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Retention of the B(3)–X (X = Br, I) bond in *closo*-*o*-carborane derivatives after nucleophilic attack. The first synthesis of $[3\text{-X-7-R-7,8-}nido\text{-C}_2\text{B}_9\text{H}_{10}]^-$ (X = Br, I). Crystal structure of $[\text{HNMe}_3][3\text{-I-7,8-}nido\text{-C}_2\text{B}_9\text{H}_{11}]$

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Abstract

The synthesis of new 3-halogeno *nido* derivatives of *o*-carborane, $[3\text{-X-7-R-7,8-}nido\text{-C}_2\text{B}_9\text{H}_{10}]^-$ (X = Br, I; R = H, CH_3, C_6H_5) is described, through deboronation of the compounds $3\text{-X-1-R-1,2-}closo\text{-C}_2\text{B}_{10}\text{H}_{10}$, previously synthesised in our laboratory. These *nido* products have been fully characterised using ^{1}H-, ^{11}B- and ^{13}C-NMR spectroscopies, MALDI-TOF and, for $[3\text{-I-7,8-}nido\text{-C}_2\text{B}_9\text{H}_{11}]^-$ by an X-ray crystallographic study. The influences of the halogen moiety on both the B(3) resonance and that of the bridge proton are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *nido* Carborane derivatives; Deboronation; Iodinated ligands

1. Introduction

Recently, the chemistry of boron-halogenated carboranes has received considerable attention, as evidenced by many relevant publications [1]. Previously, we have reported the synthesis of a series of 3-iodo and 3-bromo *closo*-*o*-carboranes and demonstrated that they could be excellent starting compounds for the preparation of new carborane-derivatives following substitution reactions [2]. More recently, the reactivity of 3-I-*o*-carborane towards Mg, Cu, Cu in the presence of PPh_3, $[Ni(PPh_3)_3]$, or $[Pd(PPh_3)_4]$ has also been studied in our group to establish the suitability of B-iodine substituted carboranes as sources of new derivatives [3]. In spite of the fact that halogenated *nido* carboranes have potential relevance to important topics such as radioiodine carry and as boron neutron capture therapy (BNCT) reagents [4]; relatively few iodinated and brominated *nido* carboranes are known. The iodination of $[7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_{12}]^-$ was first reported by Hawthorne et al. in 1965, [5] an electrophilic substitution at the 9-position of the open face of the *nido* precursor. The synthesis of 9,11 disubstituted $[7,8\text{-}nido\text{-C}_2\text{B}_9\text{H}_{12}]^-$ was later described either by electrophilic halogenation with iodine [6,7] and bromine [7] or through the reaction of the anion with *N*-halosuccinimide (iodo and bromo) [8]. The synthesis of the 5-iodo-derivative, has also been described, [9,7] and, recently, some *nido* carborane species have been radioiodinated for labelling studies [10].

In this work, we describe the synthesis of new 3-halogeno *nido* derivatives of *o*-carborane, $[3\text{-X-7-R-7,8-}nido\text{-C}_2\text{B}_9\text{H}_{10}]^-$ (X = Br, I; R = H, CH_3, C_6H_5), through the deboronation of the appropriate $3\text{-X-1-R-1,2-}closo\text{-C}_2\text{B}_{10}\text{H}_{10}$, compounds previously synthesised in our laboratory [2].

2. Results and discussion

Since the best method of obtaining halocarboranes is by electrophilic halogenation with iodine or bromine of the boron atom vertices, the most common halogenated

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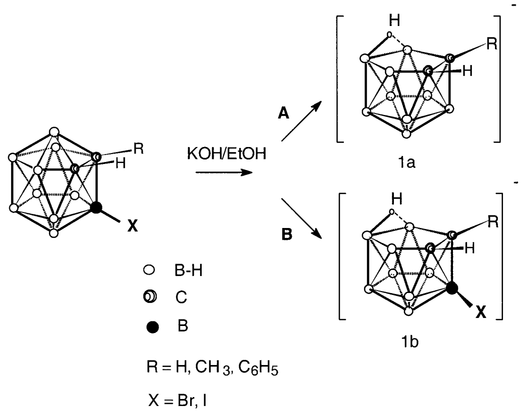
nido carboranes are those substituted at the 9 and 11 positions, the sites of highest electron density as a result of their position in the open pentagonal face of the *nido* cluster [5]. Consequently, producing iodo and bromo derivatives substituted in other positions of the *nido* cluster is relatively difficult, due to the unsusceptibility of these sites to electrophilic attack. As far as we are aware, bromination of a *nido* carborane is only known at the 9 and 11 positions. For iodocarboranes the *nido* anion enantiomers 5-I-*nido*-7,8-dicarbaundecaborate and 6-I-*nido*-7,8-dicarbaundecaborate have additionally been obtained, through the deboronation of 9-I-*o*-carborane with KOH [7] or tetrabutylammonium fluoride hydrate, TBAFH [9]. In this paper we describe the deboronation with EtO^- in EtOH of a series of *closo* derivatives of *o*-carborane 3-X-1-R-*closo*-1,2-$C_2B_{10}H_{10}$ (X = Br, I; R = H, CH_3, C_6H_5) iodinated or brominated at the 3-position, i.e. that connected both cluster carbon atoms. As it is well established, the deboronation of an icosahedral *closo*-*o*-carborane cluster always takes place at the 3 or 6 positions, equivalent in the case of non-B-substitution. However, the equivalence is removed in our case, because B(3) is halogenated. Therefore, one of the aims of this work was to establish which deboronation path, either the elimination of the B(3)–X vertex (X = I, Br) or the removal of the B(6)–H vertex (Scheme 1), would be followed.

Hawthorne et al. established that the partial degradation of 3-R-*closo*-compounds (R = Et, Ph) [11] by nucleophilic attack with ethanolic hydroxide ion at reflux temperature took place at the non-substituted boron atom, due to the steric demand of the R group, thus affording partially degraded products in which the organic substituent remains attached to boron(3). Hawthorne later reported [12] that B–OR carborane derivatives can also undergo degradation under basic conditions with retention of the substituent, but that, for substituted carboranes such as 3-($CH_2(CH_2)_2OH$)-1,2-*closo*-$C_2B_{10}H_{11}$, the B(3) vertex was removed. In general it has been shown that the deboronation of 3-substituted *ortho*-carboranes, 3-R-1,2-*closo*-$C_2B_{10}H_{11}$ in alcoholic KOH solution gives either $[3\text{-R-7,8-}nido\text{-}C_2B_9H_{11}]^-$ (R = Ph, Et, NC, NHR) or $[7,8\text{-}closo\text{-}C_2B_9H_{12}]^-$ (R = OH) or both possible *nido* anions when R = NH_2 [13]. Therefore, it is apparent that the outcome of nucleophilic attack is not just affected by steric considerations, and that electronic effects should also be taken into account. Fox et al. [9] calculated the Mulliken charges for some halogenated *closo* carboranes and demonstrated that the boron atom removed remains the one bearing the highest positive charge, thus the preferred site for nucleophilic attack.



Scheme 1. Possible paths of the degradation process in B-derivatives.

In our case, B(3) is either substituted with iodine or bromine. Both are electron-withdrawing atoms that can deplete electron density on B(3) making this atom more susceptible to nucleophilic attack; in contrast, they are also bulky atoms, which could prevent B(3) removal by steric effects, forcing attack at B(6) instead.

The *closo* halogenated compounds 3-X-1-R-1,2-*closo*-$C_2B_{10}H_{10}$ (X = Br, I; R = H, Me, Ph) have been used as starting materials. The deboronation of these compounds with KOH–EtOH under reflux conditions for 3 h and subsequent precipitation with $[HNMe_3]Cl$ led to the formation of $[HNMe_3][3\text{-X-1-R-7,8-}nido\text{-}C_2B_9H_{10}]$ (X = Br, I; R = H, Me, Ph; compounds **I**–**VI**) in good to high yield (Scheme 1b). Therefore, it is clear that nucleophilic attack takes place at the non-substituted atom B(6) leaving B(3)–X intact. This can be interpreted either in terms of the bulkiness of the substituent or the π back-donation power (the mesomeric (+M) effect) of the halogen atoms. Given that the lone pairs of weakly electronegative elements like iodine are reasonably basic in terms of Lewis acid–base theory, they could interact fairly efficiently with the tangential p-orbitals on B(3) transferring electron density to this atom, [2] thus causing B(6) to become the atom most susceptible to nucleophilic attack.

Compounds **I**–**VI** represent the first examples of 3-halogeno *nido* derivatives of *o*-carborane, and they can be used as precursors to synthesise carborane-containing macromolecules. **I**–**VI** have been fully characterised using ^1H-, ^{11}B-, ^{13}C-NMR spectroscopy, and, in the case of $[3\text{-I-7,8-}nido\text{-}C_2B_9H_{11}]^-$, MALDI-TOF and X-ray diffraction. The MALDI-TOF spectrum (Fig. 1) shows a peak with isotopic distribution at $m/z = 260.39$ corresponding to $[IC_2B_9H_{11}]^-$. A peak at 127.05 corresponding to lost iodine is also observed.

2.1. The B(3)–X influence on the bridging proton

The bridging proton in $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$ derivatives is relatively acidic and can be removed by the addition of strong base. Comparing the chemical shift of this bridging proton in unsubstituted $[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$, −2.90 ppm, with that in $[3\text{-X-7,8-}nido\text{-}C_2B_9H_{11}]^-$ (X = I, $\delta = -2.67$ ppm; X = Br, $\delta = -2.68$

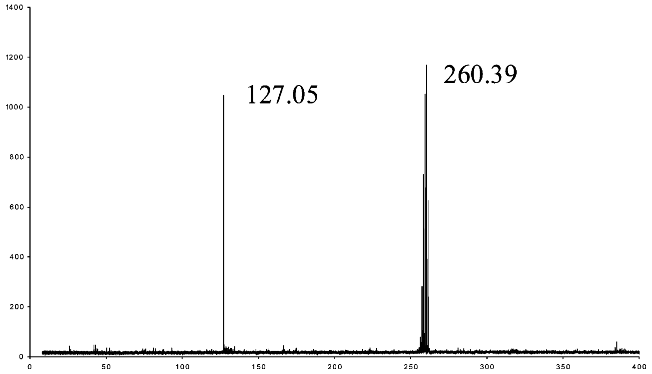


Fig. 1. MALDI-TOF of [HNMe$_3$][3-I-7,8-C$_2$B$_9$H$_{11}$] (**I**).

ppm) we observe that, although the variation is small, the presence of an halogen group on B(3) moves δ to lower field. The effect is similar for both iodine and bromine. The same phenomenon is apparent for [3-X-7-Me-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^-$ (X = I, Br) in which the BHB resonance is found at the same position in both species, in both cases at lower field than in to [7-Me-7,8-*nido*-C$_2$B$_9$H$_{11}$]$^-$. Moreover, this pattern also extends to the C$_{\text{cluster}}$–Ph derivatives (see Table 1). It is also noteworthy that, when a halogen group is substituted on B(3), in most cases the bridge proton appears in the ^{1}H{^{11}B}-NMR spectrum as a multiplet instead of the broad singlet usually observed in *nido* carboranes.

2.2. The B(3)–X substitution influence on the ^{11}B-NMR spectrum

The presence of an iodine substituent on B(3) in [3-I-7,8-*nido*-C$_2$B$_9$H$_{11}$]$^-$ ($\delta_{B(3)} = -28.8$), causes the resonance to appear at higher field in comparison to the unsubstituted anion [7,8-*nido*-C$_2$B$_9$H$_{12}$]$^-$ ($\delta_{B(3)} = -17.4$). In contrast, a bromine substituted on B(3) shifts the resonance to lower field; [3-Br-7,8-*nido*-C$_2$B$_9$H$_{11}$]$^-$ ($\delta_{B(3)} = -14.2$). The same effect was earlier observed in the case of halogeno *closo*-carborane derivatives [2]. We also note that the influence of a carbon substituent, either methyl or phenyl, on the chemical shift of B(3) in 3-I or 3-Br-*nido*-carborane is comparable in both cases, causing a shift to low field of ca. 5 ppm in the iodo case and ca. 3 ppm in the bromo case ($\delta_{\text{B3–I,C–Me}} = -23.1$, $\delta_{\text{B3–I,C–Ph}} = -23.6$; $\delta_{\text{B3–Br,C–Me}} = -11.1$, $\delta_{\text{B3–Br,C–Ph}} = -10.9$) (see Table 2).

Table 1
Chemical shifts of bridge BHB protons in halogenated *nido*-carboranes

	C$_{\text{cluster}}$–H (ppm)	C$_{\text{cluster}}$–Me (ppm)	C$_{\text{cluster}}$–Ph (ppm)
B(3)–H	−2.90	−2.71	−2.46
B(3)–I	−2.67	−2.54	−2.31
B(3)–Br	−2.68	−2.54	−2.31

Table 2
^{11}B-NMR data of B(3) in [3-X-7-R-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^-$ (X = Br, I; R = H, CH$_3$, C$_6$H$_5$) compounds (**I**–**VI**)

Compound	[3-X-R-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^-$		
	X, R	δ (B(3)–X) (ppm)	Δ (ppm)
[C$_2$B$_9$H$_{12}$]$^-$	–, H	−17.4	0
(**I**)	I, H	−28.8	−11.4
(**II**)	Br, H	−14.2	+3.2
(**III**)	I, Me	−23.1	−5.7
(**IV**)	I, Ph	−23.6	−6.2
(**V**)	Br, Me	−11.1	+6.3
(**VI**)	Br, Ph	−10.9	+6.5

The ^{11}B{^{1}H}-NMR spectrum of [3-I-7,8-*nido*-C$_2$B$_9$H$_{11}$]$^-$ displays a 2:2:2:1:1:1 pattern (low field to high field) in the range −9.3 to −35.8 ppm characteristic of [7,8-*nido*-C$_2$B$_9$H$_{12}$]$^-$ species, [15] with the resonances sufficiently separated enough to permit their unambiguous assignment by means of ^{11}B{^{1}H}–^{11}B{^{1}H} COSY. The peak at −34.1 ppm is easily assigned to B(10) since it appears as a doublet of doublets in the ^{11}B-NMR spectrum due to coupling with the H bridge as well as the *exo*-H. The peak at −35.8 ppm, at highest field, corresponds to B(1), the position antipodal to the open face (Fig. 2). The spectrum also exhibits a singlet at −28.8 ppm corresponding to B(3). With the resonances due to B(1), B(3) and B(10) thus established, analysis of the cross peak easily allowed the assignment of the 2:2:2:1:1:1 pattern to B(9,11): B(5,6): B(2,4): B(3): B(10): B(1), respectively (see Fig. 3).

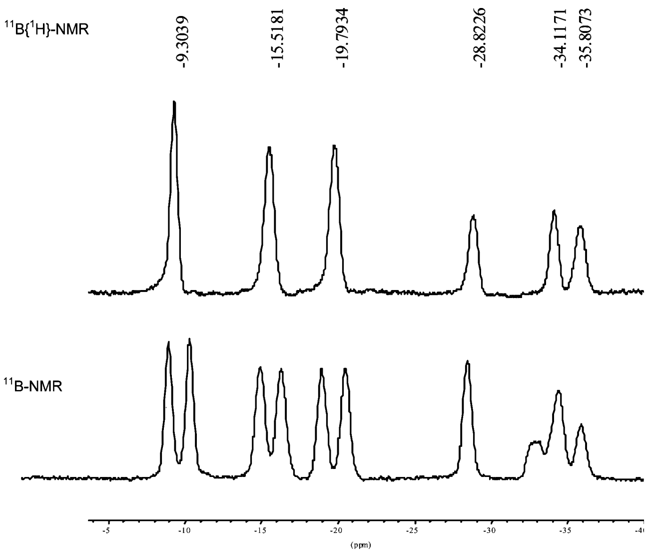


Fig. 2. Comparison of ^{11}B- and ^{11}B{^{1}H}-NMR spectra of [HNMe$_3$][3-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] (**I**).

Table 3
Selected interatomic distances (Å) and angles (°) for [HNMe$_3$][3-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] (**I**)

Interatomic distances	
I(1)–B(3)	2.163(10)
B(1)–B(4)	1.744(13)
B(1)–B(3)	1.755(14)
B(1)–B(2)	1.772(14)
B(1)–B(6)	1.808(14)
B(1)–B(5)	1.817(14)
B(2)–C(7)	1.729(13)
B(2)–B(6)	1.730(14)
B(2)–B(3)	1.762(15)
B(2)–B(11)	1.776(14)
B(3)–C(8)	1.700(12)
B(3)–C(7)	1.707(13)
B(3)–B(4)	1.787(13)
B(4)–C(8)	1.721(11)
B(4)–B(5)	1.747(14)
B(4)–B(9)	1.792(13)
B(5)–B(10)	1.773(14)
B(5)–B(9)	1.782(14)
B(5)–B(6)	1.823(14)
B(6)–B(11)	1.744(13)
B(6)–B(10)	1.795(14)
C(7)–C(8)	1.555(13)
C(7)–B(11)	1.613(14)
C(8)–B(9)	1.636(14)
B(9)–B(10)	1.857(16)
B(9)–H(10A)	1.37(10)
B(10)–B(11)	1.845(15)
B(10)–H(10A)	1.17(10)
C(21)–N(1)	1.514(12)
C(22)–N(1)	1.481(12)
C(23)–N(1)	1.495(12)
N(1)–H(1N)	0.88(9)
Interatomic angles	
B(4)–B(1)–B(3)	61.4(6)
B(3)–B(1)–B(2)	59.9(6)
B(2)–B(1)–B(6)	57.8(6)
B(4)–B(1)–B(5)	58.7(5)
B(6)–B(1)–B(5)	60.4(6)
C(7)–B(2)–B(3)	58.5(5)
B(6)–B(2)–B(1)	62.1(6)
B(3)–B(2)–B(1)	59.6(6)
C(7)–B(2)–B(11)	54.8(5)
B(6)–B(2)–B(11)	59.7(6)
C(8)–B(3)–C(7)	54.3(5)
C(7)–B(3)–B(2)	59.8(6)
B(1)–B(3)–B(2)	60.5(6)
C(8)–B(3)–B(4)	59.1(5)
B(1)–B(3)–B(4)	59.0(5)
C(8)–B(3)–I(1)	123.1(6)
C(7)–B(3)–I(1)	125.6(6)
B(1)–B(3)–I(1)	124.9(6)
B(2)–B(3)–I(1)	123.2(6)
B(4)–B(3)–I(1)	122.1(6)
B(1)–B(4)–B(5)	62.7(6)
C(8)–B(4)–B(3)	57.9(5)
B(1)–B(4)–B(3)	59.6(5)
C(8)–B(4)–B(9)	55.5(5)
B(5)–B(4)–B(9)	60.5(6)
B(4)–B(5)–B(9)	61.0(6)
B(10)–B(5)–B(9)	63.0(6)
B(4)–B(5)–B(1)	58.5(5)
B(10)–B(5)–B(6)	59.9(6)
B(1)–B(5)–B(6)	59.5(6)
B(2)–B(6)–B(11)	61.5(6)
B(11)–B(6)–B(10)	62.8(6)
B(2)–B(6)–B(1)	60.1(6)
B(10)–B(6)–B(5)	58.7(6)
B(1)–B(6)–B(5)	60.1(5)
C(8)–C(7)–B(11)	116.0(8)
C(8)–C(7)–B(3)	62.6(6)
B(11)–C(7)–B(2)	64.1(6)
B(3)–C(7)–B(2)	61.7(6)
C(7)–C(8)–B(9)	111.3(8)
C(7)–C(8)–B(3)	63.1(6)
B(9)–C(8)–B(4)	64.5(6)
B(3)–C(8)–B(4)	63.0(5)
C(8)–B(9)–B(4)	60.1(5)
B(5)–B(9)–B(4)	58.5(5)
C(8)–B(9)–B(10)	106.3(8)
B(5)–B(9)–B(10)	58.3(6)
B(5)–B(10)–B(6)	61.4(6)
B(6)–B(10)–B(11)	57.2(6)
B(5)–B(10)–B(9)	58.7(6)
B(11)–B(10)–B(9)	101.1(7)
C(7)–B(11)–B(2)	61.1(6)
B(6)–B(11)–B(2)	58.9(5)
C(7)–B(11)–B(10)	105.0(7)
B(6)–B(11)–B(10)	59.9(6)
C(22)–N(1)–C(23)	112.1(8)
C(22)–N(1)–C(21)	111.5(8)
C(23)–N(1)–C(21)	111.1(7)
C(22)–N(1)–H(1N)	108(6)
C(23)–N(1)–H(1N)	108(6)
C(21)–N(1)–H(1N)	106(6)

2.3. Description of the structure of [HNMe$_3$][3-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] (*I*)

Only three crystal structures of iodinated *nido* compounds, [HNMe$_3$][9,11-I$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$] [6], [HNMe$_3$][9-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] [6] and Cs[7-(*p*-C$_6$H$_4$NCS)-9-I-7,8-*nido*-C$_2$B$_9$H$_{11}$]. [4] have been reported. That of [HNMe$_3$][3-I-7,8-*nido*-C$_2$B$_9$H$_{11}$] (**I**), reported here, is the first in which the iodine is not attached to one of the symmetry equivalent positions 9 or 11.

The salt **I** crystallise as ion pairs (Fig. 4) with no close inter-ion contacts. The anion has the anticipated *nido* icosahedral geometry with the iodine substituent at position 3. Table 3 lists selected interatomic distances and angles. B(3)–I is 2.163(10) Å, wholly typical of similar distances in the literature [14]. Molecular parameters within the *nido* cage are consistent with those in the parent compound [7,8-*nido*-C$_2$B$_9$H$_{12}$]$^-$ [15], with C(7)–C(8) 1.555(13) Å. The atom H(10A) appears to be intermediate between *endo* on B10 and bridging between B(10) and B(9), B(9)–H(10A) 1.37(10) Å, B(10)–H(10A) 1.17(10) Å. All other distances and angles, and those in the cation, are quite normal.

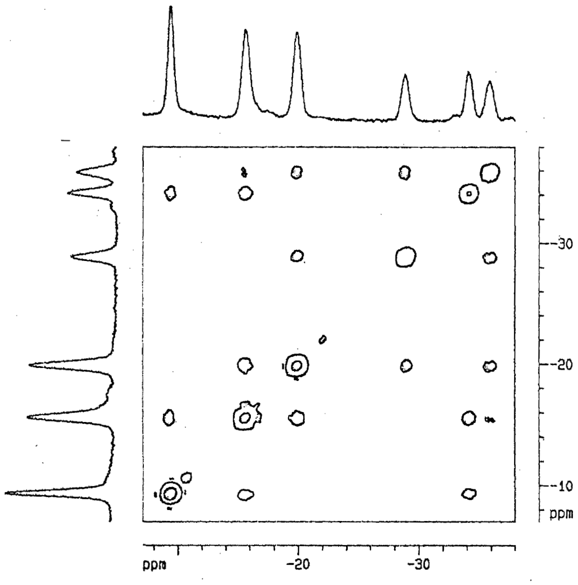


Fig. 3. $^{11}B\{^{1}H\}-^{11}B\{^{1}H\}$ COSY spectrum of $[HNMe_3][3\text{-}I\text{-}7,8\text{-}$*nido*$\text{-}C_2B_9H_{11}]$ (**I**).

3. Experimental

3.1. Instrumentation

Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H- and $^{1}H\{^{11}B\}$-NMR (300.13 MHz), $^{13}C\{^{1}H\}$-NMR (75.47 MHz) and ^{11}B-NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were recorded from CD_3COCD_3 solutions at 25 °C. Chemical shift values for ^{11}B-NMR spectra were referenced to external $BF_3 \cdot OEt_2$ and those for ^{1}H-, $^{1}H\{^{11}B\}$- and $^{13}C\{^{1}H\}$-NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are in Hz. MS spectra were recorded using a Bruker Biflex MALDI-TOF mass spectrometer.

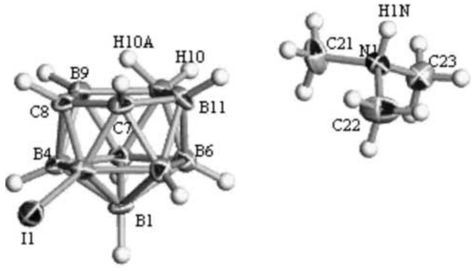


Fig. 4. Perspective view of the ion pair $[HNMe_3][3\text{-}I\text{-}7,8\text{-}$*nido*$\text{-}C_2B_9H_{11}]$ (**I**).

3.2. Materials

Unless otherwise noted, all manipulations were carried out under a dinitrogen atmosphere using standard vacuum line techniques. 3-I-*o*-carborane, [16] 3-I-1-Me-*o*-carborane, [2] 3-I-1-Ph-*o*-carborane, [2] 3-Br-*o*-carborane, [17] 3-Br-1-Me-*o*-carborane, [2] 3-Br-1-Ph-*o*-carborane, [2] were synthesised according to the bibliography. Ethanol, KOH and $[HNMe_3]Cl$ were purchased from commercial sources and used as received.

3.3. Trimethylammonium 3-iodo-7,8-dicarba-*nido*-undecaborate (*I*)

A solution of 1.95 g (7.2 mmol) of 3-iodo-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol was heated under reflux for 3 h. The alcohol was then distilled off and the residue was dissolved in water (50 ml), neutralised and precipitated with aqueous $[HNMe_3]Cl$. After filtration, the solid was washed with cold water (2 × 15 ml) and hexane (2 × 15 ml) yielding compound **I** as a white powder. Yield 2.0 g (87%). Anal. Calc. for $C_5H_{21}B_9NI$: C, 18.81; H, 6.62; N, 4.38. Found: C, 19.53; H, 6.76; N, 4.21%. IR: ν $[cm^{-1}] = 3163$ (N–H), 2518 (B–H). $^{1}H\{^{11}B\}$-NMR: $\delta = 3.22$ (s, 9H, $HN(CH_3)_3$), 3.00–0.00 (br m, 8H, $B–H_{terminal}$), 1.95 (br s, 2H, $C_{cluster}–H$), −2.67 (br m, 1H, $B–H_{bridge}$). $^{13}C\{^{1}H\}$-NMR: $\delta = 48.0$ ($C_{cluster}$), 45.2 (s, $HN(CH_3)_3$). ^{11}B-NMR: $\delta = -9.3$ (d, $^{1}J(B,H) = 139$, 2B, B(9,11)), −15.5 (d, $^{1}J(B,H) = 136$, 2B, B(5,6)), −19.8 (d, $^{1}J(B,H) = 153$, 2B, B(2,4)), −28.8 (s, 1B, B(3)), −34.1 (dd, $^{1}J(B,H_{terminal}) = 138$, $^{1}J(B,H_{bridge}) = 55$, 1B, B(10)), −35.8 (d, $^{1}J(B,H) = 154$, 1B, B(1)).

3.4. Trimethylammonium 3-bromo-7,8-dicarba-*nido*-undecaborate (*II*)

Similarly were reacted 1.60 g (7.2 mmol) of 3-bromo-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. Work-up gave compound **II**. Yield 1.62 g (83%). Anal. Calc. for $C_5H_{21}B_9NBr$: C, 58.57; H, 4.13; N, 2.73. Found: C, 59.20; H, 4.12; N, 2.70%. IR: ν $[cm^{-1}] = 3167$ (N–H), 2514 (B–H). $^{1}H\{^{11}B\}$-NMR: $\delta = 3.21$ (s, 9H, $HN(CH_3)_3$), 3.0–0.0 (br m, 8H, $B–H_{terminal}$), 1.95 (br s, 2H, $C_{cluster}–H$), −2.68 (br m, 1H, $B–H_{bridge}$). $^{13}C\{^{1}H\}$-NMR: $\delta = 47.0$ ($C_{cluster}$), 45.2 (s, $HN(CH_3)_3$). ^{11}B-NMR: $\delta = -10.0$ (d, $^{1}J(B,H) = 137.6$, 2B), −14.2 (s, 1B), −16.1 (d, $^{1}J(B,H) = 137.6$, 2B), −20.7 (s, $^{1}J(B,H) = 152.1$, 2B), −36.6 (d, $^{1}J(B,H) = 137.2$, 2B).

Table 4
Details of structural study of [HNMe$_3$][3-I-7,8-*nido*-$C_2B_9H_{11}$] (**I**)

Empirical formula	$C_5H_{21}B_9IN$
Formula weight	319.42
Temperature (K)	160(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	11.9951(16)
b (Å)	12.640(3)
c (Å)	9.6449(17)
β (°)	94.070(13)
Volume (Å^3)	1458.6(4)
Z	4
D_{calc} (Mg m^{-3})	1.455
Absorption coefficient (mm^{-1})	2.161
$F(000)$	624
Crystal size (mm^3)	0.06 × 0.32 × 0.28
θ range for data collection (°)	2.34–25.00
Index ranges	$-14 \le h \le 14$, $-1 \le k \le 15$, $-1 \le l \le 11$
Reflections collected	3306
Independent reflections	2545 [$R_{int} = 0.0709$]
Completeness to $\theta = 25.00°$	99.2%
Absorption correction	Empirical
Max/min transmission	1.00, 0.7195
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2545/10/182
Goodness-of-fit on F^2	1.116
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0544$, $wR_2 = 0.1324$
R indices (all data)	$R_1 = 0.0853$, $wR_2 = 0.1536$
Largest difference peak, hole (e Å^{-3})	1.630, −1.688

3.5. Trimethylammonium 3-iodo-7-methyl-7,8-dicarba-nido-undecaborate (*III*)

In the same manner were reacted 2.05 g (7.2 mmol) of 3-iodo-1-methyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. Work-up gave compound **III**. Yield 1.90 g (79%). Anal. Calc. for $C_6H_{23}B_9NI$: C, 21.61; H, 6.95; N, 4.20. Found: C, 21.71; H, 6.95; N, 4.19%. IR: ν [cm^{-1}] = 3155 (N–H), 2962–2860 (C_{alk}–H), 2523 (B–H). $^1H\{^{11}B\}$-NMR: δ = 3.21 (s, 9H, HN(CH$_3$)$_3$), 3.0–0.0 (br m, 8H, B–H$_{terminal}$), 1.61 (br s, 2H, C$_{cluster}$–H), 1.50 (s, 3H, CH$_3$), −2.54 (br m, 1H, B–H$_{bridge}$). $^{13}C\{^1H\}$-NMR: δ = 52.1 (C$_{cluster}$), 45.2 (s, HN(CH$_3$)$_3$), 25.1 (s, CH$_3$). ^{11}B-NMR: δ = −8.5 (d, ^1J(B,H) = 153, 1B), −10.3 (d, ^1J(B,H) = 153, 1B), −16.2 (d, ^1J(B,H) = 173, 2B), −18.4 (d, ^1J(B,H) = 115, 1B), −19.1 (d, ^1J(B,H) = 115, 1B), −23.1 (s, 1B), −34.1 (d, ^1J(B,H) = 115, 2B).

3.6. Trimethylammonium 3-iodo-7-phenyl-7,8-dicarba-nido-undecaborate (*IV*)

Similarly were reacted 2.5 g (7.2 mmol) of 3-iodo-1-phenyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. After working-up compound **IV** was obtained. Yield 2.0 g (70%). Anal. Calc. for $C_{11}H_{25}B_9NI$: C, 33.40; H, 6.37; N, 3.54. Found: C, 33.84; H, 6.38; N, 3.55%. IR: ν [cm^{-1}] = 3100 (N–H), 2524 (B–H). $^1H\{^{11}B\}$-NMR: δ = 7.20–6.90 (br m, 5H, C–H$_{aryl}$), 3.21 (s, 9H, HN(CH$_3$)$_3$), 3.0–0.0 (br m, 8H, B–H$_{terminal}$), 2.40 (br s, 2H, C$_{cluster}$–H), −2.31 (br s, 1H, B–H$_{bridge}$). $^{13}C\{^1H\}$-NMR: δ = 144.1, 127.5, 126.6, 124.9 (C$_{aryl}$), 47.1 (C$_{cluster}$), 45.5 (s, HN(CH$_3$)$_3$). ^{11}B-NMR: δ = −6.2 (d, ^1J(B,H) = 138, 1B), −9.9 (d, ^1J(B,H) = 138, 1B), −15.8 (d, ^1J(B,H) = 167, 1B), −17.05 (d, ^1J(B,H) = 146, 1B), −19.1 (d, ^1J(B,H) = 145, 2 B), −23.6 (s, 1B), −33.3 (d, ^1J(B,H) = 143, 2B).

3.7. Trimethylammonium 3-bromo-7-methyl-7,8-dicarba-nido-undecaborate (*V*)

In the same manner were reacted 1.71 g (7.2 mmol) of 3-bromo-1-methyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. Work-up gave compound **V**. Yield 1.55 g (75%). Anal. Calc. for $C_6H_{23}B_9NBr$: C, 25.16; H, 8.09; N, 4.89. Found: C, 25.26; H, 8.06; N, 4.80%. IR: ν [cm^{-1}] = 3165 (N–H), 2900–2749 (C_{alk}–H), 2524 (B–H). $^1H\{^{11}B\}$-NMR: δ = 3.18 (s, 9H, HN(CH$_3$)$_3$), 3.0–0.0 (br m, 8H, B–H$_{terminal}$), 1.97 (br s, 2H, C$_{cluster}$–H), 1.43 (s, 3H, CH$_3$), −2.54 (br m, 1H, B–H$_{bridge}$). $^{13}C\{^1H\}$-NMR: δ = 52.1 (C$_{cluster}$), 45.2 (s, HN(CH$_3$)$_3$), 25.4 (s, CH$_3$). ^{11}B-NMR: δ = −8.6 (d, ^1J(B,H) = 135, 1B), −11.1 (d, ^1J(B,H) = 146, 1B), −11.1 (s, 1B), −17.3 (d, ^1J(B,H) = 145, 2B), −18.6 (d, ^1J(B,H) = 151, 1B), −20.2 (d, ^1J(B,H) = 158, 1B), −35.85 (d, ^1J(B,H) = 131, 2B).

3.8. Trimethylammonium 3-bromo-7-phenyl-7,8-dicarba-nido-undecaborate (*VI*)

Similarly were reacted 2.15 g (7.2 mmol) of 3-bromo-1-phenyl-1,2-dicarba-*closo*-dodecaborane and 2.0 g (36 mmol) of KOH in 60 ml of ethanol. After working-up compound **VI** was obtained. Yield 1.50 g (69%). Anal. Calc. for $C_{11}H_{25}B_9NBr$: C, 37.9; H,7.2; N, 4.01. Found: C, 38.0; H, 7.3; N, 4.09%. IR: ν [cm^{-1}] = 3165 (N–H), 2527 (B–H). $^1H\{^{11}B\}$-NMR: δ = 7.20–6.90 (br m, 5H, C–H$_{aryl}$), 3.20 (s, 9H, HN(CH$_3$)$_3$), 3.0–0.0 (br m, 8H, B–H$_{terminal}$), 2.37 (br s, 2H, C$_{cluster}$–H), −2.31 (br s, 1H, B–H$_{bridge}$). $^{13}C\{^1H\}$-NMR: δ = 143.4, 127.2, 126.8, 124.5 (C$_{aryl}$), 47.2 (C$_{cluster}$), 45.3 (s, HN(CH$_3$)$_3$). ^{11}B-NMR: δ = −6.6 (d, ^1J(B,H) = 140, 1B), −10.9 (d, 1B), −10.9 (s, 1B), −17.1 (d, ^1J(B,H) = 139, 2B), −19.7 (d, ^1J(B,H) = 183, 1B), −19.9 (d, ^1J(B,H) = 180, 1 B), −35.1 (d, ^1J(B,H) = 135, 2B).

3.9. X-ray crystallographic study of *I*

A single crystal was mounted on a glass fibre and studied using a Bruker P4 diffractometer [18] operating with graphite-monochromated Mo–K_{α} radiation ($\lambda = 0.71069$ Å) with cooling via an Oxford Cryostreams device. Intensity data were collected using ω scans. No significant deviation of the intensities of standard reflections periodically remeasured was detected. Data were corrected for absorption effects by psi scans. The structure was solved by direct methods and difference Fourier methods and refined [19] by full-matrix least-squares. Cage H atoms and the ammonium H atom were located from a difference Fourier map. *Exo*-H atoms on the cage were restrained to 1.10(2) Å from boron or 1.15(2) Å from carbon, but the atoms H(10A) and H(1N) were allowed free refinement. Methyl H atoms were set in idealised positions. All H atom displacement parameters were treated as riding on their respective bound atom, with U_H set at $1.2 \times U_B$, $1.2 \times U_{C_{cage}}$ or $1.5 \times C_{methyl}$. Table 4 lists relevant data.

4. Supporting information available

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC no. 169772. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) H. Lee, C.B. Knobler, M.F. Hawthorne, Chem. Commun. 24 (2000) 2485;
(b) J.H. Morris, K.W. Henderson, V.A. Ol'shevskaya, J. Chem. Soc. Dalton Trans. (1998) 1951;
(c) C.-W. Tsang, Q. Yang, E. Tung-Po Sze, T.C.W. Mak, D.T.W. Chan, Z. Xie, Inorg. Chem. 39 (2000) 3582;
(d) W. Keller, G. Sawitzki, W. Haubold, Inorg. Chem. 39 (2000) 1282.
[2] C. Viñas, G. Barberà, J.M. Oliva, F. Teixidor, A.J. Welch, G.M. Rosair, Inorg. Chem. 40 (2001) 6555.
[3] C. Viñas, G. Barbera, F. Teixidor, J. Organomet. Chem. 642 (2002) 16.
[4] E.A. Mizusawa, M.R. Thompson, M.F. Hawthorne, Inorg. Chem. 24 (1985) 1911.
[5] F.P. Olsen, M.F. Hawthorne, Inorg. Chem. 4 (1965) 1839.
[6] R.H. Pak, R.R. Kane, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 33 (1994) 5355.
[7] G.K. Semin, L.I. Zakharkin, S.I. Kuznetsov, G.G. Zhigareva, E.V. Bryukhova, Russ. J. Gen. Chem. 68 (1998) 919.
[8] E.C. Santos, A.B. Pinkerton, S.A. Kinkead, P.K. Hurlburt, S.A. Jasper, C.W. Sellers, J.C. Huffman, L.J. Todd, Polyhedron 19 (2000) 1777.
[9] M.A. Fox, K. Wade, J. Organomet. Chem. 573 (1999) 279.
[10] M.F. Hawthorne, A. Maderna, Chem. Rev. 99 (1999) 3421.
[11] M.F. Hawthorne, P.A. Wegner, J. Am. Chem. Soc. 90 (1968) 896.
[12] W. Chen, J.J. Rockwell, C.B. Knobler, D.E. Harwell, M.F. Hawthorne, Polyhedron 18 (1999) 1725.
[13] (a) L.I. Zakharkin, V.A. Ol'shevskaya, D.D. Sulaymankulova, V.A. Antonovich, Bull. Acad. Sci. USSR Div. Chem. Sci. (1991) 1026;
(b) L.I. Zakharkin, V.A. Ol'shevskaya, D.D. Sulaymankulova, Russ. Chem. Bull. 42 (1993) 1395;
(c) V.A. Brattsev, S.P. Knyazev, G.N. Danilova, T.N. Vostrikova, V.I. Stanko, J. Gen. Chem. USSR 46 (1976) 2627.
[14] Z. Zheng, W. Jiang, A.A. Zinn, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 34 (1995) 2095 (and references therein).
[15] J. Buchanan, E.J.M. Hamilton, D. Reed, A.J. Welch, J. Chem. Soc. Dalton Trans. (1990) 677.
[16] J. Li, C.F. Logan, M. Jones, Jr., Inorg. Chem. 30 (1991) 4866.
[17] J. Li, M. Jones, Jr., Inorg. Chem. 29 (1990) 4162.
[18] Siemens Analytical Instruments, Inc., Madison, WI, USA 1996.
[19] G.M. Sheldrick, SHELXTL Version 5.1. Bruker AXS Inc., Madison, WI, USA, 1999.