Contributions to the Chemistry of Boron, 231[◇]

Synthesis and Structures of Borylated Hydrazines[☆]

Herbert Hommer, Heinrich Nöth*, Hermann Sachdev, Martin Schmidt, and Holger Schwenk

Institut für Anorganische Chemie der Universität München,
Meiserstraße 1, D-80333 München, Germany

Received June 12, 1995

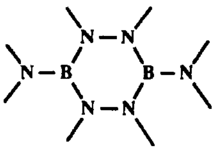
Key Words: Hydrazines, *N,N'*-bis(diphenylboryl)-*N,N'*-dimethyl-, *N,N*-bis(diphenylboryl)-*N',N'*-dimethyl-, *N,N'*-bis(dimethylphenylsilyl)-, *N,N'*-bis(chloromesitylboryl)-*N*-phenyl-*N'*-(trimethylsilyl)- / 1,2,4,5,3,6-Tetrazadiborinane, 1,2,4,5-tetrakis(*tert*-butyldimethylsilyl)-3,6-difluoro- / Triazadiborolidine, dihydro-, derivative

The diboration of the diazene $PhN{=}NSiMe_3$ (**15**) by diborane(4) derivatives provides a new synthetic route to *N,N'*-diborylated hydrazines. The product formed depends on the type of the diborane(4) compound. Thus, addition of dimesityldiboron dichloride to **15** in a 1:1 ratio afforded (mesClB)PhN−N($SiMe_3$)(BClmes) (**16**) while bis(dimethylamino)diboron dichloride was found to react in a 1:2 ratio to give a triazadiborolidine derivative **17**. In addition, it was demonstrated that in the solid state $Me_2N{-}N(BPh_2)_2$ (**8**) is a derivative of a three-membered dihydroazadiboriridine **C** while its isomer, (Ph_2B)MeN−NMe(BPh_2) (**7**), forms no BN coordinative bond. The new 3,6-difluoro-1,2,4,5-tetraza-3,6-diborine **13** shows a twist conformation. The molecular structures of all these compounds were determined by X-ray crystal structure analysis, and the influence of the B substituent on the conformation is discussed.

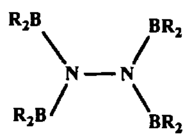
Hydrazine itself as well as its organyl derivatives usually adopt the *gauche* conformation as a consequence of interactions between lone pairs of electrons at the adjacent nitrogen atoms and polar bonds[2]. The dihedral angle RNNR (R = H, alkyl, aryl) depends, however, on the bulkiness of groups R and can be influenced by incorporating the N−N unit into ring systems. Moreover, the configuration at the N atoms can be altered and controlled e.g. by using acyl substituents. Thus, *N,N'*-diformylhydrazine shows tricoordinated planar N atoms and *trans*-oriented formyl groups[3]. This planarization also occurs when boryl groups are introduced as substituents. Compound **1** was the first example where this was demonstrated by X-ray crystallography[4]. The tetraborylated compound **2** containes also tricoordinated planar nitrogen atoms, and its $B_2N(N)$ groups are almost perpendicularly oriented to one another[5]. Further examples are compounds **3**, **4**[6], **5**[7], and **6**[8].

All these compounds show no tendency to dimerize or oligomerize due to electronic and/or steric effects of the substituents. However, it has been shown for compounds of type $Me_2N{-}N(BR_2)_2$ (R = Ph) that they contain tri- and tetra-coordinated boron atoms or that they are fluxional (R = Me)[9]. In either of the two cases it was not possible to discern between the two equilibria as depicted in equation (1).

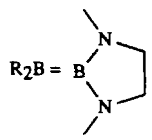
So far it is still an open question which of these equilibria are operative[9]. For this reason we investigated the structures of (diphenylboryl)hydrazines in the solid state and we report in this paper also on a new synthetic route to borylated hydrazines.

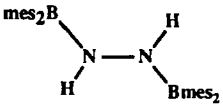


1

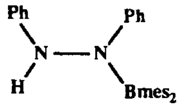


2

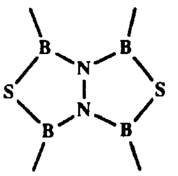




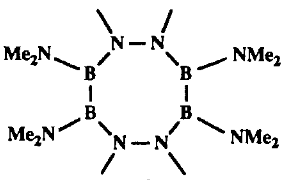
3



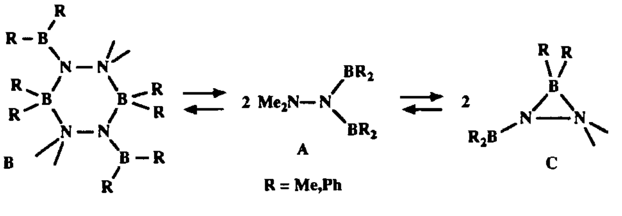
4



5



6

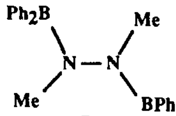


(1)

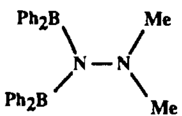
[◇] Part 230: Ref.[1].

(Diphenylboryl)hydrazines

The synthesis of compounds $Ph_2B(Me)N-N(Me)BPh_2$ (**7**) and $(Ph_2B)_2N-NMe_2$ (**8**) is already described[9]. However, it remained an open question whether compound **8** is present in solution in the form of **B** or **C**.

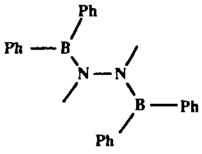


7

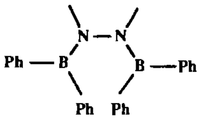


8

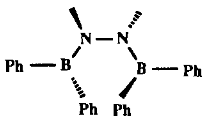
The bis(diphenylboryl)hydrazine **7** was already anticipated by its ^{11}B-NMR spectrum to feature tricoordinated boron atoms in solution ($\delta^{11}B = 41.5$). There is only a single ^{1}H-NMR signal for the Me groups and a multiplet for the phenyl protons. The ^{13}C-NMR spectrum shows two sets of signals for the phenyl groups and one resonance for the methyl carbon atoms ($\delta^{13}C = 40.1$). These data are consistent with a molecule of C_{2h}, C_{2v} or C_2 symmetry (see formulas **D** to **F**) and hindered rotation about the BN bonds, but they do not allow to us to distinguish between these three possibilities. However, for steric reasons it is very unlikely that the phenyl groups in compound **7** are coplanar with the planar BNNB skeleton, and, therefore, the *gauche* conformation **F** having C_2 symmetry is the most likely alternative. Since compound **7** crystallized readily its structure was determined by X-ray-crystallographic methods. Figure 1 depicts the result.



D C_{2h}



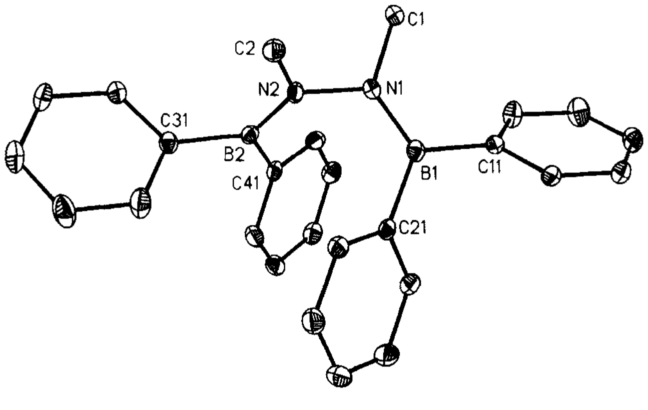
E C_{2v}



F C_2

The sum of bond angles at B and N is 360°, and these atoms can consequently be regarded as being sp^2-hybridized. However, they are not located in a plane with *trans* orientation of the Ph_2B groups as the formyl groups in *N,N'*-diformylhydrazine[3]. Actually, the B–N–N–B dihedral angle is 60.2°, proving the *gauche* conformation of the molecule. The bond angles C–N–B (126.4, 124.9°) reflect the steric demand of the diphenylboryl groups. Single BC bond lengths of sp^2-sp^2 type (average 1.583 Å) are present, and this is in consonance with a torsion of the benzene rings out of the respective N_2BC planes by 41 or 48° and 107.3 or 94.3°, respectively. The BN bonds are short, indicate BN-π bonding, and stress the argument for hindered rotation about these bonds. The NN bond in **7** was found to be 1.435 Å which is 0.02 Å shorter than in hydrazine itself[10]. This small effect is most likely due to the rehybridization of the N atoms from sp^3 in hydrazine to sp^2 in **7**. The *gauche* conformation found for the solid state seems to be retained in solution in consonance with the NMR data.

Figure 1. ORTEP plot of the molecular structure of **7** in the crystal. H atoms omitted for clarity. Thermal ellipsoids represented on the 25% probability scale. Estimated standard deviations are given in parentheses. – Selected bond lengths [Å]: N1–N2 1.435(3), B1–N1 1.403(4), B2–N2 1.397(4), N1–C1 1.468(3), N2–C2 1.469(3), B1–C11 1.583(4), B1–C21 1.585(4), B2–C31 1.584(6), B2–C41 1.581(4). – Selected bond angles [°]: B1–N1–N2 121.7(2), N1–N2–B2 122.9(2), C1–N1–B1 126.4(2), C1–N1–B1 120.2(3), C31–B2–N2 118.2(3), C41–B2–N2 122.5(3). – Dihedral angles [°]: B1–N1–N2–B2 –60.3; C1–N1–N2–C2 –66.7



In contrast to compound **7**, the isomer **8** exhibits in solution three ^{1}H- and ^{13}C-NMR signals each for the methyl groups, and 15 ^{13}C-NMR signals as well as a broad signal for the boron-bound C atom. If there were four different phenyl groups in **8** a total of 24 resonances would be expected, and since actually only 16 were observed this suggests that two out of four phenyl groups are equivalent. Consequently, some signals must be isochronous. Moreover, three ^{11}B resonances ($\delta = 39.3$, 31.0, 13.2) are observed, which indicate two tricoordinated boron atoms and one tetracoordinated boron atom. These data are not compatible with the presence of a single molecule in solution but with an equilibrium **A**/**B**/**C** as depicted by eq. (1) if only monomeric species are involved. If we assume free rotation about the respective BC bonds three kinds of Ph_2B groups are present in solution.

From the NMR data an equilibrium constant $K = [\mathbf{C}]/[\mathbf{A}] = 2.33$ has was derived which points to the three-membered isomer of **8**. In order to definitely exclude a dimeric species $(\mathbf{8})_2$ in solution and to determine the true structure of compound **8** an X-ray structural analysis was performed. The results are shown in Figure 2.

The three-membered N_2B ring is the most striking feature of the molecular structure of compound **8**. The ring contains a tetracoordinated B and N atom as well as tricoordinated nitrogen atom. The second diphenylboryl group functions as an exocyclic substituent. The three-membered ring is rather unsymmetrical primarily due to the two significantly different ring BN bond lengths. Both are clearly single bonds, the shorter one corresponds with the BN bond length found in cubic boron nitride[11] and the longer with a BN coordinate bond[12]. The NN bond length is practically the same as in hydrazine[10], a result not necessarily anticipated because one would expect a shortening of this bond if one of the two nitrogen atoms becomes sp^2-hybridized. This effect is counterbalanced, however, by the formation of a tetracoordinated N atom.

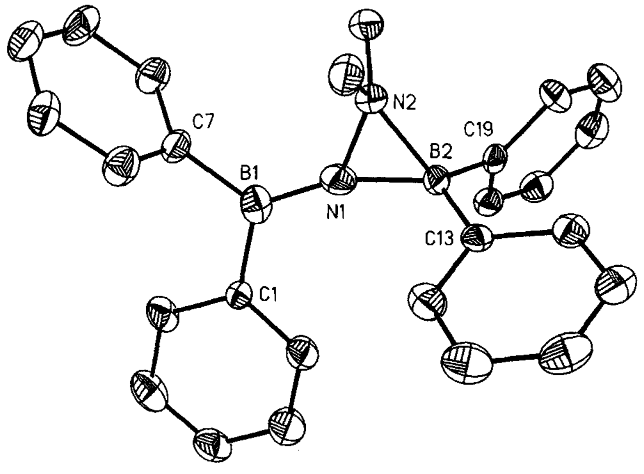


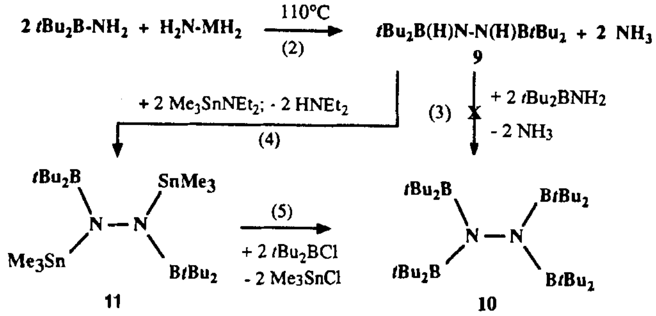
Figure 2. ORTEP plot of the molecular structure of **8** in the crystal. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represented on the 25% probability scale. Esd's in parentheses. – Selected bond lengths [Å]: N1–N2 1.46(1); N1–B1 1.34(1), N2–B2 1.65(1), N1–B2 1.55(1), N2–C25 1.49(1), N2–C26 1.47(1), B1–C1 1.63(1), B1–C7 1.59(1), B2–C13 1.61(1), B2–C19 1.59(1). – Selected bond angles [°]: B1–N1–B2 162.4(7), B1–N1–N2 126.8(7), B2–N1–N2 66.8(5), B2–N2–N1 59.1(5), N1–N2–C25 113.2(6), N1–N2–C26 116.5(6), B2–N2–C25 118.3(7), B2–N2–C26 121.7(6), N1–B1–C1 118.9(8), N1–B1–C7 122.3(9), C1–B1–C7 118.7(7), N2–B2–C13 114.2(6), N2–B2–C19 113.1(6), C13–B2–C19 119.3(8), N1–B2–N2 54.9(5), N1–B2–C13 116.4(7), N1–B2–C19 121.5(6). – Dihedral angles: B1–N1–N2–B2 –170.1, C1–B1–N1–N2 –176.1

In contrast to the endocyclic BN bond of compound **8** the length of the exocyclic BN bond (1.34 Å) is typical of a strong BN bond with a high π-bond character. Indeed, the planes N(N)BB and C_2BN are almost coplanar (interplanar angle 5.8 °) with one another allowing almost optimal conditions for BN π-bonding. The two BC bond lengths to the *exocyclic* diphenylboryl groups are significantly different. This is due to the fact that one of the phenyl groups is almost coplanar with the C_2BN plane (angle between planes 5.9 °), exhibiting a short BC bond length while the longer one belongs to the phenyl group that is twisted out of this plane by 102.1 °. The former BC bond is obviously involved in BC π-bonding. The BC bonds of the tetracoordinated boron atoms are of equivalent length and lie in the typical range of tetracoordinated arylboron compounds (1.6–1.7 Å)[13].

N,N′-Bis(di-*tert*-butylboryl)hydrazine (9)

So far no tetraborylated hydrazine has been described except compound **2**. Attempts to prepare $(Me_2B)_2N-N(BMe_2)_2$ failed in our hands due to ready BMe_3 formation from the anticipated tetrakis(dimethylboryl)hydrazine. Larger organyl groups may possibly prevent the elimination of BR_3. For this reason we attempted the synthesis of tetrakis(di-*tert*-butylboryl)hydrazine (**10**). The transamination at 110°C described by equations (2) and (3) did not lead to the formation of compound **10** but gave good yields of the *N,N′*-diborylated hydrazine **9**.

Compound **9** is a low-melting solid, and its ^{11}B-NMR signal at δ = 47.4 proves the presence of a C_2BN structural unit with a tricoordinated boron atom[14]. There are two ^1H and four ^{13}C resonances in the ^1H- and ^{13}C-NMR spectrum of the compound, respectively, indicating that there are two kinds of *tert*-butyl groups which most likely result from hindered rotation about the BN bonds. This would be in accord with a C_2 symmetry of the molecule.



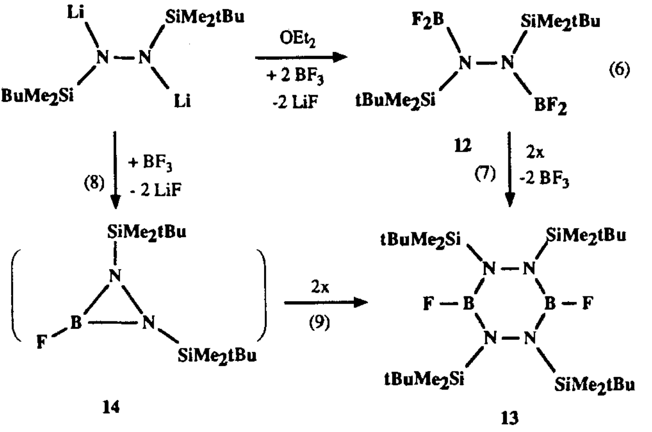
Since further transamination of **9** by treatment with tBu_2BNH_2 was not achieved we used the more basic amide Me_3SnNEt_2, which should lead to the formation of compound **11** as a more reactive borylhydrazine. However, a reaction as described by equation (4) did not proceed at temperatures up to 100 °C. This failure is most likely due to steric hindrance resulting from the di-*tert*-butylboryl groups which prevent the electrophilic attack of the Me_3Sn unit on the hydrazino moiety or of its Et_2N group on the NH protons of compound **9**. Consequently, a reaction of **11** with a di-*tert*-butylboron halide to produce eventually **10** could not be investigated.

(Fluoroboryl)hydrazines

Recently, a number of hydrazinoboranes containing BF bonds were reported[15]. They were obtained by reaction of *N*-lithiohydrazines with $BF_3 \cdot OEt_2$. We also used this route for the preparation of (fluoroboryl)hydrazines. The reaction described by equation (6) provided the oily compound **12** in yields up to 93%. Compound **12** decomposed during distillation with formation of BF_3 and the tetrazadiborine **13**. This latter compound was more readily prepared by a reaction described by eq. (8) and (9). Actually, we had expected the diazaboriridine **14** as product of reaction (8), due to the bulky substituents at the hydrazino nitrogen atoms, but this was not the case, and **13** was formed instead.

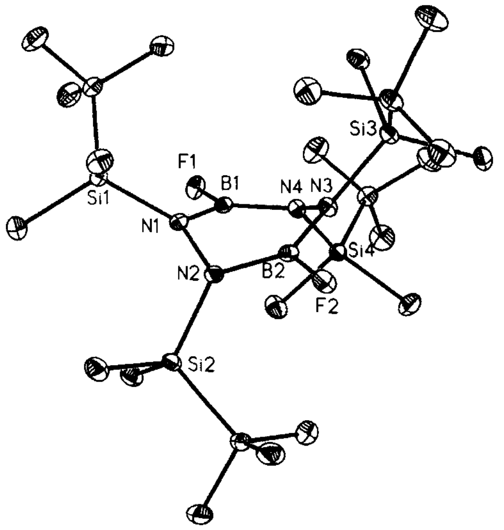
Compound **12** shows a single resonance in the ^{11}B-NMR spectrum at δ = 20.4 which is in accordance with a F_2BN structure element[14]. ^1H- and ^{13}C-NMR data are compatible with the suggested six-membered ring structure of C_2 symmetry. $\delta^{29}Si$ = 22.7 indicates a Si nucleus which is deshielded by 18 ppm relative to the starting *N,N′*-disilylhydrazine. This effect is most likely due to the trigonal-planar nitrogen atoms and BN π-bonding in compound **13** and is in accordance with two ^{19}F-NMR signals at δ = –117.3

and −121.2. $^{19}F^{11}B$ coupling cannot be observed, but this is not unusual for aminodifluoroboranes[14].



The ^{11}B resonance for compound **13** at δ = 30.6 lies in the range for a N_2BF structural unit in an unstrained environment as expected for a six-membered B_2N_4 ring system[15a,16]. However, there are twice as many ^1H- and ^{13}C-NMR signals than expected for the suggested structure, irrespective of whether the six-membered ring would be present in planar, twisted, or in a boat conformation. The most likely reason for this observation is the presence of rotamers resulting from steric overcrowding. However, there was no merging of these signals at temperatures up to 80 °C.

Figure 3. ORTEP representation of the molecular structure of compound **13**. Thermal ellipsoids are represented on the 25% probability scale. H atoms are omitted for clarity. Esd's in parentheses. − Selected bond lengths [Å]: B1−F1 1.350(3), B2−F2 1.353(3), B1−N1 1.422(3), B1−N4 1.423(3), B2−N2 1.435(3), B2−N3 1.418(3), N1−N2 1.488(3), N3−N4 1.490(3), N1−Si1 1.785(2), N2−Si2 1.780(2), N3−Si3 1.783(2), N4−Si4 1.780(2). − Selected bond angles [°]: N1−B1−N4 123.0(2), B1−N1−N2 112.5(2), N1−N2−B2 11.8(2), N2−B2−N3 123.3(2), B2−N3−N4 112.3(2), N3−N4−B1 11.8(2), F1−B1−N1 118.0(2), F2−B2−N3 118.5(2), B1−N1−Si1 119.9(2), N1−N2−Si2 117.0(1), B2−N3−Si3 128.2(2), N3−N4−Si4 118.4(1). − Dihedral angles [°]: Si1−N1−N2−Si2 −90.4, Si3−N3−N4−Si4 −78.1

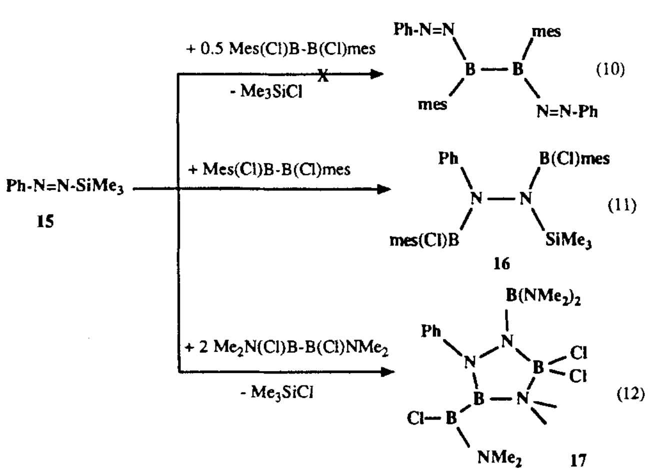


The X-ray structure determination of compound **13** revealed a six-membered ring system as shown in Figure 3. The molecule itself has no crystallographically imposed symmetry but adopts almost D_2-point group symmetry. Amongst the structural parameters of interest are the NN bonds. Their lengths slightly exceed that of the NN bond of hydrazine itself in spite of the fact that the four nitrogen atoms are all present in an almost trigonal-planar environment (sum of bond angles is 353° on average). However, the twist conformation gives evidence that the *gauche* effect is still operative. The dihedral angles were found to be −43.7° for B1−N1−N2−B2, −44.4° for B1−N4−N3−B2, −90.4° for Si1−N1−N2−Si2, and −78.1° for Si3−N3−N4−Si4. As expected for a compound of a diaminoboryl type we observe longer BN bonds than in the borylhydrazine **7**. Thus, the relatively long NN bonds as well as the deviation from full planarity at the N atoms seem to result from the steric interaction of the bulky silyl groups.

A New Route to Boryl-Substituted Hydrazines

So far boryl-substituted hydrazines were obtained from the respective hydrazine and a boron halide or a borane, a thioborane, or an aminoborane[17]. Also silylated hydrazines or *N*-lithiohydrazines were used in reactions with boron halides $R_{3-n}BHal_n$ to achieve the synthesis of these types of compounds[9,15]. We now came across a new route to hydrazinoboranes in our studies related to boryldiazenes[18]. We observed that the silyldiazene **15** acts as an oxidizing species. The boron-boron bond of the diborane (4) derivative is opened and the diazene reduced to an *N,N'*-bis(boryl)diazane, e. g. an *N,N'*-bis(boryl)hydrazine.

Thus, the blue hexane solution of PhN=NSiMe$_3$[19] was rapidly decolorized when treated at −40 °C with *B,B'*-dichloro-*B,B'*-dimesityldiborane(4). This color change already indicated that the SiN bond of the diazene was left untouched because boryl-substituted diazenes are orange to dark red in color[18] and this *excludes* a reaction according to equation (10).



Actually, the starting materials did not react in a 2:1 but in a 1:1 molar ratio with the formation of the *N,N'*-bis(chloromesitylboryl)hydrazine **16** as the sole product as described by equation (11).

In contrast to the reaction of mes(Cl)B−B(Cl)mes with the diazene **15** we found that $Me_2N(Cl)B-B(Cl)NMe_2$ reacts significantly slower. No reaction with $PhN=NSiMe_3$ occurred at −40 °C in hexane solution, but at 10 °C the formation of Me_3SiCl started. At 10 °C a colorless precipitate formed. For a quantitative conversion of the blue diazene into the colorless solid a molar ratio of 2:1 was required. Consequently, this reaction takes a different route than that described by equation (11). NMR spectroscopy revealed not only the formation of Me_3SiCl in solution but also that the product **17** is devoid of the Me_3Si substituent. Compound **17** shows three signals in its ^{11}B-NMR spectrum at δ = 39.3, 29.7, and 10.8 in a 2:2:1 intensity ratio. Moreover, there are seven signals for the Me groups in the ^{1}H-NMR spectrum besides signals for the phenyl group. Although these data prove the presence of a tetracoordinated boron atom and two tricoordinated boron moieties no definite conclusion could be drawn concerning the structure of the compound which should have the composition $B_4(NMe_2)_4Cl_3N_2Ph$ (**17**). Therefore, the structure of this molecule was determined by X-ray crystallography.

Figure 4. ORTEP representation of the molecular structure of the diborylhydrazine **16**. Esd's in parentheses. Thermal ellipsoids depicted on the 25% probability scale. − Selected bond lengths [A]: N1−N2 1.461(4), N1−B2 1.387(5), N1−C1 1.442(4), N2−B1 1.400(5), N2−Si1 1.813(3), B1−C10 1.571(6), B1−Cl1 1.805(4), B2−C19 1.579(5), B2−Cl2 1.790(4). − Selected bond angles [°]: B2−N1−N2 123.0(3), B2−N1−C1 123.1(3), C1−N1−N2 113.9(2), B−N2−Si1 126.1(2), N1−N2−Si1 118.8(7), N2−B1−C10 128.8(3), N2−B1−C21 115.2(3), C10−B1−Cl1 116.0(3), C19−B2−Cl2 118.0(3). − Dihedral angle [°]: Si1−N2−N1−C1 97.6

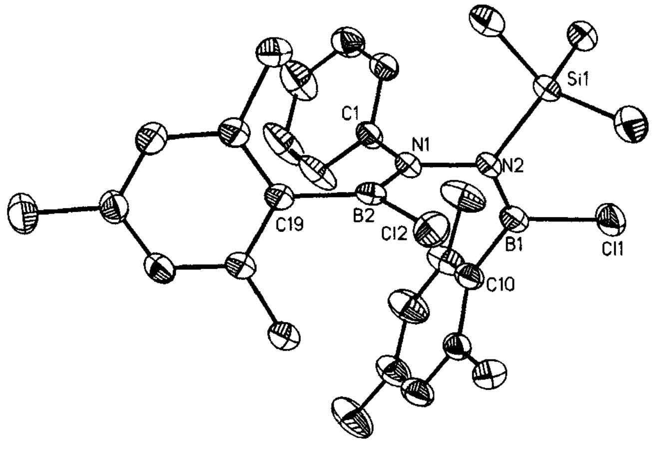
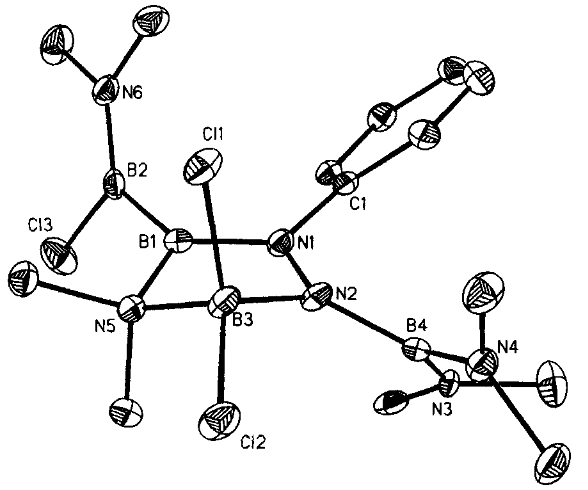


Figure 4 represents the molecular structure of **17**. It features a five-membered B_2N_3 ring in envelope conformation with an angle of 142.9° between the planes B1N1N2N5 and N2B3N5. All boron atoms in molecule **17** are strictly planarly coordinated except the tetracoordinated one, and this is almost the case also for all tricoordinated nitrogen atoms [sum of bond angles varying from 359.6° (N4) to 357.9° (N1)]. The shortest BN bond in the five-membered ring indicates double bond characteristics [B1−N1 = 1.404(6) Å]. Next comes the $B(sp^3)$-$N(sp^2)$ bond, followed by the $B(sp^2)-N(sp^3)$ bond B1−N5, and the longest bond joins atoms B3 and N5 which are both of the sp^3 type. As expected, the ring bond angles at the tetracoordinated atoms B3 (102.2°) and N5 (99.4°) are more acute than those of the tricoordinated atoms which is largest at atom N1 (113.5°).

Figure 5. ORTEP representation of the molecular structure of **17**. Esd's in parentheses. Thermal ellipsoids are represented on the 25% probability scale. − Selected bond lengths [Å]: N1−N2 1.447(5), N2−B3 1.484(6), B3−N5 1.626(6), N5−B1 1.548(6), N1−C1 1.435(5), N2−B4 1.461(6), B4−N3 1.454(6), B4−N4 1.424(6), B3−Cl1 1.909(5), B3−Cl2 1.834(5), B1−B2 1.693(7),B2−Cl3 1.834(5), B2−N6 1.363(6). − Selected bond angles [°]: B1−N1−N2 113.5(3), N1−N2−B3 104.4(3), N1−N2−B4 120.5(3), B3−N2−B4 133.8(4), N2−B3−N5 102.2(3), Cl1−B3−Cl2 108.7(2), B3−N5−B1 99.4(3), N5−B1−N1 106.2(4), B1−B2−Cl3 115.6(3), B1−B2−N6 124.4(4), B2−B1−N5 124.1(4). − Interplanar angles [°]: C1−C6/B1,N1,N2 138.7, N3,B4,N4/N1,N2,B3 35.6, N6,B2,Cl3/N1,B1,N5 67.6



Although there seems to be no reason why the BCl bonds at atom B3 should be different they nevertheless show a significant difference [1.909(5) and 1.834(5) Å]. On the other hand, the B−Cl bond at the trigonal boron atom is much shorter [1.814(5) Å], and also the BN bond at this atom [1.363(6) Å] is the shortest in this molecule and reflects strong π-bonding. In consonance with this bonding situation is the small angle of only 1.3° between the planes of atoms C7C8N6 and Cl3B2B1. Atom B4 can be regarded as the center of a triaminoborane, and indeed the BN bond lengths, although slightly different, are close to those found in $B(NMe_2)_3$[20]. This holds also for the twisting of the Me_2N groups out of the BN_3 plane. Finally, the B1−B2 bond is on the short side for a single bond in electron-precise polyboranes[21].

Discussion

The X-ray structural results on the borylated hydrazines demonstrate the effect of BN π-bonding on the conformation of these molecules. All hydrazinoboranes reported here contain tricoordinated B atoms and N atoms of the hydrazine unit suggesting BN π-bonding irrespective of the fact that the B atoms carry additional amino or hydrazino groups. However, compound **8** is a rare example of intramolecular BN coordination leading to a three-membered dihydrodiazaboriridine ring. Due to this structure the dihedral angle B−N−N−B is −170.1 °. Structural features of hydrazinoboranes were discussed in depth by Power[6], and the data reported in this paper are complementary. B−N−N−B torsion angles of the new compounds vary from 18.9 to 170.1° (Table 1). This extends the range considerably as previously observed for compounds **3** (25.9°) and **4** (88.7°) or for Ph(H)N−N(H)Ph (87°)[6] and reflects the structure of the molecules and the steric demand of the substitutents at the N atoms. BN π-bonding influences the length of the NN bond which is shorter for compounds **7** and **3** in spite of the considerable different B−N−N−B torsion angles. This bond is even shorter in *N,N'*-diphenylhydrazine which features also short NC bonds. This was attributed to electron delocalization[6]. Thus, several factors contribute to the length of the NN bond and the conformation of hydrazinoboranes. On the other hand, the BN bond length of the hydrazino unit is clearly dependent on the remaining substituent at the tricoordinated boron atom and increases in the order $B(Cl)NMe_2 < BR_2 < B(F)(N<) < B(NMe_2)_2$, e. g. with increasing electron density at the boron atom, a result that is supported by other structural data of aminoboranes[22].

Table 1. Dihedral angles τ(B−N−N−B) [°] and BN bond lengths [A] of borylated hydrazines

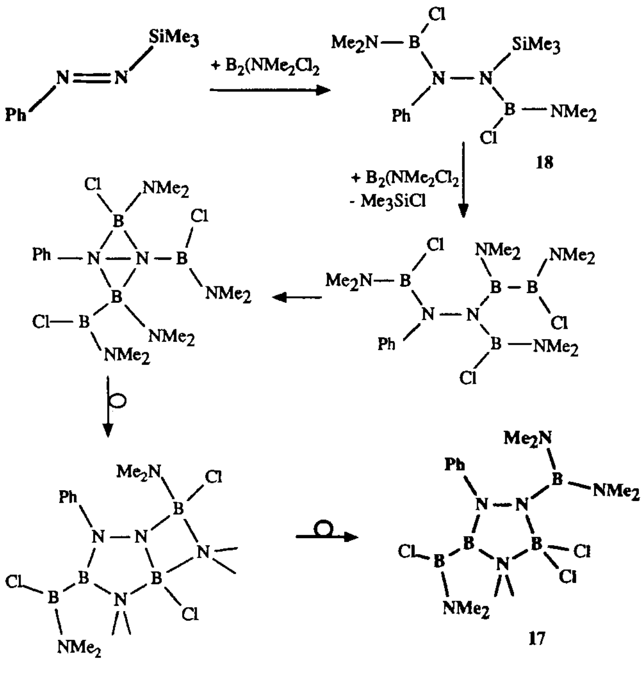
Compound	7	8	16	17	13
τ(B-N-N-B)	-60.2	170.1	100.5	-18.9/-45.3	-43.7/-44.4
d(B-N)	1.404(4)	1.36(1)	1.387(5)	1.403(6)	1.422(1)
	1.396(4)	1.64(1)	1.400(5)	1.484(5)	1.425(2)
		1.55		1.461(6)	1.423(2)
d(N-N)	1.435(3)	1.46(1)	1.461(4)	1.447(5)	1.418(3)
					1.488(3)
					1.490(3)

The synthesis of the hydrazinoboranes **7**, **8**, **12**, and **13** followed conventional ways except that a stannylhydrazine was employed for the preparation of **7**. Stannylamines are often superior to silylamines and even lithium amides to effect BN bond formation[23]. This is due to the fact that homogeneous reaction conditions can be provided in unpolar solvents, and that SnN bond polarity exceeds SiN bond polarity.

A new method for the preparation of *N,N'*-diborylated hydrazines is now available, the *N,N'*-diboration of a N=N bond by diborane(4) compounds. Two rather different examples are presented. The reaction described by e. q. (11) proceeds quantitatively to afford the *N,N'*-diborylated hydrazine **16**. Although one of its boron atoms is quite acidic as demonstrated by its ^{11}B-NMR signal (δ = 46.1)[14] neither an intramolecular association as in **8** nor an intermolecular dimerization occurs. This is obviously due to the pronounced steric effect of the mesityl group which has been successfully utilized by Power et al.[24] in their studies of low-coordinated molecules.

In contrast, $Me_2N(Cl)B-B(Cl)NMe_2$ reacts with $PhN=NSiMe_3$ quite differently. Nevertheless, an effective diboration of this diazene to compound **17** was achieved. We assume that the first step in the reaction described by eq. (12) is also a diboration of the diazene followed by SiN bond cleavage of the adduct **18** with a second molecule of $Me_2N(Cl)B-B(Cl)NMe_2$. Rearrangement of the substituents similar to a dyotopic rearrangement leads to the final product **17** (Scheme 1).

Scheme 1



It is evident that a detailed study of this new method is necessary to exploit its scope, its chemoselectivity and regiospecificity. It will also be interesting to find out wether this diboration can be metal-catalyzed as observed for the diboration of alkynes[25] and alkenes[26] with 2-(1,3,2-dioxaboranyl)-1,3,2-dioxaborolanes.

We are grateful to *Fonds der Chemischen Industrie*, *BASF Aktiengesellschaft*, and *Chemetall GmbH* for generous support. We also are indebted to Mrs. *D. Ewald*, Mrs. *E. Kiesewetter*, Mr. *P. Mayer*, and Mr. *S. Huber* for recording many spectra, and Mrs. *R. Hallmann* for experimental assistance.

Experimental

Schlenk techniques were used in all experiments with argon gas as a blanket. Solvents were dried by standard procedures. The preparation of Me_3SnNEt_2[27], tBuMe$_2$Si(Li)N−N(Li)SiMe$_2t$Bu[28], $Me_2N-N(SnMe_3)_2$, $(Me_3Sn)HN-NH(SnMe_3)$[30], tBu$_2$B−NH$_2$[30], and $PhN=NSiMe_3$[19] were prepared according to literature procedures. − IR: Nicolet 520 FT-IR. − MS: Atlas CH7. − NMR: Bruker AC-P 200 (^{11}B, ^{14}N, ^{119}Sn), Jeol GSX 270 (^{1}H, ^{13}C); standards: iTMS, $eBF_3 \cdot OEt_2$, $SnMe_4$. − X-ray analyses: Siemens P4 and Nicolet R3m diffractometer, Mo-K_α radiation, graphite monochromator.

N,N'-Bis(diphenylboryl)-N,N'-dimethylhydrazine (**7**). – a) A solution of Me(H)N–N(H)Me (0.51 g, 8.5 mmol) in 100 ml of benzene was metalated by slowly adding with stirring a solution of LiBu (10.9 ml, 1.56 M in hexane). A light yellow precipitate formed. The suspension was then heated to 50 °C, and a solution of diphenylboron bromide (4.15 g, 17.0 mmol) in 50 ml of benzene was added. An orange color developed. The suspension was kept at reflux for 1 h, the insoluble material was collected by filtration and, after addition of 70 ml of CH_2Cl_2, removed by centrifugation. The volume of the clear solution was reduced to about 1/3 by evaporation of the solvent in vacuo, and crystals separated from this solution on cooling to 0 °C. Yield: 1.22 g of **7** (37%).

b)$Me_3Sn(Me)N-N(Me)SnMe_3$ (2.78 g, 7.2 mmol) was dissolved in 40 ml of CH_2Cl_2, and a solution of Ph_2BBr (3.54 g, 14.5 mmol) in 20 ml of CH_2Cl_2 was added with stirring. The reaction was complete after 3 h (^{11}B NMR). Workup as described for **8**. Yield: 1.20 g of (43%), m. p. 122–124 °C. – NMR ($CDCl_3$): δ^1H = 3.26 (s, 6 H), 7.22–7.28 (m, 20 H). – $\delta^{11}B$ = 41.4. – $\delta^{13}C$ = 40.14 (NCH_3), 127.08, 127.40, 127.57, 128.31, 132.07, 133.25 (Ph), 149.74, 142.3 (br, CB). – $C_{26}H_{26}B_2N_2$ (388.1): calcd. C 80.46, H 6.75, N 7.22; found C 78.60, H 7.01, N 7.28.

N,N-Bis(diphenylboryl)-N,N'-dimethylhydrazine (**8**): To a solution of $Me_2N-N(SnMe_3)_2$ (2.71 g, 7.0 mmol) in 50 ml of CH_2Cl_2, a solution of Ph_2BBr (3.44 g, 14.1 mmol) in 20 ml of dichloromethane was added with stirring within 1 h. During this time the solution turned orange. Me_3SnBr formation was monitored by ^{119}Sn-NMR spectroscopy (δ = 128) and was quantitative after 1 h. The solvent was removed from the solution in vacuo, followed by extraction of the residue with hexane. The oil which remained after all volatile material had been evaporated in vacuo was treated with CH_2Cl_2/C_6H_6 (1:1) to afford 1.43 g of **8** (52%), m. p. 128–130 °C. – NMR ($CDCl_3$): δ^1H = 2.47, 1.10, 2.55, 1.73 (three s, NCH_3, a total of 6 H), 7.31–8.06 (m, C_6H_5, 20 H). – $\delta^{11}B$ = 13.2, 31.0, 39.3 (1:1:1). – $\delta^{13}C$ = 47.62, 49.44, 51.03 (NCH_3); 127.14, 127.39, 127.47, 127.90, 129.02, 129.09, 129.49, 131.29, 133.37, 133.49, 133.81, 134.97, 135.60, 135.85, 141.53 (Ph).

N,N'-Bis(di-ter-butylboryl)hydrazine (**9**): tBu_2BNH_2[27] (6.75 g, 47.9 mmol) and hydrazine (770 mg, 23.9 mmol) were dissolved in 100 ml of toluene. The solution was heated at reflux for 2 h, and liberated NH_3 was carried away by a slow stream of Ar. Vacuum was then applied to evaporate all volatile material. A white solid remained which was crystallized from pentane, yield: 6.1 g of **9** (91%), m. p. 51–53 °C. – NMR (C_6D_6): δ^1H = 1.02 (s, 18 H, CH_3), 1.17 (s, 18 H, CH_3), 6.08 (br, s, 2 H, NH). – $\delta^{11}B$ = 43.4 – $\delta^{13}C$ = 21.68 (br, CMe_3), 22.84 (br, CMe_3), 28.82 (CMe_3), 29.62 (CMe_3). – MS: 280 [M^+, ^{11}B]. – $C_{18}H_{38}B_2N_2$ (280.1): calcd. C 68.61, H 13.67, N 10.00; found C 68.08, H 12.73, N 8.36.

N,N'-Bis(tert-butyldimethylsilyl)-N,N'-bis(difluoroboryl)-hydrazine (**12**): *N,N'*-Bis(*tert*-butyldimethylsilyl)-*N,N'*-dilithiohydrazine (3.93 g, 13.0 mmol) was suspended in 30 ml of ether and the suspension cooled to −78 °C. $BF_3 \cdot OEt_2$ (3.7 g, 26 mmol) was dropped slowly to the stirred suspension of the lithium hydrazine. After the addition the mixture was allowed to attain ambient temp. followed by heating to reflux for 8 h. Insoluble material was then removed by filtration, the ether evaporated from the filtrate and the non-volatile residue washed with 5 ml of benzene. The oily product, **12**, could not be further purified by distillation in vacuo due to decomposition to **13**, which occured with BF_3 elimination. Yield: 4.3 g of **12** (93%). The compound fumed in air. – NMR (C_6D_6): δ^1H = 0.12 (s, 6 H $SiMe_2$), 0.91 (s, 9 H, CMe_3). – $\delta^{11}B$ = 20.4 ($h_{1/2}$ = 290 Hz). – $\delta^{13}C$ = −4.13 ($SiMe_2$), 27.24 ($SiCMe_3$). – $\delta^{19}F$ = −121.17, −117.26. – $\delta^{29}Si$ = 22.72. – $C_{12}H_{30}B_2F_4N_2Si_2$ (356.2): calcd. C 40.47, H 8.49, N 7.87; found C 40.99, H 8.91, N 8.96.

1,2,4,5-Tetrakis(tert-butyldimethylsilyl)-3,6-difluoro-1,2,4,5,3,6-tetrazadiborinane (**13**): $tBuMe_2Si(Li)N-N(Li)SiMe_2tBu$ (6.92 g, 23 mmol) was suspended in 30 ml of ether at −78 °C, and $BF_3 \cdot OEt_2$ was added (3.26 g, 23 mmol dissolved in 20 ml of ether) with stirring. ^{11}B-NMR spectroscopy revealed the sole formation of **13** after 5 h. Ether was then distilled from the suspension and 50 ml of hexane was added to the residue. The resulting suspension was kept at reflux for 4 d. After filtration and extraction of the solid with hot benzene 5.5 g of **13** (81%), m. p. 127–178 °C, separated from the combined solutions at 7 °C. – NMR (C_6D_6): δ^1H = 1.05 (s, 9 H, CMe_3), 0.29 (s, 6 H, $SiMe_2$). – $\delta^{11}B$ = 30.6, $h_{1/2}$ = 545 Hz. – $\delta^{13}C$ = −2.38, −3.10 ($SiMe_2$), 27.8 (CMe_3). – $\delta^{19}F$ = −105.5. – $\delta^{27}Si$ = 16.38. – IR (cm^{-1}): 2961 (s), 2932 (s). 2900 (s), 2884 (s), 1474 (s), 1466 (s), 1418 (s), 1410 (s), 1384 (s), 1343 (s), 1332 (s), 1287 (s), 1261 (m), 1065 (w), 996 (m), 835 (s), 824 (s), 810 (s), 699 (m), 671 (m). – $C_{24}H_{60}B_2F_2N_4Si_4$ (576.7): calcd. C 49.98, H 10.49, N 9.71; found C 48.44, H 10.51, N 9.11.

N,N'-Bis(chloromesitylboryl)-N-phenyl-N'-(trimethylsilyl)hydrazine (**16**): Dichlorodimesityldiborane(4) (1.00 g, 3.02 mmol) was dissolved in 40 ml hexane. To the stirred solution was added at −40 °C a solution of phenyl(trimethylsilyl)diazene[15] (0.72 g, 4.04 mmol) in 15 ml of hexane. The blue color of the diazene disappeared quickly but remained after addition of about 3/4 of the diazene solution. After warming to ambient temp. overnight two ^{11}B-NMR signals (δ = 40.8, 46.1) were observed. The blue color of the solution remained unchanged during 3 more days. The volume of the solution was then reduced in vacuo to about 30 ml, and the solution was then kept at −50 °C. The precipitate that formed was isolated and recrystallized from 30 ml of hexane. Yield: 1.44 g of **16** (94%), m. p. 141–142 °C. Additional **16** was isolated by further reducing the volume of the solution. Total yield: 70%. – NMR ($CDCl_3$): δ^1H = 0.83 (s, 9 H, $SiMe_3$), 1.14, 1.84, 2.18, 2.19, 2.29, 2.57, (s, 3 H each), 6.47, 6.49, 6.74, 6.84 (s, *m*-H of mes), 6.57, 6.59 (m, *o*-CH of Ph), 6.96–7.04 (m, m, *p*-H, 3 H). – $\delta^{11}B$ = 40.8, 46.1 (1:1). – $\delta^{13}C$ = 3.1 ($SiMe_3$), 20.2, 21.0, 21.2, 22.1, 22.4, 22.8 (*o*-, *p*-CH_3 of mes), 125.3 (*m*-C, Ph), 125.6 (*p*-C, Ph), 126.6, 127.1, 127.2, 127.6 (*m*-C of mes), 127.7 (*o*-C, Ph), 137.4, 137.9, 138.2 (1:2:1, *o*-C of mes), 139.5, 139.6 (*p*-C, mes), 146.4 (*i*-C, Ph). – $\delta^{29}Si$ = 19.5. – $C_{27}H_{36}B_2Cl_2N_2Si$ (509.2): calcd. C 63.69, H 7.13, N 5.50; found C 63.97, H 7.27, N 5.48.

4-[Bis(dimethylamino)boryl]-5,5-dichloro-2-[chloro(dimethylamino)boryl]-1,1-dimethyl-3-phenyl-1-azonia-3,4-diaza-2-bora-5-boratacyclopentane (**17**): A solution of $B_2Cl_2(NMe_2)_2$ (0.80 g, 4.4 mmol) in 30 ml of hexane was dropped into a stirred solution of $PhN{=}NSiMe_3$ (0.8 ml, 4.4 mmol) in 20 ml of hexane at −40 °C. No reaction occurred up to a temp. of −20 °C. At −10 °C a change in the ^{11}B-NMR spectrum indicated the beginnig of a reaction. At 10 °C the ^1H-NMR signal of Me_3SiCl appeared as well as a colorless precipitate which was isolated at ambient temp. The blue solution was cooled to −20 °C, and the crystals which separated were isolated after a week. Total yield: 0.83 g of **17** (1.88 mmol, 84%), m. p. 163 °C. – NMR ($CDCl_3$): δ^1H = 2.09, 2.16, 2.35, 2.39, 2.46, 2.50, 2.56 (NMe, 24 H), 6.8, 7.0 (m), 7.3 (m), 5 H). – $\delta^{11}B$ = 39.3 [br, $BCl(NMe_3)$], 29.7 (BN_3), 10.8 (N_2BCl_2). – $C_{14}H_{29}B_4Cl_3N_6$ (431.0): calcd. C 39.01, H 6.78, N 19.50; found C 38.83, H 6.71, N 19.46.

X-ray Structure Determinations: Single crystals were sealed in glass capillaries under argon. The setting angles of 15 to 20 cen-

Table 2. Crystal data and data related to data collection and structure solution of the diborylhydrazines

Compound	**7**	**8**	**13**	**16**	**17**
Formula	$C_{26}H_{26}B_2N_2$	$C_{26}H_{26}B_2N_2$	$C_{24}H_{60}B_2F_2N_4Si_4$	$C_{27}H_{36}B_2Cl_2N_2Si$	$C_{14}H_{29}B_4Cl_3N_6$
Form. wght.	388.1	388.1	576.7	509.2	431.0
Cryst. size (mm)	0.4 x 0.35 x 0.3	0.56 x 0.4 x 0.3	0.5 x 0.4 x 0.35	0.6 x 0.5 x 0.4	0.5 x 0.4 x 0.3
Cryst. system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	10.435(2)	11.845(7)	10.159(2)	9.406(7)	9.853(6)
b [Å]	12.156(2)	10.301(3)	10.931(3)	12.504(8)	12.883(9)
c [Å]	17.441(4)	19.24(2)	17.586(4)	13.047(5)	17.974(7)
α [°]	90	90	89.61(2)	87.68(4)	90
β [°]	98.61(1)	104.81(2)	76.22(2)	76.67(5)	99.08(4)
γ [°]	90	90	65.56(1)	78.68(6)	90
V [Å^3]	2187.4(7)	2270(2)	1717.4(7)	1464(1)	2253(2)
Z	4	4	2	2	4
$d_{calc.}$ [Mg/m^3]	1.179	1.136	1.115	1.155	1.271
μ (mm^{-1})	0.067	0.065	0.204	0.280	0.418
F (000)	824	824	632	540	904
T [K]	183	243	293	298	200
2 θ [°]	4 - 48	3 - 39	2.5 - 48	3.2 - 45	3.9 - 46.1
Indcx range	h, k, ± l	h, k, ± l	h, ± k, ± l	h, ± k, ± l	h, k, ± l
Refl. collect.	3839	2366	6100	4118	3344
Refl. indep.	3310	1935	5341	3833	3132
Refl.obs.[>4σF)]	2078	1389	4140	3367	2372
R	0.051	0.077	0.040	0.060	0.057
wR2	0.116	0.081 0.218	0.096	0.157	0.144
GOOF	1.039	1.96	1.038	1.027	1.003
diff. peak [e/Å^3]	0.183	0.52	0.370	0.326	0.328

tered reflections were used for the determination of the dimensions of the unit cell, and data collection was performed by using ω scans and variable scan speed. The structures were solved by direct methods, nonhydrogen atoms were refined anisotropically and H atoms in calculated positions as a riding model. Programs: SHELXTL PC plus and SHELXL 93. A summary of the data is given in Table 2. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Leopoldshafen-Eggenstein, Germany, on quoting the depository number CSD-404202–404206, the names of the authors and the journal citation.

☆ Dedicated to Professor *H. P. Fritz* on the occasion of his 65th birthday.

[1] A. Lang, H. Nöth, M. Schmidt, *Chem. Ber.* **1995**, *128*, 751–762.

[2] S. Wolfe, *Acc. Chem. Res.* **1972**, *5*, 102–111.

[3] Y. Tomiie, C. H. Koo, I. Nitta, *Acta Crystallogr.* **1958**, *11*, 774.

[4] J. C. Huffman, H. Fußstetter, H. Nöth, R. Schaeffer, *Z. Naturforsch., Part B*, **1976**, *31*, 289–293.

[5] P. C. Bharara, H. Nöth, *Z. Naturforsch., Part B*, **1979**, *34*, 1352–1356.

[6] D. C. Pestana, P. P. Power, *Inorg. Chem.* **1991**, *30*, 528–535.

[7] H. Nöth, R. Ullmann, *Chem. Ber.* **1975**, *108*, 3125–3131.

[8] B. Thiele, P. Paetzold, U. Englert, *Chem. Ber.* **1992**, *125*, 2681–1686.

[9] H. Fußstetter, H. Nöth, *Liebigs Ann.* **1981**, 633–641; H. Nöth, W. Regnet, H. Riehl, R. Standfest, *Chem. Ber.* **1971**, *104*, 722.

[10] R. L. Collin, W. N. Lipscomb, *Acta Crystallogr.* **1951**, *4*, 10; W. H. Beamer, *J. Am. Chem. Soc.* **1948**, *70*, 2979.

[11] R. H. Wentorf, *J. Chem. Phys.* **1957**, *26*, 956.

[12] S. Geller, R. E. Hughes, J. L. Hoard, *Acta Crystallogr.* **1951**, *4*, 380–385; P. M. Kuznesof, R. C. Kuczkowski, *Inorg. Chem.* **1978**, *17*, 2308–2311; P. Paetzold, Ch. von Plotho, G. Schmid, R. Boese, *Z. Naturforsch., Part B*, **1984**, *39*, 1069–1075; H. Nöth, S. Weber, *ibid.* **1983**, *38*, 1460–1464.

[13] G. M. Giandomenico, J. C. Dewan, S. J. Lippard, *J. Am. Chem. Soc.* **1981**, *103*, 1407–1412; S. Gambarotta, M. Pasquale, C. Floriani, A. Chiesa-Villa, G. Guastini, *Inorg. Chem.*, **1981**, *20*, 1173–1178.

[14] H. Nöth, B. Wrackmeyer, *NMR-Spectroscopy of Boron Compounds*, vol. 14, *NMR Basic Principles and Applications* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer Publ., Heidelberg, Berlin, New York, **1978**.

[15] [15a] M. Geschwentner, G. Elter, A. Meller, *Z. Naturforsch., Part B*, **1994**, *49*, 459–464. – [15b] K. Bode, U. Klingebiel, M. Noltemeyer, H. Witte-Abel, *Z. Anorg. Allg. Chem.* **1995**, *621*, 500–505.

[16] F. Kumpfmüller, D. Kölle, H. Nöth, H. Pommerening, R. Staudigl, *Chem. Ber.* **1985**, *118*, 483–494.

[17] H. Nöth, W. Regnet, *Chem. Ber.* **1969**, *102*, 167–179; H. Nöth, W. Winterstein, *ibid.* **1978**, *111*, 2469–2479; H. Nöth, W. Winterstein, *ibid.* **1978**, *111*, 2465–2468.

[18] A. Denk, Diploma Thesis, University of Munich, **1989**.

[19] W. Schneid, PhD Thesis, University of Munich, **1993**.

[20] G. Schmid, R. Boese, D. Bläser, *Z. Naturforsch., Part B*, **1982**, *37*, 1230–1233.

[21] D. Loderer, G. Linti, H. Nöth, *Chem. Ber.* **1994**, *127*, 1909–1922.

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

[23] T. Franz, E. Hanecker, H. Nöth, W. Stöcker, W. Storch, G. Winter, *Chem. Ber.* **1986**, *119*, 900–916, and references cited therein.

[24] P. P. Power, *Angew. Chem.* **1990**, *102*, 527–538; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 449.

[25] T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 11018–11019.

[26] P. Nguyen, G. Lesley, N. Taylor, T. B. Marder, N. Pickett, W. Clegg, M. R. Elsegood, N. C. Norman, *Inorg. Chem.* **1994**, *33*, 4623.

[27] C. M. Wright, E. L. Muetterties, *Inorg. Synth.* **1967**, *10*, 137–139.

[28] H. Nöth, H. Sachdev, M. Schmidt, H. Schwenk, *Chem. Ber.* **1995**, *128*, 105–113.

[29] St. Diemer, PhD Thesis, University of Munich, **1993**.

[30] U. Höbel, H. Nöth, H. Prigge, *Chem. Ber.* **1986**, *119*, 325–337.

[95083]