

Synthesis and Structure of Pyrrolidinobromodiboranes(4)

Yong Nie, Hans Pritzkow, and Walter Siebert

Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Reprint requests to Prof. W. Siebert.

Fax: + 49-(0)6221/545609.

E-mail: walter.siebert@urz.uni-heidelberg.de

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Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 65th birthday

The reaction of tetrapyrrolidinodiborane(4) (**1**) with BBr_3 in a 1:1 molar ratio yields a mixture of 1,2-dibromo-1,2-dipyrrolidinodiborane(4) (**2**) and bromotripyrrolidino-diborane(4) (**3**), while a 1:2 molar ratio leads in Et_2O to compound **2** as the main product along with a small amount of $[(\text{C}_4\text{H}_8\text{N})_2\text{B}_2\text{Br}_3(\text{OEt})]$ (**4**). The new compounds have been characterized by NMR and MS data, as well as by X-ray structure analyses of **2** and **4**, of which the former exhibits an interesting polymorphism phenomenon.

Key words: Boron, Borane, Diborane(4), Polymorphism

Introduction

Diborane(4) derivatives are interesting reagents in organic synthesis. In particular the tetraalkoxydiborane(4) compounds are used for various transition metal-catalyzed addition and insertion reactions into multiple bonds [1]. The B-halogeno-diborane(4) derivatives display a rich chemistry and serve as starting compounds for, among others, oligoboranes which are obtained via dehalogenation reactions. A unique structural interplay between the resulting *cyclo*- and *polyhedral* boron compounds has been demonstrated [2]. While the existence of the postulated *cyclo*-(Me_2NB)₄ [3] (from B_4Cl_4 and Me_2NH) with a planar structure has not been confirmed [4], attempts [2, 5] have been made to obtain its analogs by the dehalogenation of diborane(4) reagents $\text{R}(\text{Cl})\text{B}-\text{B}(\text{Cl})\text{R}$ ($\text{R} = \text{NMe}_2$ [6], NEt_2 [5, 7]) with $\text{NaK}_{2,8}$. However, the planar *cyclo*-tetraboranes were not obtained, which is in accord with the calculations [8] which indicate

that planar B_4 rings are unstable. Instead, the dehalogenation reaction of $\text{Me}_2\text{N}(\text{Cl})\text{B}-\text{B}(\text{Cl})\text{NMe}_2$ produces orange-red *cyclo*-(Me_2NB)₆ [5] with a chair-like structure, which was first reported in 1980 [9] as a side product in the dehalogenation of $(\text{Me}_2\text{N})_2\text{BCl}$. The dechlorination reaction of $\text{Et}_2\text{N}(\text{Cl})\text{B}-\text{B}(\text{Cl})\text{NEt}_2$ leads to green, polyhedral $(\text{Et}_2\text{NB})_6$ in 40% yield [5], which was first obtained in low yield by dehalogenating Et_2NBCl_2 . At elevated temperatures, it rearranged into its cyclic isomer [10].

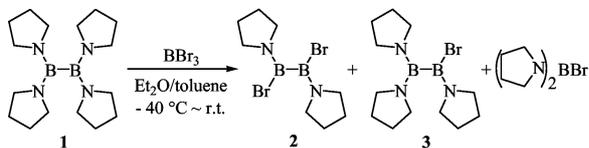
The sterically more hindered $i\text{Pr}_2\text{N}(\text{Cl})\text{B}-\text{B}(\text{Cl})\text{NiPr}_2$ allows the formation of blue folded *cyclo*-($i\text{Pr}_2\text{NB}$)₄, and in the case of the corresponding 2,2,6,6-tetramethylpiperidino (tmp) compound the yellow tetrahedral (tmpB)₄ is produced [11]. Interestingly, the codehalogenation of a 1:1 mixture of Me_2NBCl_2 and $\text{Me}_2\text{N}(\text{Cl})\text{B}-\text{B}(\text{Cl})\text{NMe}_2$ affords in low yield colorless $(\text{Me}_2\text{N})_2\text{B}_4[\text{B}(\text{NMe}_2)_2]_2$ [12] with a planar B_4 rhomb having a unique electronic structure. It is available in good yield [13, 14] by dehalogenating 1,3-dichloro-1,3,5-tris-(dimethylamino)triborane(5) [15].

Considering the similarity between pyrrolidino, dimethylamino and diethylamino groups, one might expect that the dehalogenation of 1,2-dichloro-1,2-dipyrrolidinodiborane(4) would give cyclic or polyhedral aminoboranes $(\text{C}_4\text{H}_8\text{NB})_n$ ($n = 4, 6$). However, the reaction did not lead to any definite product [5], and it was anticipated that the more reactive 1,2-dibromo-1,2-dipyrrolidinodiborane(4) (**2**) could yield better results. Herein we report on the reactions of tetrapyrrolidinodiborane(4) (**1**) with BBr_3 , which lead to the formation of compound **2** and the byproduct $[(\text{C}_4\text{H}_8\text{N})_2\text{B}_2\text{Br}_3(\text{OEt})]$ (**4**).

Results and Discussion

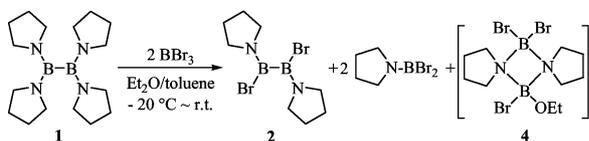
To obtain compound **2**, we started from tetrapyrrolidinodiborane(4) (**1**), which was prepared in high yield (90%) by a combination of the literature methods [**1** from $(\text{C}_4\text{H}_8\text{N})_2\text{BCl}$ and $\text{NaK}_{2,8}$, 46% [16], and **1** from $(\text{C}_4\text{H}_8\text{N})_2\text{BBr}$ and Na , 50% [17]] by using the two more reactive starting compounds, $(\text{C}_4\text{H}_8\text{N})_2\text{BBr}$ and $\text{NaK}_{2,8}$. The reaction of **1** with 1 equiv. of BBr_3 did not afford pure **2**, but a mixture of **2** and the monobromodiborane(4) species **3** (Scheme 1), as characterized by mass spectrometry which gave the molecular ion peaks for **2** and **3**, respectively. In addition, $(\text{C}_4\text{H}_8\text{N})_2\text{BBr}$ was detected (^{11}B NMR and MS).

This indicates that, in contrast to the results in the literature [6] on the reaction with tetrakis(dimethylamino)diborane(4), 1 equiv. of BBr_3 in the present case is not enough to completely replace two pyrrolidino groups in **1**.



Scheme 1.

When 2 equiv. of BBr_3 were used (Scheme 2), colorless **2** was obtained in 69% yield. A very small amount of **4** was also formed. The identity of both compounds has been confirmed by X-ray structure analyses (see below).



Scheme 2.

The formation of **4** results obviously from the Et_2O solvent used (see Experimental Section), which can react with $(\text{C}_4\text{H}_8\text{N})\text{BBr}_2$, produced in the reaction and identified by ^{11}B NMR and MS, to give $(\text{C}_4\text{H}_8\text{N})\text{B}(\text{OEt})\text{Br}$, which further reacts with $(\text{C}_4\text{H}_8\text{N})\text{BBr}_2$ to afford **4**. It is unlikely that $(\text{C}_4\text{H}_8\text{N})\text{BBr}_2$ dimerizes to form $[\text{C}_4\text{H}_8\text{NBBR}_2]_2$ [18] which then reacts with Et_2O to give **4**. The same reaction in toluene (Scheme 2) gives pure **2** in similar yield (64%). Compound **2** shows polymorphism (or dimorphism) phenomena: from a hexane/toluene solution (-28°C) it crystallizes as **2'** in the orthorhombic space group $P2_12_12$ (determined at 103(2) K), while neat **2** on cooling (-30°C) crystallizes as **2''** in the triclinic space group $P1\bar{1}$ (determined at 293(2) K).

Fig. 1 shows only **2'** (orthorhombic), as the bond lengths and angles are similar in **2'** and **2''**, which differ in their conformation. The B-Br bond lengths [1.981(2) in **2'** and 1.978(2) Å in **2''**] are similar to those in $\text{B}_2(\text{NMe})_2\text{Br}_2$ [1.979(13) Å] [19] as to the B-B bond distances [1.696(4) in **2'**, 1.684(3) in **2''** Å] [1.682(16) Å in $\text{B}_2(\text{NMe})_2\text{Br}_2$], but are shorter than those in the starting compound **1** (1.739 Å) [17]. The shorter B-N bond lengths [1.381(2) in **2'**, 1.371(2) in **2''**, cf. 1.424/1.427 Å in **1**] indicate a stronger B-N

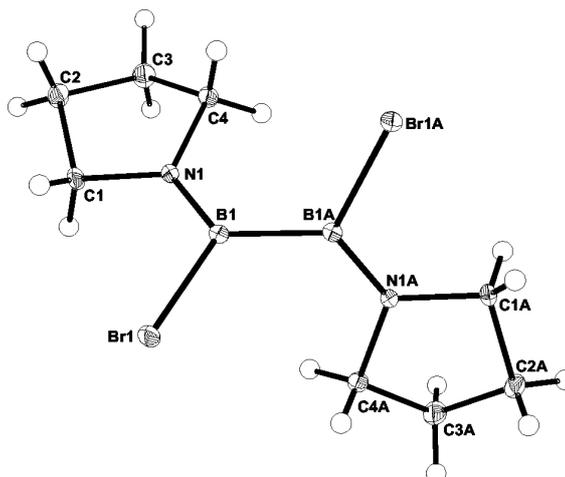


Fig. 1. Molecular structure of **2** in the orthorhombic phase **2'**. Selected bond lengths [Å]: Br1-B1 1.981(2), N1-B1 1.381(2), B1-B1A 1.696(4). [Data for the triclinic phase **2''**: Br-B 1.978(2), N-B 1.370(2), B-B 1.684(3)].

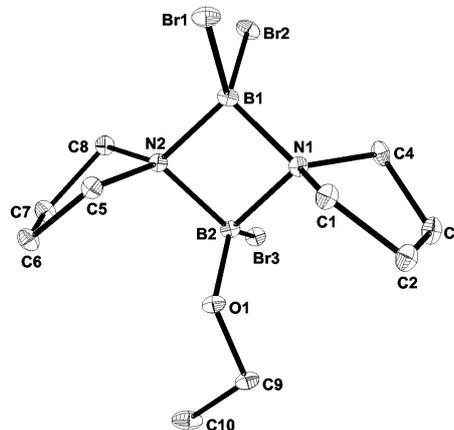


Fig. 2. Molecular structure of **4**, hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Br1-B1 2.012(3), Br2-B1 2.013(3), Br3-B2 2.045(3), N1-B1 1.578(4), N1-B2 1.655(3), N2-B1 1.580(3), N2-B2 1.618(3), O(1)-B(2) 1.375(3); B1-N1-B2 86.7(4), B1-N2-B2 88.0(2), N2-B2-N1 89.1(2), N1-B1-N2, 93.3(2).

π interaction in **2** than in **1** because of replacement of the two pyrrolidino in **1** by two bromine atoms. This is consistent with the results in 1,3-dichloro-1,3,5-tris(dimethylamino)triborane(5) and the corresponding bromine and iodine analogs [15]. The torsion angles Br1-B1-B1A-Br1A and N1-B1-B1A-N2 in **2'** are $-122.8(2)$ and $-122.8(3)^\circ$, respectively, while the corresponding values in **2''** are $-86.3(15)$ and $-82.9(19)^\circ$, respectively.

The structure of **4** is shown in Fig. 2. The four-membered B-N-B-N ring is not planar but folded (tor-

sion angle B1-N2-B2-N1: 12.5°). The B2-Br3 bond length of 2.045 Å is longer than those in **2**, and also slightly longer than the B1-Br1 and B1-Br2 distances (2.012/2.013 Å), due to the different orientation of the pyrrolidino rings and the steric requirements of the OEt group. The presence of the OEt group also influences the B-N bond lengths: the distances B2-N1 and B2-N2 (1.655/1.618 Å) are longer than those involving B1 atom (1.578/1.580 Å, respectively). However, the B-Br and B-N bond lengths in **4** are similar to those in the related structure [C₄H₈BBR₂]₂ (av. B-Br distance 1.999, B-N 1.603 Å) [20].

The results of the dehalogenation experiments with **2** show that the reactions with NaK_{2,8} in hexane or toluene afford mixtures, in which surprisingly small amounts **1** could be identified by a comparison of its NMR and HR-MS data with those of an authentic sample.

Experimental Section

All reactions and manipulations were performed in dry glassware under nitrogen using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. NMR spectra were recorded on a Bruker DRX 200 spectrometer (¹H: 200.13 MHz, ¹¹B: 64.21 MHz, ¹³C: 50.32 MHz) in CDCl₃. Et₂O•BF₃ was used as external standard for ¹¹B NMR. As internal references for ¹H and ¹³C NMR, the signals of CDCl₃ were used and shifts were calculated relative to TMS. MS: ZAB-2F VH Micromass CTD spectrometer, and a JEOL MS Station JMS 700 spectrometer. Compound **1** was prepared according to literature procedures [16, 17].

1,2-Dibromo-1,2-dipyrrolidino-diborane(4) (**2**)

a) To a solution of (C₄H₈N)₄B₂ (3.2 g, 10.6 mmol) in Et₂O (20 ml) at -40 °C was added a solution of BBr₃ (2.7 g, 10.7 mmol) in toluene (15 ml) within 20 min. The mixture was stirred for 4 h and then overnight at r.t. After the removal of the solvents under reduced pressure, the yellow residue was distilled to give a colorless liquid [(C₄H₈N)₂BBr, 2.1 g, 84%] at 70 °C/5 × 10⁻² torr, and a colorless oil (2.0 g) at 100 °C/6 × 10⁻² torr, identified to be a mixture of **2** and **3**. ¹H NMR (CDCl₃): δ = 1.6 (NCH₂CH₂), 1.8 (NCH₂CH₂), 3.3 (NCH₂CH₂), 3.5 (NCH₂CH₂); All signals are overlapping and broad. ¹¹B NMR (CDCl₃): δ = 36.2 (br.); -¹³C NMR (CDCl₃): δ = 25.6, 25.8, 26.7, 27.1 (NCH₂CH₂), 49.5, 49.8, 50.6, 51.4 (NCH₂). - EI-MS: *m/z* (%) = 322 (22) [2⁺], 311 (32) [3⁺], 241 (53) [2⁺ - Br], 232 (80) [3⁺ - Br], 163 (32) [2⁺ - 2Br + 1], 151 (100) [3⁺ - 2Br]. - HR-MS (EI): *m/z* = 311.1325 [3⁺]; calcd. for ¹²C₁₂¹H₂₄¹¹B₂⁷⁹Br¹⁴N₃ 311.1340 (Δ*m* = -1.5 mmu).

Table 1. Crystal data and details of data collection and structure solution of **2'**, **2''** and **4**.

	2'	2''	4
Empirical formula	C ₈ H ₁₆ B ₂ Br ₂ N ₂	C ₈ H ₁₆ B ₂ Br ₂ N ₂	C ₁₀ H ₂₁ B ₂ Br ₃ N ₂ O
Formula weight	321.67	321.67	446.64
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 1 bar	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	11.2890(6)	6.8944(5)	10.9113(10)
<i>b</i> [Å]	11.6672(6)	8.0273(6)	10.3105(10)
<i>c</i> [Å]	4.6012(3)	11.7240(9)	13.4627(12)
<i>α</i> [°]	90	99.210(2)	90
<i>β</i> [°]	90	102.527(2)	91.344
<i>γ</i> [°]	90	91.176(2)	90
<i>V</i> [Å ³]	606.03(6)	624.21(8)	1514.2(2)
<i>Z</i>	2	2	4
<i>ρ</i> (calcd.), [g/cm ³]	1.763	1.711	1.959
<i>μ</i> [mm ⁻¹]	6.651	6.458	7.982
<i>F</i> (000)	316	316	872
Crystal size [mm]	0.45 × 0.12 × 0.10	0.60 × 0.14 × 0.12	0.52 × 0.27 × 0.13
<i>Θ</i> _{max} [°]	32.03	32.00	32.00
Temp, [K]	103(2)	293(2)	103(2)
Refl. collected	9541	10729	5134
Refl. indep.[<i>R</i> _{int}]	2085 [0.035]	4211 [0.027]	5134 [0.030]
Refl. observed	1983	3351	4167
parameters	97	200	247
GOOF	1.060	1.037	1.055
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0194	0.0268	0.0320
<i>wR</i> 2 (all data)	0.0469	0.0654	0.0779
Min./max. resid. [eÅ ⁻³]	-0.308/1.138	-0.543/0.749	-0.615/1.701

b) Analogous procedure as described above. (C₄H₈N)₄B₂ (3.3 g, 10.9 mmol), BBr₃ (5.5 g, 21.9 mmol). The colorless residue was distilled to give a colorless liquid as the first fraction at 30 °C/2 × 10⁻¹ torr, which contained (C₄H₈N)BBR₂ (1.62 g, 31%) and a very small amount of **4**. The second fraction at 90 °C/7 × 10⁻² torr (1.08 g) was a mixture of (C₄H₈N)BBR₂ and **2**, the third fraction, obtained at 110 °C/7 × 10⁻² torr as a colorless oil, was identified to be **2** (2.44 g, 69%). ¹H NMR (CDCl₃): 1.82 (t, ³*J* = 6.8 Hz, 4 H, NCH₂CH₂), 1.85 (t, ³*J* = 6.8 Hz, 4 H, NCH₂CH₂), 3.33 (t, ³*J* = 6.8 Hz, 4 H, NCH₂), 3.46 (t, ³*J* = 6.8 Hz, 4 H, NCH₂). - ¹¹B NMR (CDCl₃): δ = 35.8. - ¹³C NMR (CDCl₃): δ = 25.6, 27.1 (NCH₂CH₂), 50.6, 51.4 (NCH₂). - EI-MS: *m/z* (%) = 322 (43) [M⁺], 241 (100) [M⁺ - Br]. - HR-MS (EI): *m/z* = 319.9819 [M⁺]; calcd. for ¹²C₈¹H₁₆¹¹B₂⁷⁹Br¹⁴N₂ 319.9866 (Δ*m* = -4.7 mmu). On cooling the first fraction (ca. -40 °C) colorless crystals of **4** were formed. Attempts to measure the melting point was not successful because of the presence of liquid (C₄H₈N)BBR₂ at ambient temperature. Different types of crystals of **2** (m.p. 78–80 °C) were obtained by cooling either the neat compound or its hexane/toluene (1:1, v/v) solution.

X-ray structure determinations

The crystal data and details of data collection and structure solution are listed in Table 1. The intensity data were collected with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scans). Data were corrected for Lorenz-polarization

and absorption effects (semiempirical, SADABS [21]). The structures were solved by direct methods (SHELXS-86) [22] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97) [22]. All non-hydrogen atoms were refined anisotropically. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center: CCDC-267548 (**2'**), –267549 (**2''**), –267550 (**4**), –267551 [(CH₃)₂NB]₆. Copies of the data can be obtained free of charge on application to The

Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44 (1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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