

Mercury-Sensitized Photolysis of Small Boranes and Carboranes

Jeffrey S. Plotkin, Robert J. Astheimer, and Larry G. Sneddon*

Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104.

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Abstract: The gas-phase mercury-photosensitized reactions of a variety of small boranes and carboranes at 2537 Å were investigated. In certain cases, it was found that these reactions resulted in the formation of the corresponding boron-boron coupled boranes or carboranes. The photolysis of diborane(6) was found to produce tetraborane(10) in high yield. The photolysis of pentaborane(9) resulted in the formation of the three previously known coupled boranes [1,1'-(B₅H₈)₂, 2,2'-(B₅H₈)₂, and 1,2'-(B₅H₈)₂], while the photolysis of 1-CH₃B₅H₈ yielded the previously unknown coupled compound 2,2'-(1-CH₃B₅H₇)₂ (I). Likewise, the photolysis of 2,4-C₂B₅H₇ gave an 84% yield of a mixture of the six possible boron-boron bonded isomers of the coupled cage system: 3,3'-(2,4-C₂B₅H₆)₂ (II), 5,5'-(2,4-C₂B₅H₆)₂ (III), 1,1'-(2,4-C₂B₅H₆)₂ (IV), 1,3'-(2,4-C₂B₅H₆)₂ (V), 1,5'-(2,4-C₂B₅H₆)₂ (VI), and 3,5'-(2,4-C₂B₅H₆)₂ (VII). The boron-11 and boron-11 spin decoupled ¹H NMR spectra of these six closely related compounds (II-VII) are described and analyzed. In addition, it was shown that each of these isomers can rearrange at 400 °C to produce an equilibrium mixture of all six isomers. Cophotolysis of 1,5-C₂B₃H₅ and 1,6-C₂B₄H₆ resulted in the formation of two mixed cage coupled carboranes: 2',2-(1',5'-C₂B₃H₄-1,6-C₂B₄H₅) (VIII) and 1',2-(1',5'-C₂B₃H₄-1,6-C₂B₄H₅) (IX). The mercury-sensitized photolyses of 2-CH₃B₅H₈, B₆H₁₀, 2,3-C₂B₄H₈, and 2,3-(CH₃)₂C₂B₄H₆ were also investigated and are discussed.

Introduction

Although the synthetic advances of recent years have resulted in the generation of a wide variety of new polyhedral boron cage systems, there still remain relatively few examples of multicage compounds which are joined by two-center two-electron boron-boron bonds. The previously reported compounds have included several coupled boranes, 2,2'-(B₄H₉)₂,¹ (B₅H₈)₂² (three isomers), carboranes, 2,2'-(1,5-C₂B₃H₄)₂,³ 4,4'-(1,2-C₂B₁₀H₁₁)₂,⁴ 3,8'-(1,2-C₂B₁₀H₁₁-5',6'-C₂B₈H₁₁)₂,⁴ and thiaboranes, (1-SB₉H₈)₂ (two isomers),⁵ (1-SB₉H₈-1'-SB₁₁H₁₀)₂,⁵ (1-SB₉H₈-1,7-C₂B₁₀H₁₁)₂.⁵ The various approaches which have been employed for their synthesis have ranged from chemical oxidation⁴ or pyrolysis^{2c,3,5} to the use of electric discharges,^{2a,b} but in most cases coupled cage products were obtained in only moderate to low yields. We previously reported preliminary results indicating that the gas-phase photolysis at 2537 Å of either B₅H₉ or 2,4-C₂B₅H₇ in the presence of mercury vapor, results in the formation of the corresponding boron-boron bonded coupled boranes and carboranes.⁶ The use of this technique for producing multicage products has now been explored with a variety of small boranes and carboranes, and full details of this work are presented in this paper.

Experimental Section

Materials. The small closo carboranes, 1,5-C₂B₃H₅, 1,6-C₂B₄H₆, and 2,4-C₂B₅H₇, were purchased from Chemical Systems Inc. and purified by vacuum line fraction or gas-liquid chromatography before use. Pentaborane(9) was obtained from laboratory stock while B₂H₆,⁷ 1-CH₃B₅H₈,⁸ 2-CH₃B₅H₈,⁸ B₆H₁₀,⁹ 2-CH₃B₆H₉,⁹ 2,3-C₂B₄H₈,¹⁰ and 2,3-(CH₃)₂C₂B₄H₆¹¹ were all prepared and purified by literature methods.

Physical Measurements and Chromatography. ¹¹B NMR spectra at 32.1 MHz and ¹H NMR spectra at 100 MHz were obtained on a JEOL PS-100 pulse Fourier transform spectrometer and are presented in Tables I and II, respectively. The 70.6-MHz ¹¹B NMR spectrum of compound VI was performed on a Varian Associates HR-220 spectrometer. Unit and high-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer interfaced to a DS50-S data system. Infrared spectra were recorded on a Perkin-Elmer 521 infrared spectrophotometer (Table III). Gas-liquid chromatography (GLC) was conducted on either a F & M Model 700 gas chromatograph using a 10 ft × 0.25 in. 30% Apiezon L on Chromosorb W (100/120 mesh) column or a Varian Aerograph Model 920

gas chromatograph equipped with a 20 ft × 0.25 in 6% tricresyl phosphate (TCP) on Chromosorb P (60/80 mesh) column. Thin layer chromatography (TLC) was performed on 0.5 mm (20 × 20 cm) silica gel plates (Merck). Elemental analyses were performed by Galbraith Laboratories, Inc. All melting points are uncorrected.

General Procedure. All operations were performed using standard high-vacuum techniques¹² except where otherwise indicated. The radiation source in each experiment was a Griffin-Rayonet photochemical reactor equipped with 16 2537-Å lamps. Photochemical reactions were carried out using one of the two procedures described below.

The first method involved the photolysis of the substrates under static conditions. The reactor consisted of a cylindrical quartz tube (30 cm × 7 cm diameter) equipped with a greaseless stopcock. Attached to the bottom of the tube was a small cold finger which was shielded to prevent photolysis in the liquid phase. In a typical reaction, the reactor was charged with a borane or carborane and ~5 drops of mercury. The reactor was then placed inside the Rayonet where the cold finger was cooled by immersion in an appropriate slush bath, thus allowing the trapping of the less volatile products. In most cases, photolytic reactions were continued until the buildup of decomposition products (usually a white polymer) on the walls of the reactor in the photolysis zone was severe enough that the reaction was retarded.

The second method employed the circulating photolysis apparatus shown in Figure 1. The reactor is all glass (V = 1.84 L), and is designed to continually circulate gaseous substrates through a quartz tube (30 cm × 7 cm diameter) photolysis zone (Q) by the action of a magnetically driven (M) glass circulating pump (P). The mercury vapor emanates from the shielded side arm (S) of the quartz tube. When the reaction is in progress, the photolysis tube and the side arm become warmed slightly, thus ensuring a good flow of mercury vapor in the photolysis region. After the substrates pass through the reaction zone, they immediately exit through the bottom of the reactor and enter the quenching trap (T). The temperature of this trap can then be adjusted to allow selected trapping of the desired species. A mercury manometer (not shown) is also attached to the system to allow monitoring of any pressure changes during a reaction. The system is completely grease-free with Teflon stopcocks and O-ring joints placed as indicated in the figure and is attached to a standard high-vacuum line.

All yields presented are based upon reactant consumed.

Photolysis of B₂H₆. A 20.0-mmol sample of B₂H₆ was photolyzed for 5 h in the circulating reactor while the quenching trap was maintained at -131 °C. After removal of the accumulated hydrogen, the volatile products of the reaction were separated by vacuum line fractionation through a -131 °C trap to give 13.6 mmol of unreacted B₂H₆ and 2.3 mmol of B₄H₁₀ (72% yield).

Table 1. 32.1-MHz ^{11}B NMR Data

compd ^a	$\delta, ^b$ ppm (J, Hz)	rel areas
2,2'-(1- $\text{CH}_3\text{B}_5\text{H}_7$) ₂ (I)	-10.0, -12.0 (113), -42.2	2:6:2
3,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) ₂ (II)	8.9, 4.9 (176), -20.9 (183)	2:4:4
5,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) ₂ (III)	8.4 (183), 7.9, 6.0 (157), -20.3 (178)	2:2:2:4
1,1'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) ₂ (IV)	7.9 (183), 5.0 (171), -19.1 (183), -19.1	2:4:2:2
1,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) ₂ (V)	8.1 (157), 5.2 (167), -17.6 (181), -20.6 (178)	1:4:1:2 ^c
1,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) ₂ (VI)	8.7 (196), 6.2 (174), -14.4, ^s -17.8 (176), -20.2 (181)	2:3:1:1:2 ^d
3,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) ₂ (VII)	8.6 (176), 5.4 (183), -20.2 (181)	1:3:4 ^e
2',2'-(1',5'- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$) (VIII)	2.6 (183), -11.2 (167), -16.6 (189)	2:1:2 ^f
1',2'-(1',5'- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$) (IX)	5.6 (189), -11.1, -16.3 (200), -22.9 (178)	3:1:2:1

^a All samples were run in CS_2 solvent with C_6D_6 lock, except I (pure C_6D_6). ^b All chemical shifts are relative to external $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$; a negative sign indicates an upfield shift. ^c Owing to their broad nature, the singlet resonances due to the substituted boron atoms are not clearly visible and are not listed in the table; however, integration reveals that the 1 boron peak is under the resonances at -17.6 to -20.6 ppm while the 3' boron resonance is under the bands at 8.1-5.2 ppm. ^d The broad singlet ascribed to the substituted 5' boron is not listed because it cannot be seen clearly, although integration indicates that it is beneath the low-field group of resonances at 8.7-6.2 ppm. ^e The singlets from the 3 and 5' boron atoms are not listed in the table because their broad nature and overlap with other peaks prohibit a measurement of their chemical shifts; however, integration reveals that they are both present at 8.6-5.4 ppm. ^f The singlets due to the 2 and 2' substituted borons are not listed because they are not clearly visible; integration indicates, however, that they are present underneath peaks at 2.6 and -11.2 to -16.6 ppm, respectively. ^g Very broad resonance, $W_{1/2} = 370$ Hz.

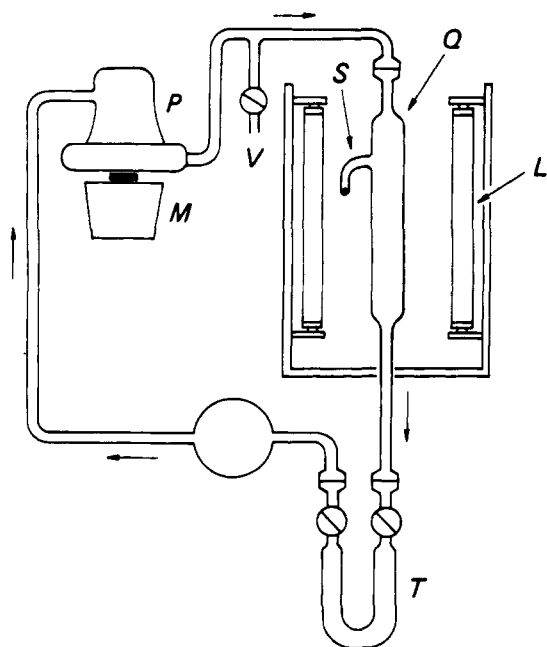


Figure 1. Schematic representation of reactor flow system (arrows indicate direction of gas flow): P, glass pump; M, magnetic stirrer; V, vacuum pump; S, mercury-filled side arm; Q, quartz reactor; L, ultraviolet lamps; T, removable product quenching trap.

In separate experiments, it was found that, when the quenching trap was maintained at higher temperatures, e.g., -112 °C, in addition to B_4H_{10} , small amounts of B_5H_9 and B_5H_{11} were also formed in the reaction.

Photolysis of B_5H_9 . Separate reactions were carried out using both of the photolytic reactors discussed above. Best results were obtained when B_5H_9 (8.6 mmol) was photolyzed for 5 h in the circulating system with periodic removal of the hydrogen while the quenching trap was maintained at ~ 15 °C. When the reaction was terminated, the volatile products were then separated by vacuum line fractionation through a -46 °C trap. Only unreacted B_5H_9 (6.9 mmol) passed, while remaining in the trap was 30.5 mg (28.5% yield) of a clear, low-volatile, air-sensitive liquid. Separation of this material on the Apiezon L column at 125 °C gave the following known compounds: 1,1'-(B_5H_8)₂, $R_v = 0.35$, 6%; 1,2'-(B_5H_8)₂, $R_v = 0.51$, 33%; 2,2'-(B_5H_8)₂, $R_v = 0.57$, 60%; $\text{B}_{10}\text{H}_{14}$, $R_v = 1.0$, trace 1%. All products were identified by comparison of their ^{11}B and ^1H NMR spectra with literature values.²

Lower yields for this reaction were obtained when the static reactor was employed. For example, when 2.7 mmol of B_5H_9 was photolyzed

in a small quartz tube ($V = 205$ mL) with the bottom maintained at 0 °C, extensive decomposition material was deposited after only 2 h and the reaction was terminated. Separation of the volatile products showed that 1.5 mmol of B_5H_9 had been consumed and that 16.8 mg (17% yield) of coupled products was produced. Also produced in this reaction was a nonvolatile oily material which was not characterized.

Photolysis of 1- $\text{CH}_3\text{B}_5\text{H}_8$. Photolysis of 5.4 mmol of 1- $\text{CH}_3\text{B}_5\text{H}_8$ in the circulating reactor for 10 h with the quenching trap maintained at 0 °C resulted in the consumption of 2.2 mmol of 1- $\text{CH}_3\text{B}_5\text{H}_8$ and yielded 163 mg (48% yield) of a product which would not pass a -46 °C trap. GLC analysis of this material on the Apiezon L column at 125 °C showed it to consist of predominantly (60%) one compound which was characterized as 2,2'-(1- $\text{CH}_3\text{B}_5\text{H}_7$)₂ (I), $R_v = 0.64$ (relative to $\text{B}_{10}\text{H}_{14} = 1.0$), liquid. The composition of I was confirmed by high-resolution mass measurement: calcd for $^{12}\text{C}_2^{11}\text{B}_{10}^1\text{H}_{20}$ 154.2496, found 154.2500. The ^{11}B NMR spectrum of I (Table 1) establishes that this compound consists of two 1- $\text{CH}_3\text{B}_5\text{H}_7$ units bonded through their basal 2,2' boron positions. The spectrum is similar in appearance to the spectrum of the parent compound, 2,2'-(B_5H_8)₂,^{2d,13} with the exception that the apex 1,1' resonance of intensity 2 at -42.2 ppm now appears as a singlet due to the methyl substitution. The boron-11 spin decoupled ^1H NMR spectrum (Table II) is also consistent with the proposed structure. Also formed as minor products in this reaction were several isomers of $(\text{CH}_3)_2\text{B}_{10}\text{H}_{12}$ which were each produced in much lower yields (<10%).

Photolysis of 2- $\text{CH}_3\text{B}_5\text{H}_8$. Photolysis of 5.8 mmol of 2- $\text{CH}_3\text{B}_5\text{H}_8$ in the circulating reactor for 10 h with the quenching trap maintained at 0 °C resulted in the consumption of 3.6 mmol of 2- $\text{CH}_3\text{B}_5\text{H}_8$ and produced 181 mg (51% yield) of products which would not pass a -46 °C trap. Since there are seven possible boron-boron bonded isomers of (2- $\text{CH}_3\text{B}_5\text{H}_7$)₂ possible, the reaction produces a very complex mixture of products and individual isomers which were not characterized. Mass spectra, ^{11}B NMR, and GLC analysis of this mixture all indicated, however, that this mixture contained the desired coupled cage products, along with smaller amounts of dimethyl derivatives of decaborane(14).

Photolysis of B_6H_{10} . Hexaborane(10) (6.4 mmol) was photolyzed in the circulating system for 8 h with the cold trap maintained at 0 °C. This resulted in the formation of a large amount of nonvolatile, orange polymer coating the walls of the reaction tube. Vacuum line fractionation of the volatile reaction materials through -31, -78, -112, and -146 °C traps gave $n\text{-B}_5\text{H}_{15}$ (trace), unreacted B_6H_{10} (3.5 mmol), B_5H_9 (0.1 mmol), and B_2H_6 (0.1 mmol), respectively. Similar experiments with 2- $\text{CH}_3\text{B}_6\text{H}_9$ gave analogous results. Since no evidence was found for the formation of a coupled hexaborane(10) product, several additional reactions were performed under varying conditions, e.g., different cold trap temperatures or at higher pressures (obtained by the addition of N_2 gas), but all reactions gave results as above.

Photolysis of 2,4- $\text{C}_2\text{B}_5\text{H}_7$. The initial mercury-sensitized photolytic reactions of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ were carried out under static conditions. In

Table II. 100-MHz ¹H NMR Data

compd ^a	δ, ^b ppm (rel area)	assignment
I	2.61 (6)	3,3',4,4',5,5' B-H
	0.43 (6)	-CH ₃
II	-2.22 (8)	B-H-B
	5.79 (4) ^c	2,2',4,4' C-H
	4.40 (4)	5,5',6,6' B-H
III	0.28 (4) <i>J</i> = 178 Hz ^d	1,1',7,7' B-H
	5.60 (4)	2,2',4,4' C-H
	5.09 (2)	3,3' B-H
IV	4.24 (2)	6,6' B-H
	0.19 (4) <i>J</i> = 178 Hz ^d	1,1',7,7' B-H
	5.26 (4) ^c	2,2',4,4' C-H
V	4.68 (2)	3,3' B-H
	3.95 (4)	5,5',6,6' B-H
	0.00 (2) <i>J</i> = 178 Hz ^d	7,7' B-H
VI	5.71 (2) ^c	2,4 C-H
	5.11 (3) ^c	2',4' C-H and 3 B-H
	4.34 (2)	5,6 B-H
VII	4.04 (2)	5',6' B-H
	0.34 (1)	7 B-H
	-0.21 (2)	1',7' B-H
VIII	5.64 (2) ^c	2,4 C-H
	5.35 (1) ^c	2' or 4' C-H
	4.98 (2)	2' or 4' C-H and 3 B-H ^e
IX	4.84 (1) ^c	3' B-H
	4.29 (2) ^c	5,6 B-H
	3.89 (1) ^c	6' B-H
X	0.25 (1)	7 B-H
	-0.23 (2)	1',7' B-H
	5.66 (4) ^c	2,2',4,4' C-H
XI	5.12 (1)	3' B-H
	4.34 (3)	5,6,6' B-H
	0.23 (4) <i>J</i> = 178 Hz ^d	1,1',7,7' B-H
XII	5.67 (2)	1',5' C-H
	3.87 (2)	3',4' B-H
	3.01 (2)	1,6 C-H
XIII	2.14 (1)	4 B-H
	1.90 (2)	3,5 B-H
	5.61 (1)	5' C-H
XIV	3.90 (3)	2',3',4' B-H
	3.20 (2)	1,6 C-H
	2.16 (2)	3,5 B-H
XV	1.98 (1)	4 B-H

^a All samples were run in CS₂ solvent with C₆D₆ lock, except I (pure C₆D₆). ^b All chemical shifts were measured from the ¹¹B spin-decoupled spectra. A negative sign indicates an upfield shift in parts per million from internal Me₄Si. ^c Unresolved multiplet due to proton-proton coupling. ^d Coupling constants (*J*_{HB}) were recorded only if they could be accurately measured in the ¹¹B coupled spectra. ^e Estimated from overlapping peaks.

a typical reaction, 4.9 mmol of 2,4-C₂B₅H₇ was photolyzed in the static reactor for 4 h while the cold finger was maintained at 15–20 °C. After the reaction was terminated, the volatile material was removed in vacuo and fractionated through a -63 °C trap. Passing this trap was 2.6 mmol of unreacted 2,4-C₂B₅H₇ while remaining in the trap was 92 mg (47% yield) of coupled cage products of the general formula (2,4-C₂B₅H₆)₂ (Anal. Calcd: C, 28.57; H 7.14; B, 64.29. Found: C, 28.43; H, 7.27; B 63.26). GLC separation of this material on the TCP column at 112 °C gave the following six isomers (retention volumes are relative to 2,4-C₂B₅H₇ = 1.0): 3,3'-(2,4-C₂B₅H₆)₂ (II), *R_v* = 16.33, mp 46.5–47.5 °C, 13%; 5,5'-(2,4-C₂B₅H₆)₂ (III), *R_v* = 8.55, liquid, 11%; 1,1'-(2,4-C₂B₅H₆)₂ (IV), *R_v* = 7.33, mp 38.5–39.5 °C, 3%; 1,3'-(2,4-C₂B₅H₆)₂ (V), *R_v* = 11.44, liquid, 22%; 1,5'-(2,4-C₂B₅H₆)₂ (VI), *R_v* = 9.11, liquid, 12%; 3,5'-(2,4-C₂B₅H₆)₂ (VII), *R_v* = 12.33, liquid, 39%.

Table III. Infrared Spectra (cm⁻¹)

I ^a	2950 (w), 2920 (w), 2850 (w), 2600 (vs), 1800 (w, br), 1470 (sh), 1430 (sh), 1400 (s), 1310 (w), 1210 (w), 1080 (w), 1005 (m), 975 (w), 905 (s), 855 (w), 805 (w, br)
II ^b	3090 (w), 2600 (vs), 1180 (w), 1108 (m), 1038 (s), 1015 (sh), 936 (m), 898 (m), 878 (sh), 851 (w)
III ^b	3090 (w), 2605 (vs), 1280 (w), 1185 (m), 1160 (sh), 1145 (m), 1055 (sh), 1040 (s), 940 (w), 895 (w), 862 (m), 642 (m)
IV ^b	3095 (w), 2600 (vs), 1286 (w), 1190 (m), 1140 (w), 1065 (sh), 1042 (s), 1028 (sh), 938 (w), 880 (w), 665 (m)
V ^a	3095 (w), 2602 (vs), 1195 (m), 1120 (m), 1042 (s), 940 (w), 903 (w), 877 (w), 788 (w), 700 (w)
VI ^b	3092 (w), 2600 (vs), 1192 (s), 1168 (s), 1143 (sh), 1040 (s), 1004 (w), 962 (m), 933 (w), 874 (w), 851 (w), 820 (w), 796 (m), 782 (w), 721 (w), 700 (m), 648 (m)
VII ^a	3098 (w), 2630 (sh), 2610 (vs), 1320 (w), 1198 (s), 1129 (m), 1121 (m), 1045 (s), 950 (w), 902 (w), 879 (m), 840 (w), 830 (w), 792 (m), 700 (w), 682 (m)
VIII ^c	3150 (w), 2640 (vs), 2598 (vs), 1336 (w), 1322 (w), 1260 (w), 1188 (m), 1135 (s), 1082 (s), 1020 (m), 970 (w), 902 (m), 875 (m), 836 (m), 798 (m), 775 (w), 748 (w)
IX ^c	2650 (s), 2600 (vs), 1150 (m), 1110 (m), 1058 (s), 930 (w), 905 (w), 850 (m)

^a Thin film on NaCl plates. ^b Solution (CCl₄ vs. CCl₄). ^c Solution (CS₂ vs. CS₂).

Exact mass measurements for II–VII: calcd for ¹²C₄¹¹B₁₀¹H₁₂ 170.1866; found II, 170.1872; III, 170.1885; IV, 170.1889; V, 170.1870; VI, 170.1883; VII, 170.1876. Anal. Calcd: C, 28.57; H, 7.14. Found: V, C, 28.32; H, 7.27; VII, C, 28.53; H, 7.34.

Also produced in the above reaction was a viscous, oily material (~20 mg) which remained in the photolysis reactor. This was extracted from the reactor with methylene chloride and chromatographed on silica gel TLC plates. The plate was first developed in hexanes giving one band (*R_f* 0.75), then in CCl₄, which yielded a second band (*R_f* 1.0), and finally additional material was obtained by extracting the origin with ethyl acetate. The mass spectrum of the material contained in the first band contained two boron envelopes with cutoffs at *m/e* 254 and 338, corresponding to three-cage, C₂B₅H₆-C₂B₅H₅-C₂B₅H₆ and four-cage C₂B₅H₆-(C₂B₅H₅)₂-C₂B₅H₆ compounds. The three-cage compounds could then be separated from the four-cage compounds by vacuum line sublimation at 65 °C onto a 0 °C cold finger. Mass spectra could not be obtained for either the second TLC band nor for the material extracted from the origin owing to the nonvolatile nature of these materials; however, the ¹¹B NMR spectra of all these materials were remarkably similar suggesting that the latter bands consisted of larger oligomers of 2,4-C₂B₅H₇.

Larger amounts of the two cage compounds could be obtained by use of the photochemical flow system. This resulted in not only higher yields, but also greater selectivity. For example, when 7.4 mmol of 2,4-C₂B₅H₇ was irradiated for 2.5 h with the cold trap maintained at 15 °C, 181 mg of (2,4-C₂B₅H₆)₂ (84% yield) along with 4.9 mmol of unreacted 2,4-C₂B₅H₇ was obtained. Little if any of the larger linked cage systems which were formed under the static conditions described above were obtained.

Direct Photolysis of (2,4-C₂B₅H₆)₂. A pure sample (10 mg) of (2,4-C₂B₅H₆)₂ was irradiated for 4 h under static conditions. Virtually all of the starting two-cage compounds were consumed, while an oily material had formed on the walls of the reaction tube. This material was extracted with methylene chloride and chromatographed on silica gel TLC plates; using CCl₄ as the eluant gave one band (*R_f* 1.0). The ¹¹B NMR spectrum of this material together with its nonvolatile nature indicated that this oil consisted of not the expected four-cage compounds but rather larger oligomers of 2,4-C₂B₅H₇.

Photolysis of 1,5-C₂B₃H₅. The flow system was charged with 4.9 mmol of 1,5-C₂B₃H₅ which was then irradiated for 1 h with the cold trap maintained at -45 °C. Almost immediately the reaction tube

became coated with a white, polymeric material indicating that the 1,5-C₂B₃H₅ was undergoing extensive decomposition. After the reaction was terminated, vacuum line fractionation of the volatiles through a -95 °C trap gave 4.4 mmol of unreacted 1,5-C₂B₃H₅ and a trace amount of a lower volatile material which stopped at the -95 °C trap. This material showed a mass spectral cutoff at *m/e* 122 corresponding to the formula (C₂B₃H₄)₂, but owing to the extremely small amounts of this compound complete characterization was not possible.

Photolysis of 1,6-C₂B₄H₆. The quartz photolysis tube was charged with 10.9 mmol of 1,6-C₂B₄H₆ and then photolyzed for 6 h, which resulted in extensive decomposition of the carborane leaving the tube coated with a white, polymeric material. Fractionation of the volatile materials through a -78 °C trap gave 9.9 mmol of unreacted 1,6-C₂B₄H₆ while stopping in the trap was a small amount of product. A mass spectrum of this material contained a boron envelope at *m/e* 134 and a much less intense envelope at *m/e* 148. These masses correspond to the formulas C₂B₃H₄-C₂B₄H₅ and CH₃C₂B₃H₃-C₂B₄H₅, respectively.

Cophotolysis of 1,5-C₂B₃H₅ and 1,6-C₂B₄H₆. The photochemical flow system was charged with an equimolar mixture of 1,5-C₂B₃H₅ (4.9 mmol) and 1,6-C₂B₄H₆ (5.0 mmol) and irradiated for 2 h while the cold trap was kept at -30 °C. After termination of the reaction, vacuum line fractionation through a -78 °C trap yielded 3.9 mmol of unreacted 1,5-C₂B₃H₅, 4.1 mmol of unreacted 1,6-C₂B₄H₆, and 3 mg (2.4% yield) of a lower volatile product which stopped in the -78 °C trap. The mass spectrum of this material contained a cutoff at *m/e* 134 corresponding to the mixed coupled carborane C₂B₃H₄-C₂B₄H₅. Gas chromatography of this material on the TCP column at 60 °C gave two compounds: the B-B bonded isomer 2',2-(1',5'-C₂B₃H₄-1,6-C₂B₄H₅) (VIII), liquid, *R_v* = 7.0 (relative to 1,6-C₂B₄H₆ = 1.0), calcd mass ¹²C₄¹¹B₇¹H₉ 134.1353, found 134.1350, 80%, and the C-B bonded isomer 1',2-(1',5'-C₂B₃H₄-1,6-C₂B₄H₅) (IX), liquid, *R_v* = 6.0, found mass 134.1363, 20%.

Photolysis of 2,3-(CH₃)₂C₂B₄H₆ and 2,3-C₂B₄H₈. The nido carborane 2,3-(CH₃)₂C₂B₄H₆ (3.5 mmol) was condensed into the quartz photolysis tube and irradiated for 6 h under static conditions with the cold finger maintained at 15-20 °C. Since the vapor pressure of 2,3-(CH₃)₂C₂B₄H₆ at the reactor temperature of ca. 40 °C is ~2.6 cm, some of the carborane remains in the liquid phase at the bottom of the cold finger. Extra care was taken to shield the cold finger to prevent direct photolysis of the liquid 2,3-(CH₃)₂C₂B₄H₆. After photolysis the tube had become coated with a clear yellow polymer while a very low volatile oil had formed in the cold finger. In order to transfer this oil under vacuum the entire pathway leading to a tared removable trap was warmed to ~50 °C by a heat tape. The trap was maintained at -22 °C until all the unreacted 2,3-(CH₃)₂C₂B₄H₆ (0.8 mmol) had passed, after which time the -22 °C slush was replaced with a -196 °C trap and pumping was continued overnight yielding 130 mg (47% yield) of product. A high-resolution mass spectrum indicates an elemental composition of ¹²C₈¹¹B₈¹H₂₂ (calcd 206.2466, found 206.2465), which is expected for the corresponding coupled product [2,3-(CH₃)₂C₂B₄H₅]₂. This oil decomposes slowly at room temperature giving off hydrogen and leaving a nonvolatile yellow residue. Owing to this thermal instability and the large number of possible B-B bonded isomers it was not possible to separate and characterize each individual isomer. However, the spectroscopic data of this isomer mixture also supports the proposed coupled carborane [2,3-(CH₃)₂C₂B₄H₅]₂ structure. For example, the ¹¹B NMR spectrum consists of a very broad resonance centered at -6.9 ppm, which is in the range expected for basal boron resonances in a 2,3-(CH₃)₂-C₂B₄H₅ unit (2,3-(CH₃)₂C₂B₄H₆ = -3.7 and -7.2 ppm),¹⁴ and a broad doublet at -43.3 ppm which is characteristic of an apex position in that cage system (2,3-(CH₃)₂C₂B₄H₆ = -47.7 ppm). In addition, the ¹H NMR contains a broad methyl resonance (intensity 12) at 1.42 ppm and a broad resonance at -2.76 ppm of intensity 4 arising from bridge hydrogens. Finally, the infrared spectrum of this mixture contains the expected CH₃ (2950 cm⁻¹), BH (2575 cm⁻¹), and bridge hydrogen (1920 cm⁻¹) bands.

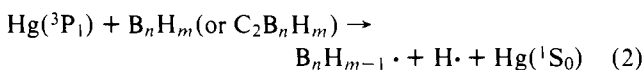
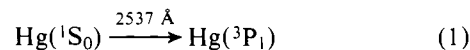
In a separate experiment 3.7 mmol of the parent nido carborane, 2,3-C₂B₄H₈, was photolyzed for 5 h while the cold finger of the quartz tube was kept at 15 °C. Decomposition of the carborane had occurred leaving the tube coated with a white, polymeric material. Vacuum line fractionation of the volatiles through a -78 °C trap gave a trace amount of product which quickly decomposed at room temperature. No evidence was found for any coupled compounds.

Thermal Rearrangement of (2,4-C₂B₅H₆)₂ Isomers. A 3-mg sample of 3,5'-(2,4-C₂B₅H₆)₂ (VII) was sealed in an evacuated Pyrex tube and heated to 400 °C for 2 h. Analysis of the resulting sample by GLC on the TCP column showed that all six isomers were now present. These six compounds, II-VII, were formed at 400 °C in a relative distribution of 3,3' (0.18), 5,5' (1.00), 1,1' (0.95), 1,3' (0.93), 1,5' (2.17), 3,5' (1.15). This is within experimental error the statistical distribution expected for the coupling of 2,4-C₂B₅H₇ cages in a completely random fashion (discounting coupling through carbon), i.e., 3,3' (0.25), 5,5' (1.00), 1,1' (1.00), 1,3' (1.00), 1,5' (2.00), 3,5' (1.00). Reheating another sample of pure 3,5'-(2,4-C₂B₅H₆)₂ for 24 h at 400 °C gave the same result.

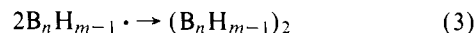
Results and Discussion

The mercury-sensitized photolyses at 2537 Å of a number of small boranes (B₂H₆, B₅H₉, 1-CH₃B₅H₈, 2-CH₃B₅H₈, and B₆H₁₀) and carboranes (1,5-C₂B₃H₅, 1,6-C₂B₄H₆, 2,4-C₂B₅H₇, 2,3-C₂B₄H₈, and 2,3-(CH₃)₂C₂B₄H₆) have now been investigated under a variety of conditions. These studies have demonstrated that in certain cases these reactions can be used as a convenient method of preparing the corresponding boron-boron coupled borane or carborane.¹⁵

The technique is based on the fact that excited-state (³P₁) Hg atoms which are formed by the absorption of 2537-Å radiation have sufficient energy to induce the dissociation of boron-hydrogen bonds:¹⁶

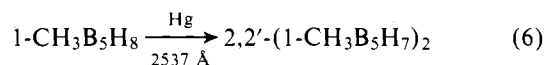
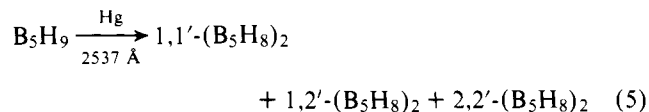
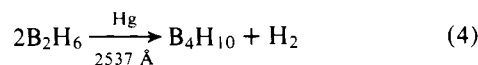


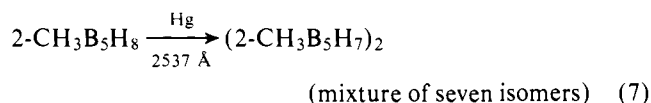
Recombination of the resulting borane (or carborane) radicals then results in the formation of the corresponding boron-boron coupled product:



This reaction sequence is analogous to those mechanisms which have been proposed to explain the reactions of (³P₁) mercury atoms with alkanes,^{15a,b} silanes,¹⁷ and germanes¹⁸ and is consistent with results presented herein.

The mercury-sensitized photochemistry of diborane(6) was originally investigated by Hirata and Gunning in 1957.¹⁵ They examined the kinetics of this system under static conditions and found that tetraborane(10) was the major product with smaller amounts of pentaboranes also being formed. This reaction was reexamined in order to determine if it could be used as a convenient synthetic procedure for producing B₄H₁₀, and it was found that, when the photochemical flow system was employed for the photolysis of B₂H₆, B₄H₁₀ could be obtained in over 72% yield. It should also be noted that the use of an appropriate slush bath (e.g., -131 °C) around the quenching trap completely suppresses the formation of other products, while the use of warmer temperatures (e.g., -112 °C) apparently allows secondary photolysis of the incompletely trapped B₄H₁₀, which in the presence of B₂H₆ gives substantial amounts of B₅H₉ and B₅H₁₁. Thus a certain selectivity of products can be obtained with careful adjustment of reaction parameters.





The reaction of B_5H_9 with $\text{Hg}(^3\text{P}_1)$ atoms (eq 5) in either the static or flow photochemical systems was found to generate the corresponding boron-boron coupled products in reasonable yields (~17–30%). We had originally thought that this product consisted of only the 2,2'-(B_5H_8)₂ isomer,⁶ but upon closer examination we found that in addition to 2,2'-(B_5H_8)₂, which was the major product, the other two possible isomers, 1,2'-(B_5H_8)₂ and 1,1'-(B_5H_8)₂, were also generated. The compound 1,1'-(B_5H_8)₂ was originally prepared by passing B_5H_9 through an electric discharge,^{2a,b} while 2,2'-(B_5H_8)₂ has been prepared in trace amounts by the slow pyrolysis of B_5H_9 in the presence of diborane.^{2c} The third isomer, 1,2'-(B_5H_8)₂, was originally found, along with 2,2'-(B_5H_8)₂, in the remains of old B_5H_9 tanks;^{2d} however, no synthetic method for producing this isomer has heretofore been developed.²⁹ Thus the photochemical methods described here represent a viable synthetic technique for the production of these latter two compounds and will allow extensive investigations of the chemistry of these substances.

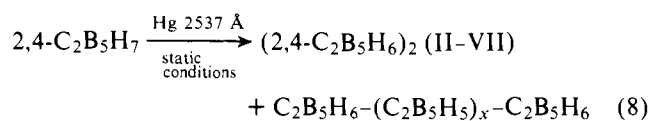
Likewise, the photolysis of 1- $\text{CH}_3\text{B}_5\text{H}_8$ (eq 6) also yields the corresponding coupled product, 2,2'-(1- $\text{CH}_3\text{B}_5\text{H}_7$)₂ (I), although in substantially larger amounts. Because the apex borons are unavailable for further bonding due to their methyl substitution, only one B-B bonded product is possible. This feature along with the increased yield makes this new compound particularly attractive for further chemical studies.

The photolysis of 2- $\text{CH}_3\text{B}_5\text{H}_8$ was also investigated and found to give coupled cage products in similar yields as 1- $\text{CH}_3\text{B}_5\text{H}_8$, but, because of the complexity of the reaction, which would be expected to produce seven different isomers of (2- $\text{CH}_3\text{B}_5\text{H}_7$)₂, the individual compounds were not characterized.

With the expectation of synthesizing the new boron hydride (B_6H_9)₂, the mercury-sensitized photolyses of hexaborane(10) and (2- $\text{CH}_3\text{B}_6\text{H}_9$) were investigated. Unfortunately the desired coupled compound was not found; the only volatile products obtained were small amounts of B_2H_6 , B_5H_9 , and $n\text{-B}_9\text{H}_{15}$. Apparently, hexaborane(10) is photolytically unstable at 2537 Å since irradiation even in the absence of mercury vapor also gave extensive decomposition.

Results similar to those described above were obtained from the mercury-sensitized photolysis of various small carboranes. Again, it was found that in certain cases these reactions led to the formation of coupled cage products in good yields. Except for the boron-carbon linked compound, 1',2-(1',5'- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$), all coupled compounds produced in these reactions were found to be linked by boron-boron bonds and no evidence was found for the formation of any carbon-carbon linked cage compounds. These findings are consistent with the known distinct electrophilic character of ($^3\text{P}_1$) mercury atoms¹³ and also with the relative bond strengths of C-H bonds (98 kcal)¹⁹ vs. B-H bonds (~91 kcal).¹⁹

Perhaps the most interesting results were obtained from the mercury-sensitized photolysis of 2,4- $\text{C}_2\text{B}_5\text{H}_7$. Initial reactions were performed under static conditions and were found to yield two different types of products, according to the equation

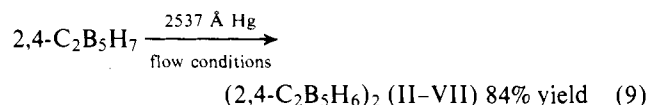


The primary products of the reaction (47% yield) are the six boron-boron linked isomers of the coupled cage carborane: 3,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$)₂ (II), 5,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$)₂ (III), 1,1'-(

2,4- $\text{C}_2\text{B}_5\text{H}_6$)₂ (IV), 1,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$)₂ (V), 1,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) (VI), and 3,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$)₂ (VII). These isomers were readily separated by gas chromatography and characterized with the aid of their spectroscopic data which is discussed below. Surprisingly these six isomers were not produced in the ratio expected for a statistically random attack (i.e., 1 (3,3'):4 (5,5'):4 (1,1'):4 (1,3'):8 (1,5'):4 (3,5')) but instead were obtained in a 5.0:4.2:1.0:8.3:4.6:15.0 ratio. This apparently indicates that the order of preference of attack of ($^3\text{P}_1$) Hg atoms upon the -BH sites is 3 > 5,6 > 1,7, but, given the fact that once formed the carborane radicals could undergo skeletal rearrangement or intramolecular hydrogen migration, this distribution may instead reflect the relative stabilities of the carborane radicals.

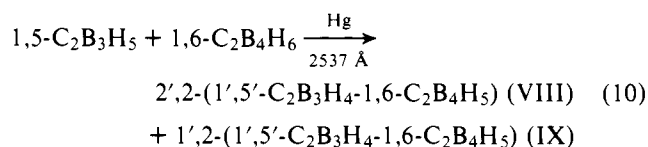
A second set of products obtained from reaction 8 consisted of a viscous oil which was found to be a complex isomer mixture of trimers, tetramers, and larger oligomers of 2,4- $\text{C}_2\text{B}_5\text{H}_7$. It should be emphasized that each set of these multicage compounds should consist of a mixture of all the possible boron-boron bonded isomers. For example, for the three cage system there are 18 possible combinations, while the four cage system should have 64 isomers. This presents a very complex separation problem and individual isomers of these systems could, therefore, not be separated and characterized. These multicage compounds are probably formed by secondary photolysis of the coupled carboranes, II-VII, and indeed, when a mixture of these carboranes was photolyzed in the absence of additional 2,4- $\text{C}_2\text{B}_5\text{H}_7$, they were rapidly converted to higher cage systems.

Clearly, the photolysis of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ under the static conditions given in reaction 8 yielded a variety of interesting and potentially useful compounds, but, if the reaction was to be synthetically useful, it was necessary to obtain both higher yields and greater specificity of products. Both of these goals were attained by employing the circulating photolysis system. For example, when 2,4- $\text{C}_2\text{B}_5\text{H}_7$ is photolyzed in this reactor with the cold trap maintained at 15 °C the two cage coupled compounds II-VII are produced in over 84% yield, while almost no multicage products are obtained.



Using this flow system we are now able to produce multi-gram quantities of these coupled carboranes, thus enabling extensive investigations of their physical and chemical properties. In this regard, we have been especially interested in the transition-metal chemistry of these coupled cage systems and have recently demonstrated that the thermal reaction of ($\eta\text{-C}_5\text{H}_5$)Co(CO)₂ with (2,4- $\text{C}_2\text{B}_5\text{H}_6$)₂ results in the formation of a variety of new multicage, multimetal complexes. Full details of this work are described elsewhere.²⁰

Photolyses of the two smallest closo carboranes, 1,5- $\text{C}_2\text{B}_3\text{H}_5$ and 1,6- $\text{C}_2\text{B}_4\text{H}_6$, were less successful and resulted primarily in decomposition. Only trace amounts of volatile products were isolated and characterization of these compounds was not possible. It was found, however, that irradiation of an equimolar mixture of 1,5- $\text{C}_2\text{B}_3\text{H}_5$ and 1,6- $\text{C}_2\text{B}_4\text{H}_6$ resulted in the formation of mixed cage coupled carboranes in 2.4% yield.



The reaction mixture was separated by gas chromatography into two compounds, the boron-boron linked compound 2',2-(1',5'- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$) (VIII) and the carbon-boron

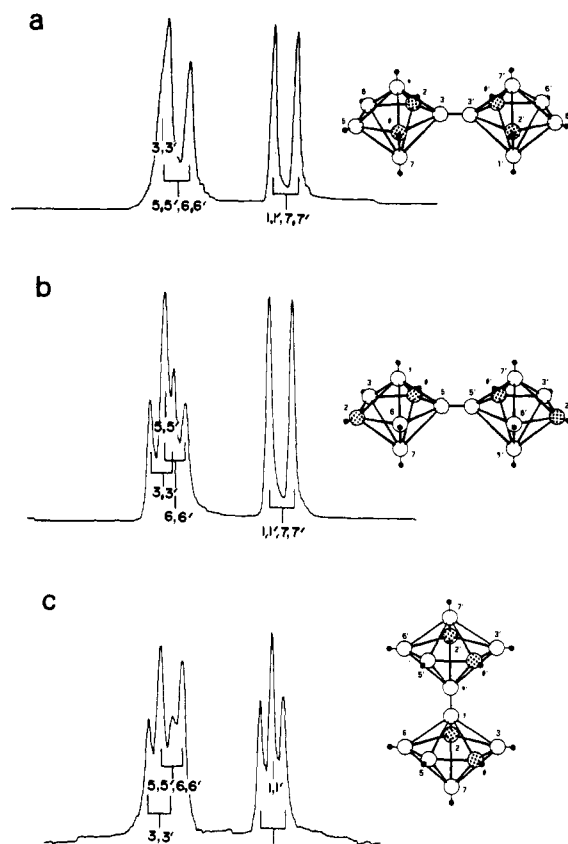
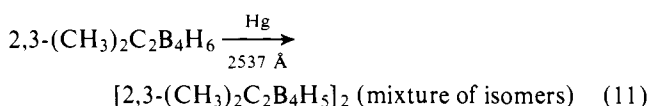


Figure 2. 32.1-MHz ^{11}B NMR of compounds: (a) 3,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (II), (b) 5,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (III), and (c) 1,1'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (IV).

bonded isomer 1',2-(1',5'- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$) (IX). The latter compound is the only example found in this study where bonding occurs at a carbon site.

The photolysis of nido 2,3- $\text{C}_2\text{B}_4\text{H}_8$ leads to decomposition without the formation of any coupled carboranes; however, the reaction of the C,C-dimethylated derivative, 2,3-(CH_3) $_2$ - $\text{C}_2\text{B}_4\text{H}_6$, with $\text{Hg}(\text{P})$ atoms results in the formation of an isomeric mixture of coupled compounds with the general formula of [2,3-(CH_3) $_2\text{C}_2\text{B}_4\text{H}_5$] $_2$ in 47% yield:



This material is a very low volatile oil which decomposes slowly at room temperature giving off hydrogen and leaving a yellow, nonvolatile residue. Because of this thermal instability and the possibility of seven different B-B coupled isomers the individual isomers were not characterized but the spectroscopic data (given in the Experimental Section) is consistent with an isomeric mixture of two 2,3-(CH_3) $_2\text{C}_2\text{B}_4\text{H}_5$ units joined by boron-boron bonds. Furthermore, this material reacts chemically similar to the parent compound 2,3-(CH_3) $_2\text{C}_2\text{B}_4\text{H}_6$.²¹ For example, the material can be readily deprotonated by reaction with sodium hydride in tetrahydrofuran. Further reaction of the resulting anion with cobaltous chloride and sodium cyclopentadienide, followed by an oxidative workup, results in the formation of several new linked cage cobaltacarboranes, including the first example of a coupled cage metallocarborane, 4,5'-[2,3-(CH_3) $_2$ -1,2,3(η - C_5H_5)Co- B_4H_3] $_2$.²⁰

Characterization and Properties of Coupled Carboranes. The structures of the three symmetrically linked isomers, 3,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$, 5,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$, and 1,1'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$, were easily determined by examination of their characteristic

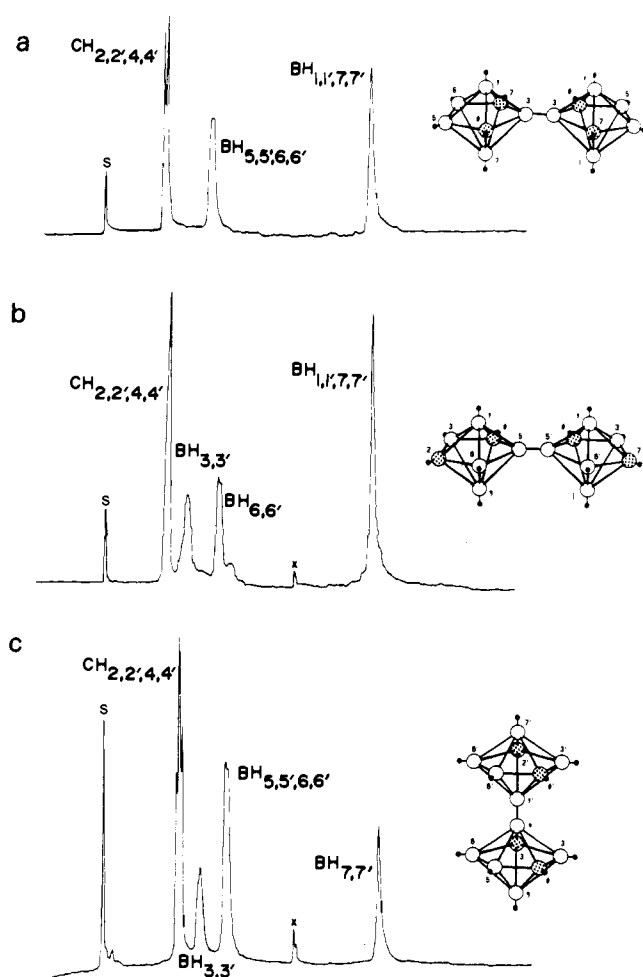


Figure 3. ^{11}B decoupled 100-MHz ^1H NMR of compounds: (a) 3,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (II), (b) 5,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (III), and (c) 1,1'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (IV). The resonance labeled S is residual benzene.

^{11}B NMR spectra (Figure 2). In each case the resonance due to the equivalent substituted borons is present as a sharp singlet. The remaining resonances can also be unambiguously assigned by analogy to previously reported ^{11}B NMR spectra of other boron-substituted 2,4- $\text{C}_2\text{B}_5\text{H}_7$ derivatives.²² The corresponding ^{11}B spin-decoupled 100-MHz ^1H NMR spectra shown in Figure 3 again confirm that all three isomers are linked via boron-boron bonds, since the presence of C-H resonances of total intensity 4 in each spectrum rules out carbon-carbon or carbon-boron bonding. The remainder of each spectrum can be assigned in a straightforward manner as given in the figure. It should be noted that the chemical shifts of the proton resonances of 1,1'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ are shifted 0.3–0.5 ppm upfield in comparison to similar resonances in 3,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ and 5,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$. This upfield shift of the proton resonances of the 2,4- $\text{C}_2\text{B}_5\text{H}_6$ cage unit bonded to the apex position of the second 2,4- $\text{C}_2\text{B}_5\text{H}_6$ cage is in agreement with predictions based on ring current calculations.²³ A similar upfield shift has previously been observed for the methyl and mercapto proton resonances in the apex substituted compounds, 1- CH_3 -2,4- $\text{C}_2\text{B}_5\text{H}_6$ ^{22a} and 1-SH-2,4- $\text{C}_2\text{B}_5\text{H}_6$.^{22c} This effect is of great value in interpreting the ^1H NMR spectra of the asymmetrically linked isomers.

The ^{11}B and ^1H NMR spectra of 1,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (V), 1,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (VI), and 3,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (VII) are naturally much more complex in comparison to the spectra of the symmetrical isomers II–IV owing to the increased number of inequivalent -BH positions and are deserving of a more detailed analysis. For example, the ^{11}B NMR spectrum of

compound V (Figure 4a) is heavily overlapped and a structural characterization cannot be made on the basis of this spectrum alone. Nevertheless, valuable structural information can be obtained. The upfield portion consists of two doublets of intensities 1 and 2, indicating that the bonding occurs at an apex boron on just one of the 2,4- $C_2B_5H_6$ cages. The expected sharp singlet due to the substituted apex boron is, however, not apparent, even though an integration of this portion of the spectrum reveals its presence underneath the two upfield resonances. Evidently, the singlet resonance in this case is broadened considerably. This is, in fact, a general phenomenon observed in every compound reported in this study which contained cages linked by two chemically inequivalent borons. That is, in contrast to the spectra of symmetrical isomers II-IV which were linked by chemically equivalent borons and gave sharp boron singlet resonances, the boron-11 spectra of the asymmetrical isomers V-VII have boron singlet resonances which are considerably broadened, making their exact location in the spectra sometimes difficult.

Similar effects have been seen for compounds previously reported in the literature. For instance, in the ^{11}B NMR spectra of the symmetrically coupled 1,1'-(B_5H_8) $_2$ ²⁴ and 2,2'-(B_5H_8) $_2$ ^{2d,13,25} the singlet is present as a sharp resonance, while in the published spectrum^{2d} of the asymmetric 1,2'-(B_5H_8) $_2$ both singlets are broadened substantially.

This peak broadening may be caused by one of several effects. One possibility is that there is extensive coupling between the two chemically inequivalent borons in the two-center two-electron B-B bond. Boron-boron coupling between borons connected by three-center bonds has previously been observed. For example, in B_5H_9 the coupling constant between the basal and apex borons has been measured as $J_{11B11B} = 19.4$ Hz.²⁶ No coupling constants between two boron atoms in a two-center two-electron bonding situation have ever been measured; however, theoretical calculations predict that such a coupling constant would be ~ 80 Hz²⁷ and could easily account for the broadening observed.

Another possible cause is that the interaction of two chemically different boron nuclei linked via a two-center two-electron bond could severely perturb the symmetries of the effective electrical field gradient around each nuclei and thus shorten the spin-lattice relaxation rates with the end result being extensive broadening of the resonances. At this time, it is not possible to determine which, if either, of these effects is responsible for the broadening observed but this phenomenon is still under investigation and will be reported at a later time.³⁰

As mentioned above, the ^{11}B NMR spectrum of V gives only partial information concerning the sites of linkage of the two cages in this isomer. Examination of the ^{11}B spin-decoupled 1H NMR (Figure 5a), however, does allow the unambiguous structural assignment of compound V. Because the proton resonances of the cage unit bonded to the apex position of the second 2,4- $C_2B_5H_6$ unit are shifted upfield, as was discussed above, the 1H NMR spectrum is greatly simplified and almost all resonances are completely resolvable as shown in the figure.

The upfield portion of the ^{11}B NMR spectrum of VI (Figure 4b) is similar to that of compound V, suggesting that again bonding occurs at an apex boron position on just one of the 2,4- $C_2B_5H_6$ cages. A very broad peak which is attributed to the singlet resonance of the substituted apex boron is seen at -14.4 ppm. When the boron-11 spectrum of this compound was taken at 70.6 MHz this broad resonance was clearly separated and shown to have an integrated intensity of 1 with a half-width of 370 Hz. Again, final confirmation of the bonding sites in this isomer comes from the ^{11}B spin-decoupled 1H NMR shown in Figure 5b. The three -CH resonances, which are present in a 2:1:1 ratio, are diagnostic of the bonding ar-

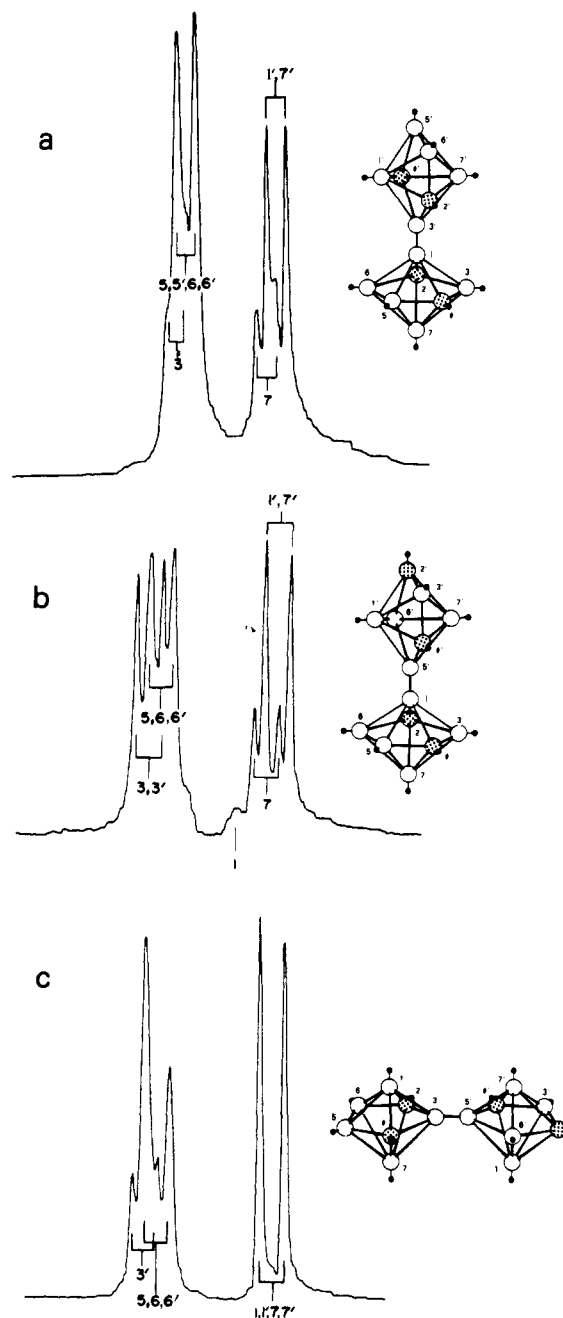


Figure 4. 32.1-MHz ^{11}B NMR of compounds: (a) 1,3'-(2,4- $C_2B_5H_6$) $_2$ (V), (b) 1,5'-(2,4- $C_2B_5H_6$) $_2$ (VI), and (c) 3,5'-(2,4- $C_2B_5H_6$) $_2$ (VII).

angement, since there are only two possible boron-boron linked combinations that will have as many as three inequivalent -CH groups: 3,5'-(2,4- $C_2B_5H_6$) $_2$ and 1,5'-(2,4- $C_2B_5H_6$) $_2$. The latter structure is clearly favored by the ^{11}B NMR data and by the fact that again two apex -BH resonances are present in the 1H NMR spectrum at 0.25 and -0.23 ppm in a 1:2 ratio. Like compound V, the upfield shift of the proton resonances of the 2,4- $C_2B_5H_6$ cage bound to an apex cage position greatly simplifies the spectrum and allows the identification of the other resonances expected for 1,5'-(2,4- $C_2B_5H_6$) $_2$, as shown in the figure.

In the ^{11}B NMR spectrum of VII, a doublet of intensity 4 at -20.2 ppm arises from the coincidental overlap of the resonances from 1,7- and 1',7'-BH groups and rules those positions out as possible substitution sites. Thus, the compound must be the 3,5'-(2,4- $C_2B_5H_6$) $_2$ isomer, although it is not possible to clearly identify either of the boron singlet reso-

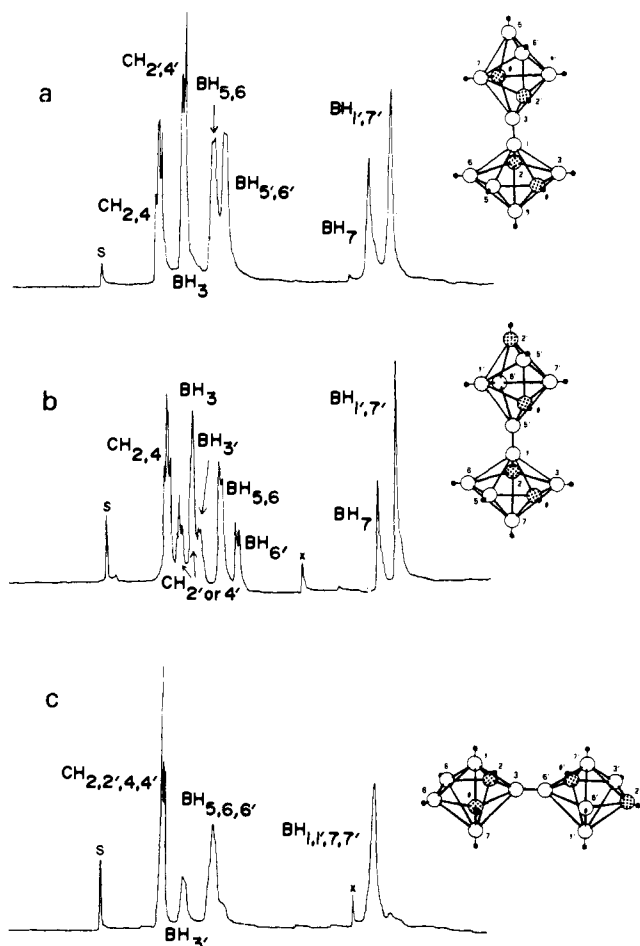


Figure 5. ^{11}B decoupled 100-MHz ^1H NMR of compounds: (a) 1,3'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (V), (b) 1,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (VI), and (c) 3,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ (VII). The resonance labeled S is residual benzene.

nances. The ^1H NMR spectrum (Figure 5c) supports this conclusion, although only one $-\text{CH}$ resonance of intensity 4 is observed instead of three expected resonances. This results because the upfield shift of the proton resonances of one cage, which simplified the spectra of compounds V and VI, does not occur since neither of the cages is apex substituted. Several of the remaining resonances are also overlapped and are assigned as indicated in the figure.

These six new coupled carboranes (II–VII) were found to be both air and water stable and, in addition, to possess a remarkable thermal stability. For example, samples which were subjected to temperatures of up to 425 $^\circ\text{C}$ under vacuum for several hours showed no evidence of decomposition. It was observed, however, that at elevated temperatures these carboranes rearranged to establish equilibrium mixtures of all six boron–boron coupled isomers. For example, GLC analysis of a mixture obtained by heating a pure sample of 3,5'-(2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ at 400 $^\circ\text{C}$ for 2 h showed it to contain all six isomers in the statistical distribution expected based on the number of like boron atoms. Reheating the sample for an additional 24 h at 400 $^\circ\text{C}$ resulted in no further change.

Similar rearrangements have been observed in other substituted 2,4- $\text{C}_2\text{B}_5\text{H}_7$ cage systems. For example, Onak has found that heating the B-substituted methyl derivatives of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ to 300 $^\circ\text{C}$ will establish an equilibrium mixture of all three methylated isomers.²⁸ However, in contrast to our observations, the three $\text{CH}_3\text{C}_2\text{B}_5\text{H}_6$ isomers were not formed in a statistical distribution, but rather the methyl group exhibited a preference of $3 > 1,7 > 5,6$. It may well be that the relatively mild conditions employed in that study did not allow

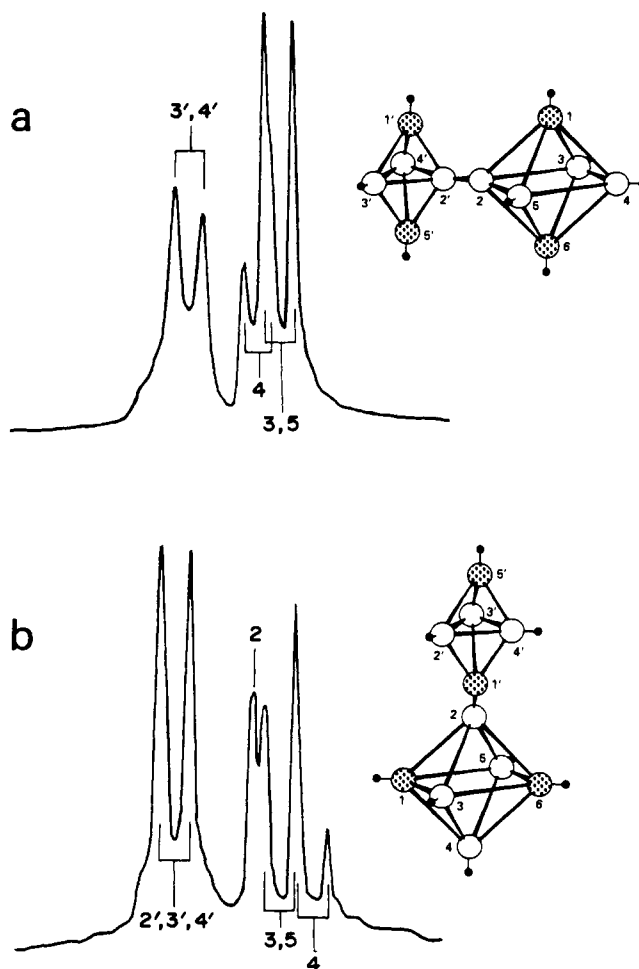


Figure 6. 32.1-MHz ^{11}B NMR of compounds: (a) 2',2-(1',5'- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$) (VIII) and (b) 1',2-(1',5'- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$) (IX).

complete rearrangement to occur and that further heating at higher temperatures might have resulted in the formation of a statistically random mixture.

The mechanism of this rearrangement has not been established, but any intermolecular process in which the boron–boron bond is broken followed by a recombination of the resulting $\text{C}_2\text{B}_5\text{H}_6$ units can be ruled out by the absence of any three or four cage compounds, both of which are known to be stable, following rearrangement. Onak has proposed²⁸ that the mechanism for the rearrangement of B-substituted methyl 2,4- $\text{C}_2\text{B}_5\text{H}_7$ derivatives may involve an intramolecular skeletal shifting of the 2,4- $\text{C}_2\text{B}_5\text{H}_7$ framework. This mechanism could also explain the rearrangement of the (2,4- $\text{C}_2\text{B}_5\text{H}_6$) $_2$ isomers; however, a direct shift mechanism via a three-center transition state in which one carborane boron adopts a bridging position between two borons on the second cage is also a possibility. This would allow migration of the cages between the various boron positions without requiring skeletal rearrangement. We have proposed that just such a direct shift mechanism is needed to account for rearrangements observed in certain coupled cobalt derivatives of these carboranes.²⁰

The bonding arrangements of the new mixed coupled carborane 1,5- $\text{C}_2\text{B}_3\text{H}_4$ -1,6- $\text{C}_2\text{B}_4\text{H}_5$ isomers can also be determined by inspection of their ^{11}B and ^1H NMR spectra. The proposed boron–boron bonded structure for VIII is supported by the ^{11}B NMR spectrum (Figure 6a), which shows a doublet at 2.6 ppm due to the equivalent 3'4'-BH groups on the 1,5- $\text{C}_2\text{B}_3\text{H}_4$ cage (1,5- $\text{C}_2\text{B}_3\text{H}_5 = 1.4$ ppm)^{22a} and two doublets at -11.2 and -16.6 ppm which are characteristic of a B-substituted derivative of 1,6- $\text{C}_2\text{B}_4\text{H}_6$ (1,6- $\text{C}_2\text{B}_4\text{H}_6 = -18.9$

ppm).^{22a} Once again, since the two borons linking the two cages are chemically inequivalent, their resonances are broadened so that no readily identifiable singlets are apparent in the spectrum. Integration of the spectrum reveals that one of the singlets lies under the doublet at 2.6 ppm and perhaps is the cause of the unusual broadness at the base of this doublet, while the other singlet overlaps the doublet at -16.6 ppm.

The ¹¹B spin-decoupled ¹H NMR is also consistent with the proposed structure, showing one CH resonance of intensity 2 at 5.67 ppm due to the 1',5'-CH resonances on the 1',5'-C₂B₃H₄ cage (1,5-C₂B₃H₅, CH = 4.6 ppm)^{22a} and a second CH resonance of intensity 2 at 3.01 ppm due to the 1,6-CH resonances on the 1,6-C₂B₄H₅ cage (1,6-C₂B₄H₆, CH = 3.1 ppm).^{22a} The spectrum also contains a resonance of intensity 2 at 3.87 ppm due to the 3',4'-BH protons, and two resonances at 2.14 and 1.90 ppm of intensities 1 and 2 due to the 4- and 3,5-BH groups, respectively.

In contrast to the ¹¹B NMR spectrum of VIII, the spectra of IX (Figure 6b) shows a sharp singlet of intensity 1 at -11.1 ppm. Since the formation of any boron-boron linkage between these cages should result in broadened singlet resonances, the appearance of this sharp singlet in the spectrum suggests that instead the two cages are linked by a C-B bond. The remainder of the spectrum is also consistent with this interpretation, showing a doublet of intensity 3 at 5.6 ppm, indicating that the 1,5-C₂B₃H₄ cage must be bonded at a carbon site, and two additional doublets at -16.3 and -22.9 ppm (intensity 2:1) which are again characteristic of B-substituted derivatives of 1,6-C₂B₄H₆.

The ¹H NMR also supports the proposed structure showing a CH resonance of intensity 1 at 5.61 due to the unsubstituted 5'-CH of the 1',5'-C₂B₃H₄ unit, and a CH of intensity 2 at 3.20 ppm which is assigned to the two unsubstituted 1,6-CH groups of the 1,6-C₂B₄H₆ cage. The resonance due to the three equivalent 2',3',4'-BH groups occurs at 3.90 ppm and peaks at 2.16 and 1.98 ppm (intensities 2 and 1) are assigned to the 3,5- and 4-BH groups, respectively.

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References and Notes

- (1) J. Dobson, D. Gaines, and R. Schaeffer, *J. Am. Chem. Soc.*, **87**, 4072 (1965).
- (2) (a) R. N. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.* **47**, 996 (1961); (b) R. N. Grimes and W. N. Lipscomb, *ibid.*, **48**, 496 (1962); (c) J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, **9**, 2161 (1970); (d) D. Gaines, T. V. Iorns, and E. N. Clevenger, *ibid.*, **10**, 1096 (1971).
- (3) (a) A. B. Burg and T. J. Reilly, *Inorg. Chem.*, **11**, 1962 (1972); (b) R. C. Dobbie, E. W. Distefano, M. Black, J. B. Leach, and T. Onak, *J. Organomet. Chem.*, **114**, 233 (1976).
- (4) Z. Janousek, S. Hermanek, J. Plešek, and B. Stibr, *Collect. Czech. Chem. Commun.*, **39**, 2363 (1974).
- (5) W. R. Pretzer and R. W. Rudolph, *Inorg. Chem.*, **15**, 1779 (1976).
- (6) J. S. Plotkin and L. G. Sneddon, *J. Chem. Soc., Chem. Commun.*, **95** (1976).
- (7) B. J. Duke, J. R. Gilbert, and I. A. Read, *J. Chem. Soc.*, 540 (1974).
- (8) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).
- (9) H. D. Johnson, II, V. T. Brice, and S. G. Shore, *Inorg. Chem.*, **12**, 689 (1973).
- (10) T. Onak, R. P. Drake, and G. B. Dinks, *Inorg. Chem.*, **3**, 1686 (1964).
- (11) T. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).
- (12) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969.
- (13) R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **11**, 1242 (1972).
- (14) T. P. Onak, R. E. William, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).
- (15) Some evidence has previously been obtained that coupled carboranes are produced in low yield from pyrolysis reactions. R. E. Williams, F. J. Gerhart, G. I. Hickey, and J. F. Ditter, *U.S. C.F.S.T.I., AD Rep.*, 693314 (1969).
- (16) (a) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, 1967; (b) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, **1**, 209 (1973); (c) T. Hirata and H. E. Gunning, *J. Chem. Phys.*, **27**, 477 (1957).
- (17) (a) H. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964); (b) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).
- (18) G. A. Gibbon, Y. Rousseau, C. H. Van Dyke, and G. J. Mains, *Inorg. Chem.*, **5**, 114 (1966).
- (19) W. L. Jolly, "The Principles of Inorganic Chemistry", McGraw-Hill, New York, 1976, p 41.
- (20) J. S. Plotkin and L. G. Sneddon, *Inorg. Chem.*, in press.
- (21) (a) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974); (b) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Matthew, and G. J. Palenik, *J. Am. Chem. Soc.*, **95**, 3046 (1973); (c) R. N. Grimes, W. J. Rademaker, M. L. Demmiston, R. F. Bryan, and P. T. Green, *ibid.*, **94**, 1865 (1972); (d) K.-S. Wong, J. R. Bowser, J. R. Pipal, and R. N. Grimes, *ibid.*, **100**, 5045 (1978); (e) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *ibid.*, **98**, 4818 (1976); (f) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976).
- (22) (a) R. N. Grimes, *J. Am. Chem. Soc.*, **88**, 1895 (1966); (b) R. Warren, D. Paquin, T. Onak, G. Dunks, and J. R. Spielman, *Inorg. Chem.*, **9**, 2285 (1970); (c) J. S. Plotkin and L. G. Sneddon, *J. Am. Chem. Soc.*, **99**, 3911 (1977).
- (23) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1797 (1969).
- (24) R. N. Grimes, Ph.D. Thesis, University of Minnesota, Minneapolis, 1962.
- (25) R. R. Rietz and R. Schaeffer, *J. Am. Chem. Soc.*, **95**, 4580 (1973).
- (26) J. D. Odom, P. D. Ellis, and H. C. Walsh, *J. Am. Chem. Soc.*, **93**, 3529 (1971).
- (27) J. Kroner and B. Wrackmeyer, *J. Chem. Soc., Faraday Trans.*, **72**, 2283 (1976).
- (28) A. P. Fung and T. Onak, *J. Am. Chem. Soc.*, **99**, 5512 (1977).
- (29) Note added at proof. After this paper was in press, a new method for the selective synthesis of 1,2'-(B₅H₆)₂ and 2,2'-(B₅H₆)₂ was reported: D. F. Gaines, M. W. Jorgensen, and M. A. Kulzick, *J. Chem. Soc., Chem. Commun.*, **380** (1979).
- (30) Note added at proof. After this paper was in press, boron-11 NMR spectra at 115.5 MHz were obtained on all compounds, confirming the assignments given, and indicating that broadening of the resonances of the linked borons in the asymmetrically coupled compounds is due to ¹¹B-¹¹B coupling. Full details will be reported elsewhere.