tem at −45°. The system was pumped further at room temperature for 2 min. The volatile components were ether and ammonia; no boron hydride compound was detected in volatiles. Ammonia retained in the solid residue was 4.8 mmol or the ratio $NH_3$(retained)/$B_5H_9$ was 2.2.

**Acknowledgment.** Support of this work by the National Cancer Institute through Grant CA-07989 and by the National Science Foundation through Grant GP-14873 is gratefully acknowledged.

# Synthesis, Structure, and Reactions of 1,2-Dicarbapentaborane(7)[1]

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**Abstract:** The carborane 1,2-dicarba-*nido*-pentaborane(7) has been obtained from the reaction of tetraborane(10) with acetylene and structurally characterized. The compound is stable in the vapor phase at 50° and in dilute hydrocarbon solutions, but the neat liquid rapidly and irreversibly polymerizes without evolution of hydrogen. Polymerization is also induced by ethereal solvents, hydrogen chloride, and certain other reagents. The carborane is highly reactive toward $B_4H_{10}$ or $B_2H_6$ in the absence of acetylene. Reaction with acetylene yields 2,3,4,5-$C_4B_2H_6$ and with ethylene produces alkylboranes. The carborane forms a stable 1:1 adduct with triethylamine. Bromine apparently adds to the C–C bond of $C_2B_3H_7$, while excess $Br_2$ attacks the boron portion of the molecule and destroys the cage. Iron pentacarbonyl and $C_2B_3H_7$ react under ultraviolet light to produce the complex ($\pi$-$C_2B_3H_7$)Fe(CO)$_3$ which contains the planar dicarbacyclopentaboranyl(2−) ligand, an isoelectronic analog of $C_5H_5^-$.

Of the many known carborane cage systems, most represent isoelectronic and isostructural analogs of known boron hydrides or polyhedral borane anions. For example, the entire hexaborane series ($B_6H_{10}$, 2-$CB_5H_9$, 2,3-$C_2B_4H_8$, 2,3,4-$C_3B_3H_7$, and 2,3,4,5-$C_4B_2H_6$) has been characterized, each species having a pentagonal-pyramidal structure with 0–4 bridge hydrogen atoms.[2] Carborane analogs of smaller boron hydrides were unknown prior to the present work, although Lipscomb has predicted,[3] from MO arguments, the existence of square-pyramidal carboranes isoelectronic with $B_5H_9$. A preliminary communication[4] from this laboratory reported the isolation and structural characterization of the first such molecule, 1,2-$C_2B_3H_7$. In this paper we describe the preparation of this compound and some of the most significant aspects of its chemistry as it has developed thus far.

## Results and Discussion

**Synthesis.** The reaction of tetraborane(10) with acetylene in the gas phase at 50° has been described in detail, and the formation of the methyl derivatives of 2,3,4-$C_3B_3H_7$ in this system has been examined kinetically.[5] In our early studies of this reaction it was allowed to run to completion, which at 50° requires 4–5 hr when the $C_2H_2$:$B_4H_{10}$ ratio is 1:1, but several days for a 10:1 mixture. More recent work has disclosed that a substantially different product mixture is obtained when the reaction is quenched well before completion. The major difference, in comparison with reactions over longer periods, is the recovery of 1,2-$C_2B_3H_7$ in substantial yield. This new compound is actually the predominant volatile product (10% yield[6] based on boron consumed) obtained from a 10:1 $C_2H_2$–$B_4H_{10}$ mixture after 24 hr at 50°. These observations are explained by the subsequent findings that pure $C_2B_3H_7$ reacts readily with $B_4H_{10}$ and $B_2H_6$ at 50° (see Experimental Section) and much more slowly with $C_2H_2$, as discussed below. In the presence of a large excess of $C_2H_2$, the rapid $C_2H_2$–$B_4H_{10}$ interaction[7] dominates the system, in effect protecting the $C_2B_3H_7$ from attack by $B_4H_{10}$. Consequently, a prerequisite to the synthesis of $C_2B_3H_7$ in reasonable yield is a $C_2H_2$:$B_4H_{10}$ mole ratio of at least 2:1, with optimum conditions depending on a complex interrelationship between partial pressures of reactants, temperature, and reaction time.

**Structure.** A square-pyramidal structure analogous to $B_5H_9$ (Figure 1) has been postulated from spectroscopic evidence,[4] and the preliminary results of a microwave study in progress elsewhere are consistent with this structure.[8] The $^{11}$B and $^1$H nmr spectra of

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(1) Abstracted in part from the Ph.D. Dissertation of D. A. F., University of Virginia, 1970, and presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract INOR 8.

(2) For a recent review, see R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(4) D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 1438 (1970).

(5) D. A. Franz and R. N. Grimes, *ibid.*, **93**, 387 (1971), and references cited therein.

(6) Actual yields of $C_2B_3H_7$ have ranged as high as 20% at low partial pressures of reactants. However, under these conditions the absolute quantity of $C_2B_3H_7$ produced is inconveniently small.

(7) Kinetic studies[5] have indicated that the actual species reacting with $C_2H_2$ is $B_4H_8$, a highly reactive intermediate produced from $B_4H_{10}$ in the gas phase.

(8) R. A. Beaudet, private communication. We thank Professor Beaudet for permission to quote these results prior to publiction.

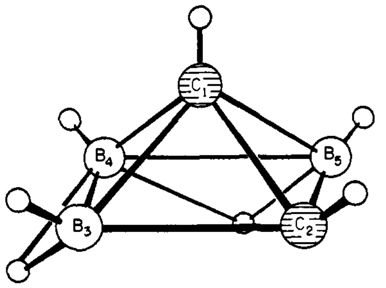

Figure 1. Proposed structure of 1,2-$C_2B_3H_7$.

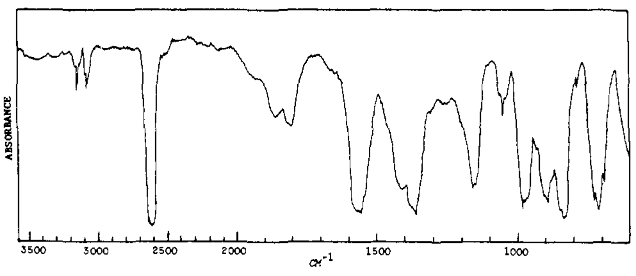

Figure 2. Gas-phase infrared spectrum of 1,2-$C_2B_3H_7$ (30-Torr pressure).

1,2-$C_2B_3H_7$ have been presented earlier,[4] as has the $^1H$ nmr spectrum of 1,2-$D_2C_2B_3H_5$ (obtained from the reaction of $C_2D_2$ with $B_4H_{10}$). The mass spectra of both compounds are listed in Table I. The presence of two deuterium atoms in the latter carborane is clearly indicated; since nmr and infrared evidence indicates that only the carbon atoms are deuterated, the presence of two carbon and three boron atoms is established.

**Table I.** Partial Mass Spectra of 1,2-$C_2B_3H_7$ and 1,2-$D_2C_2B_3H_5$

| | Relative intensity | |
|---|---|---|
| *m/e* | $C_2B_3H_7$ | $D_2C_2B_3H_5$ |
| 67 | | 0.5 |
| 66 | | 22.4 |
| 65 | 0.4 | 80.0 |
| 64 | 24.6 | 100.0 |
| 63 | 94.7 | 100.0 |
| 62 | 100.0 | 87.1 |
| 61 | 93.0 | 52.9 |
| 60 | 57.9 | 34.1 |
| 59 | 33.3 | 29.4 |
| 58 | 28.1 | 21.2 |
| 57 | 14.0 | 9.4 |
| 56 | 5.3 | 2.4 |

The infrared spectra of these compounds are similar except for the C–H stretching absorptions at 3150 and 3075 cm$^{-1}$ in the $C_2B_3H_7$ spectrum (Figure 2), which are absent in the deuterated species. The presence of two such bands at unusually high frequencies (C–H stretching bands in carboranes, when present, are virtually always below 3100 cm$^{-1}$) suggests a relatively large C–C bond order in this molecule. This observation is supported by the reaction chemistry of $C_2B_3H_7$, which is strongly suggestive of an ethylene-like carbon–carbon bond.

**Thermal Stability and Polymerization.** Dicarbapentaborane(7) is a colorless liquid, somewhat more volatile than pentaborane(9). The compound is unchanged over extended periods at 50° in the vapor phase but at 110° is completely degraded to tan solids, hydrogen, and diborane. In the liquid state at 25°, $C_2B_3H_7$ irreversibly polymerizes within minutes to a white solid, $(C_2B_3H_7)_x$, without evolution of $H_2$ or other volatile products. In the presence of certain reagents such as HCl, diglyme, or tetrahydrofuran (THF), polymerization of the liquid carborane is more rapid, occurring within seconds. Thus, the condensation of dry HCl with an equivalent amount of liquid $C_2B_3H_7$ yields a white nonvolatile solid in which essentially all of the HCl is incorporated. In contrast, THF catalyzes the polymerization of $C_2B_3H_7$ but can be quantitatively recovered from the reaction.

Solutions of $C_2B_3H_7$ in toluene, pentane, hexane, or carbon tetrachloride are relatively stable, at least at concentrations below 0.1 *M*, and do not exhibit detectable polymer formation. Even in these solvents, however, polymerization can be induced by bromine (see below) or HCl. As in the reaction of HCl with neat liquid $C_2B_3H_7$, treatment of a solution of $C_2B_3H_7$ in hexane with an equivalent amount of dry HCl at 25° yields a white, nonvolatile, air-flammable solid in which all of the HCl is retained. This reaction occurs only in the liquid carborane or in solution, since vapor-phase mixtures of $C_2B_3H_7$ and HCl are virtually unchanged over periods of a few hours.

Even in the gas phase, $C_2B_3H_7$ slowly polymerizes in the presence of THF vapor; thus, when equimolar quantities of gaseous THF and $C_2B_3H_7$ were allowed to stand at 25°, only 17% of the original $C_2B_3H_7$ remained after 15 hr, while nearly all of the THF was recovered. Again, no $H_2$ was detected.

Attempts at direct structural characterization of these polymeric products have met with little success thus far, but the weight of evidence suggests that polymerization of $C_2B_3H_7$ involves the C–C link in the molecule. If this bond is of approximately double bond character, as suggested earlier (and supported by chemical evidence discussed below), the polymerization may be mechanistically related to the formation of olefin-based polymers such as polyethylene. This hypothesis receives some support from the fact that the polymerization is not accompanied by significant evolution of $H_2$, implying that this process is very different from the usual sort of boron hydride condensations which typically release considerable quantities of $H_2$.

**Reactions with Acetylene and Ethylene.** The gas-phase interaction of $C_2B_3H_7$ with $C_2H_2$ at 50° yields one significant volatile product, the parent *nido*-carborane 2,3,4,5-tetracarbahexaborane(6). This material is identical with the compound isolated by Onak and Wong[9] from the fast-flow pyrolysis of tetramethylenediborane(6). Although the insertion of acetylene into boron

$$C_2B_3H_7 + C_2H_2 \longrightarrow \underset{(5\text{–}10\%)}{C_4B_2H_6} + \text{solids}$$

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[9] T. P. Onak and G. T. F. Wong, *J. Amer. Chem. Soc.*, **92**, 5226 (1970).

hydride frameworks to produce two-carbon carboranes is well known,[2] this reaction is the first example of acetylene insertion into a carborane cage to form a four-carbon system. Further studies of reactions of this type, including the use of tracer techniques, are in progress and will be reported elsewhere.

The reaction of $C_2B_3H_7$ with excess ethylene in the gas phase at 90° yields primarily 1,1′,2,2′-tetraethyldiborane, triethylboron, and a nonvolatile liquid which condenses onto the reactor walls in small droplets.

$$C_2B_3H_7 + C_2H_4 \longrightarrow B(C_2H_5)_3 + B_2H_2(C_2H_5)_4$$

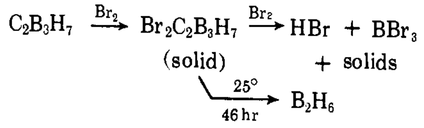
No $H_2$ is evolved, and the reaction consumes approximately 4 mol of $C_2H_4$ per mole of $C_2B_3H_7$. In contrast to the reaction with acetylene, there is no evidence of carbon insertion in this system, and the products indicate that the dominant process is gas-phase hydroboration of the ethylenic double bond.

**Reaction with Triethylamine.** Dicarbapentaborane(7) and excess triethylamine in toluene react irreversibly to form a stable 1:1 adduct, as established by the reaction stoichiometry and by tensiometric titration. No detectable $H_2$ or other side products are formed.

$$C_2B_3H_7 + :N(C_2H_5)_3 \longrightarrow C_2B_3H_7:N(C_2H_5)_3$$

The adduct is a white nonvolatile solid whose 32.1-MHz $^{11}B$ nmr spectrum (see Experimental Section) suggests that the $C_2B_3H_7$ structure is substantially altered, possibly incorporating a cyclic $C_2B_3H_7$ moiety stabilized by the transfer of electronic charge from the amine.[10] Treatment of the solid adduct with an equivalent amount of HCl vapor converts it to a glass and releases $H_2$ (50% yield based on HCl consumed), with nearly quantitative consumption of the HCl. Further studies of $C_2B_3H_7$–amine interactions are in progress and will be reported at a later date.

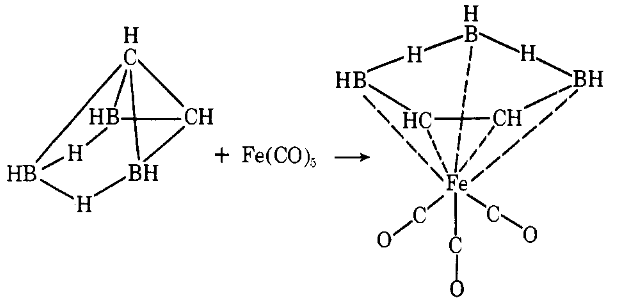
**Bromination.** The treatment of $C_2B_3H_7$ with bromine, in the gas phase or in solution, results in rapid consumption of the $Br_2$ in a ratio of at least 2 mol of halogen per mole of carborane. Significantly, no HBr or $H_2$ is released during the slow addition of the first mole equivalent of $Br_2$, indicating that the halogen adds across the carbon–carbon bond without displacement of hydrogen. This observation strongly supports the suggestion of a C–C link of double bond character in $C_2B_3H_7$, as discussed above. The product of the 1:1 addition is a white nonvolatile solid, which on standing at room temperature slowly evolves diborane (but not $H_2$). Addition of a second mole of $Br_2$ to this solid generates considerable quantities of HBr and $BBr_3$.



$$C_2B_3H_7 \xrightarrow{Br_2} \underset{\text{(solid)}}{Br_2C_2B_3H_7} \xrightarrow{Br_2} HBr + BBr_3 + \text{solids};\quad Br_2C_2B_3H_7 \xrightarrow[46\text{ hr}]{25°} B_2H_6$$

It seems probable that addition of the first mole of $Br_2$ to $C_2B_3H_7$ takes place selectively at the carbon–carbon bond, with attack on the boron portion of the molecule occurring only after the C–C bond is completely halogenated. It is not certain whether the nonvolatile 1:1 addition product is monomeric or polymeric, but evidence suggesting a polymer has been obtained. Thus, hydrolysis of the 1:1 product formed in pentane solution produced bromoalkanes and hydrogen. Extraction of the aqueous solution with ether yielded a white solid whose mass spectrum indicated the presence of brominated polymeric species of molecular weight ~400.

**Reaction with Iron Pentacarbonyl.** $Fe(CO)_5$ and $C_2B_3H_7$ react under ultraviolet light to form the complex $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$, identical with the compound obtained earlier[11] from *nido*-2,3-$C_2B_4H_8$ and $Fe(CO)_5$. In contrast to the latter reaction, which also gave $(\pi\text{-}C_2B_4H_6)Fe(CO)_3$,[11] no other complexes were detected in the present work. Significantly, no measurable $H_2$ was produced. Since $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$ is an isoelectronic analog of the known $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ cation, it is reasonable to regard it as an $Fe(CO)_3^{2+}$ unit $\pi$ bonded to an essentially planar $C_2B_3H_7^{2-}$ ligand. The proposed structure is consistent with nmr, infrared, and mass spectroscopic evidence presented in a previous communication.[11]



If one accepts the assignment of a formal −2 charge to the carborane ring, which is then isoelectronic with $C_5H_5^-$, the above reaction may be viewed as a two-electron reduction of pyramidal $C_2B_3H_7$ to planar $C_2B_3H_7^{2-}$. This suggests that it may be possible to generate the free $C_2B_3H_7^{2-}$ ion by chemical or electrolytic reduction of $C_2B_3H_7$ in solution, a hypothesis which is presently under investigation.

**Other Attempted Reactions of $C_2B_3H_7$.** In view of the apparent square pyramidal structure of $C_2B_3H_7$, an insertion reaction with trimethylboron was anticipated, producing methyl derivatives of the polyhedral carborane 1,2-dicarba-*closo*-hexaborane(6) (1,2-$C_2B_4H_6$). However, an equimolar mixture of $C_2B_3H_7$ and $(CH_3)_3B$ at 80° for 26 hr gave only methyldiboranes, solids, and $H_2$, with no carborane recovered.

Attempts to effect the deprotonation of $C_2B_3H_7$ with NaH and $NaAlH_2(C_2H_5)_2$ were not entirely conclusive due to the extreme tendency of the carborane to polymerize in ethereal solutions, but no more than

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(10) A formal $C_2B_3H_7^{2-}$ planar ligand, isoelectronic with $C_5H_5^-$, has been postulated in the $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$ complex (see below and ref 11 and 11a).

(11) R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 261 (1971).

(11a) NOTE ADDED IN PROOF. The structure postulated for $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$ in ref 11 has been confirmed by a single-crystal X-ray diffraction study in the laboratory of Professor Riley Schaeffer at Indiana University. The structure, which has been refined to an *R* factor of 1.9, contains a $C_2B_3H_7$ ring in which the boron and carbon atoms are virtually coplanar; the bridge protons are substantially out of the ring plane on the side opposite the iron atom. We are grateful to Mr. J. P. Brennan, Dr. Larry Sneddon, and Professor Schaeffer for permission to quote these results prior to publication.

traces of $H_2$ have been detected in any experiments involving $C_2B_3H_7$ and these reagents. The tentative conclusion from such observations is that $C_2B_3H_7$ is considerably more resistant to deprotonation than are the related compounds 2,3-$C_2B_4H_8$ and $B_5H_9$, which react with metal hydrides to produce the $C_2B_4H_7^-$ and $B_5H_8^-$ ions, respectively.[12-14]

## Experimental Section

All work including gas chromatography was conducted in Pyrex vacuum lines using standard high-vacuum techniques. Gas-phase reactions were run in round-bottom Pyrex reactors fitted with 5-mm Teflon vacuum stopcocks.

**Materials.** Diborane (Matheson) and acetylene (Matheson) were purified by repeated fractionation through a −128° trap. Tetraborane was synthesized by the method of Gaines and Schaeffer.[15] Typically, about 10 g of $(CH_3)_4NB_3H_8$ (Callery Chemical Co.) was added over an 8-hr period to polyphosphoric acid at 45° in an evacuated, three-neck 2000-ml flask. The mixture was constantly stirred for an additional 24 hr by a direct drive vacuum stirrer (Chesapeake), and volatile products were removed to the vacuum line by pumping through two −196° traps. Tetraborane was separated in pure form from the product mixture by fractionation through a −95° trap which removed all higher boranes and then by passage into a −128° trap which condensed $B_4H_{10}$ but permitted diborane to pass. Approximately 20–24 mmol of $B_4H_{10}$ was thus prepared from 10 g of $(CH_3)_4NB_3H_8$.

Dideuterioacetylene was obtained by dropping $D_2O$ (Strohler Isotopes, 99.4% deuterium content) onto calcium carbide in an evacuated two-neck bulb and was purified by repeated fractionation through a −128° trap. Sodium hydride (Metal Hydrides, Inc.), obtained as a 61% dispersion in mineral oil, and sodium diethyldihydroaluminate (Ethyl Corp.) were used as received. Diglyme (Ansul) and tetrahydrofuran (Eastman) were distilled from $LiAlH_4$ *in vacuo* into the reaction bulb immediately before use. All other solvents were reagent grade and used as received.

Hydrogen chloride was produced from NaCl and $H_2SO_4$ and purified by passage through a trap at −128°. Iron pentacarbonyl (Alfa) was purified by vacuum fractionation through a trap at −63° to remove traces of impurities, which were not retained at that temperature. Trimethylboron was obtained from accumulated laboratory stock. All reactants were checked for purity by infrared and/or mass spectroscopy prior to use.

**Instrumentation.** Infrared, mass, and nmr spectra were recorded on Beckman IR-8, Hitachi Perkin-Elmer RMU-6, and Varian HA-100 spectrometers, respectively. Gas-phase ir spectra were obtained in a 31-cc infrared cell with 10-cm path length, fitted with sodium chloride windows. Nmr samples were prepared on the vacuum line by sealing measured amounts of the compounds (and solvent when necessary) into previously evacuated sample tubes. Gas chromatographic separation of volatile reaction products was accomplished on a 9.8 ft × 0.25 in. column (30% Kel-F on Chromosorb W) with helium as carrier gas.

**Computer Simulation of Nmr Spectra.** Computer-drawn boron-11 and proton nmr spectra of 1,2-$C_2B_3H_7$ and 1,2-$D_2C_2B_3H_5$ have been presented in a preliminary communication.[4] The Algol program utilized in these simulations, originally written by T. Phil Pitner of this department, utilizes a Lorentzian line shape to calculate intensity ($y$ coordinate) as a function of chemical shift ($x$ coordinate). After the complete spectral contribution of each resonance is calculated and stored, a summation procedure determines and normalizes the overall spectrum to be printed out by the Calcomp plotter. The reproduced spectrum corresponds exactly in size to that recorded by the Varian HA-100. Data which must be fed to the computer include an assumed line width at mid-height (the same width for all peaks), relative intensities (areas), chemical shifts, and the chemical shift range of the spectrum. In order to reproduce the $^1H$ nmr spectrum of $C_2B_3H_7$, the program was modified to accommodate variable line widths, since H–B resonances tend to be broader than H–C resonances.

**Synthesis of 1,2-Dicarbapentaborane(7).** Typically, 25.5 mmol of $C_2H_2$ and 5.15 mmol of $B_4H_{10}$ were copyrolyzed at 50° in a 1000-ml Pyrex bulb. The products which passed a −95° trap but condensed at −128° were chromatographed at 25° (see above) to give 0.51 mmol of pure $C_2B_3H_7$ (10% yield). The retention volume of $C_2B_3H_7$ is 0.70 relative to $B_5H_9$ and 1.5 relative to $B_4H_{10}$ on the Kel-F column.

**Pyrolysis of 1,2-Dicarbapentaborane(7).** Chromatographically pure $C_2B_3H_7$ (0.50 mmol) was pyrolyzed in a 520-ml reactor at 50° for 22 hr. Recovered $C_2B_3H_7$ measured 0.45 mmol (90%). No other volatile species were detected by gas chromatography, and no evidence of nonvolatile material was observed. Pyrolysis of 0.61 mmol of $C_2B_3H_7$ at 110° in a 216-ml reactor for 4 hr yielded 0.27 mmol of $H_2$ and 0.0058 mmol of $B_2H_6$; no starting material was recovered.

**Reactions with Diborane and Tetraborane.** A mixture of 0.47 mmol of $C_2B_3H_7$ and 0.47 mmol of $B_2H_6$ was heated at 50° for 1 hr in a 216-ml bulb. Unreacted $B_2H_6$ (0.17 mmol), but no $C_2B_3H_7$, was recovered. When a similar experiment was monitored in a gas ir cell, the presence of a reaction intermediate was indicated by a band at 1300 $cm^{-1}$ which disappeared after 1 hr. No $H_2$ or other volatile products were detected, but a translucent coating was observed on the reactor walls.

The reaction of 0.16 mmol of $C_2B_3H_7$ with 0.62 mmol of $B_4H_{10}$ in a 216-ml reactor at 50° for 1 hr gave $H_2$ (0.075 mmol), 2-$CH_3$-2-$CB_5H_8$ (0.0048 mmol), and a small quantity of white solid. Unreacted $B_4H_{10}$ (0.41 mmol) was recovered, but no $C_2B_3H_7$ remained.

**Reactions with Hydrogen Chloride.** Gaseous $C_2B_3H_7$ (0.090 mmol), in the presence of HCl vapor (0.090 mmol) in a 500-ml reactor at 25°, was repeatedly condensed in a liquid nitrogen bath and allowed to warm to room temperature. After four such condensation–vaporizations over a 10-min period the carborane had completely converted to a white solid polymer, and essentially no HCl remained, as monitored by an attached manometer. No measurable $H_2$ was produced.

A solution of 0.123 mmol of $C_2B_3H_7$ in 0.8 ml of hexane was unchanged after 30 min at 25° *in vacuo*. Addition of 0.123 mmol of dry HCl to this solution (by condensation at −196° and subsequent warming to 25°) caused immediate precipitation of a white nonvolatile air-flammable solid. No $C_2B_3H_7$ and only a trace (<0.02 mmol) of HCl remained, and no $H_2$ was detected.

A gas-phase mixture of 0.141 mmol of $C_2B_3H_7$ and 0.138 mmol of HCl was allowed to stand in a 300-ml Pyrex bulb at 25° for 14 hr. No solid formation was observed. Except for $H_2$ (0.015 mmol), no volatile products were detected, and 0.117 mmol of $C_2B_3H_7$ and 0.124 mmol of HCl were recovered.

**Reactions with Tetrahydrofuran.** Pure $C_2B_3H_7$ (0.15 mmol) and 0.12 mmol of THF were cocondensed at −196° and allowed to warm to 25°. A white nonvolatile solid formed immediately following melting of the mixture, and no liquid was observed after the reaction. Work-up of the mixture after 15 hr at 25° gave 0.10 mmol of recovered THF but no $C_2B_3H_7$. No $H_2$ was detected.

A gas-phase mixture of 0.139 mmol each of $C_2B_3H_7$ and THF in 300 ml gave, after 15 hr at 25°, approximately 0.12 mmol of THF but only 0.024 mmol of $C_2B_3H_7$. No other volatile materials were detected.

**Reaction with Acetylene.** A gas-phase mixture of $C_2B_3H_7$ (0.40 mmol) and $C_2H_2$ (5.21 mmol) in a 500-ml Pyrex bulb equipped with a Teflon stopcock was allowed to stand at 50°. After 24 hr the reactor wall was coated with a white nonvolatile solid. Unreacted $C_2H_2$ (4.68 mmol) was recovered by distillation of the volatile products through a −128° trap. The condensate at −128° was separated by glpc at 65°, giving 0.104 mmol of unreacted $C_2B_3H_7$, 0.019 mmol of 2,3,4,5-$C_4B_2H_6$ (6.4% yield), and 0.002 mmol of 2,3-$(CH_3)_2$-2,3,4-$C_3B_3H_5$. The $C_4B_2H_6$ was identified from an exact mass determination on an AEI MS-9 double-focusing mass spectrometer (calcd for $^{12}C_4{}^{11}B_2{}^1H_6$, 76.0656; found, 76.0658, calcd for $^{13}C^{12}C_3{}^{11}B_2{}^1H_6$, 77.0689; found, 77.0690) and by comparison of its ir and mass spectra with those of the authentic compound[9] (we thank Professor Onak for supplying these spectra for comparison).

**Reaction with Ethylene.** A mixture of 0.354 mmol of $C_2B_3H_7$ and 1.69 mmol of $C_2H_4$ in a 250-ml bulb was maintained at 90° for 2 hr. The reaction appeared well under way after 30 min as judged by the formation of droplets of a nonvolatile liquid which has not been investigated. Work-up of the volatile contents gave 0.57 mmol of $C_2H_4$, ~0.10 mmol of $C_2B_3H_7$, and 0.175 mmol of a mixture of triethylboron and tetraethyldiborane which was iden-

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(12) T. P. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

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tified by ir and mass spectroscopy. These components were not separated but were present in approximately equal amounts as estimated from the spectroscopic data. A trace of $H_2$ (<0.005 mmol) was detected.

**Reaction with Triethylamine.** A solution of $C_2B_3H_7$ (0.440 mmol) in 2.7 ml of toluene was prepared and triethylamine was added to it in small increments at 0°. The formation of a 1:1 adduct was indicated by the overall stoichiometry of the reaction and by the decrease in total pressure over the solution as the amine was added up to 0.44 mmol, with no further significant change as more amine was introduced to the solution. A total of 1.10 mmol of amine was added, after which time the mixture was maintained at 0° for 40 hr. The volatile materials consisted of 0.58 mmol of $(C_2H_5)_3N$, ~0.007 mmol of $H_2$, and solvent. No $C_2B_3H_7$ was recovered. The 32.1-MHz $^{11}B$ nmr spectrum of the nonvolatile white solid adduct in toluene solution consists of a broad symmetrical envelope centered at $\delta$ +12.0 ppm relative to $BF_3 \cdot O(C_2H_5)_2$, at the center of which is an apparent doublet having a coupling constant of 73 Hz, with faint shoulders on either side. Comparison with the very different $^{11}B$ nmr spectrum[4] of 1,2-$C_2B_3H_7$, which contains boron resonances centered at $\delta$ +21.7 and +23.7, implies a gross structural difference between the adduct and the parent carborane. The spectrum of the adduct, however, is unfortunately not sufficiently resolved to permit more detailed interpretation.

A 0.201-mmol sample of the solid adduct was placed in contact with an equimolar quantity of HCl vapor at 25° for 20 min, during which time 0.091 mmol of $H_2$ was released. Less than 0.01 mmol of HCl was recovered. The appearance of the adduct changed from a white solid to a clear glass during the reaction.

**Reactions with Bromine. A. Gas Phase.** Samples of 0.16 mmol of $C_2B_3H_7$ and 0.15 mmol of $Br_2$ were distilled into separate Pyrex bulbs connected by a closed greaseless stopcock. The volume of each bulb (150 ml) was sufficiently large that each reactant, at room temperature, was present entirely in the gas phase. This was necessary to ensure that the reaction would not be complicated by polymerization of liquid $C_2B_3H_7$. When both reactants had warmed to 25°, the connecting stopcock was opened; reaction began immediately, as evidenced by formation of a white solid and disappearance of the $Br_2$. After 20 min no $Br_2$ remained, but 0.020 mmol of $C_2B_3H_7$ was recovered. No $H_2$ or HBr could be detected.

The solid product is unstable at room temperature, evolving 0.038 mmol of $B_2H_6$, but no $H_2$, over a 48-hr period. On treatment of the solid with an additional 0.138 mmol of $Br_2$, 0.068 mmol of HBr and 0.042 mmol of $BBr_3$ were produced together with a trace of $H_2$. The $Br_2$ was completely consumed in the reaction.

**B. Carbon Tetrachloride Solution.** A total of 0.910 mmol of $Br_2$ was distilled in small portions into a solution of 0.489 mmol of $C_2B_3H_7$ in $CCl_4$ maintained at 0°. The $Br_2$ was quickly decolorized, and no detectable $H_2$ was evolved. The products were not investigated.

**C. Pentane Solution.** A solution of 0.354 mmol of $C_2B_3H_7$ and 0.284 mmol of $Br_2$ in 1.0 ml of dry pentane was maintained at 20° for 15 min, during which time the $Br_2$ color disappeared and all of the $C_2B_3H_7$ was consumed as shown by subsequent analysis of the volatile materials. Evaporation of the volatiles gave a white solid which slowly evolved $B_2H_6$ on standing. The solid was treated with $O_2$-free water in the vacuum line, which produced 1.1 mmol of $H_2$ and 0.011 mmol of a mixture of volatile materials whose mass spectrum indicates primarily bromoalkanes. Repeated extraction of the aqueous solution with ether gave a whitish ether-soluble solid whose mass spectrum contains a series of broad envelopes up to *m/e* ~400, the profiles of which suggest the presence of both boron and bromine.

**Reaction with Iron Pentacarbonyl.** In a typical experiment, 0.196 mmol of $C_2B_3H_7$ and 0.652 mmol of $Fe(CO)_5$ were condensed into an evacuated 500-ml Pyrex bulb and irradiated at 30° with a fluorescent lamp for 24 hr. Separation of the products by vacuum-line fractionation yielded 0.02 mmol of $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$, which was retained at −45° and was identified by comparison of its ir and mass spectra with those of authentic material.[11] $C_2B_3H_7$ (0.009 mmol) and $Fe(CO)_5$ (0.008 mmol) were recovered.

Similar experiments in the absence of ultraviolet light failed to produce any detectable carborane complex. Thus, the copyrolysis of 0.232 mmol of $C_2B_3H_7$ and 0.230 mmol of $Fe(CO)_5$ in a 250-ml reactor at 81° for 19 hr resulted principally in the decomposition of $Fe(CO)_5$ to Fe and CO, and only 0.166 mmol of $Fe(CO)_5$ remained. No $C_2B_3H_7$ was recovered.

**Reaction with Trimethylboron.** A mixture containing 0.261 mmol each of $C_2B_3H_7$ and $(CH_3)_3B$ in a 250-ml reactor, maintained at 80° for 26 hr, produced ~0.01 mmol of $H_2$, 0.183 mmol of a mixture of methyldiboranes (identified from ir and mass spectra) which was not resolved, and a nonvolatile white solid. No $C_2B_3H_7$ was recovered.

**Attempted Deprotonation with Sodium Hydride.** Numerous experiments under varying conditions were conducted, of which the following are representative. A solution of 0.513 mmol of $C_2B_3H_7$ in 5 ml of THF was added *in vacuo* to 1.55 mmol of sodium hydride dispersed in mineral oil and maintained at 24° for 21 hr. Only a trace (0.03 mmol) of $H_2$ was evolved, as measured in a calibrated Toepler system. No $C_2B_3H_7$ was recovered, and no other volatiles were found.

Condensation of 0.098 mmol of liquid $C_2B_3H_7$ over 1.85 mmol of NaH in mineral oil *in vacuo*, with the temperature maintained near 0°, produced less than 0.001 mmol of $H_2$ in 10 min, after which the $C_2B_3H_7$ was nearly quantitatively recovered (0.093 mmol). The carborane was returned to the same reactor for 24 hr at 25°, which yielded only an additional 0.002 mmol of $H_2$.

**Attempted Deprotonation with Sodium Dihydrodiethylaluminate.** The reaction of 0.167 mmol of $C_2B_3H_7$ with a large excess of $NaAlH_2(C_2H_5)_2$ in 1.5 ml of dry xylene at 25° for 30 min gave essentially only polymer. No $C_2B_3H_7$ was recovered, and less than 0.005 mmol of $H_2$ was evolved.

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