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Note

Synthesis and characterisation of the halogenated azanonaboranes [(^{i}PrNH$_2$)B$_8$H$_{10}$XNH^{i}Pr] (X = Cl, Br, I) and their unexpected hydrolysis to *hypho*-[B$_5$H$_{10}$(μ-NH^{i}Pr)]

Claudia Bauer [a], Detlef Gabel [a], Thomas D. McGrath [b], Udo Dörfler [a,*]

[a] *Department of Chemistry, University of Bremen, P.O. Box 330440, 28334 Bremen, Germany*
[b] *Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK*

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Abstract

Treatment of [(^{i}PrNH$_2$)B$_8$H$_{11}$NH^{i}Pr] with elemental halogen affords the 8-*exo*-halogen-substituted derivatives [(^{i}PrNH$_2$)B$_8$H$_{10}$XNH^{i}Pr] (X = Cl, Br, I). The structures of all three compounds are confirmed by NMR spectroscopy and mass spectrometry, and (for X = Br) by an X-ray diffraction study. The bromoazanonaborane undergoes hydrolytic decomposition to the new five-vertex compound [B$_5$H$_{10}$(μ-NH^{i}Pr)] of *hypho*-type structure.

Keywords: Azanonaboranes; Halogenation; Hydrolysis; *hypho*-Clusters; Crystal structures

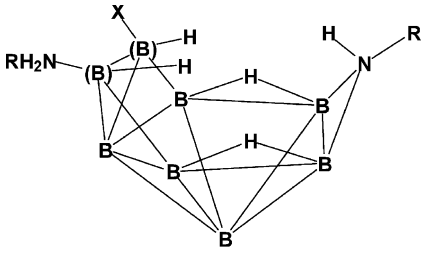
1. Introduction

The eight-boron atom species [(EtNH$_2$)B$_8$H$_{11}$NHEt] (**1a**) was first synthesised in 1962 [1], and was structurally identified in 1963 [2]. It has a structure based on an eight-vertex cluster of *hypho*-type character [3] bearing two amine-derived residues: one amine ligand in an *exo* terminal position, and one amino ligand in a bridging position (Scheme 1).

It has been shown that members of this *hypho*-type family [(RNH$_2$)B$_8$H$_{11}$NHR] [R = Et (**1a**), ^{i}Pr (**1b**)] constitute a good entry into azacarbaborane [4] and azametallaborane chemistry [5]. In order to develop the chemistry of azametallaboranes containing seven or eight boron atoms we have become interested in the use of compounds **1** as starting substrates. Here we report the syntheses of halogen-substituted derivatives of the azanonaborane [(^{i}PrNH$_2$)B$_8$H$_{11}$NH^{i}Pr] (**1b**) [6], which were obtained in good yield from its reaction with elemental chlorine, bromine or iodine, and the isolation of an unexpected *hypho*-structured pentaborane which is formed upon hydrolysis of these new haloboranes.

2. Results and discussion

Chlorine-substituted **2** is formed by gentle passage of a stream of chlorine through a CH_2Cl_2 solution of **1b** at − 78 °C, whilst treatment of the same solution at



	R	X
1a	Et	H
1b	^{i}Pr	H
2	^{i}Pr	Cl
3	^{i}Pr	Br
4	^{i}Pr	I

Scheme 1.

* Corresponding author. Tel.: +49-421-218 2375; fax: +49-421-218 2871.
E-mail address: doerfler@chemie.uni-bremen.de (U. Dörfler).

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Table 1
Selected NMR parameters [a] for compounds **1b**, **2**–**4**

Position	**1b**		**2**		**3**		**4**	
	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$
(1)	+1.6	+2.53	+2.6	+2.69	+3.4	+2.92	+4.7	+3.28
(2)	−55.6	−0.63	−56.7	−0.68	−55.9	−0.67	−55.5	−0.68
(3)	−21.5	+1.29	−24.3	+0.74	−23.8	+0.72	−24.1	+0.70
(4)	−31.8	+0.73	−31.5	+0.74	−30.7	+0.72	−31.4	+1.00
(5)	−11.1	+2.53	−10.1	+2.33	−10.7	+2.46	−11.1	+2.60
(6)	−11.1	+2.53	−12.7	+2.47	−12.1	+2.46	−11.1	+2.45
(7)	−33.6	+0.73	−33.3	+1.02	−32.1	+1.08	−31.4	+1.30
(8)	−31.8	−0.63 [b]	−16.4	+1.41 [b]	−21.0	+1.37 [b]	−31.4	+1.30 [b]
		+0.45						
(4,5)		−2.09		−1.85		−1.81		−1.73
(6,7)		−2.14		−2.16		−2.09		−1.99
N(5,6) [c]		−1.68 [d]		−1.85 [e]		−1.08 [f]		−1.74 [g]
N(3) [h]		+4.03 [i]		+4.24 [j]		+4.27 [k]		+4.27 [l]
		+4.03		+3.98		+3.95		+4.02

[a] In $CDCl_3$ at 20 °C.
[b] *endo* H atom.
[c] {^{i}PrNH} substituent site.
[d] CH at +52.8 (δ_C), +3.53 (δ_H); CH_3 at +21.2 and +21.1 (δ_C), +1.40 (mean) (δ_H).
[e] CH at +53.3 (δ_C), +2.50 (δ_H); CH_3 at +21.7 (δ_C), +1.42 (mean) (δ_H).
[f] CH at +53.3 (δ_C), +2.47 (δ_H); CH_3 at +21.8 (δ_C), +1.43 (mean) (δ_H).
[g] CH at +53.4 (δ_C), +2.55 (δ_H); CH_3 at +22.0 (δ_C), +1.47 (mean) (δ_H).
[h] {^{i}PrNH$_2$} substituent site.
[i] CH at +52.2 (δ_C), +3.43 (δ_H); CH_3 at +21.2 and +21.1 (δ_C), +1.05 (mean) (δ_H).
[j] CH at +51.3 (δ_C), +3.47 (δ_H); CH_3 at +21.0 (δ_C), +1.04 (mean) (δ_H).
[k] CH at +51.4 (δ_C), +3.44 (δ_H); CH_3 at +21.1 (δ_C), +1.03 (mean) (δ_H).
[l] CH at +51.5 (δ_C), +3.48 (δ_H); CH_3 at +21.2 (δ_C), +1.06 (mean) (δ_H).

−78 °C with 1 equiv. of bromine or iodine results in the formation of **3** and **4**, respectively.

$$[(^{i}PrNH_2)B_8H_{11}NH^{i}Pr] + X_2 \rightarrow [(^{i}PrNH_2)B_8H_{10}XNH^{i}Pr] + HX \quad (X = Cl, Br, I)$$

All three halogen-substituted azanonaboranes are obtained as colourless solids. Reaction of **1b** with an excess of bromine yields a mixture of several compounds including monosubstituted **3** (as observed by NMR spectroscopy). Separation of the mono- and apparently disubstituted products by various methods was unsuccessful.

The ^{11}B and ^{1}H NMR data for halogen-substituted compounds **2**–**4** are summarised in Table 1, along with the corresponding parameters for the starting material **1b** [6]. These data for compounds **2**–**4** were readily assigned by one- and two-dimensional homo- and hetero-nuclear correlation techniques and were consistent with the molecular structure of **3** determined in the X-ray work (see below). The influence of the halogen atom on the basic shielding patterns of compounds **2**–**4** appears to be relatively localised. Compared to the unsubstituted parent **1b** there is a downfield shift of 15.4 ppm for the chlorine-substituted boron atom B(8) in **2**. Bromo- and iodo-substitution likewise produce downfield shifts of 10.8 and 0.4 ppm, respectively. There are no other significant patterns of changes in chemical shift for the other boron atoms in **2**–**4** relative to the starting material. Similar halogen-dependent changes in ^{11}B chemical shift have been observed in other boranes (for example, $B_{10}H_{14}$ [7]). It was not possible to determine by NMR spectroscopy whether the *exo* or the *endo* hydrogen atom at B(8) had been replaced by halogen. It is known that these H atoms resonate at $\delta(^{1}H) = +0.45$ (*exo*) and -0.63 (*endo*) in **1b**. In compounds **2**–**4** the chemical shifts of the remaining H atom at B(8) are $\delta(^{1}H) = +1.41$ (**2**), $+1.37$ (**3**) and $+1.30$ (**4**). These values are also highly affected by the presence of the halogen atom itself and hence the position (*exo* or *endo*) could not be established by NMR spectroscopy alone. Accordingly, a structural study of the brominated derivative **3** was performed. The structure obtained by X-ray diffraction crystallography is shown in Fig. 1 and selected geometric parameters are listed in Table 2.

Compound **3** is seen to retain the overall parent *hypho*-type [$(RNH_2)B_8H_{11}NHR$] architecture, with one H atom replaced by bromine. This bromine substituent is confirmed to be bonded to B(8) and is found in an *exo* position. The boron–bromine distance B(8)–Br(1) in **3** is 2.043(8) Å, significantly longer than the B–Br distance in, for example, [$MeNB_{11}H_{11}Br$] (1.949(9) Å)

[8] and $[(PMe_2Ph)_2B_{10}H_{11}Br]$ (1.986(4) Å) [9], but falls within the expected ranges (ca. 1.88–2.06 Å) [10], albeit towards the longer end of this range. Interboron distances in compounds **1b** [6] and **3** are essentially identical within experimental error, and the additional bromo substituent does not significantly influence the gross structure.

Although the halogen-substituted derivatives **2**–**4** are air-stable, treatment with water-contaminated solvents results in cluster decomposition to form mainly boric acid. Additionally we found a further product in small yield, which could be identified by NMR spectroscopy and mass spectrometry (see Section 3) as $[B_5H_{10}(\mu\text{-}NH^iPr)]$ (**5a**, Fig. 2). At first sight this product might be regarded as a derivative of *arachno*-B_5H_{11} [11], with the μ-H atom bridging the B(3)–B(4) connectivity (*arachno*-B_5 numbering) replaced by a {μ-NH^iPr} residue. However, the NHR group is not isoelectronic with an electron-deficient bridging hydrogen but is instead an electron-precise moiety which is formally attached to two skeletal boron atoms via one normal covalent bond and one dative bond allowing the NHR unit to provide three electrons to the cage. Electron-counting considerations then indicate **5a** to be of *hypho* structure, derived from hypothetical *hypho*-B_5H_{13}.

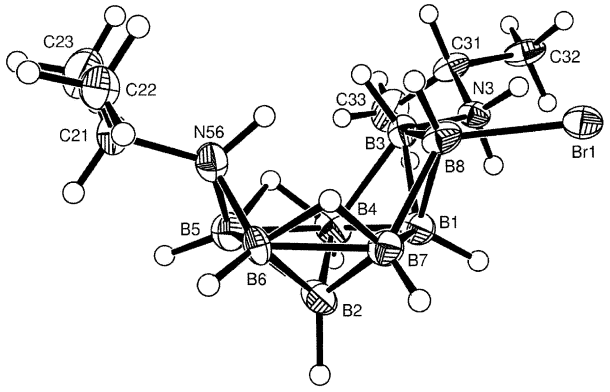

Fig. 1. An ORTEP drawing of the crystallographically determined molecular structure of **3** with displacement ellipsoids shown at 50% probability. For clarity hydrogen atoms are drawn as circles with an arbitrary small radius.

Table 2
Selected interatomic distances (Å) and interbond angles (°) for $[(^iPrNH_2)B_8H_{10}BrNH^iPr]$ (**3**) in **3**·$CHCl_3$

Bond distances			
Br(1)–B(8)	2.043(8)	B(7)–B(8)	1.879(11)
B(3)–B(4)	1.879(10)	B(3)–N(3)	1.578(8)
B(3)–B(8)	1.912(10)	B(5)–N(56)	1.561(10)
B(5)–B(6)	1.943(12)	B(6)–N(56)	1.553(10)
Bond angles			
B(3)–B(8)–Br(1)	115.6(4)	N(3)–B(3)–B(1)	112.4(5)
B(1)–B(8)–Br(1)	111.7(5)	N(3)–B(3)–B(4)	117.4(5)
B(7)–B(8)–Br(1)	117.1(5)	N(3)–B(3)–B(8)	115.3(5)
B(3)–B(1)–B(8)	68.5(5)	B(1)–B(3)–B(8)	55.7(4)
B(8)–B(1)–B(7)	66.1(4)	B(5)–N(56)–B(6)	77.2(5)

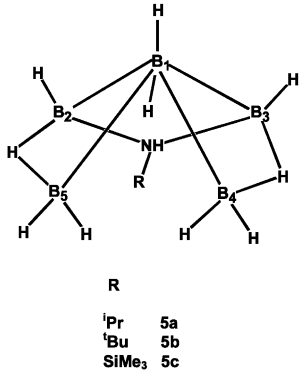

Fig. 2. Structure of *hypho*-$[B_5H_{10}(\mu\text{-}NHR)]$ species (**5**).

Two species related to **5a** have been reported by Gaines and co-workers [12]. The compounds $[B_5H_{10}(\mu\text{-}NHR)]$ (R = ^{t}Bu, **5b**; R = $SiMe_3$, **5c**) were obtained from the reaction of 2-Br-B_5H_8 with the corresponding $RSiMe_3$ reagents in CH_2Cl_2. Although **5c** was only identified as a trace impurity, **5b** was fully characterised, including an X-ray diffraction study.

The ^{11}B and ^1H NMR parameters for **5a** were independently assigned fully by one- and two-dimensional NMR experiments and its ^{11}B NMR data correspond closely with those reported [12] for **5b**. It is of interest to compare the ^{11}B chemical shifts for **5a** (and **5b**) with the equivalent data for the *hypho*-$[B_5H_{12}]^-$ anion [13]. The boron atoms of the latter resonate at δ −57.6 (B1) and −15.9 (B2–5), whereas for compounds **5** the peak positions are around δ −58 (B1), −16 (B2,3) and −9 (B4,5). Thus it appears that it is those basal boron atoms B(4,5), *distant* from the μ-NHR group in compounds **5**, which are most affected by the presence of the amino moiety. This may indicate some more subtle electronic interaction of the μ-NHR unit with the cluster than simple considerations would suggest.

Yields of **5a** are low, and could not be improved even by controlled hydrolysis of **3**, thus rendering this route not yet useful to species of this type. Preliminary studies suggest that halogenated derivatives of other azanonaboranes **1** may also undergo similar degradation. However, as these findings show, the area of intermediate-size azanonaboranes continues to reveal novel chemistry. We are further exploring this potential.

3. Experimental

3.1. General

Reactions were carried out in dry solvents under dry oxygen-free dinitrogen. Chlorine, bromine and iodine were obtained commercially and $[(^iPrNH_2)B_8H_{11}NH^iPr]$ (**1b**) [6] was prepared by literature methods. NMR

spectroscopy was performed in Bruker DPX200 and AM400 instruments operating at approximately 4.7 and 9.4 T. Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^1H)$ (nominally $SiMe_4$), $\Xi = 32.083\,972$ MHz for $\delta(^{11}B)$ (nominally $[F_3B{\cdot}OEt_2]$ in $CDCl_3$) and $\Xi = 25.145\,004$ MHz for $\delta(^{13}C)$ (nominally $SiMe_4$). Ξ is as defined in Ref. [14]. Electron impact (70 eV, 200 °C) and direct chemical ionisation (reactant gas NH_3) mass spectra were recorded in a Finnigan MAT 8200.

3.2. Synthesis

3.2.1. [(^{i}PrNH$_2$)B$_8$H$_{10}$ClNH^{i}Pr] (2)

A sample of **1b** (100 mg, 0.47 mmol) was dissolved in CH_2Cl_2 (10 ml) and cooled to −78 °C. A gentle stream of chlorine was passed through the solution for 20 s. After stirring for 1 h at room temperature (r.t.) the more volatile components were removed, and the solid residue redissolved in $CHCl_3$ (5 ml). Cooling to −20 °C afforded **2** as a colourless solid [80 mg, 69%, m.p. 115–118 °C]. EI MS; m/z: 249 (M^+, 40%), 213 ($M^+ - Cl$, 6%), 43 ($^iPr^+$, 100%).

3.2.2. [(^{i}PrNH$_2$)B$_8$H$_{10}$BrNH^{i}Pr] (3)

A sample of **1b** (100 mg, 0.47 mmol) was dissolved in CH_2Cl_2 (10 ml) and cooled to −78 °C, and then a solution of Br_2 (75 mg, 24 μl, 0.47 mmol) in CH_2Cl_2 (5 ml) was added. After stirring for 1 h at r.t. the more volatile components were removed, and the solid residue redissolved in $CHCl_3$ (5 ml). At −20 °C **3** was obtained as colourless crystals [89 mg, 65%, m.p. 122–124 °C]. EI MS; m/z: 293 (M^+, 13%), 213 ($M^+ - Br$, 13%), 43 ($^iPr^+$, 100%).

3.2.3. [(^{i}PrNH$_2$)B$_8$H$_{10}$INH^{i}Pr] (4)

Similar to the procedure for compound **3**, **1b** (100 mg, 0.47 mmol) and I_2 (118 mg, 0.47 mmol) gave **4** as a colourless solid [124 mg, 78%, m.p. (dec.) 115–118 °C]. EI MS; m/z: 341 (M^+, 8%), 213 ($M^+ - I$, 57%), 43 ($^iPr^+$, 100%).

3.2.4. [B$_5$H$_{10}$(μ-NH^{i}Pr)] (5a)

A sample of **3** (89 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (10 ml) and cooled to 0 °C, and then a solution of H_2O (60 mg, 3.3 mmol) in THF (5 ml) was added. After stirring for 0.5 h at r.t. the more volatile components were removed. The resulting solid residue was extracted with $CHCl_3$ (5 ml), filtered to remove boric acid, and the filtrate purified by repeated preparative TLC. Development with hexane/CH_2Cl_2 (3:7) gave **5a** as a colourless oil (4 mg, 0.033 mmol, 11%, R_F 0.77).

NMR ($CDCl_3$, 20 °C) $\delta(^{11}B)$ [$\delta(^1H)$ for terminal H]: $BH_2(1)$ −57.8 (dd, $J_1 = 140$ Hz, $J_2 = 49$ Hz) [+1.25, −1.07], BH(2,3) −15.5 (dd, $J_1 = 141$ Hz, $J_2 = 44$ Hz) [+2.25], $BH_2(4,5)$ −8.7 (t, $J = 122$ Hz) [+1.41, +2.55]; additionally, $\delta(^1H)$ [(^{13}C)]: μ(2,5) and μ(3,4): −0.60 [–]; CH: +2.95 [54.9]; CH_3: +1.30 [20.9]; NH: +0.62 [–]. DCI MS (negative); m/z: 121 ($M^- - 1$, 80%).

3.3. X-ray diffraction study of 3·CHCl$_3$

3.3.1. Crystal data

$C_6H_{27}B_8BrN_2{\cdot}CHCl_3$, $M_r = 413.05$, triclinic, $P\bar{1}$, $a = 6.623(5)$, $b = 9.705(3)$, $c = 16.831(5)$ Å, $\alpha = 102.087(14)$, $\beta = 95.77(3)$, $\gamma = 98.55(3)°$, $V = 1036.4(8)$ Å^3, $Z = 2$, colourless block, $0.3 \times 0.4 \times 0.6$ mm, $D_{calc} = 1.324$ Mg m^{-3}, $\mu = 2.359$ mm^{-1}, $F(000) = 420$, $T = 173(2)$ K. A total of 5363 reflections was measured (Siemens P4 diffractometer, Mo Kα X-radiation, $\lambda = 0.71073$ Å) for $2.75 \le \theta \le 22.50°$ ($-7 \le h \le 6$, $-10 \le k \le 10$, $-18 \le l \le 18$), of which 2698 were unique ($R_{int} = 0.0462$). An empirical absorption correction (ψ scans) was applied ($T_{max} = 0.6176$, $T_{min} = 0.4850$).

3.3.2. Structure solution and refinement

The structure was solved by direct methods, developed by Fourier synthesis and refined anisotropically (full-matrix least-squares on F^2) using the SHELXTL/PC suite of programs [15]. One molecule of chloroform solvate was found to co-crystallise per molecule of **3**. A total of 240 parameters was refined to final $R_1 = 0.0558$, $wR_2 = 0.1295$ for 2087 data with $I > 2\sigma(I)$ and $R_1 = 0.0799$, $wR_2 = 0.1417$ for all 2698 data, and with a goodness-of-fit on $F^2 = 1.059$. Maximum and minimum residual electron density were 1.017 and −0.733 e Å^{-3}, respectively, both near Br(1).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 174693 for compound **3**·$CHCl_3$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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