Synthesis, structure, and reactivity of *C*-isopropyl-*ortho*-carborane organoboron derivatives*

S. V. Svidlov,[a,b] Ya. Z. Voloshin,[b] N. S. Yurgina,[a] T. V. Potapova,[a] A. Yu. Belyy,[c] I. V. Ananyev,[b] and Yu. N. Bubnov[a,b]*

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation*
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5085. E-mail: voloshin@ineos.ac.ru*
[c]*Higher Chemical College of the Russian Academy of Sciences, 9 Miusskaya pl., 125047 Moscow, Russian Federation*

A reaction of isopropyl-*ortho*-carborane with *n*-butyllithium, followed by treatment of the lithium derivative formed with boron trichloride, chlorodimethoxyborane, or chloropinacolatoborane furnished *C*-boryl-*ortho*-carboranes **1a**—**c**. Further functionalization of 1-Cl_2B-2-Pr^i-1,2-$C_2B_{10}H_{10}$ (**1a**) with pentafluorophenylmagnesium bromide or pentafluorophenol led to 1-$(C_6F_5)_2$B-2-Pr^i-1,2-$C_2B_{10}H_{10}$ (**2**) and (1-(C_6F_5O)B-2-Pr^i-1,2-$C_2B_{10}H_{10})_2O$ (**3**), respectively. A reaction of 1-$(MeO)_2$B-2-Pr^i-1,2-$C_2B_{10}H_{10}$ (**1b**) with the complexes of BH_3 with THF and dimethyl sulfide gave rise to carboranylborane adducts **4a**,**b**. The use of the complex of 1-H_2B-2-Pr^i-1,2-$C_2B_{10}H_{10}$ with dimethyl sulfide **4b** as a hydroboration agent in the reactions with hex-1-ene and phenylacetylene allowed us to obtain dialkyl- and di(phenylolefin)-containing *C*-isopropyl-*ortho*-carboranylboranes, respectively. The reaction of *C*-isopropyl-*ortho*-carboranyldimethoxyborane with triallylborane led to the substitution of only one of two MeO groups with the allyl one, which is explained by the steric effects of bulky carboranyl substituent in the precursor. Compounds obtained are characterized by X-ray diffraction analysis.

Key words: carboranes, carboranylboranes, perfluoroarylboranes, hydroboration.

Derivatives of icosahedral carborane $C_2B_{10}H_{12}$ are of undoubted interest for modern materials science, energetics, organic catalysis, and medicine, which is explained by their unusual chemical properties and cage-like nature.[1,2] A large amount of boron atoms in their molecules makes this type of compounds promising agents for boron neutron capture therapy of cancer.[3] Besides, a unique reactivity of organoboron compounds allows one to use them as a powerful synthetic instrument in various fields of organic, organoelement, and pharmaceutical chemistry. At the same time, the chemistry of boron derivatives with carboranyl substituents $RCB_{10}H_{10}C—BX_2$ is not yet fully developed: only several methods for the synthesis of this class of compounds are elaborated; by now, molecular and crystal structures are determined only for a limited number of compounds of a similar type.[4] It was found, that the reactivity of *C*-boron-substituted carboranes has a specific feature to readily cleave the *exo*-B—C_{core} bond in their molecules.

The purpose of the present work is the development of synthetic strategy for the preparation of *C*-isopropyl-*ortho*-carborane derivatives, the establishment of their structure (including involvement of X-ray diffraction analysis), as well as the studies of reactivity of these compounds.

Results and Discussion

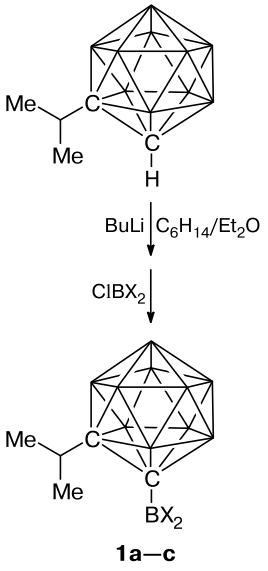
Carboranylboranes can be obtained by two principal methods: (1) the B—C bond formation *via* the reaction of haloboranes with carborane lithium derivatives and (2) interconversions of *C*-borylcarboranes[5] (thermal transformations, nucleophilic substitution, *etc*). *C*-Boryl-*ortho*-carboranes **1a**—**c** were synthesized by the first of these methods, namely, by lithiation[6,7] of isopropyl-*ortho*-carborane with butyllithium in diethyl ether with subsequent treatment of the lithium derivative formed with the corresponding chloroboranes (Scheme 1).

Dichloroborane **1a** was further functionalized using pentafluorophenylmagnesium bromide C_6F_5MgBr and pentafluorophenol C_6F_5OH as nucleophiles. The interest to such perfluorophenyl-substituted boranes is caused by the fact that this type of compounds (with two or three

* Dedicated to the 60th anniversary of A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2343—2350, October, 2014.
1066-5285/14/6310-2343

Scheme 1

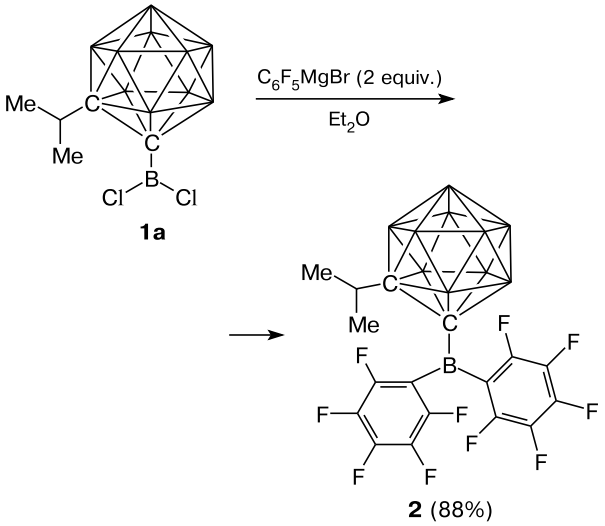


1a—c

X = Cl (**a**), MeO (**b**), chloropinacolatoborane (**c**)

perfluorophenyl groups) are capable of reversible binding molecular hydrogen in the presence of sterically hindered Lewis bases.[8] At the same time, carborane perfluorophenylboryl derivatives are not yet described in the literature. The reaction of dichlorocarboranylborane **1a** with two equivalents of C_6F_5MgBr in diethyl ether led to di(perfluorophenyl)boryl derivative **2** (Scheme 2). The $^{11}B\{^1H\}$ NMR spectrum of this compound exhibits signals for four boron atoms of the cluster fragment at δ −10.7, −6.3, −3.2, and 3.0 and a signal for the boron atom of the di(perfluorophenyl)boryl fragment at δ 73.4.

Scheme 2

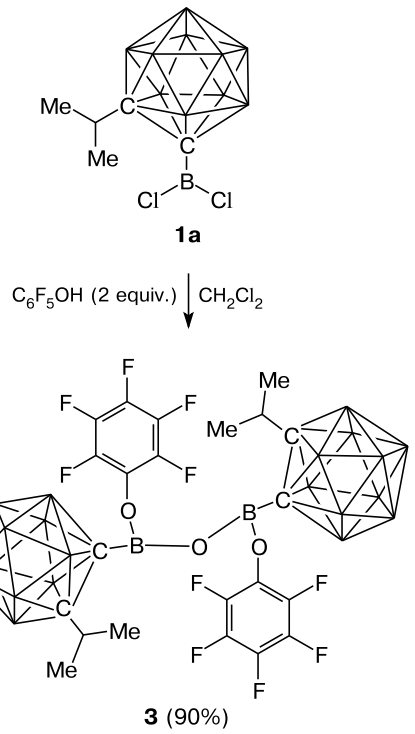


1a

2 (88%)

The use of pentafluorophenol as a nucleophile in the reaction with dichloroborane **1a** led to oxide **3** (Scheme 3), the mechanism of the formation of which, apparently, is similar to that described earlier for the reaction of pentafluorophenol with PCl_5.[9] Molecular structure of compound **3** was established by X-ray analysis.

Scheme 3

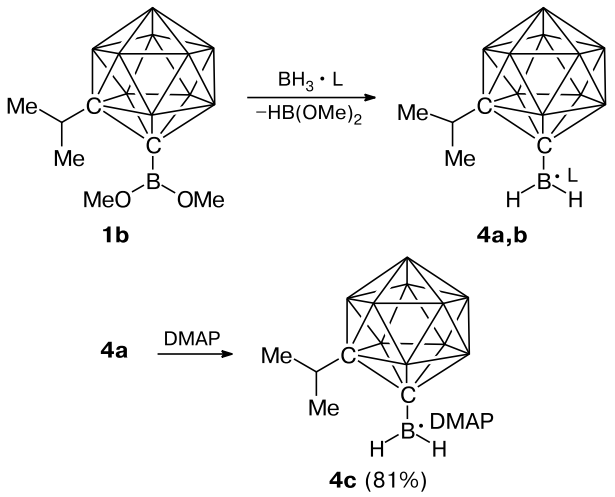


3 (90%)

The known[10] methods for the synthesis of carborane-containing boron hydrides are characterized by low or moderate yields (7—55%). We suggested and successfully used a new simple approach to the preparation of this type of compounds from methyl carboranylboronate. In particular, we found that the ester groups in (*C*-isopropyl-*ortho*-carboranyl)dimethoxyborane **1b** can be easily replaced with the hydrogen atom as a result of the reaction with derivatives of parent borane, *viz.*, the complexes of BH_3 with THF and dimethyl sulfide (Scheme 4). The reaction of borane **4a** with the equimolar amount of 4-(dimethylamino)pyridine (DMAP) in hexane gave crystals of complex **4c**, whose crystal and molecular structures were established by X-ray diffraction studies (see below).

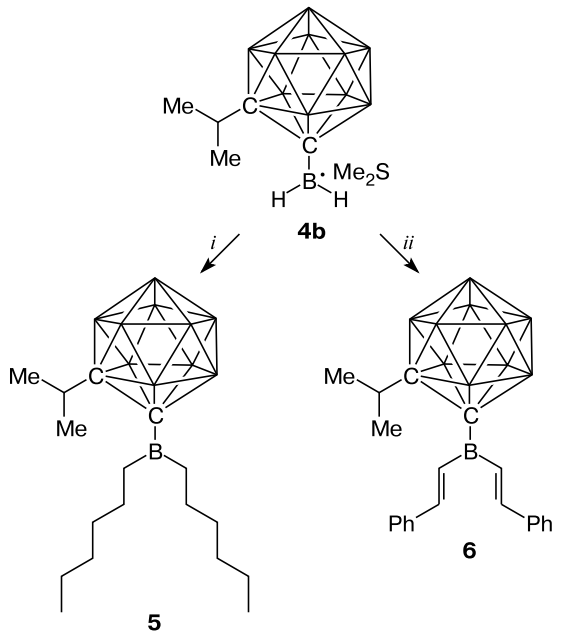
Hydroboration of hex-1-ene and phenylacetylene with the dimethyl sulfide complex of *C*-isopropyl-*ortho*-carboranylborane **4b** led to the formation of boranes **5** and **6**, respectively. The ^1H NMR spectra of the reaction mixture show that the addition proceeds regiospecifically (Scheme 5). Both hydroboration reactions are slow (48 and 72 h).

Scheme 4



L = THF (**a**), Me_2S (**b**)

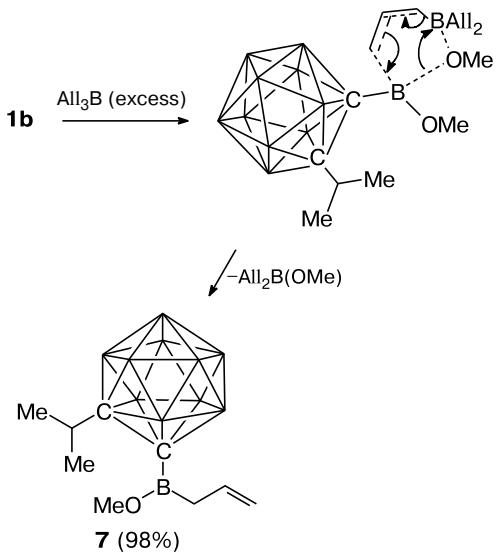
Scheme 5



i. Et_2O, hex-1-ene (2.1 equiv.); *ii*. Et_2O, Ph—≡ (2.1 equiv.).

Upon treatment of isopropyl-*ortho*-carboranyldimethoxyborane with excess of triallylborane, only one of two methoxy groups is replaced with the allyl one to give carboranylborane **7** (Scheme 6), whereas the second group remains in place even at 90 °C. This result can be explained by the steric effects of bulky carboranyl substituent, which in this case are more pronounced than in the reaction with borane complexes, since the mechanism of the methoxy-to-allyl group exchange assumes a six-membered transition state. Carrying out the reaction with excess of triallylborane at reduced pressure (200 Torr) and heating to 90 °C leads to trihomoallylboronate and a carborane-containing polymer. It is obvious that these products are formed by the radical mechanism involving molecular oxygen in trace amounts as a radical initiator.

Scheme 6



X-ray diffraction studies of *C*-isopropyl-*ortho*-carboranylboranes. The structures of obtained organoboron compounds **1a**, **1b**, **2**, **3**, and **4c** (Figs 1—5) were established by single crystal X-ray diffraction studies. Principal geometric parameters of the molecules are close to expected values and insignificantly depend on the nature of substituents in the boryl fragment (Table 1). In particular, in molecules **1a**, **1b**, **2**, and **3** with the trigonal surrounding of atom B(1), the B(1)—C(2) bond distance ranges within 1.579(2)—1.611(2) Å. At the same time, in the case of tetracoordinated boron atom in molecule **4c**, the B(13)—C(2)

Table 1. Selected geometric characteristics of molecules **1a**, **1b**, **2**, **3**, and **4c**

Characteristics	1a	1b	2	3	4c
C(1)—C(2)/Å	1.681(2)	1.676(2)	1.702(2)	1.6812(19)	1.6893(17)
C(2)—B(1)/Å	1.611(3)	1.605(2)	1.579(3)	1.589(2)	1.649(2)
B(1)—X[a]/Å	1.715	1.349	1.577	1.351	1.575
ϕ[b]/deg	93	104.7	27.9	116	90

[a] X is the atoms of a substituent at atom B(1) for all the structures except **4c**; an average value for two substituents is given, for structure **4c**, the B—N bond distance is given.

[b] The torsion angle C(1)—C(2)—B(1)—X, choosing the X so that the angle ϕ has a positive value.

bond distance is expectedly considerably longer (1.649(2) Å). In molecules **1a**, **1b**, and **3**, the plane, which is formed by substituents at the boron atom B(1), is orthogonal to the C(1)—C(2) bond in the carborane cage, whereas the corresponding dihedral angles change from 93 to 116°. Conversely, in molecule **2** this angle is considerably smaller (27.9°), that is apparently explained by the steric repulsion between the bulky pentafluorophenyl substituents and the isopropyl group. The change in the position of substituent BX_2C with respect to the C(1)—C(2) bond also leads to a slight change of this bond length. However, in contrast to *C*-arylcarboranes studied earlier,[11] the orthogonal arrangement makes this bond to be shorter (1.676(2)—1.689(2) Å) than in the case of the eclipsed conformation (1.702(2) Å). This demonstrates an exclusive influence of steric factors on the structural features of molecule **2**.

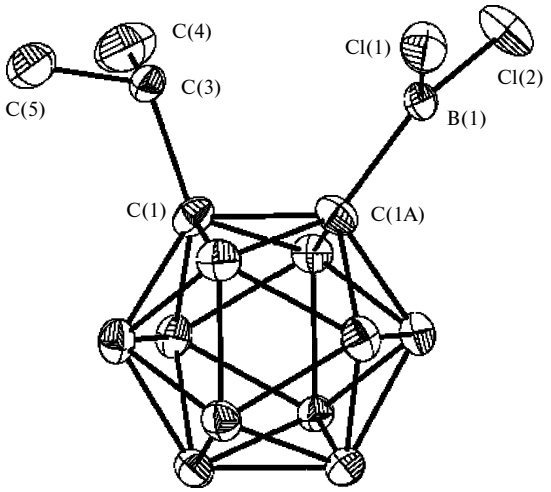


Fig. 1. General view of molecule **1a** in representation of nonhydrogen atoms with probability ellipsoids of atomic displacements (p = 50%). Hydrogen atoms are not shown.

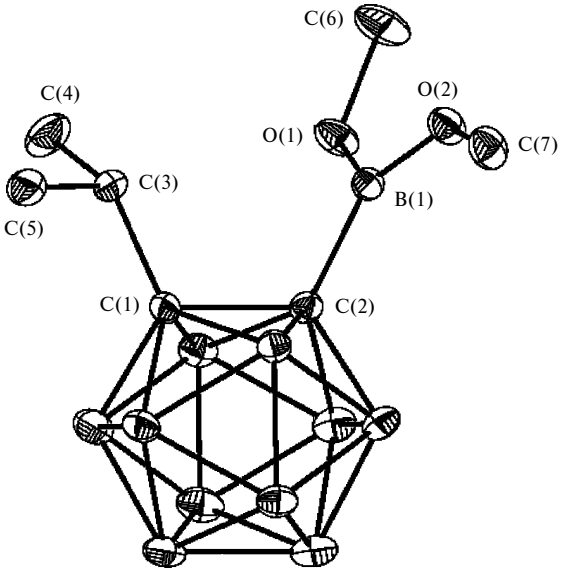


Fig. 2. General view of molecule **1b** in crystal in representation of nonhydrogen atoms with probability ellipsoids of atomic displacements (p = 50%). Hydrogen atoms are not shown.

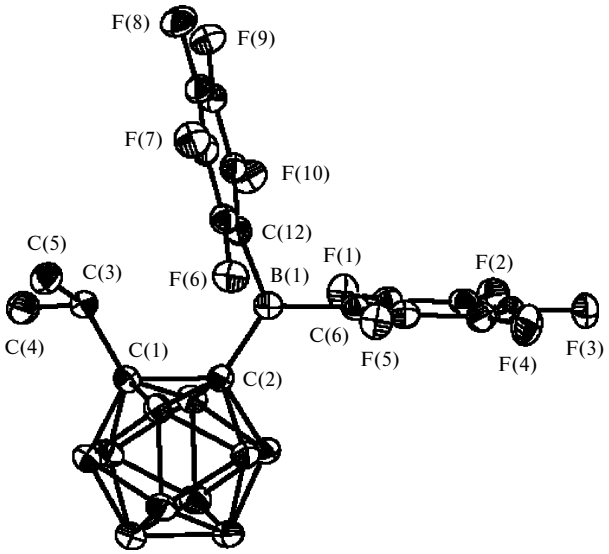


Fig. 3. General view of molecule **2** in representation of nonhydrogen atoms with probability ellipsoids of atomic displacements (p = 50%). Hydrogen atoms are not shown.

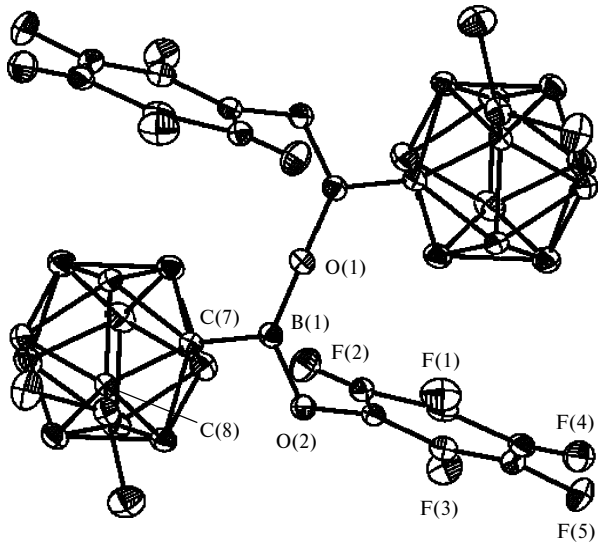


Fig. 4. General view of molecule **3** in representation of nonhydrogen atoms with probability ellipsoids of atomic displacements (p = 50%). Hydrogen atoms are not shown.

Analysis of crystal packings carried out using geometric criteria showed the absence of noticeable intermolecular interactions in all the crystals studied by X-ray diffraction analysis (see Figs 1—5), except compound **4c**. Its crystal is characterized by the stacking-interaction between the pyridine rings, combining molecules into the cen-

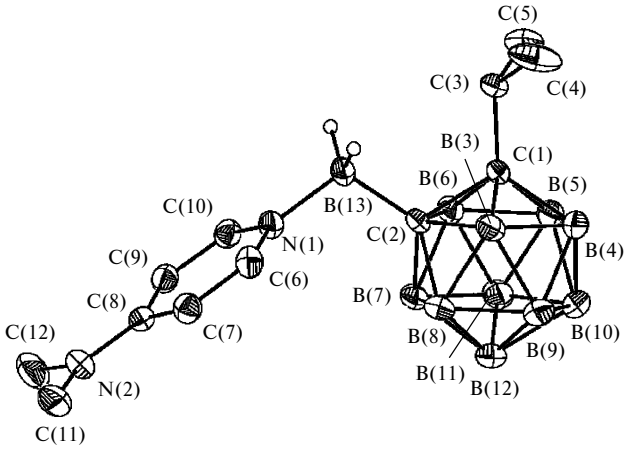


Fig. 5. General view of molecule **4c** in representation of non-hydrogen atoms with probability ellipsoids of atomic displacements ($p = 50\%$). Hydrogen atoms, except those at atom B(13), are not shown.

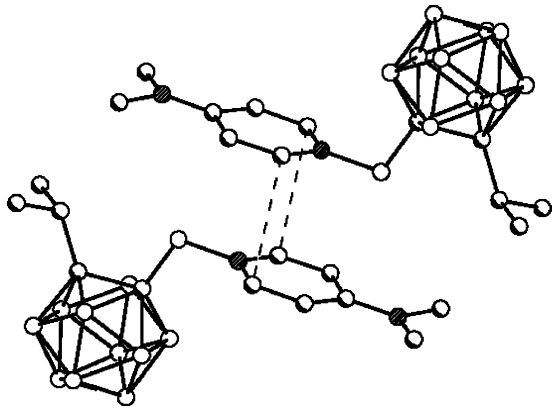


Fig. 6. Formation of centrosymmetric dimers due to the intermolecular stacking-interactions in crystal **4c**. Hydrogen atoms are not shown.

trosymmetric dimers (Fig. 6): the distance between the mean-square planes passing atoms N(1), C(6), C(7), C(8), C(9), and C(10) is ~3.51 Å and the aromatic rings are displaced with respect to each other by ~1.55 Å.

Experimental

Commercial 1.6 *M* solution of BuLi (in hexane), 1 *M* solution of BCl_3 (in hexane), C_6F_5Br, C_6F_5OH, $BH_3 \cdot SMe_2$, 4-(dimethylamino)pyridine, hex-1-ene, phenylacetylene (Aldrich) were used without additional purification. *C*-Isopropyl-*ortho*-carboranyldichloroborane (**1a**),[6] chlorodimethoxyborane,[12] chloropinacolatoborane,[13] C_6F_5MgBr,[14] $BH_3 \cdot THF$,[15] and triallylborane[16] were obtained according to the procedures published earlier.

Elemental analyses for carbon and hydrogen were performed on a Carlo Erba, model 1106 microanalyzer. ^1H, ^{11}B, and ^{13}C NMR spectra of solutions of compounds in $CDCl_3$ were recorded on a Bruker AC-200P spectrometer (200 MHz). IR spectra of solution of compounds in dichloromethane in the 400—4000 cm^{-1} region were obtained on a Bruker Alpha IR Fourier-transform spectrometer. Mass spectra were recorded on a Finnigan MAT DSQII instrument (EI, 70 eV).

All the manipulations were carried out under dry argon using thoroughly dried solvents.

1-Isopropyl-2-dimethoxyboryl-1,2-dicarba-*closo*-dodecaborane (1b). 1-Isopropyl-*ortho*-carborane (10.3 g, 0.055 mol) in diethyl ether (80 mL) was placed into a three-neck flask equipped with a dropping funnel, a thermometer, a magnetic stirrer, and a reflux condenser with an argon lock. The solution obtained was cooled to −78 °C, followed by dropwise addition of 1.6 *M* solution of butyllithium in hexane (29 mL, 0.055 mol) at such a rate that to maintain the temperature below −60 °C. After addition of BuLi, the reaction mixture was warmed-up to room temperature, stirred for 1 h, then cooled to −78 °C. A solution of chlorodimethoxyborane (6 g, 0.055 mol) in diethyl ether (10 mL) was added to the mixture at such a rate that to maintain the temperature below −65 °C. After addition of borane, the reaction mixture was warmed-up to room temperature and stirred for 10 h. A white precipitate of LiCl was filtered off, the filtrate was concentrated *in vacuo* of a water-jet pump. Fraction distillation of the oily residue (139—140 °C, 2 Torr) gave 1-isopropyl-2-dimethoxyboryl-1,2-dicarba-*closo*-dodecaborane (**1b**) (12.5 g, 92%). ^1H NMR, δ: 0.45—3.5 (br.m, 10 H, B—H); 1.29 (d, 6 H, Me, $J = 5.8$ Hz); 2.38 (m, 1 H, CH, $J = 5.8$ Hz); 3.46 (s, 6 H, OMe). $^{13}C\{^1H\}$ NMR, δ: 21.5 (s, Me); 35.2 (s, CH); 53.4 (s, OMe). $^{11}B\{^1H\}$ NMR, δ: −13.9 (br.s, B(3), B(6)); −10.7 (br.s, B(4), B(5), B(8), B(10)); −7.5 (br.s, B(7), B(11)); −3.3 (br.s, B(12)); −0.8 (br.s, B(9)); 22.8 (br.s, C—$B(OMe)_2$). Found (%): C, 32.50; H, 9.00. $C_7H_{23}B_{11}O_2$. Calculated (%): C, 32.57; H, 8.98. MS (EI, 70 eV), m/z (I_{rel} (%)): 259 $[M]^+$ (31), 185 $[M - B(OMe)_2]^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 2985, 2950 (C—H), 2580 (B—H), 1108 (B—O).

2-(1-Isopropyl-1,2-dicarba-*closo*-dodecaborane-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c). Chloropinacolatoborane (Pin) (8.1 g, 0.05 mol) was added dropwise to a solution of isopropyl-*o*-carboranyllithium (obtained according to the procedure for the synthesis of **1b**) (0.05 mol) in THF (50 mL) at −100 °C. The mixture was warmed-up to room temperature and allowed to stand for 10 h. The solvent was evaporated *in vacuo* (10 Torr), diethyl ether was added, a precipitate formed was filtered off. The filtrate was concentrated to dryness. Low-temperature crystallization from toluene gave compound **1c** as a colorless fine crystals (8.9 g, 58%). ^1H NMR, δ: 0.75—4.20 (br.m, 10 H, B—H); 1.17 (t, 3 H, Me (Pr^i), $J = 5.9$ Hz); 1.22 (s, 12 H, Me (Pin)); 2.34 (sept, 1 H, CH, $J = 5.9$ Hz). $^{13}C\{^1H\}$ NMR, δ: 14.4 (s, Me (Pr^i)); 24.1 (s, Me (Pin)); 31.4 (s, CH); 86.3 (s, C—O). $^{11}B\{^1H\}$ NMR, δ: −10.3 (br.s, B(3), B(4), B(5), B(6), B(8), B(10)); −8.1 (br.s, B(7), B(11)); −4.9 (br.s, B(12)), −0.9 (br.s, B(9)), 23.4 (br.s, C—BO_2). Found (%): C, 42.25; H, 9.42. $C_{11}H_{29}B_{11}O_2$. Calculated (%): C, 42.31; H, 9.36. MS (EI, 70 eV), m/z (I_{rel} (%)): 312 $[M]^+$ (40), 185 $[M - BPin]^+$(100). IR (CH_2Cl_2), ν/cm^{-1}: 2977, 2963 (C—H), 2572 (B—H), 1102 (B—O).

1-Isopropyl-2-dipentafluorophenylboryl-1,2-dicarba-*closo*-dodecaborane (2). Magnesium turnings (0.42 g, 0.0175 mol) in diethyl ether (50 mL) were placed into a three-neck flask equipped with a dropping funnel, a reflux condenser, and a magnetic stirrer. The mixture was activated with several drops of dibromoethane, followed by a dropwise addition of bromo-

pentafluorobenzene (2.2 mL, 0.0175 mol) with stirring. The reaction mixture was refluxed for 1 h. Pentafluorophenylmagnesium bromide obtained was added dropwise to a solution of isopropyldichloroboryl-*ortho*-carborane **1a** (2.3 g, 8.75 mmol) in benzene (30 mL). The solvent was evaporated from the reaction mixture *in vacuo* (10 Torr), pentane was added. A precipitate formed was filtered off and recrystallized from toluene, the yield was 4.1 g (88%). ^{1}H NMR, δ: 1.11 (d, 6 H, Me, J = 5.3 Hz); 2.12 (sept, 1 H, CH, J = 5.3 Hz). ^{13}C{^{1}H} NMR, δ: 22.7 (s, Me); 34.8 (s, CH). ^{11}B{^{1}H} NMR, δ: −10.7 (br.s, B(3), B(4), B(5), B(6), B(8), B(10)); −6.3 (br.s, B(7), B(11)); −3.2 (br.s, B(12)); 3.0 (br.s, B(9)); 73.4 (br.s, B(C_6F_5)$_2$). ^{19}F NMR, δ: −126.5 (m, *ortho*-F); −145.9 (m, *para*-F); −158.3 (m, *meta*-F). Found (%): C, 38.24; H, 3.18. $C_{17}H_{17}B_{11}F_{10}$. Calculated (%): C, 38.33; H, 3.22. MS (EI, 70 eV), m/z (I_{rel} (%)): 530 [M]$^+$ (37), 185 [M − B(C_6F_5)$_2$]$^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 2988, 2944, 2918 (C—H); 2610, 2569 (B—H).

Bis(*C*-isopropyl-*ortho*-carboranyl(pentafluorophenoxy)boryl)oxide (3). Isopropyl-*ortho*-carboranyldichloroborane **1a** (0.78 g, 2.9 mmol) was dissolved in dichloromethane (5 mL) in a flask equipped with a dropping funnel with an argon lock and a magnetic stirrer, followed by a dropwise addition of a solution of pentafluorophenol (1.07 g, 5.8 mmol) in dichloromethane (5 mL) with stirring. Volatile components were evaporated *in vacuo* (10 Torr). Hexane (2 mL) was added to the dark brown oil obtained. A light yellow precipitate was filtered off and the product was recrystallized from hexane. The yield was 1.02 g (90%). ^{1}H NMR, δ: 1.30 (d, 6 H, Me, J = 5.5 Hz); 2.50 (sept, 1 H, CH, J = 5.5 Hz). ^{13}C{^{1}H} NMR, δ: 24.4 (s, Me); 35.6 (s, CH). ^{11}B{^{1}H} NMR, δ: −11.3 (br.s, B(3), B(4), B(5), B(6), B(8), B(10)); −7.8 (br.s, B(7), B(11)); −4.0 (br.s, B(12)); 0.5 (br.s, B(9)); 23.1 (br.s, B—O). ^{19}F NMR, δ: −156.3 (m, 4 F, *ortho*-F); −159.6 (m, 2 F, *para*-F); −161.9 (m, 4 F, *meta*-F). Found (%): C, 34.29; H, 4.38. $C_{22}H_{34}B_{22}F_{10}O_3$. Calculated (%): C, 34.12; H, 4.43. MS (EI, 70 eV), m/z (I_{rel} (%)): 774 [M]$^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 2944, 2918, 2853 (C—H); 2578 (B—H); 1536, 1520 (C=C); 1015 (B—O).

1-Isopropyl-2-(tetrahydrofuranboryl)-1,2-dicarba-*closo*-dodecaborane (4a). Isopropyldimethoxyboryl-*ortho*-carborane **1b** (0.97 g, 4 mmol) was dissolved in THF (50 mL) in a three-neck flask equipped with a reflux condenser, a dropping funnel, and a magnetic stirrer, followed by a dropwise addition of 1.85 *M* solution of BH_3 in THF (2.1 mL) and stirring of the reaction mixture for 2 h. Then, the solvent was evaporated *in vacuo* (10 Torr) and the solid residue obtained was recrystallized from pentane. The yield of a white finely crystalline product was 1.1 g (96%). ^{1}H NMR, δ: 0.75—4.1 (br.m, 12 H, B—H); 1.1 (d, 6 H, Me, J = 5.0 Hz); 2.18 (m, 4 H, CH_2); 2.42 (sept, 1 H, CH, J = 5.0 Hz); 4.25 (t, 4 H, CH_2O, J = 5.0 Hz). ^{13}C{^{1}H} NMR, δ: 24.4 (s, Me); 25.3 (s, CH_2); 31.9 (s, CH); 79.5 (s, C—O). ^{11}B{^{1}H} NMR, δ: −10.92 (br.s, B(3), B(4), B(5), B(6), B(8), B(10)); −9.4 (br.s, B(7), B(11)); −4.2 (br.s, B(9), B(12)); 2.88 (br.s, BH_2). Found (%): C, 39.91; H, 9.98. $C_9H_{27}B_{11}O$. Calculated (%): C, 40.00; H, 10.07. MS (EI, 70 eV), m/z (I_{rel} (%)): 199 [M − THF]$^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 2984, 2952, 2944, 2896 (C—H); 2576 (B—H), 2448 (B—H (BH_2)).

1-Isopropyl-2-(dimethylsulfideboryl)-1,2-dicarba-*closo*-dodecaborane (4b). 1-Isopropyl-2-dimethoxyboryl-1,2-dicarba-*closo*-dodecaborane (**1b**) (7.3 g, 0.028 mol) was dissolved in diethyl ether (50 mL) in a three-neck flask equipped with a magnetic stirrer, a thermometer, and a dropping funnel and cooled to 0 °C. A solution of $BH_3 \cdot SMe_2$ (5 mL, 0.053 mol) in diethyl ether (10 mL) was added to the reaction mixture at room temperature and it was stirred for 1 h and then concentrated *in vacuo*. The residue was dried *in vacuo* (1—2 Torr) to obtain the target compound **4b** (7.16 g, 96%) as a clear oily liquid, sensitive to atmospheric oxygen and moisture. ^{1}H NMR, δ: 0.8—3.6 (br.m, 12 H, B—H,); 1.15 (d, 6 H, CMe, J = 6.9 Hz); 2.33 (s, 6 H, SMe); 2.48 (sept, 1 H, C—H, J = 6.9 Hz). ^{13}C{^{1}H} NMR, δ: 24.5 (s, C<u>Me</u>); 32.1 (s, CH); 25.1 (s, SMe). ^{11}B{^{1}H} NMR, δ: −10.4, −9.4, −4.14 (all br.s, B—H + BH_2). Found (%): C, 32.21; H, 9.58. $C_7H_{25}B_{11}S$. Calculated (%): C, 32.31; H, 9.68. MS (EI, 70 eV), m/z (I_{rel} (%)): 260 [M]$^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 2977, 2943, 2932, 2878 (C—H); 2573 (B—H); 2409 (B—H (BH_2)).

1-Isopropyl-2-[4-(dimethylamino)pyridineboryl]-1,2-dicarba-*closo*-dodecaborane (4c). 4-(Dimethylamino)pyridine (1 equiv.) was added to borane **4a** (0.8 g, 3 mmol) in hexane (50 mL). The reaction mixture was refluxed for 2 h. Low-temperature crystallization gave **4c** as a colorless crystalline compound. The yield was 0.7 g (81%). ^{1}H NMR, δ: 0.70—3.70 (br.m, 12 H, B—H); 1.15 (d, 6 H, CMe, J = 6.9 Hz); 2.71 (sept, 1 H, CH (Pr^i), J = 6.9 Hz); 3.14 (s, 6 H, NMe); 6.55 (d, 2 H, C—H_{arom}, J = 7.5 Hz); 7.90 (d, 2 H, C—H_{arom}, J = 7.5 Hz). ^{13}C{^{1}H} NMR, δ: 24.5 (s, C<u>Me</u>); 31.6 (s, CH (Pr^i)); 39.7 (s, NMe); 106.5 (s, *meta*-C); 147 (s, *ortho*-C); 155.6 (s, *para*-C). ^{11}B{^{1}H} NMR, δ: −10.0, −8.4, −5.3, −3.8 (all br.s, B—H + BH_2). Found (%): C, 45.11; H, 9.19. $C_{12}H_{29}B_{11}N_2$. Calculated (%): C, 45.00; H, 9.13. MS (EI, 70 eV), m/z (I_{rel} (%)): 320 [M]$^+$ (100).

2-Di(*n*-hexyl)boryl-1-isopropyl-1,2-dicarba-*closo*-dodecaborane (5). Hex-1-ene (1.2 mL, 0.010 mol) in diethyl ether (5 mL) was added dropwise to a solution of 1-isopropyl-2-(dimethylsulfideboryl)-1,2-dicarba-*closo*-dodecaborane (**4b**) (5 mL, 0.004 mol) in diethyl ether (10 mL) at 0 °C and the mixture was stirred for 48 h at room temperature. Then, the reaction mixture was concentrated *in vacuo* (10 Torr). Fraction distillation of an oily residue (130—132 °C, 0.5 Torr) gave 2-di(*n*-hexyl)boryl-1-isopropyl-1,2-dicarba-*closo*-dodecaborane (**5**) (1.3 g, 94%) as a colorless liquid. ^{1}H NMR, δ: 0.70—3.70 (br.m, 42 H, *n*-C_6H_{13} + + B—H + Me(Pr^i)); 2.22 (sept, 1 H, C—H, J = 6.9 Hz). ^{13}C{^{1}H} NMR, δ: 14.1, 15.8, 21.8, 22.6, 24.8, 34.9, 38.1 (all s). ^{11}B{^{1}H} NMR, δ: −11.4, −8.3, −4.5, −1.50 (all br.s, B—H); 69.2 (br.s, B(*n*-C_6H_{13})$_2$). Found (%): C, 55.81; H, 11.91. $C_{17}H_{43}B_{11}$. Calculated (%): C, 55.72; H, 11.83. MS (EI, 70 eV), m/z (I_{rel} (%)): 366 [M]$^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 2981, 2975, 2944, 2956 (C—H); 2576 (B—H).

1-Isopropyl-2-di(phenylethylenyl)boryl-1,2-dicarba-*closo*-dodecaborane (6). Phenylacetylene (1.0 g, 0.010 mol) was added dropwise to a solution of 1-isopropyl-2-(dimethylsulfideboryl)-1,2-dicarba-*closo*-dodecaborane (**4b**) (1.1 g, 4 mmol) in diethyl ether (10 mL) at 0 °C and the mixture was stirred for 72 h (reaction progress was monitored by ^{1}H NMR spectroscopy). The reaction mixture was concentrated to dryness. The target product **6** (1.43 g, 94%) was obtained by crystallization from hexane (30 mL) as a light yellow crystalline compound, extremely sensitive to atmospheric oxygen and moisture. ^{1}H NMR, δ: 0.80—3.50 (br.m, 10 H, B—H); 1.11 (d, 6 H, Me, J = 6.9 Hz); 2.19 (sept, 1 H, CH, J = 6.9 Hz); 7.15 (d, 2 H, BCH, J = 17.7 Hz); 7.5 (d, 2 H, C<u>H</u>Ph, J = 17.7 Hz); 7.39—7.50, 7.60—7.68 (both m, Ph). ^{13}C{^{1}H} NMR, δ: 24.7 (s, Me); 34.8 (s, CH); 128.5, 129.1, 130.8 (all s, Ph); 132.1 (br.s, BCH=); 136.9 (s, *ipso*-C, Ph); 156.8 (s, Ph<u>C</u>H=). ^{11}B{^{1}H} NMR, δ: −11.2, −8.3, −4.2, −0.9 (all br.s, B—H); 59.4 (br.s, B(HC=CHPh)$_2$). Found (%):

Table 2. Principal crystallographic and refinement parameters for compounds **1a**, **1b**, **2**, **3**, and **4c**

Parameter	**1a**	**1b**	**2**	**3**	**4c**
Molecular formula	$C_5H_{17}B_{11}Cl_2$	$C_7H_{23}B_{11}O_2$	$C_{17}H_{17}B_{11}F_{10}$	$C_{22}H_{34}B_{22}F_{10}O_3$	$C_{12}H_{29}B_{11}N_2$
Molecular weight	267.00	258.16	530.22	774.31	320.28
T/K	120	120	120	100	100
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*Pnma*	$P2_1$	$P2_1/n$	$C2/c$	$P\bar{1}$
Z	4	2	4	4	2
a/Å	12.7950(9)	6.9154(7)	9.6555(9)	18.7905(13)	9.6043(9)
b/Å	14.1447(10)	13.1723(13)	13.1802(13)	8.7596(6)	10.4412(10)
c/Å	7.7724(5)	8.3087(8)	17.6533(17)	22.3636(14)	10.9318(10)
α/deg	90.00	90.00	90.00	90.00	107.689(2)
β/deg	90.00	95.860(2)	93.641(2)	97.8193(16)	109.329(2)
γ/deg	90.00	90.00	90.00	90.00	96.875(2)
V/Å^3	1406.66(17)	752.90(13)	2242.0(4)	3646.8(4)	955.50(16)
d_{calc}/g cm^{-3}	1.261	1.139	1.571	1.410	1.113
μ/cm^{-1}	4.26	0.62	1.42	1.13	0.56
F(000)	544	272	1056	1560	340
$2\theta_{max}$/deg	58	57	58	58	58
Reflections collected	11199	5212	24281	10150	11305
Number of independent reflections	2031	2085	5951	4791	5046
Number of reflections with $I > 2\sigma(I)$	1513	1998	4150	3489	3511
Number of refined parameters	145	225	385	300	278
R_1/wR_2	0.0313/0.0873	0.0320/0.0862	0.0518/0.1331	0.0402/0.1111	0.0499/0.1451
GOF	1.014	1.048	1.003	1.029	1.028
Residual electron density ρ_{min}/ρ_{max}/e Å^{-3}	−0.210/0.308	−0.184/0.238	−0.244/0.421	−0.224/0.374	−0.207/0.294

C, 62.55; H, 7.81. $C_{21}H_{31}B_{11}$. Calculated (%): C, 62.68; H, 7.77. MS (EI, 70 eV), m/z (I_{rel} (%)): 402 $[M]^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 3050 (C—H_{arom}); 2975, 2953 (C—H); 2573 (B—H); 1560 (C=C).

2-Allylmethoxyboryl-1-isopropyl-1,2-dicarba-*closo*-dodecaborane (7). 1-Isopropyl-2-dimethoxyboryl-1,2-dicarba-*closo*-dodecaborane (**1b**) (0.8 g, 3 mmol) and triallylborane (0.84 mL, 5 mmol) were placed in a two-neck flask equipped with a magnetic stirrer and a reflux condenser with an argon lock. The reaction mixture was stirred for 2 h, volatile components were evaporated *in vacuo* (10 Torr) to obtain the target product (0.86 g, 98%) as a clear oily liquid. ^{1}H NMR, δ: 0.8—3.5 (br.m, 10 H, B—H); 1.13 (d, 6 H, Me, J = 6.9 Hz); 2.15 (d, 2 H, CH_2, J = 7.4 Hz); 2.28 (sept, 1 H, CH, J = 6.9 Hz); 3.91 (s, 3 H, OMe); 5.04—5.87 (m, 2 H, CH_2); 5.77 (ddt, 1 H, =CH, J_{trans} = 17.3 Hz, J_{cis} = 9.8 Hz, J = 7.4 Hz). ^{13}C{^{1}H} NMR (50.32 MHz), δ: 24.4 (s, Me); 33.1 (br.s, CH_2); 34.3 (s, CH); 55.5 (s, Me); 117.9 (s, CH=$\underline{C}H_2$); 130.4 (s, $\underline{C}$H=CH_2). ^{11}B{^{1}H} NMR, δ: −11.4, −8.4, −4.4, −0.9 (all br.s, B—H); 43.3 (br.s, B(OMe)All). Found (%): C, 40.15; H, 9.47. $C_9H_{25}B_{11}O$. Calculated (%): C, 40.30; H, 9.40. MS (EI, 70 eV), m/z (I_{rel} (%)): 269 $[M]^+$ (100). IR (CH_2Cl_2), ν/cm^{-1}: 2981, 2944 (C—H); 2575 (B—H).

X-ray diffraction studies of compounds 1a, **1b**, and **2** were performed on a SMART 1000 CCD diffractometer (graphite monochromator, Mo-Kα radiation, ω-scan technique). The structures **3** and **4c** were solved using an APEX II CCD diffractometer (graphite monochromator, Mo-Kα radiation, ω-scan technique). All the structure were solved by direct method and refined by the least squares method in anisotropic full-matrix approximation on F^2_{hkl}. In crystal of **1a**, molecules are located on the crystallographic plane m, which leads to the overlap of the Pr^i and BCl_2 groups. The superposition of these group is also retained in the case of noncentrosymmetric group $Pna2_1$, that indicates the independence of the static disordering from the crystal symmetry. Apparently, the disordering is explained by the absence of strong nonvalent interactions for these substituents, capable of discrimination of these functional groups when forming the crystal. Positions of hydrogen atoms at boron atoms of the carboranyl group were localized from the difference Fourier-syntheses of electron density and refined in isotropic approximation, other hydrogen atoms were placed in geometrically calculated positions. Principal crystallographic data and parameters of refinement are given in Table 2. All the calculations were carried out using the SHELXTL PLUS software.[17]

The full X-ray diffraction data are available from the Cambridge Structural Database (CCDC 1010870—1010874, www.ccdc.ac.uk).

References

1. R. N. Grimes, *Carboranes*, 2nd ed., Academic Press, Oxford, 2011, 1247 p.
2. (a) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane, *New J. Chem.*, 2011, **35**, 1955; (b) N. S. Hosmane, *Boron Science. New Technologies and Applications*, CRC Press, New York, 2012, 850 p.

3. R. F. Barth, M. G. H. Vicente, O. K. Harling, W. S. Kiger, K. J. Riley, P. J. Binns, F. M. Wagner, M. Suzuki, T. Aihara, I. Kato, S. Kawabata, *Radiat. Oncol.*, 2012, **7**, 146.
4. (a) L. Weber, Ja. Kahlert, R. Brockhinke, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, R. A. Harder, M. A. Fox, *Chem. Eur. J.*, 2012, **18**, 8347; (b) L. Weber, Ja. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, R. A. Harder, P. J. Low, M. A. Fox, *Dalton Trans.*, 2013, **42**, 2266.
5. (a) B. M. Mikhailov, E. A. Shagova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1972, **21**, 1407 [*Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1972, 1450]; (b) B. M. Mikhailov, E. A. Shagova, *Zh. Obshch. Khim.*, 1975, **45**, 1052 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 1975, **45**].
6. (a) S. Y. Erdyakov, Ya. Z. Voloshin, I. G. Makarenko, E. G. Lebed, T. V. Potapova, A. V. Ignatenko, A. V. Vologzhanina, M. E. Gurskii, Yu. N. Bubnov, *Inorg. Chem. Commun.*, 2009, **12**, 135; (b) B. M. Mikhailov, E. A. Shagova, T. V. Potapova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1970, **19**, 1923 [*Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1970, 2048].
7. Ya. Z. Voloshin, S. Yu. Erdyakov, I. G. Makarenko, E. G. Lebed´, T. V. Potapova, S. V. Svidlov, Z. A. Starikova, E. V. Pol´shin, M. E. Gurskii, Yu. N. Bubnov, *Russ. Chem. Bull.* (*Int. Ed.*), 2007, **56**, 1787 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 1724].
8. G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science*, 2006, **134**, 1124.
9. D. B. Denney, D. Z. Denney, L.-T. Liu, *Phosphorus Sulfur Related Elem.*, 1982, **13**, 1.
10. (a) G. B. Dunks, R. J. Wiersema, M. F. Hawthorne, *J. Am. Chem. Soc.*, 1973, **95**, 3174; (b) D. N. Rai, C. R. Venkatachelam, R. W. Rudolph, *Syn. React. Inorg. Met.*, 1973, **3**, 129.
11. I. V. Glukhov, K. A. Lyssenko, A. A. Korlyukov, M. Yu. Antipin, *Faraday Discuss.*, 2007, **135**, 203.
12. R. B. Castle, D. S. Matteson, *J. Am. Chem. Soc.*, 1968, **90**, 2194.
13. G. E. Herberich, A. Fisher, *Organometallics*, 1996, **15**, 58.
14. E. Nield, R. Stephens, J. C. Tatlow, *J. Chem. Soc.*, 1959, 166.
15. W. Lippert, H. Nöth, W. Ponikwar, T. Seifert, *Eur. J. Inorg. Chem.*, 1999, 817.
16. L. I. Zakharkin, V. I. Stanko, *Bull. Acad. Sci. USSR*, *Div. Chem. Sci.* (*Engl. Transl.*), 1960, **9**, 1774 [*Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1960, 1896].
17. G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

Received July 4, 2014;
in revised form August 20, 2014