CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200802669

On the Track of Novel Triel-Stabilised Silylaminoiminoborenes

Holger Ott, Christoph Matthes, Arne Ringe, Jörg Magull, Dietmar Stalke, and Uwe Klingebiel*[a]

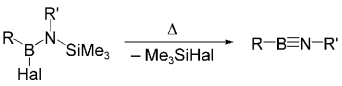
Abstract: Reactions between the halogen triels $AlClMe_2$, $AlBr_3$, $GaCl_3$ and the silylaminofluoroboranes $(Me_3Si)_2N$-B(F)NRSiMe$_3$ (R = SiMe$_3$, CMe$_3$) afforded the silylaminoiminoborenes, which were isolated as the triel adducts, such as $Me_3Si(Cl_3Ga)NB$-NRSiMe$_3$ (**6**). In order to extent this reaction path to other fluoroboranes, novel aryl- and silyl-substituted diaminofluoroboranes were synthesised. Because almost no open-chain diaminofluoroboranes had been structurally characterised previously, corresponding fluoroboranes containing no silyl groups were crystallised for purposes of comparison. In complex reactions with the arylsilylaminofluoroboranes [(2,6-(*i*Pr)$_2$C$_6$H$_3$)(Me$_3$Si)NB(F)NR$_2$, R = *i*Pr, *i*Bu], amine adducts of borenium salts such as [(*i*Pr)$_2$NH→B(Bu)NH-2,6-(*i*Pr)$_2$C$_6$H$_3$]$^+$AlCl$_4^-$ (**13**) were obtained.

Keywords: aluminium · diaminofluoroboranes · gallium · iminoborenes · X-ray diffraction

Introduction

Even though B–N and C–C units are isoelectronic, comparison of their chemical properties shows significant differences. Amine–borane (H_3N–BH_3) is a solid at room temperature, for example, whereas ethane (H_3C–CH_3) is a gas. The differences between the B–N and C–C bonds can be ascribed to their different polarities.[1] Ethane is non-polar, whereas amine–borane (H_3B–NH_3) has a large dipole moment. The simplest unsaturated B–N compound is aminoborane (H_2N=BH_2), which is isoelectronic with ethene. It is unstable and readily forms cyclic ring compounds such as the cyclohexane analogue (H_2N–BH_2)$_3$ and can only be stabilised by shielding the double bond with bulky groups.[2] The chemistry of iminoborines (-B≡N-), which are isovalence electronic with -C≡C-, is in many respects similar to that of the alkynes: they oligomerise, polymerise and undergo addition of HX. However, the polarity and weakness of the B–N bonds results in higher reactivity.[2,3]

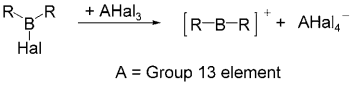
A widely used method to generate dicoordinated boron atoms in iminoborines is the elimination of halosilanes from the corresponding silylaminohaloborane [Eq. (1)].[3b,f]



(1)

The elimination often requires heating of the starting material. Sometimes temperatures up to 500 °C are necessary. Because iminoborines are thermodynamically unstable with respect to their oligomerisation, cyclodiborazanes or higher cyclisation products are isolated.[2,4] The elimination in normally becoming more difficult with increasing boron halogen bond strength from B–I to B–F compounds.[3d]

The synthesis of silylaminoborinium cations is of special interest because of the weak Si–N bond, which can easily be cleaved. Therefore, all members of the series [(Me$_3$Si)$_{4-n}$-(Me$_3$C)$_n$N$_2$B]$^+$BBr$_4^-$ have been synthesised by use of excess tribromoborane [general synthetic route Eq. (2)].[3a,c,d]



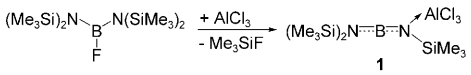
(2)

Recently, we investigated the reaction between [(Me$_3$Si)$_2$N]$_2$BF and $AlCl_3$ and isolated the silylaminoimino-

[a] H. Ott, Dr. C. Matthes, Dr. A. Ringe, Prof. Dr. J. Magull, Prof. Dr. D. Stalke, Prof. Dr. U. Klingebiel
Institut für Anorganische Chemie
Georg-August-Universität Göttingen
Tammannstraße 4, 37077 Göttingen (Germany)
Fax: (+49) 551-39-3052
E-mail: uklinge@gwdg.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200802669.

borene (**1**) as the first aluminium adduct of an iminoborene that could also be investigated by X-ray diffraction [Eq. (3)].[5]

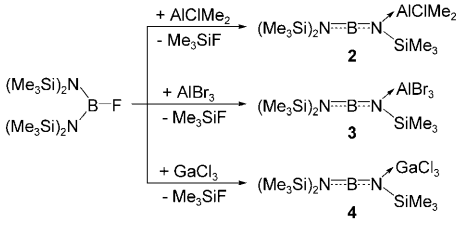


(3)

This formation of a stabilised aminoiminoborene and not of a borinium cation prompted the idea to combine the fluorosilane elimination of as yet unknown silylaminofluoroboranes with the addition of halo-triels to prepare novel and so far inaccessible aminoiminoborenes.

Results and Discussion

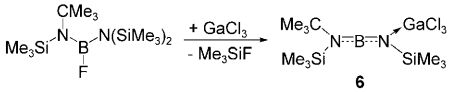
Bis(trimethylsilyl)amino- and [*tert*-butyl(trimethylsilyl)amino]-(trimethylsilyl)iminoborene triel adducts: In order to establish the reaction route to triel stabilised aminoiminoborenes as shown in Equation 3, bis[bis(trimethylsilyl)amino]fluoroborane was treated with Me_2AlCl, $AlBr_3$ and $GaCl_3$. This led to the formation of the triel adducts of the bis(trimethylsilyl)aminotrimethylsilyliminoborenes **2**–**4**, with fluorotrimethylsilane acting as the leaving group [Eq. (4)]. We can deduce that this synthetic route can be applied more generally for group 13 halides (except boron) to yield the silylamino-silyliminoborenes.



(4)

Abstract in German: *Die Reaktion von Halogentrielen ($AlClMe_2$, $AlBr_3$ und $GaCl_3$) mit Silylaminofluorboranen $(Me_3Si)_2NB(F)NRSiMe_3$ ($R = SiMe_3$, CMe_3) ergab Silylaminoiminoborene, die als Trieladdukte isoliert wurden (z.B. $Me_3Si(Cl_3Ga)NBNRSiMe_3$ (**6**)). Um diese Syntheseroute auf andere Fluorborane auszuweiten wurden aryl- und silyl-substituierte Diaminofluorborane synthetisiert. Zu Vergleichszwecken wurden ebenso die zugehörigen nichtsilylierten Verbindungen kristallisiert, da bislang kaum offenkettige Diaminofluorborane strukturell charakterisiert wurden. Aminaddukte von Boreniumsalzen z.B. $[(iPr)_2NH{\rightarrow}B(Bu)NH\text{-}2,6\text{-}(iPr)_2C_6H_3]^+AlCl_4^-$ (**13**) konnten in komplexen Reaktionen mit Arylsilylaminofluorboranen $[(2,6\text{-}(iPr)_2C_6H_3)(Me_3Si)NB(F)NR_2$, $R = iPr$, $iBu]$ erhalten werden.*

Analogously to the synthesis of the asymmetrical silyliminoborene trichloroalane adduct $Me_3C(Me_3Si)N{=}B{=}N(AlCl_3)SiMe_3$ (**5**),[5] the reaction between $Me_3C(Me_3Si)NB(F)\text{-}N(SiMe_3)_2$ and $GaCl_3$ yielded the [*tert*-butyl(trimethylsilyl)amino]-trimethylsilyliminoborene $GaCl_3$ adduct **6** [Eq. (5)].



(5)

Again, the imine group is formed at the bis(trimethylsilyl)-substituted nitrogen atom, as is also observed in the corresponding $AlCl_3$ adduct **5**.[5] This emphasises the original finding that the silyl groups show a stronger inductive effect[6] than the *t*Bu substituents, leading to a stronger Lewis basic nitrogen atom at the $N(SiMe_3)_2$ site rather than at the $N(SiMe_3)tBu$ site. This was verified by a natural bond order (NBO) analysis of the starting material in which the disilylated nitrogen atom shows a much higher negative charge than the asymmetrically substituted $N(SiMe_3)tBu$ nitrogen atom (−1.60 e vs −1.21 e).[5] This trend is not surprising, because various charge density investigations of compounds with silicon atoms in positions adjacent to first row elements show high positive integrated charges at the silicon atoms (above +2 e).[7] This is normally balanced by partial negative charges on the neighbouring atoms. The most electronegative atom among those, the nitrogen atom in this case, carries the highest charge.

Surprisingly, it is well established in amine chemistry that silyl substitution decreases the donor strength and basicity of the amine relative to the carbon analogues, which at first sight contradicts the findings above.[8] The reason for this is the drastic change in the hybridisation of the nitrogen atom if a silyl substituent is present.[9] The sp^3-hybridised lone pair of the nitrogen atom becomes less nucleophilic on changing to an sp^2 hybridisation state with silyl substituents.[3c] This causes a decreased reactivity. In our case, though, sp^2 hybridisation is already present at both nitrogen atoms in the starting materials so that the selectivity found for **5** and **6** is based only on the nitrogen atom charges, so the nucleophilic attack proceeds at the disilylated amine.

Single crystals of **6** were obtained from a diethyl ether solution. The adduct **6** (Figure 1) crystallises in the monoclinic space group $P2_1/n$ and is isomorphous with the $AlCl_3$ analogue.[5] It consists of well-separated monomers that display $SiMe_3/tBu$ disorder. The site occupation factor ratio refined to 0.7:0.3, which prevents a detailed analysis on the amino substituent part. Nevertheless, clear tendencies are visible. The mean B–N bond length to the amino nitrogen atom (N2) is longer (135 pm) than that to the imino nitrogen atom (N1, 133 pm). These are exactly in the range of related Lewis acid base adducts of silylaminoiminoborenes[5] and carboaminoiminoborenes.[10] The N-B-N unit is almost linear, and the four atoms of the R_2NB units on each side of the molecule lie in the same plane. Both planes are close to

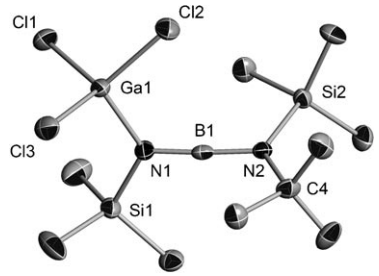
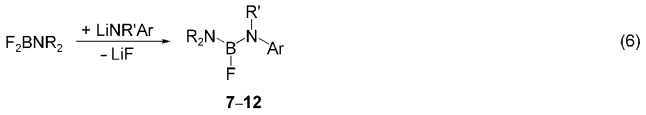


Figure 1. Molecular structure of [*tert*-butyl(trimethylsilyl)amino]-(trimethylsilyl)iminoborene trichlorogallium adduct (**6**). Disordered parts of the molecule, as well as hydrogen atoms, are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level.

orthogonal (85°), so an allene-type bonding situation can be assumed. The Ga–N bond length (194 pm) is in the range of the sum of the covalent radii (195 pm[11]) and exactly the same as that in a gallium carboiminoborene adduct[9a] (194 pm).

New arylaminofluoroboranes: The formation of **1**–**6** prompted the investigation of the analogous triel reactions with novel silylaminofluoroboranes. For reasons of comparison, we also synthesised related hydrogen- or carbo-substituted arylaminofluoroboranes. We prepared the (arylamino)-alkylaminofluoroboranes **7**–**10** and the (silylarylamino)-alkylaminofluoroboranes **11** and **12** by treatment of diisopropyl-, diisobutyl- and (trimethylsilyl)methylaminodifluoroboranes with lithium 2,6-diisopropylanilide, isopropylanilide and trimethylsilylanilide [Eq. (6) and Table 1] by the synthetic route of Kölle and Nöth.[3c,12]



(6)

7–**12**

Table 1. Residues for compounds **7**–**12**.

	7	**8**	**9**	**10**	**11**	**12**
R	*i*Pr	*i*Bu	Me/$SiMe_3$	*i*Pr	*i*Pr	*i*Bu
R′	H	H	H	*i*Pr	$SiMe_3$	$SiMe_3$

The diaminofluoroboranes can be synthesised in excellent yields and purities because they can easily be distilled and crystallised. Crystal structural analyses of four model compounds (**7**, **9**, **10**, **11**) give further insight into the bonding situation in diaminofluoroboranes, of which only a few examples had previously been structurally characterised by X-ray methods.[13] They were chosen in order to investigate the influence of substituents either with different steric demand or that were believed to stabilise the borane. Crystals of the diaminofluoroboranes were obtained from *n*-hexane solutions and were measured on a Bruker Smart Apex II diffractometer with use of graphite monochromated molybdenum radiation. Crystallographic details are shown in Table 2, and selected interatomic distances and angles in **7**, **9**,[14] **10** and **11** are listed in Table 3. The atom labelling is consistent throughout the molecular structures and can be taken from Figures 2 and 3.

The central structural motif of all diaminofluoroboranes is a planar NB(F)N unit with an sp^2 hybridised boron atom (mean deviation from idealised plane: 0.09 pm; sum of the bond angles: 360.0°). Remarkably, two different constitutional arrangements of the aryl substituents can be observed. In **7** and **9**, the aryl ring is oriented *cis* to the fluorine atom (**7**, Figure 2), whereas in **10** and **11** it is arranged in the *trans* position (**11**, Figure 3). Thus, once the second substituent of the arylamine is not a hydrogen atom, the sterically disfavoured position *trans* to the fluorine atom (from now on the reference atom for *cis*/*trans* nomenclature will be F) is occupied by the aryl ring. The bulk of this substituent is reduced through its adoption of an orientation in which the ring plane forms almost a 90° angle with the NB(F)N unit (**10**: 94.8°; **11**: 91.2°). Accordingly, the steric demand of the isopropyl groups of the second amino substituent is minimised by a conformation in which the hydrogen atom at C(*trans*) lie in the NB(F)N plane and face the aryl ring (isopropyl "shovels" bent away from the aryl ring). Exactly the opposite orientation is present in **7** (isopropyl "shovels" bent away from the fluorine atom) if the aryl substituent points to the side with the fluorine atom (*cis*). Consequently, both bulky groups (Dip and TMS) in **9** are oriented towards the fluorine atom (*cis*).

The steric demand of the substituents can be monitored by means of the N1-B1-N2 bond angle. In **9** the *trans* groups are small (H and Me) and the narrowest bond angle can be found [124.8(2)°]. This angle widens in **7** [126.9(1)°] and **10** [128.0(2)°], whereas in **11** the N1-B1-N2 angle is as much as 132.9(3)°. The differences between **10** and **11** can be ascribed to the different aryl ring tilts (see above; almost perfectly rectangular with respect to the boron plane in **11**) and the hybridisation of the connected nitrogen atom.

The degrees of sp^2 hybridisation (fully or partly sp^3) at both nitrogen atoms, as well as the dihedral angles between the p_z orbitals, determine the extent of π interaction with the unoccupied p_z orbital of the boron atom. These orbitals are almost ideally aligned (angles between orbitals: N1, B1 = 3.4°; N2, B1 = 1.4°) and perfect sp^2 hybridisation is present at both nitrogen atoms (sum of the bond angles: 360.0°) in **7**. Both B–N bond lengths are therefore short [B1–N1: 141.4(2) pm; B1–N2: 139.6(2) pm] in relation to a standard B–N single bond (149 pm[15]) but far from values found for aminoiminoborenes (ca. 133 pm[5,9]). Nevertheless, they are comparable to the formal single bonds in a supermesityl-substituted aminoiminoborine[16] [139.2(5) pm] and in a bis(trimethyl)silylaminodisilylamino-substituted fluoroborane[17] [143.4(1) and 144.2(1) pm]. According to Paetzold, who suggested a value of 141 pm as a typical $R_2B{=}NR_2$ bond length, we have to classify the B–N bonds in **7**, **9**, **10** and **11** likewise.[2]

Table 2. Crystallographic details for **6**, **7**, **9**, **10** and **11** (100(2) K) and for **13** and **16** (133(2) K).

Compound	**6**	**7**	**9**	**10**	**11**	**13**	**16**
CCDC no.	713642	713643	713644	713645	713646	713647	713648
empirical formula	$C_{10}H_{27}BCl_3GaN_2Si_2$	$C_{18}H_{32}BFN_2$	$C_{16}H_{30}BFN_2Si$	$C_{21}H_{38}BFN_2$	$C_{21}H_{40}BFN_2Si$	$C_{22}H_{42}AlBCl_4N2$	$C_8H_{19}AlCl_3N$
molecular weight [g mol^{-1}]	418.40	306.27	308.32	348.34	378.45	514.17	262.57
crystal system				monoclinic			
space group	$P2_1/n$	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [pm]	814.5(1)	1714.7(1)	663.2(1)	3232.4(1)	1698.9(1)	1504.2(3)	8224.4(5)
b [pm]	1918.5(2)	1100.3(1)	995.5(1)	1830.6(1)	1419.5(1)	1022.4(2)	9425.4(5)
c [pm]	12.967(1)	2170.1(2)	2832.9(4)	3016.1(2)	1944.0(1)	2003.0(4)	1762.7(1)
β [°]	91.690(1)	112.593(1)	90.720(2)	102.514(1)	90.383(1)	111.89(3)	91.772(5)
V [nm^3]	2.0253(3)	3.7802(6)	1.8701(4)	17.4231(12)	4.6879(4)	2.8584(10)	1.3658(2)
Z	4	8	4	32	8	4	4
ρ_{calcd} [Mg m^{-3}]	1.372	1.076	1.095	1.062	1.072	1.195	1.277
μ [mm^{-1}]	1.863	0.069	0.130	0.067	0.115	0.457	0.699
θ range [°]	2.64- 26.68	2.25–25.35	2.50–25.33	2.21–25.36	1.87–26.04	1.46–25.91	2.31–24.68
completeness	0.999	0.999	0.997	0.998	0.999	0.994	0.986
no. reflections	23740	13521	16421	64214	66018	25115	18792
unique reflections (R_{int})	4325 (0.0226)	3470 (0.0373)	3392 (0.0568)	15952 (0.0574)	9242 (0.0394)	5523 (0.0774)	2290 (0.0542)
data/restraints/parameters	4325/416/266	3470/0/232	3392/1/201	15952/0/941	9242/4/509	5523/0/288	2290/0/122
goodness of fit	1.094	1.009	1.066	1.010	1.071	0.999	1.050
R_1 [$I > 2\sigma(I)$]	0.0215	0.0401	0.0431	0.0517	0.0392	0.0469	0.0216
wR_2 (all data)	0.0508	0.0982	0.1055	0.1494	0.1022	0.1093	0.0589
largest diff. peak/hole [e Å^{-3}]	0.275/−0.197	0.169/−0.187	0.237/−0.243	0.469/−0.189	0.277/−0.272	0.382/−0.413	0.252/−0.244

Table 3. Selected interatomic distances [pm] and angles [°] in compounds **7**, **9**, **10** and **11**.

	7	**9**	**10**[a]	**11**[a]
B–F	136.8(2)	135.8(3)	136.4(3)	137.1(2)
B–N1	141.4(2)	140.3(3)	142.9(2)	143.5(2)
B–N2	139.6(2)	141.4(3)	140.9(3)	140.9(2)
N1–C1	143.4(2)	143.4(2)	143.5(3)	144.6(2)
N1–R′	83.2(19)[b]	89.1(9)[b]	149.0(3)	177.6(1)
N2–R_{cis}	148.0(2)	174.5(2)	148.5(3)	148.9(2)
N2–R_{trans}	148.0(2)	148.2(2)	147.7(3)	147.7(2)
N1-B-N2	126.9(1)	124.8(2)	128.0(2)	132.9(2)
F-B-N1	114.7(2)	116.3(2)	115.5(2)	111.8(1)
F-B-N2	118.4(2)	118.9(2)	116.6(2)	115.4(2)
B-N1-C1	125.4(2)	126.8(2)	123.5(2)	124.1(1)

[a] Value averaged over four (**10**) or two (**11**) molecules in the asymmetric unit. [b] H atom positions were taken from the final difference map and refined.

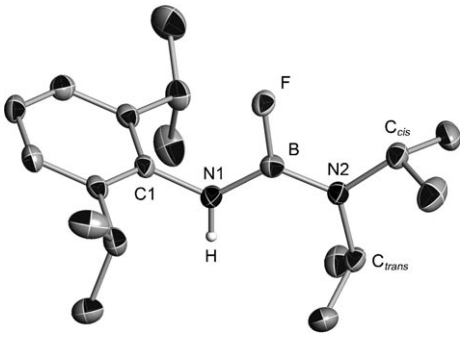


Figure 2. Molecular structure of di(isopropyl)amino-2,6-di(isopropyl)anilino-fluoroborane (**7**). Disordered parts of the molecule and constrained hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level.

The trimethylsilyl substitution in **9** causes a slight pyramidalisation at N2 (sum of the bond angles: 357.4°) in which the silyl group is bent out of the NB(F)NC plane. This also

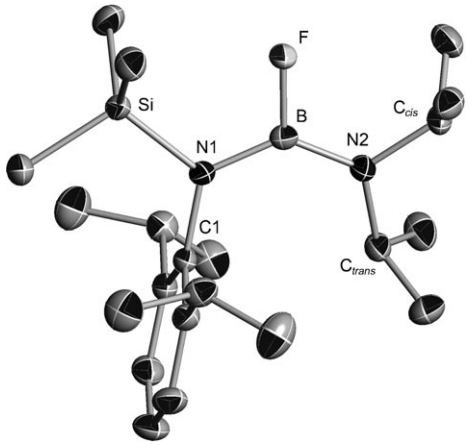


Figure 3. Molecular structure of di(isopropyl)amino-[*N*-trimethylsilyl-2,6-di(isopropyl)anilino]fluoroborane (**11**, only one molecule in the asymmetric unit shown). Hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level.

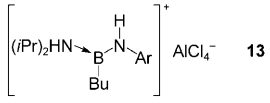
leads to an imperfect overlap of the p_z orbitals (16.7°) and, together with the increased steric demand of the silyl substituent, to the longest B–N2 bond [141.4(3) pm] in the series presented here. In the two compounds (**7** and **9**) the aryl rings are tilted by 65° and 75° relative to the NB(F)N planes and do not participate in the π stabilisation of the boron atoms. The same is true for **10** and **11** (values see above).

As soon as the aryl groups are arranged *trans*, increases in the B–N1 bond lengths are evident [**10**: 142.9(2) pm; **11**: 143.5(2) pm]. This can be explained by the need for ideal arrangements of the sterically demanding groups. The methyl groups of the N-bound isopropyl substituent in **10** point towards the fluorine atom. The halide resides at the bisection of the two methyl groups. The aryl ring is thereby forced

further out of the NB(F)N plane because of the isopropyl groups on the aryl substituent, which interfere with the other amine substituent. This leads to a slight pyramidalisation at N1 (sum of the bond angles: 359.1°) and a tilt between the lone pair orbital and the boron p_z orbital of 27.5°. The trimethylsilyl group in **11** is even more bulky, but because of the longer Si–N bond [177.6(1) pm] relative to the C–N bond in **10** [149.0(3) pm] the nitrogen atom stays sp^2 hybridised (sum of the bond angles: 359.9°) with only a slight p orbital tilt (3°).

The bulky substituents even influence the B–F bond lengths. The longest is found in **11** [137.1(2) pm], whereas the sterically least affected **9** shows the shortest B–F bond [135.8(3) pm]. The halide–boron bond lengths can be compared to the related cases in the tetrasilyl-substituted aminofluoroborane[16] [137.1(1) pm] and also to the maximum in the histogram of reported B–F single bonds (136 pm) with a tricoordinate boron atom.[18]

Conversions with $AlCl_3$: With the novel silyl-substituted diaminofluoroboranes to hand, we attempted the same conversion with trichloroalane, which led to the triel stabilised aminoiminoborenes **1** and **5**. Firstly, trimethylsilyl[2,6-di(isopropyl)phenyl]amino-di(isopropyl)aminofluoroborane (**11**) was treated with one equivalent of $AlCl_3$ in diethyl ether and dichloromethane. Elimination of Me_3SiF was detected in the NMR spectra, but it was impossible to isolate the desired product. However, we grew crystals of a by-product or decomposition product at 0°C from the resulting polymeride. The borinium cation **13** with $AlCl_4^-$ as counter-ion was characterised as a di(isopropyl)-amine adduct in the crystal structural analysis.



13

According to Nöth's nomenclature, **13** would correctly be called a borenium cation.[3c] Nöth reported several possible routes to related tricoordinated boron cations in his review, but we cannot yet explain the mechanism of the borenium cation formation. Interestingly, repeated reactions always led to the same results.

Compound **13** crystallises in the monoclinic space group $P2_1/c$ with one ion pair in the asymmetric unit (Figure 4). It belongs to the class of the rare examples of borenium cations characterised by X-ray diffraction. To the best of our knowledge, it is even the first crystal structure of a borenium cation in which the boron atom is not part of a ring system.

The boron atom is sp^2 hybridised (sum of the bond angles: 360.0°) with all connected atoms in the same plane (mean deviation from idealised plane: 0.79 pm). The same is true for the tricoordinated nitrogen atom N1 (mean deviation from idealised plane: 0.15 pm; sum of the bond angles: 360.0°), and an almost perfectly aligned p_z orbital orientation between B and N1 is adopted (tilt angle: 3°). In addition, the butyl chain participates in the π-stabilisation of the boron atom through hyperconjugation (angle between C14-C13-B and C13B(N2)N1 plane: 93.8°). The longest carbon–carbon bond can thus be found between C13–C14 [C13–C14: 154.3(3) pm; C14–C15: 149.1(4) pm; C15–C16: 151.2(4) pm]. The boron–carbon bond is 156.4(3) pm long and just slightly shorter than a standard B–C single bond (158 pm[14]).

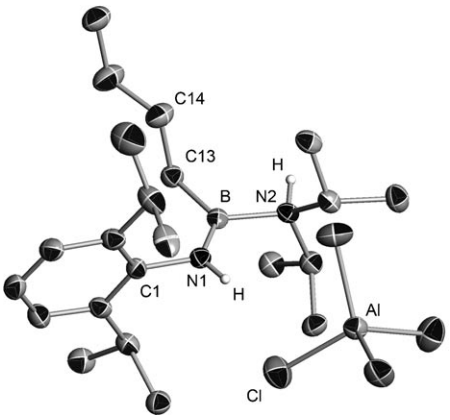
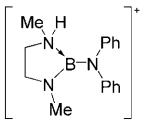


Figure 4. Molecular structure of di(isopropyl)amine-2,6-di(isopropyl)anilino-*n*-butyl-borenium tetrachloroaluminate (**13**). Disordered parts of the molecule and constrained hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level.

The boron nitrogen bond lengths differ significantly as a result of the two bonding modes present in **13**. B–N1 can be classified as a π-interaction-reinforced single bond [137.8(3) pm]. The bond length is in the range between those found for the diaminofluoroboranes and the aminoiminoborenes. However, it is close to the value of the related B–N bond [138.6(3) pm] reported for 1,3-dimethyl-2-(diphenylamino)-1,3,2-diazaborolidinium triflate (**14**), which is one of the structurally characterised borenium cations.[19]

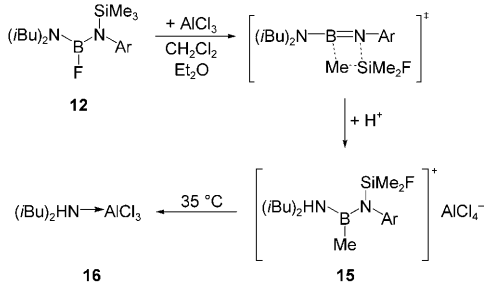


14

The second B–N bond is much longer and a coordinative interaction (B–N2: 157.1(3) pm). It is thus on the same scale as those of amine-boranes (R_3B–NR_3) selected by Paetzold as model compounds for a boron nitrogen single bond (158 pm).[2] The corresponding bond in **14** is shorter [154.7(3) pm], most probably due to the limited flexibility of the donating aminoethylene side chain. Moreover, we have to emphasise that no interactions between the $AlCl_4^-$ anions and the borenium cations are present in the solid state. The aluminium chlorine distances are thus in the normal range of 211.9(1) to 214.9(1) pm.

Even though we had not been able to isolate the desired aminoiminoborene when using the silylarylaminofluoroborane **11**, we performed the same reaction with the isobutyl-substituted starting material **12**. Once more the fluorosilane elimination takes place in the initial reaction step, but it is followed by the addition of Me_3SiF to the iminoborine, which results in a methyl substitution at the boron atom and

a dimethylfluorosilane group at the aryl-substituted nitrogen atom. In the final conversion the isobutylamino nitrogen atom was protonated[20] and below 0 °C it was possible to isolate di(isobutyl)amine adduct of [(*N*-dimethylfluorosilyl)-2,6-di(isopropyl)anilino)]-methylborenium tetrachloroaluminate (**15**) from the resulting residual oil as a crystalline material (Scheme 1). Unfortunately, no useful structure model could be refined because of the poor crystal quality; only the atom connectivity could be deduced from the diffraction experiment. The borenium salt **15** is thermally unstable above room temperature; under these conditions the di(isopropyl)amine trichloroalane adduct (**16**) was isolated (Scheme 1).



Scheme 1. Putative reaction sequence for the formation of di(isobutyl)amine adduct of [(*N*-dimethylfluorosilyl)-2,6-di(isopropyl)anilino)]-methylborenium tetrachloroaluminate (**15**) and the di(isobutyl)amine trichloroalane adduct **16**.

The amine triel adduct **16** crystallises in the monoclinic space group $P2_1/c$ with one formula unit in the asymmetric unit (Figure 5). The nitrogen aluminium donor bond is

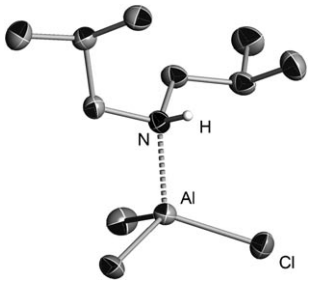


Figure 5. Molecular structure of the di(isobutyl)amine trichloroalane adduct **16**. Constrained hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level.

196.0(1) pm long and slightly shorter than the comparable bonds in methylamine [193.6(4) pm],[21] trimethylamine [196(1) pm][22] and diphenylamine [198.3(4) pm][23] adducts. The aluminium chlorine bond lengths vary between 211.5(1) and 212.8(1) pm and are in the normal range.

Conclusion

We can conclude that the novel direct synthetic route to triel stabilised aminoiminoborenes can be easily extended to a variety of halogen triels. Unfortunately, the aryl-substituted diaminofluoroboranes proved to be inappropriate starting materials in similar reactions. Nevertheless, we were able to study the bonding situations in a series of diaminofluoroboranes. In complex reactions with those starting materials we could only isolate by-products or decomposition products. Even so, the isolated compounds were structurally interesting.

Experimental Section

All experiments were performed in oven-dried glassware under purified nitrogen or argon with use of standard inert gas and vacuum line techniques. All NMR spectra were measured at room temperature on a Bruker AVANCE 200 or DPX 500 spectrometer with $SiMe_4$, $BF_3{\cdot}Et_2O$, $Al(NO_3)_3$ or C_6F_6 as external standards. Mass spectra were obtained with a MAT 95 spectrometer. The progress of the reactions was checked by ^{19}F NMR spectroscopy. The purities of the compounds were confirmed by NMR spectroscopy and gas chromatography.

Compounds 2–4: A solution of $AlClMe_2$ (0.1 mol) in *n*-hexane (100 mL) (**2**), of tribromoalane (0.1 mol) in diethyl ether (50 mL) (**3**) or of trichloride gallium (0.1 mol) in *n*-hexane (50 mL) (**4**) was added to bis-[bis(trimethylsilyl)amine]fluoroborane (0.1 mol) in *n*-hexane (50 mL). The reaction mixture was heated at reflux for 48 h and compounds **2–4** were isolated by distillation and recrystallisation from *n*-hexane.

Chlorodimethylalano(trimethylsilyl)iminobis-(trimethylsilyl)aminoborene (2): Yield 91%; m.p. 42 °C; ^1H NMR ($CDCl_3$): $\delta = -0.32$ (s, 6H; AlMe_2), 0.10 [s, 18H; N(SiMe_3)$_2$], 0.42 ppm (s, 9H; AlNSiMe_3); ^{13}C NMR ($CDCl_3$): $\delta = 1.03$ (AlMe_2), 1.94 [N(SiMe_3)$_2$], 2.48 ppm (AlNSiMe_3); ^{11}B NMR ($CDCl_3$): $\delta = 33.63$ ppm; ^{27}Al NMR ($CDCl_3$): $\delta = 63.24$ ppm; ^{29}Si NMR ($CDCl_3$): $\delta = 11.15$ (AlN*Si*Me$_3$), 12.85 ppm [N(*Si*Me$_3$)$_2$]; MS (EI): *m*/*z* (%): 350 $[M]^+$ (8), 335 $[M-Me]^+$ (45), 315 $[M-Cl]^+$ (5), 259 $[M-AlClMe_2]^+$ (20).

Tribromoalano(trimethylsilyl)imino-bis(trimethylsilyl)aminoborene (3): Yield 95%; m.p. 122 °C; ^1H NMR ($CDCl_3$): $\delta = 0.39$ [s, 18H; N(SiMe_3)$_2$], 0.51 ppm (s, 9H; AlNSiMe_3); ^{13}C NMR ($CDCl_3$): $\delta = 1.94$ [N(SiMe_3)$_2$], 2.30 ppm (AlNSiMe_3); ^{11}B NMR ($CDCl_3$): $\delta = 26.19$ ppm; ^{27}Al NMR ($CDCl_3$): $\delta = 91.47$ ppm; ^{29}Si NMR ($CDCl_3$): $\delta = 13.70$ [AlN*Si*Me$_3$], 15.74 ppm [N(*Si*Me$_3$)$_2$].

Trichlorogallano(trimethylsilyl)imino-bis(trimethylsilyl)aminoborene (4): Yield 82%; m.p. 157 °C; ^1H NMR ($CDCl_3$): $\delta = 0.33$ (s, 9H; GaNSiMe_3), 0.36 ppm [s, 18H; N(SiMe_3)$_2$]; ^{13}C NMR ($CDCl_3$): $\delta = 1.74$ [N(SiMe_3)$_2$], 1.83 ppm (GaNSiMe_3); ^{11}B NMR ($CDCl_3$): $\delta = 30.10$ ppm; ^{29}Si NMR ($CDCl_3$): $\delta = 13.68$ (GaN*Si*Me$_3$), 15.67 ppm [N(*Si*Me$_3$)$_2$].

Trichlorogallano(trimethylsilyl)imino-[*tert*-butyl(trimethylsilyl)amino]-borane (6): A solution of trichlorogallium (0.1 mol) in diethyl ether (50 mL) was added to *tert*-butyl(trimethylsilyl)amino-bis(trimethylsilyl)amino-fluoroborane (0.1 mol) in diethyl ether (50 mL). The reaction mixture was heated under reflux for 24 h. The crystalline compound **4** was obtained after removal of the solvent in vacuo and recrystallisation of the residue from *n*-hexane. Yield 98%; m.p. 72 °C; ^1H NMR ($CDCl_3$): $\delta =$ 0.40 (s, 9H; CNSiMe_3), 0.44 (s, 9H; GaNSiMe_3), 1.47 ppm (s, 9H; NCMe_3); ^{13}C NMR ($CDCl_3$): $\delta = 1.93$ (CNSiMe_3), 2.30 (GaNSiMe_3), 32.64 (NCMe_3), 58.54 ppm (NCMe_3); ^{11}B NMR ($CDCl_3$): $\delta = 31.92$ ppm; ^{29}Si NMR ($CDCl_3$): $\delta = 11.77$ (GaN*Si*Me$_3$), 14.26 ppm (CN*Si*Me$_3$).

Compounds 7–12: A *n*BuLi solution (15% in *n*-hexane, 0.2 mol) was added at 0 °C variously to 2,6-di(isopropyl)aniline (0.2 mol; **7–9**), to (*N*-isopropyl)-2,6-di(isopropyl)aniline (0.2 mol; **10**) or to (*N*-trimethylsilyl)-2,6-di(isopropyl)aniline (0.2 mol; **11**, **12**) in *n*-hexane (100 mL). After the

system had been heated at reflux for 2 h, the lithium anilide was dissolved in THF (100 mL) and slowly added variously to di(isopropyl)amino-difluoroborane (**7**, **10**, **11**), to di(isobutyl)amino-difluoroborane (**8**, **12**) or to (trimethylsilyl)methylamino-difluoroborane (**9**[13]) (0.2 mol) and the mixture was heated to reflux for 3 h. The crude product was separated from LiF by condensation of the volatile components into a cooling trap in vacuo. Compounds **7**–**12** were purified by distillation and recrystallisation from *n*-hexane.

Di(isopropyl)amino-2,6-di(isopropyl)anilino-fluoroborane (7): Yield 97%; m.p. 83°C; b.p. 70°C (0.01 mbar); ^{1}H NMR ($CDCl_3$): $\delta=1.19$ (d, $^3J_{H,H}=6.8$ Hz, 12H; C−CHMe_2), 1.19 (d, $^3J_{H,H}=6.8$ Hz, 12H; N−CHMe_2), 3.27 (sept, $^3J_{H,H}=6.8$ Hz, 2H; C−C*H*Me$_2$), 3.37 (sept, $^3J_{H,H}=6.8$ Hz, 2H; N−C*H*Me$_2$), 3.39 (d, $^3J_{H,F}=0.6$ Hz, 1H; N*H*), 7.02–7.11 ppm (m, 3H; arom. C*H*); ^{13}C NMR ($CDCl_3$): $\delta=22.43$ (N−CHMe_2), 23.40 (C−CHMe_2), 28.51 (C−CHMe$_2$), 44.58 (N−CHMe$_2$), 122.88 (*m*-*C*), 125.10 (*p*-*C*), 132.43 (*o*-*C*), 145.11 ppm (*i*-*C*); ^{11}B NMR ($CDCl_3$): $\delta=21.78$ ppm; ^{19}F NMR ($CDCl_3$): $\delta=28.98$ ppm; MS (EI): *m*/*z* (%): 306 $[M]^+$ (20), 205 (100) $[M-N(CHMe_2)_2]^+$.

Di(isobutyl)amino-2,6-di(isopropyl)anilino-fluoroborane (8): Yield 95%; m.p. 81°C; b.p. 80°C (0.01 mbar); ^{1}H NMR ($CDCl_3$): $\delta=0.91$ (d, $^3J_{H,H}=6.6$ Hz, 12H; CH_2−CHMe_2), 1.19 (d, $^3J_{H,H}=6.9$ Hz, 12H; C−CHMe_2), 1.88 (m, 2H; CH_2−C*H*Me$_2$), 2.72 (d, $^3J_{H,H}=7.4$ Hz, 4H; CH_2−CHMe$_2$), 3.29 (sept, $^3J_{H,F}=6.9$ Hz, 2H; C−C*H*Me$_2$), 3.49 (d, $^3J_{H,F}=17.2$ Hz, 1H; N*H*), 7.13–7.36 ppm (m, 3H; arom. C*H*); ^{11}B NMR ($CDCl_3$): $\delta=21.99$ ppm; ^{13}C NMR ($CDCl_3$): $\delta=20.13$ (CH_2−CHMe_2), 23.46 (C−CHMe_2), 26.93 (CH_2−CHMe$_2$), 28.43 (C−CHMe$_2$), 53.56 (CH_2−CHMe$_2$), 122.85 (*m*-*C*), 125.17 (*p*-*C*), 136.04 (*o*-*C*), 145.13 ppm (*i*-*C*); ^{19}F NMR ($CDCl_3$): $\delta=22.75$ ppm; MS (EI): *m*/*z* (%): 334 $[M]^+$ (18), 291 $[M-CHMe_2]^+$ (18).

Di(isopropyl)amino-(*N*-2,6-tri(isopropyl)anilino)-fluoroborane (10): Yield 97%; b.p. 110°C (0.01 mbar); ^{1}H NMR ($CDCl_3$): $\delta=0.92$ [d, $^3J_{H,H}=6.7$ Hz, 12H; N−(CHMe_2)$_2$], 1.19 (d, $^3J_{H,H}=6.8$ Hz, 6H; C−CHMe_2), 1.22 (d, $^3J_{H,H}=6.8$ Hz, 6H; C−CHMe_2), 1.29 (dd, $^3J_{H,H}=6.7$, $^3J_{H,F}=1.9$ Hz, 6H; C−CHMe_2), 3.00 [sept, $^3J_{H,H}=6.7$ Hz, 2H; N−(C*H*Me$_2$)$_2$], 3.02 (sept, $^3J_{H,H}=6.7$ Hz, 2H; N−C*H*Me$_2$), 3.30 (sept, $^3J_{H,H}=6.8$ Hz, 2H; C−C*H*Me$_2$), 7.01–7.15 ppm (m, 3H; arom. C*H*); ^{13}C NMR ($CDCl_3$): $\delta=22.56$ (d, $^3J_{C,F}=4.3$ Hz; N−CHMe_2), 22.87 [N−(CHMe_2)$_2$], 23.46 (C−CHMe$_2$), 24.64 (C−CHMe$_2$), 27.78 (C−CHMe$_2$), 44.35 [N−(CHMe$_2$)$_2$], 55.29 (N−CHMe$_2$), 124.26 (*m*-*C*), 125.54 (*p*-*C*), 142.14 (*o*-*C*), 146.94 ppm (*i*-*C*); ^{11}B NMR ($CDCl_3$): $\delta=23.39$ ppm; ^{19}F NMR ($CDCl_3$): $\delta=48.86$ ppm; MS (EI): *m*/*z* (%): 348 (15) $[M]^+$, 333 (100) $[M-Me]^+$.

Di(isopropyl)amino-(*N*-trimethylsilyl-2,6-di(isopropyl)anilino)-fluoroborane (11): Yield 95%; m.p. 83°C; b.p. 80°C (0.01 mbar); ^{1}H NMR ($CDCl_3$): $\delta=0.10$ [d, $^5J_{H,F}=2.2$ Hz, 9H; Si(CH_3)$_3$], 0.97 [d, $^3J_{H,H}=6.5$ Hz, 12H; C−CH(CH_3)$_2$], 1.18 [d, $^3J_{H,H}=6.8$ Hz, 6H; N−CH(CH_3)$_2$], 1.25 [d, $^3J_{H,H}=6.8$ Hz, 6H; N−CH(CH_3)$_2$], 2.94 (sept, $^3J_{H,H}=6.5$ Hz, 2H; C−C*H*Me$_2$), 3.41 (sept, $^3J_{H,H}=6.8$ Hz, 2H; N−C*H*Me$_2$), 6.8–7.07 ppm (m, 3H; arom. C*H*); ^{13}C NMR ($CDCl_3$): $\delta=1.75$ [Si(CH_3)$_3$], 22.44 [C−CH(CH_3)$_2$], 24.19 [N−CH(CH_3)$_2$], 25.20 [N−CH(CH_3)$_2$], 27.77 [C−CHMe$_2$], 44.07 [d, $^3J_{C,F}=2.4$ Hz, N−CHMe$_2$], 123.59 (*p*-*C*), 124.99 (*m*-*C*), 140.81 (*o*-*C*), 145.74 ppm (*i*-*C*); ^{11}B NMR ($CDCl_3$): $\delta=22.61$ ppm; ^{19}F NMR ($CDCl_3$): $\delta=53.00$ ppm; ^{29}Si NMR ($CDCl_3$): $\delta=8.30$ ppm (d, $^3J_{Si,F}=9.6$); MS (EI): *m*/*z* (%): 378 $[M]^+$ (3), 363 $[M-Me]^+$ (100), 335 $[M-CHMe_2]^+$ (90).

Di(isobutyl)amino-(*N*-trimethylsilyl-2,6-di(isopropyl)anilino)-fluoroborane (12): Yield 88%; b.p. 89°C (0.01 mbar); ^{1}H NMR ($CDCl_3$): $\delta=0.15$ [d, $^5J_{H,F}=2.2$ Hz, 9H; Si(CH_3)$_3$], 0.71 [d, $^3J_{H,H}=6.7$ Hz, 12H; C−CH(CH_3)$_2$], 1.22 [d, $^3J_{H,H}=6.9$ Hz, 6H; CH_2−CH(CH_3)$_2$], 1.25 [d, $^3J_{H,H}=6.9$ Hz, 6H; CH_2−CH(CH_3)$_2$], 2.43 (d, $^3J_{H,H}=6.1$ Hz, 4H; CH_2CHMe$_2$), 2.92 (sept, $^3J_{H,H}=6.7$ Hz, 2H; C−C*H*Me$_2$), 3.39 (m, 2H; CH_2C*H*Me$_2$), 7.06–7.13 ppm (m, 3H; arom. C*H*); ^{11}B NMR ($CDCl_3$): $\delta=21.73$ ppm; ^{13}C NMR ($CDCl_3$): $\delta=1.75$ [d, $^4J_{C,F}=4.5$ Hz, Si(CH_3)$_3$], 20.18 [C−CH(CH_3)$_2$], 24.28 [CH_2CH(CH_3)$_2$], 25.09 [CH_2CH(CH_3)$_2$], 27.29 (C−CHMe$_2$), 27.81 (CH_2CHMe$_2$), 52.56 (d, $^3J_{C,F}=4.7$ Hz; CH_2CHMe$_2$), 123.16 (*p*-*C*), 125.25 (*m*-*C*), 140.75 (d, $^4J_{C,F}=8.4$ Hz; *o*-*C*), 145.87 ppm (*i*-*C*); ^{19}F NMR ($CDCl_3$): $\delta=46.06$ ppm; ^{29}Si NMR ($CDCl_3$): $\delta=8.00$ ppm (d, $^3J_{Si,F}=9.5$ Hz); MS (EI): *m*/*z* (%): 406 $[M]^+$ (6), 391 $[M-Me]^+$ (18), 363 $[M-CHMe_2]^+$ (100).

Compounds 13, 15 and 16: A solution of trichloroalane (0.1 mol) in diethyl ether (50 mL) was added at −20°C to a solution either of **11** (0.1 mol) in diethyl ether (100 mL) or of **12** (0.1 mol) in diethyl ether (50 mL) and dichloromethane (50 mL), and the mixture was stirred for 4 h at 0°C. Compounds **13** and **15** were crystallised from diethyl ether at 0°C and **16** at room temperature.

Di(isopropyl)amine-2,6-di(isopropyl)anilino-*n*-butyl-borenium tetrachloroaluminate (13): Yield 20%; decomposition at 25°C.

Di(isobutyl)amine-[(*N*-dimethylfluorosilyl)-2,6-di(isopropyl)anilino)]-methylborenium tetrachloroaluminate (15): Yield 18%; decomposition at 38°C; MS (EI): *m*/*z* (%): 407 $[M-AlCl_4]^+$ (10), 278 $[M-NH(iBu)_2]^+$ (30).

Di(isobutyl)amine aluminium (16): M.p. 77°C; ^{1}H NMR ($CDCl_3$): $\delta=1.06$ (d, $^3J_{H,H}=6.7$ Hz, 12H; CHMe_2), 2.19 (m, 2H; C*H*Me$_2$), 2.94 ppm (m, 4H; CH_2); ^{13}C NMR ($CDCl_3$): $\delta=20.24$ (CHMe_2), 25.63 (*C*HMe$_2$), 56.04 ppm (CH_2); ^{27}Al NMR ($CDCl_3$): $\delta=103.41$ ppm.

Crystal structure determination: Single crystals were selected from Schlenk flasks under argon and covered with perfluorated polyether oil on a microscope slide, which in the case of **6** was cooled with a nitrogen gas flow by use of the X-TEMP 2.[24] Suitable crystals were mounted on the tip of a glass fibre fixed to a goniometer head and shock-cooled with the crystal cooling device. All data were collected with use of monochromated $Mo_{K\alpha}$ radiation ($\lambda=71.073$ pm) variously with a Bruker TXS rotating anode (**6**), a Bruker Smart Apex II with D8 goniometer (**7**, **9**, **10**, **11**) or a Stoe IPDS II with image plate detector (**13**, **16**).

Bruker system: The cell determination was performed with the aid of the APEX2 program package (Bruker AXS, 2007) followed by integration with SAINT (Bruker AXS, 2007). SADABS (Bruker AXS, 2006) was used for the empirical absorption correction.

IPDS system: The cell determination and integration was done with the aid of X-AREA (Stoe & Cie, 2002) software.

The data were reduced in XPREP and the structures were solved by direct methods with SHELXS.[25] The refinement against F^2 was done with SHELXL.[26]

CCDC-713642 (**6**), 713643 (**7**), 713644 (**9**), 713645 (**10**), 713646 (**11**), 713647 (**13**) and 713648 (**16**) 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.

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgesellschaft, the Volkswagen Stiftung, the Fonds der Chemischen Industrie (H.O.), and CHEMETALL GmbH Frankfurt.

[1] For example, a) U. Flierler, D. Leusser, H. Ott, G. Kehr, G. Erker, S. Grimme, D. Stalke, *Chem. Eur. J.* **2009**, *15*, 4595–4601, preceding paper; b) K.-A. Østby, G. Gundersen, A. Haaland, H. Nöth, *Dalton Trans.* **2005**, 2284–2291; c) K.-A. Østby, A. Haaland, G. Gundersen, H. Nöth, *Organometallics* **2005**, *24*, 5318–5328; d) A. Beste, O. Krämer, A. Gerhard, G. Frenking, *Eur. J. Inorg. Chem.* **1999**, 2037–2045; e) V. Jonas, G. Frenking, M. T. Reetz, *J. Am. Chem. Soc.* **1994**, *116*, 8141–8753; f) A. Haaland, *Angew. Chem.* **1985**, *97*, 1017–1032; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992–1007.

[2] P. Paetzold, *Adv. Inorg. Chem.* **1987**, *31*, 123–170.

[3] a) P. Kölle, H. Nöth, *Chem. Ber.* **1986**, *119*, 3849–3855; b) M. Haase, U. Klingebiel, *Angew. Chem.* **1985**, *97*, 335–336; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 324; c) P. Kölle, H. Nöth, *Chem. Rev.* **1985**, *85*, 399–418; d) H. Nöth, S. Weber, B. Rasthofer, C. Narula, A. Konstantinov, *Pure Appl. Chem.* **1983**, *55*, 1453–1461; e) P. Paetzold, A. Richter, T. Thijssen, S. Würtenberg, *Chem. Ber.* **1979**, *112*, 3811–3827.

[4] a) P. Geymayer, E. G. Rochow, U. Wannagat, *Angew. Chem.* **1964**, *76*, 499–500; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 633; b) C. R. Russ, A. G. MacDiarmid, *Angew. Chem.* **1964**, *76*, 500–501; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 509.
[5] H. Ott, C. Matthes, S. Schmatz, U. Klingebiel, D. Stalke, *Z. Naturforsch. B* **2008**, *63*, 1023–1026.
[6] For example: a) E. Heilbronner, V. Hornung, F. H. Pinkerton, S. F. Thames, *Helv. Chim. Acta* **1972**, *55*, 289–302; b) H. Bock, H. Alt, H. Seidl, *J. Am. Chem. Soc.* **1969**, *91*, 355–361; c) H. Bock, H. Alt, H. Seidl, *Angew. Chem.* **1968**, *80*, 906–907; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 885–886; d) H. Bock, H. Seidl, *J. Am. Chem. Soc.* **1968**, *90*, 5694–5700.
[7] a) H. Ott, C. Däschlein, D. Leusser, D. Schildbach, T. Seibel, D. Stalke, C. Strohmann, *J. Am. Chem. Soc.* **2008**, *130*, 11901–11911; b) N. W. Mitzel, K. Vojinovic, R. Fröhlich, T. Foerster, H. E. Robertson, K. B. Boriseko, D. W. H. Rankin, *J. Am. Chem. Soc.* **2005**, *127*, 13705–13713; c) N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, *126*, 5563–5568; d) N. Kocher, C. Selinka, D. Leusser, D. Kost, I. Kahlikhman, D. Stalke, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1777–1793; e) C. Lecomte, M. Souhassou, S. Pillet, *J. Mol. Struct.* **2003**, *647*, 53–64.
[8] G. Huber, H. Schmidbaur, *Z. Naturforsch. B* **1998**, *53*, 1103–1108 and references therein.
[9] a) E. A. V. Ebsworth, *Acc. Chem. Res.* **1987**, *20*, 295–301; b) H. Bürger, *Angew. Chem.* **1973**, *85*, 519–532; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 474–486.
[10] a) B. Böck, U. Braun, T. Habereder, P. Mayer, H. Nöth, *Z. Naturforsch. B* **2004**, *59*, 681–684; b) H. Nöth, W. Rattay, U. Wietelmann, *Chem. Ber.* **1987**, *120*, 859–861.
[11] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–768.
[12] P. Kölle, H. Nöth, *Chem. Rev.* **1985**, *85*, 399–418.
[13] Only one other compound without further inorganic substituents or ring systems at the nitrogen atoms connected to the boron atom is reported to the best of our knowledge (see ref. [16]).
[14] Synthesis already published (see W. Luthin, J.-G. Stratmann, G. Elter, A. Meller, A. Heine, H. Gornitzka, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1995–2000)
[15] P. Rademacher, *Strukturen organischer Moleküle*, VCH, Weinheim, **1987**.
[16] W. Luthin, G. Elter, A. Heine, D. Stalke, G. M. Sheldrick, A. Meller, *Z. Anorg. Allg. Chem.* **1992**, *608*, 147–152.
[17] C. Matthes, U. Klingebiel, S. Deuerlein, H. Ott, D. Stalke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2402–2410.
[18] Cambridge Structural Database, v5.29 (November 2007), Cambridge Crystallographic Data Centre, Cambridge, **2007**.
[19] C. K. Narula, H. Nöth, *Inorg. Chem.* **1984**, *23*, 4147–4152.
[20] The $AlCl_3/CH_2Cl_2$ mixture is a possible source for the required protons (see O. Graalmann, M. Hesse, U. Klingebiel, W. Clegg, M. Haase, G. M. Sheldrick, *Angew. Chem.* **1983**, *95*, 630–631; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 621–622; O. Graalmann, M. Hesse, U. Klingebiel, W. Clegg, M. Haase, G. M. Sheldrick, *Angew. Chem. Suppl.* **1983**, *22*, 874–886).
[21] W. Clegg, U. Klingebiel, J. Neemann, G. M. Sheldrick, *J. Organomet. Chem.* **1983**, *249*, 47–54.
[22] D. F. Grant, R. C. G. Killean, J. L. Lawrence, *Acta Crystallogr. Sect. B* **1969**, *25*, 377–379.
[23] N. Burford, R. G. Hicks, B. W. Royan, B. Borecka, T. S. Cameron, *Acta Crystallogr. Sect. C* **1991**, *47*, 1066–1067.
[24] a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171–178; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615–619.
[25] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.
[26] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

Received: December 18, 2008
Published online: March 23, 2009

