

Table I. Energy of the d → d Band for Low-Spin Square-Planar Ni(tetraamine)²⁺ Complexes in Aqueous Solution

ligand	no. of bridges	$\nu(d \rightarrow d)$, cm ⁻¹
[14]aneN ₄ ^a	0	22 470
Me ₄ [14]aneN ₄ ^b	0	19 570
2	1	21 690
3	2	23 260

^a Data taken from ref 5. ^b 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane. Data taken from ref 12.

seems unlikely since extraction of the aqueous solution with hot chloroform failed to transfer any of these normally chloroform soluble species³ into the organic phase. There are at least two possible reactions for this: The effect of the bridge may simply be to impose a prohibitive steric barrier toward the addition of axial substituents; however, this is improbable since the addition of excess cyanide ion results in the liberation of the ligand and the formation of Ni(CN)₄²⁻, in the usual way, after only a few minutes of heating. Alternatively, the effect of the bridge may be to reduce ligand flexibility to the point where the macrocyclic hole is incapable of expanding to accept the slightly larger high-spin nickel(II) ion. In this case one would expect the in-plane ligand field to be enhanced upon the introduction of the bridge. In fact this is observed. The frequency of the single d → d absorption band in the spectra of low-spin nickel(II) complexes is related to the in-plane ligand field strengths, with higher frequencies being indicative of higher ligand field strengths.¹¹ In Table I the ligand field absorptions of nonbridged, monobridged, and dibridged complexes are compared, and the correlation which exists between increased bridging and increased ligand field strength, at least in this series of compounds, can readily be seen. The low-spin nickel(II) complex of N,N',N'',N'''-Me₄[14]aneN₄ is chosen for inclusion in the table since it is the only complex involving tertiary nitrogen donors in a macrocyclic array for which data are available.¹²

Attempts to induce the Ni(2)(ClO₄)₂ system to fold, by refluxing it in ethanolic solution with the potentially cis-bidentate ligand 1,10-phenanthroline, were unsuccessful, which suggests that this manner of bridging provides an effective means of blocking the possibility of a macrocycle folding. Preliminary experiments on the [13]aneN₄ system have already shown that corresponding bridged products can be derived from this system also.

Registry No. 1, 295-37-4; 2, 72952-82-0; 2·4HCl, 72952-83-1; Ni(2)(ClO₄)₂, 72984-97-5; 3·4HCl, 72952-84-2; Ni(3)(ClO₄)₂, 72967-86-3; 1,2-dibromoethane, 106-93-4.

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A New Synthetic Method for 2-Alkylpentaboranes(9)

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Following the synthesis of μ -SiMe₃B₅H₈,¹ the first example of a group 4 element bridging two adjacent boron atoms in a borane by a three-center two-electron bond, a number of other bridge-substituted group 4 derivatives of pentaborane(9),

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Table I. Energy Differences between Related Molecular Orbitals for Isomers of SiH₃B₅H₈, CH₃B₅H₈, and FB₅H₈

MO ^a	substituent	$\Delta_{1,2}$, ^b eV	$\Delta_{2,\mu}$, ^c eV
3e	CH ₃	+0.15	-0.96
	SiH ₃	-0.33	-0.29
	F	-2.08	
e _x	CH ₃	+1.13	+1.73
	SiH ₃	+0.66	+1.25
	F	+0.38	
a _{1x}	CH ₃	+1.12	+1.05
	SiH ₃	+1.50	-0.14
	F	-1.91	

^a Idealized molecular orbital symmetry assignment. ^b (Energy of MO of 1-XB₅H₈) - (energy of MO of 2-XB₅H₈) = $\Delta_{1,2}$; positive values imply a net stabilization. ^c (Energy of MO of 2-XB₅H₈) - (energy of MO of μ -XB₅H₈) = $\Delta_{2,\mu}$.

including μ -SiR₃⁻, μ -GeR₃⁻, μ -SnR₃⁻, and μ -PbR₃B₅H₈, have been prepared.^{1,2} Attempts to prepare the corresponding carbon-bridged derivatives, μ -CR₃B₅H₈, under conditions similar to those utilized in the preparation of the other bridged group 4 derivatives were, however, notably unsuccessful. We report here the results of Fenske-Hall molecular orbital calculations³ on μ -CH₃B₅H₈ and the synthesis of 2-allylpentaborane(9), 2-[CH₂CHCH₂]B₅H₈, and 2-benzylpentaborane(9), 2-[C₆H₅CH₂]B₅H₈, via synthetic routes that appear to require the formation of short-lived carbon-bridged intermediates.

Results and Discussion

Recent theoretical calculations, having proven useful in rationalizing the reactivity and relative stabilities of known pentaborane(9) derivatives,^{4a} were extended to include the unknown μ -CH₃B₅H₈ in order to reveal any anomalous changes in the energy levels of the MO's or the charge distributions. In accord with previous semiempirical calculations based on photoelectron spectral data,^{4b} an examination of the shifts of three primary molecular orbitals, cage 3e, substituent e_x, and substituent-boron σ bond a_{1x}, allows a qualitative understanding of the observed trends in isomer stabilities since the other MO energy values generally remain invariant. The differences in the calculated energies of these respective MO's in 2-CH₃- and μ -CH₃B₅H₈ (unknown) as compared to the 2-SiH₃- and μ -SiH₃B₅H₈ (least stable) couple are tabulated in Table I. These results, in contrast to the striking differences between 2-FB₅H₈ and the unknown 1-FB₅H₈, suggested that the nonexistence of μ -CH₃B₅H₈ could not be attributed to energy differences.

Calculations also showed the individual atom charges on carbon in the known 1- and 2-CH₃B₅H₈'s and the unknown μ -CH₃B₅H₈ to be -0.152, -0.246, and -0.064 e, respectively, and on silicon in the 1-, 2-, and μ -SiH₃B₅H₈'s to be +0.810, +0.726, and +0.907 e, respectively. The relative trends for carbon and silicon are virtually identical except that carbon is negatively charged and the silicon is positively charged. The charges on both carbon and silicon are most positive in the bridged position. This tendency for positive charge to increase on the substituent when it is located in a bridged position suggested that further synthetic investigations were warranted.

The supposition⁵ that only relatively electropositive groups can occupy bridged positions led to the examination of reactions of B₅H₈⁻ with organic compounds known to produce relatively stable carbonium ions. Due to the spatial require-

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Table II. ^{11}B NMR Chemical Shifts and Coupling Constants for $2\text{-C}_6\text{H}_5\text{CH}_2\text{B}_5\text{H}_8$ and $2\text{-CH}_2\text{CHCH}_2\text{B}_5\text{H}_8$

	B(1)	B(2)	B(3,5)	B(4)
$2\text{-C}_6\text{H}_5\text{CH}_2\text{B}_5\text{H}_8$				
δ , ppm	-52.32	+1.83	-14.12	-18.79
J , Hz	17.3		164	
$2\text{-CH}_2\text{CHCH}_2\text{B}_5\text{H}_8$				
δ , ppm	-52.52	+0.45	-14.43	-18.82
J , Hz	175		166	166

ments of the pentaborane(9) cage, primary carbon reagents, allyl iodide and benzyl bromide, were the first choices to be investigated. Both of these compounds reacted with the B_5H_8^- anion. The products obtained were not the desired μ -substituted but rather the thermodynamically stable 2-substituted pentaborane(9) derivatives. These results suggest that the μ -allyl and μ -benzyl B_5H_8 derivatives are formed but then rapidly isomerize to the corresponding 2-substituted derivatives by a much lower activation energy pathway than is available for μ -silyl- and μ -germyl- B_5H_8 derivatives. In the silyl- and germyl- B_5H_8 compounds the μ isomers are produced initially and are easily purified, but they isomerize irreversibly to the corresponding 2-isomers by low-energy thermolysis and at ambient by a Lewis base catalyzed (diethyl ether) route. Low-temperature ^{11}B NMR studies of the allyl iodide and benzyl bromide reactions with KB_5H_8 showed only the presence of the B_5H_8^- anion and the 2-substituted products. This indicates that the μ -allyl- and μ -benzyl- B_5H_8 derivatives are thermodynamically unstable with respect to the corresponding 2-substituted derivatives and also isomerize to them at rates that are comparable to the rates of formation of the μ -derivative.

Experimental Section

High-vacuum techniques were used in handling all pentaborane(9) derivatives.⁶ Dimethyl ether, diethyl ether, and pentane were distilled from LiAlH_4 directly into the reaction flask. *n*-Butyllithium in hexane solution, KH dispersion in oil, benzyl bromide, and allyl iodide were used as received from conventional sources.

The Bruker WH-270 Fourier transform spectrometer (270 MHz for ^1H spectra, 86.7 MHz for ^{11}B spectra) was used to obtain the NMR data. Chemical shifts were referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$ and Me_4Si , downfield shifts having positive values. Mass spectra were obtained on an AEI-902 spectrometer. Infrared spectra were obtained by using a Perkin-Elmer Model 700 spectrometer.

$2\text{-C}_6\text{H}_5\text{CH}_2\text{B}_5\text{H}_8$. In a dimethyl ether solution, 23 mmol of KB_5H_8 was prepared as previously described.⁷ The KB_5H_8 was rigorously freed of dimethyl ether by successive washings with pentane followed by high-vacuum pumping at -30°C . Then ca. 30 mL of pentane and 23 mmol of benzyl bromide were condensed into the reaction flask. The reaction mixture was warmed from -30 to 0°C over a 1-h period and then warmed from 0°C to room temperature over a 3-h period. Isolation of the $2\text{-C}_6\text{H}_5\text{CH}_2\text{B}_5\text{H}_8$ was accomplished by distillation and condensation in a trap at -30°C . Final purification was by slow distillation and condensation in a trap at -10°C with the remaining contaminants distilling past. The yield of $2\text{-C}_6\text{H}_5\text{CH}_2\text{B}_5\text{H}_8$ was 11%. By observation of this reaction in an NMR tube, it was determined that the reaction proceeds at ca. 0°C .

The compound is a colorless liquid with no measurable vapor pressure at room temperature. The mass spectrum exhibited a cutoff at m/e 154, corresponding to $^{11}\text{B}_5\text{H}_8^{12}\text{C}_7\text{H}_7$; m/e calcd, 154.1637; obsd, 154.1639. ^{11}B NMR chemical shifts and coupling constants are listed in Table II, and the ^1H NMR spectrum is shown in Figure 1. The infrared spectra were measured as a thin film at ambient temperature. Absorptions occurred at 3090 (w), 3075 (w), 3010 (m), and 2905 (w) (C-H stretch), 2605 (vs) (B-H), 1940 (vw), 1865 (vw), 1790 (m) (B-H-B), 1595 (s), 1485 (s), 1465 (s), 1395 (vs), 1248 (m), 1120 (w), 1080 (w), 1063 (w), 1020 (w), 1008 (w), 975 (vw),

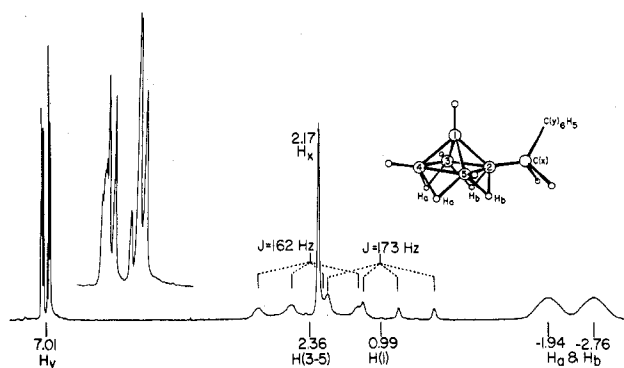


Figure 1. The ^1H NMR spectrum of $2\text{-C}_6\text{H}_5\text{CH}_2\text{B}_5\text{H}_8$ at 270 MHz. Coupling patterns and constants for ^{11}B -H are shown above the spectrum, while chemical shifts and assignments are shown below.

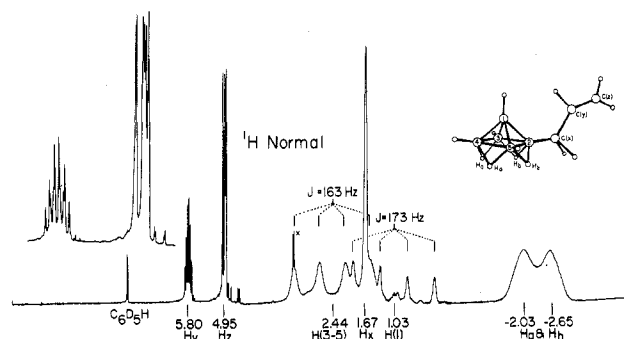


Figure 2. The ^1H NMR spectrum of $2\text{-CH}_2\text{CHCH}_2\text{B}_5\text{H}_8$ at 270 MHz. Coupling patterns and constants for ^{11}B -H are shown above while chemical shifts and assignments are shown below the spectrum.

950 (vw), 880 (vs), 850 (w), 790 (vw), 740 (m), 725 (w), and 695 (s) (± 10) cm^{-1} .

$2\text{-CH}_2\text{CHCH}_2\text{B}_5\text{H}_8$. In a diethyl ether solution, 20 mmol of LiB_5H_8 was prepared as previously described.⁸ Then ca. 21 mmol of $\text{CH}_2\text{CHCH}_2\text{I}$ was condensed in the reaction flask. The solution was then slowly warmed from -78°C to room temperature over a period of ca. 6 h. During this time, the reaction solution became bright yellow and an off-white milky precipitate formed. Conventional high-vacuum distillation through a -30°C trap and condensation in a -50°C trap produced nearly pure $2\text{-CH}_2\text{CHCH}_2\text{B}_5\text{H}_8$. To obtain a ^1H NMR pure product, however, very slow distillation through a trap at -50°C and condensation in a trap at -63°C was necessary. The yield of $2\text{-CH}_2\text{CHCH}_2\text{B}_5\text{H}_8$ was 13%. In an NMR tube experiment, it was determined that this reaction proceeds at ca. -30°C .

The compound is a colorless liquid at room temperature. The mass spectrum exhibited a cutoff at m/e 104, corresponding to $^{11}\text{B}_5\text{H}_8^{12}\text{C}_3\text{H}_5$; m/e calcd, 104.1483; obsd, 104.1480. ^{11}B NMR chemical shifts and coupling constants are listed in Table II. The ^1H NMR spectrum is shown in Figure 2. Upon decoupling of B(2), the methylenic group at 1.67 ppm sharpens to a doublet demonstrating that the point of attachment is at the saturated carbon. The infrared spectrum was measured in a 10-cm cell in the gas phase at ambient temperature. Absorptions occurred at 3110 (m), 3000 (w), and 2835 (w) (C-H stretch), 2600 (vs) (B-H), 1820 (w) (B-H-B), 1650 (m), 1440 (s), 1255 (vw), 1210 (vw), 1160 (m), 1100 (2), 1060 (vw), 1030 (vw), 1000 (w), and 995 (s) (± 10) cm^{-1} .

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Registry No. $2\text{-C}_6\text{H}_5\text{CH}_2\text{B}_5\text{H}_8$, 73002-61-6; $2\text{-CH}_2\text{CHCH}_2\text{B}_5\text{H}_8$, 72985-57-0; KB_5H_8 , 12447-53-9; LiB_5H_8 , 34370-18-8; benzyl bromide, 100-39-0; $\text{CH}_2\text{CHCH}_2\text{I}$, 556-56-9; $1\text{-CH}_3\text{B}_5\text{H}_8$, 19495-55-7; $1\text{-SiH}_3\text{B}_5\text{H}_8$, 28556-29-8; $1\text{-FB}_5\text{H}_8$, 30624-36-3; $2\text{-CH}_3\text{B}_5\text{H}_8$, 23753-74-4; $2\text{-SiH}_3\text{B}_5\text{H}_8$, 22142-52-5; $2\text{-FB}_5\text{H}_8$, 20199-86-4; $\mu\text{-CH}_3\text{B}_5\text{H}_8$, 72985-80-9; $\mu\text{-SiH}_3\text{B}_5\text{H}_8$, 22044-27-5.

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