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Grigoriy S. Kazakov, Igor B. Sivaev, Kyrill Yu. Suponitsky, Alexey D. Kirilin, Vladimir I. Bregadze, Alan J. Welch

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$\text{H}_2\text{O, MeCN, } r.t.$

$X = \text{Cl, Br, I}$
Facile Synthesis of \textit{closo-nido} Bis(carborane) and Its Highly Regioselective Halogenation

Grigoriy S. Kazakov\textsuperscript{a,b}, Igor B. Sivaev\textsuperscript{a1}, Kyrill Yu. Suponitsky\textsuperscript{a}, Alexey D. Kirilin\textsuperscript{b}, Vladimir I. Bregadze\textsuperscript{a} and Alan J. Welch\textsuperscript{c}

\textsuperscript{a} A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., Moscow, 119991, Russia  
\textsuperscript{b} M.V. Lomonosov Moscow University of Fine Chemical Technology, 1 Malaya Pirogovskaya Str., Moscow, 119435, Russia  
\textsuperscript{c} Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK

Abstract. 1,1’-Bis(ortho-carborane) undergoes mild deboronation in solution in the presence of water with formation of the [7-(1’\textprime,2’\textprime-\textit{closo}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{11}-1’)-7,8-\textit{nido}-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10}]- (1) anion. The chlorination of 1 with \textit{N}-chlorosuccinimide in acetonitrile proceeds highly regioselectively to give [7-(1’\textprime,2’\textprime-\textit{closo}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{11}-1’)-9-Cl-7,8-\textit{nido}-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10}]\textsuperscript{-} (2) as the main product, whereas its bromination and iodination with elemental halogens results exclusively in [7-(1’\textprime,2’\textprime-\textit{closo}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{11}-1’)-9-X-7,8-\textit{nido}-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10}], X = Br (3) and I (4), respectively. The structure of [Me\textsubscript{3}NH][7-(1’\textprime,2’\textprime-\textit{closo}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{11}-1’)-9-X-7,8-\textit{nido}-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10}] was determined by single-crystal X-ray diffraction.

Key words: 1,1’-Bis(ortho-carborane); Deboration; \textit{closo-nido}-Carborane; Regioselective halogenation

1. Introduction

1,1’-Bis(ortho-carborane) was first prepared by Hawthorne more than 50 years ago via insertion of diacetylene into decaborane frameworks [1]. However, despite some interesting results, to date its chemistry remains relatively unexplored in comparison with not only the parent \textit{ortho}-carborane [2], but with some other polyhedral boranes, such as carba-\textit{closo}-dodecaborate [3], \textit{closo}-dodecaborate [4], \textit{closo}-decaborate [5], bis(dicarbolide) complexes of transition metals [6] and even with rather exotic [B\textsubscript{6}H\textsubscript{6}]\textsuperscript{2-} [7], [B\textsubscript{20}H\textsubscript{18}]\textsuperscript{2-} [8] and [SnB\textsubscript{11}H\textsubscript{11}]\textsuperscript{2-} [9] anions. One of the limiting factors hampering development of 1,1’-bis(ortho-carborane) chemistry was the absence of convenient methods for its synthesis. The turning point was

\textsuperscript{1} Corresponding author.  
E-mail address: sivaev@ineos.ac.ru (I.B. Sivaev).
copper-coupling two parent ortho-carborane units that was initially proposed by Zakharkin [10] and successfully realized later by Hawthorne [11] and Xie [12]. Similarly to the parent ortho-carborane, the CH groups in 1,1′-bis(ortho-carborane) have acidic character and can be easily deprotonated to produce the corresponding dianion which has been used as C,C′-chelating [13-15] or C,C′-bridging [16] ligand to complex a variety of transition metal fragments. Unlike the transition metal complexes C-substituted derivatives of 1,1′-bis(ortho-carborane) with non-transition elements are very rare. To date, syntheses of only a few such compounds have been reported including 2,2′-dimethyl [1a,17] and 2,2′-di( hydroxymethyl) [18] derivatives as well as cyclic derivatives with μ-CH(OH) [19], μ-PPh [20] and μ-AsMe [20,21] bridging fragments. Aiming to expand the range of organic derivatives of 1,1′-bis(ortho-carborane) we found that some of prepared compounds undergo partial deboronation during a work-up procedure. An additional study demonstrated that the parent 1,1′-bis(ortho-carborane) itself can be partially deboronated under mild conditions.

In this contribution we report mild monodeboronation of 1,1′-bis(ortho-carborane) to the 

\[
[7-(1′,2′-closo-C_2B_{10}H_{11}-1′)-7,8-nido-C_2B_9H_{11}]^- \] 

anion and regiospecific halogenation of the latter resulting in monohalogen derivatives 

\[
[7-(1′,2′-closo-C_2B_{10}H_{11}-1′)-9-X-7,8-nido-C_2B_9H_{10}]^- \] 

(X = Cl, Br, I).

2. Results and discussion

The nucleophile-induced removal of one boron atom (deboronation) from the parent ortho-carborane and its C-substituted derivatives resulting in the corresponding nido-carboranes is widely used as method to improve water solubility of carborane derivatives for medicinal applications [22] as well as for preparation of carborane π-ligands in metallacarborane synthesis [23]. Alkoxides and alkylamines are traditionally used as nucleophilic agents for deboronation of the ortho-carborane cage; however, use of the fluoride ion as mild deboronating agent has become more and more popular in recent years. In some cases, deboronation can proceed in the apparent absence of a nucleophile. Derivatives with carbon-bound electron-withdrawing substituents such as COR (R = H, OMe) [24] or C_6H_4NO_2 [25] were found to undergo facile deboronation in wet DMSO. Recently, the deboronation of various ortho-carboranyl amides HCB_{10}H_{11}CC(O)NRR’ in wet methanol [26] and aqueous acetonitrile [27] has been reported. Apparently, water molecules act as a nucleophile in all these cases. Moreover, slow spontaneous deboronation of some water-soluble ortho-carboranyl derivatives such as carboranyl alanine [28] or carborane-containing lactose [29] in aqueous solution is well documented and short-time heating of aqueous solutions of ortho-carboranyl carboxylic acid and its amides was proposed.
recently as a convenient route for the *closo-to-nido* transformation of water soluble carborane derivatives with electron-withdrawing substituents [30].

In 1,1’-bis(*ortho*-carborane) both *ortho*-carborane fragments are susceptible to nucleophilic attack. Preparation of both *closo-nido-* and *nido-nido*-deboronation products under treatment with KOH in refluxing ethanol has been described [31-33]. Nevertheless the deboronation proceeds selectively in a two-step process and the degree of deboronation depends on the reaction time and reagent ratio. *1-ortho*-Carboranyl group is known to have strong electron-withdrawing effect [34], therefore it could be expected that water can produce deboronation of 1,1’-bis(*ortho*-carborane). Indeed we found that reaction of 1,1’-bis(*ortho*-carborane) with water in acetonitrile under ambient conditions smoothly produces the corresponding *closo-nido* bis(carborane) \[7-(1’,2’-*closo*-C\textsubscript{2}B\textsubscript{10}H\textsubscript{11}-1’)-7,8-*nido*-C\textsubscript{2}B\textsubscript{9}H\textsubscript{11}\]- (1) isolated in almost a quantitative yield as the Me\textsubscript{3}NH\textsuperscript{+} salt (Scheme 1). It should be noted that no deboronation of the second carborane cage was found either at room temperature or under reflux conditions. This can be explained by effective suppression of the electron-withdrawal effect of the carborane cage upon its deboronation [35].

![Scheme 1](image)

Taking the \(^1\text{H}\) NMR chemical shift of the carborane CH proton as a measure of the CH acidity of *ortho*-carborane derivatives it is possible to estimate indirectly the electronic effects of various substituents attached to an *ortho*-carborane cage. In the case of 1,1’-bis(*ortho*-carborane), substitution of one of the CH hydrogens by the strongly electron-withdrawing *ortho*-carboran-1-yl group results in a significant downfield shift of the CH\textsubscript{carb} signal from 4.52 to 5.07 ppm (in acetone-\(d_6\)). After the transformation of one *closo*-carborane into a *nido*-carborane one the CH\textsubscript{carb} signals undergoes a strong upfield shift to 4.35 ppm indicating that the *nido*-carboran-7-yl group has a weak electron-releasing rather than an electron-withdrawing effect. Therefore,
the monodeboronation proceeds selectively. Likewise the reactions of 1,1′-bis(ortho-carborane) with water in methanol and dimethylsulfoxide also result in the monodeboronation with formation of \([7-(1′,2′-closo-C_2B_{10}H_{11}-1′)-7,8-nido-C_2B_9H_{11}]^−\).

It should be noted that the deboronation of 1-(para-nitrophenyl)-ortho-carborane under the same conditions (20 vol.% H\(_2\)O in MeCN) takes place much more slowly and is only complete after several days, in good agreement with the literature data [25].

Despite the fact that the closo-nido bis(carborane) was first obtained for more than forty years, there are only a few examples of its reactions in the literature. All these relate to its use as a ligand in synthesis of metallacarborane complexes of transition metals [32,33,36]. In this contribution we describe halogenation of the \([7-(1′,2′-closo-C_2B_{10}H_{11}-1′)-7,8-nido-C_2B_9H_{11}]^−\) anion.

Both closo- and nido-carboranes are known to react with various halogenating agents to give the corresponding halogen derivatives. However their reactivities are very different; for example, monoiiodination of ortho-carborane with I\(_2\) proceeds in refluxing dichloromethane only in the presence of AlCl\(_3\) as catalyst [37], whereas monoiiodination of nido-carborane with I\(_2\) in aqueous ethanol proceeds easily under ambient conditions [38]. Therefore, it could be expected that halogenation of closo-nido bis(carborane) should proceed primarily at the nido-carborane cage. Usually halogenation of a nido-carborane occurs at a facial boron atom adjacent to one of the two carbon atoms on the open face of the nido-carborane cage (positions 9 and 11) [38-40]. In the case of C-substituted nido-carboranes monohalogenation results in the formation of a mixture of \([7-R-9-X-7,8-C_2B_9H_{10}]^−\) and \([7-R-11-X-7,8-C_2B_9H_{10}]^−\) isomers. As can be expected, the isomers form in unequal amounts with the major product likely the one with the halogen residing on the boron atom closest to the unsubstituted, and hence less sterically-demanding, carbon vertex. In the case of \(R = \text{CONHCH}_2\text{Ar}\) the isomer ratio in the iodination reaction was estimated to be 4:1 based on NMR spectroscopic data [27]. The preferential formation of the less sterically-hindered isomer was supported by crystal crystallographic study of Cs[7-(p-SCNC\(_6\)H\(_4\))-9-I-7,8-C\(_2\)B\(_9\)H\(_{10}\)] [41]. However, it was recently demonstrated that even in the case of \(R = \text{Ar}\) the iodination does not proceed regiospecifically and results in a mixture of isomers [42]. Probably, less regioselectivity can be expected in the bromination and chlorination reactions.

It was reasonable to expect that in the case of such a bulky substituent as carborane, the substitution at the boron atom closest to the substituted carbon atom should be completely blocked. Indeed the reaction of \(1\) with bromine and iodine in ethanol resulted in exclusive formation of the corresponding 9-bromo- and 9-iododerivatives \([7-(1′,2′-closo-C_2B_{10}H_{11}-1′)-9-Br-7,8-nido-C_2B_9H_{10}]^−\) (3) and \([7-(1′,2′-closo-C_2B_{10}H_{11}-1′)-9-I-7,8-nido-C_2B_9H_{10}]^−\) (4), whereas the reaction \(1\) with \(N\)-chlorosuccinimide in acetonitrile at ambient temperature gave mainly \([7-
(1’,2’-closo-C₆B₁₀H₁₁-1’)-9-Cl-7,8-nido-C₂B₉H₁₀][X⁻] (2) together with a small amount (~ 10 %) of presumably the 11-chloro derivative and a trace amount of the 9,11-dichloro derivative (m/z 344.2836) (Scheme 2).

![Diagram](image)

Scheme 2

The $^{11}$B NMR spectra of compounds 2-4 reveal combined sets of signals corresponding to closo- and nido-carborane cages including singlets for the 9-substituted boron atoms at 3.3, -3.1 and -17.7 ppm for chloro, bromo and iodo derivatives, respectively. In the $^1$H NMR spectra the signal of the nido-CH$_{\text{carb}}$ group demonstrates a progressive downfield shift from 1.99 ppm for 1 to 2.46, 2.55 and 2.59 ppm for 2, 3 and 4, respectively. The signal of the closo-CH$_{\text{carb}}$ group also undergoes a downfield shift from 4.35 ppm for 1 to 4.52-4.58 ppm for 2-4, i.e. close to the chemical shift of the CH groups in ortho-carborane (4.50 ppm in acetone-$d_6$). Parenthetically this implies that halogenation of nido-carborane depress its electron-releasing effect.

The halogenation position was unequivocally established by a single crystal X-ray diffraction study of [Me₃NH][7-(1’,2’-closo-C₂B₁₀H₁₁-1’)-9-Br-7,8-nido-C₂B₉H₁₀]. General view of the anion in the structure of [Me₃NH][3] is depicted in Fig. 1. The bromine atom is attached to the B9 boron atom of the nido-carborane fragment. The relative orientation of the two carborane cages is such that the torsion angle C₈’-C₇’-C₁-C₂ is equal to 106.3(6)°, less than was found for the unsubstituted closo-nido-carborane [177.2(6)°] [33]. Nevertheless, the both orientations are close to expected local minima on the potential energy surface for rotation around C1-C7’ bond (108 and 180°).
In summary, a mild method of monodeboronation of 1,1’-bis(ortho-carborane) in the presence of water as nucleophile has been described and halogenation of the closo-nido carborane thus formed has been studied. Chlorination with N-chlorosuccinimide proceeds mainly regioselectively, whereas the reactions with elementary bromine and iodine are fully regiospecific. The crystallographic structure of [Me₃NH][7-(1’,2’-closo-C₂B₁₀H₁₁-1’)-9-X-7,8-nido-C₂BoH₁₀] was determined.

3. Experimental

3.1. Materials and methods

1,1’-bis(ortho-carborane) was prepared according to the literature procedure [12]. The reaction progress was monitored by thin-layer chromatography (Merck 60 F₂₅₄ silica gel on aluminium plates). Boron compounds were visualized using 0.5% PdCl₂ in 1 % HCl in MeOH. ¹H, ¹³C, ¹¹B and ¹¹B{¹H} NMR spectra were recorded using a Bruker Avance-400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference for ¹H NMR and ¹³C NMR spectra. ¹¹B NMR spectra were referenced to BF₃·Et₂O as the external signal. High resolution electrospray ionization mass spectra were obtained with a microOTOF II instrument (Bruker Daltonics) operating in a mass range of m/z 50-3000.
3.2. Synthesis of \([\text{Me}_3\text{NH}]_7\text{-}(1',2'-\text{closo}-\text{C}_2\text{B}_{10}\text{H}_{11}1'-1')7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}\] ((Me₃NH)[1])

To solution of 1,1'-bis(o-carborane) (0.50 g, 1.75 mmol) in acetonitrile (50 ml) water (10 ml) was added and the resulting suspension was stirred at room temperature overnight until a clear solution was formed. The solution was concentrated in vacuo to 10 ml and treated with an aqueous solution of \([\text{Me}_3\text{NH}]\text{Cl}\) (0.19 g, 2.00 mmol) resulting in the immediate formation of a white precipitate. The precipitate was isolated by filtration, washed with water (2 × 5 ml) and diethyl ether (2 × 5 ml) and dried in vacuo to obtain 0.54 g (92 %) of \([\text{Me}_3\text{NH}]_7\text{-}(1',2'-\text{closo}-\text{C}_2\text{B}_{10}\text{H}_{11}1'-1')7,8\text{-nido-C}_2\text{B}_9\text{H}_{11}\] (1), the $^1$H and $^{11}$B NMR spectra of which were identical with those of an authentic sample prepared according to the literature [11].

$^1$H NMR (acetone-$d_6$, ppm): 4.37 (1H, s, CH_{carb}), 3.24 (9H, s, (CH$_3$)$_3$NH$^+$), 1.99 (1H, s, CH_{carb}), 3.0 – 0.0 (18H, BH), -2.61 (1H, BH$_B$). $^{11}$B NMR (acetone-$d_6$, ppm): -3.9 (1B, d, $J$ = 157 Hz), -5.9 (1B, d, $J$ = 140 Hz), -8.8 (1B, d, $J$ = 130 Hz) -10.4 (5B, d, $J$ = 143 Hz), -11.2 (2B, d), -13.5 (2B, d, $J$ = 160 Hz), -16.8 (2B, d, $J$ = 133 Hz), -19.0 (1B, d, $J$ = 156 Hz), -22.7 (1B, d, $J$ = 146 Hz), -32.9 (1B, d, $J$ = 138 Hz), -35.3 (1B, d, $J$ = 141 Hz).

3.3. Synthesis of \([\text{Me}_3\text{NH}]_7\text{-}(1',2'-\text{closo}-\text{C}_2\text{B}_{10}\text{H}_{11}1'-1')9\text{-Cl-7,8-nido-C}_2\text{B}_9\text{H}_{10}\] ((Me₃NH)[2])

To solution of 1 (100 mg, 0.30 mmol) in acetonitrile (30 ml) N-chlorosuccinimide (48 mg, 0.35 mmol) was added and the reaction mixture was stirred at ambient temperature for 6 h. The solvent was removed under reduced pressure and the residue was dissolved in a mixture of water and ethanol (2 : 1 v/v, 15 ml). Ethanol was removed in vacuo and the precipitate thus formed was filtered, washed with water (2 × 10 ml) and dried in air to obtain white solid (96 mg, yield 93 %). $^1$H NMR (acetone-$d_6$, ppm): 4.53 (1H, s, CH_{carb}), 3.24 (9H, s, (CH$_3$)$_3$NH$^+$), 2.46 (1H, s, CH_{carb}), 3.0 – 0.0 (18H, BH), -2.55 (1H, BH$_B$). $^{11}$B NMR (acetone-$d_6$, ppm): -3.9 (1B, d, $J$ = 157 Hz), -5.9 (1B, d, $J$ = 140 Hz), -8.8 (1B, d, $J$ = 130 Hz) -10.4 (5B, d, $J$ = 143 Hz), -11.2 (2B, d), -13.5 (2B, d, $J$ = 160 Hz), -16.8 (2B, d, $J$ = 133 Hz), -19.0 (1B, d, $J$ = 156 Hz), -22.7 (1B, d, $J$ = 146 Hz), -32.9 (1B, d, $J$ = 138 Hz), -35.3 (1B, d, $J$ = 141 Hz).

$^{13}$C NMR (acetone-$d_6$, ppm): 82.0 (closo-CH$_{carb}$), 65.5 (closo-CH$_{carb}$), 54.3 (nido-CH$_{carb}$), 52.0 (nido-CH$_{carb}$), 45.4 ((CH$_3$)$_3$NH$^+$). HRMS-ESI (m/z) for C$_4$H$_{12}$B$_{15}$Cl: calcld 310.3225 [M$^+$], found 310.3228 [M$^+$].

3.4. Synthesis of \([\text{Me}_3\text{NH}]_7\text{-}(1',2'-\text{closo}-\text{C}_2\text{B}_{10}\text{H}_{11}1'-1')9\text{-Br-7,8-nido-C}_2\text{B}_9\text{H}_{10}\] ((Me₃NH)[3])

To solution of 1 (100 mg, 0.30 mmol) in ethanol (15 ml) a solution of Br$_2$ (17 µl, 53 mg, 0.33 mmol) in ethanol (10 ml) was added dropwise at 0 °C and stirred for 2 h. To the colourless
solution water (10 ml) was added and ethanol was removed in vacuo. The precipitate formed was filtered, washed with water (2 × 10 ml) and dried in air to obtain white solid (118 mg, yield 99 %). 1H NMR (acetone-d6, ppm): 4.55 (1H, s, CHcarb), 3.24 (9H, s, (CH3)3NH+), 2.55 (1H, s, CHcarb), 3.0 – 0.0 (18H, BH), -2.63 (1H, BHB). 11B NMR (acetone-d6, ppm): -3.1 (1B, s), -3.6 (1B, d, J = 151 Hz), -5.8 (1B, d, J = 132 Hz) -6.6 (1B, d, J = 131 Hz), -10.3 (4B, d, J = 147 Hz), -11.1 (2B, d), -13.4 (2B, d, J ~ 165 Hz), -14.3 (2B, d, J = 126 Hz), -17.6 (1B, d, J = 154 Hz), -22.8 (1B, d, J = 158 Hz), -25.8 (1B, d, J = 141 Hz), -31.3 (1B, d, J = 119 Hz), -35.7 (1B, d, J = 141 Hz). 13C NMR (acetone-d6, ppm): 81.8 (closo-Carb), 65.5 (closo-CHcarb), 55.7 (nido-CHcarb), 52.8 (nido-Carb), 45.4 ((CH3)3NH+). HRMS-ESI (m/z) for C6H21Br: calcd 354.2733 [M]+, found 354.2727 [M]+.

3.5. Synthesis of [Me3NH][7-(1′,2′-closo-C2B10H11-1′′)-9-I-7,8-nido-C2B9H10] ((Me3NH)[4])

To solution of 1 (100 mg, 0.30 mmol) in ethanol (15 ml) a solution of I2 (83 mg, 0.32 mmol) in ethanol (10 ml) was added and the reaction mixture was heated under reflux for 2 h. To the colourless reaction mixture water (10 ml) was added and ethanol was removed under reduced pressure. The precipitate formed was filtered, washed with water (2 × 10 ml) and dried in air to obtain a white solid (129 mg, yield 93 %). 1H NMR (acetone-d6, ppm): 4.59 (1H, s, CHcarb), 3.24 (9H, s, (CH3)3NH+), 2.59 (1H, s, CHcarb), 3.0 – 0.0 (18H, BH), -2.75 (1H, BHB). 11B NMR (acetone-d6, ppm): -3.62 (1B, d, J = 156 Hz), -5.0 (1B, d, J = 120 Hz), -5.7 (1B, d, J = 131 Hz), -10.3 (4B, d, J = 148 Hz), -11.2 (2B, d), -13.6 (4B, d, J ~ 190 Hz), -15.0 (1B, d, J ~ 175 Hz) -17.7 (1B, s), -22.6 (1B, d, J = 152 Hz), -25.2 (1B, d, J = 146 Hz ), -29.6 (1B, d, J = 121 Hz), -35.0 (1B, d, J = 143 Hz). 13C NMR (acetone-d6, ppm): 81.7 (closo-Carb), 65.7 (closo-CHcarb), 57.8 (nido-CHcarb), 54.4 (nido-Carb), 45.4 ((CH3)3NH+). HRMS-ESI (m/z) for C6H21BrI: calcd 402.2574 [M]+, found 402.2574 [M]+.

3.6. X-ray diffraction study

Single crystals of [Me3NH][3] suitable for the X-ray study were obtained from ethanol - water mixture. Crystal data: C6H21Br-C3H10N+, orthorhombic, space group Pbcm, a = 10.7716(11)Å, b = 21.044(2)Å, c = 9.6203(10)Å, V = 2180.7(4)Å3, Z = 4, dcalcd = 1.263 g·cm−3, μ=1.879 mm−1. 31513 reflections were collected on a SMART APEX2 CCD diffractometer [λ(Mo-Kα)=0.71073 Å, graphite monochromator, ω-scans, 2θ < 56.6°] at 120K. Analysis of measured intensities was carried out with the SAINT and SADABS programs implemented in the APEX2 program package [43]. The structure was solved by the direct methods and refined by full-matrix least-squares against F2 in the anisotropic approximation. 2865 independent
reflections \( R(\text{int}) = 0.1299 \) were used in the refinement which converged to \( wR_2 = 0.1201 \) based on \( F^2_{\text{hkl}} \) \( GOF = 1.055, R_1 = 0.0473 \) based on \( F_{\text{hkl}} \) using 1994 reflections with \( I>2\sigma(I) \). Refinement was carried out with the SHELXTL program [44]. The position of C2 atom was identified by a combination of the examination of refined isotropic thermal parameters, the length of the cage connectivities and the Vertex-Centroid Distance Method [45]. Both anion and cation occupy special positions being located on the mirror plane, and as a result are disordered over two positions. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC № 1435997).

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References


Method of mild monodeboronation of 1,1′-bis(ortho-carborane) was developed. Halogenation of closo-nido-bis(carborane) proceeds highly regioselectively. 

\[7-(1′,2′\text{-closo-C}_2\text{B}_{10}\text{H}_{11}-1′)-9-X-7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}]^- (X = \text{Cl}, \text{Br}, \text{I}) \] were prepared.