

results have been reported by Solomon, *et al.*,<sup>15,35</sup> and attributed to the  $O_2^+$  ion.

As might be expected, the X-ray diffraction pattern of the powder is very similar in both spacings and intensity distribution to that<sup>40</sup> of  $NO^+BF_4^-$ . We have indexed our pattern on the basis of an orthorhombic unit cell,  $8.77 \times 5.58 \times 7.05 \pm 0.01$  Å. Apart from the labeling of the axes, this is similar to the unit cell assigned to  $NOBF_4$  by Evans, *et al.*<sup>40</sup> ( $8.91 \times 5.68 \times 6.98$  Å). The systematic absences are consistent with the space group  $P_{nma}$  which conforms also to the observation of the  $O_2^+$  vibration in infrared absorption. The unit cell and symmetry are very similar to those previously assigned to  $NH_4BF_4$ ,  $KBF_4$ , and other compounds with the  $BaSO_4$  structure.<sup>41</sup> Details will be reported elsewhere.

**Nomenclature.** In this paper we have referred to the compounds  $O_2F_2$  and  $O_4F_2$  as oxygen fluorides, in accordance with the recommendations of one of the referees and with the concurrence of the editor of this

(40) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).

(41) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience Publishers, New York, N. Y., 1965, p 47.

journal. Their recommendations were presumably based on the conviction that, in compounds made up of two elements, the least electronegative element is to be named first. Our originally suggested nomenclature for these two compounds as fluorine peroxide and fluorine superoxide is consistent with the similarity in geometrical structure between  $H_2O_2$  and  $F_2O_2$  and the recent, though controversial, literature suggesting the possible existence of  $H_2O_3$  or  $H_2O_4$  at low temperatures. The fact that the O-O distance in  $O_2F_2$  is close to that prevailing in the cation  $O_2^+$ , however, suggests that the accepted name, dioxygenyl difluoride, is appropriate for the compound.

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## Representative Derivative Chemistry of the 1,6- and 1,10- $B_8C_2H_{10}$ Carborane System

Philip M. Garrett, James C. Smart, and M. F. Hawthorne

Contribution from the Department of Chemistry, The University of California, Riverside, California 92502. Received February 20, 1969

**Abstract:** Basic and acidic hydrolysis degrades 1,6- $B_8C_2H_{10}$  to  $B_7C_2H_{12}^-$  ion and boric acid, respectively, but similar conditions do not affect the 1,10- $B_8C_2H_{10}$  isomer. Mono and dilithio derivatives of both isomers have been prepared and subsequent reactions gave C-methyl, C-carboxylic acid, C-amine, and C-halogen derivatives. Chlorination of the 1,10- $B_8C_2H_{10}$  isomer gave perchlorinated products.

The preparation and characterization of the 1,6- $B_8C_2H_{10}$  and 1,10- $B_8C_2H_{10}$  carboranes and their C-monomethyl, C,C'-dimethyl, and C-monophenyl derivatives have been recently reported.<sup>1,2</sup> We now wish to report representative derivative chemistry of these carboranes which illustrates their general reactivities.

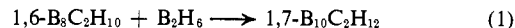
### Results and Discussion

Of the reactions of 1,6- and 1,10- $B_8C_2H_{10}$  studied to date, few have involved the boron atoms of the carborane cage, but rather the terminal boron and carbon hydrogen atoms. These two known isomers of  $B_8C_2H_{10}$  are shown in Figure 1. Two reactions which involve the carborane cage have been described elsewhere.<sup>1</sup> They are the thermal isomerization of 1,6- $B_8C_2H_{10}$  derivatives to their isomeric 1,10- $B_8C_2H_{10}$  counterparts. These rearrangements are nearly quantitative above

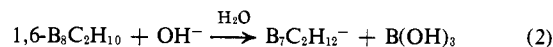
(1) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 869 (1968).

(2) P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, in press.

300°. Secondly, the hydroboration of 1,6- $B_8C_2H_{10}$  to 1,7- $B_{10}C_2H_{12}$  (eq 1) has been observed. The third



example of cage chemistry is hydrolytic degradation. Hydrolysis of 1,6- $B_8C_2H_{10}$  in basic, aqueous ethanol (eq 2) gives the known<sup>1</sup>  $B_7C_2H_{12}^-$  ion in 90% yield.



In acidic, aqueous tetrahydrofuran solution 1,6- $B_8C_2H_{10}$  degrades to boric acid. Treatment of 1,6- $B_8C_2H_{10}$  with piperidine in diethyl ether solution at 25° also produces the  $B_7C_2H_{12}^-$  ion in 51% isolated yield. However, a large difference between the degradative stabilities of the 1,6- and 1,10- $B_8C_2H_{10}$  isomers exists. Attempted basic and acidic hydrolysis of 1,10- $B_8C_2H_{10}$  under the same conditions employed in the case of the 1,6-isomer degradation afforded recovered starting material in 48 and 70% yields, respectively. Further support of this large difference in the cage stability toward degradation of these two isomers is evidenced by a 53% recovery of starting material when 1,10-

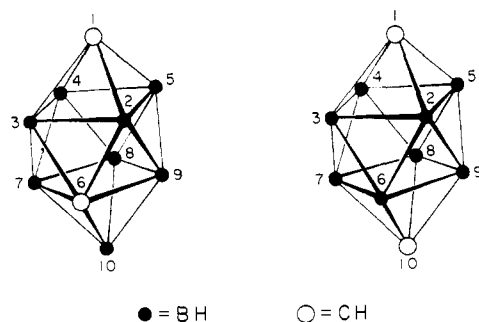
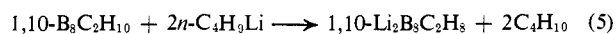
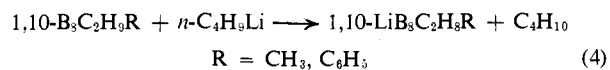
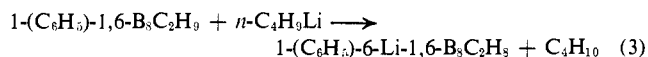


Figure 1. The structure of 1,6- and 1,10- $B_8C_2H_{10}$  carboranes.

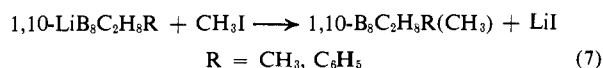
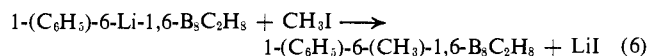
$B_8C_2H_{10}$  was heated at  $300^\circ$  for 12 hr in neat piperidine. A rationalization of the difference in the basic degradative stabilities of the 1,2- and 1,7- $B_{10}C_2H_{12}$  carboranes has been presented elsewhere.<sup>3</sup> Employing the same reasoning here for the 1,6- and 1,10- $B_8C_2H_{10}$  carboranes, one would expect the boron atom removed in the basic degradation of 1,6- $B_8C_2H_{10}$  to be one of the chemically equivalent 2- or 3- boron atoms (Figure 1) since they both have two relatively electropositive carbon atoms as nearest neighbors and hence are the most electropositive boron atoms in the polyhedron and presumably the most susceptible to attack by base. In the case of the 1,10- $B_8C_2H_{10}$  isomer, all eight boron atoms are chemically equivalent and neighbor only one carbon atom. Hence, no one site is more prone to basic attack than any other, and the ground-state charge distribution does not favor facile nucleophilic attack.

The 1,6- and 1,10- $B_8C_2H_{10}$  carboranes were found to react readily with *n*-butyllithium to give monolithio (eq 3 and 4) and dilithio (eq 5) salts. Subsequent



reactions of these lithio carborane derivatives established that the hydrogens on the carborane carbon atoms are relatively more acidic than those on boron atoms and hence are more susceptible to attack by alkyllithium reagents. Similar reactivity is seen in the case of the 1,2- and 1,7- $B_{10}C_2H_{12}$  carboranes.<sup>4-6</sup>

Methylation of these lithium carborane derivatives gave the expected methylated products as shown in eq 6 and 7. It has been established elsewhere<sup>2</sup> that pre-



viously obtained C-monomethyl-substituted 1,6- $B_8C_2H_{10}$  consists of an inseparable isomer mixture of the 1-methyl- and 6-methyl-substituted carboranes and that their relative abundance is 2:1, respectively. Treat-

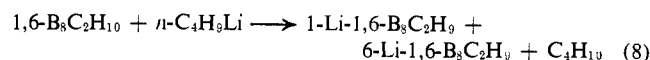
(3) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 862 (1968).

(4) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

(5) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963).

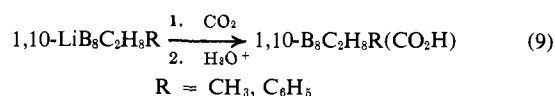
(6) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

ment of 1,6- $B_8C_2H_{10}$  with 1 mole of *n*-butyllithium (eq 8)

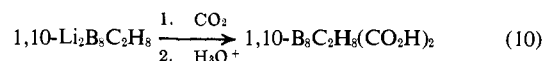


gave a monolithio salt which, when allowed to react with methyl iodide, gave a C-monomethyl-substituted 1,6- $B_8C_2H_{10}$ . The  $^1H$  nmr and infrared spectra of this material were identical with that of the known isomer mixture obtained from other sources.<sup>2</sup> Thus, products derived from the lithiocarborane derivatives of 1,6- $B_8C_2H_{10}$  favor the 1-substituted product by 2:1.

Preparation of the mono- and dicarboxylic acids of the 1,10- $B_8C_2H_{10}$  isomer is readily accomplished by treating the proper lithio carborane derivatives with carbon dioxide. The 10-monocarboxylic acids of 1-monomethyl and 1-monophenyl derivatives of 1,10- $B_8C_2H_{10}$  were prepared (eq 9) in 48 and 81% yield, re-



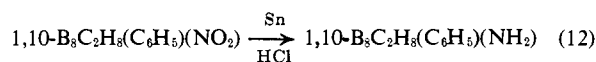
spectively. Reaction of the dilithio species derived from 1,10- $B_8C_2H_{10}$  with carbon dioxide (eq 10) gave



the 1,10-dicarboxylic acid in 90% yield. The C-monomethyl and C-monophenyl acids titrated as strong monoprotic acids with apparent  $pK_a$ 's of 4.2 and 4.1, respectively. The 1,10-dicarboxylic acid derived from 1,10- $B_8C_2H_{10}$  titrated as a strong diprotic acid which exhibited only one potentiometric inflection with an apparent  $pK_a$  of 3.8. The equivalent weight found was 107 (calcd 104.3), and hence the single inflection point observed is attributed to the second ionizable proton.

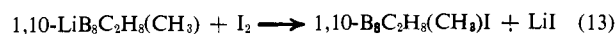
Reaction of the monolithio derivative of C-monophenyl-substituted 1,10- $B_8C_2H_{10}$  with nitrogen dioxide (eq 11) produced a light yellow oil which was not char-

acterized, but was assumed to be the C-nitro derivative. Treatment of the C-nitro derivative with tin and hydrochloric acid (eq 12) gave the 1-amino-10-phenyl deriva-



tive of 1,10- $B_8C_2H_{10}$  in 70% yield. Nonaqueous potentiometric titration of the amine in glacial acid with perchloric acid gave a single sharp end point and an equivalent weight of 215 (calcd 211.6). The amine could not be titrated as a weak base with dilute aqueous hydrochloric acid.

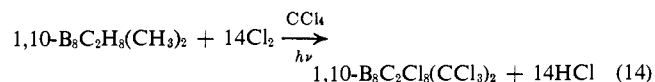
The monolithio derivative of C-monomethyl-substituted 1,10- $B_8C_2H_{10}$  reacted (eq 13) with an ether solution of iodine to give the 1-methyl-10-iodo derivative of 1,10- $B_8C_2H_{10}$  in 50% yield.



When chlorine gas was passed through a carbon tetrachloride solution of 1,10- $B_8C_2H_{10}$  and its C-monomethyl and C,C'-dimethyl derivatives, the hydrogen atoms attached to boron were rapidly displaced with chlorine, yielding volatile and air-stable chlorinated

(7) The potentiometric titrations were performed in 50% by volume aqueous ethanol with standard sodium hydroxide in the same solvent. Titration of benzoic, monochloroacetic, and trichloroacetic acid gave apparent  $pK_a$ 's of 5.7, 3.9, and 2.1, respectively.

products. Treatment of the C,C'-dimethyl-substituted 1,10-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub> with chlorine in carbon tetrachloride at the reflux temperature and in the presence of uv radiation (eq 14) afforded the perchlorinated carborane in 58%



yield. The infrared spectrum contained no C-H or B-H absorptions and its 32-Mc/sec <sup>11</sup>B nmr consisted of a singlet at +1.0 ppm (relative to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>). Chlorination of the C-monomethyl derivative under the above conditions produced about a dozen different major chlorinated products which were observed in the vapor phase chromatogram of the reaction mixture. Varying reaction conditions, such as elimination of uv radiation and chlorinating at 25°, yielded about the same number of major chlorinated products, none of which has yet been isolated as a pure compound.

A carbon tetrachloride solution of the parent carborane, 1,10-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>, gave 1,10-B<sub>8</sub>C<sub>2</sub>Cl<sub>8</sub>H<sub>2</sub> in 75% yield when chlorine was passed through the stirred solution for 48 hr at 25° and without uv irradiation. That the two hydrogen atoms on the carborane carbon atoms remained intact was established by the presence of the carborane C-H absorption at 3090 cm<sup>-1</sup> and the absence of B-H absorption in its infrared spectrum. In addition, the <sup>1</sup>H nmr spectrum of 1,10-B<sub>8</sub>C<sub>2</sub>Cl<sub>8</sub>H<sub>2</sub> in carbon tetrachloride solution contained a carborane C-H resonance at τ 4.8 (relative to tetramethylsilane). The 32-Mc/sec <sup>11</sup>B nmr of 1,10-B<sub>8</sub>C<sub>2</sub>Cl<sub>8</sub>H<sub>2</sub> in carbon tetrachloride solution consisted of a singlet at +3.1 ppm (relative to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>). The mass spectrum of 1,10-B<sub>8</sub>C<sub>2</sub>Cl<sub>8</sub>H<sub>2</sub> exhibited the parent peak at *m/e* 396 which corresponds to the <sup>11</sup>B<sub>6</sub><sup>10</sup>B<sub>2</sub><sup>12</sup>C<sub>2</sub><sup>1</sup>H<sub>2</sub><sup>37</sup>Cl<sub>2</sub><sup>35</sup>Cl<sub>6</sub><sup>+</sup> ion.

## Experimental Section

The 1,6- and 1,10-dicarba-*closo*-decaborane(10) and their C-monomethyl, C,C'-dimethyl, and C-monophenyl derivatives were prepared by literature methods.<sup>1,2</sup> Diethyl ether was Mallinckrodt Analytical reagent grade; other solvents were reagent grade and were used without further purification. *n*-Butyllithium was obtained from the Foote Mineral Co., and nitrogen dioxide from the Matheson Co.

Infrared spectra were recorded on a Beckman IR-5 spectrophotometer. Proton nmr spectra were recorded on a Varian Associates A-60 spectrometer, and the 32.0-Mc/sec boron nmr spectra were recorded on a Varian Associates HR-100 spectrometer. Mass spectra were measured on a Hitachi RMU-6 mass spectrometer. Vapor phase chromatography was performed with an Aerograph vapor phase chromatograph Model A-350-B, and potentiometric titrations were conducted with a Leeds Northrup potentiometer using a glass electrode *vs.* sce. The uv light source was a pen-ray quartz lamp produced by Ultra-violet Products, Inc., San Gabriel, Calif., Model SCT 1.

Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. All melting points were observed in sealed capillaries and are uncorrected. All reactions were carried out under an atmosphere of nitrogen.

**Hydrolysis of 1,6-Dicarba-*closo*-decaborane(10).** **A. Basic Hydrolysis.** To 100 ml of 1 *M* sodium hydroxide in 50% ethanol in water was added 250 mg (2.07 mmoles) of 1,6-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>. After the carborane dissolved, the solution was stirred for 0.5 hr at 25°. The solution was reduced in volume to 40 ml by rotary evaporation. Addition of an aqueous solution of tetramethylammonium chloride precipitated the monoanion of 1,3-dicarbaborane(13). The precipitate was filtered, washed with water, and dried under vacuum to give 350 mg or 90% of (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>[1,3-B<sub>8</sub>C<sub>2</sub>H<sub>12</sub>]<sup>-</sup>. The product was identified by comparing its infrared spectrum with an authentic sample.

**B. Acidic Hydrolysis.** In 10 ml of tetrahydrofuran was dissolved 0.25 g (2.1 mmoles) of 1,6-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub> to which 30 ml of aqueous 2 *M* hydrochloric acid was added. The solution was stirred at 25° for 10 hr and the solution was evaporated to dryness under vacuum. The white solid remaining was identified as boric acid by its infrared spectrum, 0.52 g or 50%.

**Hydrolysis of 1,10-Dicarba-*closo*-decaborane(10).** **A. Basic Hydrolysis.** To 30 ml of 1 *M* sodium hydroxide in 50:50 ethanol-water was added 250 mg (2.07 mmoles) of 1,10-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>. The solution was stirred at 25° for 1 hr, and then at 60° for 2 hr. After cooling, 100 ml of water was added and the unreacted starting material was extracted with four 20-ml portions of isopentane. The isopentane was removed under high vacuum and the 1,10-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub> was sublimed to a 80° cold finger giving 120 mg or 48% recovery.

**B. Acidic-Hydrolysis.** In 10 ml of tetrahydrofuran was dissolved 250 mg (2.1 mmoles) of 1,10-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>. To this solution was added 30 ml of aqueous 2 *M* hydrochloric acid and the resulting solution was stirred at 25° for 10 hr. Water (100 ml) was added to the solution and the starting material was extracted with four 20-ml portions of isopentane. The isopentane fractions were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under high vacuum. The recovered 1,10-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub> was sublimed to a -80° cold finger at 25° to give 175 mg or 70%.

**1-Phenyl-6-methyl-1,6-dicarba-*closo*-decaborane(10).** This is given as the general procedure for methylation. With stirring, 4.0 mmoles of *n*-butyllithium was added to 0.52 g (2.64 mmoles) of 1-(C<sub>6</sub>H<sub>5</sub>)-1,6-B<sub>8</sub>C<sub>2</sub>H<sub>9</sub> dissolved in 20 ml of ether. After stirring the solution for 1 hr, 0.45 ml (7.2 mmoles) of methyl iodide was added and the solution was refluxed for 3 hr using a Dry Ice condenser. The solvent was evaporated under vacuum and the product was distilled under high vacuum at 60°, yielding 0.49 g or 88% of 1,6-B<sub>8</sub>C<sub>2</sub>H<sub>8</sub>(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) (bp 280-281°).

*Anal.* Calcd for B<sub>8</sub>C<sub>9</sub>H<sub>16</sub>: B, 41.07; C, 51.33; H, 7.61. Found: B, 41.08; C, 51.58; H, 7.86.

**1-Phenyl-10-methyl-1,10-dicarba-*closo*-decaborane(10)** was obtained in a similar manner from 1-(C<sub>6</sub>H<sub>5</sub>)-1,10-B<sub>8</sub>C<sub>2</sub>H<sub>9</sub> in 85% yield and was purified by high-vacuum sublimation to a -80° cold finger (mp 36.0-37.0°).

*Anal.* Calcd for B<sub>8</sub>C<sub>9</sub>H<sub>16</sub>: B, 41.07; C, 51.33; H, 7.61. Found: B, 40.66; C, 50.92; H, 7.79.

**1,10-Dimethyl-1,10-dicarba-*closo*-decaborane(10)** was prepared from 1-(CH<sub>3</sub>)-1,10-B<sub>8</sub>C<sub>2</sub>H<sub>9</sub> in 62% yield and was purified by vapor phase chromatography using a 3/8 in. × 10 ft Apiezon L on 60-80 HMDS Chromosorb P column at 140°. It was identified by comparison of its infrared spectrum and boiling point with authentic material.

**1,10-Dicarba-*closo*-decaborane(10)-1,10-dicarboxylic Acid.** To 0.55 g (4.57 mmoles) of 1,10-B<sub>8</sub>C<sub>2</sub>H<sub>10</sub> dissolved in 50 ml of ether was added 9.1 mmoles of *n*-butyllithium with stirring. After stirring for 1 hr, carbon dioxide gas was bubbled through the stirred suspension for 1 hr using a Dry Ice condenser to retain the solvent. To this slurry was added 50 ml of water and the ether was evaporated under vacuum. The aqueous solution was filtered and acidified with dilute hydrochloric acid, and the product was filtered and washed with water. After drying under vacuum, the diacid weighed 0.85 g or 90%. An analytically pure sample was obtained by high-vacuum sublimation at 160° to a -80° cold finger and two recrystallizations from *n*-heptane-ether, followed by another sublimation (mp 316-317°).

*Anal.* Calcd for B<sub>8</sub>C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>: B, 41.50; C, 23.15; H, 4.80. Found: B, 41.30; C, 22.90; H, 5.03.

Potentiometric titration of 1,10-(CO<sub>2</sub>H)<sub>2</sub>-1,10-B<sub>8</sub>C<sub>2</sub>H<sub>8</sub> in 50:50 by volume ethanol-water with standard sodium hydroxide in 50:50 by volume ethanol-water gave a single sharp end point with an apparent <sup>7</sup>pK<sub>a</sub> of 3.8 (equivalent weight calcd for B<sub>8</sub>C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>, 208.6; found, 213).

**1,10-Dicarba-*closo*-decaborane(10)-1-phenyl-10-carboxylic Acid.** To 1.0 g (5.07 mmoles) of 1-(C<sub>6</sub>H<sub>5</sub>)-1,10-B<sub>8</sub>C<sub>2</sub>H<sub>9</sub> dissolved in 30 ml of ether was added 5.7 mmoles of *n*-butyllithium with stirring. The solution was stirred for 1 hr and then carbon dioxide gas was bubbled through the solution for 1 hr using a Dry Ice condenser to retain the solvent. To the slurry was added 40 ml of water and the ether was evaporated under vacuum. The aqueous solution was filtered and acidified with dilute hydrochloric acid, and the product was filtered and washed with water. The monoacid was dried under vacuum and weighed 0.98 g or 81%. Pure material was obtained by high-vacuum sublimation at 140° to a -80° cold finger and two recrystallizations from *n*-heptane-toluene, followed by a final sublimation (mp 192.5-194.0°).

*Anal.* Calcd for  $B_8C_9H_{14}O_2$ : B, 35.98; C, 44.90; H, 5.82. Found: B, 35.81; C, 44.76; H, 5.90.

Potentiometric titration of 1-( $C_6H_5$ )-10-( $CO_2H$ )-1,10- $B_8C_2H_8$  in 50:50 by volume ethanol-water with standard sodium hydroxide in 50:50 by volume ethanol-water gave a single sharp end point with an apparent  $pK_a$  of 4.1 (equivalent weight calcd for  $B_8C_9H_{14}O_2$ , 240.6; found, 242).

Using the same procedure, 1,10-dicarba-*closo*-decaborane(10)-1-methyl-10-carboxylic acid was prepared from 1-( $CH_3$ )-1,10- $B_8C_2H_8$  in 48% yield. A pure sample was obtained by high-vacuum sublimation at  $120^\circ$  to a  $-80^\circ$  cold finger and two recrystallizations from *n*-heptane, followed by another sublimation (mp 156.0–157.0°).

*Anal.* Calcd for  $B_8C_4H_{12}O_2$ : B, 48.46; C, 26.90; H, 6.72. Found: B, 48.61; C, 27.11; H, 7.08.

Potentiometric titration of 1-( $CH_3$ )-10-( $CO_2H$ )-1,10- $B_8C_2H_8$  in 50:50 by volume ethanol-water with standard sodium hydroxide in 50:50 by volume ethanol-water gave a single sharp end point with an apparent  $pK_a$  of 4.2 (equivalent weight calcd for  $B_8C_4H_{12}O_2$ , 178.5; found, 181).

**1-Iodo-10-methyl-1,10-dicarba-*closo*-decaborane(10).** To a stirred solution of 60 mg (0.45 mmole) of 1-( $CH_3$ )-1,10- $B_8C_2H_8$  in 10 ml of ether was added 0.88 mmole of *n*-butyllithium, and the solution was stirred for 1 hr. A saturated solution of iodine in ether was syringed dropwise into the solution until it became slightly colored by iodine. The reaction mixture was passed through a  $\frac{1}{2}$  in.  $\times$  6 in. silica gel chromatography column using ether as the eluent. To the solution was added 10 ml of acetonitrile, and the solution was reduced in volume to about 5 ml by rotary evaporation using a mechanical vacuum pump. The product was isolated by cooling the solution with a  $-80^\circ$  cold bath followed by rapid filtration. After washing with 1 ml of cold acetonitrile, the product was dried in air to give 57 mg or 50% of pale yellow crystalline 1-(I)-10-( $CH_3$ )- $B_8C_2H_8$ . An analytical sample was obtained by high-vacuum sublimation at  $25^\circ$  to a  $-80^\circ$  cold finger, followed by two recrystallizations from acetonitrile and a final sublimation (mp 61.0–62.0°).

*Anal.* Calcd for  $B_8C_3H_{11}I$ : B, 33.20; C, 13.83; H, 4.26; I, 48.71. Found: B, 33.03; C, 14.05; H, 4.23; I, 48.90.

**Reaction of 1,10-Dicarba-*closo*-decaborane(10) with Piperidine.** A solution of 0.49 g of 1,10- $B_8C_2H_8$  in 25 ml of distilled piperidine was sealed off under vacuum in a thick wall tube. The tube was heated at  $300^\circ$  for 12 hr. After cooling, the tube was opened and the solution was acidified with dilute hydrochloric acid, and the unreacted carborane was extracted with 100 ml of isopentane. The isopentane solution was dried over anhydrous magnesium sulfate, filtered, and reduced to 20 ml with a rotary evaporator. The remaining solvent was removed under high vacuum and the carborane was sublimed to a  $-80^\circ$  cold finger, yielding 0.26 g or 53% of recovered 1,10- $B_8C_2H_8$ .

**Reaction of 1,6-Dimethyl-1,6-dicarba-*closo*-decaborane(10) with Piperidine.** With stirring, 15 ml of distilled piperidine was added to a solution of 90.4 mg (0.61 mmole) of 1,6-( $CH_3$ )<sub>2</sub>-1,6- $B_8C_2H_8$  in 10 ml of ether. After stirring for 0.5 hr at room temperature, 15 ml of water was added and the ether was evaporated under vacuum. Addition of an aqueous solution of tetramethylammonium chloride precipitated the monoanion of 1,3-dimethyl-1,3-dicarbanonaborane(13). The precipitate was filtered, washed with water, and dried under vacuum to give 61.2 mg or 51% of  $(CH_3)_4N^+[1,3-(CH_3)_2-1,3-B_8C_2H_{10}]^-$  which was identified by comparing its infrared spectrum with an authentic sample.<sup>1</sup> No 1,6-( $CH_3$ )<sub>2</sub>-1,6- $B_8C_2H_8$  was recovered.

**Octachloro-1,10-dicarba-*closo*-decaborane(10).** The reaction was carried out in an all-glass apparatus. With stirring, chlorine was slowly passed through a solution of 200 ml of carbon tetrachloride and 0.70 g (5.75 mmoles) of 1,10- $B_8C_2H_8$  for 48 hr. The reaction was followed by gas chromatography using a  $\frac{3}{8}$  in.  $\times$  20 ft SE 30 column operating at  $150^\circ$ . The retention time of 1,10- $B_8C_2Cl_8H_2$  under these conditions was 11.0 with respect to carbon tetrachloride. The solvent was stripped under vacuum to give a

white powder which was sublimed twice under high vacuum at  $150^\circ$  to a  $-80^\circ$  cold finger to give 1.6 g or 75% of 1,10- $B_8C_2Cl_8H_2$ . An analytical sample was obtained by two more sublimations (mp 179–180°).

*Anal.* Calcd for  $B_8C_2Cl_8H_2$ : B, 21.83; C, 6.07; H, 0.51. Found: B, 21.85; C, 7.03; H, 0.51 (mass spectrum calcd for  $^{11}B_6^{10}B_2^{12}C_2^{1}H_2^{37}Cl_2^{35}Cl_6^+$ ,  $m/e$  396; found,  $m/e$  396).

**1,10-Di(trichloromethyl)octachloro-1,10-dicarba-*closo*-decaborane(10).** In an all-glass apparatus, 0.16 g (0.81 mmole) of 1,10-( $CH_2$ )<sub>2</sub>- $B_8C_2H_8$  was dissolved in 25 ml of carbon tetrachloride. Chlorine was passed through the solution for 3.5 hr while the solution was irradiated with uv light and heated at the reflux temperature. After filtering while hot, the solvent was removed under vacuum. One crystallization from methylene chloride gave 0.30 g or 58% yield of 1,10-( $CCl_3$ )<sub>2</sub>- $B_8C_2H_8$ . A pure sample was obtained by high-vacuum sublimation, followed by two recrystallizations from methylene chloride and another sublimation (mp 213–215°).

*Anal.* Calcd for  $B_8C_4Cl_{14}$ : B, 13.71; C, 7.61. Found: B, 13.71; C, 7.60; H, 0.00.

**1-Amino-10-phenyl-1,10-dicarba-*closo*-decaborane(10).** To a solution of 1.2 g (6.1 mmoles) of 1-phenyl-1,10- $B_8C_2H_8$  in 50 ml of ether was added 9.0 mmoles of *n*-butyllithium with stirring. After stirring for 1 hr the solution was cooled to  $-80^\circ$ , and 2 ml of liquid nitrogen dioxide was condensed into the solution. The solution was slowly warmed to room temperature and then stirred for 30 min. The solution was washed once with water, 25 ml of water was added, and the ether was evaporated under vacuum. The light green-yellow water-insoluble solid was dissolved in the water by adding ethyl alcohol. To this solution were added 2.0 g of tin metal and 10 ml of concentrated hydrochloric acid. The mixture was heated at the reflux temperature for 12 hr. After cooling, the solution was filtered and the alcohol was evaporated under vacuum. About 150 ml of water was added to the mixture and solid potassium hydroxide was slowly added with stirring and cooling until the solid ceased dissolving. The mixture was extracted with three 100-ml portions of ether. The combined ether phases were dried over anhydrous magnesium sulfate, filtered, and evaporated to a low volume under vacuum. The remaining solvent was removed under high vacuum and the product was sublimed from the residue at  $100^\circ$  to a  $-80^\circ$  cold finger yielding 0.90 g or 70% of 1,10- $B_8C_2H_8(C_6H_5)(NH_2)$ . An analytical sample was obtained by two recrystallizations from *n*-heptane followed by another sublimation (mp 106.0–107.5°).

*Anal.* Calcd for  $B_8C_8H_{15}N$ : B, 40.92; C, 45.38; H, 7.09; N, 6.62. Found: B, 41.11; C, 45.64; H, 7.33; N, 6.73.

Potentiometric titration of 1,10- $B_8C_2H_8(C_6H_5)(NH_2)$  in glacial acetic acid with 0.1008 *N* perchloric acid in glacial acetic acid gave a sharp end point (equivalent weight calcd for  $B_8C_8H_{15}N$ , 211.6; found, 215).

**1-Methyl- and 6-Methyl-1,6-dicarba-*closo*-decaborane(10).** In 25 ml of ether was dissolved 0.82 g (6.77 mmoles) of 1,6- $B_8C_2H_{10}$  and to this solution was added 6.9 mmoles of *n*-butyllithium with stirring. After stirring an additional hour, 2.0 ml of methyl iodide was added and the resulting solution was refluxed for 3 hr using a Dry Ice condenser. The bulk of the ether was removed under high vacuum and the remaining solvent and product were distilled from the lithium iodide. The ether solution was then vapor phase chromatographed on a  $\frac{3}{8}$  in.  $\times$  10 ft Carbowax column at  $160^\circ$ . The product was collected from the chromatograph in a U-tube maintained at  $-80^\circ$ . Under high vacuum, the product was condensed into a weighing tube giving 0.71 g or 78% yield of the isomer mixture 1-( $CH_3$ )- and 6-( $CH_3$ )-1,6- $B_8C_2H_{10}$  which contained a 2:1 ratio of 1- $CH_3$ - to 6- $CH_3$ -1,6- $B_8C_2H_{10}$  as determined by  $^1H$  nmr.

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