be expressed in the formula $[Hg(OH)]_n(NO_3)_n$ and described as polymeric mercury(II) oxonium nitrate or as *catena-μ*-hydroxo-mercury(II) nitrate.[18]

Registry No. $Hg(OH)NO_3$, 22640-45-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-3006.

(18) See nomenclature rules in *J. Amer. Chem. Soc.*, **82**, 5517 (1960).

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Studies of Boranes. XXXVIII. Reactions of Hexaborane(10) with Boron Hydride Lewis Acids[1]

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The reactions of B_6H_{10} with several borane Lewis acids, or their reactive precursors, were studied. The acids B_3H_7 and B_4H_8 react with B_6H_{10} to give *n*-B_9H_{15}. Boron isotopically labeled B_3H_7 and B_9H_{13} react with B_6H_{10} to give *n*-B_9H_{15} and $B_{15}H_{23}$ in which three and nine boron atoms, respectively, are specifically labeled. The acid, B_8H_{12}, reacts with B_6H_{10} to give a new boron hydride, $B_{14}H_{22}$. In the absence of B_6H_{10}, B_8H_{12} is shown to decompose to give $B_{16}H_{20}$ as the only volatile borane. The products of the hexaborane reactions are postulated to arise from a reaction not widely recognized in neutral boron hydride chemistry: the formation of a three-center boron bond by reaction of a hydride containing a B–B two-center bond with an acidic hydride having a readily available empty boron orbital. Reaction mechanism and structures are proposed on the basis of nmr studies.

Introduction

The unstable species BH_3, B_2H_4, B_3H_7, B_4H_8, B_8H_{12}, and B_9H_{13} are all known to form carbon monoxide adducts.[2-7] This property has been cited as evidence for the transitory existence of BH_3[2] and B_4H_8.[8] Extrapolation of this principle supports the contention that these compounds are all capable of a brief existence. For some of these materials other evidence is abundant;[9] indeed, one of them, B_8H_{12}, is an isolable compound.[10] Since many of these acids (if not all of them) appear to be intermediates in boron hydride interconversions, we have attempted to study their reactions with other boron hydrides, at low temperatures, where possible. This article describes our efforts with B_6H_{10} which because of its known Lewis basicity[11,12] seemed particularly likely to react with these species. We have already described the nearly quantitative synthesis of the new hydride $B_{15}H_{23}$ by generation of B_9H_{13} in the presence of B_6H_{10}.[13]

Experimental Section

Methods. The high-vacuum techniques used in this investigation have been described elsewhere.[14,15] Commercially available materials used in this work were purified by standard methods. The 70.6-MHz Fourier transform ^{11}B nmr spectra were obtained with a Varian Associates HR220 spectrometer using a "home-built" pulse apparatus and standard Varian variable-temperature probe accessories. Data manipulation for the instrument was accomplished by means of a Nicolet 1080 computer. Mass spectra were recorded on an AEI Model MS-9 mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer.

Preparation of Starting Materials. The compounds B_6H_{10}, B_8H_{12}, and B_8H_{18} were prepared by literature methods.[16-18] Calcium tetrafluoroborate (enriched to 96% ^{10}B by Oak Ridge National Laboratory) was converted to $^{10}B_2H_6$.[19,20] Decaborane(14), enriched to approximately 60% ^{10}B, was prepared by acidification of $KB_{10}H_{13}$ after exchange of this material with $^{10}B_2H_6$.[21] The labeled $B_{10}H_{14}$ was then converted to KB_9H_{14}[22] and to *i*-B_9H_{15} as described previously.[23]

Reactions of Hexaborane(10). Isononaborane(15). Nmr samples of $B_{15}H_{23}$ were prepared by decomposition of *i*-B_9H_{15} of normal and approximately 60% ^{10}B content in B_6H_{10} solution as described previously.[13] Spectra of CH_2Cl_2 solutions of these samples are shown in Figure 1.

Octaborane(12). Due to its extreme instability, B_8H_{12} could be accurately measured only by weight loss from a larger sample at room temperature.[24] Samples of B_8H_{12} (1.82 mmol) and B_6H_{10} (5.47 mmol) were sealed into a break-seal tube (12-mm o.d.) at

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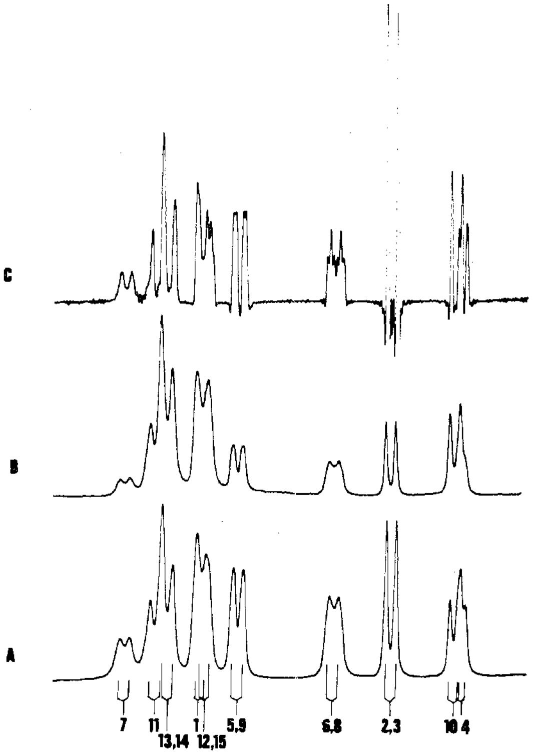

Figure 1. The 70.6-MHz ^{11}B nmr spectra of $B_{15}H_{23}$ measured in CH_2Cl_2 solution: (A) normal FT spectrum; (B) normal FT spectrum with 60% ^{10}B in B(1–9); (C) artifically line-narrowed spectrum (A. O. Clouse, D. C. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, 95, 2496 (1973)) (TC = 10).

−196°. The tube was warmed to −23° for 15 min during which much solid formed. Excess B_6H_{10} (3.71 mmol, vp at 0° = 8.0 ± 0.5 mm, lit.[16] 7.5 mm) was then removed at −23° by pumping (*ca.* 90 min) into a −196° bath. The weight of the white powder remaining in the tube corresponded to 1.74 mmol of $B_{14}H_{22}$. The white solid did not melt or show signs of decomposition after standing at 0° for 30 min but did melt to a colorless liquid at room temperature which was very unstable. At −41° a ^{11}B nmr spectrum in CH_2Cl_2 solution showed only peaks corresponding to a 1:1 mixture of B_8H_{12} and B_6H_{10} indicating complete dissociation of the adduct under these conditions. Hydrolysis with dilute hydrochloric acid and titration of $B(OH)_3$ as the D-mannitol complex gave 85.8% B (calcd for $B_{14}H_{22}$ 87.2%) and a hydrolytic H_2 to $B(OH)_3$ ratio of 2.289 (calcd 2.286).

Tetraborane(8)-Carbonyl and Octaborane(18). A mixture of B_6H_{10} (3.36 mmol) and $B_4H_8 \cdot CO$ (0.90 mmol) in a sealed breakseal tube (11-ml volume) was allowed to stand at room temperature for 3 hr. Material which passed a 0° bath and stopped in a −30° bath was identified mass spectroscopically as n-B_9H_{15} (0.85 mmol) contaminated with a small amount of $B_{10}H_{14}$. Material which passed the −30° bath and stopped at −63° was B_6H_{10} (2.34 mmol). Also identified by their infrared spectra were $BH_3 \cdot CO$ and B_2H_6. Noncondensable gas and nonvolatile residue were also obtained.

Similarly a mixture of B_8H_{18} and B_6H_{10} allowed to stand at room temperature for 1 hr gave large amounts of n-B_9H_{15} and some $B_{10}H_{14}$ identified by their mass spectra.

Triborane(7). In a 50-ml tube equipped with a stopcock, B_4H_{10} (96% ^{10}B, 2.66 mmol) and tetrahydrofuran (6.0 mmol) were allowed to remain at room temperature for 30 min. Volatile products were then pumped from the tube at −10° until only solid $B_3H_7 \cdot THF$ remained. This adduct was dissolved in B_6H_{10} (3.29 mmol), the tube was cooled to −196°, and BF_3 (7.0 mmol) was added. Only 0.05 mmol of H_2 was evolved after 90 min at −45°. After 30 additional min at 0° a total of 0.71 mmol of H_2 was formed. Labeled n-B_9H_{15} was then separated as in the previous experiment. A ^{11}B nmr spectrum of this compound is shown in Figure 2. Material which collected in a −63° bath (mostly B_8H_{12} and B_6H_{10}) was warmed to −23°. Excess B_6H_{10} was pumped from the trap at this temperature until only a white powder, presumably $B_{14}H_{22}$, remained.

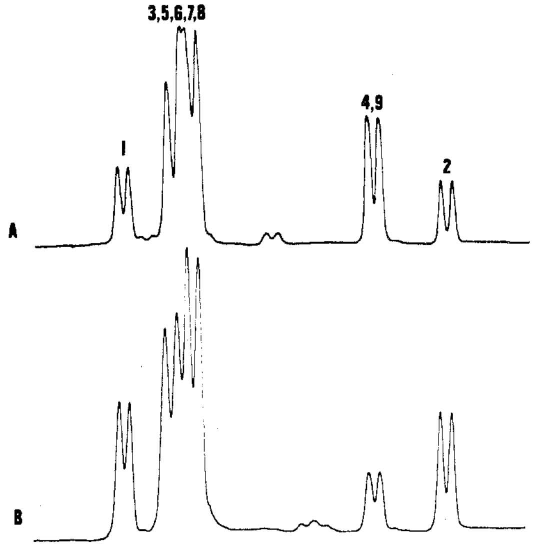

Figure 2. The 70.6-MHz ^{11}B nmr spectra of n-B_9H_{15}: (A) normal FT spectrum; (B) normal FT spectrum ^{10}B enriched in B(3,4,9).

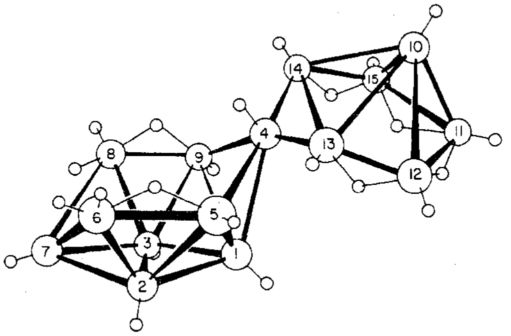

Figure 3. Proposed structure of $B_{15}H_{23}$.

A reaction conducted similarly which consumed 0.58 mmol of B_6H_{10} produced 0.33 mol of n-B_9H_{15}, 0.16 mmol of $B_{14}H_{22}$, and 0.50 mmol of H_2. Other boranes formed in these reactions were not investigated.

Decomposition of Octaborane(12). A sample of B_8H_{12} (1.49 mmol) was allowed to remain at room temperature for 3 hr during which the material solidified to a red-orange glass. After removal of H_2 (1.50 mmol) at −196°, $B_{16}H_{20}$ (0.387 mmol) was sublimed at 130°. The residue weighed 0.0632 g. Only a trace of B_8H_{12} could be recovered. The $B_{16}H_{20}$ was identified as the known isomer[25] by ir, uv, nmr, and mass spectra.

Results

Spectra of $B_{15}H_{23}$ are shown in Figure 1. A proposed structure is shown in Figure 3 in which a B_9H_{13} moiety has replaced a bridge proton in the $B_6H_{11}{}^+$ ion.[11] The chemical shifts and coupling constants of six of the nine resonances which decreased in intensity in the spectrum of the ^{10}B-labeled compound are close to corresponding resonances of $B_9H_{13}Et_2S$, the spectrum of which has already been assigned.[26] Resonances from the 4 and 5, 9 borons can be assigned by their relative intensities and comparison with ^{10}B-labeled spectrum. A comparison of these values for the two compounds is given in Table I. The resonance due to B(6,8) appears as a doublet (as in other B_9H_{13} ligand compounds[26]) with triplet fine structure suggesting that the endo terminal hydrogen coupling (^1H-^{11}B) is nearly

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[24] We have observed that B_8H_{12} pumped from highly decomposed samples is pure and therefore the only error in this method is that due to loss of a small amount of hydrogen.

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Table I. ^{11}B Chemical Shift Values[a] and Coupling Constants[b] of $B_{15}H_{23}$ and $B_9H_{13}Et_2S$

	$B_{15}H_{23}$		$B_9H_{13}Et_2S$	
Position	δ	J_{B-H}	δ	J_{B-H}
7	−21.0	150[c]	−17.5	138
11	−14.2	140		
13, 14	−11.8	146		
1	−4.7	128	−4.0	129
12, 15	−4.1	160[d]		
5, 9	3.5	139[e]	14.4	138
6, 8	24.5	113[d]	21.8	
2, 3	36.8	115	38.8	147
10	51.0	155		
4	52.2	101	25.9	131

[a] Ppm relative to $BF_3{\cdot}O(C_2H_5)_2 = 0$ ppm in CH_2Cl_2 solution. [b] Terminal proton coupling in Hz (±10 Hz). [c] This coupling was not observed in the previously published spectrum[13] measured in $CDCl_3$ solution. [d] Bridge proton coupling constants of 50 (±10) Hz were measured from triplet fine structure. [e] Bridge proton coupling constants of 50 (±10) Hz were measured from doublet fine structure.

of the same magnitude as the adjacent bridge proton coupling. The B_6H_{10} portion of the molecule is tentatively assigned on the basis of multiplicities of the bridge proton coupling resolved in the "line-narrowed" spectra as well as on the basis of intensity relationships and chemical shifts.

The reaction of B_8H_{12} with B_6H_{10} proceeds according to the measured stoichiometry

$$1.00B_6H_{10} + 1.03B_8H_{12} = 0.99B_{14}H_{22}$$

The compounds B_8H_{18}[27] and $B_4H_8{\cdot}CO$ were used as sources of the acid, B_4H_8. In the reactions of both these materials with B_6H_{10} large amounts of n-B_9H_{15} (94% yield with $B_4H_8{\cdot}CO$) and much smaller amounts of $B_{10}H_{14}$ were obtained. The following competitive reactions are suggested

$$\begin{array}{l} B_6H_{10}{\cdot}B_4H_8 \xrightarrow{-BH_3} n\text{-}B_9H_{15} \\ \qquad\qquad\quad \xrightarrow{-2H_2} B_{10}H_{14} \end{array}$$

An unstable intermediate $B_{10}H_{18}$ could be involved in either or both pathways.

The reaction of B_3H_7 with B_6H_{10} was done under conditions we have used to prepare $B_3H_7{\cdot}CO$[17] except that B_6H_{10} was substituted for carbon monoxide. The amount of H_2 produced in the decomposition of B_3H_7 by itself under these conditions[17] and under similar conditions[28] is negligible. The amount of H_2 evolved in the reaction of B_3H_7 with B_6H_{10} (0.50 mmol) agrees well with the sum of the amounts of n-B_9H_{15} and $B_{14}H_{22}$ formed (0.49 mmol). The amount of B_6H_{10} consumed in the reaction (0.58 mmol) corresponds roughly with the amount of n-B_9H_{15} plus twice the amount of n-B_9H_{15} plus twice the amount of $B_{14}H_{22}$ formed (0.65 mmol). In consistency with these data and in view of the formation of B_2H_4 adducts of weakly basic ligands when B_3H_7 adducts are allowed to react with excess ligand,[29] we propose that the products of the B_6H_{10} reaction arise from loss of H_2 from intermediate B_2H_4 and B_3H_7 adducts of B_6H_{10} as in the equations

$$B_6H_{10}{\cdot}B_3H_7 \rightarrow n\text{-}B_9H_{15} + H_2$$

$$B_6H_{10}{\cdot}B_2H_4 \rightarrow B_8H_{12} + H_2$$

The B_8H_{12} is converted to $B_{14}H_{22}$ with excess B_6H_{10}. Although ligand cleavage of n-B_9H_{15} to B_8H_{12} adducts is known,[30] it apparently does not occur readily with B_6H_{10} since n-B_9H_{15} and no B_8H_{12} (or its decomposed products) were isolated in the reactions with B_4H_8. The experiment with ^{10}B-labeled B_3H_7 gave n-B_9H_{15} labeled in the 3, 4, and 9 positions. A partial assignment of the ^{11}B nmr spectrum of n-B_9H_{15} has already been published.[31] Integration of our first spectrum of this material showed a ^{11}B content of *ca.* 10% in the B(4,9) positions and no measureable ^{11}B in the B(3) position which lies under the 5,6,7,8 peaks. The two doublets attributed to B(5,8) and B(6,7) were of nearly equal intensity. The spectrum shown in Figure 3 was obtained after further purification of the initial sample during which some scrambling of the label occurred. The ^{11}B content of the B(4,9) positions in this spectrum is *ca.* 22% and the lower field doublet of the B(5,6,7,8) set decreased in intensity. No indication of the triplet due to B(3) is observable but the increased resolution of 5,6,7,8 over the normal spectrum shows that at least partial ^{10}B substitution has occurred at B(3).

In the decomposition of B_8H_{12}, 1 mol of H_2/mol of B_8H_{12} is evolved. Since the composition of $B_{16}H_{20}$ is $(B_8H_{10})_2$, the overall composition of the only other product, nonvolatile material, is $(B_8H_{10})_x$. Furthermore, nearly equal weights of nonvolatile material and $B_{16}H_{20}$ were observed, suggesting two approximately equally favorable pathways for association of B_8 molecules, one leading to nonvolatile materials(s) and the other leading to $B_{16}H_{20}$.

Discussion

The new hydrides $B_{14}H_{22}$ and $B_{15}H_{23}$ appear to arise by formation of a three-center bond by donation of the pair of electrons in the single B–B bond in B_6H_{10} (acting as a base) into an empty (or readily vacated) boron orbital of the acids B_8H_{12} and B_9H_{13}. In this respect, these compounds are unique among the known boron hydrides in that each contain two boron frameworks apparently joined only by a single three-center bond.

In view of the formation of B_8H_{12} and B_9H_{13} adducts of B_6H_{10}, the reaction of B_3H_7 with B_6H_{10} was done in an attempt to prepare n-B_9H_{15} through loss of H_2 from an intermediate B_3H_7 adduct. The mechanism shown in Scheme I appeared sterically reasonable with models and agrees with the results of the ^{10}B-labeling experiment. The first step after the formation of the expected acid–base adduct is attack of a terminal hydrogen (with its pair of electrons) of the B_3H_7 moiety (B(3), B(4), and B(9) in a tautomeric configuration resembling that of the crystal structure of $NH_3B_3H_7$[32]) on a bridge proton of the B_6H_{10} fragment with elimination of H_2 and formation of a three-center bond. Only a slight redistribution of electrons is then required to give n-B_9H_{15}.

Octaborane(12) was also observed in the reaction. We suspect that B_8H_{12} is formed by loss of H_2 from an intermediate B_2H_4 adduct of B_6H_{10}. Indeed, a reasonable mechanism is exactly the same as that given for n-B_9H_{15} except that the doubly bridged BH_2 group (B(3)) is replaced with a bridge hydrogen atom.

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(27) Decomposition of B_8H_{18} in the presence of CO gives good yields of $B_4H_8{\cdot}CO$: J. Dobson, D. Gaines, and R. Schaeffer, *J. Amer. Chem. Soc.*, **87**, 4072 (1965).

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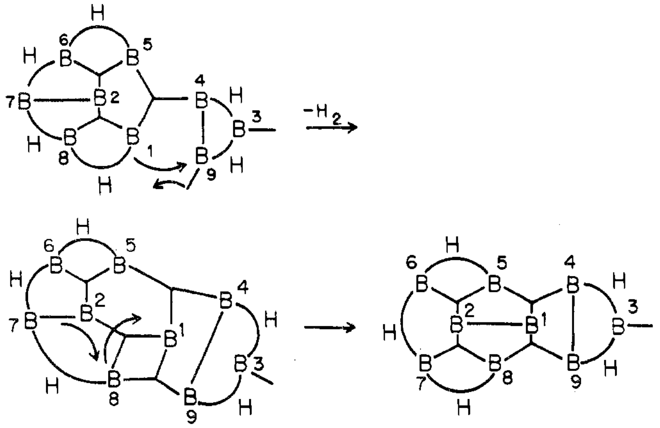
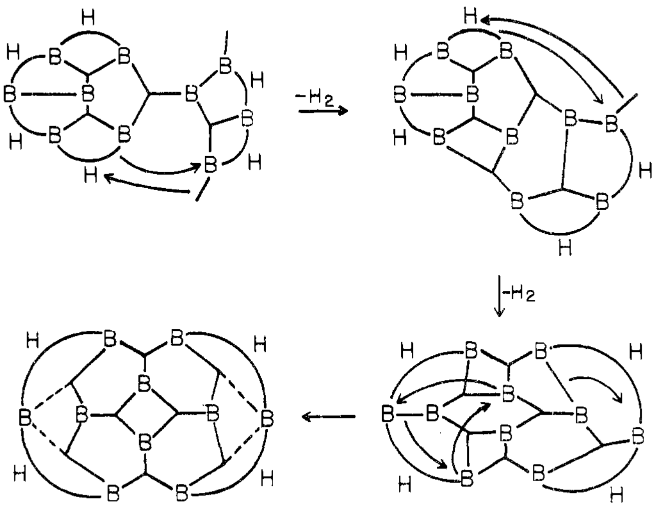
Scheme I



Scheme II



Similarly, we expected an intermediate B_4H_8 adduct of B_6H_{10} to lose H_2 to form $B_{10}H_{14}$ as in the Scheme II mechanism (also appearing very favorable with models). However, the reaction does not appear to follow this path possibly because of more favorable loss of BH_3 to form n-B_9H_{15}. The small amount of $B_{10}H_{14}$ formed in the reaction may have come from the known reaction of n-B_9H_{15} with B_2H_6.[33]

Interpretation of the data for ^{10}B scrambling in B(3,4,9)-labeled n-B_9H_{15} allows assignment of the previously unassigned B(5,8) and B(6,7) resonances. Evidence for the dissociation of n-B_9H_{15} into B_2H_6 and B_8H_{12} and demonstration of the reverse of this reaction where BH_3 inserts into the B(3) position of n-B_9H_{15} are already reported.[31,34] Furthermore, a rapid tautomerism in B_8H_{12} has been postulated to account for the equivalence of the B(3,5,6,8)[35] set in the ^{11}B nmr spectra of this compound.[18] Dissociation of BH_3 from n-B_9H_{15} with reinsertion at the tautomerically equivalent B(6,7) position in B_8H_{12} would cause an enrichment of the ^{10}B content of the B(6,7) positions and a decrease of the ^{10}B content of the B(4,9) positions with no change in the ^{10}B content of the B(3) position in n-B_9H_{15}. Since a decrease in intensity of the lower field doublet of the B(5,6,7,8) set, as well as the other changes consistent with this mechanism, is observed, this resonance can now be assigned as that due to B(6,7).

The decomposition of B_8H_{12} to give $B_{16}H_{20}$ clarifies earlier studies. Hermanek has observed that pyrolysis of $B_9H_{13}SMe_2$ gives $B_{16}H_{20}$, $B_{10}H_{14}$, and $B_{18}H_{22}$ but does not isolate B_8H_{12}.[25] Decomposition of i-B_9H_{15} yields B_9H_{12}, $B_{10}H_{14}$, and $B_{18}H_{22}$ but no $B_{16}H_{20}$.[18] Recognition of the fact that B_8H_{12} decomposes to $B_{16}H_{20}$ confirms the similarity of reaction of the two B_9H_{13} precursors. Indeed, the dimerization of an unidentified B_8 hydride has been proposed to account for the formation of $B_{16}H_{20}$ in the pyrolysis of $B_9H_{13}SMe_2$.[36]

In view of the structural importance of the two new hydrides, a crystal structure determination has been undertaken for $B_{15}H_{23}$. No satisfactory crystals have been obtained of $B_{14}H_{22}$.

Acknowledgment. The authors gratefully acknowledge support from the National Science Foundation (GP-24266X).

Registry No. B_8H_{12}, 19469-16-0; B_6H_{10}, 23777-80-2; $B_{14}H_{22}$, 52002-74-1; B_4H_8CO, 12007-71-5; n-B_9H_{15}, 19465-30-6; B_8H_{18}, 12421-66-8; B_3H_7·THF, 12544-89-7; $B_{16}H_{20}$, 28265-11-4; $B_{15}H_{23}$, 51965-60-7; $B_9H_{13}Et_2S$, 11092-87-8.

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