Rh-S-H are −14.5° in **2**). Thus, the hydrogens linked to one metal and to one sulfur remain in close proximity.

A CH_2Cl_2 solution of **2** under a stream of argon loses 2 mol of H_2 (as determined by GC) and transforms into [(triphos)Rh(μ-S)$_2$Rh(triphos)](BPh$_4$)$_2$ (**3**) ($^{31}P\{^1H\}$ NMR (CD_3COCD_3, 293 K) 24.02 ppm (J(P-Rh) = 102 Hz, doublet, triphos)). Brown crystals are precipitated by addition of ethanol. A stream of H_2 turns a solution of **3** to the original pink color, and the complex **2** is obtained quantitatively in 4 h. A preliminary X-ray analysis on **3** has confirmed the structural formulation given in Scheme I.

The ability of **3** to activate homodinuclear molecules shows up in the reaction with oxygen. When O_2 is bubbled throughout a CH_2Cl_2 solution of **3**, red crystals of the μ-SO complex [(triphos)Rh(μ-SO)$_2$Rh(triphos)](BPh$_4$)$_2$ (**4**) are obtained quantitatively. The crystal structure and characterization of **4**, prepared by a different synthetic strategy, have recently been reported by us.[6]

Current studies are under way to try to elucidate the mechanism of the present H_2 activation. This might be helpful in understanding some enzymatic hydrogenation processes that have been postulated to proceed via intermediates containing metal-hydride and protonated metal-coordinated thiolates.[7]

Registry No. **1**, 105139-41-1; **2**, 105162-41-2; **3**, 105139-43-3; **4**, 105162-43-4; S^{2-}, 18496-25-8.

Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, and bond distances and angles (4 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Articles

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Structural Characterization and Cage-Condensation Reactions of the Coupled-Cage Borane 1:2′-$[B_5H_8]_2$: New Routes to Higher Single-Cage Boranes and Carboranes

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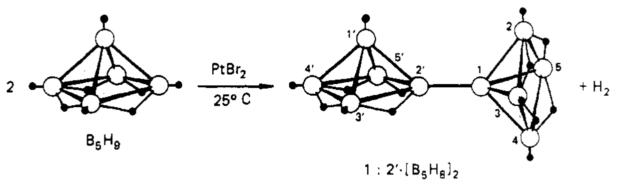
A single-crystal X-ray structure determination of 1:2′-$[B_5H_8]_2$ has confirmed that the compound has a coupled-cage structure composed of two pentaborane clusters joined apex to base by means of a two-center two-electron boron-boron bond. The utility of 1:2′-$[B_5H_8]_2$ as a precursor to larger single-cage boranes and carboranes has also been explored. It has been found that under appropriate conditions 1:2′-$[B_5H_8]_2$ will undergo coupled-cage to single-cage condensations producing important higher cage materials, such as $B_9H_{14}^-$, $B_9H_{13}\cdot SMe_2$, $B_8H_{10}\cdot NEt_3$, 1,2-$R_2C_2B_8H_8$, and $B_{12}H_{12}^{2-}$. Crystal data for 1:2′-$[B_5H_8]_2$: space group $Pna2_1$; $Z = 4$; $a = 11.020$ (4) Å, $b = 5.870$ (6) Å, $c = 14.988$ (6) Å; $V = 969.5$ Å^3. The structure was refined by full-matrix least squares to final R of 0.049 and R_w of 0.048 for the 406 unique reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We recently reported[1,2] the development of high-yield, catalytic synthetic routes to boron-boron-coupled polyhedral boranes and carboranes via transition-metal-promoted dehydrocondensation reactions. The facile formation of multicage systems is potentially of great significance in polyhedral borane chemistry since the procedures used for their syntheses provide new pathways to higher boron content materials, which avoid the problems inherent in traditional thermally induced cage growth reactions. Furthermore, if these multicage compounds could be converted to fused-cage boranes or carboranes, then this would represent an alternative to decaborane(14)-based synthetic procedures for the formation of large-cage materials.[3]

One coupled-cage system of particular interest is the coupled-pentaborane dimer 1:2′-$[B_5H_8]_2$, since the compound can now be made catalytically, in nearly quantitative yields, from the readily available small boron hydride pentaborane(9).



We report here the first structural characterization, by means of a single-crystal X-ray study, of 1:2′-$[B_5H_8]_2$ and that furthermore, under appropriate conditions, 1:2′-$[B_5H_8]_2$ will undergo multicage to single-cage rearrangements to produce a number of important higher polyhedral boranes.

Experimental Section

Materials. 1:2′-$[B_5H_8]_2$ was made by a platinum(II) bromide catalyzed dehydrodimerization reaction previously reported.[1,2] Pentaborane(9) was obtained from laboratory stock. Platinum(II) bromide, lithium triethylborohydride, and dimethyl sulfide were obtained from Aldrich Chemicals, and 2-butyne, obtained from Farchan Labs, was used as received. Decane and 2,6-lutidine were obtained from Aldrich and dried with P_2O_5 and BaO, respectively. Triethylamine was obtained from

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Table I. Data Collection and Structure Refinement Information

space group	$Pna2_1$
a, Å	11.020 (4)
b, Å	5.870 (6)
c, Å	14.988 (6)
V, Å^3	969.5
Z	4
ρ(calcd), g cm^{-3}	0.851
mol formula	$B_{10}H_{16}$
mol wt	126.2
λ(Mo Kα), Å	0.71073
scanning range, deg	$4 \leqslant 2\theta \leqslant 45$
scan mode	$\omega-2\theta$
$\pm h,\pm k,\pm l$ collected	+6,+11,±16
no. of measd intensities	1747
unique reflcns, $F_o^2 > 3\sigma(F_o^2)$	406
no. of variables	138
abs coeff μ, cm^{-1}	0.297
R	0.049
R_w	0.048

Fisher and also dried with BaO. Unless otherwise indicated all manipulations were carried out in vacuo.

Physical Measurements. Boron-11 and proton NMR spectra at 64.2 and 200 MHz, respectively, were obtained on an IBM WP200SY Fourier transform spectrometer equipped with appropriate decoupling accessories. Boron-11 NMR spectra at 115.5 MHz were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility at the University of Pennsylvania. Low- and high-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer.

Crystallographic Data for 1:2′-$[B_5H_8]_2$. Single crystals were grown by sublimation in vacuo in a sealed Pyrex tube over ~1 week at 5 °C. Since 1:2′-$[B_5H_8]_2$ melts at 18.4 °C and is also air-sensitive, it was necessary to open the Pyrex tube in a N_2 gas filled glovebag in a cold room (5 °C) in order to select a crystal. A crystal of suitable size was mounted inside a capillary tube and then transferred quickly to the diffractometer. The crystal was maintained at −50 °C during orientation and data collection with a Nonius low-temperature device. The Enraf-Nonius program SEARCH was used to obtain 25 reflections, which were then used in the program INDEX to obtain an orientation matrix for data collection. Refined cell dimensions and their standard deviations were obtained from the least-squares refinement of these 25 accurately centered reflections. On the basis of several θ scans, the mosaicity of the crystal was judged acceptable. See Table I for crystal data.

Collection and Reduction of the Data. Diffraction data were collected on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP 8/A computer, employing Mo Kα radiation from a highly oriented graphite crystal monochromator. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program BEGIN.

Solution and Refinement of the Structure. All calculations were performed on a VAX 750 computer using the Enraf-Nonius VAXSDP, Ver. 2, structure package.[4] A quadrant of data was collected over $0 \leqslant h \leqslant 6$, $0 \leqslant k \leqslant 11$, $-16 \leqslant l \leqslant 16$, which was subsequently averaged to the unique octant. The full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[5a] and those for hydrogen from Stewart.[5b] The effects of anomalous dispersion were included in F_c by using Cromer and Iber's values[6] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Direct methods, using the 11/82 version of Multan, yielded the location of the 10 boron atoms. Anisotropic refinement followed by a difference Fourier synthesis resulted in the location of all 16 hydrogen atoms. Final refinement included anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms. No absorption correction was made. Final positional

Table II. Positional Parameters and Their Estimated Standard Deviation

atom	x	y	z
B1	0.7072 (6)	0.114 (1)	0.775
B2	0.6959 (7)	−0.129 (1)	0.8338 (6)
B3	0.6846 (7)	0.144 (1)	0.8858 (5)
B4	0.8249 (6)	0.229 (1)	0.8350 (5)
B5	0.8352 (6)	−0.049 (1)	0.7821 (5)
B1′	0.6571 (6)	0.178 (1)	0.5754 (5)
B2′	0.6354 (6)	0.206 (1)	0.6848 (5)
B3′	0.5201 (7)	0.094 (1)	0.6121 (6)
B4′	0.5365 (7)	0.327 (2)	0.5371 (5)
B5′	0.6513 (6)	0.450 (1)	0.6098 (5)
H23	0.700 (5)	−0.047 (9)	0.911 (3)
H45	0.896 (4)	0.049 (9)	0.858 (3)
H34′	0.468 (4)	0.23 (1)	0.586 (4)
H34	0.794 (4)	0.181 (8)	0.918 (3)
H25	0.823 (4)	−0.191 (8)	0.841 (4)
H23′	0.517 (5)	0.163 (9)	0.699 (3)
HB2	0.639 (4)	−0.277 (9)	0.827 (3)
HB3	0.634 (5)	0.215 (9)	0.927 (3)
HB4	0.866 (4)	0.394 (9)	0.825 (4)
HB5	0.896 (5)	−0.117 (9)	0.732 (4)
HB1′	0.720 (5)	0.107 (9)	0.533 (3)
HB3′	0.461 (4)	−0.052 (9)	0.603 (4)
HB5′	0.718 (5)	0.600 (9)	0.605 (3)
HB4′	0.510 (5)	0.333 (9)	0.473 (3)
H25′	0.626 (5)	0.439 (8)	0.696 (4)
H45′	0.554 (4)	0.50 (1)	0.578 (4)

Table III. Interatomic Distances (Å)

B1–B2	1.683 (10)	B1′–B2′	1.665 (11)
B1–B3	1.686 (7)	B1′–B3′	1.680 (10)
B1–B4	1.713 (9)	B1′–B4′	1.693 (11)
B1–B5	1.708 (10)	B1′–B5′	1.680 (11)
B2–B3	1.787 (11)	B2′–B3′	1.798 (10)
B2–B5	1.783 (11)	B2′–B5′	1.827 (11)
B3–B4	1.794 (10)	B3′–B4′	1.782 (11)
B4–B5	1.815 (11)	B4′–B5′	1.818 (11)
		B1′–B2	1.660 (8)
B2–HB2	1.08 (5)	B1′–HB1′	1.03 (5)
B2–H23	1.26 (5)	B2′–H23′	1.35 (5)
B2–H25	1.45 (5)	B2′–H25′	1.38 (5)
B3–HB3	0.93 (5)	B3′–HB3′	1.08 (5)
B3–H23	1.19 (5)	B3′–H23′	1.36 (5)
B3–H34	1.32 (5)	B3′–H34′	1.07 (6)
B4–HB4	1.09 (5)	B4′–HB4′	1.01 (5)
B4–H34	1.32 (5)	B4′–H34′	1.20 (5)
B4–H45	1.36 (5)	B4′–H45′	1.18 (6)
B5–HB5	1.08 (5)	B5′–HB5′	1.15 (5)
B5–H25	1.22 (5)	B5′–H25′	1.32 (5)
B5–H45	1.44 (5)	B5′–H45′	1.21 (5)

Table IV. Selected Bond Angles (deg)

B2–B1–B3	69.1 (4)	B2′–B1′–B3′	65.0 (5)
B3–B1–B4	63.7 (4)	B3′–B1′–B4′	63.8 (8)
B4–B1–B5	64.1 (4)	B4′–B1′–B5′	65.2 (5)
B2–B1–B5	63.4 (4)	B2′–B1′–B5′	66.2 (5)
B2–B1–B2′	131.9 (6)	B2′–B1′–HB1′	139 (3)
B3–B1–B2′	134.4 (4)	B3′–B1′–HB1′	134 (3)
B4–B1–B2′	131.4 (6)	B4′–B1′–HB1′	122 (3)
B5–B1–B2′	128.7 (4)	B5′–B1′–HB1′	127 (3)
B3–B2–B5	90.7 (5)	B1′–B2′–B1	134.6 (5)
B1–B2–HB2	133 (3)	B3′–B2′–B1	135.4 (6)
B2–B3–B4	90.2 (5)	B5′–B2′–B1	135.3 (5)
B1–B3–HB3	142 (3)	B3′–B2′–B5′	89.0 (5)
B4–B4–B5	89.5 (5)	B2′–B3′–B4′	91.6 (5)
B1–B4–HB4	127 (3)	B1′–B3′–HB3′	137 (3)
B4–B5–B2	89.7 (5)	B3′–B4′–B5′	89.8 (5)
B1–B5–HB5	133 (3)	B1′–B4′–HB4′	124 (3)
B2–H23–B3	93 (3)	B4′–B5′–B2′	89.5 (5)
B3–H34–B4	86 (3)	B1′–B5′–HB5′	133 (3)
B4–H45–B5	81 (3)	B2′–H23′–B3′	83 (3)
B2–H25–B5	83 (3)	B3′–H34′–B4′	104 (4)
		B4′–H45′–B5′	99 (4)
		B2′–H25′–B5′	85 (3)

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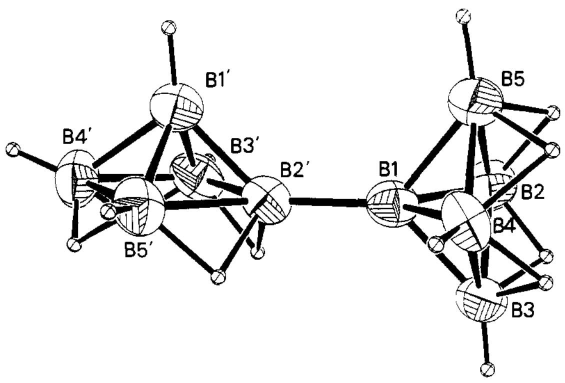

Figure 1. ORTEP drawing of the molecular structure of 1:2′-$[B_5H_8]_2$.

parameters are given in Table II. Intramolecular bond distances and selected bond angles are presented in Tables III and IV, respectively. Figure 1 gives an ORTEP view of I.

Reactions of 1:2′-$[B_5H_8]_2$. $B_9H_{14}^-$. A 100-mL reaction flask was charged with 11.0 mL (11.0 mmol) of superhydride [$LiB(C_2H_5)_3H$, 1.0 M solution in THF] and 1.36 g (10.9 mmol) of 1:2′-$[B_5H_8]_2$. The mixture was allowed to warm slowly to room temperature and then stirred for 2 h. The volatiles were removed in vacuo, leaving a white flaky solid. This material was dissolved in water, and an aqueous solution of $(CH_3)_4NCl$ was added, resulting in the precipitation of 1.92 g (10.3 mmol) of $B_9H_{14}N(CH_3)_4$ (94% yield). The product was isolated in high purity, as confirmed by comparison of its ^{11}B NMR spectra with literature data.[7]

$B_9H_{13}\cdot S(CH_3)_2$. A reaction tube was charged with 0.0955 g (0.77 mmol) of 1:2′-$[B_5H_8]_2$, 4.0 mmol of dimethyl sulfide, and 5 mL of decane. The tube was sealed under vacuum and the mixture reacted at 60 °C for 72 h. The volatile components were then removed, leaving a white powder that was identified by the ^{11}B NMR data[8] as $B_9H_{13}\cdot S(CH_3)_2$. Exactly 0.1021 g (0.59 mmol) of product had been produced, corresponding to a yield of 77%.

$B_8H_{10}\cdot NEt_3$. In a 40-mL reaction flask, 0.0655 g (0.53 mmol) of 1:2′-$[B_5H_8]_2$ was added to 3.0 mmol of triethylamine and 5 mL of decane. The mixture was allowed to warm slowly to room temperature and then stirred for 48 h. The volatile components were then removed under vacuum. Remaining in the reaction flask was 0.0953 g (0.48 mmol) of an oily product, which according to ^{11}B and ^{1}H NMR was 80% pure $B_8H_{10}\cdot NEt_3$ (contaminated with $B_9H_{13}\cdot NEt_3$). This corresponds to an ~75–85% yield of $B_8H_{10}\cdot NEt_3$. Exact mass measurement: calcd for $^{12}C_6{}^1H_{25}{}^{11}B_8{}^{14}N_1$, 199.272; found, 199.276. ^{11}B NMR (C_6D_6, 115.5 MHz), δ (relative intensity, J_{BH}): 6.51 (2, unresolved resonance), 1.91 (3, 148 Hz), −21.87 (2, 136 Hz), −30.50 (1, 136 Hz). $^1H\{^{11}B\}$ NMR (C_6D_6, 200 MHz), δ (relative intensity, assignment): 4.54 (2, BH), 4.30 (2, BH), 2.48 (6, CH_2), 1.41 (2, BH), 0.66 (9, CH_3), −1.67 (1, BHB), −4.60 (2, BHB).

1,2-$(CH_3)_2C_2B_8H_8$. In a 40-mL reaction flask, 1.7 mmol of 2,6-lutidine was added to a mixture of 0.1034 g (0.83 mmol) of 1:2′-$[B_5H_8]_2$ and 3.3 mmol of 2-butyne in three increments. After each increment the solution was slowly warmed to room temperature and stirred for 0.5 h. Following the last addition, the mixture was heated at 60 °C for 48 h. The volatile components were removed and fractionated in vacuo through a 0, −10, −196 °C trap series. This yielded a total of 0.0408 g (0.28 mmol) of 1,2-$(CH_3)_2C_2B_8H_8$[9] in the −10 °C trap, corresponding to a yield of 33%.

$B_{12}H_{12}^{2-}$. A three-necked 100-mL flask was charged with 5 mL of dried decane and 4 mL of $Et_3N\cdot BH_3$ (25 mmol). To this mixture was added, 0.91 g (7.22 mmol) of 1:2′-$[B_5H_8]_2$. The material was allowed to warm to room temperature and then stirred at 100 °C for 20 h. Hydrogen evolution necessitated frequent degassing. The volatiles were then removed, the flask was purged with argon, and the crude yellow solid that formed was removed to a frit, where it was washed with diethyl ether. The solid was then treated with 400 mL of boiling water, acidified with 2 mL of 4 N HCl, and the mixture was filtered hot. The filtrate was reduced in volume to 40 mL and cooled to 0 °C. Crystals of $[B_{12}H_{12}^{2-}][NEt_3H^+]_2$ formed, which were removed by filtration and air-dried to a free-flowing white solid (1.18 g). A second crop was similarly obtained from the mother liquor for a total of 1.44 g of $[B_{12}H_{12}^{2-}][NEt_3H^+]_2$ (4.29 mmol), a yield of 59% for the reaction. Purity was confirmed by comparison of the IR[10] and ^{11}B NMR[11] spectra with literature data.

Results and Discussion

Pentaborane(9) forms three isomeric boron–boron-coupled dehydrodimers, 1:1′-$[B_5H_8]_2$, 1:2′-$[B_5H_8]_2$, and 2:2′-$[B_5H_8]_2$. The compound 1:1′-$[B_5H_8]_2$[12] was, in fact, the first boron–boron-linked cage compound to be synthesized and was structurally characterized more than 20 years ago. The 1:2′-$[B_5H_8]_2$ and 2:2′-$[B_5H_8]_2$ isomers were originally discovered[13a] in the remains of pentaborane(9) storage tanks and assigned their coupled-cage structures on the basis of their spectral data. Although subsequent synthetic methods[13] have been developed to produce both 1:2′-$[B_5H_8]_2$ and 2:2′-$[B_5H_8]_2$, these compounds have not previously been structurally characterized.

As can be seen in the ORTEP drawing in Figure 1, a single-crystal X-ray determination has confirmed that 1:2′-$[B_5H_8]_2$ has a coupled-cage structure in which two pentaborane cages are joined apex to base (B1 to B2′) by means of an exopolyhedral boron–boron bond. This two-center, two-electron bond should be shortened relative to a three-center, two-electron interaction (~ 1.70–1.80 Å). The observed B1–B2′ distance, 1.660 (8) Å, is in agreement with this expectation and in the range observed for boron–boron linkages found in other coupled-cage systems: 1:1′-$[B_5H_8]_2$, 1.74 (6) Å;[12] 2:2′-$[1\text{-}SB_9H_8]_2$, 1.678 (5) Å;[14] 1:5′-$[B_{10}H_{13}]_2$, 1.698 (3) Å;[15] 2:2′-$[B_{10}H_{13}]_2$, 1.692 (3) Å;[16] 2:6′-$[B_{10}H_{13}]_2$, 1.679 (3) Å;[16] 1:2′-$[B_{10}H_{13}]_2$, 1.696 (4) Å;[17] 7′:7-$[2',5'\text{-}C_2B_8H_{11}][2,3\text{-}C_2B_{10}H_{11}]$, 1.681 (2) Å;[18] 2′:4-$[B_{10}H_{13}][7\text{-}\{(PMe_2Ph)_2Pt\}B_{10}H_{11}]$, 1.707 (15) Å;[19] 3′:2-$[2',4'\text{-}C_2B_5H_6][1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6]$, 1.654 (8) Å.[20]

The bond distances and angles in the two pentaborane cages are normal and are similar to, although somewhat shorter than, those observed in the parent, pentaborane(9),[21] indicating that the formation of the exopolyhedral boron–boron linkage does not perturb the cage bonding patterns significantly. Thus, the average boron–boron basal and basal–apical distances are 1.795 and 1.698 Å in the 1-B_5H_8 unit and 1.806 and 1.680 Å in the 2′-B_5H_8 cage compared to 1.751 and 1.653 Å in pentaborane(9). The basal B2–B3–B4–B5 and B2′–B3′–B4′–B5′ rings are each planar with a dihedral angle of 97.5°. The linkage atom B1 is shifted out of the B2′–B3′–B4′–B5′ plane by 0.15 Å toward B1′. There is also a noncrystallographic mirror plane bisecting B4′–B1′–B2′–B1–B3–B5 that is perpendicular to both the B2–B3–B4–B5 and B2′–B3′–B4′–B5′ planes.

As is discussed below, 1:2′-$[B_5H_8]_2$ was found to undergo a number of cage-fusion reactions forming larger single-cage systems. The closest nonbonded intercage interactions in the com-

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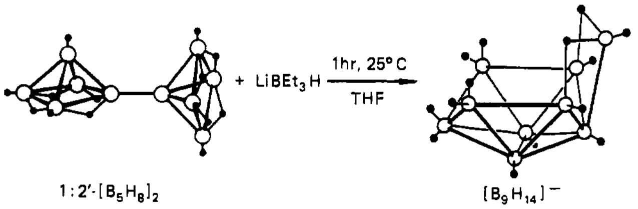
pound are those of the B2' boron with each of the atoms in the B2–B3–B4–B5 ring, average distance 3.06 Å, and B1–B1', 3.06 Å, B1–B3', 3.19 Å, and B1–B5', 3.22 Å. The B4–B5' and B2–B3' distances are quite long, 4.09 and 4.06 Å, respectively.

Previous chemical studies of 1:2'-$[B_5H_8]_2$ have focused primarily on its substitution chemistry. Gaines demonstrated[13c] that the compound readily undergoes Friedel–Crafts catalyzed halogenation to yield 1:2'-$[B_5H_8][1'\text{-}ClB_5H_7]$, although some cleavage of the boron–boron linkage, yielding 1- and 2-ClB_5H_8, was also observed. Likewise, reaction of 1:2'-$[B_5H_8]_2$ with hydrogen chloride gives complete cleavage to B_5H_9 and 2-ClB_5H_8. Gaines also reported[13c] that 1:2'-$[B_5H_8]_2$ could be deprotonated by methyllithium to yield an anion, stable only at low temperatures, which could be reacted with DCl to yield a monodeuteriated derivative of the parent compound.

Our interest in the chemistry of 1:2'-$[B_5H_8]_2$ stemmed from the possibility that this compound could be a useful precursor to larger single-cage boranes and carboranes. We have found that under suitable conditions 1:2'-$[B_5H_8]_2$ will, in fact, undergo a coupled-cage to single-cage fusion resulting in the production of a number of important cage compounds.

In contrast to the results described above for the reaction of MeLi with 1:2'-$[B_5H_8]_2$, we find that 1:2'-$[B_5H_8]_2$ reacts with lithium triethylborohydride in tetrahydrofuran solution to yield the $B_9H_{14}^-$ anion in high yields.



There is no apparent hydrogen evolution during the reaction, but the formation of BEt_3, $BH_3{\cdot}THF$, and $LiBH_4$ (when excess $LiBEt_3H$ is present) is observed in the ^{11}B NMR spectrum of the reaction in progress. These observations suggest that 1:2'-$[B_5H_8]_2$ reacts with $LiBEt_3H$ to yield the $B_{10}H_{17}^-$ anion, which is unstable, further decomposing via BH_3 loss to yield the final product.

$$1{:}2'\text{-}[B_5H_8]_2 + LiBEt_3H \rightarrow [B_{10}H_{17}^-] \xrightarrow{-BH_3} B_9H_{14}^-$$

Thus, the initial reaction of $LiBEt_3H$ with 1:2'-$[B_5H_8]_2$ would appear to involve hydride addition, rather than the deprotonation reaction that is normally observed when metal hydrides are reacted with boranes containing bridging hydrogens. Gaines also observed[22] that when pentaborane(9) is reacted with lithium triethylborohydride, no deprotonation occurs, and he discussed the possibility that the reaction may involve an initial hydride addition to form the $B_5H_{10}^-$ anion.

The above reaction sequence may also be related to the recent synthesis of $B_9H_{14}^-$ reported by Shore.[23] This route involves the reaction of $B_5H_8^-$ with B_5H_9, giving $B_9H_{14}^-$ in ~75% yields. Shore, in fact, proposed that the reaction may go through a $B_{10}H_{17}^-$ intermediate, which, as in the reaction reported herein, loses a BH_3 unit to give the final $B_9H_{14}^-$ product.

The $B_9H_{14}^-$ anion is an important precursor to many higher cage systems, including $B_9H_{13}{\cdot}L$[23,24] (L = Lewis Base), *n*-$B_{18}H_{22}$,[23,24a] $B_{10}H_{14}$,[23,25] and *nido*-$R_2C_2B_8H_{10}$.[9,23] The reaction sequence reported above is an attractive alternative to existing routes to this anion,[7,23,25,26] since $B_9H_{14}^-$ can be produced from pentaborane(9) in high yields, ~90%, and in excellent purity by using only a two-step procedure. Furthermore, this procedure should be readily adaptable for larger scale reactions.

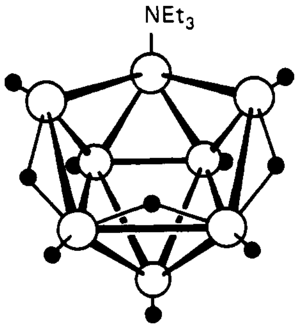
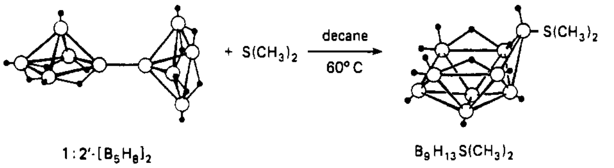


Figure 2. Proposed structure for $B_8H_{10}{\cdot}NEt_3$.

The reaction of 1:2'-$[B_5H_8]_2$ with 2 equiv of dimethyl sulfide, at ~60–70 °C was found to result in BH_3 cleavage and cage condensation to give $B_9H_{13}SMe_2$:



Also observed in this reaction was the borane adduct, $BH_3{\cdot}SMe_2$, indicating that the reaction probably occurs by initial attack at one of the basal atoms of the pentaborane(9) cages with subsequent cleavage of the $BH_3{\cdot}SMe_2$ unit. The resulting B_9H_{13} fragment could then rearrange and combine with another equivalent of SMe_2 to yield the final product. This procedure compares favorably with the production of $B_9H_{13}{\cdot}SMe_2$ from decaborane(14)[27] and should be applicable to the synthesis of a wide range of $B_9H_{13}{\cdot}L$ complexes.

When 1:2'-$[B_5H_8]_2$ was reacted with triethylamine, the cleavage of two BH_3 groups was observed, resulting in the production of $B_8H_{10}{\cdot}NEt_3$ in excellent yields.

$$1{:}2'\text{-}[B_5H_8]_2 + 3Et_3N \rightarrow B_8H_{10}NEt_3 + 2Et_3N{\cdot}BH_3$$

Although base adducts of B_8H_{12} are known ($B_8H_{12}{\cdot}NEt_3$[28] and $B_8H_{12}{\cdot}CH_3CN$[28]), compounds of the formula $B_8H_{10}{\cdot}L$ (L = Lewis base) have not previously been reported. On the basis of simple electron-counting procedures,[29] the expected structure for this cage system ($2n + 4$ skeletal electron system) would be a tricapped trigonal prism missing one vertex; however, such a structure has been confirmed in only one case: $(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$.[30] The more common structure observed for this cluster system is based on a square antiprism missing two vertices and has the same geometry observed for eight-vertex arachno species. Structurally characterized examples include, B_8H_{12},[31] $(\eta^6\text{-}(CH_3)_6C_6)FeMe_4C_4B_3H_3$,[32] and $(\eta\text{-}C_5H_5)CoPh_4C_4B_3H_3$.[33]

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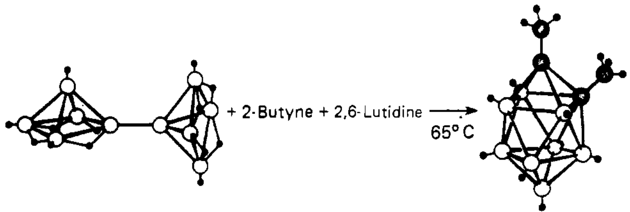
The ^{11}B NMR spectrum of $B_8H_{10}\cdot NEt_3$ consists of four resonances in a ratio of 2:3:2:1, with the peak of intensity three appearing to result from an overlapping doublet and singlet. The $^1H\{^{11}B\}$ NMR spectrum shows, in addition to the $-C_2H_5$ resonances, overlapping B–H terminal peaks and two bridge hydrogen resonances in a ratio of 2:1. These data seem most consistent with the structure shown in Figure 2, which is based on a tricapped trigonal prism missing one of the noncapping vertices; however, final structural confirmation will have to await detailed X-ray analysis.

The reaction of pentaborane(9) with alkynes in the presence of triethylamine or 2,6-lutidine has previously been developed as a good-yield synthetic route to the small carborane 2,3-$Et_2C_2B_4H_6$.[34,35] The key step in this reaction is presumed to be the cleavage of a BH_3 group from the pentaborane(9) cage to produce a B_4H_6 fragment, which can then insert the alkyne, yielding the final carborane product.

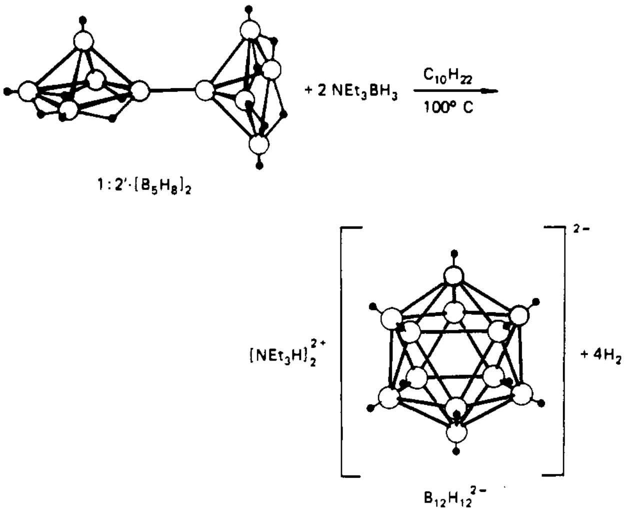
$$B_5H_9 + NEt_3 \xrightarrow{-BH_3\cdot NEt_3} [B_4H_6] \xrightarrow{RC\equiv CR} 2,3\text{-}R_2C_2B_4H_6$$

Given the results described above that 1:2′-$[B_5H_8]_2$ will undergo cleavage reactions with triethylamine to produce a B_8H_{10} fragment, a reaction with 2-butyne and 2,6-lutidine, analogous to the 2,3-$R_2C_2B_4H_6$ synthesis, was explored, and it was found that 1,2-$(CH_3)_2C_2B_8H_8$ could be produced in ~33% yield.



1:2′-$[B_5H_8]_2$ 1,2-$(CH_3)_2C_2B_8H_8$

All of the cage-condensation reactions discussed above have been accompanied by cage fragmentation of the 1:2′-$[B_5H_8]_2$ framework, producing smaller B_8 or B_9 single-cage systems. We also investigated the possibility that 1:2′-$[B_5H_8]_2$ could undergo cage-expansion reactions to yield larger cage polyhedral clusters. One of the most important higher cage systems is the very stable borane anion $B_{12}H_{12}^{2-}$. Previously, the most convenient synthetic route[10] to $B_{12}H_{12}^{2-}$ involved the thermal reaction of decaborane(14) with triethylamine–borane. We have now found that 1:2′-$[B_5H_8]_2$ can be used as a substitute for decaborane(14) in this reaction.



1:2′-$[B_5H_8]_2$

$B_{12}H_{12}^{2-}$

The reaction gives $[B_{12}H_{12}^{2-}][NEt_3H^+]_2$ in high purity with ~60% yields, compared to the 79% yields that are obtained from reactions employing decaborane(14). Although the yields are lower, the fact that pentaborane(9) is readily available makes this reaction sequence an attractive route.

In summary, the studies presented herein have resulted in the preparation of a number of important higher polyhedral boron cage systems. More importantly, however, they suggest that a new synthetic sequence involving the catalytic dehydrocondensation of a small borane or carborane, followed by a *multicage* to *single-cage* fusion reaction may be a potentially important new synthetic route to larger *single-cage* polyhedral boranes and carboranes. We are now continuing our investigations of the scope of this synthetic methodology, as well as further explorations of the chemistry of 1:2′-$[B_5H_8]_2$.

Acknowledgment. We thank the Army Research Office and the National Science Foundation for the support of this research.

Supplementary Material Available: Tables of general temperature factor expressions and least-squares planes (4 pages); a listing of structure factors (2 pages). Ordering information is given on any current masthead page.

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