Synthesis of cobalt and nickel 6,6′-diphenylbis(dicarbollides)*

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6,6′-Diphenyl derivatives of cobalt and nickel bis(dicarbollide) were synthesized starting from *nido*-carborane by the insertion—deboronation—insertion sequence of reactions. The by-products of the insertion of $PhBCl_2$ into the *nido*-carborane cage, diethyloxonium derivatives of *nido*-carborane [9-Et_2O-7,8-$C_2B_9H_{11}$] and [10-Et_2O-7,8-$C_2B_9H_{11}$], were isolated and characterized. Treatment of the latter with pyridine resulted in the elimination of one ethyl group to give the corresponding ethoxy derivatives. The structures of *nido*-carborane 10-diethyloxonium derivative and cobalt bis(dicarbollide) 6,6′-diphenyl derivative were established by X-ray diffraction analysis.

Key words: carboranes, metallacarboranes, phenyl derivatives.

The rapid development of the carborane chemistry in the 1960s in many ways was ahead of the development and introduction into everyday practice of modern instrumental methods of physicochemical analysis, first of all, nuclear magnetic resonance spectroscopy. According to the R. N. Grimes monograph,[1] only synthesis was described for the majority of carborane derivatives obtained in 1960—1970, with any of physicochemical characteristics being absent. Moreover, this problem is also present for many compounds synthesized later.[2] It was found that, in the absence of reliable methods for product identification and control of purity, synthetic procedures described in the literature in some cases can lead to the formation of mixtures of derivatives with a low content of the target product.[3] Therefore, in many cases, it is necessary to recheck previously described procedures with verification of the compounds formed.

Derivatives of transition metal bis(dicarbollide) complexes with aryl substituents in the dicarbollide ligand belt farthest from the metal atom are of interest for the design of various new materials, including metal-organic frameworks (MOFs),[4] solar cells,[5] and molecular switches.[6—8] In contrast to the aryl derivatives of transition metal bis(dicarbollide) complexes containing substituents in the dicarbollide ligand belt closest to the metal atom, which are obtained by modification of parent complexes,[9—12] derivatives with aryl substituents in the farthest dicarbollide ligand belt are prepared by assembling from the corresponding *nido*-carboranes on the metal ion. In this case, derivatives with substituents at the remotest from carbon atoms positions 9 and 12, are obtained by assembling from relatively available 5-aryl- and 5,6-diaryl-*nido*-carboranes,[4,13] while the synthesis of derivatives with substituents at position 6 adjacent to carbon atoms requires the use of much less available 3-aryl-*nido*-carboranes.[14,15] The purpose of the present work is to synthesize cobalt and nickel bis(dicarbollide) 6,6′-diphenyl derivatives and recheck the previously described procedures with characterization of all the intermediate and by-products formed.

Results and Discussion

Cobalt and nickel bis(dicarbollide) 6,6′-diphenyl derivatives were synthesized according to Scheme 1. The sequence includes the insertion of the BPh group into the *nido*-carborane cage with the formation of 3-phenyl-*ortho*-carborane, its subsequent deboronation to 3-phenyl-*nido*-carborane, and the insertion of the metal atom to form the corresponding metal complexes [6,6′-Ph_2-3,3′-Co-(1,2-$C_2B_9H_{10})_2$]$^-$ (see Ref. 14) and [6,6′-Ph_2-3,3′-Ni(1,2-$C_2B_9H_{10})_2$] (see Ref. 6).

The preparation of 3-phenyl-*ortho*-carborane by the insertion of phenylboron dichloride $PhBCl_2$ into the dicarbollide anion was described already 50 years ago,[14] however, it was characterized only by elemental analysis data and ^{1}H NMR spectroscopy. Later, a two-step syn-

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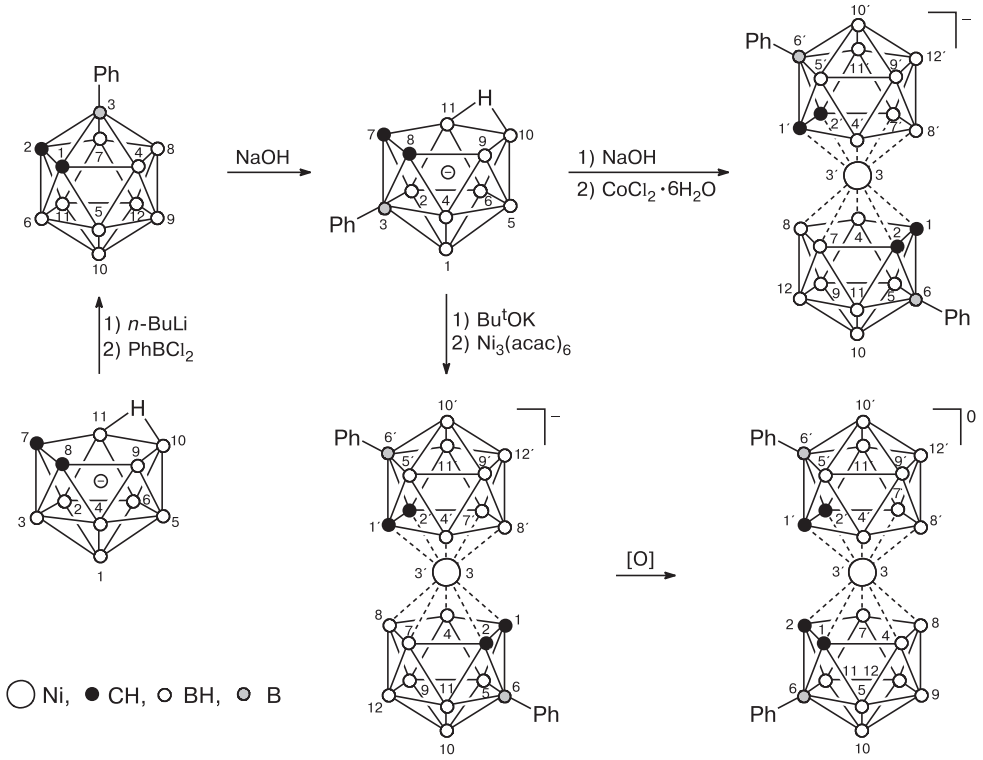
Scheme 1

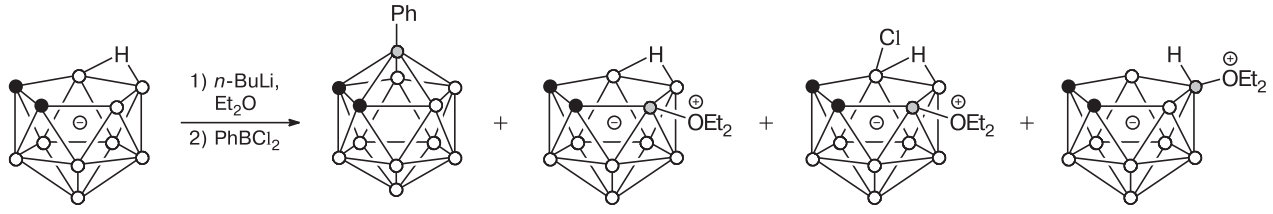


thesis of 3-phenyl-*ortho*-carborane through the insertion of boron triiodide into the dicarbollide anion with subsequent Pd-catalyzed cross-coupling of the resulting 3-iodo-*ortho*-carborane with phenylmagnesium bromide PhMgBr was described. The resulting product was fully characterized by NMR and IR spectroscopy and X-ray diffraction analysis.[15] Recently,[16] the preparation of 3-phenyl-*ortho*-carborane by the reaction of diazonium derivative $[3\text{-}N_2\text{-}1,2\text{-}C_2B_{10}H_{11}][BF_4]$ with phenylmagnesium bromide PhMgBr was described. The latter two methods are of interest for the preparation of derivatives with different substituents in the aryl ring, but since phenylboron dichloride is commercially available, the one-step method for the synthesis of 3-phenyl-*ortho*-carborane is preferred.

We found that the reaction of the deprotonated form of *nido*-carborane, obtained by treatment of potassium dodecahydro-7,8-dicarba-*nido*-undecaborate K[7,8-$C_2B_9H_{12}$] (**1**) with *n*-butyllithium, with $PhBCl_2$ in diethyl ether leads, in addition to 3-phenyl-*ortho*-carborane **2** (69% yield), to three minore uncharged products. They were isolated by column chromatography and identified as *nido*-carborane 9- and 10-diethyloxonium derivatives [9-Et_2O-7,8-$C_2B_9H_{11}$] (**3a**) and [10-Et_2O-7,8-$C_2B_9H_{11}$] (**4**), as well as 9-diethyloxonium-11-chloro derivative [9-Et_2O-11-Cl-7,8-$C_2B_9H_{10}$] (**3b**) (Scheme 2). If the synthesis is carried out in a dilute solution (four-fold dilution), the yield of the target 3-phenyl-*ortho*-carborane **2** decreases to 60%, while the yields of by-products **3** and **4** increase to 9 and 11%, respectively.

The formation of *nido*-carborane diethyloxonium derivatives results from the nucleophilic substitution reaction initiated by $PhBCl_2$ as a Lewis acid.[17] Thus, the formation of similar tetrahydrofuran derivatives of

Scheme 2



1 **2** (69%) **3a** (3%) **3b** (0.3%) **4** (5%)

nido-carborane in its reaction with $FeCl_3$ in THF was described earlier.[18] Note that no formation of by-products is observed when the insertion reaction is carried out in toluene, but the yield of 3-phenyl-*ortho*-carborane **2** decreases to 43%.

The symmetrically substituted *nido*-carborane 10-diethyloxonium derivative **4** was obtained earlier in ~25% yield in the acid-catalyzed reaction of *nido*-carborane with formaldehyde or acetaldehyde in the presence of diethyl ether.[19] We obtained a single crystal of **4** and its molecular structure was determined by X-ray diffraction analysis (Fig. 1).

The B(10)—O(1) bond length is 1.508 Å, which is slightly shorter than in the known oxonium derivatives of polyhedral boron hydrides (1.517—1.553 Å),[20—29] while the C—O bonds (1.463(3) and 1.478(4) Å) are of the same order as in other oxonium derivatives (1.417—1.515 Å). The orientation of the substituent at B(10) atom is such that the torsion angle B(9)—B(10)—O(1)—C(3) is −60.97(19)°. This orientation seems to be additionally stabilized by the detected shortened contacts H(9)...H(4C) and H(6)...H(1A) (2.26(2) and 2.49(2) Å, respectively). Since the possibility of attractive C—H...H—B interactions was repeatedly demonstrated earlier,[30—33] we performed quantum chemical calculations for compound **4**. The calculated geometry slightly differs from the experimental one: the torsion angle B(9)—B(10)—O(1)—C(3) is −40.8°, the distances H(9)...H(4C) and H(6)...H(1A) are 2.47 and 2.25 Å, respectively. However, two shortened contacts were found in both the calculation and the experiment. A topological analysis of the electron density showed that both contacts are attractive and are characterized by the energies of −1.9 and −0.8 kcal mol^{-1} for H(9)...H(4C) and H(6)...H(1A), respectively.

The unsymmetrically substituted *nido*-carborane 9-diethyloxonium derivative **3a** was not earlier described, its structure was proved by the NMR spectroscopy data. The ^{11}B NMR spectrum consists of a singlet at δ 8.1 and seven doublets at δ −13.5, −19.1, −21.5, −23.9, −25.3, −33.2, and −39.5 with a ratio of integral intensities of 1 : 2 : 1 : 1 : 1 : 1 : 1 : 1. The ^{1}H NMR spectrum contains signals at δ 4.50 and 1.48 characteristic of the ethyl groups, signals for nonequivalent CH groups of the carborane cage at δ 1.98 and 1.90, and a broad signal for the proton of the BHB bridge at δ −2.55. In the ^{13}C NMR spectrum, the signals for the ethyl groups are found at δ 78.3 and 13.3, while the signals for the carbon atoms of the carborane cage, at δ 41.7 and 34.0. The chemical shifts of the signals for the methylene groups bonded to the oxygen atom are the same in derivatives **3a** and **4**. As it was shown earlier,[34] the position of these signals is a good indicator of the strength of the electron-donating effect of polyhedral

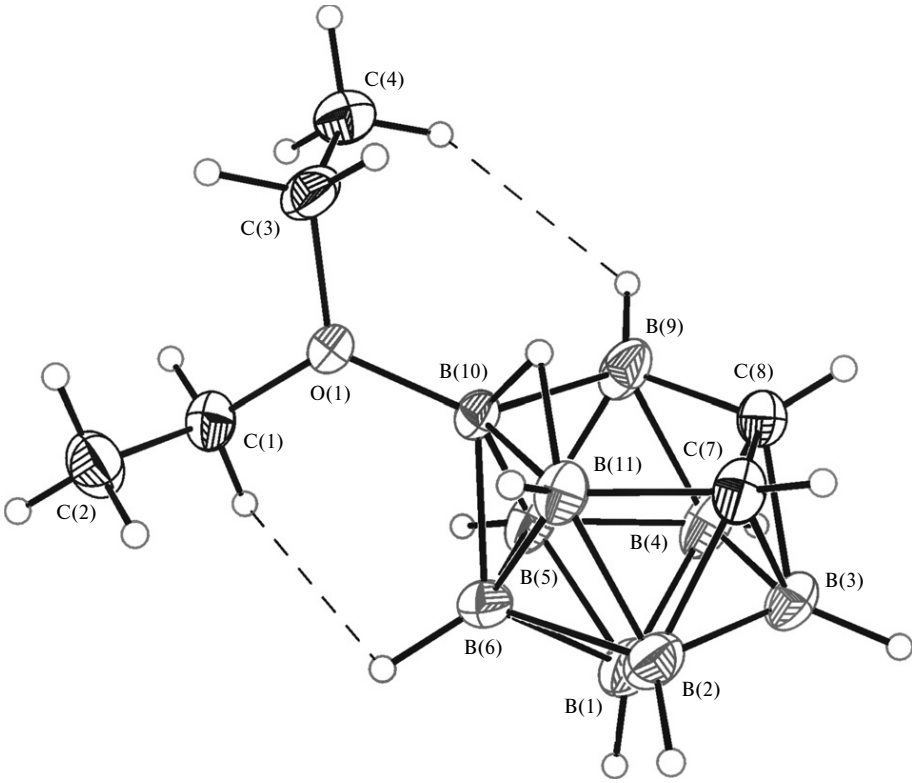
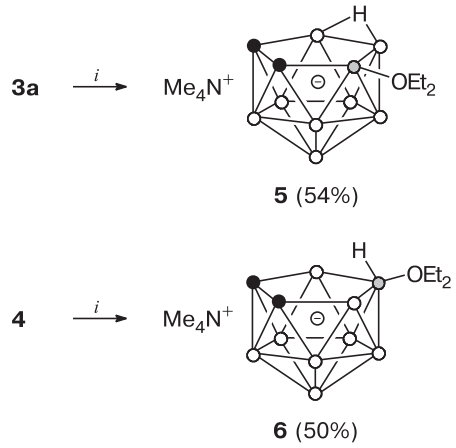


Fig. 1. A general view of molecule **4** in the representation of atoms by thermal displacement ellipsoids with a 50% probability. The dashed lines show attractive noncovalent H···H contacts.
Note. Figures 1 and 2 are available in full color on the web page of the journal (http://www.link.springer.com).

boron hydrides. Thus, it can be suggested that the electronic effects of the *nido*-carborane cage substituted at positions 9 and 10 are very close.

Cyclic oxonium derivatives of polyhedral boron hydrides are well studied because they are convenient starting compounds for the preparation of various functional derivatives.[35—37] At the same time, there are only a few published examples of diethyloxonium derivatives of polyhedral boron hydrides, including derivatives of *closo*-decaborate[38] and *closo*-dodecaborate[39] anions, *nido*-carborane,[19] and some metallaboranes[29] and metallacarboranes.[40,41] In contrast to cyclic oxonium derivatives, the reactions of diethyloxonium derivatives with nucleophiles proceed with the elimination of one ethyl group to give the corresponding ethoxy derivatives.[38,41] We found that reflux of diethyloxonium derivatives **3a** and **4** in pyridine leads to the elimination of an ethyl group and formation of ethoxy derivatives [9-EtO-7,8-$C_2B_9H_{11}$]$^-$ (**5**) and [10-EtO-7,8-$C_2B_9H_{11}$]$^-$ (**6**), respectively, which were isolated as tetramethylammonium salts (Scheme 3).

Scheme 3



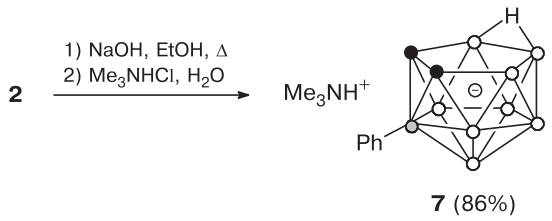
i. 1) pyridine, Δ; 2) Me_4NCl, H_2O.

The transformation of the diethyloxonium substituent into the ethoxy one leads to a noticeable upfield shift of the methylene group signals by about 1 and 15 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. At the same time, a slight downfield shift (~1—2 ppm) of the signals corresponding to the substituted boron atoms is observed in the ^{11}B NMR spectra.

The preparation of 3-phenyl-*nido*-carborane [3-Ph-7,8-$C_2B_9H_{11}$]$^-$ was also described previously,[14] but it was characterized only by ^{1}H NMR spectroscopy data. We have found that reflux of 3-phenyl-*ortho*-carborane with NaOH in ethanol gives the corresponding *nido*-carborane [3-Ph-7,8-$C_2B_9H_{11}$]$^-$ (**7**) in high yield, which was isolated as a trimethylammonium salt (Scheme 4).

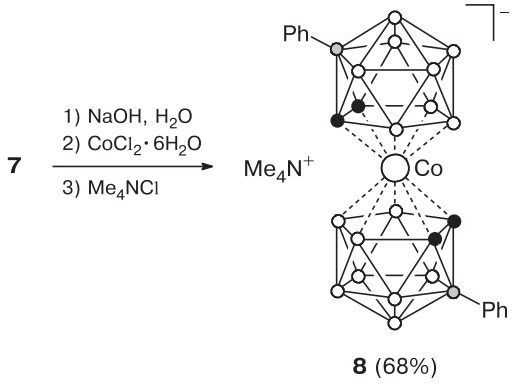
The ^{11}B NMR spectrum of (Me_3N)[**7**] in $CDCl_3$ exhibits a singlet at δ −9.9 and five doublets at δ −10.6, −16.2, −21.5, −35.0, and −36.5 with a ratio of integral intensities of 1 : 2 : 2 : 2 : 1 : 1. The ^{1}H NMR spectrum in acetone-d_6 exhibits signals for the phenyl group at δ 7.50 and 7.11, for the CH groups of the carborane cage at δ 1.88, and a broad signal for the proton of the BHB bridge at δ −2.53.

Scheme 4



6,6′-Diphenyl derivative of cobalt bis(dicarbollide) [6,6′-Ph_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$ (**8**) was obtained by deprotonation of *nido*-carborane **7** in 40% aqueous NaOH, followed by the reaction of the resulting dicarbollide anion with $CoCl_2 \cdot 6H_2O$, and isolated as a tetramethylammonium salt (Scheme 5). This method is much more convenient than the synthesis described earlier,[14] which uses sodium hydride and anhydrous $CoCl_2$, and gives a some higher yield of the target product (68% compared to 62% for the anhydrous method).

Scheme 5



The ^{11}B NMR spectrum of Me_4N[**8**] in acetone-d_6 exhibits a singlet at δ −14.1 and four doublets at δ 4.8, 2.1, −5.6, and −16.4 with a ratio of integral intensities of 2 : 2 : 8 : 2 : 4. The ^{1}H and ^{13}C NMR spectra exhibit signals for the phenyl groups, as well as for the CH groups of the carborane cage at δ 4.28 and 53.7, respectively.

The structure of Me_4N[**8**] was established by X-ray diffraction analysis (Fig. 2). The symmetrically independent part of the unit cell contains one molecule of the Me_4N^+ cation and two [6,6′-Ph2-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$ halves of anions **A** and **B**. The dicarbollide ligands in both anions are rotated by 180° relative to each other and form a transoid conformation. The phenyl

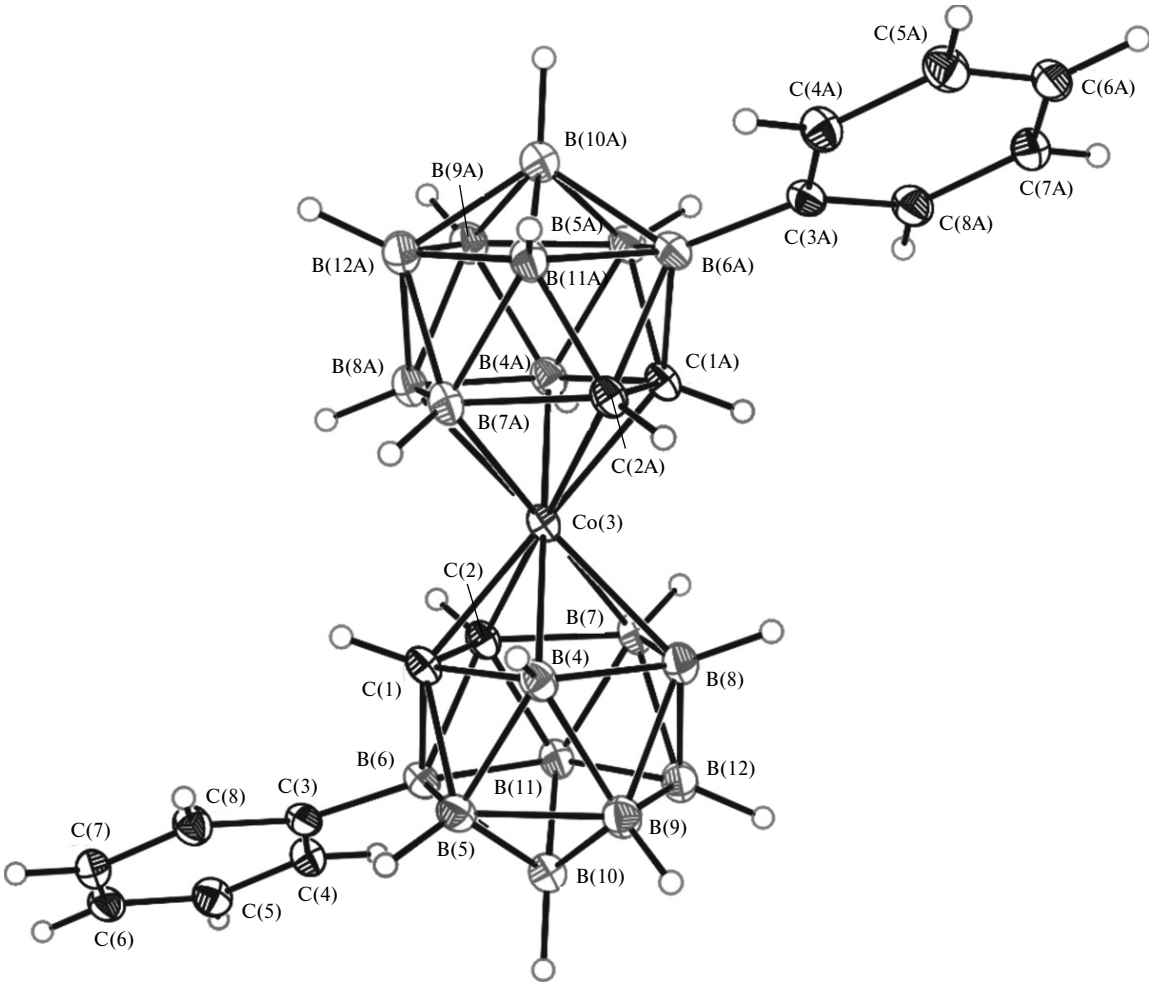


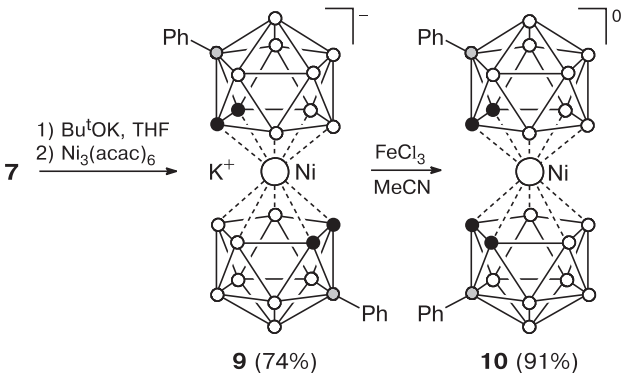
Fig. 2. A general view of the [6,6′-Ph_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$ anion (**8**) in the representation of atoms by thermal displacement ellipsoids with a 50% probability.

substituents in each anion are parallel to each other, but their rotation relative to the carborane cage is different in different anions (the torsion angles C(1)—B(6)—C(3)—C(4) are 148.8(3) and 86.1(3)° for A and B, respectively). The $C_{carb}H\cdots$HCPh and BH···HCPh contacts in the anions **A** and **B** are 2.49 and 2.41 Å and 2.29 and 2.49 Å, respectively, which is comparable with the length of the corresponding contacts in 3-phenyl-*ortho*-carborane 2 (2.48 and 2.43 Å)[15] and slightly longer than in 1-phenyl-*ortho*-carborane (2.04 and 2.15 Å).[30,42,43] The B(6)—C(Ph) bond lengths in the anions A and B are 1.574(2) and 1.576(2) Å, respectively, which is somewhat larger than the length of the corresponding B(3)—C(Ph) bond in the structure of 3-phenyl-*ortho*-carborane 2 (1.565 Å).[15]

The crystal structure is stabilized by relatively weak H...π and CH...BH interactions existing between the cation and the anion, as well as between dicarbollide anions A and B; in this case, no shortened contacts are formed between the same type of anions (**A**...**A** or **B**...**B**). The presence of interactions between two symmetrically independent molecules in a crystal or between two structural units in solvates and cocrystals was repeatedly observed earlier[44—47] and is at least one of the main driving forces for the formation of such crystal structures. In the crystal, the H...π and CH...BH contacts mentioned above (the shortest distances: H(7A)...C(8′), 2.81 Å, C(2)—H(2)...H(8′)—B(8′), 2.35 Å) cause the formation of chains along the c axis from alternating anions A and B rotated by ~90° relative to each other. Apparently, this explains the different relative orientation of phenyl substituents in anions **A** and **B**, contributing to the formation of intermolecular interactions.

In contrast to cobalt 6,6′-diphenylbis(dicarbollide), the preparation for nickel 6,6′-diphenylbis(dicarbollide) was described earlier only as a synthetic scheme and a figure of the crystal structure in the conference reports[6] without any characterization. We found that the reaction of nickel acetylacetonate $Ni_3(acac)_6$ with deprotonated 3-phenyl-*nido*-carborane in tetrahydrofuran leads to nickel(III) 6,6′-diphenylbis (dicarbollide) (**9**), the oxidation of which with ferric(III) chloride $FeCl_3$ in acetonitrile gives the desired nickel(IV) 6,6′-diphenylbis(dicarbollide) (**10**) (Scheme 6).

Scheme 6



The ^{11}B NMR spectrum of compound **10** in $CDCl_3$ exhibits a set of doublets at δ 20.8, 18.9, 4.9, and 1.9, as well as overlapped doublet and singlet at δ −7.1 with a total ratio of integral intensities of 2 : 2 : 4 : 4 : 6. The ^1H and ^{13}C NMR spectra exhibit signals for the phenyl groups, as well as for the CH groups of the carborane cage at δ 4.47 and 67.3, respectively.

Thus, we synthesized 6,6′-diphenyl derivatives of cobalt and nickel bis(dicarbollide), the separate steps of which were described in the literature,[6,14] the earlier unknown products were isolated and characterized. The by-products of the insertion of $PhBCl_2$ into the *nido*-carborane cage, the *nido*-carborane diethyloxonium derivatives [9-Et_2O-7,8-$C_2B_9H_{11}$] and [10-Et_2O-7,8-$C_2B_9H_{11}$], were detected and characterized. Treatment of the latter with pyridine leads to the elimination of one ethyl group to give the corresponding ethoxy derivatives [9-EtO-7,8-$C_2B_9H_{11}$]$^-$ and [10-EtO-7,8-$C_2B_9H_{11}$]$^-$.

Experimental

Potassium dodecahydro-7,8-dicarba-*nido*-undecaborate K[7,8-$C_2B_9H_{12}$] (**1**) was obtained as described in the literature.[48] Dichlorophenylborane $PhBCl_2$ (Acros Organics) was used without additional purification. The reactions progress was monitored by thin layer chromatography on Kieselgel 60 F245 plates (Merck), visualizing by a 0.5% solution of $PdCl_2$ in 1% HCl in a MeOH—H_2O solvent mixture (10 : 1). Acros Organics silica gel, 0.060–0.200 mm, 60 Å, was used for column chromatography. ^1H, ^{11}B, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are given relative to Me_4Si (for ^1H and ^{13}C NMR spectra) and $BF_3\cdot Et_2O$ (for ^{11}B NMR spectra). ^{11}B NMR spectra were used to determine the splitting pattern of boron signals. Mass spectra were obtained on a Kratos MS 890 mass spectrometer, high resolution mass spectra (HRMS) were obtained on a Bruker Daltonics microOTOF II mass spectrometer.

3-Phenyl-1,2-dicarba-*closo*-dodecarborane (2), 9-diethyloxonium-7,8-dicarba-*nido*-undecarborane (3a), and 10-diethyloxonium-7,8-dicarba-*nido*-undecarborane (4). ***A.*** A 2.5 *M* solution of BuLi in hexane (17.6 mL, 44.00 mmol) was added dropwise to a suspension of compound **1** (5.94 g, 40.0 mmol) in diethyl ether (150 mL) at −50 °C. The reaction mixture was allowed to warm-up to room temperature, then cool to −30 °C, followed by a dropwise addition of a solution of $PhBCl_2$ (6.20 mL, 7.63 g, 48.0 mmol) in diethyl ether (10 mL). The mixture was stirred for 100 h, the reaction progress was monitored by thin layer chromatography. Then, the reaction mixture was quenched with water (100 mL). The organic fraction was separated, dried with Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography (eluent chloroform—hexane, 3 : 1). The first, second, third, and fourth fractions were collected and concentrated on a rotary evaporator to obtain compounds **2** (5.82 g, 69%), **3a** (0.24 g, 3%), **3b** (0.03 g, 0.3%), and **4** (0.38 g, 5%), respectively.

B. A 2.5 *M* solution of BuLi in hexane (1.32 mL, 3.3 mmol) was added dropwise to a suspension of compound **1** (0.45 g, 3.00 mmol) in toluene (50 mL) at −30 °C. The reaction mixture was allowed to warm-up to room temperature, then cool to −30 °C, followed by a dropwise addition of a solution of 97% $PhBCl_2$ (0.44 mL, 0.54 g, 3.3 mmol) in toluene (5 mL). The mixture was stirred for 100 h, the reaction progress was monitored by thin layer chromatography. Then, the reaction mixture was concentrated on a rotary evaporator. The residue was dissolved in chloroform (25 mL) and passed through a layer of silica gel on a Schott filter. The system was washed with chloroform until the product was not detected by thin layer chromatography. The yield of compound **2** was 0.27 g (43%). The spectral data of compound **2** agree with the literature data.[15]

Compound 3a. ^1H NMR ($CDCl_3$), δ: 4.50 (m, 4 H, $OC\underline{H}_2CH_3$, J = 7 Hz); 1.98 (br.s, 1 H, CH_{carb}); 1.90 (br.s, 1 H, CH_{carb}), 1.48 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); −2.55 (br.s, 1 H, BHB_{bridge}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 78.3 ($O\underline{C}H_2CH_3$), 41.7 (C_{carb}), 34.0 (C_{carb}), 13.3 ($OCH_2\underline{C}H_3$). ^{11}B NMR ($CDCl_3$), δ: 8.1 (s, 1 B); −13.5 (d, 2 B, J = 138 Hz); −19.1 (d, 1 B, J = 165 Hz); −21.5 (d, 1 B, J = 154 Hz); −23.9 (d, 1 B, J = 158 Hz); −25.3 (d, 1 B, J = 180 Hz); −33.2 (dd, 1 B, J_1 = 126 Hz, J_2 = 57 Hz); −39.5 (d, 1 B, J = 140 Hz). MS (EI), found m/z 206 $[M]^+$; $C_6H_{21}B_9O$; calculated for $C_6H_{21}B_9O$: $[M]^+$ = 206.

Compound 3b. ^1H NMR ($CDCl_3$), δ: 4.49 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7 Hz); 4.48 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7 Hz);1.88 (br.s, 1 H, CH_{carb}); 1.73 (br.s, 1 H, CH_{carb}); 1.47 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); −2.37 (br.s, 1 H, BHB_{bridge}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 78.0 ($O\underline{C}H_2CH_3$), 40.8 (C_{carb}), 32.5 (C_{carb}), 13.3 ($OCH_2\underline{C}H_3$). ^{11}B NMR ($CDCl_3$), δ: 8.8 (s, 1 B, B—O); −0.9 (s, 1 B, B—Cl); −13.7 (d, 2 B, J = 144 Hz); −19.6 (d, 2 B, J = 157 Hz); −25.3 (d, 1 B, J = 138 Hz); −29.4 (d, 1 B, J = 156 Hz); −33.8 (dd, 1 B, J_1 = 130 Hz, J_2 = 47 Hz); −39.9 (d, 1 B, J = 143 Hz).

Compound 4. ^1H NMR ($CDCl_3$), δ: 4.50 (q, 4 H, $OC\underline{H}_2CH_3$, J = 7 Hz); 2.00 (br.s, 2 H, CH_{carb}); 1.54 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); 0.03 (br.s, 1 H, BHB_{bridge}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 79.9 ($O\underline{C}H_2CH_3$), 42.9 (C_{carb}), 12.9 ($OCH_2\underline{C}H_3$). ^{11}B NMR ($CDCl_3$), δ: −10.1 (s, 1 B); −12.6 (d, 2 B, J = 139 Hz); −16.6 (d, 2 B, J = 137 Hz); −21.7 (d, 2 B, J = 146 Hz); −22.1 (d, 1 B); −39.5 (d, 1 B, J = 138 Hz). MS (EI), found m/z 206 $[M]^+$; $C_6H_{21}B_9O$; calculated for $C_6H_{21}B_9O$: $[M]^+$ = 206.

Tetramethylammonium 9-ethoxyundecadecahydro-7,8-dicarba-*nido*-undecaborate (5). A solution of compound **3** (0.18 g, 0.9 mmol) in pyridine (25 mL) was refluxed for 24 h, the progress of dealkylation reaction was monitored by thin layer chromatography. The reaction mixture was concentrated on a rotary evaporator, the residue was subjected to column chromatography (eluent dichloromethane—acetone, 1 : 1). The first fraction contained unreacted starting compound **3**, the second fraction was concentrated on a rotary evaporator, the residue was dissolved in water (10 mL), the product was precipitated with a solution of Me_4NCl (0.12 g, 1.3 mmol) in water (5 mL). The preci-

pitate was collected by filtration, washed, and dried over P_2O_5 to obtain compound **5** (0.12 g, 54%). ^{1}H NMR (CD_3COCD_3), δ: 3.45 (m, 2 H, OC$\underline{H}_2$CH$_3$); 3.39 (s, 12 H, $(CH_3)_4N$); 1.53 (br.s, 1 H, CH_{carb}); 1.34 (br.s, 1 H, CH_{carb}); 0.99 (t, 3 H, OCH$_2$C$\underline{H}_3$, J = 7 Hz); −2.91 (br.s, 1 H, BHB_{bridge}). ^{13}C{^{1}H} NMR (CD_3COCD_3), δ: 63.7 (O$\underline{C}$H$_2$CH$_3$), 55.9 ($(CH_3)_4N$), 40.6 (C_{carb}), 26.7 (C_{carb}), 18.0 (OCH$_2\underline{C}$H$_3$). ^{11}B NMR (CD_3COCD_3), δ: 10.5 (s, 1 B); −12.3 (d, 1 B, J = 135 Hz); −16.2 (d, 1 B, J = 135 Hz); −19.7 (d, 1 B, J = 162 Hz); −21.6 (d, 1 B, J = 152 Hz); −25.5 (d, 2 B, J = 137 Hz); −31.0 (d, 1 B, J = 122 Hz); −38.6 (d, 1 B, J = 136 Hz). HRMS (ESI), found m/z 178.2076 [M]$^+$; $C_4H_{16}B_9O$; calculated for $C_4H_{16}B_9O$: [M]$^+$ = 178.2084.

Tetramethylammonium 10-ethoxyundecadecahydro-7,8-dicarba-*nido*-undecaborate (6). The synthesis was carried out similarly to the procedure described above using compound **4** (0.23 g, 1.1 mmol) and Me_4NCl (0.16 g, 1.7 mmol). The yield of compound **6** was 0.14 g (50%). ^{1}H NMR (CD_3COCD_3), δ: 3.47 (m, 2 H, OC$\underline{H}_2$CH$_3$); 3.41 (s, 12 H, $(CH_3)_4N$); 1.44 (br.s, 2 H, CH_{carb}); 1.01 (t, 3 H, OCH$_2$C$\underline{H}_3$, J = 7 Hz); −0.55 (br.s, 1 H, BHB_{bridge}). ^{13}C{^{1}H} NMR (CD_3COCD_3), δ: 65.6 (O$\underline{C}$H$_2$CH$_3$); 56.0 (($\underline{C}$H$_3$)$_4$N); 38.7 (C_{carb}); 17.9 (OCH$_2\underline{C}$H$_3$). ^{11}B NMR (CD_3COCD_3), δ: −9.3 (s, 1 B); −12.4 (d, 2 B, J = 135 Hz); −17.4 (d, 2 B, J = 129 Hz); −24.1 (d, 2 B, J = 151 Hz); −25.4 (d, 1 B, J = 171 Hz); −40.6 (d, 1 B, J = 138 Hz). HRMS (ESI), found m/z 178.2076 [M]$^+$; $C_4H_{16}B_9O$; calculated for $C_4H_{16}B_9O$: [M]$^+$ = 178.2084.

Trimethylammonium 3-phenylundecadecahydro-7,8-dicarba-*nido*-undecaborate (7). Sodium hydroxide (0.86 g, 21.5 mmol) was added to a solution of compound **2** (1.51 g, 7.2 mmol) in ethanol (150 mL). The mixture was refluxed for 16 h, the reaction progress was monitored by thin layer chromatography. Then, the reaction mixture was neutralized with aqueous HCl to neutral pH, filtered, and concentrated on a rotary evaporator. The residue was dissolved in water (40 mL), the product was precipitated with a solution of Me_3NHCl (1.05 g, 11.0 mmol) in water (10 mL). The resulting oily layer was extracted with dichloromethane (50 mL). The organic fraction was separated, dried with Na_2SO_4, filtered, and concentrated on a rotary evaporator to obtain compound **7** (1.67 g, 86%). ^{1}H NMR (CD_3COCD_3), δ: 7.50 (d, 2 H, H_{arom}, J = 4 Hz); 7.11 (m, 3 H, H_{arom}); 3.11 (s, 9 H, $(CH_3)_3N$); 1.88 (br.s, 2 H, CH_{carb}); −2.53 (br.s, 1 H, BHB_{bridge}). ^{11}B NMR ($CDCl_3$), δ: −9.9 (s, 1 B); −10.6 (d, 2 B, J = 147 Hz); −16.2 (d, 2 B, J = 138 Hz); −21.5 (d, 2 B, J = 145 Hz); −35.0 (d, 1 B, J = 136 Hz); −36.5 (d, 1 B, J = 149 Hz).

Tetramethylammonium 6,6′-diphenyleicosahydro-1,1′,2,2′-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (Me_4N[8]). Compound **5** (1.16 g, 4.3 mmol) was added to a freshly prepared hot 40% solution of NaOH (25 mL) in water, the mixture was stirred until the salt was completely dissolved and evolution of Me_3N ceased. Next, $CoCl_2 \cdot 6H_2O$ (2.38 g, 10.0 mmol) was added to the mixture and it was stirred for 4 h. After the addition of (100 mL), the organic phase was separated, the aqueous fraction was extracted with diethyl ether (4×50 mL). The combined organic fractions were dried with Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue was dissolved in water (50 mL) and a solution of Me_4NBr (1.54 g, 10.0 mmol) in water (10 mL) was added. The precipitate was collected by filtration, washed with water, and dried over P_2O_5 to obtain compound **8** (0.80 g, 68%) as an orange powder. ^{1}H NMR (CD_3COCD_3), δ: 7.65 (m, 4 H, H_{arom}); 7.25 (m, 6 H, H_{arom}); 4.28 (br.s, 4 H, CH_{carb}); 3.44 (s, 12 H, $(CH_3)_4N^+$); 4.0—1.0 (m, 16 H, BH). ^{13}C{^{1}H} NMR (CD_3COCD_3), δ: 133.2 (C_{arom}), 127.6 (C_{arom}), 127.3 (C_{arom}), 55.1 (($CH_3)_4N^+$); 53.7 (C_{carb}). ^{11}B NMR (CD_3COCD_3), δ: 4.8 (d, 2 B, J = 148 Hz); 2.1 (d, 2 B, J = 134 Hz); −5.6 (d, 8 B, J = 139 Hz); −14.1 (s, 2 B), −16.4 (d, 4 B, J = 151 Hz).

Potassium 6,6′-diphenyleicosahydro-1,1′,2,2′-tetracarba-3-*commo*-nickela-*closo*-tricosaborate (9). Potassium *tert*-butoxide (0.90 g, 8.0 mmol) was added to a solution of compound **5** (0.27 g, 1.0 mmol) in THF (50 mL) and the mixture was refluxed for 3 h. After the addition of $Ni_3(acac)_6$ (0.39 g, 1.5 mmol), the reflux was continued for another 14 h, monitoring the reaction progress by thin layer chromatography. Then the reaction mixture was concentrated on a rotary evaporator. The residue was dissolved in water (50 mL), the product was extracted with dichloromethane (3×50 mL). The organic fractions were separated, combined, dried with Na_2SO_4, filtered, and concentrated on a rotary evaporator to obtain compound **9** (0.19 g, 74%). ^{11}B NMR (CD_3COCD_3), δ: 15.0, 2.3, −53.3.

6,6′-Diphenyl-1,1′,2,2′-tetracarba-3-*commo*-nickela-*closo*-tricosaborane (10). A solution of $FeCl_3$ (0.18 g, 1.1 mmol) in acetonitrile (10 mL) was added dropwise to a solution of compound **8** (0.19 g, 0.4 mmol) in acetonitrile (50 mL) and the mixture was stirred for 24 h, monitoring the reaction progress by thin layer chromatography. Then, the reaction mixture was concentrated on a rotary evaporator. The residue was subjected to column chromatography (eluent dichloromethane). The first fraction was collected and concentrated on a rotary evaporator to obtain compound **10** (0.16 g, 91%). ^{1}H NMR ($CDCl_3$), δ: 7.62 (d, 4 H, *o*-H_{arom}, J = 7.1 Hz); 7.44 (t, 2 H, *p*-H_{arom}, J = 7.3 Hz); 7.37 (dd, 4 H, *m*-H_{arom}, J_1 = 7.1 Hz, J_1 = 7.3 Hz); 4.47 (br.s, 4 H, CH_{carb}). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 133.7 (C_{arom}), 130.4 (*p*-C_{arom}), 128.5 (C_{arom}), 67.3 (C_{carb}). ^{11}B NMR ($CDCl_3$), δ: 20.8 (d, 2 B, J = 181 Hz); 18.9 (d, 2 B, J = 170 Hz); 4.9 (d, 4 B, J = 140 Hz); 1.9 (d, 4 B, J = 128 Hz); −7.1 (d + s, 6 B). HRMS (ESI), found: m/z 475.3506 [M]$^-$; $C_{16}H_{30}B_{18}Ni$; calculated for $C_{16}H_{30}B_{18}Ni$: [M]$^-$ = 475.3522.

X-ray diffraction analysis of compounds 4 and Me_4N[8] was carried out on an APEX II CCD diffractometer (λ(Mo-$K\alpha$) = = 0.71073 Å, graphite monochromator, ω-scan technique) at 120 K. Single crystals of **4** and **8** suitable for X-ray diffraction experiment were obtained by crystallization from hexane—dichloromethane and hexane—dichloromethane—acetone solvent mixtures, respectively. The processing of the initial arrays of measured intensities was carried out using the SAINT and SADABS programs incorporated into the APEX2 software package.[49] The structures were solved by the direct method and refined by the full-matrix least squares method in anisotropic approximation for non-hydrogen atoms with respect to F^2_{hkl}. All the calculations were carried out using the SHELXTL and OLEX2 software packages.[50,51] The main crystallographic parameters are given in Table 1. Both structures are registered in the the Cambridge Crystallographic Data Center (CCDC 1873049 for **4** and 1903011 for Me_4N[**8**]).

Quantum chemical calculations. The molecule **4** was optimized in the PBE0/6-311G(df,pd) approximation, using the GAUSSIAN program.[52] The reliability of this approximation for modeling the structure of a wide range of organic and organoelement compounds has been demonstrated in a number of papers.[53—56] The electron density distribution obtained in the calculations was analyzed in the framework of the R. Bader "Atoms in Molecules" theory,[57] using the AIMALL program.[58] The energy of contacts was evaluated by its correlation with the potential energy density function $V(r)$ at the bond critical point ($E_{int} = 1/2V(r)$),[59,60] which is widely used for studies of various types of interactions.[61—65]

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Table 1. Crystallographic data and parameters of X-ray diffraction experiment for compound **4** and Me_4N[**8**]

Parameter	**4**	Me_4N[**8**]
Molecular formula	$C_6H_{21}B_9O$	$C_{16}H_{30}B_{18}Co^- \cdot C_4H_{12}N^+$
Molecular weight	206.52	550.05
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a/Å	13.544(3)	10.2489(11)
b/Å	13.339(3)	10.7454(11)
c/Å	13.996(3)	14.3906(15)
α/deg	90	89.435(2)
β/deg	90	72.390(2)
γ/deg	90	77.605(2)
V/Å^3	2528.5(10)	1472.8(3)
Z	8	2
d_{calc}/g cm^{-3}	1.085	1.240
Absorption coefficient, μ/mm^{-1}	0.055	0.598
F(000)	880	s572
θ range of scanning/deg	2.59—27.00	1.49—29.01
Number of reflections		
measured	19328	35781
independent	2759	7821
R_{int}	0.0477	0.0257
Completeness of reflection array (%)	100	99.8
Number of refined parameters	191	448
Number of reflections with $I \geq 2\sigma(I)$	2183	6953
GOOF	1.031	1.088
Convergence ($R_1(F)$)[a] for reflections with $I \geq 2\sigma(I)$	0.0504	0.0305
Convergence for all reflections ($wR_2(F^2)$)[b]	0.1472	0.0791
Residual electron density (ρ_{max}/ ρ_{min})/e Å^{-3}	0.406/−0.216	0.400/−0.296

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

and 18-33-20115). X-ray diffraction data and NMR spectra were obtained using equipment of the X-Ray Structural Center of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

References

1. R. N. Grimes, *Carboranes*, 3d ed., Elsevier, Amsterdam, 2016.
2. I. B. Sivaev, M. Yu. Stogniy, *Russ. Chem. Bull.*, 2019, **68**, 217.
3. J. S. Andrews, J. Zayas, M. Jones, *Inorg. Chem.*, 1985, **24**, 3715.
4. R. D. Kennedy, D. J. Clingerman, W. Morris, C. E. Wilmer, A. A. Sarjeant, C. L. Stern, M. O´Keeffe, R. Q. Snurr, J. T. Hupp, O. K. Farha, C. A. Mirkin, *Cryst. Growth Des.*, 2014, **14**, 1324.
5. A. M. Spokoyny, T. C. Li, O. K. Farha, C. W. Machan, C. She, C. L. Stern, T. J. Marks, J. T. Hupp, C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2010, **49**, 5339.
6. M. F. Hawthorne, B. M. Ramachandran, R. D. Kennedy, C. B. Knobler, *Pure Appl. Chem.*, 2006, **78**, 1299.
7. N.-N. Ma, S.-J. Li, L.-K. Yan, Y.-Q. Qiu, Z.-M. Su, *Dalton Trans.*, 2014, **43**, 5069.
8. I. B. Sivaev, *Russ. Chem. Bull.*, 2018, **67**, 1117.
9. I. Rojo, F. Teixidor, C. Viñas, R. Kivekäs, R. Sillanpää, *Chem. Eur. J.*, 2003, **9**, 4311.
10. I. P. Beletskaya, V. I. Bregadze, V. A. Ivushkin, P. V. Petrovskii, I. B. Sivaev, S. Sjöberg, G. G. Zhigareva, *J. Organomet. Chem.*, 2004, **689**, 2920.
11. V. I. Bregadze, I. D. Kosenko, I. A. Lobanova, Z. A. Starikova, I. A. Godovikov, I. B. Sivaev, *Organometallics*, 2010, **29**, 5366.
12. I. D. Kosenko, I. A. Lobanova, I. A. Godovikov, Z. A. Starikova, I. B. Sivaev, V. I. Bregadze, *J. Organomet. Chem.*, 2012, **721**, 70.
13. S. A. Anufriev, I. B. Sivaev, V. I. Bregadze, *Russ. Chem. Bull.*, 2015, **64**, 712.
14. M. F. Hawthorne, P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 896.
15. C. Viñas, G. Barbera, J. M. Oliva, F. Teixidor, A. J. Welch, G. M. Rosair, *Inorg. Chem.*, 2001, **40**, 6555.
16. D. Zhao, Z. Xie, *Chem. Sci.*, 2016, **7**, 5635.
17. I. B. Sivaev, V. I. Bregadze, *Coord. Chem. Rev.*, 2014, 270—271, 75.
18. D. C. Young, D. V. Howe, M. F. Hawthorne, *J. Am. Chem. Soc.*, 1969, **91**, 859.
19. J. Plešek, T. Jelinek, F. Mareš, S. Heřmanek, *Collect. Czech. Chem. Commun.*, 1993, **58**, 1534.
20. T. Peymann, E. Lork, D. Gabel, *Inorg. Chem.*, 1996, **35**, 1355.
21. I. B. Sivaev, N. Yu. Kulikova, E. A. Nizhnik, M. V. Vichuzhanin, Z. A. Starikova, A. A. Semioshkin, V. I. Bregadze, *J. Organomet. Chem.*, 2008, **693**, 519.

22. A. Semioshkin, V. Bregadze, I. Godovikov, A. Ilinova, J. Laskova, Z. Starikova, *J. Organomet. Chem.*, 2011, **696**, 2760.
23. R. Bernard, D. Cornu, M. Perrin, J.-P. Scharff, P. Miele, *J. Organomet. Chem.*, 2004, **689**, 2581.
24. K. Yu. Zhizhin, V. N. Mustyatsa, E. A. Malinina, N. A. Votinova, E. Yu. Matveev, L. V. Goeva, I. N. Polyakova, N. T. Kuznetsov, *Russ. J. Inorg. Chem.*, 2004, **49**, 180.
25. I. N. Klyukin, A. S. Kubasov, I. P. Limarev, A. P. Zhdanov, E. Yu. Matveev, I. N. Polyakova, R. Yu. Zhizhin, N. T. Kuznetsov, *Polyhedron*, 2015, **101**, 215.
26. J. Plešek, S. Heřmanek, A. Franken, I. Cisařova, C. Nachtigal, *Collect. Czech. Chem. Commun.*, 1997, **62**, 47.
27. J. Plešek, B. Grüner, J. Machaček, I. Cisařova, J. Časlavsky, *J. Organomet. Chem.*, 2007, **692**, 4801.
28. P. Ma, T. M. Smith, J. Zubieta, J. T. Spencer, *Inorg. Chem. Commun.*, 2014, **46**, 223.
29. P. Ma, T. M. Smith-Pellizzeri, J. Zubieta, J. T. Spencer, *J. Chem. Cryst.*, 2019; DOI: 10.1007/s10870-018-0749-8.
30. I. V. Glukhov, K. A. Lyssenko, A. A. Korlyukov, M. Yu. Antipin, *Russ. Chem. Bull.*, 2005, **54**, 547.
31. I. V. Glukhov, M. Yu. Antipin, K. A. Lyssenko, *Eur. J. Inorg. Chem.*, 2004, 1379.
32. M. Yu. Antipin, K. A. Lyssenko, V. N. Lebedev, *Inorg. Chem.*, 1998, **37**, 5834.
33. S. V. Timofeev, O. B. Zhidkova, I. B. Sivaev, Z. A. Starikova, K. Yu. Suponitsky, H. Yan, V. I. Bregadze, *J. Organomet. Chem.*, 2018, **867**, 342.
34. I. B. Sivaev, A. V. Prikaznov, S. A. Anufriev, *J. Organomet. Chem.*, 2013, **747**, 254.
35. A. A. Semioshkin, I. B. Sivaev, V. I. Bregadze, *Dalton Trans.*, 2008, 977.
36. I. B. Sivaev, V. I. Bregadze, in *Boron Science: New Technologies and Applications*, Ed. N. S. Hosmane, CRC Press, Boca Raton, 2011, p. 623.
37. A. V. Shmal´ko, Ph. D. Thesis (Chem.), Mendeleev University of Chemical Technology of Russia, Moscow, 2016, 138 pp. (in Russian).
38. I. N. Klyukin, V. V. Voinova, N. A. Selivanov, A. P. Zhdanov, K. Yu. Zhizhin, N. T. Kuznetsov, *Russ. J. Inorg. Chem.*, 2018, **63**, 1546.
39. I. B. Sivaev, A. A. Semioshkin, B. Brellochs, S. Sjöberg, V. I. Bregadze, *Polyhedron*, 2000, **19**, 627.
40. D. F. Mullica, E. L. Sappenfield, F. G. A. Stone, S. F. Woolam, *Organometallics*, 1994, **13**, 157.
41. S. Du, A. Franken, P. A. Jellis, J. A. Kautz, F. G. A. Stone, P.-Y. Yu, *J. Chem. Soc., Dalton Trans.*, 2001, 1846.
42. P. T. Brain, J. Cowie, D. J. Donohoe, D. Hnyk, D. W. H. Rankin, D. Reed, B. D. Red, H. E. Robertson, A. J. Welch, M. Hofmann, P. Schleyer, *Inorg. Chem.*, 1996, **35**, 1701.
43. R. L. Thomas, G. M. Rosiar, A. J. Welch, *Acta Cryst.*, 1996, **C52**, 1024.
44. C. B. Aakeröy, J. Desper, M. Fasulo, I. Hussain, B. Levin, N. Schultheiss, *CrystEngComm*, 2008, **10**, 1816.
45. A. B. Sheremetev, N. V. Palysaeva, M. I. Struchkova, K. Yu. Suponitsky, M. Yu. Antipin. *Eur. J. Org. Chem.*, 2012, 2266.
46. A. B. Sheremetev, V. L. Korolev, A. A. Potemkin, N. S. Aleksandrova, N. V. Palysaeva, T. H. Hoang, V. P. Sinditskii, K. Yu. Suponitsky, *Asian J. Org. Chem.*, 2016, **5**, 1388.
47. I. L. Dalinger, O. V. Serushkina, N. V. Muravyev, D. B. Meerov, E. A. Miroshnichenko, T. S. Kon´kova, K. Yu. Suponitsky, M. V. Vener, A. B. Sheremetev, *J. Mater. Chem. A*, 2018, **6**, 18669.
48. M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862.
49. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339.
50. APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, 2013.
51. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
52. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc.: Wallingford, 2004.
53. M. G. Medvedev, I. S. Bushmarinov, J. W. Sun, J. P. Perdew, K. A. Lyssenko, *Science*, 2017, **355**, 49.
54. K. Yu. Suponitsky, N. I. Burakov, A. L. Kanibolotsky, V. A. Mikhailov, *J. Phys. Chem. A*, 2016, **120**, 4179.
55. S. A. Anufriev, I. B. Sivaev, K. Yu. Suponitsky, I. A. Godovikov, V. I. Bregadze, *Eur. J. Inorg. Chem.*, 2017, 4436.
56. S. A. Erokhina, M. Yu. Stogniy, K. Yu. Suponitsky, I. D. Kosenko, I. B. Sivaev, V. I. Bregadze, *Polyhedron*, 2018, **153**, 145.
57. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990.
58. T. A. Keith, AIMAll, Version 14.11.23. TK Gristmill Software, Overland Park, 2014 (http://aim.tkgristmill.com).
59. E. Espinosa, I. Alkorta, I. Rozas, J. Elguero, E. Molins, *Chem. Phys. Lett.*, 2001, **336**, 457.
60. E. Espinosa, E. Molins, C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170.
61. A. B. Sheremetev, N. S. Aleksandrova, K. Yu. Suponitsky, M. Yu. Antipin, V. A. Tartakovsky, *Mendeleev. Commun.*, 2010, **20**, 249.
62. K. Y. Suponitsky, K. A. Lyssenko, I. V. Ananyev, A. M. Kozeev, A. B. Sheremetev, *Cryst. Growth Des.*, 2014, **14**, 4439.
63. S. A. Anufriev, I. B. Sivaev, K. Yu. Suponitsky, V. I. Bregadze, *J. Organomet. Chem.*, 2017, **849—850**, 315.
64. A. O. Dmitrienko, V. A. Karnoukhova, A. A. Potemkin, M. I. Struchkova, I. A. Kryazhevskikh, K. Yu. Suponitsky, *Chem. Heterocycl. Compd.*, 2017, **53**, 532.
65. I. L. Dalinger, K. Yu. Suponitsky, T. K. Shkineva, D. B. Lempert, A. B. Sheremetev, *J. Mater. Chem. A*, 2018, **6**, 14780.

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