Inorg. Chem. **2006**, *45*, 336–340

Inorganic Chemistry

Article

Synthesis and Structural Characterization of Symmetrical *closo*-4,7-I_2-1,2-$C_2B_{10}H_{10}$ and [$(CH_3)_3NH$][*nido*-2,4-I_2-7,8-$C_2B_9H_{10}$]

Bhaskar M. Ramachandran, Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095

Received August 15, 2005

The boron-atom insertion reaction of *nido*-9,11-I_2-7,8-$C_2B_9H_9^{2-}$, with the $HBCl_2$:SMe_2 complex yields *closo*-4,7-I_2-1,2-$C_2B_{10}H_{10}$, **1**, in excellent yield. Although the two boron atoms (B3 and B6) nearest to the carbon atoms in **1** are equally available for attack by nucleophiles, the boron-degradation reaction of **1** with alkoxide ion occurs only at the B6 vertex, yielding regioselectively [$(CH_3)_3NH$][*nido*-2,4-I_2-7,8-$C_2B_9H_{10}$], **2**. The molecular structures of **1** and **2** have been determined by X-ray diffraction studies. Crystallographic data are as follows. For **1**, monoclinic, space group $P2_1/n$, $a = 6.9199(19)$ Å, $b = 23.9560(7)$ Å, $c = 7.2870(2)$ Å, $\beta = 94.081(4)°$, $V = 1204.9(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.18$ g cm^{-3}, $R = 0.020$, $R_w = 0.0610$; for **2**, orthorhombic, space group $Pca2_1$, $a = 14.1141(7)$ Å, $b = 7.0276(4)$ Å, $c = 16.4602(9)$ Å, $V = 1632.7(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.81$ gcm^{-3}, $R = 0.022$, $R_w = 0.0623$

Introduction

The utility of 1,2-dicarba-*closo*-dodecaborane (*o*-carborane) as a building block for macrocyclic and supramolecular assemblies has been the focus of many recent reports.[1] The acidity of the C–H vertexes of *o*-carborane enables the formation of hydrogen bonds[2] used in the generation of supramolecular structures. This, coupled with the symmetry of the icosahedral carborane cage and the high thermal and chemical stability, has led to its use as a desirable building unit with many promising applications.[3] A vital factor for the further development of this field is the ability to selectively introduce diverse functional groups at boron vertexes of the *o*-carborane cage.

The acidic nature of the C–H vertexes of the *o*-carborane cage facilitates a versatile range of substitution variations at these positions by common organometallic reagents, while leaving the relatively hydridic B–H vertexes unaffected.[4] However, functionalization of the boron vertexes is comparatively less straightforward, but a predisposition to apparent electrophilic substitution reactions provides a similarity to aromatic arene systems.[5] The two boron atoms (B3 and B6) closest to the carbon atoms on the cage are the most electron-poor and hence are attacked by a variety of nucleophiles, such as alkoxide[6] and fluoride[7] anions, in the presence of protons. The resulting nido-carborane, *nido*-7,8-$C_2B_9H_{12}^-$, lacks one of the two boron atoms adjacent to the two carbon atoms in the closo-carborane. Treatment of the *nido*-7,8-$C_2B_9H_{12}^-$ ion with a base, such as NaH or *n*-BuLi, yields the corresponding dicarbollide dianion *nido*-7,8-$C_2B_9H_{11}^{2-}$. Functionalization of the B3 vertex of the *o*-carborane cage may be achieved by reconstruction of this closo-cage with the insertion of a substituted boron-atom electrophile into a dicarbollide dianion, as demonstrated by Hawthorne et. al. in 1968.[8] Another route for the introduction of substituents on the boron vertexes involves the reaction of B-iodinated *o*-carboranes with a variety of Grignard reagents under Pd-catalyzed cross-coupling conditions to form a B–C bond.[9] The most commonly employed method for the introduction of iodine at the boron vertexes of the *o*-carborane cage involves electrophilic iodination of

---

(1) (a) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267. (b) Lee, H.; Knobler, C. B.; Hawthorne, M. F. *Chem. Commun.* **2000**, 2485.

(2) (a) Kruglyak, L. I.; Kalinin, V. N.; Rys, E. G.; Zakharkin, L. I.; Shatenstein, A. I. *Zh. Obshch. Khim.* **1972**, *42*, 2670. (b) Leites, L. A. *Chem. Rev.* **1992**, *92*, 279.

(3) (a) Hawthorne, M. F. *Pure Appl. Chem.* **1991**, *63*, 327. (b) Brown, A.; Colquhoun, H. M.; Daniels, J. A.; MacBride, J. A. H.; Stephenson, I. R.; Wade, K. *J. Mater. Chem.* **1992**, *2*, 793.

(4) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.

(5) (a) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209. (b) Grushin, V. V.; Bregadze, V. I.; Kalinin, V. N. *J. Organomet. Chem.* **1988**, *20*, 1.

(6) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

(7) (a) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812. (b) Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; ColquHoun, H. M.; Wade, K. *Polyhedron* **1996**, *15*, 565. (c) Getman, T. D. *Inorg. Chem.* **1998**, *37*, 3422. (d) Yoo, J.; Hwang, J. W.; Do, Y. *Inorg. Chem.* **2001**, *40*, 568.

(8) Hawthorne, M. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 896.

10.1021/ic051395w CCC: $33.50

© 2006 American Chemical Society

Published on Web 11/17/2005

o-carborane with iodine or iodine monochloride (ICl) in the presence of $AlCl_3$ and methylene chloride as solvent.[9a,10] Another way to introduce iodine atoms onto boron atoms is by the double displacement reaction of boron triiodide with the dicarbollide dianion *nido*-7,8-$C_2B_9H_{12}^{2-}$.[9a] Recently, Endo et al.[11] have utilized a combination of the boron-atom insertion reaction and the electrophilic iodination reaction in the regioselective synthesis of 3,6,9-triiodo- and 3,6,9,-12-tetraiodo-*o*-carborane.

The significance and the wide-ranging applications of this field of chemistry led us to reinvestigate a previously[12] reported diiodo nido-carborane salt, $[(CH_3)_3NH]$[*nido*-9,11-I_2-7,8-$C_2B_9H_{10}$], **3**, prepared by the initial rapid electrophilic attack of formal I^+ upon the open face of the *nido*-7,8-$C_2B_9H_{12}^-$ ion. The application of these easily formed iodinated nido-carborane compounds as both radioiodine carriers and as precursors for boron neutron capture therapy (BNCT) agents[13] remains under investigation. Herein, we wish to report the synthesis and structural determination of two new symmetrical iodinated compounds, *closo*-4,7-I_2-1,2-$C_2B_{10}H_{10}$, **1**, formed unexpectedly during the boron insertion with the dicarbollide dianion *nido*-7,8-$C_2B_9H_{11}^{2-}$ and the nido-carborane salt $[(CH_3)_3NH]$[*nido*-2,4-I_2-7,8-$C_2B_9H_{10}$], **2**, which is formed regioselectively when **1** is subjected to the stereoselective deboronation reaction with alcoholic base.

Experimental Section

General Considerations. Standard Schlenk line and glovebox techniques were employed for the manipulation of water- and air-sensitive reagents and products. Solvents used were reagent-grade, dried over an appropriate drying agent, and distilled under nitrogen. Ether and *n*-hexane were distilled from a sodium−benzophenone still prior to use. **3** was prepared by previously reported literature methods.[12] Boron triiodide and dichloroborane−methyl sulfide complex were obtained from Aldrich Chemical Co. and used as received. *n*-Butyllithium was obtained from Acros Chemical Co. and used as received.

Physical Measurements. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker ARX 500 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to signals of residual ^1H and ^{13}C present in deuterated solvents. Chemical shift values for ^{11}B NMR spectra were referenced relative to external $BF_3{\cdot}OEt_2$ ($\delta = 0.0$ ppm with negative values indicating an upfield shift). Mass spectra were obtained using a VG Autospec (EI) and an electrospray mass spectrometer.

Preparation of *closo*-4,7-I_2-1,2-$C_2B_{10}H_{10}$, 1. The salt $[(CH_3)_3NH]$[*nido*-9,11-I_2-7,8-$C_2B_9H_{10}$], **3**, (1.00 g, 2.2 mmol) was placed in 30 mL of anhydrous ethyl ether in a 100 mL three-necked flask equipped with a magnetic stir-bar, reflux condenser, and gas inlet and outlet. The system was slowly flushed with argon. A solution of 2.5 M butyllithium in hexane (1.8 mL, 4.4 mmol) was added dropwise to the stirring mixture at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature for 2 h and then refluxed for 4 h. After the reaction mixture was cooled to room-temperature, all solvent was removed under vacuo. Anhydrous hexane (50 mL) was syringed into the remaining solid followed by dichloroborane−methyl sulfide complex (0.4 mL, 3.0 mmol) at 0 °C. The mixture was stirred for an additional 6 h at room temperature and then was hydrolyzed with 10 mL of water to quench excess dichloroborane. The organic layer was separated from the mixture, dried over $MgSO_4$, and then concentrated on a rotovap. The resulting solid was purified by recrystallization from a mixture of 4:1 hexane/ethyl acetate to give **1**. Yield = 72% (0.63 g, 1.6 mmol), mp: 94−95 °C. ^1H NMR (δ, ppm, CD_2Cl_2) 4.23 (s, 2H), 3.21−1.52 (m, 8H). ^{11}B NMR (δ, ppm, CD_2Cl_2) 0.4 (d, 2B, J_{B-H} 152), −5.3 (s, 1B, J_{B-H} 157), −7.9 (d, 1B, J_{B-H} 153), −10.9 (d, 1B, J_{B-H} overlapping), −12.6 (d, 3B, J_{B-H} 170), −27.2 (s, 2B). ^{13}C NMR (δ, ppm, CD_2Cl_2) 59.7 (s, carborane *C*H). HR-EIMS: *m*/*z*: calcd 397.9802; found 397.9788.

Table 1. Crystallographic Data for Compounds **1** and **2**[a]

empirical formula	$C_2H_{10}B_{10}I_2$	$C_5H_{20}B_9I_2N$
temp	298(2) K	298(2) K
wavelength	0.71073 Å	0.71073 A
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$Pca2_1$
a	6.9199(19) Å	14.1141(7) Å
b	23.956(7) Å	7.0276(4) Å
c	7.287(2) Å	16.4602(9) Å
β	94.081(4)°	90°
V	1204.9(6) Å^3	1632.7(15) Å^3
Z	4	4
ρ_{calcd}	2.183 g cm^{-3}	1.812 g cm^{-3}
absorption coefficient	5.164 mm^{-1}	3.824 mm^{-1}
GOF on F^2	1.005	1.018
final R indices [$I > 2\sigma(I)$]	$R = 0.0199$ $R_w = 0.0608$	$R = 0.0220$ $R_w = 0.0623$

[a] $R = \Sigma\,||F_0| - |F_c||/|F_0|$. $R_w = [\Sigma\, w(|F_0| - |F_c|)^2]^{1/2}$ where $w = 1/\sigma^2|F_0|$.

Preparation of $[(CH_3)_3NH]$[*nido*-2,4-I_2-7,8-$C_2B_9H_{10}$], 2. A solution of 0.14 g (2.5 mmol, 100% excess) of potassium hydroxide in 50 mL of absolute ethanol was placed in a 100 mL three-necked flask equipped with a magnetic stir-bar, a reflux condenser, and a gas inlet and outlet. After the solution was cooled to room temperature, **1** (0.50 g, 1.3 mmol) was added and was stirred for 1 h at room temperature and then was heated to reflux temperature until hydrogen evolution ceased (2 h). After cooling, an additional 20 mL of absolute ethanol was added. The excess potassium hydroxide was precipitated as potassium carbonate by saturating the solution with a stream of carbon dioxide. The precipitate was removed by filtration and washed with five 15 mL portions of ethanol. The combined filtrate and washings were evaporated to dryness to yield the crude potassium salt, which was dissolved in water and reprecipitated as the trimethylammonium salt by the addition of 0.50 g (5.2 mmol) of trimethylamine hydrochloride in 20 mL of water. The precipitated trimethylammonium salt, **2**, was isolated by filtration, washed with 10 mL of cold water and dried in vacuo. Yield = 92% (0.51 g, 1.2 mmol), mp: 139−140 °C. ^1H NMR (δ, ppm, C_3D_6O) 3.18 (m, $(CH_3)_3$ 9H), 2.39 (s, CH, 2*H*), −3.21 (br, s, endo, 1*H*) ^{11}B NMR (δ, ppm, C_3D_6O) −9.1 (d, 2B, J_{B-H} 141), −13.7 (d, 3B, J_{B-H} 147), −31.6 (s, 3B), −33.5 (d, 1B, J_{B-H} 146). ^{13}C NMR (δ, ppm, C_3D_6O) 49.1 (s, carborane *C*H), 45.5 (s, $(CH_3)_3$. HR-ESMS: *m*/*z*: calcd 386.9716; found 386.9723.

X-Ray Crystallography. Table 1 lists a summary of crystallographic data for **1** and **2**.

Collection and Reduction of X-Ray Data for 1. A colorless crystalline cut parallelepiped obtained from a hexane/ethyl acetate

---

[9] (a) Li, J.; Logan, C. F.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 4866. (b) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095. (c) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Z. S. *J. Organomet. Chem.* **1982**, *226*, 217.

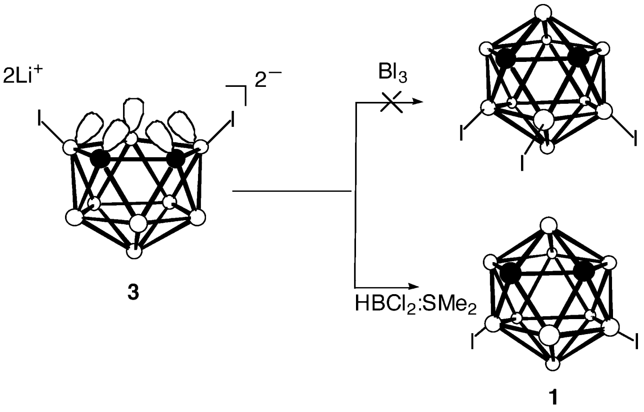
[10] Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095.

[11] Yamazaki, H.; Ohta, K.; Endo, Y. *Tetrahedron Lett.* **2005**, *46*, 3119.

[12] Pak, R. H.; Kane, R. R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1994**, *33*, 5355.

[13] Mizusawa, E. A.; Thompson, M. R.; Hawthorne, M. F. *Inorg. Chem.***1985**, *24*, 1911.

Scheme 1



solution was mounted on a thin glass fiber on a Bruker SMART 1000 ccd diffractometer. Unit cell parameters were determined from a least-squares fit of 4249 reflections (5.90° $< 2\theta <$ 56.60°). These dimensions and other parameters, including conditions of data collection, are summarized in Table 1. Data were collected at 25 °C. Of the 2904 unique reflections measured, 2732 were considered observed ($F_o > 4\sigma (F_o)$), but all reflections were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for extinction and absorption. Programs used in this work are those supplied with the Bruker SMART 1000 ccd diffractometer.

Solution and Refinement of the Structure of 1. Atoms were located by use of statistical methods. All nonhydrogen atoms were included with anisotropic displacement parameters. Position parameters of all hydrogen atoms were allowed to vary. The isotropic displacement parameters for hydrogen atoms were based on the values for the attached atoms. Scattering factors for H were obtained from Stewart et al.[14] The maximum and mininum values on a final difference electron density map were 0.52 and −0.48 e Å^{-3}.

Collection and Reduction of X-ray Data for 2. A colorless crystalline cut rod obtained from an acetone solution was mounted on a thin glass fiber on a Bruker SMART 1000 ccd diffractometer. Unit cell parameters were determined from a least-squares fit of 6495 reflections (4.95° $< 2\theta <$ 56.40°). These dimensions and other parameters, including conditions of data collection, are summarized in Table 1. Data were collected at 25 °C. Intensities did not decay during the course of the experiment. Of the 3435 unique reflections measured, 3197 were considered observed ($F_o > 4\sigma (F_o)$), but all reflections were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for extinction and absorption. Programs used in this work are those supplied with the Bruker SMART 1000 ccd diffractometer.

Solution and Refinement of the Structure for 2. Atoms were located by use of statistical methods. All non-hydrogen atoms were included with anisotropic displacement parameters. Methyl hydrogen atoms were placed in calculated positions. Position parameters of all other hydrogen atoms were allowed to vary. The isotropic displacement parameters for hydrogen atoms were based on the values for the attached atoms. Scattering factors for H were obtained from Stewart et al. The maximum and mininum values on a final difference electron density map were 0.48 and −0.42 e Å^{-3}.

Results and Discussion

Efforts to prepare a new triiodinated *o*-carborane (as shown in Scheme 1) yielded unexpected results. The reaction of *nido*-9,11-I_2-7,8-$C_2B_9H_9^{2-}$ dicarbollide dianion with BI_3 did not give the expected 3,4,7-triiodo-*o*-carborane. Instead, a new diiodo-carborane, **1**, was obtained as a single product in low yields. **1** was obtained as an air-stable white solid after recrystallization from 4:1 hexane/ethyl acetate. The composition of **1** was established by mass spectrometry, and the proposed structure is also supported by its NMR data, which were further confirmed by the crystallographic study (Figure 1). In the ^{11}B{H} NMR of **1**, the resonance at −27.2 ppm corresponds to two boron atoms and does not exhibit coupling which is consistent with the presence of two B−I bonds. Selected bond lengths and bond angles for **1** are summarized in Table 2.

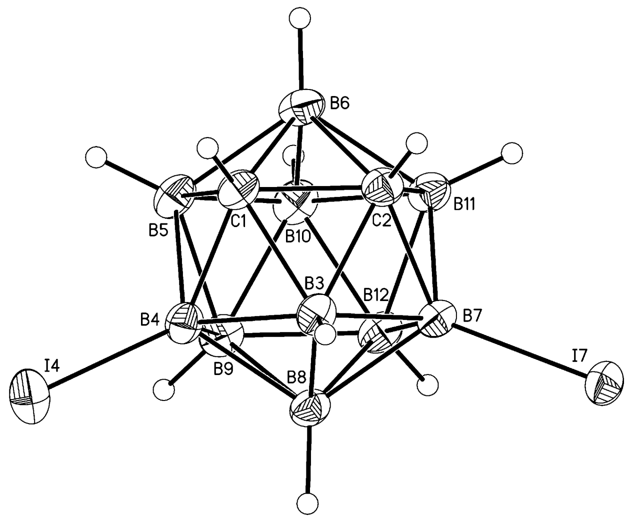


Figure 1. ORTEP representation of *closo*-4,7-I_2-1,2-$C_2B_{10}H_{10}$, **1**.

Table 2. Selected Bond Lengths and Angles for **1**

lengths (Å)		angles (deg)	
C(1)−C(2)	1.627(4)	C(1)−B(4)−I(4)	120.19(19)
C(1)−B(4)	1.692(4)	B(9)−B(4)−I(4)	126.8(2)
C(1)−B(5)	1.696(4)	B(8)−B(4)−I(4)	123.71(19)
C(1)−B(6)	1.719(4)	B(3)−B(4)−I(4)	116.62(18)
C(1)−B(3)	1.731(4)	B(5)−B(4)−I(4)	121.86(19)
C(2)−B(11)	1.690(4)	C(2)−B(7)−I(7)	119.91(18)
C(2)−B(7)	1.697(4)	B(8)−B(7)−I(7)	124.72(18)
C(2)−B(6)	1.722(4)	B(3)−B(7)−I(7)	116.90(18)
C(2)−B(3)	1.726(4)	B(12)−B(7)−I(7)	127.61(19)
B(4)−I(4)	2.165(3)	B(11)−B(7)−I(7)	121.40(19)
B(7)−I(7)	2.159(3)		

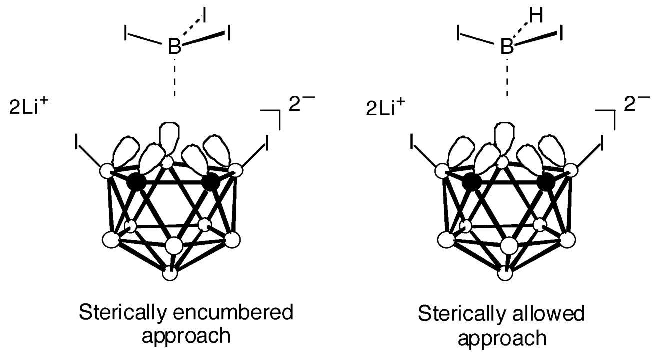
The surprising formation of **1**, instead of the expected triiodo-carborane derivative, suggested that steric hindrance may play a role in the formation of the final product. Two types of steric strain recognized by Brown[15] that may influence the formation of one product over the other are (i) a face-to-face interference due to the presence of two bulky iodine atoms on the open pentagonal face of the dianion (Scheme 2), pointing upward and away from the open face preventing the close approach of the capping reagent, called “F-strain” and (ii) the strain generated in forcing the three bulky iodine atoms in the planar boron atom (in BI_3) closer, to a near tetrahedral geometry during the capping reaction (Scheme 2), called “B-strain”, indicating the strain localized

---

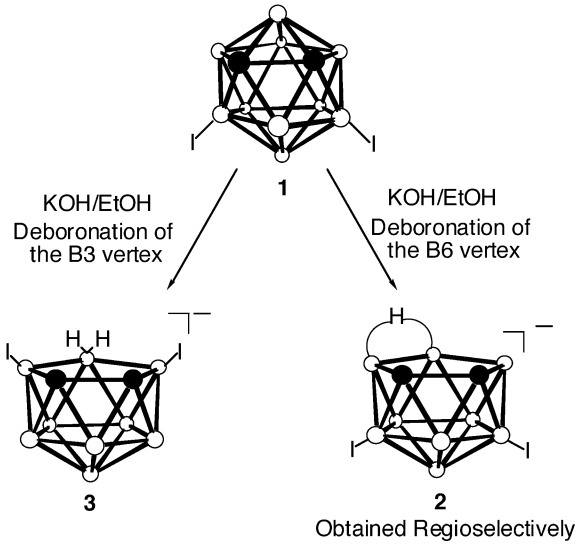
(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42* 3175.

(15) (a) Brown, H. C.; Bartholomay, H.; Taylor, M. D. *J. Am. Chem. Soc.* **1944**, *66*, 435. (b) Brown, H. C.; Fletcher, E. A. *J. Am. Chem. Soc.* **1951**, *73*, 2808.

Scheme 2



Scheme 3



at the back of the molecule. For the case under discussion, the latter B-strain may be the determining factor in the formation of the final product, which results from a B−H (from traces of HBI_2) moiety (lesser B-strain) taking part in the capping reaction (Scheme 2) rather than B−I (from BI_3) (greater B-strain). The targeted synthesis of **1** using the dichloroborane−methyl sulfide complex as the capping reagent resulted in increased yields (72%).

The above results led us to further investigate the availability of the B3 vertex of **1**, sandwiched between two iodine atoms, for further reactions. As shown previously,[6] the two boron atoms (B3 and B6) closest to the carbon atoms on the cage are the most electron-poor and hence are equally susceptible to attack by a variety of nucleophiles. As shown in Scheme 3, if the deboronation reaction occurs at the B3 vertex of **1**, the product will be the previously[12] known compound, **3**, with the 12th or the "extra hydrogen" located on the B10 vertex. The product of the deboronation reaction at the B6 vertex of **1** would produce a new diiodo-nido-compound, **2** (Figure 2), with the 12th or the "extra hydrogen" located between the B10 and B11 atoms. The base-promoted deboronation reaction of **1** resulted in the regioselective formation of **2** as a single product in high yields. This result suggests that the availability of the B3 vertex of **1**, located between two iodine atoms, to the attacking nucleophile is hindered, and the deboronation reaction occurs exclusively at the B6 vertex.

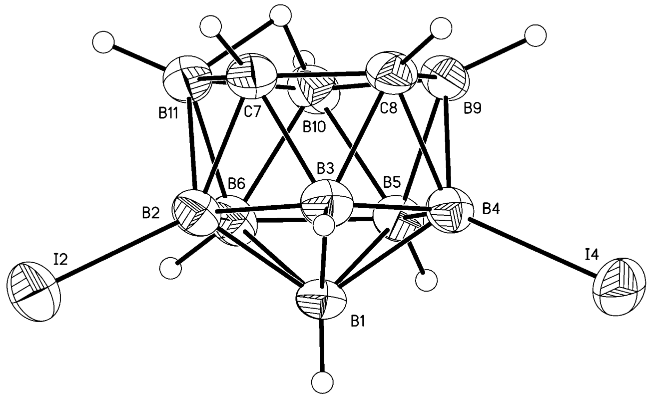


Figure 2. ORTEP representation of *nido*-2,4-I_2-7,8-$C_2B_9H_{10}^-$, **2**.

Table 3. Selected Bond Lengths and Angles for **2**

lengths (Å)		angles (deg)	
B(1)−B(2)	1.735(6)	C(7)−B(2)−I(2)	122.4(3)
B(1)−B(4)	1.756(5)	B(1)−B(2)−I(2)	122.7(2)
B(1)−B(3)	1.780(5)	B(3)−B(2)−I(2)	117.6(2)
B(1)−B(6)	1.802(5)	B(6)−B(2)−I(2)	125.2(2)
B(1)−B(5)	1.804(5)	B(11)−B(2)−I(2)	121.2(3)
B(2)−C(7)	1.688(5)	C(7)−B(3)−C(8)	53.4(2)
B(2)−B(3)	1.740(5)	C(7)−B(3)−B(2)	58.5(2)
B(2)−B(6)	1.747(5)	C(8)−B(3)−B(2)	100.8(3)
B(2)−B(11)	1.788(6)	C(7)−B(3)−B(4)	102.3(3)
B(2)−I(2)	2.198(4)	C(8)−B(3)−B(4)	58.9(2)
B(3)−C(7)	1.715(6)	B(2)−B(3)−B(4)	106.4(3)
B(3)−C(8)	1.729(6)	C(8)−B(4)−B(9)	54.8(2)
B(3)−B(4)	1.754(6)	B(5)−B(4)−B(9)	59.8(2)
B(4)−C(8)	1.714(5)	B(3)−B(4)−B(9)	107.7(3)
B(4)−B(5)	1.737(4)	B(1)−B(4)−B(9)	109.4(2)
B(4)−B(9)	1.773(5)	C(8)−B(4)−I(4)	124.1(2)
B(4)−I(4)	2.191(4)	B(5)−B(4)−I(4)	126.1(2)
B(5)−B(9)	1.751(5)	B(3)−B(4)−I(4)	116.9(2)
B(5)−B(10)	1.763(6)	B(1)−B(4)−I(4)	122.4(2)
B(5)−B(6)	1.828(6)	B(9)−B(4)−I(4)	122.9(2)
B(6)−B(11)	1.777(6)		
B(6)−B(10)	1.782(5)		
C(7)−C(8)	1.547(6)		
C(7)−B(11)	1.620(6)		
C(8)−B(9)	1.605(6)		
B(9)−B(10)	1.816(5)		
B(10)−B(11)	1.857(6)		
N(1C)-C(1C)	1.444(8)		
N(1C)-C(3C)	1.466(7)		
N(1C)-C(2C)	1.482(8)		

2 was obtained as a crystalline white product after recrystallization from acetone solution. The composition of **2** was established by mass spectrometry, and the proposed structure is also supported by its NMR data, which were further confirmed by the crystallographic data (Figure 2). In the $^{11}B\{H\}$ NMR of **2**, the resonance at −31.6 ppm does not exhibit coupling which is consistent with the presence of two B−I bonds. Selected bond lengths and bond angles for **2** are summarized in Table 3. In the monoanion, the bridging B−H−B hydrogen atom is located between B10 and B11, B10−H101 = 1.11(5) Å and B11−H101 = 1.37(5) Å. B10−H101−B11 = 97(3)°. Iodine atoms are bonded to boron atoms B2 and B4 and are meta with respect to each other. These boron atoms are also adjacent to the ortho carbon atoms C7 and C8, respectively.

Conclusion

Previously,[8] selective deboronation of the B6 vertex could be achieved by functionalizing the B3 vertex. In this study, we have systematically shown that the same results can be achieved by sterically masking the B3 vertex from the nucleophile. Compounds reported in this paper provide useful symmetrical intermediates for use as carboracycle and supramolecular precursors.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE-0111718) and equipment grants (No. CHE-9871332) and (No. CHE-9974928) for their support of this research. We also thank US Borax, Inc. for a generous grant-in aid.

Supporting Information Available: Tables of information on data collection, structure solution and refinement, atom coordinates, anisotropic displacement parameters, and all bond distances and angles of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051395W