
Crystal size [mm]	0.10 × 0.10 × 0.10	0.30 × 0.40 × 0.40
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	11.1059(8)	15.674(1)
<i>b</i> [Å]	27.428(2)	18.123(1)
<i>c</i> [Å]	11.719(1)	18.194(1)
<i>α</i> [°]	90	90
<i>β</i> [°]	105.866(1)	110.709(1)
<i>γ</i> [°]	90	90
<i>V</i> [Å ³]	3433.8(5)	4834.3(6)
<i>Z</i>	4	4
<i>ρ</i> (calcd.) [Mgm ⁻³]	1.515	1.523
<i>μ</i> [mm ⁻¹]	1.065	0.765
<i>F</i> (000)	1576	2240
Index range	−14 < <i>h</i> < 10 −35 < <i>k</i> < 35 −14 < <i>l</i> < 15	−18 < <i>h</i> < 18 −23 < <i>k</i> < 23 −22 < <i>l</i> < 22
2 θ [°]	58.46	58.86
Temperature [K]	193(2)	193(2)
Reflections collected	19865	28240
Reflections unique	6586	9522
Reflections observed (4 σ)	3029	3680
<i>R</i> (int.)	0.0743	0.0700
No. variables	342	561
Weight scheme ^[a] <i>x/y</i>	0.1034/3.4764	0.1451/0.000
GOOF	1.044	0.837
Final <i>R</i> (4 σ)	0.0788	0.0719
Final <i>wR</i> ₂	0.1947	0.1959
Largest residual peak [eÅ ⁻³]	0.953	1.530

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

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