Synthesis of 9,9′,12,12′-substituted cobalt bis(dicarbollide) derivatives*

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A partial degradation of 9,12-disubstituted derivatives of *ortho*-carboranes 9,12-X_2-1,2-$C_2B_{10}H_{10}$ (X = Br, Alk, Ar) led to the corresponding substituted *nido*-carboranes [5,6-X_2-7,8-$C_2B_9H_{10}]^-$, which on the reaction with cobalt(II) chloride gave new 9,9′,12,12′-tetrasubstituted derivatives of cobalt bis(dicarbollide) [9,9′,12,12′-X_4-3,3′-Co(1,2-$C_2B_9H_9)_2]^-$.

Key words: *ortho*-carboranes, *nido*-carboranes, cobalt bis(dicarbollide), cobalt derivatives.

In 2014, 50 years have passed since discovery of first metallacarboranes, one of which was cobalt bis(dicarbollide).[1] Due to a number of unique properties, such as high chemical stability, wide possibilities of modification *via* substitution of hydrogen atoms in the carborane cage, low nucleophilicity, as well as due to various prospects of its practical application, cobalt bis(dicarbollide) [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ became the most studied among metallacarboranes and one of the most studied polyhedral boron hydrides.[2—4] Cobalt bis(dicarbollide) derivatives are of interest for the preparation of molecular conductors. The most widespread type of molecular conductors are the radical cation salts, the structure of which is characterized by the presence of conducting stacks or layers of organic p-electron donors separated by inorganic or organometal anions. In this case, depending on the packing type of radical cations the crystals of molecular organic conductors can possess various electroconducting properties: from dielectric to metallic and even to superconducting. As a rule, anions are not directly involved in the conducting process, however, their size and shape considerably influence the packing of radical cations in the conducting layer and, therefore, the conductivity of the crystal.[5,6]

Introduction of substituents in the bis(dicarbollide) cage leads to the change in the size and shape of the anion, that greatly affects the structure of the anionic sublattice and, as a consequence, the conducting layer packing and transport characteristics of the molecular conductor crystal as a whole. The most important parameters are the size and the placement of substituents, as well as their ability to form intermolecular anion—anion and anion—cation bonds. Earlier, we have studied the influence of different 8 and 8′-positioned substituents (Cl, Br, I, OH) in cobalt bis(dicarbollide) on the crystal structure and electroconductivity of molecular conductors based on tetrathiafulvalene radical cation salts and its derivatives.[7—11] There is much less information on the influence of substituents at positions 9, 9′, 12, and 12′ of the metallacarborane cage on the structure and properties of molecular conductors.[12] Therefore, the purpose of the present work is the synthesis of new 9,9′,12,12′-tetrasubstituted derivatives of cobalt bis(dicarbollide).

Results and Discussion

In contrast to 8,8′-substituted derivatives, which are formed by a direct substitution in the parent cobalt bis(dicarbollide),[2,13] 9,9′,12,12′-substituted derivatives are synthesized by the assemblage of the corresponding *nido*-carboranes on a metal ion. *nido*-Carboranes are obtained by a partial degradation of 9,12-disubstituted derivatives of *ortho*-carborane. This approach was used earlier for the preparation of 9,9′,12,12′-tetrachloro and tetraiodo derivatives [9,9′,12,12′-X_4-3,3′-Co(1,2-$C_2B_9H_9)_2]^-$ (X = Cl,[14] I[12]). In the present work, we describe the synthesis of 9,9′,12,12′-tetrabromo, 9,9′,12,12′-tetraalkyl, and 9,9′,12,12′-tetraaryl derivatives of cobalt bis(dicarbollide).

Earlier,[15] 9,12-dibromo-*ortho*-carborane (**1a**) was obtained by treatment of *ortho*-carborane with molecular bromine in the presence of aluminum metal in carbon disulfide. Since carbon disulfide is very toxic and requires special precautions in handling, we carried out the process in refluxing dichloromethane in the presence of $AlCl_3$ (Scheme 1).

The synthesis of a number of 9,12-dialkyl and 9,12-diaryl derivatives of *ortho*-carborane by a Pd-catalyzed cross-coupling of 9,12-diiodo-*ortho*-carborane with Grignard

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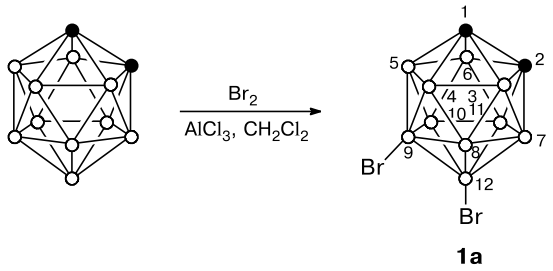
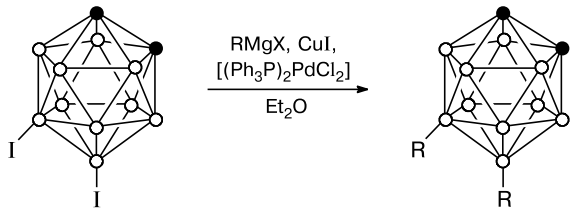
Scheme 1



1a

reagents under different conditions has been described earlier.[16—19] We obtained 9,12-dialkyl-*ortho*-carboranes 9,12-R_2-1,2-$C_2B_{10}H_{10}$ (R = Me (**2**), Et (**3a**)) by a cross-coupling of 9,12-diiodo-*ortho*-carborane (**1b**) with the corresponding Grignard reagents in the presence of $(Ph_3P)_2PdCl_2$ and CuI in diethyl ether.[16] Similar approach was also used for the preparation of 9,12-diaryl-*ortho*-carboranes **4**, **5a**, **6**, **7a** (Scheme 2).

Scheme 2



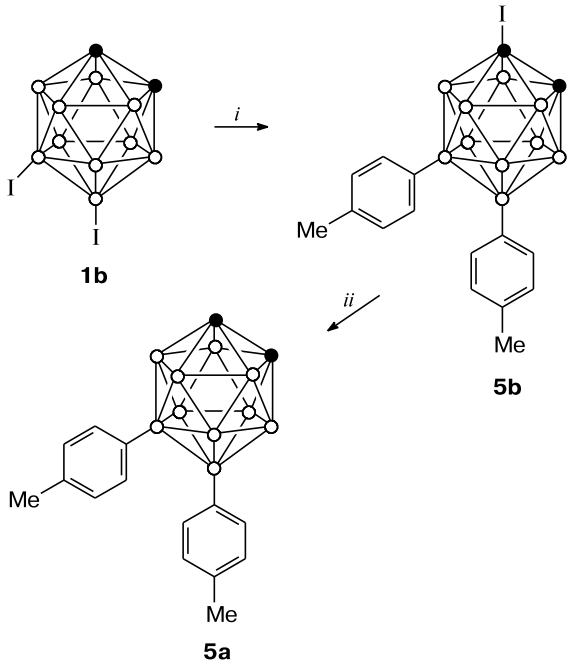
1b **2, 3a, 4, 5a, 6, 7a**

X = Br, I
R = Me (**2**), Et (**3a**), Ph (**4**), 4-MeC_6H_4 (**5a**), 4-$MeOC_6H_4$ (**6**), 4-FC_6H_4 (**7a**)

The ^{11}B NMR spectra of compounds **2**, **3a**, **4**, **5a**, **6**, **7a** contain a singlet for the *C*-substituted boron atoms in the region δ 7.2—9.5 and three doublets for the unsubstituted carborane vertices with the ratio of integral intensities 2 : 2 : 4 : 2. The ^{1}H NMR spectra exhibit broad singlets for the carborane CH groups in the region δ 3.34—3.69 and signals of the corresponding substituents.

When 9,12-diiodo-*ortho*-carborane reacted with 4-MeC_6H_4MgBr, 1-iodo-9,12-di(*p*-tolyl)-*ortho*-carborane (**5b**) was isolated from the reaction mixture. Its structure was inferred from the mass spectrometry and the ^{1}H and ^{11}B NMR spectroscopy data, which indicate the lowering of the molecular symmetry. Thus, in the ^{11}B NMR spectrum the signals for the substituted polyhedron vertices separate and are found as two singlets at δ 9.5 and 6.7. The ^{1}H NMR spectrum exhibits a double set of signals for the tolyl substituents and a signal for only one carborane CH group. Afterwards, this suggestion was confirmed by the transformation of compound **5b** to 9,12-di(*p*-tolyl)-*ortho*-carborane (**5a**) upon treatment with EtMgI with subsequent demetallation in the presence of hydrochloric acid (Scheme 3).

Scheme 3

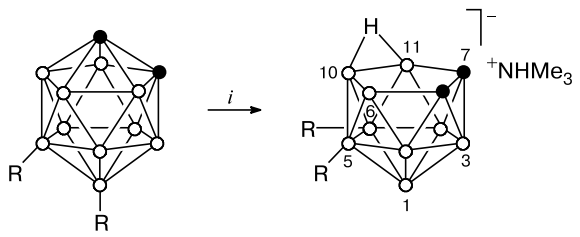


1b **5b** **5a**

Reagents: *i*. 4-MeC_6H_4MgBr, CuI, $[(Ph_3P)_2Pd]Cl_2$, Et_2O; *ii*. 1) EtMgI, Et_2O; 2) HCl/H_2O

The earlier unknown 5,6-disubstituted *nido*-carboranes **8—14** were obtained upon treatment of the corresponding 9,12-disubstituted *ortho*-carboranes **2**, **3a**, **4**, **5a**, **6**, **7a** with NaOH in refluxing ethanol and isolated as trimethylammonium salts (Scheme 4).

Scheme 4



1a, 2, 3a, 4, 5a, 6, 7a **8—14**

R = Br (**1a**, **8**), Me (**2**, **9**), Et (**3a**, **10**), Ph (**4**, **11**), 4-MeC_6H_4 (**5a**, **12**), 4-$MeOC_6H_4$ (**6**, **13**), 4-FC_6H_4 (**7a**, **14**)

Reagents: *i*. 1) NaOH/EtOH; 2) Me_3NHCl/H_2O.

The ^{11}B NMR spectra of compounds **8—14** contain singlets for the C-substituted boron atoms in the region δ –(7.6—5.4) and five doublets for the unsubstituted vertices with the ratio of integral intensities 2 : 2 : 1 : 2 : 1 : 1.

The ^{1}H NMR spectra exhibit broad singlets for the carborane CH groups in the region δ 1.53—1.94 and signals of the corresponding substituents.

Cobalt 9,9′,12,12′-tetrabromobis(dicarbollide) K[9,9′,12,12′-Br_4-3,3′-Co(1,2-$C_2B_9H_9)_2$] (K[**15**]) was obtained by the reaction of Me_3NH[**8**] with $CoCl_2 \cdot 6H_2O$ in 40% aqueous solution of NaOH with subsequent extraction with diethyl ether and precipitation from water using potassium acetate. 9,9′,12,12′-Tetraalkyl derivatives Me_4N[9,9′,12,12′-R_4-3,3′-Co(1,2-$C_2B_9H_9)_2$] (R = = Me (**16**), Et (**17**)) were obtained by the reaction of Me_3NH[5,6-R_2-7,8-$C_2B_9H_{10}$] (**9**, **10**) with anhydrous $CoCl_2$ in 1,2-dimethoxyethane using Bu^tOK as a base with subsequent precipitation from water with Me_4NCl. 9,9′,12,12′-Tetraaryl derivatives K[9,9′,12,12′-R_4-3,3′-Co(1,2-$C_2B_9H_9)_2$] (R = Ph (**18**), *p*-Tol (**19**)) were synthesized similarly, except the precipitation step since the potassium salts obtained are insoluble in water (Scheme 5).

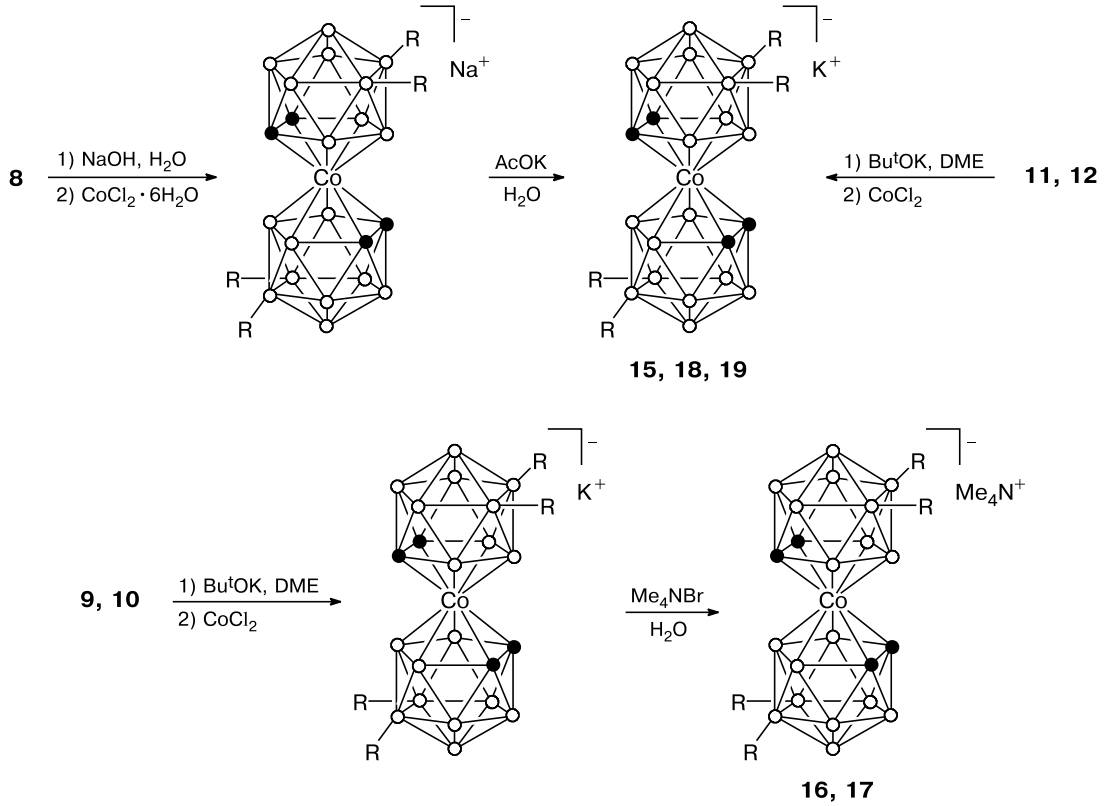
The ^{11}B NMR spectra of compounds **16**—**19** contain singlets for the *C*-substituted boron atoms in the region δ 2.7—4.7 and five doublets for the unsubstituted vertices with the ratio of integral intensities 2 : 4 : 2 : 4 : 4 : 2. The ^{1}H NMR spectra exhibit broad singlets for the carborane CH groups in the region δ 3.75—4.42 and signals of the corresponding substituents.

In conclusion, we obtained and characterized a series of new 5,6-disubstituted *nido*-carborane derivatives and 9,9′,12,12′-substituted cobalt bis(dicarbollide) derivatives.

Experimental

All the cross-coupling and complexation reactions were carried out under argon. Diethyl ether and 1,2-dimethoxyethane were distilled over sodium metal in the presence of benzophenone, dichloromethane was distilled over calcium hydride. 9,12-Diiodo-*ortho*-carborane (**1b**),[16] 4-FC_6H_4Br,[20] and $(Ph_3P)_2PdCl_2$[21] were obtained according to procedures published earlier, anhydrous $CoCl_2$ was obtained by the reaction of $CoCl_2 \cdot 6H_2O$ with $SOCl_2$. Reaction progress was monitored by thin-layer chromatography on Kieselgel 60 F245 plates (Merck). Silica gel from Acros Organics (0.060—0.200 mm, 60 Å) was used for column chromatography. ^{1}H, ^{11}B, ^{11}B{^{1}H}, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra were recorded on Bruker Avance-300, Bruker Avance-400, and Bruker AM-600 spectrometer. Chemical shifts are given relative to Me_4Si (for ^{1}H and ^{13}C NMR spectra), $BF_3 \cdot Et_2O$ (for ^{11}B NMR spectra), and $CFCl_3$ (for ^{19}F NMR spectra). ^{11}B NMR spectra were used to determine splitting patterns of boron signals (the B—H spin-spin coupling constants are not given because of partial overlap of signals, the ^{13}C—^{11}B spin-spin coupling constants are not given because of unsatisfactory resolution of signals). Mass spectra were obtained on Kratos MS 890 and Bruker Microflex LT mass spectrometers, high resolution mass spectra

Scheme 5



were obtained on a Bruker Daltonics microOTOF II mass spectrometer.

9,12-Dibromo-1,2-dicarba-*closo*-dodecaborane (1a). A solution of Br_2 (1.81 mL, 5.54 g, 34.67 mmol) in CH_2Cl_2 (50 mL) was added dropwise to a solution of 1,2-$C_2B_{10}H_{12}$ (5.00 g, 34.67 mmol) in CH_2Cl_2 (50 mL) over 15 min and the mixture was stirred until it became colorless. Then, more Br_2 (1.81 mL, 5.54 g, 34.67 mmol) in CH_2Cl_2 (50 mL) was added dropwise over 20 min, followed by the addition of $AlCl_3$ (1.00 g, 7.50 mmol). The reaction mixture was refluxed for 20 h. After the reaction was complete, the mixture was cooled and treated with a solution of $Na_2S_2O_3$ (30.00 g) in water (100 mL). The organic phase was separated, the aqueous fraction was extracted with dichloromethane (3×50 mL). The organic fractions were combined, dried with Na_2SO_4, filtered, and concentrated. The product was recrystallized from CH_2Cl_2 and dried in air to obtain compound **1a** (5.99 g, 57%). ^{1}H NMR ($CDCl_3$), δ: 3.70 (br.s, CH_{carb}). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: 0.3 (s, 2 B); −7.4 (d, 2 B); −14.4 (d, 4 B); −16.9 (d, 2 B). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 46.5. (br.s, C_{carb}).

9,12-Dimethyl-1,2-dicarba-*closo*-dodecaborane (2) was obtained according to the procedure published earlier.[16] ^{1}H NMR ($CDCl_3$), δ: 3.34 (br.s, 2 H, CH_{carb}); −0.20 (br.s, 6 H, CH_3—B). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: 7.2 (s, 2 B); −7.6 (d, 2 B); −14.1 (d, 4 B); −16.6 (d, 2 B).

9,12-Diethyl-1,2-dicarba-*closo*-dodecaborane (3a) and 9-ethyl-12-iodo-1,2-dicarba-*closo*-dodecaborane (3b). Iodoethane (0.38 mL, 1/3 of the total amount) was added to a suspension of Mg turnings (0.56 g, 22.88 mmol) in Et_2O (30 mL). Two drops of $BrCH_2CH_2Br$ were added to activate Mg. The reaction mixture was refluxed until it grew turbid, then cooled, followed by a dropwise addition of a solution of iodoethane (0.77 mL, a total of 2.23 g, 14.30 mmol) in Et_2O (30 mL) over 20 min. The mixture was refluxed for 1 h and cooled, followed by a dropwise addition of a solution of 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (1.13 g, 2.86 mmol) in Et_2O (30 mL) over 20 min. Then, the solution was stirred for 30 min, followed by the addition in one portion of CuI (0.03 g, 0.16 mmol) and $(Ph_3P)_2PdCl_2$ (0.09 g, 0.14 mmol). The solution gradually turned black. The reaction mixture was refluxed for 40 h. After the reaction was complete, the mixture was cooled and treated with 10% aqueous solution of hydrochloric acid (30 mL). The organic phase was separated. The aqueous fraction was extracted with diethyl ether (3×50 mL). The organic fractions were combined, dried with Na_2SO_4, filtered, and concentrated. The residue obtained was purified by column chromatography (eluent Et_2O). The first two fractions were collected and concentrated to obtain compound **3a** (0.20 g, 35%) and product **3b** (0.16 g, 19%), respectively. The spectral data for compound **3a** correspond to those published earlier.[16]

Compound **3b**. ^{1}H NMR ($CDCl_3$), δ: 3.82 (br.s, 1 H, CH_{carb}); 3.54 (br.s, 1 H, CH_{carb}); 0.94 (m, 3 H, $C\underline{H}_3CH_2$—B); 0.90 (m, 2 H, $CH_3C\underline{H}_2$—B). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: 9.2 (s, 1 B); −7.2 (d, 2 B); −13.4 (d, 2 B); −14.2 (d+s, 3 B); −15.6 (d, 2 B). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 50.3. (br.s, C_{carb}); 49.0 (br.s, C_{carb}); 13.3 (s, $\underline{C}H_3CH_2$—B); 11.3 (br.q, $CH_3\underline{C}H_2$—B).

9,12-Diphenyl-1,2-dicarba-*closo*-dodecaborane (4). Compound **4** was synthesized according to the procedure similar to that for compounds **3a,b**, using Mg (0.56 g, 22.88 mmol), bromobenzene (1.50 mL, 2.25 g, 14.30 mmol), 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (1.13 g, 2.86 mmol), CuI (0.03 g, 0.16 mmol), and $(Ph_3P)_2PdCl_2$ (0.09 g, 0.14 mmol). The yield of compound **4** was 0.45 g (53%). ^{1}H NMR ($CDCl_3$), δ: 7.23 (m, 4 H, *m*-$\underline{H}$—C_6H_4—B); 7.14 (m, 6 H, *p*-$\underline{H}$—C_6H_4—B and *o*-$\underline{H}$—C_6H_4—B); 3.69 (br.s, 2 H, CH_{carb}). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: 7.8 (s, 2 B); −9.2 (d, 2 B); −14.0 (d, 4 B); −16.5 (d, 2 B).

1-Iodo-9,12-di(*p*-tolyl)-1,2-dicarba-*closo*-dodecaborane (5b). Compound **5b** was obtained according to the procedure similar to that for compounds **3a,b**, using Mg (0.56 g, 22.88 mmol), *p*-MeC_6H_4Br (2.45 g, 14.30 mmol), 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (1.13 g, 2.86 mmol), CuI (0.03 g, 0.16 mmol), and $(Ph_3P)_2PdCl_2$ (0.09 g, 0.14 mmol). The yield of compound **5b** was 0.81 g (63%). ^{1}H NMR ($CDCl_3$), δ: 7.12 (d, 2 H, C_6H_4, J = 7.6 Hz); 7.07 (d, 2 H, C_6H_4, J = 7.6 Hz); 6.96 (d, 2 H, C_6H_4, J = 8.3 Hz); 6.94 (d, 2 H, C_6H_4, J = 8.3 Hz); 3.81 (br.s, 1 H, CH_{carb}); 2.26 (s, 3 H, *p*-$C\underline{H}_3$—C_6H_4—B); 2.24 (s, 3 H, *p*-$C\underline{H}_3$—C_6H_4—B). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: 9.5 (s, 1 B); 6.7 (s, 1 B); −7.2 (d, 4 B); −10.8 (d, 2 B); −12.0 (d, 2 B). MS (EI): found: m/z 450 $[M]^-$; $C_{14}H_{23}B_{10}I$; calculated 450 $[M]^-$.

9,12-Di(*p*-tolyl)-1,2-dicarba-*closo*-dodecaborane (5a). Iodoethane (0.34 mL, 0.65 g, 4.18 mmol) was added to a suspension of Mg turnings (0.16 g, 6.68 mmol) in Et_2O (40 mL). Two drops of $BrCH_2CH_2Br$ were added to activate Mg. The reaction mixture was refluxed for 1 h, the grew turbid. Then, the mixture was cooled, followed by the addition of a solution of compound **5b** (0.75 g, 1.67 mmol) in Et_2O (40 mL) over 15 min. The mixture was stirred for 30 min, refluxed for 4 h, cooled, and treated with 10% aqueous solution of hydrochloric acid (30 mL). The organic fraction was separated. The aqueous fraction was extracted with diethyl ether (3×50 mL). The organic fractions were combined, dried with Na_2SO_4, filtered, and concentrated to obtain compound **5a** (0.42 g, 78%).

Later, compound **5a** was synthesized according to the procedure for compounds **3a,b**, using Mg (1.11 g, 45.76 mmol), 4-MeC_6H_4Br (4.89 g, 28.60 mmol), 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (2.26 g, 5.72 mmol), CuI (0.06 g, 0.32 mmol), and $(Ph_3P)_2PdCl_2$ (0.18 g, 0.28 mmol). The yield of compound **5a** was 1.35 g (73%). The spectral data corresponded to those published earlier.[18]

9,12-Bis(4-methoxyphenyl)-1,2-dicarba-*closo*-dodecaborane (6) was synthesized according to the procedure similar to that for compounds **3a**,**b**, using 0.50 M solution of 4-$MeOC_6H_4MgBr$ in THF (2.11 g, 10.00 mmol; 20.00 mL of solution), 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (0.79 g, 2.00 mmol), CuI (0.03 g, 0.16 mmol), and $(Ph_3P)_2PdCl_2$ (0.09 g, 0.14 mmol). The yield of compound **6** was 0.35 g (49%). ^{1}H NMR ($CDCl_3$), δ: 7.15 (d, 4 H, *m*-$\underline{H}$—C_6H_3OMe, J = 5.5 Hz); 6.70 (d, 4 H, *o*-$\underline{H}$—C_6H_3OMe, J = 5.5 Hz); 3.75 (s, 6 H, *p*-$C\underline{H}_3O$—C_6H_4—B); 3.63 (br.s, 2 H, CH_{carb}). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: 7.8 (s, 2 B); −9.2 (d, 2 B); −14.1 (d, 4 B); −16.6 (d, 2 B).

9,12-Bis(4-fluorophenyl)-1,2-dicarba-*closo*-dodecaborane (7a) and 9-(4-fluorophenyl)-12-iodo-1,2-dicarba-*closo*-dodecaborane (7b) were synthesized according to the procedure similar to that for compounds **3a,b**, using Mg (0.56 g, 22.88 mmol), 4-FC_6H_4Br (1.58 mL, 2.50 g, 14.30 mmol), 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (1.13 g, 2.86 mmol), CuI (0.03 g, 0.16 mmol), and $(Ph_3P)_2PdCl_2$ (0.09 g, 0.14 mmol). The yield of compound **7a** was 0.31 g (33%), for compound **7b** 0.22 g (21%). The spectral data for compound **7a** corresponded to those published earlier.[19]

Compound **7b**. ^{1}H NMR ($CDCl_3$), δ: 7.41 (m, 2 H, C_6H_4); 7.00 (m, 2 H, C_6H_4); 3.98 (br.s, 1 H, CH_{carb}); 3.63 (br.s, 1 H,

CH_{carb}). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: 6.9 (s, 1 B); −7.7 (d, 2 B); −13.6 (d, 2 B); −14.5 (d+s, 3 B); −15.4 (d, 2 B). $^{19}F\{^1H\}$ NMR ($CDCl_3$), δ: −114.85 (s, *p*-*F*—C_6H_4—B).

Trimethylammonium 5,6-dibromodecahydro-7,8-dicarba-*nido*-undecaborate (8) was obtained according to the procedure published earlier.[22] ^1H NMR (CD_3COCD_3), δ: 8.86 (br.s, 1 H, $(CH_3)_3N\underline{H}$); 3.19 (d, 9 H, $(C\underline{H}_3)_3NH$, *J* = 5.1 Hz); 1.88 (br.s, 2 H, CH_{carb}); −2.09 (br.s, 1 H, H_{bridge}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: −10.7 (s+d, 4 B); −19.0 (d, 1 B); −21.9 (d, 2 B); −28.7 (d, 1 B); −34.8 (d, 1 B). $^{13}C\{^1H\}$ NMR (CD_3COCD_3), δ: 46.7 (s, $(CH_3)_3NH$); 39.3 (br.q, CH_{carb}).

Trimethylammonium 5,6-dimethyldecahydro-7,8-dicarba-*nido*-undecaborate (9). Compound **2** (0.34 g, 2.00 mmol) was added to a solution of sodium hydroxide NaOH (0.16 g, 4.00 mmol) in 96% aqueous EtOH (20 mL). The mixture was refluxed for 16 h, cooled, filtered, and neutralized with 10% aqueous solution of hydrochloric acid. A precipitate of sodium chloride was filtered off, the filtrate was concentrated. The residue was dissolved in water (10 mL), the product was precipitated by an excess of trimethylammonium chloride (Me_3NHCl) in water (10 mL). A white clotted precipitate was filtered off, washed, and dried to obtain compound **9** (0.29 g, 65%). ^1H NMR (CD_3COCD_3), δ: 3.24 (s, 9 H, $(C\underline{H}_3)_3NH$); 1.53 (br.s, 2 H, CH_{carb}); 0.03 (br.s, 6 H, CH_3—B); −2.46 (br.s, 1 H, H_{bridge}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: −7.6 (s, 2 B); −9.9 (d, 2 B); −18.6 (d, 1 B); −21.2 (d, 2 B); −28.9 (d, 1 B); −34.2 (d, 1 B). $^{13}C\{^1H\}$ NMR (CD_3COCD_3), δ: 46.2 (s, $(CH_3)_3NH$); 38.5 (br.q, CH_{carb}); 2.2 (br.q, CH_3—B). MS (EI): found: *m/z* 161 [M − − Me_3N − H_2]$^-$; $C_4H_{15}B_9$; calculated 161 [M − Me_3N − H_2]$^-$.

Trimethylammonium 5,6-diethyldecahydro-7,8-dicarba-*nido*-undecaborate (10) was obtained according to the procedure similar to that for compound **9**, using NaOH (0.07 g, 1.80 mmol) and compound **3a** (0.18 g, 0.90 mmol). The yield of compound **10** was 0.11 g (49%). ^1H NMR (CD_3COCD_3), δ: 3.24 (s, 9 H, $(C\underline{H}_3)_3NH$); 1.55 (br.s, 2 H, CH_{carb}); 0.83 (m, 6 H, $C\underline{H}_3CH_2$—B); 0.52 (m, 4 H, $CH_3C\underline{H}_2$—B); −2.54 (br.s, 1 H, H_{bridge}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: −5.4 (s, 2 B); −10.9 (d, 2 B); −18.8 (d, 1 B); −21.2 (d, 2 B); −30.4 (d, 1 B); −35.7 (d, 1 B). $^{13}C\{^1H\}$ NMR (CD_3COCD_3), δ: 45.3 (s, $(CH_3)_3NH$); 37.3 (br.q, CH_{carb}); 14.2 (s, $\underline{C}H_3CH_2$—B); 2.5 (br.q, $CH_3\underline{C}H_2$—B). MS (MALDI): found: *m/z* 190.4 [M − Me_3NH]$^-$; $C_6H_{20}B_9$; calculated 190.2 [M − Me_3NH]$^-$.

Trimethylammonium 5,6-diphenyldecahydro-7,8-dicarba-*nido*-undecaborate (11) was obtained according to the procedure similar to that for compound **9**, using NaOH (0.10 g, 2.42 mmol) and compound **4** (0.36 g, 1.21 mmol). The yield of compound **11** was 0.27 g (65%). ^1H NMR (CD_3COCD_3), δ: 7.33 (m, 4 H, *m*-$\underline{H}$—C_6H_4—B); 6.83 (m, 6 H, *p*- and *o*-*H*—C_6H_4—B); 3.11 (s, 9 H, $(C\underline{H}_3)_3NH$); 1.92 (br.s, 2 H, CH_{carb}); −2.04 (br.s, 1 H, H_{bridge}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: −6.2 (s, 2 B); −10.0 (d, 2 B); −18.4 (d, 1 B); −21.2 (d, 2 B); −30.3 (d, 1 B); −35.9 (d, 1 B).

Trimethylammonium 5,6-di(*p*-tolyl)decahydro-7,8-dicarba-*nido*-undecaborate (12) was obtained according to the procedure similar to that for compound **9**, using NaOH (0.50 g, 12.48 mmol) and compound **5a** (1.35 g, 4.16 mmol). The yield of compound **12** was 0.90 g (58%). ^1H NMR (CD_3COCD_3), δ: 7.22 (d, 4 H, C_6H_4, *J* = 7.6 Hz); 6.68 (d, 4 H, C_6H_4); 3.14 (s, 9 H, $(C\underline{H}_3)_3NH$); 2.11 (s, 6 H, *p*-$C\underline{H}_3C_6H_4$—B); 1.89 (br.s, 2 H, CH_{carb}); −2.06 (br.s, 1 H, H_{bridge}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: −6.1 (s, 2 B); −10.0 (d, 2 B); −18.5 (d, 1 B); −21.2 (d, 2 B); −30.2 (d, 1 B); −36.0 (d, 1 B).

Trimethylammonium 5,6-bis(4-methoxyphenyl)decahydro-7,8-dicarba-*nido*-undecaborate (13) was obtained according to the procedure similar to that for compound **9**, using NaOH (0.08 g, 1.92 mmol) and compound **6** (0.34 g, 0.96 mmol). The yield of compound **13** was 0.21 g (54%). ^1H NMR (CD_3COCD_3), δ: 7.21 (d, 4 H, *m*-$\underline{H}$—C_6H_3OMe, *J* = 7.3 Hz); 6.46 (d, 4 H, *o*-$\underline{H}$—C_6H_3OMe, *J* = 7.3 Hz); 3.62 (s, 6 H, *p*-$C\underline{H}_3OC_6H_4$—B); 3.19 (s, 9 H, $(C\underline{H}_3)_3NH$); 1.87 (br.s, 2 H, CH_{carb}); −2.08 (br.s, 1 H, H_{bridge}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: −6.2 (s, 2 B); −10.1 (d, 2 B); −18.6 (d, 1 B); −21.2 (d, 2 B); −30.2 (d, 1 B); −35.9 (d, 1 B).

Trimethylammonium 5,6-bis(4-fluorophenyl)decahydro-7,8-dicarba-*nido*-undecaborate (14) was obtained according to the procedure similar to that for compound **9**, using NaOH (0.04 g, 0.90 mmol) and compound **7** (0.15 g, 0.45 mmol). The yield of compound **14** was 0.05 g (29%). ^1H NMR (CD_3COCD_3), δ: 7.27 (m, 4 H, C_6H_4); 6.61 (m, 4 H, C_6H_4); 3.12 (s, 9 H, $(C\underline{H}_3)_3NH$); 1.94 (br.s, 2 H, CH_{carb}); −2.04 (br.s, 1 H, H_{bridge}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: −6.6 (s, 2 B); −10.0 (d, 2 B); −18.4 (d, 1 B); −21.2 (d, 2 B); −30.2 (d, 1 B); −35.8 (d, 1 B). ^{19}F (CD_3COCD_3), δ: −122.00 (s, 2 F, *p*-F—C_6H_4—B). MS (EI): found: *m/z* 321 [M − Me_3N − H_2]$^-$; $C_{14}H_{17}B_9F_2$; calculated 321 [M − Me_3N − H_2]$^-$.

Potassium 9,9′,12,12′-tetrabromooctadecahydro-1,1′,2,2′-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (15). Compound **8** (4.39 g, 12.50 mmol) was added to a freshly prepared 40% solution of NaOH in water H_2O (100 mL). After the compound was completely dissolved and triethylamine ceased to liberate, $CoCl_2 \cdot 6H_2O$ (5.95 g, 25.00 mmol) was added. The mixture was stirred for 4 h, then diluted with diethyl ether (100 mL). The organic fraction was separated, the aqueous phase was extracted with diethyl ether (4×50 mL). The organic fractions were combined, filtered, dried with Na_2SO_4, and concentrated. The residue was dissolved in water, the product was precipitated by an excess of potassium acetate. The precipitate was filtered off, washed with water, and dried to obtain compound **15** (3.90 g, 92%) as an orange powder. ^1H NMR (CD_3COCD_3), δ: 4.23 (br.s, 2 H, CH_{carb}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: 6.4 (d, 2 B); 2.9 (d, 2 B); −1.7 (s, 4 B); −6.9 (d, 4 B); −17.1 (d, 2 B); −23.4 (d, 2 B). $^{13}C\{^1H\}$ NMR (CD_3COCD_3), δ: 46.7 (br.s, CH_{carb}). HRMS (ESI): found: *m/z* 639.9216 [M]$^-$; $C_4H_{18}B_{18}Br_4Co$; calculated: 639.9232 [M]$^-$.

Tetramethylammonium 9,9′,12,12′-tetramethyloctadecahydro-1,1′,2,2′-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (16). Potassium *tert*-butoxide (1.39 g, 12.40 mmol) was added in one portion to a solution of compound **9** (0.27 g, 1.24 mol) in 1,2-dimethoxyethane (40 mL). The suspension was stirred for 30 min. Then, anhydrous $CoCl_2$ (1.61 g, 1.24 mmol) was added in one portion. The solution was refluxed for 20 h. After the reaction was complete, the mixture was cooled, filtered, and concentrated. The residue was dissolved in water, the product was precipitated by an excess of NMe_4Br in water. The precipitate was filtered off, washed, and dried to obtain compound **16** (0.25 g, 89%) as a brown powder. ^1H NMR (CD_3COCD_3), δ: 3.75 (br.s, 4 H, CH_{carb}); 3.47 (br.s, 12 H, $N(CH_3)_4$); 0.08 (br.s, 12 H, CH_3—B). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: 9.5 (d, 2 B); 2.7 (d+s, 6 B); −5.3 (d, 4 B); −17.3 (d, 4 B), −23.6 (d, 2 B). $^{13}C\{^1H\}$ NMR (CD_3COCD_3), δ: 55.2 (t, $N(CH_3)_4$); 45.4 (br.s, CH_{carb}); 3.4 (br.q, CH_3—B). HRMS (ESI): found: *m/z* 380.3488 [M]$^-$; $C_8H_{30}B_{18}Co$; calculated 380.3475 [M]$^-$.

Tetramethylammonium 9,9′,12,12′-tetraethyloctadecahydro-1,1′,2,2′-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (17) was obtained according to the procedure similar to that for

compound **16**, using compound **10** (0.07 g, 0.28 mmol), Bu^tOK (0.31 g, 2.80 mmol), and $CoCl_2$ (0.36 g, 2.80 mmol). The yield of compound **17** was 0.06 g (84%), a brown powder. ^1H NMR (CD_3COCD_3), δ: 3.78 (br.s, 4 H, CH_{carb}); 3.45 (br.s, 12 H, $N(CH_3)_4$); 0.85 (br.s, 12 H, $C\underline{H}_3CH_2$—B); 0.59 (br.m, 8 H, $CH_3C\underline{H}_2$—B). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: 8.2 (d, 2 B); 4.7 (s, 4 B); 1.1 (d, 2 B); −6.0 (d, 4 B); −18.2 (d, 4 B); −23.7 (d, 2 B). $^{13}C\{^1H\}$ NMR (CD_3COCD_3), δ: 56.8 (t, $(CH_3)_4N$); 47.2 (br.s, CH_{carb}); 15.0 (s, $\underline{C}H_3CH_2$—B); 13.1 (br.q, $CH_3\underline{C}H_2$—B). HRMS (ESI): found: *m/z* 436.4088 $[M]^-$; $C_{12}H_{38}B_{18}Co$; calculated 436.4103 $[M]^-$.

Potassium 9,9′,12,12′-tetraphenyloctadecahydro-1,1′,2,2′-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (18) was obtained according to the procedure similar to that for compound **16**, but after evaporation of dimethoxyethane, the residue obtained was washed with water. The reaction used compound **11** (0.20 g, 0.58 mmol), Bu^tOK (0.65 g, 5.80 mmol), and $CoCl_2$ (0.74 g, 5.80 mmol). The yield of compound **18** was 0.17 g (88%), a dark brown powder. ^1H NMR (CD_3COCD_3), δ: 7.37 (br.s, 8 H, *m*-$\underline{H}$—C_6H_4—B); 6.98 (br.s, 12 H, *o*- and *p*-$\underline{H}$—C_6H_4—B); 4.42 (br.s, 4 H, CH_{carb}). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: 6.9 (d, 2 B); 3.7 (s, 4 B); 0.2 (d, 2 B); −5.5 (d, 4 B); −17.2 (d, 4 B); −23.9 (d, 2 B).

Potassium 9,9′,12,12′-tetra(*p*-tolyl)octadecahydro-1,1′,2,2′-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (19) was obtained according to the procedure similar to that for compound **18**, using compound **12** (0.85 g, 2.27 mmol), Bu^tOK (2.55 g, 22.70 mmol), and $CoCl_2$ (2.95 g, 22.70 mmol). The yield of compound **19** was 0.54 g (65%), a dark brown powder. ^1H NMR (CD_3COCD_3), δ: 7.24 (m, 8 H, C_6H_4); 6.79 (m, 8 H, C_6H_4); 4.16 (br.s, 4 H, CH_{carb}); 2.16 (br.s, 12 H, *p*-$C\underline{H}_3C_6H_4$—B). $^{11}B\{^1H\}$ NMR (CD_3COCD_3), δ: 6.8 (d, 2 B); 3.9 (s, 4 B); 0.2 (d, 2 B); −5.5 (d, 4 B); −17.1 (d, 4 B); −23.5 (d, 2 B). $^{13}C\{^1H\}$ NMR (CD_3COCD_3), δ: 141.8 (br.q, C—B); 133.7 (s, $\underline{C}$—CH_3); 133.2 (s, CH); 126.9 (s, CH); 47.3 (br.s, CH_{carb}); 20.3 (s, CH_3). HRMS (ESI): found: *m/z* 684.4742 $[M]^-$; $C_{32}H_{46}B_{18}Co$; calculated 684.4742 $[M]^-$.

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