



Synthesis and structure of halogen derivatives of 9-trimethylammonio-7,8-dicarba-*nido*-undecaborane [9-Me₃N-7,8-C₂B₉H₁₁]

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ABSTRACT

Halogenation of the charge-compensated *nido*-carborane [9-Me₃N-7,8-C₂B₉H₁₁] (**1**) with elemental halogens X₂ (X = Cl, Br, I) was investigated. Derivatives of **1** with substitution degree varying from one to three were synthesized and characterized by ¹H and ¹¹B NMR. In all compounds positions of substitution were determined by ¹¹B–¹¹B COSY NMR. Structures of [11-I-9-Me₃N-7,8-C₂B₉H₁₀], [6,11-Br₂-9-Me₃N-7,8-C₂B₉H₉] and [1,6,11-Br₃-9-Me₃N-7,8-C₂B₉H₈] were established using single crystal X-ray diffraction.

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1. Introduction

Due to their chemical variability *nido*-carboranes attract attention as versatile ligands for synthesis of transition metal complexes. The dicarbollide ligands [7,8-R₂-7,8-C₂B₉H₉]²⁻ are isolobal with the Cp⁻ anion. However, the extra charge of the dicarbollide ligand results in the change of total charge or magnetic properties of π-dicarbollide complexes in comparison with their metallocene analogues. This problem can be solved using monoanionic ligands [9-L-7,8-R₂-7,8-C₂B₉H₈]⁻ (L – a charge compensating moiety such as Me₂S⁺, Me₃N⁺ or C₅H₅N⁺) [1–4] instead of [7,8-R₂-7,8-C₂B₉H₉]²⁻. Thus study of chemistry and modification of charge-compensated dicarbollide ligands and metallacompounds on their base is of great interest. At present various metallacarboranes containing the Me₂S⁺-group have been synthesized [5–9]. Further modification could be reached by two ways: an introduction of substituents directly into the cage of metallacarborane [10] or a preliminary modification of the carborane ligand followed by formation of the substituted metallacarborane [11–13]. Each of these approaches leads to metallacarboranes with substituents in different positions of the cage. Recently we described the halogenation of [9-Me₂S-7,8-C₂B₉H₁₁] [11]. Here we report the study of

the reaction of another member of a series of charge-compensated *nido*-carboranes – the 9-trimethylammonio-7,8-dicarba-*nido*-undecaborane [9-Me₃N-7,8-C₂B₉H₁₁] (**1**) with various halogens.

2. Results and discussion

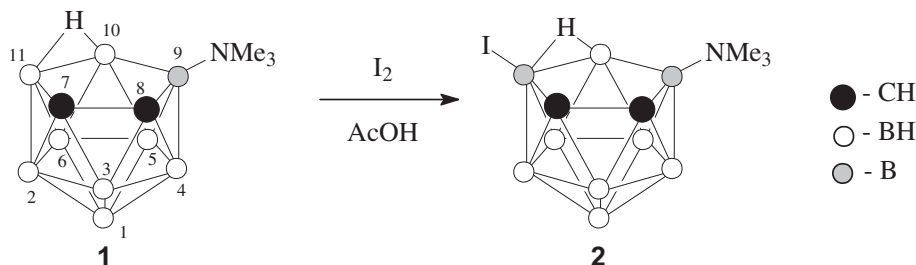
It is known that halogenation of the parent 7,8-dicarba-*nido*-undecaborate results in the substitution at positions 9 and 11 of the cage [12,14,15]. The iodination of charge-compensated *nido*-carboranes [9-L-7,8-C₂B₉H₁₀]⁻ (L = Me₂S⁺ or C₅H₅N⁺) proceeds at the position 11 as well [11,13]. Based on these data it could be expected that the halogenation of **1** will proceed in a similar way. As in the case of other charge-compensated *nido*-carboranes the reaction of **1** with iodine proceeds only under rather strong conditions. Reaction of **1** with elemental iodine in acetic acid under reflux produces [11-I-9-Me₃N-7,8-C₂B₉H₁₀] (**2**) as a single product isolated in 88% yield. The structure of **2** was determined using a single crystal X-ray diffraction (Fig. 1) and ¹¹B–¹¹B COSY NMR spectroscopy (see Fig. S1).

It was reported earlier that the bromination of [9-Me₂S-7,8-C₂B₉H₁₁] gave products of substitution both in «upper» and «lower»¹ belts of the carborane cage [11]. In a similar way the reaction of **1** with

¹ Here and further, a «lower» belt is a pentagon including positions 2–6, while an «upper» belt is a pentagon including positions 7–11.

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the equimolar amount of elemental bromine in methylene dichloride at $-25\text{ }^{\circ}\text{C}$ gave a mixture of two isomers (81 and 11% yield). Based on ^{11}B – ^{11}B COSY NMR spectroscopy (Figs. S2 and S3, respectively) the major isomer was found to be [11-Br-9-Me₃N-7,8-C₂B₉H₁₀] (**3**), whereas the minor one was [6-Br-9-Me₃N-7,8-C₂B₉H₁₀] (**4**).



It is reasonable to suppose that the use of an excess of bromine should result in a derivative containing bromine substituents both at the positions 6 and 11. Indeed, [6,11-Br₂-9-Me₃N-7,8-C₂B₉H₉] (**5**) was isolated as one of the two products from the reaction of **1** with the excess of elemental bromine in methylene dichloride. The second product was [1,6,11-Br₃-9-Me₃N-7,8-C₂B₉H₈] (**6**) containing the third bromine substituent at position 1 opposite to the open face of the cage. It is the first example of substitution at the B(1) position in *nido*-carboranes. It should be noted that all bromine atoms in **6** are situated in *meta*-positions to the primarily Me₃N-substituent. Low yields could be explained by an extensive decomposition of the initial [9-Me₃N-7,8-C₂B₉H₁₁]. The structures of **5** and **6** were determined using the single crystal X-ray diffraction (Figs. 2 and 3, respectively) and ^{11}B – ^{11}B COSY NMR spectroscopy (Figs. S4 and S5, respectively).

The reaction of **1** with the equimolar amount of elemental chlorine at $-25\text{ }^{\circ}\text{C}$ in methylene dichloride produced a mixture of two isomeric products [11-Cl-9-Me₃N-7,8-C₂B₉H₁₀] (**7**) and [6-Cl-9-Me₃N-7,8-C₂B₉H₁₀] (**8**) in molar ratio 1:3. It is surprising that the major product in this reaction was found to be [6-Cl-9-Me₃N-7,8-C₂B₉H₁₀] (**8**) while in all previous cases of halogenation of charge-compensated carboranes the 11-substituted derivatives were single or major products.

The only product [6,11-Cl₂-9-Me₃N-7,8-C₂B₉H₉] (**9**) was isolated from the reaction of **1** with the excess of chlorine. The

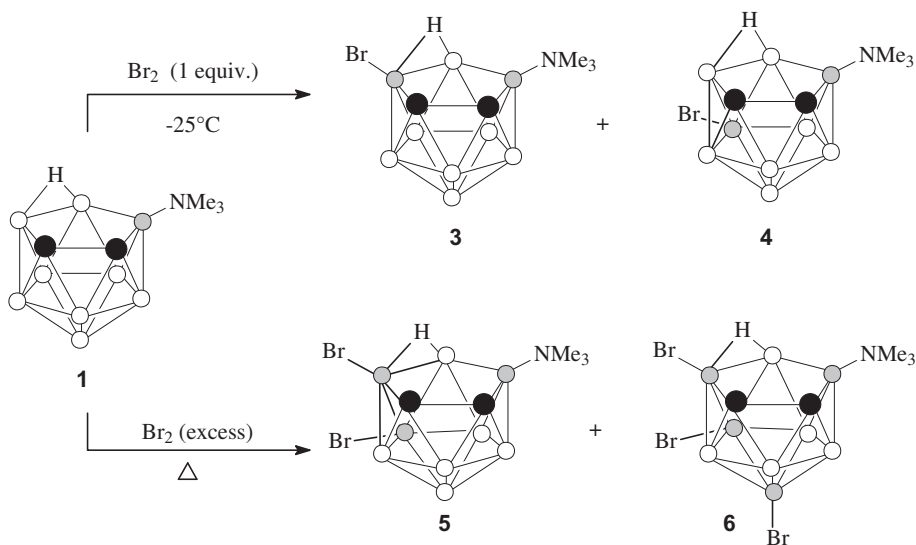
2.1. NMR spectra

The assignments of signals in the ^{11}B NMR spectra of all the compounds **1**–**9** were carried out using ^{11}B – ^{11}B COSY NMR spectroscopy and was based on characteristic high-field doublets

of B(1), B(10) and singlet of B(9). The comparison of the ^{11}B NMR spectra of compounds **2**–**9** (see Table 1) shows that only the iodine atom shifts the signal corresponding to the substituted boron atom B(11) to a high field at -26.3 ppm (-16.9 ppm for [9-Me₃N-7,8-C₂B₉H₁₁]). Meanwhile the halogen atoms Cl and Br shift the signals of substituted boron atoms to a low field.

According to the spectra of the isomeric bromo derivatives **3** and **4** the introduction of the bromo substituent at position 6 or 11 does not change significantly the spectrum pattern except the low-field shifts of the signals of the ipso-atoms B(11) and B(6) by $\Delta\delta_{\text{ipso}}$ 6.6 ppm and $\Delta\delta_{\text{ipso}}$ 8.1 ppm, respectively. ^{11}B NMR spectrum of the 6,11-dibromo derivative **5** resembles spectra of **3** and **4** except the appearance of an additional singlet from the second bromo-substituted boron atom. Additionally, in case of **6** the strong low-field shift of the signal corresponding to the B(1) atom by $\Delta\delta_{\text{ipso}}$ 12.9 ppm takes place.

Spectral patterns observed for the chloro derivatives **7** and **8** are similar to those found for bromo analogues **3** and **4**. However, the Cl atoms shift the signals corresponding to the B(11) and B(6) atoms to a much more lower field by $\Delta\delta_{\text{ipso}}$ 13.4 ppm and $\Delta\delta_{\text{ipso}}$ 15.0 ppm for **7** and **8**, respectively. The $\Delta\delta_{\text{ipso}}$ values for **3**, **4**, **7** and **8** are close to those observed for halogen derivatives of boranes and carboranes [16].



positions of substitutions in all chloro derivatives were determined using ^{11}B – ^{11}B COSY NMR spectroscopy (Figs. S6, S7 and S8, respectively).

The difference between the chemical shifts of signals of other boron atoms in **2**–**9** and the chemical shifts of the corresponding signals of the parent **1** does not exceed 4.1 ppm.

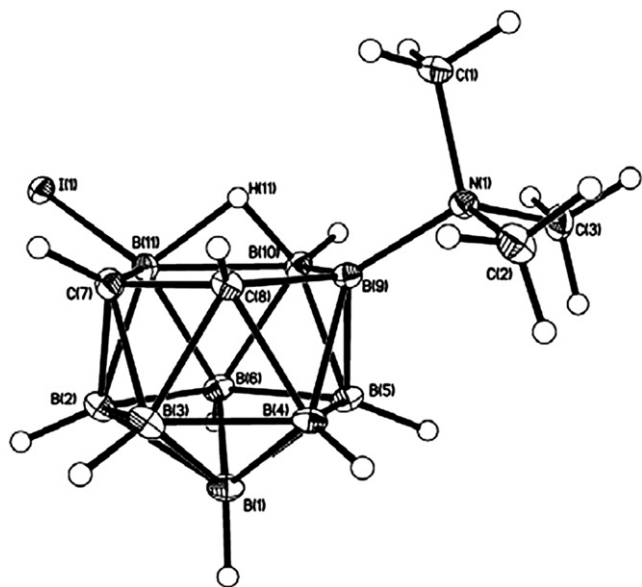


Fig. 1. Molecular structure of [11-I-9-Me₃N-7,8-C₂B₉H₁₀] (**2**). Selected bond length (Å): B(9)–N 1.574(3), B(11)–I 2.191(3), N–C(1) 1.503(3), N–C(2) 1.499(3), N–C(3) 1.497(3).

The ¹H NMR spectra of all the compounds contain signals of $-(CH_3)_3N$, CH_{carb} -groups, BH -protons and the broad signal of the bridge *extra*-hydrogen atom $B(\mu^2-H)$. It should be noted that the chemical shift of the bridge-hydrogen atom is not influenced by the nature of the halogen used but highly depends on the position and degree of substitution. The $B(\mu^2-H)$ signal in the spectra of 11-halogeno derivatives **2**, **3** and **7** is displaced by approximately 1.5 ppm to the low field relative to the parent compound **1** (see Table 2). In case of the 6-chloro derivative **8** the displacement is less and forms 0.7 ppm. The substitution at both positions 6 and 11 in the compounds **5** and **9** displaces the chemical shift of the extra hydrogen by 2.0 ppm to the low field. The most dramatic displacement by 2.7 ppm in the extra hydrogen shift is observed in the ¹H NMR spectrum of 1,6,11-tribromo derivative **6**. Thus the more the substituents, the more significant the displacement of the chemical shift of the extra hydrogen is. This fact correlates well

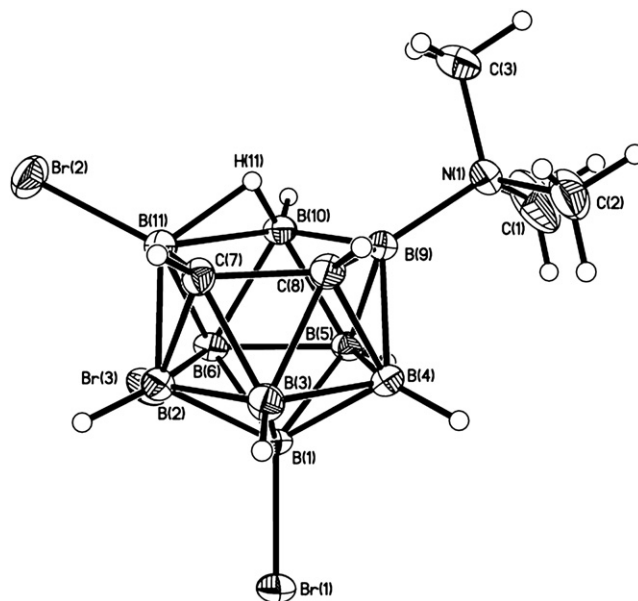


Fig. 3. Molecular structure of [1,6,11-Br₃-9-Me₃N-7,8-C₂B₉H₈] (**6**). Selected bond length (Å): B(9)–N 1.586(5), B(11)–Br(2) 1.950(4), B(6)–Br(3) 1.959(4), B(1)–Br(1) 1.968(4), N–C(1) 1.475(6), N–C(2) 1.488(5), N–C(3) 1.488(5).

with the results of our previous investigation on the halogenation of [9-Me₂S-7,8-C₂B₉H₁₁] [11].

2.2. X-ray structure

Molecular crystal structures of compounds **2**, **5**, and **6** were determined by single crystal X-ray diffraction. The iodo-derivatives **2** and [9-Me₂S-11-I-7,8-C₂B₉H₁₀] [11] were found to be isomorphous. The B–I bond length in **2** is 2.191(3) Å, that is very close to a similar bonds found in [9-Me₂S-11-I-7,8-C₂B₉H₁₀] and [9-Py-11-I-7,8-C₂B₉H₁₀] (2.197(3) Å) [11] and [13b], respectively) and some shorter than in (Me₃NH)[nido-9-I-7,8-C₂B₉H₁₁] (2.309(9) Å) [14b]. The B–Br bond lengths in **5** (1.958(5) and 1.987(6)) and **6** (1.950(4), 1.959(4), and 1.968(4)) lie in the same range as the similar bonds in [9-Me₂S-11-Br-7,8-C₂B₉H₁₀] (1.9855(17) Å) and [9-Me₂S-6,11-Br₂-7,8-C₂B₉H₉] (1.978(3) and 1.971(2) Å) [11], [3-Cp-4-Me₂S-7,8-Br₂-3,1,2-FeC₂B₉H₈] (1.992(3) and 1.998(3) Å) [17], [Et₄N][4,4',7,7'-Br₄-3,3'-Co(1,2-C₂B₉H₉)₂] (av. 1.983 Å) [12], (BEDT-TTF)₂[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂], (BEDT-TTF)₂[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] and (BMDT-TTF)₄[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (av. 1.993 Å) [18] and some shorter than those found in [2,2,2,2-(CNBu^t)₄-2,3-Br₂-2,1-MoCB₁₀H₁₀] (2.003 Å) [19].

It is interesting to note short intermolecular Br...Br contacts in the crystal structure of [6,11-Br₂-9-Me₃N-7,8-C₂B₉H₉] (**5**) and [9-Me₃N-1,6,11-Br₃-7,8-C₂B₉H₈] (**6**). In complex **6**, strong Br1...Br1' contacts (3.480(1) Å) (sum of their Van der Waals radii 3.94 Å [20]) leads to the formation of double layers parallel to *bc* plane. These layers are connected to each other by weaker Br2...Br3' contacts (3.606(1) Å) (Fig. 4a). In the structure **5**, Br1...Br1' contacts (3.794(1) Å) connect molecules to similar double layers (also parallel to *bc* plane) (Fig. 4b).

3. Experimental

[9-Me₃N-7,8-B₉C₂H₁₁] (**1**) was prepared using the literature procedure [1]. All other reagents were commercially available and used without further purification. ¹H and ¹¹B NMR spectra were recorded with a Bruker Avance 400 spectrometer at ambient temperature. Proton chemical shifts were referenced to residual

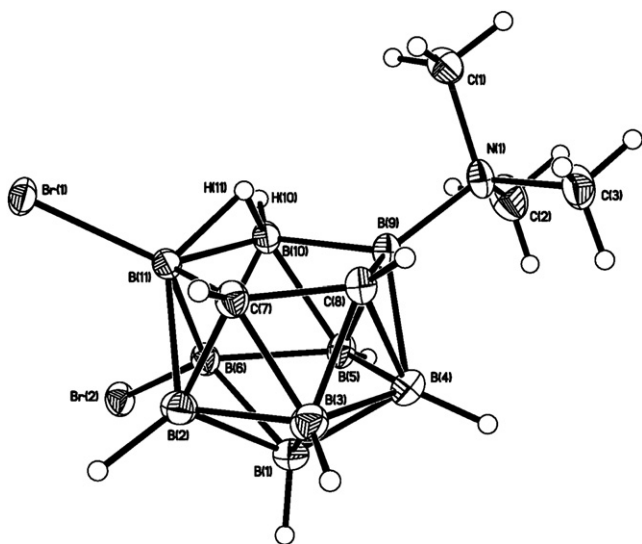


Fig. 2. Molecular structure of [6,11-Br₂-9-Me₃N-7,8-C₂B₉H₉] (**5**). Selected bond length (Å): B(9)–N 1.563(7), B(11)–Br(1) 1.958(5), B(6)–Br(2) 1.987(6), N–C(1) 1.517(7), N–C(2) 1.491(7), N–C(3) 1.500(7).

Table 1
¹¹B NMR shifts for compounds 1–9.

Compound	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	B(9)	B(10)	B(11)
1 [9-Me ₃ N-7,8-C ₂ B ₉ H ₁₁]	-38.6	-16.9	-18.9	-24.4	-5.2	-27.3	5.4	-32.1	-16.9
2 [11-I-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-37.6	-14.2	-17.7	-25.8	-6.4	-23.8	5.9	-31.4	-26.3
3 [11-Br-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-38.7	-16.1	-18.6	-27.7	-8.6	-24.7	6.2	-33.4	-10.3
4 [6-Br-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-37.0	-16.2	-19.6	-24.3	-4.4	-19.2	6.2	-30.1	-16.2
5 [6,11-Br ₂ -9-Me ₃ N-7,8-C ₂ B ₉ H ₉]	-37.0	-15.4	-19.8	-27.0	-7.3	-17.4	6.0	-31.0	-10.4
6 [1,6,11-Br ₃ -9-Me ₃ N-7,8-C ₂ B ₉ H ₈]	-25.7	-14.8	-18.5	-25.7	-5.8	-16.0	5.0	-30.8	-10.9
7 [11-Cl-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-39.2	-16.4	-19.0	-24.8	-9.2	-29.0	5.9	-34.1	-3.5
8 [6-Cl-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-37.3	-16.6	-20.3	-24.6	-4.5	-12.3	5.9	-30.8	-16.6
9 [6,11-Cl ₂ -9-Me ₃ N-7,8-C ₂ B ₉ H ₉]	-37.8	-15.8	-21.1	-28.5	-7.8	-11.3	5.2	-32.3	-4.6

protons in the lock solvents (CDCl₃ 7.26 ppm; acetone-*d*₆ 2.05 ppm vs (CH₃)₄Si). Boron chemical shifts were referenced externally to BF₃·OEt₂. Elemental analyses were performed at the Laboratory of Microanalysis of Institute of Organoelement Compounds (Moscow).

11-I-9-Me₃N-7,8-C₂B₉H₁₀ (**2**). Iodine (1.96 g, 7.72 mmol) was added to a solution of 9-Me₃N-7,8-C₂B₉H₁₁ (0.96 g, 5 mmol) in 50 ml of acetic acid. The mixture was refluxed for 6 h. The solvent was removed *in vacuo*, to leave a brown solid. The solid was dissolved in methylene dichloride and washed with an aqueous solution of Na₂S₂O₃·5H₂O. The organic layer was dried over Na₂SO₄. The product was purified by column chromatography on silica (eluent hexane:CH₂Cl₂, 1:1) to give **2** (1.39 g, 88%). Anal. Calc. for C₅H₁₉B₉NI: C 18.92; H 6.03; B 30.65; N 4.41. Found: C 19.38; H 6.08; B 29.87; N 4.15. M.p. 208–210 °C.

¹H NMR (CDCl₃, ppm), δ: 3.07 (s, 9H, Me₃N); 2.45 (s, 1H, CH_{carb}); 2.32 (s, 1H, CH_{carb}); 3.3–0.2 (br. m, 9H, BH); -1.5 ÷ -2.3 (br s, 1H, H_{extra}).

¹¹B NMR (CDCl₃, ppm), δ: 5.9 (s, 1B, B(9)); -6.4 (d, 1B, B(5), J_{B-H} = 140 Hz); -14.2 (d, 1B, B(2), J_{B-H} = 154 Hz); -17.7 (d, 1B, B(3), J_{B-H} = 169 Hz); -23.8 (d, 1B, B(6), J_{B-H} = 148 Hz); -25.8 (d, 1B, B(4), J_{B-H} = 161 Hz); -26.3 (s, 1B, B(11)); -31.4 (d, 1B, B(10), J_{B-H} = 141 Hz); -37.6 (d, 1B, B(1), J_{B-H} = 154 Hz).

11-Br-9-Me₃N-7,8-C₂B₉H₁₀ (**3**) and 6-Br-9-Me₃N-7,8-C₂B₉H₁₀ (**4**). A solution of bromine (0.8 g, 5 mmol) in 5 ml CH₂Cl₂ was added to a solution of 9-Me₃N-7,8-C₂B₉H₁₁ (0.96 g, 5 mmol) in 30 ml of CH₂Cl₂ at -22 °C for 30 min. The mixture was stirred for a couple of hours. The final solution was treated with an aqueous solution of NaHCO₃. The organic layer was dried over Na₂SO₄. The solvent was removed *in vacuo*, the crude product was chromatographed on silica (eluent CHCl₃). Yield of **3**: 1.1 g, 81%; yield of **4**: 0.15 g, 11%.

11-Br-9-Me₃N-7,8-C₂B₉H₁₀ (**3**). Anal. Calc. for C₅H₁₉B₉BrN: C 22.21; H 7.08; B 35.98; N 5.18. Found: C 22.30; H 7.25; B 35.83; N 5.04. ¹H NMR (acetone-*d*₆, ppm), δ: 3.17 (s, 9H, Me₃N); 2.76 (s, 2H, 2CH_{carb}); 2.7–0.0 (br. m, 9H, BH); -1.3 ÷ -2.2 (br s, 1H, H_{extra}). ¹¹B NMR (acetone-*d*₆, ppm), δ: 3.2 (s, 1B, B(9)); -8.6 (d, 1B, B(5), J_{B-H} = 146 Hz); -10.3 (s, 1B, B(11)); -16.1 (d, 1B, B(2), J_{B-H} = 159 Hz); -18.6 (d, 1B, B(3), J_{B-H} = 166 Hz); -24.3 (d, 1B, B(6), J_{B-H} = 146 Hz); -27.7 (d, 1B, B(4), J_{B-H} = 150 Hz); -33.4 (d, 1B, B(10), J_{B-H} = 140); -38.7 (d, 1B, B(1), J_{B-H} = 148 Hz).

Table 2
¹H NMR shifts of the bridge-hydrogen, for 1–3 and 5–9.

Compound	δ B(μ ² -H), ppm	ΔH _{extra} comparing with 1, ppm
1 [9-Me ₃ N-7,8-C ₂ B ₉ H ₁₁]	-2.8 ÷ -3.7	–
8 [6-Cl-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-2.0 ÷ -3.0	0.7
2 [11-I-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-1.5 ÷ -2.3	1.4
3 [11-Br-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-1.2 ÷ -2.2	1.5
7 [11-Cl-9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀]	-1.3 ÷ -2.2	1.5
5 [6,11-Br ₂ -9-Me ₃ N-7,8-C ₂ B ₉ H ₉]	-0.8 ÷ -1.7	2.0
9 [6,11-Cl ₂ -9-Me ₃ N-7,8-C ₂ B ₉ H ₉]	-0.7 ÷ -1.8	2.0
6 [1,6,11-Br ₃ -9-Me ₃ N-7,8-C ₂ B ₉ H ₈]	-0.2 ÷ -0.9	2.7

6-Br-9-Me₃N-7,8-C₂B₉H₁₀ (**4**). ¹H NMR (acetone-*d*₆, ppm), δ: 3.16 (s, 9H, Me₃N); 2.71 (s, 2H, 2CH_{carb}); 2.7–0.2 (br. m, 9H, BH). ¹¹B NMR (acetone-*d*₆, ppm), δ: 6.2 (s, 1B, B(9)); -4.4 (d, 1B, B(5), J_{B-H} = 150 Hz); -16.2 (d, 2B, B(11, 2), J_{B-H} = 147 Hz); -19.2 (s, 1B, B(6)); -19.6 (d, 1B, B(3), J_{B-H} = 161 Hz); -24.3 (d, 1B, B(4), J_{B-H} = 156 Hz); -30.1 (d, 1B, B(10), J_{B-H} = 124); -37.0 (d, 1B, B(1), J_{B-H} = 144 Hz).

6,11-Br₂-9-Me₃N-7,8-C₂B₉H₉ (**5**) and 1,6,11-Br₃-9-Me₃N-7,8-C₂B₉H₈ (**6**). Bromine (12 g, 75 mmol) was added to a solution of 9-Me₃N-7,8-C₂B₉H₁₁ (0.96 g, 5 mmol) in 40 ml of methylene dichloride. The mixture was stirred at room temperature for 30 min, then refluxed for 6 h. The reaction mixture was washed with an aqueous solution of Na₂S₂O₃·5H₂O and treated with an aqueous solution of NaHCO₃. The organic layer was dried over Na₂SO₄. Products were separated by column chromatography on silica (eluent CHCl₃). Yield of **5**: 0.21 g, 12%; yield of **6**: 0.26 g, 12%.

6,11-Br₂-9-Me₃N-7,8-C₂B₉H₉ (**5**). ¹H NMR (acetone-*d*₆, ppm), δ: 3.21 (s, 9H, Me₃N); 2.82 (s, 1H, CH_{carb}); 2.51 (s, 1H, CH_{carb}); 2.9–0.3 (br. m, 9H, BH); -0.8 ÷ -1.7 (br s, 1H, H_{extra}). ¹¹B NMR (acetone-*d*₆, ppm), δ: 6.0 (s, 1B, B(9)); -7.3 (d, 1B, B(5), J_{B-H} = 140 Hz); -10.4 (s, 1B, B(11)); -15.4 (d, 1B, B(2), J_{B-H} = 160 Hz); -17.4 (s, 1B, B(6)); -19.8 (d, 1B, B(3), J_{B-H} = 168 Hz); -27.0 (d, B(4), J_{B-H} = 155 Hz); -31.0 (d, 1B, B(10), J_{B-H} = 139 Hz); -37.0 (d, 1B, B(1), J_{B-H} = 147 Hz).

1,6,11-Br₃-9-Me₃N-7,8-C₂B₉H₈ (**6**). ¹H NMR (acetone-*d*₆, ppm), δ: 3.21 (s, 9H, Me₃N); 2.82 (s, 1H, CH_{carb}); 2.51 (s, 1H, CH_{carb}); 2.7–0.2 (br. m, 9H, BH); -0.2 ÷ -0.9 (br s, 1H, H_{extra}). ¹¹B NMR (acetone-*d*₆, ppm), δ: 5.0 (s, 1B, B(9)); -5.8 (d, 1B, B(5), J_{B-H} = 144 Hz); -10.9 (s, 1B, B(11)); -14.8 (d, 1B, B(2), J_{B-H} = 183 Hz); -16.0 (s, 1B, B(6)); -18.5 (d, 1B, B(3), J_{B-H} = 174 Hz); -25.7 (s, 1B, B(1), d, B(4), J_{B-H} = 140 Hz); -30.8 (d, 1B, B(10), J_{B-H} = 140 Hz).

11-Cl-9-Me₃N-7,8-C₂B₉H₁₀ (**7**) and 6-Cl-9-Me₃N-7,8-C₂B₉H₁₀ (**8**). A solution of chlorine (0.56 g, 7.82 mmol) in 10.7 ml CCl₄ was slowly added to a solution of 9-Me₃N-7,8-C₂B₉H₁₁ (0.96 g, 5 mmol) in 40 ml of CH₂Cl₂ at -25 °C. The reaction mixture slowly warmed to room temperature and treated with an aqueous solution of NaHCO₃. The organic layer was dried over Na₂SO₄. The solvent was removed *in vacuo*, crude products **7** and **8** were isolated by column chromatography on silica and eluted with CHCl₃. Yield of **7**: 0.16 g, 14%; yield of **8**: 0.47 g, 42%.

11-Cl-9-Me₃N-7,8-C₂B₉H₁₀ (**7**). Anal. Calc for C₅H₁₉B₉NCl: C 26.58; H 8.48; B 43.06. Found: C 26.35; H 8.00; B 42.49. ¹H NMR (acetone-*d*₆, ppm), δ: 3.17 (s, 9H, Me₃N); 2.72 (s, 1H, CH_{carb}); 2.17 (s, 1H, CH_{carb}); 2.6–0.0 (br. m, 9H, BH); -1.3 ÷ -2.2 (br s, 1H, H_{extra}). ¹¹B NMR (acetone-*d*₆, ppm), δ: 5.9 (s, 1B, B(9)); -3.5 (s, 1B, B(11)); -9.1 (d, 1B, B(5), J_{B-H} = 137 Hz); -16.4 (d, 1B, B(2), J_{B-H} = 156 Hz); -19.0 (d, 1B, B(3), J_{B-H} = 166 Hz); -24.8 (d, 1B, B(6), J_{B-H} = 141 Hz); -29.0 (d, 1B, B(4), J_{B-H} = 153 Hz); -34.1 (d, 1B, B(10), J_{B-H} = 129); -39.2 (d, 1B, B(1), J_{B-H} = 148 Hz).

6-Cl-9-Me₃N-7,8-C₂B₉H₁₀ (**8**). Anal. Calc for C₅H₁₉B₉NCl: C 26.58; H 8.48; B 43.06; N 6.20. Found: C 26.35; H 8.41; B 42.68; N 5.86.

¹H NMR (acetone-*d*₆, ppm), δ: 3.15 (s, 9H, Me₃N); 2.59 (s, 1H, CH_{carb}); 2.7–0.2 (br. m, 9H, BH); -2.1 ÷ -3.0 (br s, 1H, H_{extra}).

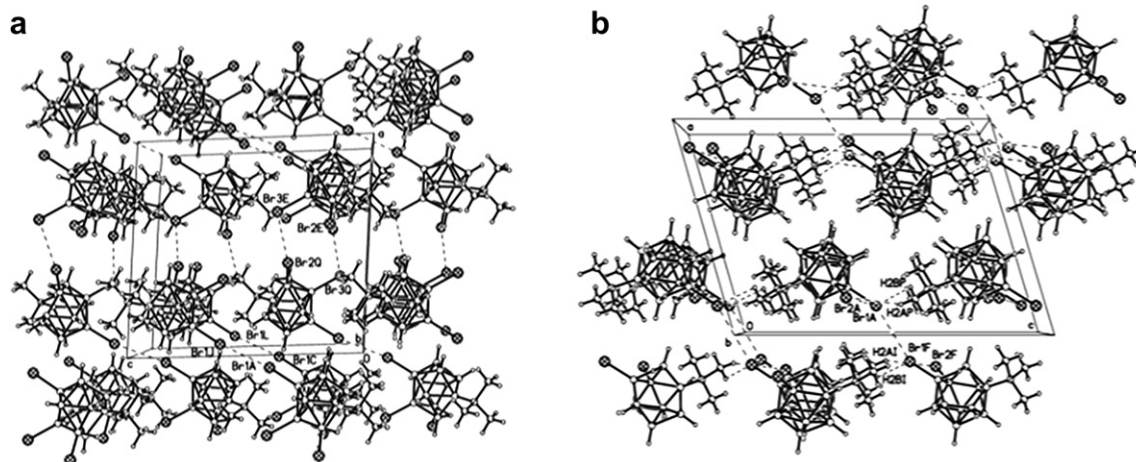


Fig. 4. (a) The double layers in crystal structure 6; (b) The double layers in crystal structure 5.

^{11}B NMR (acetone- d_6 , ppm), δ : 5.9 (s, 1B, B(9)); –4.5 (d, 1B, B(5), $J_{\text{B-H}} = 141$ Hz); –12.3 (s, 1B, B(6)); –16.6 (d, 2B, B(2), B(11), $J_{\text{B-H}} = 151$ Hz); –20.3 (d, 1B, B(3), $J_{\text{B-H}} = 166$ Hz); –24.6 (d, 1B, B(4), $J_{\text{B-H}} = 151$ Hz); –30.8 (d, 1B, B(10), $J_{\text{B-H}} = 130$ Hz); –37.3 (d, 1B, B(1), $J_{\text{B-H}} = 146$ Hz).

6,11-Cl₂-9-Me₃N-7,8-C₂B₉H₉ (**9**). A solution of chlorine (3.55 g, 50 mmol) in 46.72 ml CCl₄ was added to a solution of 9-Me₃N-7,8-C₂B₉H₁₁ (0.96 g, 5 mmol) in 50 ml of CH₂Cl₂ at –25 °C for 4.5 h. The reaction mixture was slowly warmed to room temperature and

Table 3

Crystal data and structure refinement for [1,6,11-Br₃-9-Me₃N-7,8-C₂B₉H₉] (**6**), [11-*l*-9-Me₃N-7,8-C₂B₉H₁₀] (**2**) and [6,11-Br₂-9-Me₃N-7,8-C₂B₉H₉] (**5**).

Compound	11- <i>l</i> -9-Me ₃ N-7,8-C ₂ B ₉ H ₁₀ (2)	6,11-Br ₂ -9-Me ₃ N-7,8-C ₂ B ₉ H ₉ (5)	1,6,11-Br ₃ -9-Me ₃ N-7,8-C ₂ B ₉ H ₉ (6)
Empiric formula	C ₅ H ₁₉ B ₉ IN	C ₅ H ₁₈ B ₉ Br ₂ N	C ₅ H ₁₇ B ₉ Br ₃ N
Formula weight	317.40	349.31	428.22
Space group	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>P2₁/c</i>
<i>a</i> /Å	13.232(1)	12.388(2)	12.504(2)
<i>b</i> /Å	11.836(1)	6.9973(9)	9.111(2)
<i>c</i> /Å	17.397(2)	17.528(2)	13.633(2)
α /deg	90	90	90
β /deg	90	106.295(2)	94.418(3)
γ /deg	90	90	90
<i>V</i> /Å ³	2724.7(5)	1458.3(3)	1548.5(5)
<i>Z</i>	8	4	4
<i>D</i> _{calc.} /g·cm ^{–3}	1.548	1.591	1.837
Colour, habit	Colourless needle	Colourless needle	Colourless needle
Crystal size (mm)	0.35 × 0.20 × 0.15	0.35 × 0.25 × 0.25	0.35 × 0.25 × 0.15
μ /cm ^{–1}	2.313	5.526	7.787
<i>T</i> _{min} / <i>T</i> _{max}	0.575/0.701	0.205/0.251	0.114/0.312
2 θ _{max}	56	54	52
Total number of reflections collected	28887	14375	14438
Independent reflections (Rint)	3266 (0.0549)	3126 (0.0351)	3034 (0.0397)
<i>R</i> ₁ (Number of reflections with <i>I</i> > 2 σ (<i>I</i>))	0.0252(2733)	0.0502(2478)	0.0301(2368)
<i>wR</i> ₂	0.0570	0.1312	0.0703
Number of parameters refined	156	155	174
<i>a</i>	0.0203	0.0518	0.0316
<i>b</i>	2.9759	5.2158	1.1768
<i>G</i> OF	1.015	1.168	1.044
<i>F</i> (000)	1232	680	816

$$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP, P = 1/3(F_o^2 + 2F_c^2).$$

treated with an aqueous solution of Na₂S₂O₃·5H₂O, then washed with an aqueous solution of NaHCO₃. The organic layer was dried over Na₂SO₄. The solvent was removed *in vacuo*, the product **9** was purified by column chromatography on silica (eluent CHCl₃:CH₂Cl₂, 3:1). Yield of **9**: 0.34 g, 26%. Anal. Calc for C₅H₁₈B₉NCl₂: C 23.06; H 6.97; B 37.36, N 5.38. Found: C 23.48; H 7.00; B 36.8, N 5.35.

^1H NMR (acetone- d_6 , ppm), δ : 3.19 (s, 9H, Me₃N); 2.67 (s, 1H, CH_{carb}); 2.40 (s, 1H, CH_{carb}); 2.7–0.2 (br. m, 9H, BH); –0.8 ÷ –1.6 (br s, 1H, H_{extra}).

^{11}B NMR (acetone- d_6 , ppm), δ : 5.2 (s, 1B, B(9)); –4.6 (s, 1B, B(11)); –7.8 (d, 1B, B(5), $J_{\text{B-H}} = 141$ Hz); –11.3 (s, 1B, B(6)); –15.8 (d, 1B, B(2), $J_{\text{B-H}} = 153$ Hz); –21.1 (d, 1B, B(3), $J_{\text{B-H}} = 173$ Hz); –28.5 (d, B(4), $J_{\text{B-H}} = 153$ Hz); –33.3 (d, 1B, B(10), $J_{\text{B-H}} = 111$ Hz); –37.8 (d, 1B, B(1), $J_{\text{B-H}} = 144$ Hz).

3.1. X-ray diffraction study

Experimental data for all compounds were collected on Bruker APEX II CCD area detector at 100 K (λ Mo K_{α} radiation, ω -scanning). Absorption correlations were allowed using SADABS software [21]. The structures were solved using direct method; all non-hydrogen atoms were located in difference electron density maps and refined based on F^2_{hkl} with anisotropic displacement parameters. All hydrogen atoms (except hydrogen atoms in Me₃N-groups positioned geometrically) were located in difference electron density maps and refined using a riding model with $U(H) = 1.2 U(X)$, $U(X)$ – equivalent thermal parameters of the corresponding atoms of the carborane cage.

All calculations were carried out with the use of the SHELXTL PLUS 5 program package [22]. The data collection and refinement parameters are summarized in Table 3.

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Appendix. Supplementary material

CCDC 754810, 754811 and 754812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.04.004

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