Synthesis of dihalo derivatives of the 7,8-dimethyldecahydro-7,8-dicarba-*nido*-undecaborate anion

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Treatment of potassium 7,8-dimethyldecahydro-7,8-dicarba-*nido*-undecaborate with *N*-chloro- and *N*-bromosuccinimides in acetonitrile or with an excess of iodine in methanol gave the corresponding dihalo derivatives $[9,11\text{-}X_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (X = Cl, Br, or I), which were isolated as alkylammonium salts. The compound $(Me_3NH)^+[9,11\text{-}I_2\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_9]^-$ was synthesized by a reaction of $K^+[7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]^-$ with an excess of iodine in methanol. The compounds obtained were characterized by IR and NMR (^1H, ^{11}B, and $^{11}B—^{11}B$ COSY) spectroscopy.

Key words: carboranes, 7,8-dimethyldecahydro-7,8-dicarba-*nido*-undecaborate, halogenation, NMR spectroscopy.

The dicarbollide anion $[7,8\text{-}C_2B_9H_{11}]^{2-}$ (**1**) is widely used as a ligand in organometallic chemistry because of its similarity with the cyclopentadienide anion $[C_5H_5]^-$ (Cp), to which it is formally isolobal. The dicarbollide anion has long been known[1] to stabilize transition metal cations in very high oxidation states. Substitution in the cyclopentadienide anion changes the steric and electronic properties of the ligand. The pentamethylcyclopentadienide ligand $[C_5Me_5]^-$ (Cp*) is known to be larger and a stronger electron donor than the cyclopentadienide ligand. Analogously, substitution in the dicarbollide anion will change the steric and electronic properties of the ligand. That is why constantly growing interest exists today in the synthesis of substituted dicarbollide ligands and in investigations of the effects of their electronic and steric properties on the structures and properties of metal complexes with these ligands.

Sterically overcrowded dicarbollide ligands containing two or more substituents in the pentagonal face are of great interest for the synthesis of metal complexes with unusual coordination spheres. In contrast to the cyclopentadienide ligand, the substituents in the pentagonal face of the dicarbollide ligand are not coplanar with the ligand but are directed from the center of the icosahedron, which substantially diminishes the "cone angle" of the ligand. In some cases, steric repulsion between bulky substituents in the pentagonal face of the dicarbollide ligand can cause ligand rearrangement.[2—4]

The goal of this work was to obtain tetrasubstituted 7,8-dicarba-*nido*-undecaborate derivatives $[9,11\text{-}X_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (X = Cl, Br, or I) containing in the pentagonal face methyl and halogen substituents bound to the C and B atoms of the carborane framework, respectively, and perform comparative analysis of the effects of various substituents on the spectroscopic characteristics of the compounds obtained.

Results and Discussion

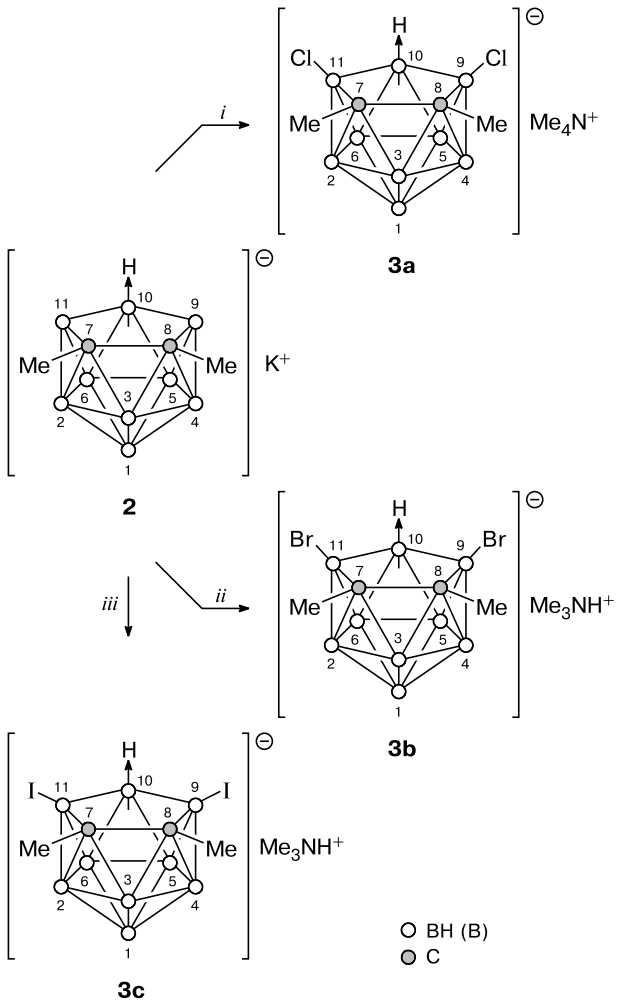
Tetrasubstituted 7,8-dicarba-*nido*-undecaborate derivatives were obtained by introduction of additional substituents (halogen atoms) into the pentagonal plane of 7,8-dimethyl-7,8-dicarba-*nido*-undecaborate anion $[7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (**2**).[5] Dichloro and dibromo derivatives were synthesized from potassium undecaborate **2** by the action of an excess of *N*-chloro- and *N*-bromosuccinimide, respectively, in acetonitrile as described earlier for the halogenation of the unsubstituted anion **1** (see Ref. 6). The reaction of potassium 7,8-dimethyl-7,8-dicarba-*nido*-undecaborate with a fourfold excess of *N*-chlorosuccinimide under reflux for 3 h gave a B(9,11)-dichloro derivative isolated as the tetramethylammonium salt $(Me_4N)^+[9,11\text{-}Cl_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (**3a**) in 46% yield (Scheme 1). The bromination of potassium salt **2** with an excess of *N*-bromosuccinimide occurred more easily (room temperature,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 888—891, May, 2007.

1066-5285/07/5605-0922

10 min), giving a dibromo derivative isolated as the trimethylammonium salt $(Me_3NH)^+[9,11\text{-}Br_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (**3b**) in 19% yield.

Scheme 1



3a 2 3b 3c

Reagents and conditions: *i*. 1) NCS (4 equiv.), MeCN, t_b, 3 h, 2) Me_4NBr; *ii*. 1) NBS (2.2 equiv.), MeCN, 10 min, 2) Me_3NHCl; *iii*. 1) I_2 (2.5 equiv.), MeOH, 12 h, 2) Me_3NHCl.

The diiodo derivative $(Me_3NH)^+[9,11\text{-}I_2\text{-}7,8\text{-}(Me)_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (**3c**) was synthesized as described earlier for the iodination of the unsubstituted anion **1** (see Ref. 7) and $[7,8\text{-}Ph_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (see Ref. 4): the reaction of potassium salt **2** with an excess of iodine in methanol at room temperature for 12 h followed by treatment of the reaction mixture with trimethylammonium chloride gave product **3c** in 73% yield.

The compositions and structures of compounds **3a**—**c** were determined by elemental analysis and IR and NMR spectroscopy. The IR spectra of products **3a**—**c** contain intense absorption bands at 770—870 cm^{-1} due to the B—Cl, B—Br, and B—I stretching vibrations, which confirms the presence of halogen atoms in their molecules. The high-frequency spectral range shows bands corresponding to the B—H (2500—2550 cm^{-1}) and C—H stretching vibrations (2960—3030 cm^{-1}).

The ^1H NMR spectra of compounds **3a**—**c** contain broad signals for BH groups at δ 0.0—2.0; the signals for the methyl substituents monotonically shift downfield when moving from dichloro derivative **3a** (δ 1.45) to diiodo derivative **3c** (δ 1.53). The spectra also exhibit singlets for the methyl groups of the methylammonium cations at δ 3.1—3.5.

In the ^{11}B NMR spectra, the signals for the B(9) and B(11) atoms bearing the halogen atoms appear as singlets, while the signals for the other B atoms are doublets. The high-field doublets of doublets were assigned to the B(10) atom bound to two H atoms. The positions of the substituents in compounds **3a**—**c** were unambiguously determined from ^{11}B—^{11}B COSY NMR data. A comparative stick diagram of the chemical shifts for compounds **2** and **3a**—**c** is shown in Fig. 1. It should be noted that the signals for the unsubstituted B atoms monotonically shift downfield in the series of derivatives **3a**—**c** and that their chemical shifts change virtually linearly.

It was also interesting to compare the effects of the methyl substituents on the spectroscopic characteristics of halo derivatives $[9,11\text{-}X_2\text{-}7,8\text{-}R_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_8]^-$ (**3a**—**c**, **4a**—**c**: R = Me (**3**) and H (**4**); X = Cl (**a**), Br (**b**), and I (**c**)). A comparative analysis of the ^{11}B NMR spectra of compounds **3a**—**c** and **4a**—**c** (see Ref. 6) revealed that the presence of the methyl groups at the C(7) and C(8) atoms in the carborane framework causes a substantial downfield shift of the signal for the B(3) atom (by 7.2—8.0 ppm) and of the signals for the B(2) and B(4) atoms (by 3.9—4.6 ppm). Similar downfield shifts of

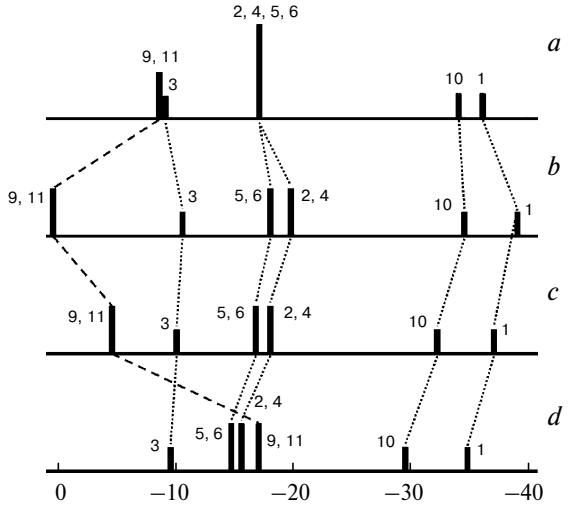
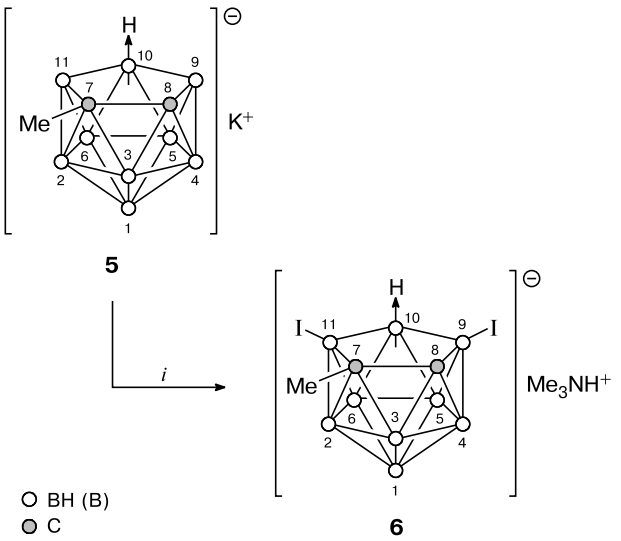


Fig. 1. Stick diagram of the ^{11}B NMR chemical shifts for compounds **2** (*a*), **3a** (*b*), **3b** (*c*), and **3c** (*d*).

the signals for the B(3), B(2), and B(4) atoms in methyl have been noted earlier for a number of other derivatives of anions **1** and **2** (see Refs 8, 9) and is likely to be characteristic.

Iodination of $K^+[7\text{-Me-}7,8\text{-}C_2B_9H_{11}]^-$ (**5**) with an excess of elemental iodine under the conditions of the iodination of potassium salt **2** gave a diiodo derivative isolated as the trimethylammonium salt $(Me_3NH)^+[9,11\text{-}I_2\text{-}7\text{-Me-}7,8\text{-}C_2B_9C_2H_9]^-$ (**6**) in 31% yield (Scheme 2).

Scheme 2



Reagents and conditions: *i.* 1) I_2 (2.5 equiv.), MeOH, 12 h, 2) Me_3NHCl.

The structure and composition of compound **6** were determined by elemental analysis and IR and NMR (^1H, ^{11}B, and $^{11}B—^{11}B$ COSY) spectroscopy.

The ^{11}B NMR spectrum of compound **6** contains two signals for the nonequivalent B(9) and B(11) atoms bound to the I atoms at δ −18.6 and −20.6, respectively. The nonequivalence of the boron atoms is due to the asymmetry of the compound and the presence of the methyl group at the C(7) atom. To correctly assign the signals for the B(9) and B(11) atoms in the spectrum of compound **6**, we compared δ(B(9), B(11)) for the 9,11-diiodinated dicarbaundecaborate anion **2c** and its dimethyl derivative **3c** and concluded that introduction of methyl substituents into a carborane framework causes a downfield shift of the signals for the B(9) and B(11) atoms, which are near the fragment C—Me. Therefore, in the ^{11}B NMR spectrum of the anion $[9,11\text{-}I_2\text{-}7\text{-Me-}7,8\text{-}B_9C_2H_9]^-$, the signal at δ −18.6 relates to the boron atom that is near the C—Me group (*i.e.*, B(11) atom), while the signal at δ −20.6 relates to the B(9) atom. The signals of the other B atoms were assigned from $^{11}B—^{11}B$ COSY data.

Experimental

IR spectra were recorded on a Protégé-460 spectrophotometer (pellets with KBr). ^1H and ^{11}B NMR spectra were recorded on a Bruker Avance-400 spectrometer. $^{11}B—^{11}B$ COSY NMR spectra were recorded on a Bruker Avance-500 spectrometer. ^1H and ^{11}B chemical shifts are referenced to Me_4Si and $Et_2O \cdot BF_3$, respectively. Potassium salts of the *C*-methyl derivatives of the 7,8-dicarba-*nido*-undecaborate(−1) anion were prepared as described earlier.[5]

Tetramethylammonium 9,11-dichloro-7,8-dimethyloctahydro-7,8-dicarba-*nido*-undecaborate, $(Me_4N)^+[9,11\text{-}Cl_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (3a). Chlorosuccinimide (0.45 g, 3.40 mmol, 4 equiv.) was added to a solution of $K^+[7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (0.17 g, 0.85 mmol) in anhydrous acetonitrile (15 mL). The reaction mixture was refluxed for 3 h and concentrated to a quarter of the volume. An aqueous solution of tetramethylammonium bromide was added and the resulting precipitate was filtered off, washed with water (3×15 mL), and dried over $CaCl_2$. The yield of $(Me_4N)^+[9,11\text{-}Cl_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ was 0.12 g (0.39 mmol, 46%). Found (%): C, 31.25; H, 9.03; B, 31.85; N, 4.61; Cl, 23.62. $C_8H_{26}B_9Cl_2N$. Calculated (%): C, 31.55; H, 8.61; B, 31.95; N, 4.60; Cl, 23.29. ^1H NMR (acetone-d_6), δ: 3.44 (s, 12 H, Me_4N^+); 1.45 (s, 6 H, CMe_{carb}); 2.00—0.00 (m, 8 H, BH). ^{11}B NMR (acetone-d_6), δ: 0.8 (s, 2 B, B(9), B(11)); −10.8 (d, 1 B, B(3), J = 162 Hz); −17.9 (d, 2 B, B(5), B(6), J = 144 Hz); −19.6 (d, 2 B, B(2), B(4), J = 152 Hz); −34.2 (dd, 1 B, B(10), J = 126 Hz, J = 37 Hz); −38.8 (d, 1 B, B(1), J = 144 Hz). IR (KBr), ν/cm^{-1}: 3015 w, 2972 m, 2935 s, 2869 w, 2545 vs, 1483 vs, 1449 s, 1415 m, 1383 m, 1370 m, 1289 w, 1200 w, 1160 w, 1094 w, 1063 w, 1027 w, 1003 w, 950 vs, 914 w, 874 m, 856 m, 819 vs, 777 w, 741 w, 719 w, 681 w, 613 w, 600 w.

Trimethylammonium 9,11-dibromo-7,8-dimethyloctahydro-7,8-dicarba-*nido*-undecaborate, $(Me_3NH)^+[9,11\text{-}Br_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (3b). Bromosuccinimide (0.97 g, 5.46 mmol, 2.2 equiv.) was added to a solution of $K^+[7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (0.50 g, 2.48 mmol) in anhydrous acetonitrile (10 mL). The reaction mixture was stirred for 10 min and concentrated to a quarter of the volume. An aqueous solution of trimethylammonium chloride was added and the resulting precipitate was filtered off, washed with water (3×15 mL), and dried over $CaCl_2$. The yield of $(Me_3NH)^+[9,11\text{-}Br_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ was 0.18 g (0.47 mmol, 19%). Found (%): C, 22.43; H, 6.24; B, 25.87 N, 3.62; Br, 41.33. $C_7H_{24}B_9Br_2N$. Calculated (%): C, 22.16; H, 6.38; B, 25.65; N, 3.69; Br, 42.12. ^1H NMR (acetone-d_6), δ: 3.17 (s, 9 H, Me_3NH^+); 1.49 (s, 6 H, CMe_{carb}); 2.00—0.00 (m, 8 H, BH). ^{11}B NMR (acetone-d_6), δ: −4.7 (s, 2 B, B(9), B(11)); −10.3 (d, 1 B, B(3), J = 159 Hz); −16.7 (d, 2 B, B(5), B(6), J = 152 Hz); −18.0 (d, 2 B, B(2), B(4), J = 171 Hz); −32.5 (dd, 1 B, B(10), J = 138 Hz, J = 41 Hz); −37.7 (d, 1 B, B(1), J = 138 Hz). IR (KBr), ν/cm^{-1}: 3038 w, 3025 w, 3017 w, 2977 m, 2934 s, 2867 w, 2810 w, 2788 w, 2728 w, 2549 vs, 2530 vs, 1477 s, 1466 vs, 1451 s, 1416 s, 1400 w, 1380 w, 1370 s, 1253 w, 1230 w, 1197 w, 1086 w, 1063 w, 1043 m, 1000 w, 971 s, 950 w, 932 s, 901 w, 869 m, 840 m, 797 s, 771 s, 710 m, 676 m, 609 m, 594 m, 560 w, 517 w, 483 w.

Trimethylammonium 9,11-diiodo-7,8-dimethyloctahydro-7,8-dicarba-*nido*-undecaborate, $(Me_3NH)^+[9,11\text{-}I_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ (3c). A solution of iodine (1.58 g, 6.25 mmol, 2.5 equiv.) in anhydrous methanol (20 mL) was added to a solution of $K^+[7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (0.50 g, 2.50 mmol) in

anhydrous methanol (10 mL). The reaction mixture was stirred for 12 h, washed with aqueous sodium sulfite, and concentrated to a quarter of the volume. An excess of aqueous trimethylammonium chloride was added and the resulting precipitate was filtered off, washed with water (3×10 mL), and dried over $CaCl_2$. The yield of $(Me_3NH)^+[9,11\text{-}I_2\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8]^-$ was 0.86 g (1.82 mmol, 73%), m.p. 122—124 °C. Found (%): C, 17.94; H, 5.23; B, 20.48; N, 3.05; I, 53.62. $C_7H_{24}B_9I_2N$. Calculated (%): C, 17.76; H, 5.11; B, 20.55; N, 2.96; I, 53.62. ^{1}H NMR (acetone-d_6), δ: 3.17 (s, 9 H, Me_3NH^+); 1.53 (s, 6 H, CMe_{carb}); 2.00—0.00 (m, 8 H, BH). ^{11}B NMR (acetone-d_6), δ: −9.6 (d, 1 B, B(3), J = 159 Hz); −14.8 (d, 2 B, B(5), B(6), J = 143 Hz); −15.6 (d, 2 B, B(2), B(4), J = 144 Hz); −17.4 (s, 2 B, B(9), B(11)); −29.6 (dd, 1 B, B(10), J = 140 Hz, J = 33 Hz); −35.7 (d, 1 B, B(1), J = 147 Hz). IR (KBr), ν/cm^{-1}: 3022 w, 2967 m, 2927 s, 2863 w, 2542 vs, 1474 s, 1465 vs, 1450 vs, 1413 w, 1380 s, 1366 vs, 1250 w, 1227 w, 1180 w, 1083 w, 1060 w, 1040 w, 997 w, 970 s, 928 s, 898 w, 867 m, 837 m, 790 s, 762 s, 707 m, 673 m, 590 m, 560 w, 480 w.

Trimethylammonium 9,11-diiodo-7-methylnonahydro-7,8-dicarba-*nido*-undecaborate, $(Me_3NH)^+[9,11\text{-}I_2\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_9]^-$ (6) was obtained analogously from $K^+[7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]^-$ and iodine in anhydrous methanol. The yield was 31%, m.p. 148—152 °C. Found (%): C, 16.04; H, 5.27; B, 21.03; N, 3.06; I, 55.47. $C_6H_{22}B_9I_2N$. Calculated (%): C, 15.70; H, 4.81; B, 21.23; N, 3.05; I, 55.25. ^{1}H NMR (acetone-d_6), δ: 3.20 (s, 9 H, Me_3NH^+); 2.26 (s, 1 H, CH_{carb}); 1.54 (s, 3 H, CMe_{carb}); 2.00—0.00 (m, 8 H, BH). ^{11}B NMR (acetone-d_6), δ: −12.7 (d, 1 B, B(3), J = 163 Hz); −14.4 (d, 1 B, B(5), $J \approx$ 139 Hz); −14.7 (d, 1 B, B(6), $J \approx$ 145 Hz); −18.6 (s, 1 B, B(11)); −19.3 (d, 1 B, B(4), J = 183 Hz); −20.6 (s, 1 B, B(9)); −28.9 (dd, 1 B, B(10), J = 140 Hz, J = 138 Hz); −35.6 (d, 1 B, B(1), J = 151 Hz). IR (KBr), ν/cm^{-1}: 3075 s, 3030 m, 2980 w, 2958 w, 2925 m, 2863 w, 2792 w, 2745 w, 2550 vs, 2523 vs, 1476 vs, 1465 vs, 1449 vs, 1413 m, 1373 s, 1250 w, 1147 w, 1073 w, 1043 w, 1001 w, 976 vs, 953 m, 920 vs, 853 w, 827 s, 795 s, 767 m, 700 m, 668 m, 600 m.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 07-03-00712).

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Received January 11, 2007;
in revised form April 4, 2007