

RECENT ADVANCES IN THE CHEMISTRY OF BORON HYDRIDES*

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ABSTRACT

The Lewis base behaviour of B_6H_{10} is reported with a number of Lewis acids including BCl_3 , BBr_3 , BI_3 , AlR_3 ($R = Me, Et, i-Bu$), B_3H_7 , B_4H_8 , B_8H_{12} , and $i-B_9H_{13}$. A new preparation of B_6H_9Br is reported as well as the new compounds B_6H_9I , B_6H_8BrI , $B_6H_8I_2$ and related species with CH_3 as well as halogen. Structures have been redetermined for a number of boron hydrides. The asymmetric location of the unique bridging proton in B_5H_{11} has been established. The structures of SiH_3 and CH_3 pentaboranes have been determined by electron diffraction for both the 1 and 2 substituted isomers. Significant bond shortening occurs for SiH_3 in the 1 position.

The intent of this paper is to present an overview of progress in the study of the simple hydrides of boron since the first meeting at Prague in 1971. Since most of the active workers concerned with this chemistry are present at the meeting, relatively little time will be devoted to the discussion of results from other laboratories. Certain high spots deserve mention but a number of interesting recent developments will be presented by their originators later in this meeting. I shall concentrate largely on structural and synthetic studies carried out at Indiana University.

Three advances in the chemistry of the boranes deserve special mention. Hermanek reported in 1972 that the partial hydrolysis of $B_{16}H_{20}$ led to the formation of the previously unknown $B_{14}H_{18}$. In a second particularly interesting development Davison and co-workers reported in 1972 the synthesis of the $\mu-Fe(CO)_4-B_6H_{10}$ molecule¹. The consequences of this observation are developed more fully below. Finally, Professor Davison has kindly allowed me to quote some recent results from his laboratory that I believe to be of considerable significance and general interest. Briefly, he has been able to produce decaborane in 10–30 per cent yield by reaction of silver fluoroborate or silver nitrate with the lithium salt of pentaborane-9. Further development of this reaction could have exciting implications on the economics of decaborane synthesis.

SYNTHESIS

The possibility of protonation of B_6H_{10} to form salts containing $B_6H_{11}^+$

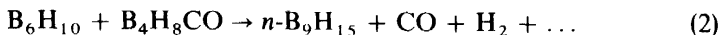
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was predicted as early as 1958 by Lipscomb². However, despite numerous attempts no such salts were reported until 1972³. Evidence of possible general Lewis basicity of B_6H_{10} has been scanty indeed. G. L. Brubaker in a 1971 thesis reported failure to obtain evidence for a complex with BF_3 but was able to show the formation of a 1:1 complex between B_6H_{10} and BCl_3 which was unstable at higher temperatures. On the publication by Davison of the synthesis of $Fe(CO)_4B_6H_{10}$, it became obvious that this boron hydride might be a relatively versatile general Lewis base towards suitable Lewis acids including other boron hydrides. A substantial number of examples of such behaviour have now been observed.

X-ray determination of the structure of $PtCl_2(B_6H_{10})_2$ by Brennan *et al.*⁴ clearly demonstrates the similarity between hexaborane and more widely recognized Lewis bases as ligands. It at once becomes obvious that the use of suitable boron hydrides with readily available orbitals should result in formation of new and interesting species and this expectation has been fully realized.

When $i-B_9H_{15}$ is allowed to decompose in the presence of B_6H_{10} the stable crystalline $B_{15}H_{23}$ is formed. Structural studies of this molecule are currently under way⁵. The molecule crystallizes in the space group P_{bcm} with eight molecules per unit cell. A complete doubly redundant data set of apparently good quality has been collected for the crystalline material but technical difficulties have prevented structural elucidation at the present time. We view it as likely that the molecule consists of simple three-centre bond formation between one of the exposed boron atoms of $i-B_9H_{13}$ and the single bond of B_6H_{10} .

Similarly, B_8H_{12} is known to act as a Lewis acid. For example, this highly unstable hydride is stabilized by solution in diethyl ether. Reaction occurs with B_6H_{10} in 1:1 ratio to form a solid substance. The resulting material dissociates on solution into the component molecules. Attempts to obtain crystalline species have thus far been to no avail. Generation of either B_3H_7 or B_4H_8 in the presence of B_6H_{10} leads to formation of $n-B_9H_{15}$. The fate of the extra boron atom in the case of the B_4H_8 reaction is as yet unknown.



If a B_3H_7 source enriched in ^{10}B is used, the resulting nonaborane is specifically labelled in the 3, 4, 9 positions.

An obvious reaction of interest would be the addition of simple borane, BH_3 , to B_6H_{10} . On first glance this reaction might be expected to lead to the formation of B_7H_{13} . However, the fact that no heptaboranes have been isolated and identified suggested long ago that these molecules were either unstable or highly reactive. Examination of the expected B_7H_{13} structure which would result by simple addition of BH_3 to the electron pair suggests that the reversal of the reaction to form the starting products might be particularly easy. In contrast, hydrogen loss to form the B_7H_{11} molecule presents a different problem. Attempts to write good valence structures for the B_7H_{11} moiety lead to the conclusion that no really good structures can be written. In contrast, it is possible to write structures with a vacant

orbital. Failure to isolate B_7H_{11} might then be a result simply of its high chemical reactivity (analogous in its way to the chemical reactivity of BH_3). Attempts to produce neutral B_7 species at low temperatures were totally unsuccessful.

We consequently turned to an attempt to trap any possible B_7 intermediate by further reaction with B_6H_{10} . B_6H_{10} was heated with diborane and to our delight a new molecule $B_{13}H_{19}$ was isolated. When hexaborane was heated in the absence of diborane, $B_{13}H_{19}$ was still produced. It is possible that our speculation concerning the mechanism is totally wrong but we cannot exclude the possibility that sufficient quantities of diborane for reaction are generated by decomposition of B_6H_{10} . Overall yields of the $B_{13}H_{19}$ species are in any event very low.

The structure of $B_{13}H_{19}$ has been determined by x-ray crystallography, Figure 1⁶.

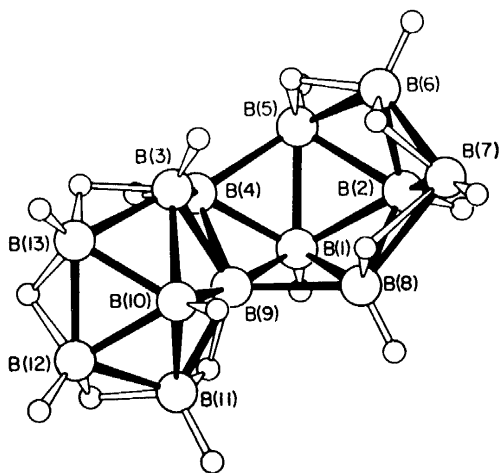
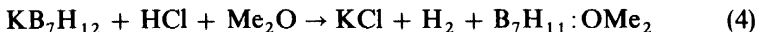
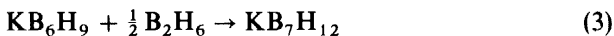


Figure 1

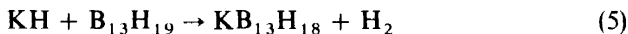
Several alternative pathways have been tried for the synthesis of $B_{13}H_{19}$ in better yield. The most satisfactory method yet devised depends on the prior formation of a B_7 species. For this purpose we have prepared KB_7H_{12} by the method of Shore⁷. Treatment of this with anhydrous hydrogen



chloride in dimethyl ether results in evolution of hydrogen. The resulting heptaborane complex is not isolated but presumably is the 1:1 complex of B_7H_{11} with dimethyl ether. Removal of excess solvent followed by treatment with BF_3 and excess hexaborane results in formation of $B_{13}H_{19}$. A 47 per cent yield of $B_{13}H_{19}$ based on hexaborane consumed was obtained. However, conversion on the basis of the potassium salt is only four per cent. Apparently, a substantial fraction of the initial hexaborane is regenerated in the course

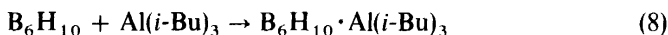
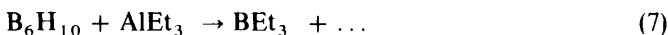
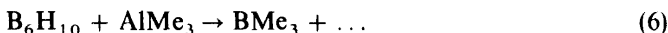
of the reaction. The low conversion is annoying but it should be pointed out that the most difficult material to obtain is hexaborane-10 and the reaction is relatively efficient with respect to this reagent. Other reaction schemes are still being studied.

The new hydride $B_{13}H_{19}$ offers a possible starting point for the synthesis of hitherto unknown boranes of higher molecular weight. Reaction with potassium hydride results in hydrogen evolution and formation of what appears to be $KB_{13}H_{18}$.



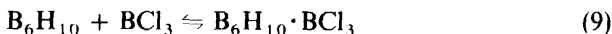
Addition of diborane to the resulting solution produces a material with a distinctive n.m.r. spectrum but acidification of the resulting product regenerates only $B_{13}H_{19}$. Examination of the structure of $B_{13}H_{19}$ suggests that borane addition to form $B_{14}H_{22}$ is likely to be difficult. Further study of these reactions will be undertaken in the near future. Degradative reactions as possible routes to B_{11} and B_{12} hydrides will also be studied.

Reaction of hexaborane with simple Lewis acids has been studied in some detail. Hexaborane reacts readily with aluminium alkyls. In the case of the methyl and ethyl derivatives, only extensive alkylation of the borane is achieved and only trimethyl boron and triethyl boron can be isolated.



On the other hand, triisobutyl aluminium forms a simple 1:1 adduct.

Reactions of the boron halides with B_6H_{10} have also been examined in some detail. We have confirmed the earlier reports that BF_3 is unreactive. BCl_3 readily produces a solid deposit from excess boron trichloride. The reaction apparently has a substantial temperature coefficient since complete dissociation occurs at room temperature. Reaction of hexaborane with

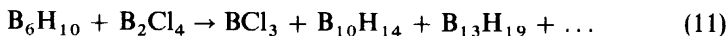


boron bromide results in immediate precipitation of a white solid which only slowly dissolves in excess boron tribromide. On standing at room temperature the hexaborane is converted in 80 per cent yield to the monobromide.



In contrast, direct bromination of hexaborane produces only ten per cent yield of the same compound. Reaction of hexaborane with boron triiodide proceeds in a fashion somewhat different from that of the other halides. The first product is apparently the monoiodide, B_6H_9I , but further reaction takes place in this case. A crystalline diiodide can be separated which has been examined in a preliminary crystallographic study. The crystals are in space group P_{21}/c with four molecules per unit cell. Complete solution of the structure should present no problems. Perhaps most interesting and surprising is the fact that $B_{13}H_{19}$ can be isolated as a minor byproduct of the reaction.

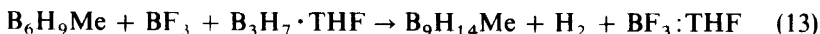
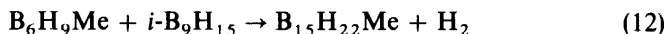
Reaction of B_6H_{10} with diboron tetrachloride proceeds by a different pathway. Boron trichloride is isolated as well as $B_{10}H_{14}$ and $B_{13}H_{19}$.



Other unidentified products are also formed. Reaction of hexaborane with aluminium trichloride results in the formation of $B_{10}H_{14}$.

With a variety of substituted hexaboranes available, it was of interest to us to examine reactions of these with Lewis acids. Several series of reactions have now been studied. Boron triiodide reacts with methyl, bromo or iodo hexaborane to produce iodinated products. Both a mono and diiodide derivatives of the methyl compound can be obtained. In reaction with bromo hexaborane, halogen replacement occurs to form monoiodohexaborane. In addition, direct halogen substitution takes place to form the new compound B_6H_8IBr . Reaction with iodo hexaborane produces the previously mentioned diiodide, $B_6H_8I_2$.

Several attempts have been made to produce products by reaction of bromohexaborane with Lewis acids. Thus far we have been unable to demonstrate reactions with B_8H_{12} , B_3H_7 derivatives, or boron tribromide. In contrast, methyl hexaborane retains considerable Lewis basicity. Decomposition of *i*- B_9H_{15} in the presence of $B_6H_9CH_3$ results in the formation of what appeared to be monomethyl $B_{15}H_{23}$ derivatives. Proton n.m.r. spectra indicate that at least three isomers are formed in the reaction but we have not yet been able to separate individual components. Similarly, reaction with B_3H_7 generated from ligand species results in the formation of two isomers, as yet unseparable, of *n*- $B_9H_{14}CH_3$. Finally, reaction of $B_6H_9CH_3$



with boron bromide produces a mixture of two isomers of $B_6H_8BrCH_3$.



It is our present belief that the differences in reactivity of methyl and bromo hexaborane are dependent upon electronic rather than steric differences. Further structural work and additional studies to clarify the matter are contemplated.

STRUCTURAL STUDIES

About two years ago we constructed new apparatus for the growth and maintenance of crystals at low temperature on an automated Picker x-ray diffractometer. We wished to test the crystal-growing characteristics of the new apparatus and decided to carry out these tests on several of the boron hydrides with structures previously determined by Professor Lipscomb. Most of the structures of interest had been investigated by the film technique and in several instances incomplete data were available. Ultimately, structures of B_5H_9 , B_5H_{11} , B_6H_{10} and *n*- B_9H_{15} were redetermined. Needless to say,

all structures were reconfirmed but with substantially reduced margins for error. Only one of them is worth comment at this time although ultimately the details of all redeterminations will be presented. In passing, it is worth recording for those tempted to try their luck that we have repeated Lipscomb's efforts to grow crystals of B_6H_{12} without success. Furthermore, we have succeeded in loading capillaries with B_8H_{14} but once again cannot obtain crystals. In both cases, the materials appeared to become viscous and eventually glass at low temperatures.

A significant point of interest did emerge from the restudy of pentaborane-11. This molecule has been of considerable interest since it is the first in which a 'unique' terminal hydrogen was observed. The uniqueness of this hydrogen is twofold: first it displays a strikingly smaller coupling constant in n.m.r. than normal terminal hydrogens and secondly, although bonded to B(1), it resides much closer to both the B(2) and B(5) positions than normal non-bonded interactions would allow. The hydrogen is thus somewhere intermediate between terminal and bridging. Of equal interest is the apparent asymmetry of its position relative to a possible mirror plane in the molecule. In the original work by Lipscomb *et al.*, the hydrogen was 1.75 Å from the B(2) but only 1.58 Å from B(5)⁸. Subsequent re-refinement by Lipscomb of the original data led to distances of 1.77 and 1.68 respectively, with standard deviations ± 0.19 Å⁹. X-ray diffraction measurements of 776 reflections were made and compared with the 299 photographically estimated by Lipscomb *et al.* Refinement proceeded to $R_0 = 0.058$ for the 683 non-zero data. Table 1 shows pertinent distances for the unique hydrogen interactions and associated boron asymmetry.

Table 1. Selected bond distances in B_5H_{11}

B_4-B_5	1.80	$H_{\mu}-B_5$	1.55
B_2-B_3	1.75	$H_{\mu}-B_2$	1.83
$\sigma B-B \pm 0.003, \sigma B-H \pm 0.02$			

Both differences in boron-boron bond distance and bridge asymmetry are approximately 15 times the standard deviations. There can be little residual doubt concerning the asymmetry of this molecule in the solid state. Examination of non-bonded distances in the crystal lattice fails to give obvious packing effects which might lead to distortion. Nevertheless, a detailed structure of the gas phase molecule would be desirable. We have recently learned that a microwave investigation of this structure is underway. This is a difficult task and if no structure is forthcoming, an electron diffraction study of the molecule will be undertaken in our laboratory.

In view of the failure of B_6H_{12} to crystallize, an attempt has been made to determine its structure by electron diffraction. Unfortunately, the electron diffraction data can be equally well fitted with either of the two proposed structures. We appear to be fated to depend upon the nuclear magnetic resonance evidence for the structure of this molecule.

Structural studies by electron diffraction of four substituted pentaboranes are also substantially completed. The problem of interest here is the relative stability of the 1 and 2 substituted isomers of various derivatives. We chose

to examine the four methyl and silyl substituted pentaboranes-9. The pertinent values of R_gM-B distance are given in *Table 2*. Note that the C—B distance in the more stable 2- isomer equals the distance in the 1-substituted isomer within two σ but the shortening of the Si—B bond is over 30 σ . These values are nicely consistent with the assumption that extra interaction of the silicon 3d orbitals is most favourable for the 1-substituted

Table 2. B—C and B—Si distances for isomers of $B_5H_8MH_3$

	B—SiH ₃	B—CH ₃
1-	1.981 ± 0.005	1.595 ± 0.005
2-	2.006 ± 0.004	1.592 ± 0.005
Δ	0.0520	0.003
	Uncertainties = 3 σ	

isomer and of course a similar analogous contribution from carbon would be of insignificant magnitude. It should be pointed out that these results are consistent with unpublished extended Hückel calculations by Dr Steven Zumdahl which lead to greater stability of the 1-silyl isomer by nearly 0.4 eV¹⁰.

Further structural information is now available for the highly unstable B_8H_{14} molecule. We have obtained both 70.6 MHz boron spectra and 220 MHz proton spectra for this compound. The normal boron spectrum of B_8H_{14} consists of three doublets of intensity 2:4:2. The central doublet splits into asymmetric triplets under line-narrowing conditions. Thus, in the first approximation the molecule appears to contain no BH_2 groups. The proton spectra show only two bridging hydrogens thus suggesting that the four additional hydrogens may be of the unique type observed in pentaborane-11. Preliminary analysis of the data leads to a coupling constant of about 55 Hz for these B—H bonds. *Table 3* shows a comparison of normal and unique bridging for a variety of compounds.

Table 3. Bridge and 'unique' coupling constants for a variety of boranes

Compound	$J_{11B-11H}$ (Hz)	$J_{11B-11H^u}$ (Hz)
B_2H_6	46	
B_6H_{10} (1, 3)	40	
(2, 4)	29	
B_5H_9	35–38	
B_5H_{11}	36	51
B_6H_{12} (3, 6)	48	
(1, 4)	28	
<i>i</i> - B_9H_{15}	48	
$B_9H_{13}CO$	40	55
$B_{10}H_{14}$	40	

Approx. range (30–50 Hz) (50–60 Hz)

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