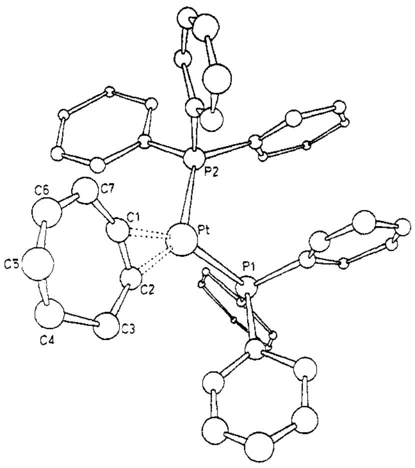

Figure 1. The overall stereochemistry of (cycloheptyne)Pt$(PPh_3)_2$.

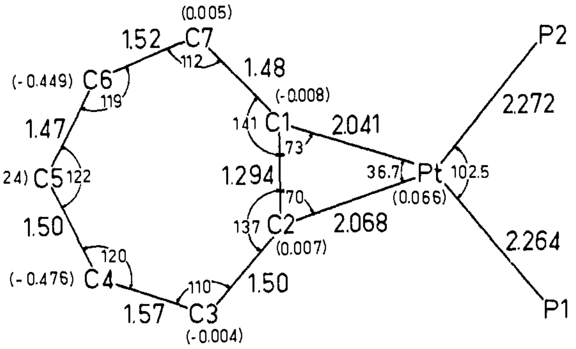

Figure 2. Important bond lengths (ångströms) and bond angles (degrees) for (cycloheptyne)Pt$(PPh_3)_2$. Deviations from the least-squares plane through C(1), C(2), C(3), and C(7) are shown in parentheses.

age. Although the aliphatic C–C distances in the cycloheptyne ring are normal, significant deviations from the tetrahedral angle occur at C(4), C(5), and C(6), presumably in an attempt to relieve ring strain. Atoms C(1), C(2), C(3), and C(7) are coplanar within experimental error and C(5) is only 0.024 Å above this plane. The cycloheptyne ring can, therefore, be described as having a distorted chair conformation.

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M. A. Bennett,* G. B. Robertson, P. O. Whimp, T. Yoshida
Research School of Chemistry
The Australian National University
Canberra, A.C.T., 2600, Australia
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Addition of Diborane(6) to Boron Hydride Anions. New Syntheses of Hexaborane(12) and Pentaborane(11)

Sir:

In recent years, the conjugate bases of B_5H_9, B_6H_{10}, and B_4H_{10} ($B_5H_8^-$,[1-4] $B_6H_9^-$,[3,4] and $B_4H_9^-$ [5-7]) have been

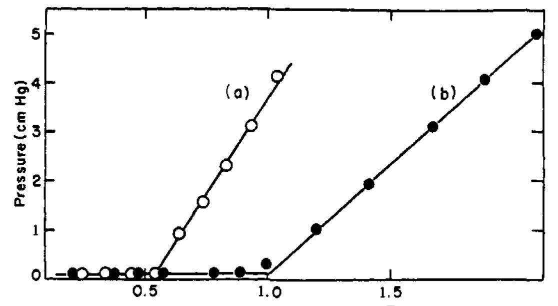

Figure 1. Tensiometric titrations of $B_5H_8^-$ with B_2H_6 at −78° in $(C_2H_5)_2O$: (a) completed in one day, (b) sufficient time allowed for complete reaction of each increment (see text).

prepared and characterized. The Lewis basicity of these species makes them potentially valuable synthetic reagents, as has been demonstrated for $B_5H_8^-$.[2,8-10] At this time we wish to report a sequence of reactions in which the BH_3 group adds to these bases in a way which apparently expands the polyhedral framework. Thus, we have observed that diborane(6) reacts in a 0.5 *M* ratio with $B_4H_9^-$, $B_5H_8^-$, and $B_6H_9^-$ to produce $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$, respectively. From the first two anions we have obtained B_5H_{11} and B_6H_{12}, respectively, in good yields (60–70%) by treatment with anhydrous liquid hydrogen chloride. These syntheses of B_5H_{11} and B_6H_{12} are summarized by the following equations.

$$MB_5H_8 + {}^1/_2B_2H_6 \xrightarrow[(CH_3)_2O]{-78^\circ} MB_6H_{11} \tag{1a}$$

$$MB_6H_{11} + HCl(l) \xrightarrow{-110^\circ} B_6H_{12} + MCl \tag{1b}$$

$$KB_4H_9 + {}^1/_2B_2H_6 \xrightarrow[(C_2H_5)_2O]{-35^\circ} KB_5H_{12} \tag{2a}$$

$$KB_5H_{12} + HCl(l) \xrightarrow{-110^\circ} B_5H_{11} + H_2 + KCl \tag{2b}$$

Treatment of $B_7H_{12}^-$ with HCl yields B_6H_{10} as the major product; minor components are still under study. In view of the commercial availability of B_5H_9,[11] the reactions outlined above (1a, 1b) make B_6H_{12} conveniently available in the laboratory for the first time. Furthermore, the reactions outlined for the preparation of B_5H_{11} provide an attractive alternative to currently employed procedures.[12]

Tensiometric titrations of LiB_5H_8 or KB_5H_8 at −78° in diethyl ether (Figure 1) with B_2H_6 clearly reveal a

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two-step reaction sequence showing an overall 1:1 stoichiometry. Diborane(6) adds rapidly and irreversibly up to a mole ratio of 0.5 (eq 1a); however, in the range 0.5:1–1:1, days are required for complete reaction. The final products of this reaction include B_6H_{10} and $B_{10}H_{14}$.[2,13]

A 1:1 stoichiometry for the reaction of B_2H_6 with $B_5H_8^-$ has previously been reported, but the fact that the reaction proceeds in two steps was unrecognized. Unsymmetrical cleavage of B_2H_6 by $B_5H_8^-$ to produce an isomer of B_6H_{10} was proposed.[2] Unsymmetrical cleavage is clearly inconsistent with the results of the present study; no evidence now exists to support the formation of the proposed isomer of B_6H_{10}.

The boron-11 nmr spectrum of LiB_6H_{11} formed according to eq 1a is shown in Figure 2. The unsymmetrical "doublet" near 0 ppm appears to be a singlet of relative intensity one overlapping a doublet of relative intensity two.[13a] This interpretation is supported by the boron-11 nmr spectrum of a specifically labeled $B_6H_{11}^-$ prepared by adding B_2H_6 of normal isotopic composition to $B_5H_8^-$ containing 96% boron-10. Only a single unresolved peak was observed with a chemical shift corresponding to the larger (downfield) arm of the unsymmetrical "doublet." The boron-11 nmr spectrum thus suggests a structure in which the added BH_3 group has entered the vacant bridge site in the base of the $B_5H_8^-$ unit. Lack of resolvable spin coupling for the resonance due to the added boron atom could be the result of a rapid tautomerism which scrambles the terminal hydrogens on this boron and the bridging hydrogens in the remainder of the anion. Thermal decoupling may also be involved.[14]

Conversion of $B_6H_{11}^-$ to B_6H_{12} was accomplished using the potassium salt prepared in $(CH_3)_2O$. In 2.0 ml of $(CH_3)_2O$, 1.91 mmol of KB_5H_8 was prepared from KH and B_5H_9.[4] Diborane(6), 1.00 mmol, was condensed in at −196° and allowed to react at −78° for about 10–20 min. Solvent was distilled away until solvent removal became prohibitively slow at −35°. Liquid anhydrous hydrogen chloride was then added and stirred at −110° until the viscous residue dissolved and a white solid formed. A 63% yield of B_6H_{12} (1.2 mmol) was obtained through fractionation of the product mixture which contained B_4H_{10} and B_5H_9 as the main contaminants. The identity and purity of the product were established by its vapor pressure at 0°, 17 mm (lit. 17 mm,[15a] 17.1 mm[15b]), infrared spectrum,[15] and boron-11 nmr spectrum.[15a]

To a 1.59-mmol sample of KB_4H_9 in 1.8 ml of $(C_2H_5)_2O$, a 1.18-mmol quantity of B_2H_6 was added and allowed to react at −35°. The reaction was complete in several hours, as determined by monitoring the pressure in the system. Excess B_2H_6 (0.41 mmol) was recovered, thereby establishing a molar reaction ratio of $0.97BH_3:1.0B_4H_9^-$. The bulk of the solvent was distilled away from the reaction vessel at −78°. Additional solvent was removed by warming to −35° briefly. Liquid anhydrous HCl was added at −196° and 1.47 mmol of hydrogen was evolved in about 20 min at −110° (92% of theory). Pentaborane(11) was obtained in 69% yield (1.08 mmol) by fractional condensation. The vapor pressure was 49 mm at 0° (lit.[16] 52.8 mm) and infrared[16,17] and 32.1-MHz boron-11[18] spectra agreed well with previous reports.

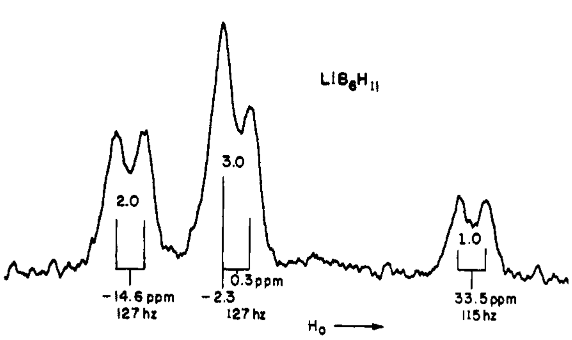

Figure 2. Boron-11 nmr spectrum (32.1 MHz) of LiB_6H_{11} at −20°. Chemical shifts are relative to $BF_3 \cdot O(C_2H_5)_2$.

The boron-11 nmr spectrum of KB_5H_{12} consists of two apparent singlets in the area ratio of 3.9:1.0, suggesting a square-pyramidal arrangement of boron atoms (on the nmr time scale) in the anion. The chemical shifts are 16.6 and 58.6 ppm, respectively (relative to $BF_3 \cdot O(C_2H_5)_2$).

A dichloromethane solution containing 0.92 mmol of $(n\text{-}C_4H_9)_4NB_6H_9$[19] was titrated tensiometrically at −78° with B_2H_6. The stoichiometry of the reaction as determined from the tensiometric curve, which showed a sharp break, was 0.54 mol of B_2H_6/mol of $B_6H_9^-$. Furthermore, the quantity of excess B_2H_6 recovered and measured agreed well with this reaction ratio. At this point we are not prepared to discuss the boron-11 nmr spectra of $B_7H_{12}^-$, but the spectra of samples prepared and maintained at low temperature show that no $B_6H_9^-$ is present.

The reactions described herein offer the possibility of a general systematic method for the stepwise buildup of boron hydride frameworks through repetition of the three-step sequence: (1) generation of boron hydride anion, (2) addition of BH_3, and (3) conversion to neutral hydride. Work is in progress to extend this reaction sequence to other related systems.

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(13a) Note Added in Proof. This conclusion has been verified by observing the boron-11 nmr spectrum while simultaneously irradiating the sample at the proton resonance frequency using a white noise decoupler. With the protons spin decoupled, this region of the spectrum shows two singlets with the expected chemical shifts and with the relative areas of the higher field to lower field peak equal to two.

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H. D. Johnson, II, S. G. Shore*
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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