ion in solution maintains the structure of a 10-atom icosahedral fragment. Bridge hydrogen tautomerism may involve rapid interconversion between structures like those presented in Figure 4. Similar mechanisms have been proposed for bridge hydrogen tautomerism in B_6H_{10} and $B_{11}H_{14}^-$.[12,13]

The relative chemical shifts of the different types of boron-11 nuclei in the spectra of four decaborane species have now been determined.[14-16] The interrelationships of this chemical shift information are illustrated in Figure 5. It is observed that the weighted average of the boron chemical shifts for each molecule is found at higher field in the order $B_{10}H_{14} < B_{10}H_{13}^- < B_{10}H_{15}^- < B_{10}H_{14}^{2-}$. From left to right in this series is the most probable order for increasing electron density available for bonding in the decaborane cage framework. It is also observed that the B(1,3), B(5,7,8,10), and B(6,9) resonances gradually change to higher field while the B(2,4) resonance changes to lower field as one looks at the spectra in the order $B_{10}H_{14}$, $B_{10}H_{13}^-$, $B_{10}H_{15}^-$, and $B_{10}H_{14}^{2-}$, respectively.

Registry No. $Na[B_{10}H_{15}]$, 12008-67-2; $Ph_4As[B_{10}H_{15}]$, 39301-43-4.

Acknowledgments. This work was generously supported in part by the Office of Naval Research and in part by the National Science Foundation, Grant GP-33267X. We also wish to thank Mr. Ron Garber for his assistance in obtaining some of the nmr spectra.

[12] J. C. Carter and N. L. Mock, *J. Amer. Chem. Soc.*, 91, 5891 (1969).

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Preparation of Bis(*B*-hydroxy) Derivatives of 1,8-Dimethyl-*closo*-dicarbaundecaborane(11). Their Properties and Derivative Chemistry[1]

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In the reaction of 1,8-$(CH_3)_2C_2B_9H_9$ with chromic acid in benzene at 0° a bis(hydroxy) derivative [1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$] is formed. Spectral, structural, and chemical evidence indicates the two hydroxy groups are on adjacent B(3,7) positions. In addition, the bis(hydroxy)carborane on pyrolysis dimerizes to give two carborane polyhedra linked *via* two bridging oxygen atoms at the B(3,3′,7,7′) positions of 1,8-$(CH_3)_2C_2B_9H_9$. Pyrolysis in the presence of an organic diol such as *pyrocatechol* produces a carborane polyhedron linked *via* two oxygen bridges to the organic ligand, *i.e.*, phenyl ring.

Introduction

A large body of literature exists, in which C-substituted derivatives of the carborane series $C_2B_nH_{n+2}$ have been prepared. The derivative chemistry of the carborane series has been the subject of extensive reviews.[2,3] By comparison there are only a few B-substituted derivatives reported, in which the substituent is other than a halogen atom. The majority of these are derivatives of the icosahedral carborane $C_2B_{10}H_{12}$ and include *B*-alkyl, alkylamino, and alkoxy derivatives.[4]

We wish to report the first class of B-substituted derivatives of the 1,8-$(CH_3)_2C_2B_9H_9$ carborane. In the preparation of the *nido*-$(CH_3)_2C_2B_7H_{11}$ carborane *via* the sequence of degradation reactions of the $(CH_3)_2C_2B_{10}H_{10}$ outlined by Hawthorne[5] one of the intermediate steps involved the reaction of 1,8-$(CH_3)_2C_2B_9H_9$ with chromic acid in toluene. From this reaction sequence we have isolated a bis(hydroxy) derivative (I), $(CH_3)_2C_2B_9H_7(OH)_2$, 1,8-dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11).[6] The only prior reports in the literature of *B*-hydroxy derivatives were the synthesis of 1-methyl-*B*-hydroxy-1,2-carborane and the *B*-hydroxy-1,2-carborane by reaction of nitric acid with the respective 1,2-$B_{10}C_2H_{12}$ at 20°.[7,8] There are no reported B-substituted derivatives of the 1,8-dicarba-*closo*-undecaborane(11) family.

Experimental Section

Methods and Materials. 1,8-Dimethyl-1,8-dicarba-*closo*-undecaborane(11) was prepared by literature method.[9] All solvents were reagent grade and used without further purification. Pyrocatechol was obtained from Eastman Kodak and 2,3-butanediol from Aldrich Chemical; both were used as received. Deuterium chloride was prepared by a standard reaction using D_2O and benzoyl chloride.

Infrared spectra were obtained on either a Perkin-Elmer 337 or a

[1] Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

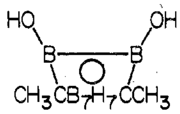
[2] R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

[3] R. E. Williams, "Progress in Boron Chemistry," Vol. 2, R. J. Brotherton and H. Steinberg, Ed., Pergamon Press, New York, N. Y., 1970, pp 37-119.

[4] See ref 2, p 198.

[5] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 90, 869 (1968).

[6] We have adopted the following formula to indicate the structure of 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$



[7] L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1713 (1965); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1694 (1965).

[8] (a) L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *Zh. Obshch. Khim.*, 36, 1786 (1966); (b) L. I. Zakharkin, V. N. Kalinin, and V. V. Gedymin, *ibid.*, 40, 2653 (1970); (c) *J. Organometal. Chem.*, 16, 371 (1969).

[9] (a) M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorg. Syn.*, 10, 100 (1967); (b) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 90, 869 (1968).

Perkin-Elmer 521. Mass spectra were measured on a low-resolution MS-902 mass spectrometer. Proton nmr spectra were recorded on a Varian Associates A-60 spectrometer. The 32.1-MHz boron nmr spectra were recorded on a Varian Associates HA-100 spectrometer and the 28.9-MHz decoupled boron nmr spectra were recorded on a Bruker HR-90 spectrometer.

Analyses were conducted by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

All reactions (except pyrolyses) were conducted under an atmosphere of nitrogen, and subsequent product work-ups required either a nitrogen atmosphere or minimum exposure to air.

Preparation of 1,8-Dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11). In a 500-ml, three-neck flask equipped with a nitrogen inlet, magnetic stirring bar, and addition funnel was dissolved 1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) (8.0 g, 0.05 mol) in 55 ml of glacial acetic acid with stirring. After dissolution 110 ml of water and 85 ml of benzene were added and the resulting mixture was chilled to 0°. A solution of sodium dichromate (15 g, 0.05 mol) in 85 ml of 2 *N* H_2SO_4 was added dropwise over a 15-min period. After complete addition of the dichromate, the mixture was stirred for an additional 15 min at 0°. The apparatus was opened to the atmosphere, the solution was poured into a separatory funnel, and the layers quickly separated. The aqueous phase was washed four times with 30-ml portions of benzene and the combined benzene fractions were dried over magnesium sulfate. The benzene was removed at room temperature using a mechanical pump until a solid residue was obtained. The residue was vacuum dried at about 60° for 2 additional hr. The residue was recrystallized from about 100 ml of CCl_4 under nitrogen to give 3.1 g (31%, 16 mmol) of product (mp 164–169°). *Anal.* Calcd for $B_9C_4H_{15}O_2$: C, 25.00; H, 7.81. Found: C, 24.34; H, 6.98.

Preparation of $[(CH_3)_2C_2B_9H_7O]_2$. 1,8-Dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane (0.2 g, 0.001 mol) was placed in a reaction tube (17 × 120 mm Pyrex test tube with attached standard taper 14/20 joint at one end) under nitrogen. The tube was capped with a gas inlet adapter and evacuated, and the bottom portion was immersed in an oil bath heated at 200°. After 45 min the tube was removed from the oil bath, allowed to cool, and opened to the air. The residue was recrystallized from acetonitrile to give 0.06 g (31%, 0.00031 mol) of product (mp 273–275°). *Anal.* Calcd for $B_{18}C_8H_{26}O_2$: C, 27.59; H, 7.47. Found: C, 27.72; H, 8.17.

Reaction of 1,8(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ with Pyrocatechol. 1,8-Dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11) (0.3 g, 0.0016 mol) and pyrotacheol (2.7 g, 0.025 mol) were mixed in a reaction tube in a nitrogen atmosphere. The tube was capped with a gas inlet adapter and evacuated, and the bottom portion was immersed in an oil bath heated to 180°. After 30 min the tube was removed from the oil bath, allowed to cool, and opened to the air. The solid was washed thoroughly with water to remove unreacted pyrocatechol and then air-dried. The crude product was sublimed at 70° to a cold-water cold finger to give 0.3 g (75%, 1.2 mmol) of product (mp 102–105°). *Anal.* Calcd for $B_9C_{10}H_{17}O_2$: C, 45.11; H, 6.39. Found: C, 45.48; H, 6.44.

Reaction of 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ with 2,3-Butanediol. 1,8-Dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11) (0.2 g, 0.001 mol) and 2,3-butanediol (1.0 g, 0.01 mol) were placed in a reaction tube in a nitrogen atmosphere. The tube was capped with a gas inlet adapter and evacuated, and the bottom portion was immersed in an oil bath heated at 155°. After 60 min the tube was removed from the oil bath, allowed to cool, and opened to the air. The crude material was transferred to the top of an alumina column 13 cm in length and 1 cm in diameter. Methylene chloride was used as an eluent and the product was taken off the column with the first 35 ml of eluent. The CH_2Cl_2 was removed using a mechanical pump and the solid residue was sublimed at 80° to a cold-water cold finger to give 0.06 g (24%, 0.24 mmol) of pure product (mp 80–82°). *Anal.* Calcd for $B_9C_8H_{21}O_2$: C, 39.02; H, 8.54. Found: C, 39.13; H, 8.87.

Preparation of 1,8-Dimethyl-3,7-dihydroxy-bromo-1,8-dicarba-*closo*-undecaborane(11). In a nitrogen atmosphere a 100-ml, three-neck flask fitted with a magnetic stirring bar, reflux condenser, and nitrogen inlet was loaded with aluminum chloride (0.04 g, 0.0003 mol), 1,8-dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11) (0.3 g, 0.0016 mol), and 25 ml of methylene chloride. The carborane was dissolved with stirring and then bromine (0.46 g, 0.0058 mol) was added. The stirred solution was refluxed for 24 hr. The flask was cooled to room temperature and the solution was filtered under nitrogen. The solvent was removed at room temperature using a mechanical pump and the solid residue was recrystallized from CCl_4 to give 0.16 g (55%, 0.88 mmol) of product (mp 163–166°). *Anal.* Calcd for $B_9C_4H_{14}O_2Br$: C, 17.71; H, 5.17. Found: C, 17.50; H, 5.07.

Deuterium Exchange on 1,8-Dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11). In a nitrogen atmosphere, a Schlenk tube fitted with a magnetic stirring bar and bubbler tube was loaded with 1,8-dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11) (0.1 g, 0.005 mol). The carborane was dissolved with stirring in 25 ml of methylene chloride and then DCl was passed in through the bubbler for 10 min (the flow rate was determined by placing the trap with the DCl in a Dry Ice–acetone bath and letting the DCl pass into the solution under its own vapor pressure). The solution was stirred for an additional 10 min and then the solvent and residual DCl were removed at room temperature using a mechanical pump. This left a dry, white solid that was not purified further. Purity was determined by nmr and ir analysis.

Preparation of 1,8-Dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11) Using Sodium Periodate. In a 100-ml, three-neck flask equipped with an addition funnel, nitrogen inlet, and magnetic stirring bar was dissolved 1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) (1.0 g, 0.0062 mol) in 10 ml of glacial acetic acid. After dissolution, 20 ml of benzene was added and the resulting solution was cooled to 0°. A solution of sodium periodate (1.4 g, 0.0065 mol) in 15 ml of water was then added dropwise over a 10-min period. After complete addition of the periodate the mixture was stirred an additional 15 min at 0°. The solution was transferred to a separatory funnel and the layers quickly separated. The aqueous layer was washed twice with 15 ml of benzene each time and the combined benzene fractions dried over magnesium sulfate. The solution was filtered and the bulk of the benzene was removed using a mechanical pump. The dark red liquid residue was dissolved in 50 ml of pentane, a small amount of mercury was added, and the solution was stirred until the red color was completely gone. The solution was filtered and the pentane removed using a mechanical pump. The residue was vacuum dried at about 60° for an additional 30 min. The white solid residue was recrystallized from CCl_4 to give 0.37 g (31%, 0.0019 mol) of product.

Results and Discussion

Various aspects of the chemistry of the 1,8-*closo*-$C_2B_9H_{11}$ have been explored in recent years. One of the earlier reactions published was the degradation of the 1,8-*closo*-$C_2B_9H_{11}$ with oxidizing agents to produce the open-cage structure 1,3-$C_2B_7H_{13}$.[10] The reaction of carboranes with oxidizing agents to undergo a degradation reaction producing smaller open-cage structures is a general one.[2] Either

$$C_2B_9H_{11} + 6H_2O \rightarrow C_2B_7H_{13} + 2B(OH)_3 + 4H^+ + 4e^- \qquad (1)$$

aqueous ferric ion or chromic acid has been used to prepare the $C_2B_7H_{13}$ by degradation of 1,8-$C_2B_9H_{11}$. By observing stringent air-free conditions the reaction of the 1,8-*closo*-$(CH_3)_2C_2B_9H_9$ in a two-phase solvent system of chromic acid and benzene at 0° gives a 31% yield of a new substituted carborane 1,8-dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11) (I). The isolation of the bis(hydroxy) derivative of the *closo*-$(CH_3)_2C_2B_9H_9$ carborane may be due to formation of a proposed chromate–carborane complex formed in the reaction of 1,8-$(CH_3)_2C_2B_9H_9$ and chromic acid, which on hydrolysis yields the 1,8-$(CH_3)_2C_2B_9H_7(OH)_2$ rather than undergoing complete oxidation to the $(CH_3)_2$-$C_2B_7H_{11}$. The preparation of the new hydroxy-substituted carborane can also be accomplished by using a mixture of sodium periodate and acetic acid in lieu of the chromic acid medium.

The product from the reaction of the oxidizing agent and the *closo*-$(CH_3)_2C_2B_9H_9$ has the correct analysis and molecular weight to indicate the formation of 1,8-$(CH_3)_2C_2B_9H_7$-$(OH)_2$. The product is isolated from the organic benzene layer in the reaction medium. Evaporation of solvent and sublimation of the residue gave only a negligible amount of the expected product, $(CH_3)_2C_2B_7H_{11}$. Recrystallization of

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[10] P. M. Garrett, T. A. George, and M. F. Hawthorne, *Inorg. Chem.*, 8, 2008 (1969).

the sublimate residue under an inert atmosphere in dry, air-free benzene yields clear, cubic crystals. These observations represent a new departure from the general reactions of the *closo*-carboranes with oxidizing agents and led us to a more detailed study of the bis(hydroxy) adduct of $1,8-(CH_3)_2C_2B_9H_9$.

Initial attempts were made to compare the reactivity of the bis(hydroxy)carborane I with the chemistry of the known *B*-hydroxycarborane systems of the icosahedral carboranes.[7,8] For example, Zakharkin[7] reported the preparation of the methoxy derivative by reaction of 3-hydroxydimethylcarborane with liquid ammonia followed by treatment with methyl iodide. However, reaction of the bis(hydroxy)carborane I with base in polar solvents leads primarily to the isolation of the $(CH_3)_2C_2B_7H_{11}$ in nearly 40% yield indicating the OH groups in the bis(hydroxy)carborane are located at the adjacent boron positions, B(3,7). The product from the reaction with base was identified by comparison of its physical and spectral data with a sample of $(CH_3)_2C_2B_7H_{11}$ of known purity. The instability of the carborane I in base may be due in part to the tendency of the closo 11-atom carborane polyhedra to undergo a cage-opening reaction in basic media and to the reactivity of the highly positive centers on the boron atoms directly bonded to the -OH groups, which make them particularly susceptible to attack by nucleophilic reagents. The following data substantiate the proposed structure for the bis(hydroxy)carborane shown in Figure 1.

Infrared Spectra. The infrared spectrum of the bis(hydroxy)carborane I contains a strong terminal B-H stretch at 2550 cm^{-1}. Neither KBr mull spectra nor solution spectra show any indication of an absorption band at 1600-2100 cm^{-1}, which would be indicative of a B-H-B grouping or a band at 2300 cm^{-1} indicative of a BH_2 group. A strong, broad band in the KBr spectrum of carborane I at 3600-3100 cm^{-1} is assigned to the OH stretch. The spectrum of the bis(hydroxy)carborane recovered after stirring in a solution of CH_2Cl_2 saturated with DCl indicated that the broad band at 3600-3100 cm^{-1} nearly disappeared and that, in addition, a new broad band appeared at 2550 cm^{-1}, which can be attributed to an O-D stretch. Further, if the solution ir spectra are taken in a dry nonpolar solvent such as benzene, a sharp band occurs at 3575 cm^{-1}, which is assigned to the O-H absorption and has a 20-cm^{-1} width at half-peak height.

In addition to the assigned O-H stretch there is a band at 1230 cm^{-1} with a width of 25 cm^{-1} at half-peak height, which is assigned to the B-O stretch. This assignment is consistent with previous studies on boric acid, trimethyl borate,[11] and the 3-hydroxycarboranes isolated by Zakharkin.[8b]

The infrared spectral data, the microanalytical and molecular weight data, and the conversion of the bis(hydroxy)carborane I into the open-cage structure $(CH_3)_2C_2B_7H_{11}$ strongly suggest that the basic structure for the bis(hydroxy)carborane I is as shown in Figure 1. The two hydroxyl groups are tentatively assigned to the B(3,7) positions, since the removal of these two boron atoms generates the open-cage $(CH_3)_2C_2B_7H_{11}$.

Mass Spectra. The mass spectrum of $1,8-(3,7)-(CH_3)_2C_2B_9H_7(OH)_2$ (I) was obtained on an MS-902 low-resolution instrument with a heated inlet. The $1,8-(3,7)-(CH_3)_2C_2B_9H_7(OH)_2$ slowly sublimes at 60° (10^{-3} mm). The mass spectrum cuts off sharply at a *m/e* 194 corresponding to the parent ion ($^{11}B_9{}^{12}C_4{}^{16}O_2{}^1H_{15}{}^+$). The second most abundant envelope occurs with cutoff at *m/e* 166 and corresponds to the loss of a *B*-OH moiety from the parent molecule.

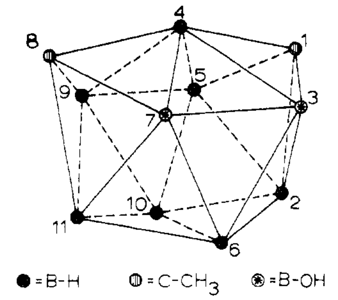

Figure 1. Numbering system and proposed structure for the 1,8-dimethyl-(3,7)-dihydroxy-1,8-dicarba-*closo*-undecaborane(11).

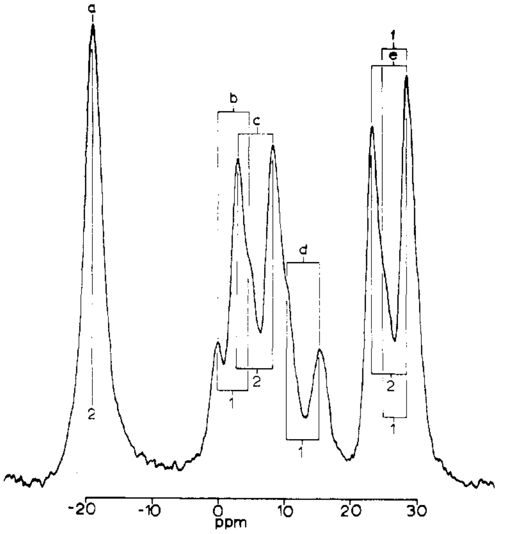

Figure 2. The 32.1-MHz ^{11}B nmr spectrum of $1,8-(3,7)-(CH_3)_2C_2B_9H_7(OH)_2$ in acetone. Chemical shifts relative to boron trifluoride etherate (coupling constants, Hz): (a) −19.2 ppm, (b) 1.9 ppm (151), (c) +5.3 ppm (169), (d) +12.6 ppm (157), (e) +25.4 ppm (170), and (f) +26.1 ppm (132).

Mass spectra were also obtained for the deuterium-substituted carborane-exchanged products. The parent ion molecule weight had increased by 2 mass units to *m/e* 196 corresponding to $^{11}B_9{}^{12}C_4{}^{16}O_2{}^1H_{13}{}^2D_2{}^+$. The mass spectral data and ir data indicate that the two hydroxyl protons are easily exchanged while the rate of any B-H exchange is extremely slow, if at all.

Since the infrared data indicate that any protons exchanged are those bonded to oxygen and not boron, we suggest that there are no B-H-B hydrogens available for exchange and any protons, which undergo rapid exchange, are those bonded to oxygen.

Nmr Spectra. The 32.1-MHz ^{11}B nmr spectrum of $1,8-(3,7)-(CH_3)_2C_2B_9H_7(OH)_2$ is shown in Figure 2. The data presented so far indicate the two hydroxy groups are located on adjacent boron atoms B(3,7). Using the structure shown in Figure 1 this gives six different sets of boron atoms, three of intensity 1 (B(4), B(6), B(10)) and three of intensity 2 (B(3,7), B(5,9), B(2,11)). The 32.1-MHz ^{11}B nmr spectrum indicates six different boron environments and consists of a broad singlet at low field of intensity 2, which is assigned to the B(3,7) atoms, and a series of overlapping doublets of relative intensity 1:2:1:2:1 at higher field. The presence of six different types of boron atoms, which is clearly indicated in the ^{11}B nmr spectrum, is in agreement with the proposed structure in Figure 1.

Using a Bruker HF-90 with a broad-band decoupler operating at 90 MHz at 800-cps bandwidth the decoupled

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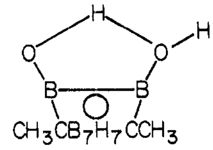
(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 348.

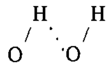
proton spectrum of the ^{11}B nmr shows five distinct singlets of intensity ratio 2:1:2:1:3. The low-field singlet of intensity 2 is assigned to the B(3,7) atoms, which have terminal OH groups, while the high-field singlet of intensity 3 arises from the accidental overlap of two sets of boron atoms of relative intensity 2:1.

The 60-MHz ^1H nmr spectrum of I in $CDCl_3$ shows two peaks at −2.10 and −4.81 ppm, with relative intensity of 3:1. The ^1H nmr in chloroform is both temperature and concentration dependent. At room temperature the peak at −4.81 ppm is assigned to the terminal hydrogen on the O-H group, while the peak at −2.10 ppm lies in the expected range for methyl groups bonded to carbon atoms in carboranes. At −60° in the ^1H nmr spectrum of I in $CDCl_3$ the chemical shift of the proton assigned to the OH group broadens slightly and shifts to lower field to −6.96 ppm indicating the two hydroxyl protons are still in equivalent environments even at low temperatures. In acetone-d_6 at 25° the ^1H nmr consists, apparently, of only one peak at −2.05 ppm, which is assigned to the methyl groups of I. However, as the temperature is lowered, two peaks of equal intensity begin to appear at lower field in addition to the peak at −2.05 ppm. The two new peaks, which appear only at low temperatures, are assigned to the protons of the hydroxy groups. At −20° the two peaks appear at −4.63 and −8.29 ppm and eventually at −60° shift to −5.43 and −8.80 ppm. The variable-temperature ^1H nmr is shown in Figure 3.

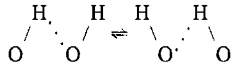
The interpretation of the low-temperature ^1H nmr in acetone-d_6 invokes the possibility of the O-H· · ·O hydrogen-bonded structure



At room temperature in $CDCl_3$ a rapid isomerization occurs in which the bridge and terminal hydroxy protons are equilibrated. A possible mechanism for the isomerization involves the rearrangement of the



bridging hydrogen bond, in which the terminal and bridging positions alternate. Hydrogen bonds of this type are estimated to have energies on the order of 3-7 kcal. 5,8-Dihydroxy-1,4-naphthoquinone has been studied in detail and shows a similar hydrogen-bonding phenomenon.[12] The appearance of two peaks at low temperature in acetone-d_6, but not in chloroform-*d*, may be due to the stabilization of the bridged structure by the formation of a hydrogen bond between the oxygen in acetone and the terminal O-H proton. We note the same effect in the ^1H nmr of pyrocatechol, in which two different types of hydroxy protons are found in the ^1H nmr in acetone-d_6.



These data as well as chemical information discussed previously suggest that the product from the reaction of 1,8-*closo*-$(CH_3)_2C_2B_9H_9$ and chromic acid in benzene has the structure shown in Figure 1.

Although the mechanism of formation of the 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ is unknown, we believe the mode of preparation, the degradation by base to the $(CH_3)_2C_2B_7H_{11}$, and the stated physical evidence indicate the formation of the carborane I may be an intermediate step involved in the preparation of $(CH_3)_2C_2B_7H_{11}$ *via* oxidation of the 1,8-*closo*-$(CH_3)_2C_2B_9H_9$ as proposed by Hawthorne. The actual intermediate involved may be described as a transition metal-oxy complex, in which the metal is bonded to the B(3,7) borons in the carborane 1,8-$(CH_3)_2C_2B_9H_9$ through two bridging oxygen atoms. Oxidation of the metal-carborane complex would yield the expected $(CH_3)_2C_2B_7H_{11}$, whereas hydrolysis of the metal-oxygen bond would yield the bis(hydroxy)carborane I. Although chromic acid and IO_4^- have been used to produce the bis(hydroxy)carborane, we have been unable to find an oxidizing agent, which would produce a stable derivative of the proposed metal-oxygen intermediate. A more detailed description of the chemistry of the 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ carborane follows.

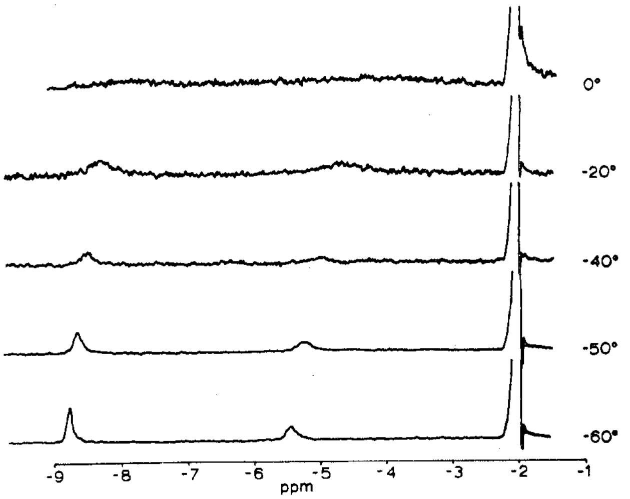


Figure 3. The variable-temperature 60-MHz ^1H nmr spectrum of 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ in acetone.

Halogenation Reactions. The reaction of 1,8-(3,7)-$(CH_3)_2$-$C_2B_9H_7(OH)_2$ with bromine under various conditions leads to monobromo substitution and no evidence of any di- or trihalo products was found. Microanalytical data and mass spectral data indicate only one bromine atom is taken up for each molecule of carborane I. The position of bromination favored may be at either the B(6) or B(10) atoms. These are the only borons not adjacent to the more electronegative carbons. The B(OH) groups can have either an electron-withdrawing inductive effect, in which case bromination occurs at B(10), or the hydroxy groups may be strongly electron releasing as in phenol, in which case bromination occurs at B(6). An X-ray structure is in progress on the bromo derivative.

Examination of the ^{11}B nmr of the bromo-substituted derivative allows us to propose a partial assignment for the ^{11}B nmr of the 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$. The 32.1-MHz ^{11}B nmr of the bromo derivative shown in Figure 4 is similar to the parent carborane shown in Figure 2. In the ^{11}B nmr of the bis(hydroxy)carborane I the spectrum consists of a low-field singlet, assigned to the B(3,7) boron atoms, and a multiplet group at higher field. The multiplet group at higher field consists of two multiplets, the first of total intensity 4 in a ratio of 1:2:1 and the second of total intensity 3 in a ratio of doublets 2:1. The ^{11}B nmr of the bromo derivative has the same gross structural features, except that in the high-field multiplet the doublet of intensity 1 has been reduced to a singlet at 14.0 ppm (intensity 1) and the doublet of intensity 2 shifts to +22.4 ppm. Based on this

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(12) J. R. Bolton, A. Carrington, and P. E. Todd, *Mol. Phys.*, 6, 169 (1963).

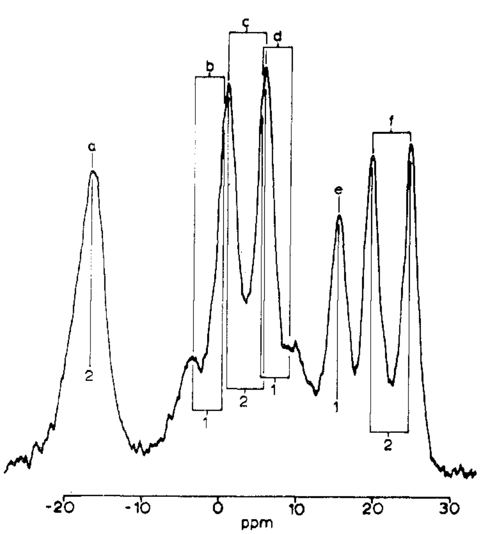
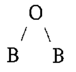


Figure 4. The 32.1-MHz ^{11}B nmr spectrum of 1,8-(3,7)-$(CH_3)_2$-$C_2B_9H_6Br(OH)_2$ in CH_2Cl_2-acetone. Chemical shifts relative to boron trifluoride etherate (coupling constants, Hz): (a) −16.7 ppm, (b) −1.3 ppm (126), (c) +3.4 ppm (156), (d) +7.5 ppm (119), (e) +15.5 ppm, and (f) +22.4 ppm (161).

evidence the boron of intensity 1 at highest field in the 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ spectrum is assigned to the B(10) or B(6) atom. This is in direct contrast to the parent carborane, 1,8-(3,7)-$(CH_3)_2C_2B_9H_9$, where the unique seven-coordinate boron B(4) is assigned to a single high-field doublet at +17.3 ppm ($J = 169$ cps) at 19.3 MHz.

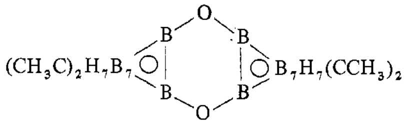
The spin-decoupled spectrum of the brominated derivative of the carborane I has six distinct singlets in the ^{11}B nmr. The singlets are in a ratio of 2:1:2:1:1:2 at −16.7, −1.1, 3.7, 7.0, 16.0, and 22.8 ppm, respectively. The singlet of intensity 2 at −16.7 ppm has been assigned to B(3,7) and the singlet of intensity 1 at 16.0 ppm has been assigned to B(10) or B(6).

Condensation Reactions. As already noted the 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ can be isolated in pure form with some difficulty by sublimation at 60° (0.001 mm). However, on heating at temperatures above 100° or attempted dissolution in hot solvents at temperatures exceeding 150° the bis(hydroxy)carborane dimerizes with loss of water to form two B_9C_2 units linked *via* two



$$\begin{array}{c} O \\ / \quad \backslash \\ B \quad\; B \end{array}$$

bridging units on adjacent boron atoms. The proposed structure of the dimer (II) is written as



II

The tentative structural assignment is based on the infrared spectrum, which has no -OH stretching bands near the region of 3600-3100 cm^{-1}, but does retain the B-O stretch assigned to the band at 1225 cm^{-1}. The low-resolution mass spectrum of the pyrolysis product has a parent ion peak at *m/e* 352 corresponding to $^{11}B_{18}{}^{12}C_8{}^{16}O_2{}^{1}H_{26}{}^{+}$ as well as a relatively abundant fragment at *m/e* 176 which has been assigned to the $^{11}B_9{}^{12}C_4{}^{16}O_1{}^{1}H_{13}{}^{+}$. The fragment represents the product of the homolytic cleavage of the pyrolysis product of the dimer II.

Although the 32.1-MHz ^{11}B nmr of the dimer II is less well resolved than the 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$, the gross structural features are the same. There is a large broad singlet of intensity 4 at low field (−13.7 ppm relative to boron trifluoride etherate) which is assigned to the four boron atoms (B(3), B(3′), B(7), B(7′)) linked *via* the oxygen bridges. The remainder of the ^{11}B nmr consists of a group of peaks at higher field of total intensity 14. The high-field group consists of two multiplets of relative intensity 8:6 at +3.9 and +18.9 ppm relative to boron trifluoride etherate.

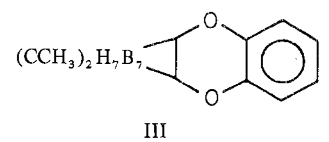
Table I. Mass Spectral Data for Products of Condensation Reactions

Carborane	Organic ligand	Mass spectral cutoff
I	I	352
I	*o*-Pyrocatechol	268
I	Ethylene glycol	220
I	2,3-Butanediol	248
I	1-Phenyl-1,2-ethanediol	296
I	1,2-Cyclohexanediol	274

The ^{1}H nmr spectrum of II is an interesting one having two singlets in a 2.5:1 ratio at −2.73 and −2.24 ppm relative to TMS. These are in the expected range for methyl groups bonded to the carbon atoms in carborane. Although the microanalytical data and molecular weight data indicate a pure substance, the possibility of two different isomers formed from the pyrolysis reaction cannot be discounted. On coupling through oxygen bridges the two B_9C_2 units can adopt two possible conformations about the oxygen linkage. The cage B_9C_2 units may be linked *via* two oxygens so that both cage units face up in the same direction. In this case the four methyl groups are in the same environment related by a mirror plane and a twofold axis of rotation. In the second isomer one carborane unit may face up and the second face down. The four methyl groups are again in identical environments being related by a center of inversion but are in environments distinctly different from the first isomer. This would give rise to two different singlets in the ^{1}H nmr spectrum. The respective isomers are referred to as cis and trans configurations. This would indicate the ^{11}B nmr spectrum of II is really two closely related boron nmr spectra in a ratio of 2.5:1. Based on comparative models of the two isomers the structure with the least amount of steric interactions between neighboring B-H units or methyl groups is the trans isomer. Attempts at separation using thin-layer chromatography have so far been unsuccessful.

The condensation reaction of the carborane 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ appears to be a general one, which can involve the reaction of the bis(hydroxy)carborane with an organic moiety. The organic ligand must contain two hydroxy groups preferably in positions adjacent to each other. A list of derivatives prepared so far is found in Table I.

A reaction typical of this series is one between *o*-pyrocatechol and the 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$



III

The mass spectrum has a cutoff at *m/e* 268 corresponding to $^{11}B_9{}^{12}C_{10}{}^{16}O_2{}^{17}H_1{}^{+}$. Primary fragments indicate the presence of $(CH_3)_2C_2B_9H_7(O)_2{}^{+}$. The infrared spectrum of the pyrolysis product III has no O-H stretch but does retain the B-O stretch at 1275 cm^{-1}. The overall structure of the 32.1-MHz ^{11}B nmr is similar to the starting material and con-

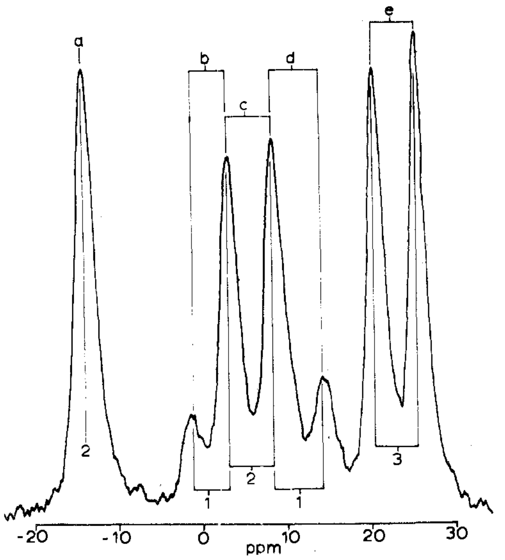


Figure 5. The 32.1-MHz ^{11}B nmr spectrum in acetone of the condensation product from the reaction of pyrocatechol and 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$. Chemical shifts relative to boron trifluoride etherate (coupling constants, Hz): (a) −14.2 ppm, (b) +0.4 ppm (128), (c) +4.9 ppm (170), (d) +11.1 ppm (160), and (e) +21.9 ppm (150).

sists of five individual peaks at −14.2 ppm (2), +0.4 ppm (1), +4.9 ppm (2), +11.6 ppm (1), and +21.9 ppm (3). The spectrum is shown in Figure 5. The doublet of intensity 3 at highest field arises from the accidental overlap of the two individual doublets of intensity 2 and 1 found in the ^{11}B nmr of the parent carborane 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$. The ^{11}B nmr indicates the structural B_9 carborane unit is maintained. The proposed structure of the catechol derivative is shown in Figure 6.

The chemistry of the pyrolysis product of pyrocatechol is similar to that of an activated benzene ring. Under mild conditions a dinitro product (position of nitration undetermined) is obtained from reaction of the pyrolysis product with a solution of nitric and sulfuric acids.

Other condensation reactions include the product from the pyrolysis of 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$ and 2,3-butanediol. The 2,3-butanediol consisted of 85% *dl* mixture and 15% meso. Of interest in this reaction was the proton nmr of the condensation product. The microanalytical data, mass spectral cutoff at *m/e* 248, and a ^{11}B nmr similar to that of the pyrocatechol reaction product indicated the condensation product had been formed. However, the 60-MHz ^1H nmr indicated that the sole isomer formed had the methyl groups trans to each other. The ^1H nmr spectrum shown in Figure 7 clearly shows the two different methyl groups, which are split by the trans hydrogen ($J = 6$ Hz). The reactions of stereospecific glycols such as *dl*-butanediol or *meso*-butanediol are being used as probes for determining possible mechanisms for the condensation reaction.

Furthermore, we have extended this general reaction sequence to produce successfully both $(CH_3)_2C_2B_9H_8(OH)$ and the $(CH_3)_2C_2B_9H_7(OH)_2$ *via* reaction of $(CH_3)_2C_2B_9H_9$ with IO_4^- in acid media.[13] The possibility of selective or stepwise removal of the B(OH) groups followed by replacement with transition metal ions is also being investigated.

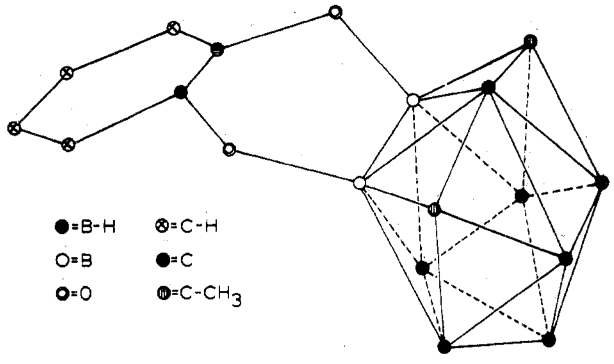


Figure 6. Proposed structure for the pyrolysis product of pyrocatechol and 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$.

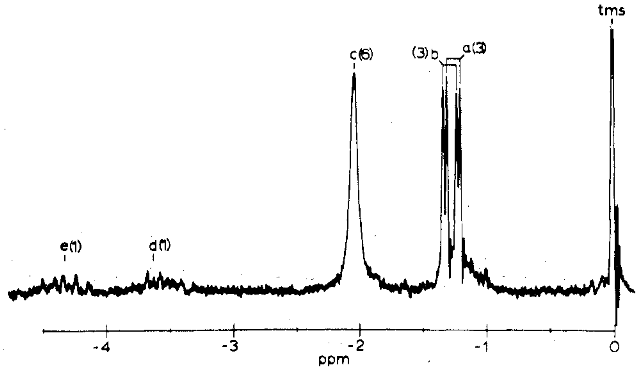


Figure 7. The 60-MHz ^1H nmr spectrum in CD_2Cl_2 of the condensation product from the reaction of 2,3-butanediol and 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$. Relative areas are given in parentheses in the figure. Chemical shifts relative to tetramethylsilane (coupling constants, Hz): (a) −1.25 ppm (6), (b) −1.28 ppm (6), (c) −2.05 ppm, (d) −3.67 ppm (complex), and (e) −4.34 ppm (complex).

Registry No. 1,8-$(CH_3)_2C_2B_9H_9$, 17764-85-1; 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$, 40618-03-9; $[(CH_3)_2C_2B_9H_7O]_2$, 40633-54-3; $C_6H_4(OH)_2$, 120-80-9; 1,8-(3,7)-$(CH_3)_2$-$C_2B_9H_7(O_2C_6H_4)$, 40736-40-1; $CH_3CH(OH)CH(OH)CH_3$, 513-85-9; 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(O_2C_4H_8)$, 40618-04-0; 1,8-(3,7)-$(CH_3)_2C_2B_9H_6(OH)_2Br$-10, 40633-55-4.

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(13) F. R. Scholer and G. D. Mercer, to be submitted for publication.