INCREMENTAL IODINATION OF THE EIGHT-VERTEX *closo* MONOCARBORANE ANION [*closo*-1-CB_7H_8]$^-$: PREPARATION AND CHARACTERIZATION OF [*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ AND [*closo*-1-CB_7H_2-2,3,4,6,7,8-I_6]$^-$, AND THE SYNTHESIS OF THE FIRST EIGHT-VERTEX C-METHYLATED CARBORANE ANION [1-CH_3-*closo*-1-CB_7H_4-6,7,8-I_3]$^-$

Radim DOSTÁL[a1,b,*], Michael G. S. LONDESBOROUGH[a2,*], Magdalena KVÍČALOVÁ[a3], Jan MACHÁČEK[a4], Ivana CÍSAŘOVÁ[c] and Zbyněk JANOUŠEK[a5]

[a] *Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, v.v.i., 250 68 Řež, Czech Republic; e-mail: [1] dostal@iic.cas.cz, [2] michaell@iic.cas.cz, [3] magda@iic.cas.cz, [4] jmach@iic.cas.cz, [5] janousek@iic.cas.cz*

[b] *University of Pardubice, Faculty of Chemical Technology, Department of General and Inorganic Chemistry, Studentská 573, 532 10 Pardubice, Czech Republic*

[c] *Charles University, Faculty of Science, Department of Inorganic Chemistry, Hlavova 2030, 128 40 Prague, Czech Republic; e-mail: cisarova@natur.cuni.cz*

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Dedicated to Dr. Bohumil Štíbr on the occasion of his 70th birthday in recognition of his major contributions to cluster borane chemistry.

Iodination of [*closo*-1-CB_7H_8]$^-$ (anion **1**) with elemental iodine under various controlled conditions yields a continuum from mono- to hexaiodinated derivatives including the previously unknown [*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (anion **5**) and [*closo*-1-CB_7H_2-2,3,4,6,7,8-I_6]$^-$ (anion **8**). These species, characterized by mass spectrometry and NMR spectroscopy, and, in the case of **8**, by single-crystal X-ray diffraction, provide insight into the fluxional molecular behavior of anion **1** in solution. Investigation of direct electrophilic substitution on the carbon-vertex of anion **1** using standard conditions and reagents (deprotonation by BuLi followed by addition of electrophile) proved futile, but the same conditions when using the new triiodo-deravitive anion **5** resulted in the formation of the first eight-vertex C-methylated carborane anion [1-CH_3-*closo*-1-CB_7H_4-6,7,8-I_3]$^-$ (anion **9**), in 60% yield.

Keywords: Carboranes; Monocarborane anions; Eight-vertex; Low nucleophilic and weakly coordinating anions; Halogen derivatives; Electrophilic substitution; Iodination.

One of the remarkable properties of closed polyhedral boron hydride frameworks is their high chemical and thermal stability. For example, cesium

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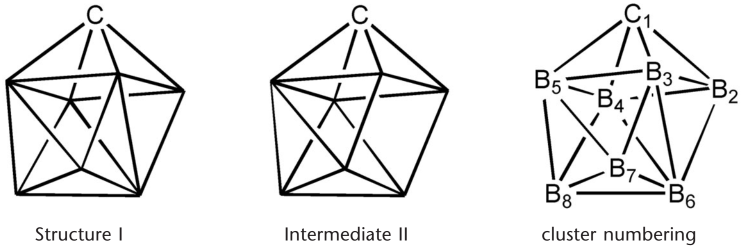
salts of [*closo*-$B_{10}H_{10}$]$^{2-}$ and [*closo*-$B_{12}H_{12}$]$^{2-}$ can be heated to 600 °C without decomposition, and may be recovered unchanged after several hours of heating in solution with aqueous acids and bases[1]. All *closo* boron hydrides have a double-negative charge associated with them that is delocalized within their cluster structures. This charge can be changed by the nominal replacement of {BH}$^-$ vertices from the cluster by isolobal neutral heteroatom units, such as {CH}. Thus, incorporation of two {CH}-vertices into the cluster via, typically, addition of alkynes into decaborane[2], leads to neutral compounds such as *closo*-$C_2B_{10}H_{12}$, and the introduction of a single carbon-vertex, most commonly via reaction of decaborane with aldehydes[3,9,12,13], give singly charged monocarborane species. The single-negative charge carried by the monocarboranes remains delocalized within its cluster framework, and suitably substituted anions of this class are among the least nucleophilic and the most weakly coordinating of all known anions[4]. For these reasons significant resources have gone into the investigation of the [$CB_{11}H_{12}$]$^-$ anion, supplemented, more recently, by an increase in interest about the [CB_9H_{10}]$^-$ anion and its derivatives[5–8]. The chemistry of even smaller *closo* monocarborane anions has been, until recently, an almost unexplored area; its development inhibited by the complicated syntheses of such species[9]. The break-through came by what was later to be known as the Brellochs reaction[10], *nido*-$B_{10}H_{14}$ with formaldehyde to give the [*arachno*-6-CB_9H_{14}]$^-$ anion, which provided an easy and high-yield entry into open-cage monocarborane systems. Recently, the optimization of this synthesis was reported together with new routes to a family of 'smaller *closo* cages' including eight- and nine-vertex *closo* monocarborane anions [1-CB_7H_8]$^-$ and [4-CB_8H_9]$^-$ [11–14] and it is first of these latter two anions, the eight-vertex [*closo*-1-CB_7H_8]$^-$ (anion **1** – see Scheme 1 for numbering), that is the focus of our interest here.

[*closo*-1-CB_7H_8]$^-$ has recently been shown to be a versatile reagent in the formation of carborane-transitional metal complexes on reaction with a series of metal carbonyls ({$M(CO)_4$} where M = Fe, Ru, Mn, Re)[15–17]. This study documented the insertion of metal fragments into the {CB_7} structure of **1** and, indeed, the incorporation of a carbon atom from the carbonyl-metal ligand to give a unique {*nido*-1,9-C_2B_7} moiety[15]. These new metallacarboranes were structurally characterized by single-crystal X-ray diffraction[15–17], but the precise structure of anion **1** itself is still not clear. As yet, no single-crystal X-ray structure of the parent anion exists, but its static solid-state cluster structure is presumed to be as I shown in Scheme 1. However, in solution the ^{11}B NMR spectrum of **1** is simpler (just two resonance peaks of relative intensity 4:3) than that expected for a molecule with structure I. This discrepancy can be rationalized only by the molecular fluxionality of **1** via a diamond-square-diamond mechanism with an intermediate II that results in the lower-belt positions B(6, 7 and 8) becoming equivalent and the upper-belt B(2, 3, 4 and 5) also becoming equivalent[18]. Several attempts, mainly by Kennedy et al.[19], have been made to "freeze" this molecular fluxionality in an effort to confirm the structure of **1** and elucidate the conformations of any intermediates. Low temperature ^{11}B NMR spectroscopy (180 K in CD_2Cl_2 solution) showed[19] no sign of any definitive emergence of a 2:2:1:1:1 relative intensity ratio that would be expected for a static structure I. However, a single-crystal X-ray structure of the phenyl-C derivative of **1**: [1-(C_6H_5)-*closo*-1-CB_7H_7][NEt_4] (compound **2**) did reveal[12,20] a molecular cluster framework as I shown in Scheme 1. Nevertheless, ^{11}B NMR spectroscopy shows **2** to be similarly fluxional in solution[12]. A further strategy pursued by Kennedy et al.[19] was the preparation and subsequent structural study of iodinated derivatives of anion **1**. To this end, two iodo derivatives of **1** were synthesized and characterized as [PPh_4]$^+$ salts of [*closo*-1-CB_7H_7-7-I]$^-$ (compound **3**) and [*closo*-1-CB_7H_6-7,8-I_2]$^-$ (compound **4**). The single-crystal X-ray structures of both **3** and **4** share the same static molecular cluster framework as I in Scheme 1. However, in solution the large iodine substituents were reported neither to hinder nor to remarkably slow the same molecular fluxionality seen in solutions of **1** and **2**.

In this contribution, we describe the progressive iodination of the anion **1** beyond the mono- and disubstituted deravitives prepared by Kennedy et al. and present evidence for the tri-, tetra-, penta- and hexaiodinated derivatives. Additionally, we show that in the case of the triiodinated species, [*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (anion **5**), the cluster {CH}-vertex is activated to the



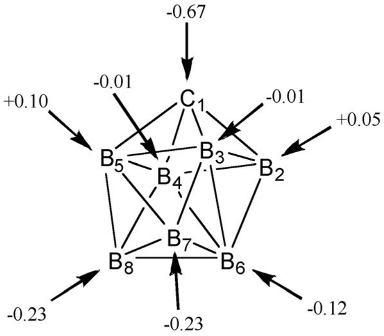
SCHEME 1

Representation of the skeletal molecular structure of [*closo*-1-CB_7H_8]$^-$ (anion **1**): As its static solid-state structure I, as its proposed intermediate in fluxionality II and its numbering system extent that direct substitution at that vertex can be achieved; a feat not possible with the parent anion **1**.

RESULTS AND DISCUSSION

Incremental Iodination of [closo-1-CB_7H_8]⁻ (Anion 1)

The previously reported[19] [*closo*-1-CB_7H_7-7-I]⁻ (anion **3**) and [*closo*-1-CB_7H_6-7,8-I_2]⁻ (anion **4**) result from the straightforward iodination of a dichloromethane solution of anion **1** with a slight excess of elemental iodine. Under these conditions, anions **3** and **4** form in a 2:1 relative concentration ratio. Considering the stoichiometry of the reaction, the fact that both the di- and monoiodinated derivatives form simultaneously suggests that there is a little preference to iodination at these two cluster positions. A natural population analysis (NPA) of charge distribution in anion **1** (Scheme 2) indeed shows positions B(7) and B(8) as jointly having the most negative charge, making these cluster sites in equal measure the most susceptible toward electrophilic substitution, and therefore rationalizing the experimental observation of simultaneous formation of **3** and **4**. Further NPA calculations (see Table I in Supplementary Data) suggest that incremental iodine additions to the cluster do not significantly change the atomic charge distributions, and therefore by analysis of the data provided in Scheme 2, we might expect there to be a barrier to further iodination after the formation of the diiodo derivative. This provides a simple yet reasonable explanation as to why Kennedy's original iodination of anion **1** stopped with the formation of **4**. We thence became interested in whether



SCHEME 2
Schematic showing the NPA atomic charge distributions of [*closo*-1-CB_7H_8]⁻ (anion **1**)

it would be possible to manipulate conditions such as to facilitate further iodination of anion **1**.

On repeating the original synthesis of **3** and **4**, we found that by extending the reaction time from 2 to 24 h, a new trisubstituted species was formed, isolated in 1% yield, that we later identified by means of mass spectrometry and multinuclear NMR spectroscopy as [*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (anion **5**). Room temperature NMR measurements reveal two resonance peaks in the ^{11}B-{^1H} spectrum; the same molecular symmetry (and therefore the same molecular fluxionality) as seen for parent anion **1** but with the upfield shift of the intensity 3 peak representative of the lower-belt B(6,7,8) nuclei and the downfield shift of the intensity 4 peak representative of the upper-belt B(2,3,4,5) nuclei. The intensity 3 resonance peak is a singlet in the ^{11}B spectrum, confirming the iodonation of the B(6), B(7) and B(8) cluster positions and verifying the proposed structure shown in Fig. 1. The mass spectrum of **5** is consistent with the empirical formula [$CB_7H_5I_3$]$^-$. Variable temperature NMR experiments conducted on **5** showed that even at 180 K the fluxional molecular dynamics evident at room temperature do not stop and that the presence of the three iodine substituents bares no mitigating effect on its process. These observations on the molecular dynamics of **5**, so clear from the NMR spectroscopic study, lead to one other profound conclusion, that there is no mixing of vertices between the lower B(6,7,8) belt and the upper B(2,3,4,5) belt, adding experimental support to the previously published hypothesis[18] on the molecular fluxionality of anion **1** based on calculations and theory.

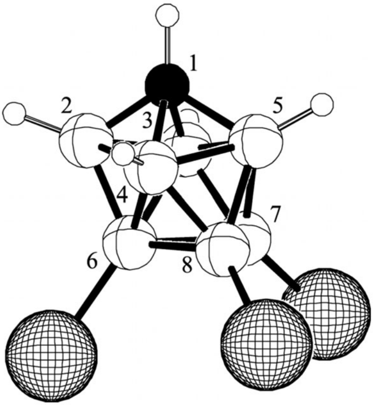


FIG. 1
Turbomole geometrically-optimalized static gas-phase structure for [*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (anion **5**)

The yield of **5** sharply increases to 70% in a single-product reaction involving the parent anion **1** with the common iodinating agent N-iodosuccinimide. Interestingly, in a preliminary attempt to increase the yield of **5** by driving the original reaction conditions, refluxing dichloromethane and now three molar equivalents of iodine, mass spectrometry revealed not only the increased formation of **5**, but also the generation of previously unknown tetraiodo and pentaiodo derivatives. Both were detected in mass spectra of the reaction products after crude separation on a silica column. The former of these new species, clearly visible in the ES mass spectrum as a typical envelope with a most-populated mass peak at 600 *m*/*z* representative of a species with an empirical formula $[CB_7H_4I_4]^-$ (anion **6**), and the latter identified in the MS as an envelope with a most-populated mass peak at 726 *m*/*z*, a value matching the empirical formula $[CB_7H_3I_5]^-$ (anion **7**).

Table I, which shows the incremental iodination enthalpy ΔH_{inc} of anion **1**, reveals the iodination of the anion **1** to be exothermic, but less so with the increasing number of iodine atoms in the molecule, indicative of the forcing experimental conditions required to iodinate past diiodination. Furthermore, from the substitution of the fifth to the seventh iodine atom, the difference is small and unequivocal. This suggests that while the first

TABLE I
Calculated iodination enthalpies of parent anion **1** and its iodo derivatives

Compound	*E*, Eh	ΔH_{iod}, kJ mol^{-1}	$\Delta H/n(I)$, kJ mol^{-1}	ΔH_{inc}, kJ mol^{-1}
$7\text{-}I\text{-}CB_7H_7^-$	–512.9993	–118.0893	–118.0893	–118.0863
$7,8\text{-}I_2\text{-}CB_7H_6^-$	–809.6230	–231.3562	–115.6781	–113.2669
$6,7,8\text{-}I_3\text{-}CB_7H_5^-$	–1106.2443	–338.5608	–112.8536	–107.2046
$2,6,7,8\text{-}I_4\text{-}CB_7H_4^-$	–1402.8635	–440.1895	–110.0474	
$3,6,7,8\text{-}I_4\text{-}CB_7H_4^-$	–1402.8636	–440.4306	–110.1077	–102.2073
$5,6,7,8\text{-}I_4\text{-}CB_7H_4^-$	–1402.8637	–440.7682	–110.1920	
$3,4,6,7,8\text{-}I_5\text{-}CB_7H_3^-$	–1699.4820	–539.9480	–107.9896	
$2,5,6,7,8\text{-}I_5\text{-}CB_7H_3^-$	–1699.4820	–539.9843	–107.9969	–99.2161
$2,3,6,7,8\text{-}I_5\text{-}CB_7H_3^-$	–1699.4826	–541.6030	–108.3206	
$3,5,6,7,8\text{-}I_5\text{-}CB_7H_3^-$	–1699.4828	–542.2715	–108.4543	–101.5033
$2,3,4,6,7,8\text{-}I_6\text{-}CB_7H_2^-$	–1996.1010	–641.2409	–106.8735	–100.0367
$2,3,4,5,6,7,8\text{-}I_7\text{-}CB_7H^-$	–2292.7201	–742.6825	–106.0975	–100.3743

few iodination steps are thermodynamically separated, if the conditions of iodination to the fifth degree are reached, then further iodination or even per-iodination is feasible if not probable.

Emboldened both by these computational postulations and by the observations of **6** and **7** we endeavored to see whether, by application of yet more forceful reaction conditions, further iodination of **1** could be achieved. Thus, using a nine-molar excess of iodine and changing to a higher boiling-point solvent (1,2-dichloroethane), the conditions were found to led to the formation, after 48 h, of the hexaiodo derivative [*closo*-1-CB_7H_2-2,3,4,6,7,8-I_6]$^-$ (anion **8**). Anion **8** was structurally characterized by NMR spectroscopy, mass spectrometry and, as its $[Bu_4N]^+$ salt, by single-crystal X-ray diffraction. The last of these methods revealed a molecular conformation as shown in Fig. 2.

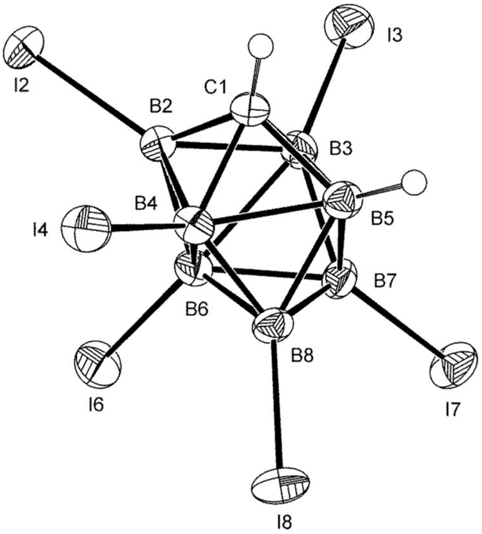


FIG. 2

View of the independent anion **8** from the single-crystal X-ray diffraction structure of the $(Bu_4N)^+$ salt of [*closo*-1-CB_7H_2-2,3,4,6,7,8-I_6]$^-$ (anion **8**). Displacement ellipsoids are drawn on 50% probability level and H atoms shown as small circles of arbitrary radii. Selected bond distances (in Å) and angles (°): C1–B2 1.531(6), C1–B5 1.618(6), C1–B4 1.672(6), C1–B3 1.684(6), B2–B6 1.654(6), B2–B4 1.819(6), B2–B3 1.827(6), B3–B7 1.677(6), B3–B5 1.884(6), B3–B6 1.955(6), B4–B8 1.671(6), B4–B5 1.891(6), B4–B6 1.966(6), B5–B8 1.789(6), B5–B7 1.790(6), B6–B8 1.805(6), B6–B7 1.809(6), B7–B8 1.608(6), B2–C1–B5 114.2(3), B2–C1–B4 69.1(3), B5–C1–B4 70.1(3), B2–C1–B3 69.1(3), B5–C1–B3 69.6(3), B4–C1–B3 99.5(3); B–I range 2.125(4)–2.163(4)

From the X-ray crystal structure, the single boron-vertex in **8** not to have been iodinated is B(5), which might be expected on the basis of the NPA of charge distribution (see Scheme 2 and Table I in Supplementary Data). In solution, the hexaiodo anion **8** is fluxional and, on evidence of its ^{11}B NMR spectrum, fluxional in the same habit as the parent anion **1** and triiodo anion **5**. The ^{11}B NMR spectrum of **8** consists of one singlet representing the three lower-belt B(6,7,8) nuclei, shifted only slightly downfield from its equivalent in the spectrum for **5**. The resonance peak representing the upper-belt B(2,3,4,5) nuclei in **5** is now split into three separate peaks of relative intensity 1:1:2, representative of the symmetry seen in the crystal structure of **8**. The mass spectrum is also consistent with the empirical formula $[CB_7H_2I_6]^-$, i.e. 851 *m*/*z*.

Interestingly, despite the suggestion from the computational study that per-iodination is likely if the conditions are pushed past penta-iodination, no evidence was found for the formation of a periodinated derivative of anion **1**. However this is by no means extraordinary or unexpected: Computationally derived data in such cases only give an indication of thermodynamic stability of products. Kinetic inhibition of the final iodination, which will involve a more restricted access to the relevant cluster site than the previous iodinations in the sequence, may be an important factor.

Carbon-Vertex Substitution on [closo-1-CB$_7$H$_5$-6,7,8-I$_3$]$^-$ (Anion 5)

There is an interest in monocarboranes with alkyl and aryl substituents on the cluster carbon-vertex in connection with the synthesis of rod-like structures for use in larger molecular assemblies[8]. In this context, we set about investigating carbon-vertex substitution of anion **1**. There are two general methods to go about this: Direct substitution of the parent anion via deprotonation of the cluster {CH}-vertex followed by electrophilic attack, or selection of the appropriate aldehyde used in the Brellochs synthesis. This latter method led to the only known C-substituted *closo*-{CB$_7$} species, [1-(C$_6$H$_5$)-*closo*-1-CB$_7$H$_7$]$^-$, made in 49% yield starting from the reaction of *nido*-decaborane(14) with benzaldehyde[12,20]. Direct substitution, which is the common method used to prepare C-substituted derivatives for [*closo*-CB$_{11}$H$_{12}$]$^-$ and [*closo*-CB$_9$H$_{10}$]$^-$ anions[21,22], usually involves deprotonation by BuLi followed by electrophilic attack. Such a method proved unsuccessful with anion **1**, even with the use of BuLi in conjunction with ultra-sound and Schlosser's base (mixture of *n*-butyllithium and potassium *tert*-butoxide)[23]. If, however, these standard conditions were applied not to **1** but to the triiodo deravitive, anion **5**, then substitution at the carbon-vertex proved successful. Thus, cluster C–H deprotonation with *n*-BuLi at –70 °C in THF followed by the slow addition of CH_3I led to the formation of the single product [1-CH_3-*closo*-1-CB_7H_4-6,7,8-I_3]$^-$ (anion **9**; Fig. 3); the first eight-verrtex C-substituted monocarborane member prepared by direct substitution. After purification on a silica-gel column, anion **9** was isolated in 60% yield and characterized by multi-nuclear NMR spectroscopy and mass spectrometry.

As with anions **1** and **5**, NMR spectroscopy shows anion **9** to be fluxional, with just two resonance peaks in its ^{11}B-{^1H} spectrum of relative intensity ratio 4:3. The intensity 3 peak in the ^{11}B NMR spectrum is a singlet and thus evidence that the 3 iodide cluster ligands remain on the lower-belt cage positions, B(6,7,8). The relative positions of the intensity 3 and 4 peaks for anions **1**, **5** and **9** are interesting to compare. Scheme 3 presents the line diagrams of the ^{11}B-{^1H} spectra for anions **1**, **5** and **9**. In the parent anion **1** the two peaks are well separated. Substitution of the three lower-belt positions B(6,7,8) leads to the upfield shift of the intensity 3 peak and the downfield shift of the intensity 4 peak. One may expect that substitution with an electronegative ligand (electronegativity Pauling scale B = 2.04, I = 2.66) would result in a deshielding of the B(6,7,8) nuclei and a corresponding downfield chemical shift in the ^{11}B NMR spectrum. However, due to the importance of relativistic spin-orbit effects on the I-^{11}B chemical shifts (heavy atom effect)^{24}, which are known to overcompensate the

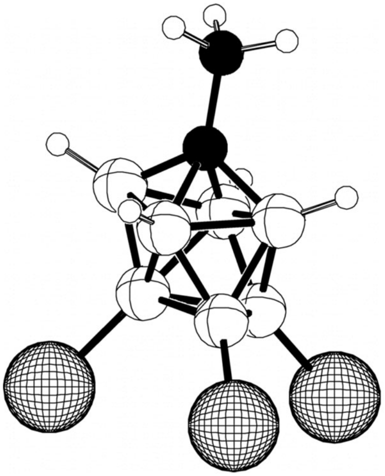
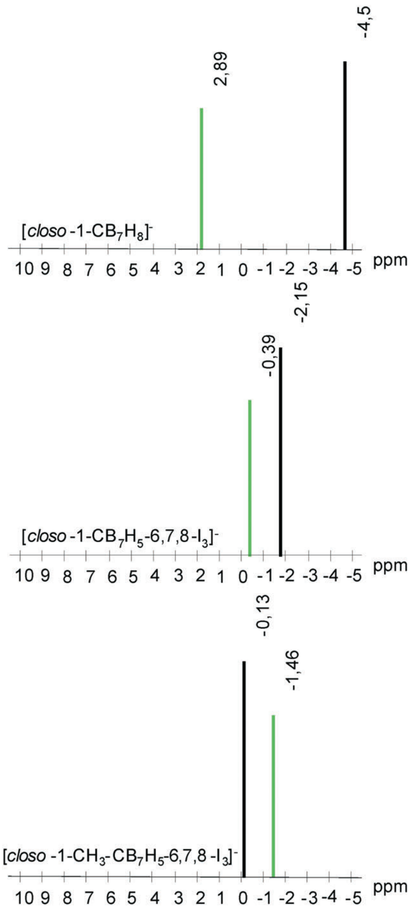


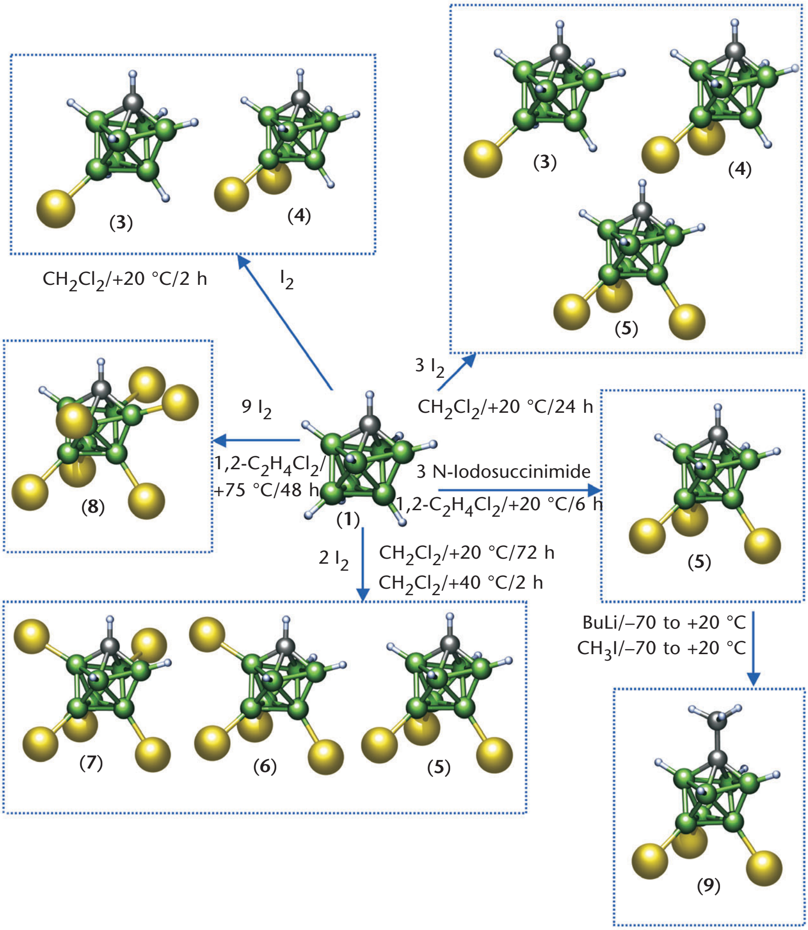
FIG. 3

Turbomole geometrically-optimalized static gas-phase structure for [1-CH_3-*closo*-1-CB_7H_4-6,7,8-I_3]$^-$ (anion **9**) trends caused by the greater electronegativity of heavier halogen substituents[24], there is an overall increase in shielding of the B(6,7,8) nuclei, and a resultant upfield shift of their ^{11}B NMR peak is observed. It is instead the upper-belt B(2,3,4,5) nuclei that experience deshielding, suggesting that triiodination has an influence on all seven boron nuclei. This trend is amplified by the methylation of the single cluster carbon vertex as shown in Scheme 3.



SCHEME 3
Line diagrams representative of the ^{11}B-{^{1}H} NMR spectra for anions **1**, **5** and **9** (from top to bottom)

Why carbon-vertex methylation occurs so readily with anion **5** and not at all with parent anion **1** is reasonably linked to the effect of the iodide substituents on the carborane cage, their presence conceivably resulting in an increase in the acidity of the cluster C–H bond. Computational calculations support this postulation. The gas-phase proton affinities shown in Table II in Supplementary Data indicate a stabilizing effect of the iodine



SCHEME 4

Reaction scheme summarizing all derivitives isolated from the iodination of the [*closo*-1-CB_7H_8]$^-$ (anion **1**) and the conditions of their formation. For detailed synthetic procedures of anions **5** to **9** please see Experimental. For syntheses of anions **3** and **4** see ref.[19]

atoms on the deprotonated dianion. Data from the single-crystal X-ray diffraction studies show an initial increase in the cluster C–H bond length with incremental iodination, suggesting higher bond polarization with increasing number of iodide substituents, followed by a significant decrease for the hexaiodo derivative (monoiodo derivative, anion **3**, 0.96 Å [19]; diiodo derivative, anion **4**, 0.98 Å [19]; hexaiodo derivative, anion **9**, 0.88 Å). However, this trend in bond polarity of the undissociated acids is likely to be of less relevance than the stabilities of the dissociated Lewis acid-base pair.

CONCLUSION

This study describes the conditions under which incremental iodination of the [*closo*-1-CB_7H_8]$^-$ (anion **1**) can be made (Scheme 4 for a summary) and discusses the implications that the structural studies have on the fluxional molecular dynamics shared by parent anion **1** and all its iodine derivatives. Additionally, we herein describe the direct C-substitution of anion **5**, a procedure not possible for the parent anion **1**. We currently are focusing our attention on probing the versatility of this method; preliminary results show that it works well with variety of electrophiles to produce benzyl and other C-substituted derivatives. We hope to report on these and other developments in the future.

EXPERIMENTAL

General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver[25], although some operations, such as column LC, were carried out in air. Aldrich 1,2-dichloroethane was dried over molecular 4A sieves and kept under inert atmosphere. THF was freshly distilled with sodium diphenylketyl before use. NMR spectra were recorded in acetonitrile-d_3. Other chemicals were reagent or analytical grade and were used as purchased. Column chromatography was carried out using silica gel (Aldrich 230–400 mesh) as the stationary phase. All R_F values quoted arise from analytical TLC monitoring of column chromatography products using Silufol silica TLC plates as a stationary phase and an eluting phase of 100% CH_2Cl_2 solvent. Mass spectra were obtained using a Thermo-Finnigan LCQ-Fleet ion trap instrument using electrospray ionization (ESI) with detection of negative ions. Samples dissolved in acetonitrile (concentrations approximately 100 ng ml^{-1}) were introduced to the ion source by infusion of 5 μl min^{-1}, source voltage 5.28 kV, tube lens voltage –84.8 V, capillary voltage –30.0 V, drying temperature was 188 °C, drying gas flow 8 l min^{-1}, auxiliary gas pressure 6 bar. ^{1}H, ^{13}C and ^{11}B NMR spectroscopy was performed on Varian Mercury 400Plus instrument. The spectra of all compounds were measured immediately after dissolution. The peak assignments are based on [^{11}B-^{11}B]-COSY and ^{1}H-{^{11}B(selective)} NMR experiments. ^{11}B NMR (128.3 MHz) chemical shifts are given in ppm to high-frequency (low field) to $F_3B·OEt_2$ as the external reference. Residual solvent ^1H resonances were used as internal secondary standards. ^1H (400 MHz) and ^{13}C NMR (100.6 MHz) chemical shifts were measured relative to the residual protons from acetonitrile-d_3 and referenced to Me_4Si.

Preparation of $[Bu_4N]^+$[*closo*-1-CB_7H_8]$^-$ (Compound **1**)

Compound **1** was prepared from commercially available *nido*-$B_{10}H_{14}$ using the literature method[14].

Preparation of $[Bu_4N]^+$[*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (compound **5**) using 3 molar equivalents of I_2

$[Bu_4N]^+$[*closo*-1-CB_7H_8]$^-$ (**1**; 0.11 g, 0.33 mmol) was dissolved in dichloromethane (20 ml) in a three-necked 100-ml round-bottom flask. Elemental iodine (0.25 g, 0.99 mmol) was added against a stream of argon, and the reaction mixture was stirred at ambient temperature for 24 h. A 10% aqueous solution of Na_2SO_3 (20 ml) was subsequently added and the combined mixture shaken until the red color disappeared. The individual layers were afterwards separated and the aqueous layer extracted with CH_2Cl_2 (3 × 20 ml). The combined CH_2Cl_2 layers were then evaporated to dryness on a rotary evaporator, resulting in formation of slightly yellow crystals. These crystals were dissolved in a small amount of CH_2Cl_2 and passed through a silica gel-column using CH_2Cl_2 as a mobile phase. A minor fraction with R_F 0.14 was collected and evaporated to dryness to give white crystals identified by ^{11}B and ^1H-{^{11}B} NMR as $[Bu_4N]^+$[*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (compound **5**). Yield 10 mg (1%). ^{11}B NMR: –0.39 (s, 3 B, B6-B8), –2.15 (d, 162, 4 B, B2-B5). ^1H-{^{11}B} NMR: 4.68 (s, 1 H, H1), 2.75 (s, 4 H, H2-H5), (Bu_4N^+) 3.05 (t, 8 H), 1.57 (q, 8 H), 1.32 (q, 8 H), 0.95 (t, 12 H). ^{13}C-{^1H} NMR: 59.09, 24.08, 20.12, 13.59 (Bu_4N^+). ESI MS (–) *m/z*: 473.92 (100%) for $CB_7H_5I_3$ (473.43).

Preparation of $[Bu_4N]^+$[*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (Compound 5) using N-Iodosuccinimide

$[Bu_4N]^+$[*closo*-1-CB_7H_8]$^-$ (**1**; 0.5 g, 1,48 mmol) was dissolved in dichloroethane (20 ml) in a three-necked 100-ml round-bottom flask. N-Iodosuccinimide (1.3 g, 5.78 mmol) was added against a stream of argon and the reaction mixture was stirred at ambient temperature for 6 h. A 10% aqueous solution of Na_2SO_3 (20 ml) was subsequently added and the combined mixture shaken until the red color disappeared. The individual layers were thence separated and the aqueous layer extracted with CH_2Cl_2 (3 × 20 ml). The combined dichloroethane and CH_2Cl_2 layers were then evaporated to dryness on a rotary evaporator, leading to the formation of small yellow crystals. These crystals were dissolved in a small amount of CH_2Cl_2 and passed through a silica-gel column using CH_2Cl_2 as a mobile phase. The major fraction with R_F 0.14 was collected and evaporated to dryness to give white crystals identified by ^{11}B and ^1H-{^{11}B} NMR as $[Bu_4N]^+$[*closo*-1-CB_7H_5-6,7,8-I_3]$^-$ (compound **5**). Yield 0.69 g (69%). ^{11}B NMR: –0.39 (s, 3 B, B6-B8), –2.15 (d, 162, 4 B, B2-B5). ^1H-{^{11}B} NMR: 4.68 (s, 1 H, H1), 2.75 (s, 4 H, H2-H5), (Bu_4N^+) 3.05 (t, 8 H), 1.57 (q, 8 H), 1.32 (q, 8 H), 0.95 (t, 12 H). ^{13}C-{^1H} NMR: 59.09, 24.08, 20.12, 13.59 (Bu_4N^+). ESI MS (–) *m/z*: 473.92 (100%) for $CB_7H_5I_3$ (473.43).

Preparation of $[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_4\text{-}I_4]^-$ (Compound 6) and $[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_3\text{-}I_5]^-$ (compound 7)

$[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_8]^-$ (**1**; 0.11 g, 0.33 mmol) was dissolved in dichloromethane (20 ml) in a three-necked 100-ml round-bottom flask. Elemental iodine (0.25 g, 0.99 mmol) was added against a stream of argon, and the reaction mixture was stirred at ambient temperature for 72 h and after that at 40 °C further 2 h. A 10% aqueous solution of Na_2SO_3 (20 ml) was subsequently added and the combined mixture shaken until the red color disappeared. The individual layers were thence separated and the aqueous layer extracted with CH_2Cl_2 (3 × 20 ml). The combined CH_2Cl_2 layers were then evaporated to dryness on a rotary evaporator, leading to the isolation of slightly yellow crystals. These crystals were dissolved in a small amount of CH_2Cl_2 and passed through a silica-gel column using CH_2Cl_2–hexane 2:1 as a mobile phase. Two main fractions (R_F 0.4 and 0.38) were collected and evaporated to dryness and white crystals were identified by ESI MS (–) as $[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_4\text{-}I_4]^-$ (compound **6**) *m/z* 600.82 (100%) for $CB_7H_4I_4$ (600.65) and $[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_3\text{-}I_5]^-$ (compound **7**) *m/z* 726.52 (100%) for $CB_7H_3I_5$ (726.54).

Preparation of $[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_2\text{-}2,3,4,6,7,8\text{-}I_6]^-$ (Compound 8)

$[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_8]^-$ (**1**; 0.1 g, 0.31 mmol) was dissolved in dichloroethane (20 ml) in a three-necked 100-ml round-bottom flask, to which a water condenser was attached. Elemental iodine (0.7 g, 2.76 mmol) was added against a stream of argon and the reaction mixture was stirred at 75 °C for 48 h. A 10% aqueous solution of Na_2SO_3 (20 ml) was subsequently added and the combined mixture shaken until the red color disappeared. The individual layers were thence separated and the aqueous layer extracted with CH_2Cl_2 (3 × 20 ml). The combined dichloroethane and CH_2Cl_2 layers were then evaporated to dryness on a rotary evaporator, resulting in the formation of slightly yellow crystals. These crystals were dissolved in a small amount of CH_2Cl_2 and passed through a silica-gel column using CH_2Cl_2 as a mobile phase. The main fraction with R_F 0.24 was collected and evaporated to dryness and slightly yellow crystals were identified by ^{11}B and $^{1}H\text{-}\{^{11}B\}$ NMR as $[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_2\text{-}2,3,4,6,7,8\text{-}I_6]^-$ (compound **8**). Yield 0.20 g (60%). ^{11}B NMR: 1.23 (s, 3 B, B6-B8), –3.46 (d, 162, 1 B, B5) –6,38 (s, 1 B, B3) –11.07 (s, 2 B, B2-B4). $^{1}H\text{-}\{^{11}B\}$ NMR: 5.30 (s, 1 H, H1), 3.25 (s, 1 H, H5), (Bu_4N^+) 3.10 (t, 8 H), 1.62 (q, 8 H), 1.37 (q, 8 H), 0.99 (t, 12 H). $^{13}C\text{-}\{^{1}H\}$ NMR: 59.10, 24.10, 20.14, 13.63 (Bu_4N^+). ESI MS (–) *m/z*: 851.50 (100%) for $CB_7H_2I_6$ (851.12).

Preparation of $[Bu_4N]^+[1\text{-}CH_3\text{-}\textit{closo}\text{-}1\text{-}CB_7H_4\text{-}6,7,8\text{-}I_3]^-$ (Compound 9)

$[Bu_4N]^+[\textit{closo}\text{-}1\text{-}CB_7H_5\text{-}6,7,8\text{-}I_3]^-$ (**5**; 0.2 g, 0.28 mmol) was dissolved in freshly distilled THF (20 ml) in a three-necked 50-ml round-bottom flask. The solution was cooled to –70 °C and 1.1 M *n*-BuLi in hexanes (0.4 ml, 0.44 mmol) was added dropwise. The solution was warmed to room temperature and stirred for a further 40 min. After this time, the solution was again cooled to –70 °C and CH_3I (0.8 ml, 12.6 mmol) was added dropwise. The reaction mixture slowly turned yellow upon warming to + 20 °C, at which temperature the mixture was stirred for further 12 h. EtOH (0.2 ml) was then added to quench any unreacted BuLi, after which all solvents were removed on a rotary evaporator, resulting in the isolation of a yellow oily liquid. This liquid was then diluted with a small amount of CH_2Cl_2 and passed through a silica-gel column using CH_2Cl_2 as a mobile phase. The main fraction from this separation with R_F 0.32 was collected and evaporated to dryness, giving a slightly yellowcolored oil identified by ^{11}B and ^{1}H-{^{11}B} NMR as $[Bu_4N]^+[1\text{-}CH_3\text{-}closo\text{-}1\text{-}CB_7H_4\text{-}6,7,8\text{-}I_3]^-$ (compound **9**). Yield 0.12 g (62%). ^{11}B NMR: –0.13 (d, 39, 4 B, B2-B5), –1.46 (s, 3 B, B6-B8). ^{1}H-{^{11}B} NMR: 2.71 (s, 4 H, H2-H5), 2.12 (s, 3 H, CH_3), (Bu_4N^+) 3.09 (t, 8 H), 1.61 (q, 8 H), 1.32 (q, 8 H), 0.94 (t, 12 H). ^{13}C-{^{1}H} NMR: 23.72 (s, CH_3), 64.17, 26.45, 22.09, 15.62 (Bu_4N^+). ESI MS (–) *m/z*: 487.92 (100%) for $C_2B_7H_7I_3$ (487.46).

X-ray Crystallography

Crystal data for compound **9**: $C_{16}H_{36}N{\cdot}CH_2B_7I_6$, M = 1093.55, monoclinic, $C2/c$ (No. 16), a = 20.9806(2) Å, b = 12.83720(10) Å, c = 27.0606(3) Å, β = 108.7707(6)°, V = 6900.65(11) Å^3 , Z = 8, D_x = 2.105 Mg m^{-3}. A yellow crystal of dimensions 0.37 × 0.25 × 0.2 mm was mounted into Lindemann capillary and measured at Nonius KappaCCD diffractometer by monochromatized MoKα radiation (λ = 0.71073 Å) at 150(2) K. Absorption corrections were carried out, using Gaussian integration from crystal shape[26] (μ = 5.41 mm^{-1}).

T_{min} = 0.176, T_{max} = 0.375; a total of 65376 measured reflections in the range h = –27 to 27, k = –16 to 16, l = –35 to 34 (θ_{max} = 27.5°), from which 7924 were unique (R_{int} = 0.049) and 6800 observed according to the $I > 2\sigma(I)$ criterion. Cell parameters from 51824 reflections (θ = 1–27.5°). The structure was solved by direct methods (SIR92 [27]) and refined by full-matrix least squares based on F^2 (SHELXL97 [28]). The hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors either H_{iso}(H) = 1.2 U_{eq}(pivot atom) or H_{iso}(H) = 1.5 U_{eq}(pivot atom) for methyl moiety. The refinement converged (Δ/σ_{max} = 0.001) to R = 0.028 for 6800 observed reflections and $wR(F^2)$ = 0.065, GOF = 1.09 for 293 parameters and all 7924 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 1.38, $\Delta\rho_{min}$ –1.03 e Å^{-3}).

CCDC 766240 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Computational Details

The structures of the parent anion **1** and its derivatives were optimized using the Turbomole[29,30] quantum chemistry package. The second order Møller–Plesset perturbation theory (MP2)[31] was used within the frame of the resolution of identity (RI) approximation[32]. Triple-zeta basis set with polarization functions def2-TZVP [33] was employed along with the corresponding auxiliary basis[34]. Charge distribution in the molecules was estimated by natural population analysis (NPA)[35].

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