

## PREPARATION OF [closo-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> BY DICHLOROCARBENE INSERTION INTO [nido-B<sub>11</sub>H<sub>14</sub>]<sup>-</sup>

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*Dedicated to the memory of Professor Stanislav Heřmánek.*

In strongly basic media, the [nido-B<sub>11</sub>H<sub>14</sub>]<sup>-</sup> anion reacts with the haloforms. Dehydrogenation to [closo-B<sub>11</sub>H<sub>11</sub>]<sup>2-</sup> is the only reaction observed with iodoform. With chloroform and bromoform, the cage is expanded by dihalocarbene insertion. The dominant products are the [closo-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> and the [2-Br-closo-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion, respectively. The chief side product is the [closo-B<sub>11</sub>H<sub>11</sub>]<sup>2-</sup> anion, which results from dehydrogenation of the starting material. It was identified by <sup>11</sup>B NMR spectroscopy and isolated after acidic aqueous workup in the form of the [nido-7-OH-B<sub>11</sub>H<sub>13</sub>]<sup>-</sup> anion. Since the starting [nido-B<sub>11</sub>H<sub>14</sub>]<sup>-</sup> anion is available from NaBH<sub>4</sub> and BF<sub>3</sub>·Et<sub>2</sub>O in 50% yield, its conversion to [closo-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> with chloroform and base in a 40% yield represents a useful laboratory route to the numerous known but previously very expensive derivatives of [closo-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup>, highly prized for their very low nucleophilicity.

**Keywords:** Boranes; Carboranes; [closo-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion; Dihalocarbenes; Haloforms.

The [closo-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion<sup>1</sup> (**1**) serves as a starting material for the preparation of many extremely weakly nucleophilic anions<sup>2,3</sup>, interesting for their ability to stabilize highly electrophilic and/or oxidizing cations and for possible practical applications as catalyst counterions in olefin polymerization, as electrolytes in lithium ion batteries, *etc.* A few examples of such “inert” anions are [closo-CB<sub>11</sub>H<sub>n</sub>Hal<sub>12-n</sub>]<sup>-</sup> (refs<sup>4,5</sup>), [closo-CB<sub>11</sub>Me<sub>12</sub>]<sup>-</sup> (ref.<sup>6</sup>), and [closo-CB<sub>11</sub>(CF<sub>3</sub>)<sub>12</sub>]<sup>-</sup> (ref.<sup>7</sup>). Unfortunately, all these useful anions are presently very expensive because of the high cost of **1**, and this severely limits their utility. The best available route<sup>8</sup> to **1** uses a quite expensive starting material, B<sub>10</sub>H<sub>14</sub>, and involves several steps.

We now describe a simple one-step synthesis of the Me<sub>3</sub>NH<sup>+</sup> salt of **1** in 40% yield from the Me<sub>3</sub>NH<sup>+</sup> salt of [*nido*-B<sub>11</sub>H<sub>14</sub>]<sup>-</sup> (**2**), which is in turn accessible<sup>9</sup> in 50% yield from NaBH<sub>4</sub> and BF<sub>3</sub>·Et<sub>2</sub>O. The insertion of a single carbon atom into the cage is accomplished by the use of dichlorocarbene, generated *in situ* from chloroform and a base. In the presence of nucleophiles, the insertion reaction leads to derivatives of (**1**) carrying the nucleophile in position 2 (see Fig. 1 for position labels); these have been characterized as their bis(triphenylphosphine)iminium [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PNP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sup>+</sup>(PNP<sup>+</sup>) salts. The carbene insertion reaction promises to be general.

## EXPERIMENTAL

### General

The PNP<sup>+</sup> salts (<sup>31</sup>P NMR signal at 22.25 ppm) of the new anions were prepared by reaction of other salts with aqueous PNP<sup>+</sup>Cl<sup>-</sup>. HPLC separations were done on a Waters 600 instrument with an ELS detector (SEDEX 65), employing a reverse phase C<sub>18</sub> column and a mobile phase based on methanol and water (MeOH/H<sub>2</sub>O mixture, 10 l; NEt<sub>3</sub>, 70 ml; HOAc, 100 ml). Electrospray negative ion mass spectra were obtained on acetonitrile solutions with a Hewlett-Packard 5989 API/ES/MS instrument (the most intense peak in each spectrum is listed). NMR spectra (δ, ppm) were measured in CDCl<sub>3</sub>. <sup>1</sup>H spectra showed indistinct broad peaks for BH protons; only CH protons are listed. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P spectra were measured with a 500 MHz Varian Unity Inova instrument; positive shifts are downfield and are expressed against TMS and H<sub>3</sub>PO<sub>4</sub> standards. <sup>11</sup>B, <sup>11</sup>B{<sup>1</sup>H}, and <sup>11</sup>B-<sup>11</sup>B COSY spectra were measured with a 300 MHz Varian VXR 300 instrument. Assignment of the boron signals to individual vertices (shown in parentheses) and the position of the substituent were estab-

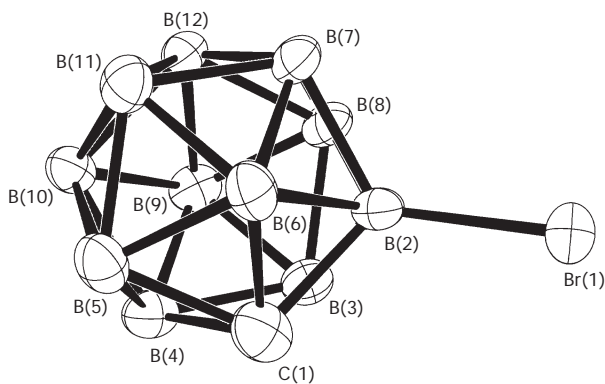


FIG. 1  
ORTEP representation of **7** in PNP<sup>+</sup>[2-Br-*closo*-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup>

lished by  $^{11}\text{B}$ - $^{11}\text{B}$  COSY NMR. The signals of B atoms without an attached H are labeled with s; the reference is  $\text{B}(\text{OMe})_3$  at 18.1 ppm. Elemental analyses were performed on PNP<sup>+</sup> salts by Desert Analytics, Tucson, AZ.

#### Reaction of $\text{Na}^+$ Salt of **2** with $\text{CHCl}_3$ and Base

In a 2 l two-neck flask the  $\text{Me}_3\text{NH}^+$  salt of **2** (ref.<sup>9</sup>) (20 g, 0.104 mol) was dissolved in THF (200 ml) under an argon atmosphere. The solution was cooled to 0 °C and NaH (95%, 23 g, 0.91 mol) was added carefully. After stirring 30 min at room temperature, the mixture was evaporated to dryness under reduced pressure and THF (400 ml) and  $\text{CHCl}_3$  (30 ml, 0.375 mol) were added. The reaction mixture was stirred for 2 h at ambient temperature. EtOH (80 ml) was added dropwise at 0 °C and stirring was continued for 4 h at room temperature. Water (600 ml) was added and THF was evaporated under reduced pressure. The solution was acidified by addition of 10% HCl. Residual THF and EtOH were removed under reduced pressure. After addition of  $\text{Me}_3\text{NH}^+\text{Cl}^-$  (20 g, 0.2 mol) a white solid precipitated. It was separated and dried under reduced pressure to yield colorless  $\text{Me}_3\text{NH}^+$  salt of **1** (8.9 g, 42%), usually containing a few % of the 2-chloro derivative **3** as judged by  $^{11}\text{B}$  NMR. If desired, this can be removed by crystallization from hot water/methanol (9 : 1).

A small amount of **3** was isolated from the crude reaction mixture by HPLC using a  $\text{MeOH}/\text{H}_2\text{O}$  (1 : 1) eluent. The elution times were 20 min for **1** and 26 min for **3**. After evaporation of methanol from the slow fraction and addition of CsCl (1 g), the aqueous layer was extracted three times with diethyl ether, the combined ether layers were evaporated to dryness, the residue was dissolved in water (50 ml) and a saturated solution of  $\text{PNP}^+\text{Cl}^-$  in water (30 ml) was added to precipitate the PNP salt of **3**, which was then dried under reduced pressure. MS (*z/e*): 177. NMR:  $^{11}\text{B}\{^1\text{H}\}$ : -6.0 (2 s), -7.1 (12), -12.9 (7,11), -14.4 (3,6,8,10), -16.4 (4,5), -17.8 (9);  $^1\text{H}$ : 2.68  $\text{CH}_{\text{cage}}$ ,  $^{13}\text{C}$ : 49.3.

$\text{Me}_4\text{N}^+\text{Cl}^-$  (10 g, 92 mmol) was added to the filtrate left after the separation of the  $\text{Me}_3\text{NH}^+$  salt of **1**, and the resulting white precipitate was separated, dried under reduced pressure, and crystallized from water/MeOH to yield the  $\text{Me}_4\text{N}^+$  salt of the 2-ethoxy derivative **4** (1.1 g, 4%). MS (*z/e*): 185. NMR:  $^{11}\text{B}\{^1\text{H}\}$ : 1.4 (2 s), -10.1 (12), -16.0 (7,11), -17.3 (3,6,8,10), -18.9 (4,5), -22.9 (9);  $^1\text{H}$ : 3.72 (q)  $\text{CH}_2$ , 2.54  $\text{CH}_{\text{cage}}$ , 1.45 (t)  $\text{CH}_3$ ;  $^{13}\text{C}$ : 65.1  $\text{CH}_2$ , 53.1  $\text{C}_{\text{cage}}$ , 17.9  $\text{CH}_3$ . IR (Cs salt): 3 055, 2 968, 2 924, 2 532, 1 439, 1 213, 1 105, 1 019, 724, 692  $\text{cm}^{-1}$ . For  $\text{C}_{39}\text{H}_{46}\text{B}_{11}\text{NOP}_2$  (725.7) calculated: 64.6% C, 6.4% H, 1.9% N; found: 64.6% C, 6.2% H, 1.9% N.

#### Reaction of $\text{Li}^+$ Salt of **2** with $\text{CHCl}_3$ and Base in the Presence of $\text{Me}_3\text{N}$

In a 250 ml two-neck flask the  $\text{Me}_3\text{NH}^+$  salt of **2** (1 g, 5.2 mmol) was dissolved in THF (20 ml) under an argon atmosphere. The solution was cooled to -78 °C and *n*-BuLi (10 ml, 16 mmol) was added dropwise. After stirring 1 h at room temperature, the solution was cooled to -78 °C and  $\text{CHCl}_3$  (2 ml, 24 mmol) was added, and the reaction mixture was allowed to stir overnight at room temperature. The THF was removed under reduced pressure, the residue was taken up in water (50 ml), and acidified by addition of 10% HCl. A yellow solid was filtered and washed three times with 10 ml portions of water and dried in vacuum to yield the known<sup>10</sup> pale yellow 2-trimethylammonio derivative **5** (200 mg, 19%).  $\text{Me}_3\text{NH}^+\text{Cl}^-$  (1 g, 10 mmol) was added to the filtrate, a white solid was filtered, washed three times with 10 ml portions of water, and dried under reduced pressure to recover colorless starting material, the  $\text{Me}_3\text{NH}^+$  salt of **2** (300 mg, 30%).

Reaction of **2** with CCl<sub>3</sub>COONa in Water

The Me<sub>3</sub>NH<sup>+</sup> salt of **2** (50 mg, 0.26 mmol) was dissolved in carefully degassed water (30 ml), sodium trichloroacetate (9 g, 49 mmol) was added, and the reaction mixture was refluxed and vigorously stirred for 8 h. Initially, Me<sub>3</sub>N escaped, and during the first 6 h, formation of CHCl<sub>3</sub> was observed; it was trapped in a Dean-Stark trap and identified by NMR. The reaction mixture was extracted with diethyl ether three times, the combined organic layers were dried over sodium sulfate, and the solvent was evaporated to yield a slightly pink precipitate. This was dissolved in methanol for HPLC separation, which afforded **1** (12% yield) and the known<sup>11</sup> oxaborane **6** (47% yield).

Reaction of Na<sup>+</sup> Salt of **2** with CHBr<sub>3</sub> and Base

In a 250 ml two-neck flask the Me<sub>3</sub>NH<sup>+</sup> salt of **2** (1 g, 5.2 mmol) was dissolved in dry THF (10 ml) under an argon atmosphere. The solution was cooled to 0 °C and NaH (95%, 1.2 g, 48 mmol) was added. After stirring 15 min at room temperature, the mixture was evaporated to dryness under reduced pressure. THF (20 ml) was added to the residue, the suspension was cooled to 0 °C, and CHBr<sub>3</sub> (2 ml, 22.9 mmol) was added. Ethanol (2 ml) was added slowly and the mixture was stirred overnight. After addition of ethanol (5 ml) and water (40 ml), THF and ethanol were removed under reduced pressure and Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> (1 g, 9.2 mmol) was added to the solution. A pale yellow solid precipitated and was dried under reduced pressure. The dry solid was dissolved in methanol (12 ml) and filtered. The filtrate was injected on an HPLC column and a MeOH/H<sub>2</sub>O (55 : 45) mixture was used to separate **1** (*R<sub>F</sub>* 14.2) from the 2-bromo derivative **7** (*R<sub>F</sub>* 19.7).

MeOH was removed under reduced pressure from the combined MeOH/H<sub>2</sub>O fractions containing **1** and the aqueous solution was extracted three times with diethyl ether (40 ml). The combined ether extracts were evaporated to dryness and the colorless oil was dissolved in water (50 ml). After addition of a solution of Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> (0.5 g, 4.6 mmol) in H<sub>2</sub>O (20 ml), the white Me<sub>4</sub>N<sup>+</sup> salt of **1** was filtered and dried under reduced pressure (0.12 g, 11%). The same treatment of the combined fractions containing **7** yielded 0.45 g (29%) of product. MS (*z/e*): 222. NMR: <sup>11</sup>B{<sup>1</sup>H}: -6.4 (12), -12.3 (7,11), -13.6 (3,6), -14.0 (2 s,8,10), -15.9 (4,5), -17.0 (9); <sup>1</sup>H: 2.71 CH<sub>cage</sub>; <sup>13</sup>C: 55.0. IR (Cs salt): 2 572, 2 529, 2 504, 1 454, 1 261, 1 093, 1 020, 799 cm<sup>-1</sup>. For C<sub>37</sub>H<sub>41</sub>B<sub>11</sub>BrNP<sub>2</sub> (760.5) calculated: 58.4% C, 5.4% H, 1.8% N; found: 58.5% C, 5.6% H, 2.0% N.

Reaction of Na<sup>+</sup> Salt of **2** with CHI<sub>3</sub> and Base

In a 250 ml two-neck flask the Me<sub>3</sub>NH<sup>+</sup> salt of **2** (1 g, 5.2 mmol) was dissolved in THF (20 ml) under an argon atmosphere. The solution was cooled to -78 °C, and NaH (95%, 0.9 g, 36 mmol) was added. After stirring 15 min at room temperature, the mixture was evaporated to dryness under reduced pressure. THF (40 ml) was added to the residue, the suspension was cooled to -78 °C, and CHI<sub>3</sub> (6 g, 15.3 mmol) was added. The reaction mixture was stirred overnight at room temperature. Ethanol (10 ml) and water (50 ml) were added, and the THF and the ethanol were removed under reduced pressure. The solution was acidified by addition of 10% HCl. After filtration Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> (0.57 g, 5.2 mmol) in H<sub>2</sub>O (20 ml) was added to the filtrate and the white precipitate was filtered and dried under reduced pressure. The residue was crystallized from CH<sub>3</sub>CN/H<sub>2</sub>O to yield colorless crystals of the known<sup>12</sup> Me<sub>4</sub>N<sup>+</sup>[7-OH-B<sub>11</sub>H<sub>13</sub>]<sup>-</sup> (**8**; 290 mg, 25%).

## Crystallography

Colorless crystals of **7** were examined under light hydrocarbon oil. The specimen crystal was mounted with silicone vacuum grease to a thin glass fiber affixed to a tapered copper mounting pin and transferred to the goniometer of a Siemens SMART CCD diffractometer equipped with a locally modified LT-2a low-temperature apparatus operating at 135 K.

Cell parameters were determined using reflections harvested from three orthogonal sets of  $20\ 0.3^\circ\ \omega$  scans and refined utilizing 8 092 reflections with  $I > 10\sigma(I)$  chosen from 73 747 in the entire data set. An arbitrary hemisphere of data was collected to  $0.68\ \text{\AA}$  using  $0.3^\circ\ \omega$  scans measured for 30 s for two correlated 30-s exposures. Data were truncated to  $0.77\ \text{\AA}$  during refinement due to poor agreement at higher resolution. This limit left 17 592 unique reflections, 14 056 with  $I > 10\sigma(I)$ ; 99% of the unique data were measured. All data were corrected for Lorentz and polarization effects, as well as for absorption; for a summary, see Table I.

Structure solution agrees with the assignment of the substituent location in position 2, next to the carbon atom. Solution by direct methods in centrosymmetric space group  $P2_1/n$  revealed much of the non-hydrogen structure, which consists of two carborane and two  $\text{PNP}^+$  units,  $Z = 8$ . Missing atoms were located by subsequent cycles of least-squares refinement followed with calculation of a difference Fourier map. Non-hydrogen atoms were refined using parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 times the equivalent isotropic thermal parameter of the parent atom. Hydrogens attached to C(1) of the carboranes were located by difference electron density map and constrained in subsequent cycles of least-squares refinement. No significant features were present in the final difference electron density map.

Positional disorder is present for carbon C(1) in each carborane. Two sites were identified by inspection of thermal parameters and bond lengths. Bond lengths were compared to average values for  $\text{CB}_{11}$  dodecahedron cages taken from the Cambridge Structural Database<sup>13</sup>. Forty-seven crystal structures of this type are archived. The average boron–boron edge length is  $1.77(2)\ \text{\AA}$  while carbon–boron edges average  $1.71(3)\ \text{\AA}$ . Our values for **7** are presented in Table II and it is clear that two edges are shorter. In molecule 1, the B(2)–B(7) and B(2)–C(1) edge lengths are  $1.736(9)$  and  $1.725(9)\ \text{\AA}$ , respectively, much shorter than the  $1.768\ \text{\AA}$  average for the remaining edges emanating from B(2). Thermal parameters are also unusual for these two atoms (Table III). The value for B(7),  $0.0284\ \text{\AA}^2$ , is smaller than the  $0.0306\ \text{\AA}^2$  average for B(3), B(6), and B(8). For C(1), the thermal parameter is  $0.0388$ , much larger than the average for the three unaffected atoms. We conclude that insufficient electron density is modeled at B(7) and too much is modeled at C(1). Taken in concert with the bond lengths, the implication is that these sites share occupancy between a boron and a carbon. Similar observations can be made for vertices C(1) and B(3) of molecule 2. Attempts to model two atoms, B and C, at these sites were unsuccessful. With the high non-crystallographic symmetry of the molecule, this disorder does not alter the structure.

Crystallographic data for the structure **7** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-163555. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

TABLE I  
Crystallographic data

Empirical formula	C <sub>37</sub> H <sub>41</sub> B <sub>11</sub> BrNP <sub>2</sub>
Formula mass	760.47
Crystal color, habit	colorless parallelepiped
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	28.072(3)
<i>b</i> , Å	9.9765(9)
<i>c</i> , Å	28.145(2)
α, °	90
β, °	103.141(2)
γ, °	90
<i>V</i> , Å <sup>3</sup> ; <i>Z</i>	7 675.7(12); 8
ρ <sub>calc</sub> , g cm <sup>-3</sup>	1.316
μ, mm <sup>-1</sup>	1.184
Transmission coeff.	0.8240 and 0.7031
<i>T</i> , K	135(2)
λ, Å	0.71073 MoKα
Reflections collected	73 747
Unique reflections	17 592 ( <i>R</i> (int) = 0.0564)
Reflections observed	14 056
<i>R</i> index <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0867
<i>R</i> indices <sup>a</sup> (all data)	<i>R</i> 1 = 0.1043, <i>wR</i> 2 = 0.2294
Weighting coefficients <sup>d</sup>	<i>a</i> = 0.0001, <i>b</i> = 2.8565
Goodness-of-fit <sup>c</sup> on <i>F</i> <sup>2</sup>	1.184
Extinction coefficient	0.00109(11)

$$^a R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}}; ^b w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP],$$

where  $P = (F_o^2 + 2F_c^2) / 3$ ; <sup>c</sup> GooF =  $S = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{(M - N)}}$ , where *M* is the number of reflections and *N* is the number of parameters refined.

## RESULTS AND DISCUSSION

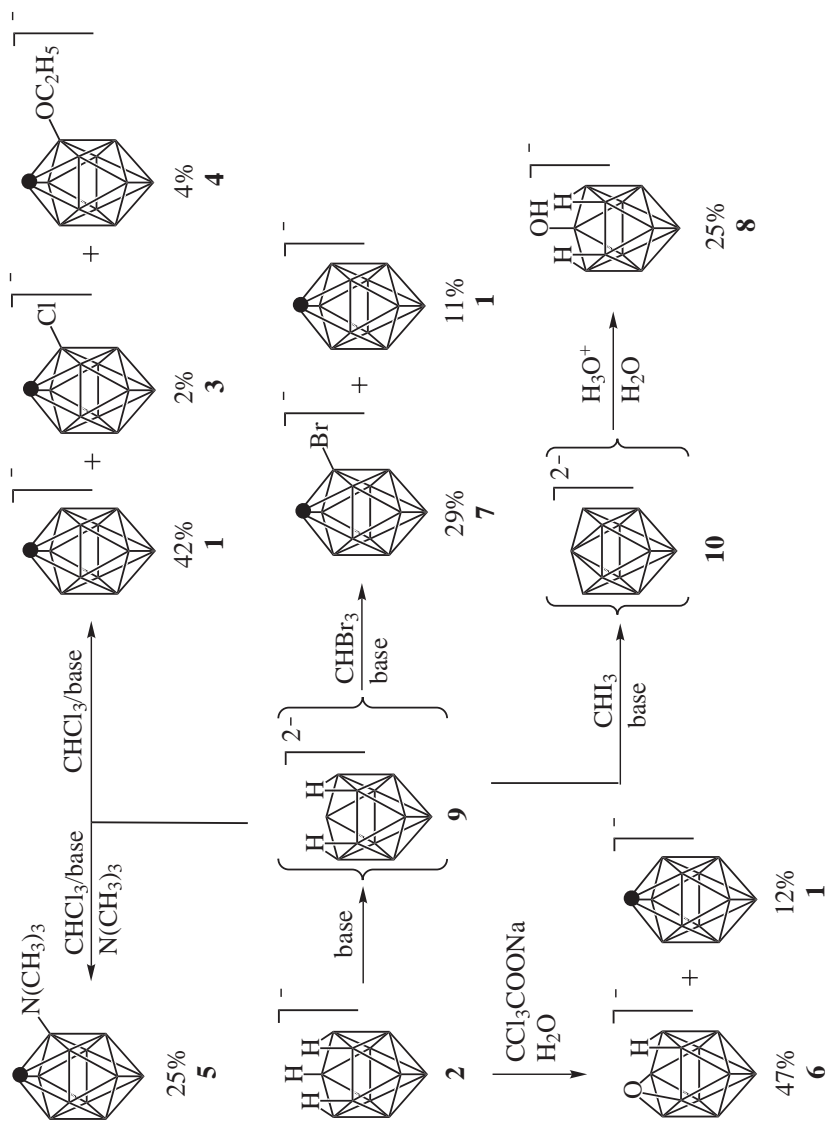
The initial point of our work was the realization that the 11-vertex cage of **2** represents an ideal starting cluster for the synthesis of **1**, both because it is cheap and easy to prepare on laboratory scale<sup>9</sup>, and because only one additional vertex needs to be inserted into it. The stoichiometry of the desired transformation of **2** into **1** requires the addition of one carbon atom and the removal of two hydrogen atoms. Formally, this is accomplished by addition of a dihalocarbene,  $\text{CHal}_2$ , and removal of two  $\text{HHal}$  units. The carbene can be generated in situ from a suitable precursor, and the hydrogen halide would be taken up by a base. The actual observations are summarized in Scheme 1. Although in the end we have not found conditions under which the reaction proceeds quantitatively with the desired stoichiometry, the concept has served us well as a guiding principle.

TABLE II  
Bond lengths to B(2), Å

Bond length	Molecule 1	Molecule 2
B(2)–B(3)	1.778(9)	1.742(10)
B(2)–B(6)	1.754(10)	1.781(12)
B(2)–B(7)	1.736(9)	1.761(11)
B(2)–B(8)	1.771(10)	1.752(10)
B(2)–C(1)	1.725(9)	1.723(10)

TABLE III  
Equivalent isotropic thermal parameters, Å<sup>2</sup>

Atom	Molecule 1	Molecule 2
B(3)	0.0309(14)	0.0353(16)
B(6)	0.0303(14)	0.0388(17)
B(7)	0.0284(14)	0.0379(17)
B(8)	0.0306(14)	0.0364(16)
C(1)	0.0388(15)	0.0423(16)



SCHEME 1

Reactions of **2** with the haloforms and base. Each polyhedron vertex carries a hydrogen atom that is not shown. The vertex marked with a dot is a carbon atom, the others are boron atoms



During considerable experimentation with the insertion of dihalocarbenes from different sources into **2** under various conditions, we found that the desired **1** is indeed often formed, but usually in a low yield. The yields of **1** were optimized when the reaction solution was very strongly basic, such that the starting borane was present in the deprotonated form shown in curly brackets as an intermediate in Scheme 1, the  $[nido-B_{11}H_{13}]^{2-}$  dianion (**9**). In the absence of strong base, an insertion reaction still occurred in some cases, but little **1** was formed. Thus, sodium trichloroacetate, a common thermal precursor for dichlorocarbene, mostly produced an oxygen instead of a carbon insertion product. In aqueous solution, it reacted with **2** to give the known<sup>11</sup> oxaborane anion  $[nido-OB_{11}H_{12}]^-$  (**6**) in 47% yield, while **1** was formed in only 12% yield. The yield of **6** in this reaction is higher than previously reported in another synthesis<sup>11</sup>, but for our purposes this product did not appear useful.

Given the need for a strongly basic reaction medium, the use of the inexpensive haloforms, known to react with base to yield dihalocarbenes, suggested itself. The base would thus serve the double function of generating both the dianion **9** and the dihalocarbene reagent. Among the solvents compatible with the presence of a strong base, ethers appear to be optimal. Low solubility excluded the use of certain counterions, such as  $(CH_3)_4N^+$ , and we found it best to work with the sodium salt in tetrahydrofuran. The published<sup>9</sup> procedure for the synthesis of **2** furnishes this starting material in the form of a sodium salt, but our efforts to purify this without first converting it to a salt of another cation were not successful. The dry sodium salt is pyrophoric and unpleasant to work with, and in the end we found it best to convert the solvated sodium salt into the easily isolated and purified  $(CH_3)_3NH^+$  salt and then reconvert the latter back to the former *in situ*, by reaction with a  $Na^+$ -containing base and evaporation of the amine.

If the trimethylamine liberated in the reversion procedure is not thoroughly removed, the yield of the desired product drops dramatically, and the known<sup>10</sup> zwitterion 2- $(CH_3)_3N-closo-CB_{11}H_{11}$  (**5**) forms instead. The carbene insertion reaction of a pure  $(CH_3)_3NH^+$  salt of **2** produces **5** as the only significant icosahedral product, in  $\approx 25\%$  yield after correction for recovered **2**. Although this product probably could be converted to **1**, it is simpler to avoid the presence of trimethylamine in the reaction mixture, and this direction was not pursued further.

Since **1** is stable to trimethylamine, and since boron 2 is its least reactive vertex, the above result suggested that the nucleophilic attack by  $Me_3N$  in position 2 occurs at an earlier stage in the reaction sequence, and that it might be advisable to minimize the concentration of other strong

nucleophiles in the reaction mixture as well. This requirement limited the choice of strong bases needed for the deprotonation of **2** to **9**. The insoluble NaH appeared ideal. It deprotonated **2** in THF smoothly, but addition of chloroform failed to produce any **1**, and **2** was recovered. Apparently, the extremely low solubility of NaH did not allow it to deprotonate chloroform, which is a relatively weak acid, and dichlorocarbene was not formed. A compromise seemed inevitable, and we tried the addition of various bases that are soluble in THF, such as butyllithium and sodium alkoxides. These reactions all produced **1**.

The procedure ultimately identified as best used sodium ethoxide, generated *in situ* from excess NaH by the addition of ethanol. Under these conditions, the reaction was fast, the isolation of pure **1** was facile, the yield of the (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> salt of **1** from the (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> salt of **2** was ≈40%, and the procedure was easily performed on large scale (we have used as much as 100 g of **2** in a single run). Perhaps not surprisingly in view of the reaction with Me<sub>3</sub>N noted above, small amounts of two impurities were always present in the crude reaction mixture. One (≈5% by <sup>11</sup>B NMR) was [2-C<sub>2</sub>H<sub>5</sub>O-*closo*-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> (**4**), whose (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> salt was isolated in 4% yield and fully characterized. The other was a minute amount (≈2% by <sup>11</sup>B NMR) of [2-Cl-*closo*-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> (**3**). This impurity was not fully characterized, but <sup>11</sup>B-<sup>11</sup>B COSY NMR leaves no doubt of either structure. Both byproducts can be removed by crystallization, and the <sup>11</sup>B NMR spectrum of the final product **1** revealed no detectable impurities.

The principal side product is [*closo*-B<sub>11</sub>H<sub>11</sub>]<sup>2-</sup> (**10**), identified in the crude reaction mixture by <sup>11</sup>B NMR (≈20%), but not isolated. Upon acidic aqueous workup, **10** is converted to [*nido*-7-OH-B<sub>11</sub>H<sub>13</sub>]<sup>-</sup> (**8**)<sup>12</sup> and easily removed. The formation of **10** formally corresponds to a dehydrogenation of a *nido* to a *closo* borane dianion, and we suspect that this process is triggered by electron transfer from the *nido* dianion **9** to chloroform. This observation suggests that it might be possible to increase the yield of the desired product **1** in the future by the use of a carbene precursor that cannot act as an electron acceptor.

This interpretation of the origin of the byproduct **10** is supported by observations made when iodoform was substituted for chloroform under otherwise identical reaction conditions. This much better electron acceptor yielded **10** as the only product and it is possible that it, and other polyiodinated alkanes, could find general use as mild dehydrogenating agents for the conversion of *nido* to *closo* dianions.

Under the same conditions, the dominant (29%) product obtained with bromoform was [2-Br-*closo*-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (**7**). Its structure was established by <sup>11</sup>B-<sup>1</sup>B COSY NMR and a single-crystal X-ray diffraction analysis. The yield of **1** in the reaction with bromoform was only 11%. It is tempting to attribute the increased production of **7** at the expense of **1** to the increased nucleophilicity of the bromide relative to the chloride anion. It thus appears that among the haloforms tested, chloroform is not only the cheapest but also the best dihalocarbene precursor for the conversion of **2** to **1**.

Finally, although **1** may be the most important monocarba-*closo*-borane anion at the moment, it seemed of interest to establish the scope of the carbene insertion reaction. A series of preliminary experiments has been most encouraging in that insertion of various halogenated carbenes into **2** yielded the 1-substituted anions [1-R-*closo*-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup>, and their insertion into [*arachno*-B<sub>9</sub>H<sub>14</sub>]<sup>-</sup>, readily accessible from B<sub>10</sub>H<sub>14</sub> (refs<sup>14,15</sup>), yielded the 1-substituted anions [1-R-*nido*-CB<sub>9</sub>H<sub>11</sub>]<sup>-</sup>. Insertion into the neutral B<sub>10</sub>H<sub>14</sub> itself yielded [*closo*-CB<sub>10</sub>H<sub>11</sub>]<sup>-</sup>. These results will be reported in full elsewhere.

## CONCLUSIONS

The [*closo*-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion (**1**) is now accessible from NaBH<sub>4</sub>, BF<sub>3</sub>·Et<sub>2</sub>O, CHCl<sub>3</sub>, and NaH in two simple steps in an overall yield of 20%. The key new reaction is the insertion of a carbon atom in the form of a carbene into the boron cage of the [*nido*-B<sub>11</sub>H<sub>14</sub>]<sup>-</sup> anion (**2**). This process appears to be general. We have also prepared several derivatives of **1** carrying a single substituent at the least reactive boron vertex **2**.

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