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Diborane (4) derivatives via coupling of amine monobromocyanoboranes: Study of the bromination of amine cyanoborane and molecular structures of the amine dibromocyanoboranes

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Abstract

The first examples of diborane (4) compounds derived from amine cyanoboranes are described. A series of monobromo derivatives of amine cyanoboranes (A:BHBrCN), and dibromo derivatives (A:BBr_2CN), **1**–**7**, were prepared. Lithiation of the monobromo derivative of trimethylamine cyanoborane, using *n*-BuLi, did not produce the C-lithiated intermediate $Li^+[CH_2NMe_2BHBrCN]^-$, but instead the B-lithiated intermediate $Li^+[Me_3NBHCN]^-$, was obtained. This intermediate, when allowed to react for 16 h, coupled with the un-lithiated trimethylamine monobromocyanoborane ($Me_3NBHBrCN$) and resulted in diborane (4) derivative formation as the 2LiBr complex. The same result was obtained when one equiv of the trimethylamine monobromocyanoborane was added to the reaction mixture 1 h after lithiation. Following the same procedure, novel diborane (4) derivatives of amine cyanoboranes were successfully obtained, **8**–**11**, as their 2LiBr complexes from the monobromo derivatives of the corresponding amine cyanoboranes. Molecular structures of the trimethylamine dibromocyanoborane, **6**, and the triethylamine dibromocyanoborane, **7**, were determined using X-ray crystallography.

Keywords: Amine monobromocyanoboranes; Amine dibromocyanoboranes; Crystal structures; B-lithiation; B–B bond formation; Diboron (4) compounds

1. Introduction

Diboron compounds with a boron–boron single bond are important intermediates, and their structural complexity lies between simple monoboron derivatives and polyhedral electron-deficient compounds. Since the initial discovery of B_2Cl_2 by Stock et al. [1], a continual effort has been focused on the synthesis of diboron compounds, particularly the single derivatives of B_2X_2 type. These boron containing compounds provide the simplest examples of catenation in boron chemistry and offer suitable systems to study properties of the covalent B–B bond and the characteristic chemistry of compounds containing this linkage. Diboron derivatives have been utilized as synthetic intermediates, functional molecules, functional polymers, and biologically active compounds [2]. Diboration, the addition of diboron tetrahalides B_2X_4 ($X = F$, Cl, Br), to unsaturated

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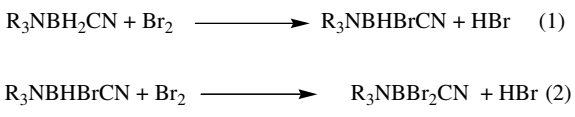
hydrocarbons is a straightforward method to introduce boryl groups into organic molecules, but their synthetic use has been severely limited because of the instability and limited availability of the reagents [2]. Diboron compounds can also be used in boron neutron capture therapy (BNCT), first proposed in 1936 [3]. Critical to the development of BNCT is the synthesis of boron-containing compounds that selectively target tumor cells [4]. Numerous boron-containing compounds have been tested [5–8]. These agents may be categorized into those containing a single boron atom and those containing multiple boron atoms as boron clusters having B–B bonds. The advantage of the latter is that higher boron concentration in a tumor can be achieved [9]. Herein, we report a novel method for the preparation of diborane (4) derivatives of amine cyanoboranes, the first example of B–B diboron compounds derived from such compounds. Amine and phosphine cyanoboranes are an intriguing group of compounds that have inspired extensive biological screening. The promising early results led to the synthesis of a large number derivatives, some of which have been shown in model studies to have potent antitumor [10–15], anti-inflammatory [16–18], hypolipidemic [11,19], anti-hyperlipidemic [20], anti-ostoeoporotic [21], anti-neoplastic [22–24], BNCT [25], and other promising biological activities [26,27]. In the present study, the diborane (4) derivatives of the corresponding amine cyanoborane were synthesized as their 2LiBr complexes from of the monobromo derivative of the corresponding amine cyanoborane, followed by B–B coupling using elemental sodium or *n*-BuLi. Although numerous bromo derivatives of amine and phosphine cyanoboranes have been synthesized [28], no molecular structure determinations for such derivatives have been presented. In this work, two molecular structures of the prepared amine dibromocyanoborane derivatives **6** and **7** are presented.



Scheme 1. Preparation of amine monobromo and dibromocyanoborane derivatives from amine cyanoboranes.

2. Results and discussion

2.1. Synthesis of amine monobromocyanoboranes and dibromocyanoboranes

Reaction of the corresponding alkyl amine cyanoborane ($R_3NBH_2C{\equiv}N$), with 1.2 equiv. of Br_2 in double distilled water (DDW) at 0 °C for a period of 4 h, produced the monobromo derivatives ($R_3NBHBrC{\equiv}N$), **1**–**5**, in high purity and excellent yields (Scheme 1, Table 1). Performing the same reaction with 2.2 equiv. of Br_2 and allowing the reaction to warm to room temperature with stirring for 16 h, produced total conversion of the corresponding amine cyanoboranes to the dibrominated derivatives ($R_3NBBr_2C{\equiv}N$), **6**–**7**, in high purity and excellent yields (Scheme 1, Table 1). Though it is known that some trigonal R_2BH compounds react with HBr to generate the bromine substituted derivative, R_2BBr, with elimination of H_2 [29], our stoichiometry indicates that this is not so in the present case. The HBr produced from reaction of Br_2 with the amine cyanoborane (R_3NBH_2CN) (Scheme 1, eq 1), does not react with the monobrominated derivative ($R_3NBHBrCN$) to produce the dibrominated derivative (R_3NBBr_2CN), whereas, another equiv of Br_2 is necessary to produce the dibrominated derivative (Scheme 1, eq 2). Also, when the number of equiv. of Br_2 in the reaction of the amine cyanoborane was reduced to less than one equiv., a mixture of the starting material and amine monobromocyanoborane was obtained.

Table 1
Amine monobromocyanoboranes **1**–**5**, amine dibromocyanoboranes, **6**–**7**, and the 2LiBr complexed diborane (4) derivatives of amine cyanoboranes, **8**–**11**

Compound	*R*	*R′*	*R″*	δ_{ppm} (m)-^{11}B	δ_{ppm} (m)-^{11}B for A:BH_2CN	Yield (%)[a]
1	Me	Me	Me	−6.90 (d)	−14.92 (t)	95
2	Et	Me	Me	−9.34 (d)	−15.98 (t)[24]	94
3	Et	Et	Et	−9.34 (d)	−19.72 (t)	97
4	Bu	Me	Me	−11.75 (d)	−15.98 (t)[24]	94
5	Pen	Me	Me	−11.79 (d)	−15.93 (t)[24]	92
6[*]	Me	Me	Me	−9.89 (s)	−14.92 (t)	98
7[*]	Et	Et	Et	−10.88 (s)	−19.72 (t)	98
8	Me	Me	Me	−11.75 (d)	−14.92 (t)	80
9	Et	Et	Et	−11.39 (d)	−19.72 (t)	82
10	Bu	Me	Me	−11.04 (d)	−15.98 (t)[24]	78
11	Pen	Me	Me	−12.25 (d)	−15.93 (t)[24]	82

[a] Isolated yield.
[*] Crystalline product.

2.2. Synthesis of diborane (4) derivative of trimethylamine cyanoborane using n-BuLi

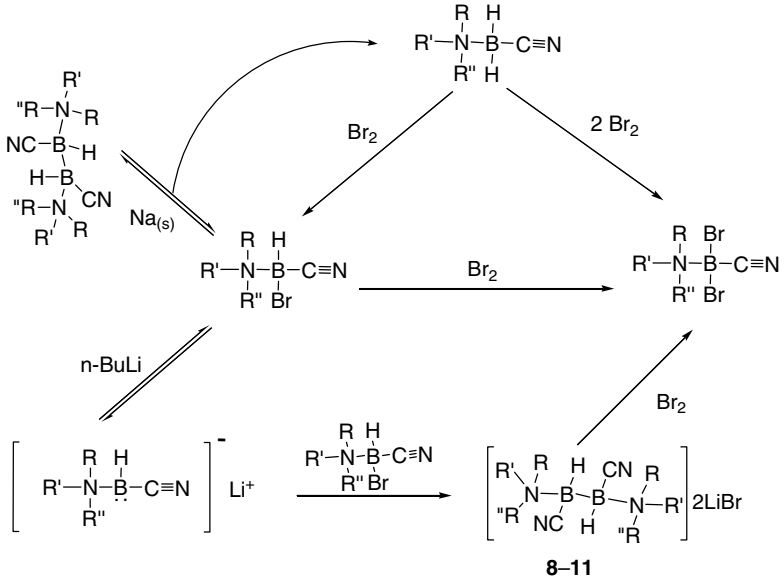
Following the previously published procedure for the C-lithiation of trimethylamine cyanoborane [29], the trimethylamine monobromocyanoborane derivative ($Me_3NBHBrC{\equiv}N$) using *s*-BuLi or *t*-BuLi produced a mixture of the C-lithiated intermediate $Li^+[CH_2N(Me)_2BHBrCN]^-$ and a new B-lithiated intermediate $Li^+[Me_3NBHCN]^-$ as determined by the formation of a mixture of the ethyldimethylamine monobromocyanoborane and a new product, **8**, after stirring the reaction mixture for 16 h at room temperature. However, using 3 equiv. of *n*-BuLi, only the B-lithiated intermediate was produced. Allowing the reaction mixture to warm to room temperature with stirring for 16 h, produced coupling of the B-lithiated intermediate with the un-lithiated trimethylamine monobromocyanoborane (Scheme 2), and the diborane (4) derivative, **8**, as the 2LiBr complex was formed in high purity and in good yield (Scheme 2, Table 1). The natures of the complex were confirmed by both elemental analysis and by mass spectroscopy (see Section 4). The same product was obtained when 1 equiv. of trimethylamine monobromocyanoborane was added 1 h after lithiation.

2.3. Synthesis of diborane (4) derivative of trimethylamine cyanoborane using elemental sodium

Dehalogination of haloborane amines with sodium to give the B–B diboron compounds was previously reported by Abu-Ali et al. [30]. Bis(pyrrolidino)bromoborane was debrominated to give the B–B coupled product, tetra(pyrrolidino)diborane (4). We tried this procedure, and obtained the diborane (4) derivative of trimethylamine cyanoborane. However, in addition to the coupling product, the monobromo derivative was partially reduced and the trimethylamine cyanoborane was obtained as by-product. This was the major drawback with elemental sodium (Scheme 2).

2.4. Synthesis of diborane (4) derivatives of other amine cyanoboranes

A series of diboron (4) derivatives of amine cyanoboranes were prepared as their 2LiBr complexes using the *n*-BuLi method with different amine monobromocyanoboranes, such as triethylamine, *n*-butyldimethylamine, and dimethylpentylamine, to give the corresponding diborane (4) derivatives, **9**–**11**, as their 2LiBr complexes in high purity and good yields. (Scheme 2, Table 1). Attempted coupling of the amine dibromocyanoboranes under the same reaction conditions failed to give the expected dibromodiborane (4) derivative. Only starting reagent was obtained. When sodium was used for coupling the amine dibromocyanoborane monomers, a mixture of the starting material, the diborane (4) derivative, the amine monobromocyanoborane, and the nonbrominated amine cyanoborane were produced. From these results it may be concluded that the dibromodiborane (4) derivatives are not stable or cannot be obtained by using any of these methods. The instability of the dibromodiborane (4) derivatives may be explained in terms of the steric hindrance caused by the large bromine atoms that replaces the hydrogen atoms in the diborane (4) derivatives.



Scheme 2. Preparation of compounds **8–11** from the corresponding amine cyanoboranes.

2.5. Bromination of the diborane (4) derivatives of amine cyanoboranes

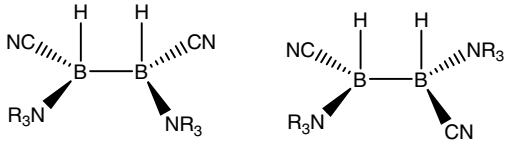
Brominating the diborane (4) derivatives of amine cyanoboranes, **8**–**11**, with excess of Br_2 in DDW, did not give the expected dibromodiborane (4) derivative. Instead the B–B bond was cleaved, and the dibrominated monomer (R_3NBBr_2CN) was obtained as a precipitate (Scheme 2). Adding one equivalent of bromine produced a mixture of the amine dibromocyanoborane, **6**, and the diborane (4) compound **8**. This confirms the instability of dibromodiborane (4) compounds, and explains the failure of B–B coupling of the amine dibromocyanoborane derivatives.

2.6. Crystallography

Crystals suitable for crystallographic X-ray analysis could not be obtained for the BH–BH compounds, possibly due to the formation of diastereomers because of the two chiral boron atoms (Scheme 3).

Crystals suitable for X-ray structure determination were obtained for compounds **6** and **7**. Their molecular structures were determined by single-crystal X-ray diffraction. The results of the diffraction analysis, crystal data, and details of the structure determination are shown in Figs. 1 and 2, and the data are summarized in Table 2.

Molecular structures of the two compounds **6** and **7** were determined at ca. 110 K with relatively high precision. They represent two independent and internally consistent determinations. The covalent parameters exhibit standard values characteristic to boron in tetrahedral sp^3 hybridization. Those of the N-BBr_2-C≡N are of a particular significance in the present context, and are summarized in Table 3. The observed data are comparable to those found in related compounds that contain the N-BBr_2-C fragment [31–36]. The conformation around the boron atom is nearly ideally tetrahedral, with Br–B–Br and N–B–C bond angles of 109°, and the conformation around the carbon atom in B–C≡N moiety is nearly linear with B–C≡N bond angles of 178.5° and 176.7°.



Scheme 3. Two possible diastereomers for compounds **8**–**11**.

2.7. Spectroscopic analysis

All the compounds were fully characterized by ^1H, ^{11}B, and ^{13}C NMR, FT-IR, mass spectra, elemental analysis and melting point. The ^1H and ^{13}C NMR spectra for compounds **1**–**7** showed an expected downfield shift of the CH_2-N and CH_3-N peaks due to the replacement of the hydrogen atom in the corresponding amine cyanoborane (A:BH_2CN) by inductive bromine atom (see Section 4). Diastereomeric peaks for the carbon atom of the N-CH_2 fragment appeared in all ^{13}C spectra for compounds **1–5**, due to the presence of the chiral boron-atom in the monobromo derivatives (see Section 4). In the ^{11}B, similar downfield shifts were observed, and the multiplicity due to BH coupling changed from triplet for BH_2 in the amine cyanoborane, to doublet and singlet for the monobromo and dibromo derivatives, respectively (Table 1). In the diboron (4) derivatives, **8**–**11**, the ^1H and ^{13}C NMR spectra showed an expected upfield shift compared to the monobromo derivatives for the CH_2-N and CH_3-N peaks due to the absence of the inductive bromine atom. In the ^{11}B, similar upfield shifts were observed. A comparison between the ^{11}B chemical shifts of the diboron compounds and the ^{11}B chemical shifts of the corresponding amine

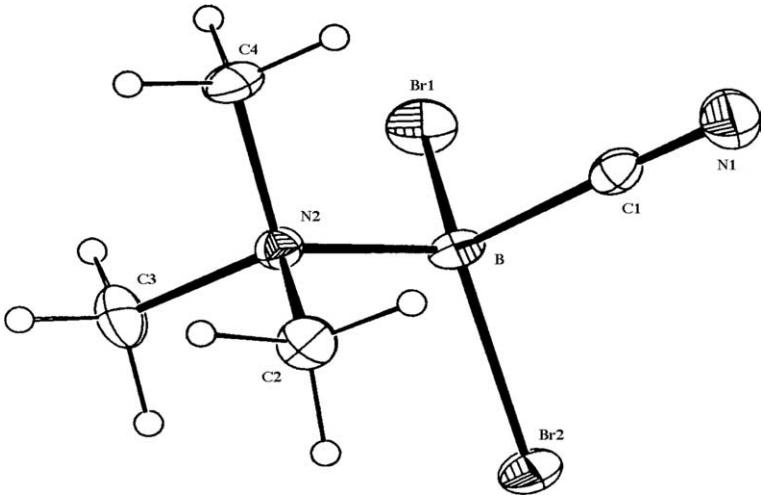


Fig. 1. The molecular structure of compound **6**.

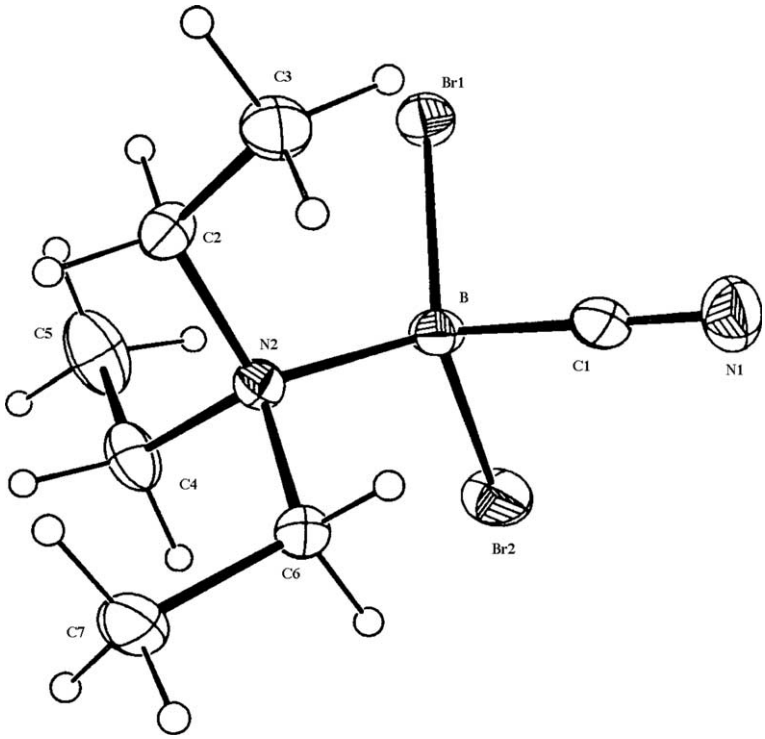


Fig. 2. The molecular structure of compound **7**.

Table 2
Crystal data and structure refinement for compounds **6** and **7**

	6	**7**
Formula	$C_4H_9BBr_2N_2$	$C_7H_{15}BBr_2N_2$
Fw	255.76	297.84
Habit	Plates	Prisms
Color	Colorless	Colorless
Temp. K	110(2)	110(2)
Radiation	Mo Kα	Mo Kα
Crystal size (mm)	$0.25\times0.25\times0.15$	$0.20\times0.15\times0.15$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	10.2102(2)	8.0103(2)
b (Å)	6.72510(10)	11.7302(3)
c (Å)	12.3776(3)	11.8342(4)
α (°)	90.00	90.00
β (°)	92.1910(8)	90.00
γ (°)	90.00	90.00
V Å^3	849.28(3)	1111.97(5)
Z	4	4
μ (mm^{-1})	9.466	7.244
2θ Range (°)	2.3–27.8	2.4–27.8
No. of unique reflcns	1985	1502
No. of restraints	0	0.917
hkl limits	0, 13/0, 8/−16−16	0, 9/0, 15/0,15
No. of parameters	85	109
No. of reflcns with $[I>2\sigma(I)]$	1814	1414
Final R indices[a] $[I>2\sigma(I)]$		
R_1	0.0294	0.0259
wR_2	0.0737	0.0609
$\lvert\Delta\rho\rvert$(e Å^{-3})	⩽0.130	⩽0.090
GOF	1.132	0.917

[a] $R_1=\sum\|F_o|-|F_c\|/\sum|F_o|.\ wR_2=\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 3
Covalent parameters of the N-BBr_2-C≡N in compounds **6** and **7**

	6	**7**
B–N(sp^3)/Å	1.592	1.613
B–C(sp^2)/Å	1.594	1.596
B—Br/Å	2.013, 2.019	2.016, 2.027
C≡N/Å	1.118	1.134
Br–B–Br/°	109.21	109.2
N–B–C/°	109.2	111.1
N–B–Br/°	111.1, 110.92	113.8, 110.6
C–B–Br/°	108.6, 107.8	106.5, 105.3
B–C≡N/°	178.5	176.7

cyanoboranes (A:BH_2CN), showed a downfield shift of the former. This is expected due to replacement of the hydrogen atom by electronegative boron-atom. The multiplicity of the ^{11}B peak was a doublet in all the diboron (4) compounds due to BH coupling in the BH–BH fragment (Table 1). The IR vibrations are in the expected range: (2923–2962 cm^{-1}) C–H, (2358–2361 cm^{-1}) C≡N (1456–1478 cm^{-1}) C–N, and (603–608 cm^{-1}) B–Br stretching vibrations. Molecular weights (GC–MS and LC–MS) were observed for all compounds **1**–**11**. In particular, **8**–**11**, LCMS data showed molecular weights corresponding to the [B–B].2LiBr complex, confirming the elemental analysis, and peaks showing consecutive losses of one and two LiBr. In addition, peaks of 102 and 104 were also observed, representing the (N_2-B–B-$(CN)_2$) and the (N_2-BH–BH-$(CN)_2$) fragments, respectively.

3. Conclusion

Diboron (4) derivatives have been utilized as synthetic intermediates, functional molecules, functional polymers, ^{10}B carriers for boron neutron capture therapy (BNCT), and biologically active compounds. As precursors for novel diboron derivatives of amine cyanoboranes, a series of mono and dibrominated amine cyanoboranes, **1**–**7**, were prepared in high purity and excellent yields. Molecular structures of compounds **6** and **7** were determined by single-crystal X-ray diffraction. B–B diboron compounds of amine cyanoboranes, **8**–**11**, as their 2LiBr complexes were successfully synthesized through coupling of the corresponding amine monobromocyanoborane derivatives using *n*-BuLi.

4. Experimental

4.1. Syntheses

4.1.1. General comments

All coupling reactions were carried out under nitrogen. Solvents were dried by the usual methods and distilled before use. All other chemicals were obtained from Sigma–Aldrich and used as received without any further purification. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded in $CDCl_3$ and D_2O solution on a Varian Unity Spectrometer (300, 75, 96 MHz) using Me_4Si as an internal standard. Infrared spectra were run for samples in NaCl cells on a Bruker Vector 22 FT-IR spectrophotometer. GC–MS analyses were performed on an HP GC–MS instrument (Model HP6890 GC/HP5971 MSD) with an electron impact detector and 30 m methyl silicon column. LC–MS analyses were performed on a Finnigan LCQDUO Thermo Quad, with electron spray detector. Melting points were measured on a Fisher Scientific melting point apparatus. Elemental analyses were performed in house at the Hebrew University Microanalysis laboratory. Me_3NBH_2CN was prepared from $Me_3N \cdot HCl$ and $NaBH_3CN$ using the literature method [31]. Et_3NBH_2CN was prepared following same procedure for preparation of Me_3NBH_2CN, but the reflux time with $NaBH_3CN$ in THF was extended to 5 days. All other amine cyanoboranes were prepared from trimethylamine cyanoborane using the previously reported C-lithiation method [24].

4.1.2. Synthesis of compounds *1*–*2*

One millimole of the desired amine cyanoborane was dissolved in 10 mL DDW, cooled to 0 °C in an ice bath, and (1.2 mmol) of Br_2 dissolved in 20 mL DDW was added drop wise. The reaction mixture was allowed to stir at 0 °C for a period of 4 h. The produced precipitate was filtrated and dried under vacuum. The products were re-crystallized using an acetone/water solvent mixture, where the acetone was allowed to evaporate slowly at room temperature for few days.

4.1.3. Synthesis of compounds *3*–*5*

One millimole of the desired amine cyanoborane was dissolved in 10 mL MeOH, cooled to 0 °C in an ice bath, and (1.2 mmol) of Br_2 dissolved in 20 mL DDW was added drop wise. The reaction mixture was allowed to stir and warm gradually to room temperature for a period of 4 h. MeOH was evaporated, and the aqueous layer was extracted with 3×20 mL of ether. The organic layers were combined, washed with brine, dried over sodium sulfate, filtered, decolorized by adding charcoal, filtrated, and concentrated under vacuum. The products were obtained as a yellowish liquid.

4.1.4. Synthesis of compounds *6*–*7*

One millimole of the desired amine cyanoborane was dissolved in 10 mL DDW, cooled to 0 °C in an ice bath, and (2.2 mmol) of Br_2 dissolved in 20 mL DDW was added drop wise. The reaction mixture was allowed to stir at 0 °C overnight. Then the produced precipitate was filtrated and dried under vacuum. The product was re-crystallized using an acetone/water solvent mixture, where the acetone was allowed to evaporate slowly at room temperature for few days.

4.1.5. Synthesis of compounds *8*–*11* using n-BuLi

One millimole of the desired amine monobromocyanoborane was dissolved in 10 mL of dry THF, cooled to −78 °C, and (1.88 mL, 3.0 mmol) of 1.6 M *n*-BuLi/hexanes solution was added drop wise. The reaction mixture was allowed to warm gradually to room temperature overnight. Then 20 mL of saturated aqueous $NaHCO_3$ solution were added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with 3×10 mL of ether. Organic layers were combined, washed with brine, dried over sodium sulfate, filtered, and concentrated under vacuum.

4.1.6. Synthesis of the diborane (4) derivative of trimethylamine monobromocyanoborane using elemental sodium [30]

A solution of trimethylamine monobromocyanoborane (0.98 g, 10 mmol) in dry toluene (2 mL) was added slowly to a highly-dispersed molten sodium (0.276 g, 12 mmol) in dry toluene (5 mL) at 110 °C. The reaction leaved under reflux for overnight. Then solvent evaporated and the mixture product was dried under vacuum.

4.2. X-ray crystallographic study

Colorless single crystals of compounds **6** and **7**, suitable for X-ray diffraction analysis were obtained from acetone/water solution mixture at 25 °C, where slow evaporation of acetone produced colorless crystal plates

for **6** and prisms for **7** after few days. The crystal data and structure refinement parameters are summarized in Table 2. All diffraction measurements were carried out on a Nonius KappaCCD diffractometer at ca. 110 K, using graphite monochromated Mo Kα ($\lambda = 0.71070$ Å) radiation and 1° φ scans. The intensity data was integrated and scaled by DENZO-SMN and SCALEPACK programs [37]. The structures were solved by direct methods (SIR-92) [38] and refined by full-matrix least-squares on F^2 (SHELXL-97) [39]. All non-hydrogen atoms were refined anisotropically; the hydrogens were located in idealized positions and allowed to ride with thermal parameters 1.2 times those of their parent carbon.

4.3. Analytical data

4.3.1. Triethylamine cyanoborane

White oil, 92% (0.129 g). ^{1}H NMR (D_2O): δ 0.27 (q, 2H, $J_{B-H} = 88.20$ Hz), δ 1.14 (t, 9H, $J = 7.2$ Hz), δ 2.94 (q, 6H, $J = 6.9$ Hz).^{13}C {^{1}H} NMR ($CDCl_3$): δ 8.53, 51.9, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −19.72 (t, $J_{B-H} = 100.86$ Hz). IR (neat, cm^{-1}): 2923 (C–H), 2358 (C≡N), 1456 (C–N). MS: *m*/*z* (%) 140 (M, 10), 115 (15), 114 (22), 101 (100), 84 (8), 71 (5). Anal. Calc. for $C_7H_{17}BN_2$: C, 60.04; H, 12.24; N, 20.00. Found: C, 59.96; H, 12.06; N, 19.97.

4.3.2. Trimethylamine monobromocyanoborane (*1*)

White solid, 95% (0.168 g), m.p. 67 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 (s), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 50.82 (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −6.90 (d, $J_{B-H} = 131.94$ Hz). IR (mineral oil, cm^{-1}): 2956 (C–H), 2359 (C≡N), 1458 (C–N), 603 (B–Br). MS: *m*/*z* (%) 179 (10), 178 (10), 177 (M, 20), 176 (18), 151 (100), 150 (85), 102 (65), 71 (10). Anal. Calc. for $C_4H_{10}BBrN_2$: C, 27.17; H, 5.70; N, 15.84; Br, 45.18. Found: C, 27.02; H, 5.78; N, 15.75; Br, 45.68.

4.3.3. Triethylamine monobromocyanoborane (*2*)

White oil, 94% (0.206 g). ^{1}H NMR ($CDCl_3$): δ 1.23 (t, 9H, $J = 7.5$ Hz), δ 3.03 (q, 6H, $J = 7.5$ Hz), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 10.12, 52.82 (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −13.83 (d, $J_{B-H} = 128.29$ Hz). IR (neat, cm^{-1}): 2947 (C–H), 2359 (C≡N), 1475 (C–N), 605 (B–Br). MS: *m*/*z* (%) 221(8), 220 (8), 219 (M, 10), 218 (8), 149 (85), 139 (4), 102 (65). Anal. Calc. for $C_7H_{16}BBrN_2$: C, 38.40; H, 7.37; N, 12.80; Br, 36.50. Found: C, 38.34; H, 7.48; N, 12.65; Br, 36.81.

4.3.4. Ethyldimethylamine monobromocyanoborane (*3*)

Yellowish oil, 97% (0.184 g) yield. ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 3H, $J = 7.2$ Hz), 2.77 (s, 6H), 3.15 (q, 2H, $J = 7.2$ Hz), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 8.69, 46.96, 47.14, 56.70, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −9.34 (d, $J_{B-H} = 131.62$ Hz). IR (neat, cm^{-1}): 2940 (C–H), 2361 (C≡N), 1469 (C–N), 603 (B–Br). MS: *m*/*z* (%) 193 (8), 192 (8), 191 (M, 10), 165 (82), 164 (60), 109 (20), 73 (5). Anal. Calc. for $C_5H_{12}BBrN_2$: C, 31.46; H, 6.34; N, 14.68; Br, 41.86. Found: C, 31.31; H, 6.42; N, 14.49; Br, 41.81.

4.3.5. Butyldimethylamine monobromocyanoborane (*4*)

Yellowish oil, 94% (0. 206 g) yield. ^{1}H NMR ($CDCl_3$): δ 0.84 (t, 3H, $J = 6.9$ Hz), 1.36 (sex, 2H, $J = 7.2$ Hz), 1.81 (pent, 2H, $J = 7.2$ Hz), 2.61 (s, 6H), 2.81(t, 2H, $J = 7.2$ Hz), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 13.94, 20.29, 24.90, 47.58, 47.72, 61.73, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −11.75 (t, $J_{B-H} = 104.4$ Hz). IR (neat, cm^{-1}): 2962 (C–H), 2352 (C≡N), 1478 (C–N), 604 (B–Br). MS: *m*/*z* (%)221(10), 220 (10), 219 (M, 20), 218 (10), 193 (100), 192 (83), 114 (30), 102 (35), 101 (25), 86 (10). Anal. Calc. for $C_7H_{16}BBrN_2$: C, 38.40; H, 7.34; N, 12.80; Br, 36.50. Found: C, 38.11; H, 7.40; N, 12.76; Br, 36.39.

4.3.6. Dimethylpentylamine monobromocyanoborane (*5*)

Yellowish oil, 92% (0.214 g) yield.^{1}H NMR ($CDCl_3$): δ 0.97 (t, 3H, $J = 7.2$ Hz), 1.25 (m, 2H), 1.35 (pent, 2H, $J = 7.2$ Hz), 1.63 (m, 2H), 2.78 (s, 6H), 3.03 (m, 2H), (HB cannot be detected). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.10, 22.46, 22.59, 29.01, 47.57, 47.70, 61.92, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −11.79 (d, $J_{B-H} = 130.1$ Hz). IR (neat, cm^{-1}): 2962 (C–H), 2358 (C≡N), 1456 (C–N), 603 (B–Br). MS: *m*/*z* (%) 235 (15), 234 (15), 233 (M, 25), 232 (15), 230 (15), 207 (7), 128 (25), 127 (40), 115 (7), 100 (30), 71 (5). Anal. Calc. for $C_8H_{18}BBrN_2$: C, 41.25; H, 7.79; N, 12.03; Br, 34.30. Found: C, 41.60; H, 7.88; N, 12.12; Br, 34.42.

4.3.7. Trimethylamine dibromocyanoborane (*6*)

White solid, 98% (0.251 g), m.p. 190 °C. ^{1}H NMR ($CDCl_3$): δ 3.08 (s), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 50.59, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −9.89 (s). IR (mineral oil, cm^{-1}): 2959 (C–H), 2359 (C≡N), 1463 (C–N), 604 (B–Br). MS: *m*/*z* (%) 260 (18), 259(12), 258 (25), 257(12), 256 (M, 10), 255(5), 242 (30), 226 (100), 176 (25), 151(20), 96 (7). Anal. Calc. for $C_4H_9BBr_2N_2$: C, 18.79; H, 3.55; N, 10.95; Br, 62.49. Found: C, 18.62; H, 3.59; N, 10.87; Br, 62.99.

4.3.8. Triethylamine dibromocyanoborane (*7*)

White solid, 98% (0.292 g), m.p. 190 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (t, 9H, $J = 7.5$ Hz), 3.47 (q, 6H, $J = 7.5$ Hz), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 11.85, 56.70, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −10.88 (s). IR (mineral oil, cm^{-1}): 2959 (C–H), 2359 (C≡N), 1463 (C–N), 604 (B–Br). MS: *m*/*z* (%) 302(30), 301 (27), 300 (35), 299 (27), 298 (M, 25), 297

(14), 272 (20), 218 (30), 138 (100), 112 (25), 101 (5). Anal. Calc. for $C_7H_{15}BBr_2N_2$: C, 28.23; H, 5.08; N, 9.41; Br, 53.66. Found: C, 27.52; H, 5.23; N, 9.27; Br, 52.25.

*4.3.9. Diborane (4) derivative of trimethylamine cyanoborane. 2LiBr (**8**)*

White solid, 80% (0.294 g), m.p. 74 °C. ^{1}H NMR (D_2O): δ 2.85 (s), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 50.79, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −11.75 (d, $J_{B-H} = 133.77$ Hz). IR (mineral oil, cm^{-1}): 2923 (C–H), 2359 (C≡N), 1456 (C–N). MS: *m/z* (%) 370 (10), 369 (20), 367(18), 366 (15, M), 365(8), 280(1), 194 (100), 192 (80), 168 (5), 152 (10), 145 (35), 144 (60), 112 (10), 104 (10), 102 (10), 88 (3), 74 (3). Anal. Calc. for $C_8H_{20}B_2Br_2Li_2N_4$: C, 26.14; H, 5.48; N, 15.24; Br, 43.48. Found: C, 26.25; H, 5.52; N, 15.33; Br, 43.58.

*4.3.10. Diborane (4) derivative of triethylamine cyanoborane. 2LiBr (**9**)*

White solid, 82% (0.369 g). ^{1}H NMR (D_2O): δ 1.31 (t, 18 H, $J = 7.2$ Hz), 3.14 (q, 12 H, $J = 7.2$ Hz), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 8.96, 51.20, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −11.39 (d, $J_{B-H} = 131.95$ Hz). IR (mineral oil, cm^{-1}): 2955 (C–H), 2358 (C≡N), 1457 (C–N). MS: *m/z* (%) 454 (15), 453 (30), 452 (22), 450 (M, 20), 449 (10),364 (15) 279 (5), 275 (25), 274 (75), 272 (100), 270 (43), 242 (32), 220 (10), 219 (30), 194 (30), 193 (17), 191 (10), 164 (12), 152 (40), 150 (23), 132 (6), 114 (10), 104 (15), 102 (26), 101 (13). Anal. Calc. for $C_{14}H_{32}B_2Br_2Li_2N_4$: C, 37.22; H, 7.14; N, 12.40; Br, 35.38. Found: C, 37.41; H, 7.20; N, 12.53; Br, 35.25.

*4.3.11. Diborane (4) derivative of n-butyldimethylamine cyanoborane. 2LiBr (**10**)*

Yellowish oil, 78% (0.352 g) yield. ^{1}H NMR ($CDCl_3$): δ 0.84 (t, 3H, $J = 6.9$ Hz), 1.36 (sex, 2H, $J = 7.2$ Hz), 1.81 (pent, 2H, $J = 7.2$ Hz), 2.61 (s, 6H), 2.81(t, 2H, $J = 7.2$ Hz), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 13.92, 20.29, 25.00, 48.58, 60.73, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −11.04 (d, $J_{B-H} =$ 130.4 Hz). IR (neat, cm^{-1}): 2957 (C–H), 2359 (C≡N), 1458 (C–N). MS: *m/z* (%) 454 (18), 453 (40), 452 (37), 450 (M, 35), 449 (18), 364 (20), 278 (100), 263 (38), 248 (38), 233 (33), 221 (40), 218 (25), 177 (15), 147 (20), 120 (13), 105 (38), 104 (25), 104 (7), 102 (10), 90 (6). Anal. Calc. for $C_{14}H_{32}B_2Br_2Li_2N_4$: C, 37.22; H, 7.14; N, 12.40; Br, 35.38. Found: C, 37.38; H, 7.23; N, 12.37; Br, 35.18.

*4.3.12. Diborane (4) derivative of dimethyl-n-pentylamine cyanoborane. 2LiBr (**11**)*

Yellowish oil, 82% (0.393 g) yield. ^{1}H NMR ($CDCl_3$): δ 0.97 (t, 3H, $J = 7.2$ Hz), 1.25 (m, 2H), 1.35 (pent, 2H, $J = 7.2$ Hz), 1.63 (m, 2H), 2.78 (s, 6H), 3.03 (m, 2H), (HB cannot be detected).^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.10, 22.46, 22.59, 29.01, 47.60, 61.92, (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ −12.25 (d, $J_{B-H} = 124.6$ Hz). IR (neat, cm^{-1}): 2956 (C–H), 2358 (C≡N), 1456 (C–N). MS: *m/z* (%) 482 (15), 481(13), 479 (35), 478 (27) 478 (M, 25), 477 (12), 393 (5), 233 (25), 232 (70), 230 (100), 207 (7), 128 (25), 127 (40), 115 (7), 104 (10), 102 (5), 100 (30), 71 (5). Anal. Calc. for $C_{16}H_{36}B_2Br_2Li_2N_4$: C, 40.05; H, 7.56; N, 11.68; Br, 33.31. Found: C, 39.98; H, 7.63; N, 11.53; Br, 33.18.

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Appendix A. Supplementary material

Crystallographic data for the crystal structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary puplication numbers CCDC-270856 (**6**) and CCDC-270857 (**7**). Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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