$$\Delta(\Delta G_{\mathrm{in}}^{\ddagger}) = {}^{*}\Delta G_{\mathrm{in}}^{\ddagger} - \Delta G_{\mathrm{in}}^{\ddagger} = \frac{3f_2}{f_2 + f_3}\left[(f_3^{*} - f_3)a_2^2 + \frac{E_s}{6}\left(\frac{a_3^{*} + \mathrm{a}_3 - 2a_2}{a_3^{*} - \mathrm{a}_3} \right) \right] \quad (7)$$

bond distance, and the subscripts 2 and 3 denote the charges on the complexes. Inasmuch as both ^{2}E and ^{4}A$_2$ states have the same t_{2g}^3 configuration, the first term in eq 7 is expected to be small.[42] Five possible cases have been described[21] for the second term of equation 7. (i) $E_s = 0$ (i.e., $\mathrm{a}_3^{*} - a_3 = 0$), so that $\Delta(\Delta G_{\mathrm{in}}^{\ddagger})$ also equals 0 and the inner-sphere barriers for the ground-state and excited-state reactions are the same. This suggests that the exchange rate for these two reactions should be nearly identical, as is observed. Also, (ii) If $a_3^{*} > a_3$ and $a_2 > {}^1/_2(a_3^{*} + a_3)$, then ${}^{*}\Delta G_{\mathrm{in}}^{\ddagger} < \Delta G_{\mathrm{in}}^{\ddagger}$. (iii) If $a_3^{*} > a_3$ but $a_2 < {}^1/_2(a_3^{*} + a_3)$, then ${}^{*}\Delta G_{\mathrm{in}}^{\ddagger} > \Delta G_{\mathrm{in}}^{\ddagger}$. (iv) If $a_3^{*} < a_3$ but $a_2 > {}^1/_2(a_3^{*} + a_)$, then ${}^{*}\Delta G_{\mathrm{in}}^{\ddagger} > \Delta G_{\mathrm{in}}^{\ddagger}$. (v) If $a_3^{*} < a_3$ but $a_2 < {}^1/_2(a_3^{*} + a_3)$, then ${}^{*}\Delta G_{\mathrm{in}}^{\ddagger} < \Delta G_{\mathrm{in}}^{\ddagger}$. The cases ii–v, which are dependent on whether the excited state has Cr–N bond lengths longer than or shorter than those in the ground-state species, are inconsequential in the present system. However, it is clear that if electron exchange involved addition of electrons to antibonding e_g^{*} orbitals, significant changes in the bond lengths and breathing force constants would take place.[40,41] Interestingly, ^{2}E does not appear to be the state involved in the reductive quenching reaction (8); a higher energy state has been suggested but not identified.[37]

$$^{*}\mathrm{Cr(bpy)_3}^{3+} + \mathrm{ROH} \rightarrow \mathrm{Cr(bpy)_3}^{2+} + \mathrm{ROH}^{+} \quad (8)$$

Involvement by the ^{4}T$_2$ state in excited-state self-exchange reactions can be ruled out due to its very short lifetime (<1 ns, probably $\sim 10^{-10}$ s);[42] the excited-state self-exchange reaction could not compete with ^{4}T$_2$ decay. Consideration should also be given to the possible involvement of the ^{2}T$_1$ excited state which has always been taken to be in thermal equilibrium with ^{2}E. Separated in energy by ~ 600 cm^{-1}, ^{2}T$_1$ constitutes $\sim 5\%$ of the population of the ^{2}T$_1$/^{2}E pair at room temperature. Although ^{2}T$_1$ and ^{2}E have the same overall t_{2g}^3 orbital population, ^{2}T$_1$ differs in that the spin density in one of the t_{2g} orbitals is drastically reduced, approximating $(\alpha)(\alpha\beta)(\square)$. In previous studies[43] of the ligand labilization of (^{2}E) Cr(bpy)$_3^{3+}$, we concluded that the ^{2}T$_1$ state was the reactive entity due to the vacant t_{2g} orbital situated in the vicinity of the interligand pockets.[44] If ^{2}T$_1$ were the sole contributor to reaction 2 and to the extent that the overall rate constant for this reaction is $\sim 10^8$–10^9 M^{-1} s^{-1}, taking into account the population of ^{2}T$_1$, k_{ex} is expected to be $\sim 10^9$–10^{10} M^{-1} s^{-1}. Unfortunately, the presently available data and the uncertainties inherent in the Marcus relationships preclude a delineation as to the reactive state in the self-exchange reactions involving the ^{2}T$_1$/^{2}E pair.

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Preparation of Aluminoborane Analogues of the Lower Boron Hydrides[1]

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Abstract: The reactions of Al(BH$_4$)$_3$ with volatile boron hydrides have been found to result in the formation of an unprecedented series of aluminoborane compounds of exceptionally high thermal stability. Reaction of Al(BH$_4$)$_3$ with B$_2$H$_6$ in benzene solution at 100 °C for 18 h produced a nonvolatile, amorphous, pyrophoric solid of empirical formula AlB$_4$H$_{11}$. This compound can also be prepared from the reaction of (CH$_3$)$_3$Al with B$_2$H$_6$ under similar conditions. On the basis of the physical and chemical properties of this compound, a polymeric structural arrangement such as that found in (AlH$_3$)$_x$ is proposed, with a borane framework similar to that of B$_5$H$_{11}$. Aluminum occupies the apex (1) BH$_2$ position in the borane cage and, as such, can polymerize through adoption of a six-coordinate, hydrogen-bridging configuration. Reaction of Al(BH$_4$)$_3$ with B$_5$H$_9$ under similar conditions gave another aluminoborane species, AlB$_5$H$_{12}$, with a similar arrangement of bridging hydrogens between aluminum atoms as proposed for AlB$_4$H$_{11}$. The reactions of AlB$_5$H$_{12}$ with H$_2$O and gaseous HCl are unusual in that the dihydroboron cation, BH$_2^+$, is apparently formed in each case. Thermal decomposition of (BH$_4$)Al(B$_3$H$_8$)$_2$, prepared from the reaction of Al(BH$_4$)$_3$ with B$_4$H$_{10}$, resulted in the formation of a third aluminoborane, AlB$_6$H$_{13}$. Reactions of AlB$_4$H$_{11}$ and AlB$_5$H$_{12}$ with BH$_4^-$ in diglyme produced the anions AlB$_5$H$_{11}^-$ and AlB$_6$H$_{12}^-$, respectively, demonstrating a strong structural similarity between members of the aluminoborane series.

Introduction

Within the last 10 years, the field of metalloborane chemistry has evolved from a study of metal BH$_4^-$ and B$_3$H$_8^-$ derivatives to an area nearing the chemical complexity and structural diversity of organometallic chemistry. Metalloboranes may be roughly classed into three major categories: (1) those involving metal-hydrogen-boron bridging, such as the aforementioned metal tetrahydroborates and octahydrotriborates; (2) those involving simple coordination to a boron–boron bond, such as (OC)$_4$Fe-B$_6$H$_{10}$[2] and *trans*-Cl$_2$Pt(B$_6$H$_{10}$)$_2$;[2,3] and (3) metalloboranes in

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which the metal atom has inserted into a borane cage framework. Examples of this most interesting class include $(OC)_3FeB_4H_8$,[4] a B_5H_9 analogue in which the iron atom occupies the apex (1) position of the borane cage. Insertion of a metal atom into a bridge hydrogen position is observed in species such as $(Ph_3P)CuB_5H_8$,[5] the structure of which can be derived from B_5H_9 by replacing one of the basal bridging hydrogen atoms with the $(Ph_3P)_2Cu$ unit. Another example of this class is the $(OC)_4FeB_2H_5^-$ anion, a B_2H_6 analogue.[6,7]

Recently, the unusual berylloborane species $(BH_4)BeB_5H_{10}$ and $Be(B_5H_{10})_2$[8-10] have been prepared and characterized. Regarded as structural analogues of a hexaborane (11) system, these compounds represent the first examples of light metal substituted metalloborane systems. In contrast, the only reports of aluminoborane systems to date have dealt with octahydrotriborate derivatives,[11,12] wlth the exception of earlier work on the anionic decaborane analogue, $AlB_{10}H_{14}^-$.[13] Inasmuch as boron and aluminum have the same valence configuration, one might suspect the existence of novel mixed aluminum–boron hydride derivatives. The tendency for aluminum to adopt a coordination number of 6 creates further possibilities in this area.

We report here the preparation of three remarkable, structurally related aluminoborane compounds from the reactions of aluminum tetrahydroborate with volatile boron hydrides in benzene solution at elevated temperatures. Although highly reactive, these species are of extremely high thermal stability, an unusual feature among metalloboranes in general. It must be noted that these compounds either are not soluble or are highly reactive when mixed with common laboratory solvents. Thus such invaluable physical structural methods as ^{11}B NMR are inapplicable. However, chemical characterization of these species gives support to the suggested structures.

Experimental Section

Materials and Analytical Methods. The extreme air and moisture sensitivity of the boron hydrides and $Al(BH_4)_3$ necessitates the exclusive use of high-vacuum techniques[14] in this study. Aluminum tetrahydroborate,[15] diborane(6),[16] and tetraborane(10)[17] were prepared by the respective literature methods. Pentaborane(9) was purchased from Callery Chemical Co., and trimethylaluminum was obtaind from ROC/RIC Chemical Co. Solvents used were of spectroscopic quality and were dried over $LiAlH_4$. Infrared spectra were obtained as Nujol mulls, using a Perkin-Elmer Model 521 grating spectrophotometer.

Volatile species were analyzed by codistillation chromatography.[18,19] Aluminoborane products were confirmed by complete elemental analysis. Hydrogen content was determined by a combination of hydrolysis and pyrolysis studies. Careful moderation of hydrolyses in dilute acidic solution is necessary to avoid the formation of black, insoluble, nonstoichiometric propducts which retain hydrogen. In the case of AlB_5H_{12}, addition of methanol was required to complete the hydrolysis, owing to the formation of $[(H_2O)_2BH_2]^+$ in solution. Aluminum was determined gravimetrically as the 8-hydroxyquinolinate, $Al(C_9H_6ON)_3$.[20] Boron was distilled as methyl borate, hydrolyzed, and titrated with standard NaOH in the presence of mannitol.[21] For each aluminoborane compound isolated, repreated analyses confirmed the empirical formula to within 1%.[22]

Table I. Preparation of Aluminoborane Compounds

$$\mathrm{Al(BH_4)_3 + {}^1/_2B_2H_6 \xrightarrow[\text{benzene, 18 h}]{100\ {}^\circ C} AlB_4H_{11} + 2H_2}$$

$$\mathrm{(CH_3)_3Al + {}^5/_2B_2H_6 \xrightarrow[\text{benzene, 40 h}]{100\ {}^\circ C} AlB_4H_{11} + (CH_3)_3B + 2H_2}$$

$$\mathrm{Al(BH_4)_3 + B_5H_9 \xrightarrow[\text{benzene, 45 h}]{80\ {}^\circ C} AlB_5H_{12} + B_2H_6 + H_2 +} \text{ decomposition products}$$

$$\left\{\begin{array}{l}\mathrm{Al(BH_4)_3 + 2B_4H_{10} \xrightarrow[\text{benzene, 67 h}]{25\ {}^\circ C} (BH_4)Al(B_3H_8)_2 + 2B_2H_6} \\ \mathrm{(BH_4)Al(B_3H_8)_2 \xrightarrow[\text{benzene, 27 h}]{100\ {}^\circ C} AlB_6H_{13} + {}^1/_2B_2H_6 + 2H_2}\end{array}\right\}$$

Table II. Reactions of Aluminoboranes

$$\mathrm{AlB_4H_{11} + 3HCl(g) \rightarrow B_4H_{10} + AlCl_3 + 2H_2}$$

$$\mathrm{AlB_5H_{12} + 4HCl(g) \rightarrow B_4H_{10} + BH_2{}^+AlCl_4{}^- + 2H_2}$$

$$\mathrm{BH_2{}^+AlCl_4{}^- + (C_2H_5)_2O(g) \rightarrow {}^1/_3BCl_3 + {}^1/_3B_2H_6 + (C_2H_5)_2O{\cdot}AlCl_3}$$

$$\mathrm{AlB_4H_{11} + 11H_2O \rightarrow 11H_2 + AlB_4(OH)_{11}}$$

$$\mathrm{AlB_5H_{12} + 10H_2O \rightarrow 10H_2 + (H_2O)_2BH_2{}^+AlB_4(OH)_{10}{}^-}$$

$$\mathrm{AlB_4H_{11} + NaBH_4 \xrightarrow[\text{diglyme, 20 h}]{50\ {}^\circ C} Na(DG)^+AlB_5H_{11}{}^- + 2H_2}$$

$$\mathrm{AlB_5H_{12} + NaBH_4 \xrightarrow[\text{diglyme, 20 h}]{50\ {}^\circ C} Na(DG)^+AlB_6H_{12}{}^- + 2H_2}$$

AlB_4H_{11} The preparation of this compound is carried out in an all-glass 250-cm^3 reaction vessel, having a medium-porosity filter disk and trap to permit purification of the sample.[22] Access to the vacuum system is provided by use of a break-off side arm and standard "tube opener". In a typical preparation, 8.88 mmol of $Al(BH_4)_3$ and 13.0 mmol of B_2H_6 were condensed into the reaction vessel, along with 15 mL of dry benzene. The reaction can also be successfully run in other hydrocarbon solvents such as hexane, but the solvent vapor pressure at 100 °C must be considered. The system was sealed off under vacuum, and the benzene solution was heated to 100 °C with continuous stirring. After 8 h the formation of a white solid was evident, but complete uptake of $Al(BH_4)_3$ required a reaction period of 18 h. Volatile products of this reaction consisted of H_2 (16.6 mmol), and unreacted B_2H_6 (8.68 mmol), corresponding to the stoichiometry shown in Table I. The white solid product of this reaction is readily purified by washing with benzene or hexane within the reaction vessel. Only trace amounts of decomposition products, such as $(BH)_x$, could be detected in the trap end of the reaction vessel. From this system, 0.5 g of pure, free-flowing finely divided solid AlB_4H_{11} was obtained, corresponding to a yield of 70% based on $Al(BH_4)_3$.

Numerous trials of the $Al(BH_4)_3/B_2H_6$ reaction indicate that this is basically a stoichiometric process complicated by the thermal instability of the reactants. In general, optimum yields of AlB_4H_{11} are obtained when a 50% excess of B_2H_6 is used. Initial pressures of B_2H_6 should ideally be in the 1.1–1.5-atm range, due to the limited solubility of this reagent. If lesser amounts of B_2H_6 are used, the yield of AlB_4H_{11} is greatly decreased, and large amounts of benzene-soluble, nonstoichiometric aluminoborane products are formed. It is most interesting to note that, in using the optimized method quoted here, a decomposition of B_2H_6 is barely evident, whereas in the absence of $Al(BH_4)_3$ thermal decomposition of B_2H_6 is extensive under the given reaction conditions. The tube should be immersed in the temperature bath only to the top of the benzene solution to reduce the possibility of decomposition on the glass walls.

Formation of AlB_4H_{11} was also observed in reactions run at room temperature for several months, without stirring. This clearly demonstrates the remarkable thermodynamic stability of the aluminoborane product (as well as kinetic inhibition in the preparative reaction). The

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$Al(BH_4)_3/B_2H_6$ reaction is discussed in greater detail elsewhere.[22]

As noted previously, AlB_4H_{11} is a very finely divided, insoluble, pyrophoric solid. It is completely nonvolatile and is thermally stable up to 140 °C. Hydrogen is the only volatile product of pyrolysis. An X-ray powder photograph demonstrated that AlB_4H_{11} is amorphous. The infrared spectrum of AlB_4H_{11} exhibited the following principal absorption bands (in cm^{-1}): 2530 (vs), 2458 (s), 2380 (s), 2350 (s), 2275 (vs), 2100 (m), 2050 (m, shoulder), 1150 (m), 1050 (w), 990 (m), 935 (m), 910 (m), 850 (w), 800 (w).

It is possible to prepare AlB_4H_{11} without the use of $Al(BH_4)_3$. Reaction of $(CH_3)_3Al$ with excess B_2H_6 (Table I) results in the generation of $Al(BH_4)_3$ "in situ", followed by reaction with B_2H_6 to yield the aluminoborane product. In the manner described previously, 8.40 mmol of $(CH_3)_3Al$ and 23.0 mmol of B_2H_6 were allowed to react for 40 h at 100 °C in benzene. This reaction afforded 0.5 g of pure AlB_4H_{11}, a yield of 73% based on $(CH_3)_3Al$. Dimethyldiboranes are also produced in a side reaction between $B(CH_3)_3$ and unreacted B_2H_6. The aluminoborane product is free of substituted methyl groups.

Reactions. The reaction of AlB_4H_{11} with gaseous HCl proceeded in agreement with the stoichiometry shown in Table II. This reaction was conducted by circulating HCl through the solid, trapping volatile products at −78 °C. Optimal yields of B_4H_{10} are obtained at low temperatures. Reactions of AlB_4H_{11} with gaseous NH_3 and methylamines were studied in a similar manner. In the NH_3, H_2NCH_3, and $HN(CH_3)_2$ reactions, a total uptake of 4 mmol of base is observed per mmol of AlB_4H_{11}, as is the case with B_5H_{11}.[23] The solid products of these reactions are generally unstable at room temperature, liberating varying amounts of hydrogen over short periods. Remarkably, no reaction was observed between AlB_4H_{11} and gaseous trimethylamine, even over prolonged periods. A symmetrical cleavage reaction, favored with trimethylamine,[24] would require rupture of the exceptionally stable AlB_4 unit in the polymer.

Hydrolysis of AlB_4H_{11} results in the liberation of 11 equiv of H_2, as shown in Table II. This is also true of the methanolysis reaction. In the latter case, *$B(OCH_3)_3$ cannot be recovered from the system prior to acidification*, further demonstrating the stability of the AlB_4 unit in solution. This unprecedented stability is also evident from the lack of borane products in pyrolysis studies.

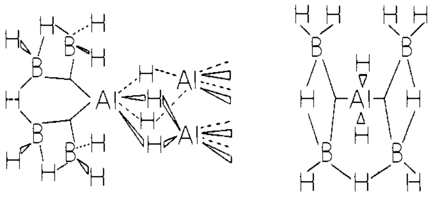
Reaction of AlB_4H_{11} with BH_4^- in diglyme results in the liberation of H_2 and formation of the anionic species $AlB_5H_{11}^-$ (Table II). Insoluble material is present throughout the reaction, and an unsolvated product could not be isolated. Formation of $AlB_5H_{11}^-$ demonstrates a structural link between AlB_4H_{11} and AlB_5H_{12} and suggested the possible existence of the latter compound.

AlB_5H_{12}. This compound is prepared from the reaction of $Al(BH_4)_3$ with excess B_5H_9 in benzene solution. Unlike the $Al(BH_4)_3/B_2H_6$ reaction, this system is clearly complex and nonstoichiometric. Varying amounts of H_2, B_2H_6, and decomposition products are produced. However, a pure aluminoborane product, solid AlB_5H_{12}, is readily obtained as the only benzene-insoluble material formed. A lower reaction temperature 80 °C is required, as decomposition of AlB_5H_{12} begins at 100 °C.

In a typical preparation, 8.56 mmol of $Al(BH_4)_3$ and 10.5 mmol of B_5H_9 were condensed into the reaction vessel with 12 mL of dry benzene. After a total reaction period of 45 h at 80 °C, volatile products included 23.3 mmol of H_2 and 6.10 mmol of B_2H_6. Pure AlB_5H_{12} was isolated from considerable amounts of soluble decomposition products by repeated washing with benzene, giving a yield of 0.5 g, or 63% based on $Al(BH_4)_3$.

Pure AlB_5H_{12} is obtained as a light yellow, finely divided solid material. It is very similar to AlB_4H_{11} in its physical characteristics. AlB_5H_{12} is not pyrophoric, although it decomposes rapidly upon contact with air or moisture. Pyrolysis results only in the liberation of H_2. An infrared spectrum showed the following absorptions (in cm^{-1}): 2530 (s, broad), 2460 (s), 2350 (m broad), 2270 (m), 2090 (m), 2030 (m), 1148 (m), 1040 (w), 990 (m), 900 (w), 850 (w), 800 (w).

Reactions. Reaction of AlB_5H_{12} with gaseous HCl (Table II) is unusual in that 4 mmol of HCl is consumed per mmol of aluminoborane. This result can be rationalized by proposing the formation of BH_2^+ through unsymmetrical cleavage of a BH_2 unit from the basal borane framework. Existence of this species was demonstrated by the reaction of the solid product with gaseous diethyl ether. Aluminum chloride etherate formed with the displacement of BH_2Cl, which rapidly disproportionated to yield stoichiometric amounts of B_2H_6 and BCl_3, as shown in the table. Small amounts of the intermediate BH_2Cl were detected by codistillation chromatography.


Section of the AlB_4H_{11} Polymer

Planar Representation of the AlB_4H_{11} Structural Unit

Figure 1. Proposed structure of AlB_4H_{11}.

Formation of BH_2^+ is also observed in the hydrolysis of AlB_5H_{12} (Table II). Addition of methanol to the hydrolysate results in the formation of CH_3OBH_2, an intermediate not observed directly, which then undergoes hydrolysis to yield an additional 2 equiv of hydrogen.

As in the case of AlB_4H_{11}, reaction of AlB_5H_{12} with BH_4^- in diglyme resulted in the insertion of boron and libration of H_2, giving the anionic species $AlB_6H_{12}^-$. An unsolvated product could not be isolated.

AlB_6H_{13}. In studying aluminum octahydrotriborate derivatives prepared by means of the $Al(BH_4)_3/B_4H_{10}$ reaction,[11] we noted that such species are unstable at room temperature with respect to loss of B_2H_6 and formation of a hydrogen-bridged aluminoborane polymer. In the case of the disubstituted species $(BH_4)Al(B_3H_8)_2$, decomposition at 100 °C results in the formation of AlB_6H_{13} in high yield.

Reaction of 4.65 mmol of B_4H_{10} with 1.44 mmol of $Al(BH_4)_3$ in benzene at 25 °C for 67 h results in the formation of 1.85 mmol of H_2 and 2.86 mmol of B_2H_6, with uptake of 2.83 mmol of B_4H_{10}. The viscous liquid product of this reaction was then heated to 100 °C in benzene solution. After only 1 h a considerable amount of white solid product had formed. After 27 h the system was analyzed and found to contain 0.76 mmol of H_2 and 0.622 mmol of B_2H_6. The white solid product of the reaction, confirmed as AlB_6H_{13}, amounted to 0.12 g, yield of 79.5% based on $Al(BH_4)_3$. Experimental data are in agreement with the stoichiometry shown in Table I. Results from extensive work on aluminum octahydrotriborate systems[22] suggest that H_2 produced in the initial $B_4H_{10}/Al(BH_4)_3$ reaction is attributable to the decomposition of $(BH_4)Al(B_3H_8)_2$ at room temperature, yielding the aluminoborane product AlB_6H_{13}. The total H_2 production is thus 2.61 mmol, in close agreement with the value of 2.88 mmol based on $Al(BH_4)_3$.

The physical characteristics of AlB_6H_{13} closely resemble those of AlB_4H_{11}. Each species is obtained as a white, finely divided, pyrophoric solid. The thermal stability of AlB_6H_{13} is also comparable to that of AlB_4H_{11}. The infrared spectrum of AlB_6H_{13} exhibited the following absorptions (in cm^{-1}): 2520 (s), 2450 (w), 2370 (m, shoulder), 2355 (m), 2260 (s, broad), 2100 (m), 1145 (m), 1040 (w), 970 (m), 925 (m), 910 (w), 840 (w).

Discussion

One of the most interesting aspects of the three aluminoborane compounds prepared is their direct relationship in empirical formulas to the "arachno" boron hydrides B_5H_{11}, B_6H_{12}, and B_7H_{13}. On this basis alone, some structural similarity between these compounds would be expected. However, differences in thermal stability of the aluminoboranes and corresponding borane analogues are enormous. Stability in the aluminoboranes is undoubtedly gained through polymerization, made possible by the ability of aluminum to adopt a coordination number of 6, as in $(AlH_3)_x$. The marked insolubility and nonvolatility of the aluminoboranes afford physical evidence of a polymeric configuration. However, for polymerization to occur, maintaining the empirical formula unit, aluminum must occupy the position of a *BH_2* group in the borane framework (i.e., a net of two terminal hydrogen atoms per aluminum is required for polymerization). Furthermore, the unusually high thermal stability is consistent only with a highly stable bonding interaction between aluminum and boron. Essentially all of the known metalloborane compounds of thermal stability comparable to that of the aluminoboranes are similar in that the metal atom is bonded to the framework exclusively by symmetrical, closed three-center bonds.[25] Systems involving hydrogen bridging between aluminum and boron are particularly unstable at high temperatures.[26] Noting this and the experi-

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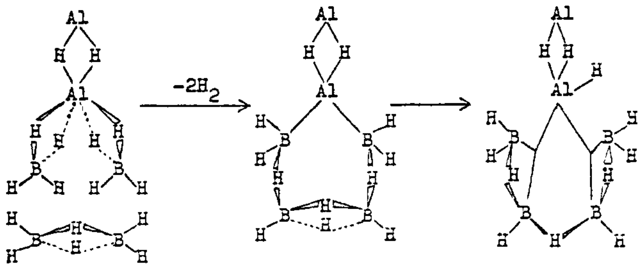

Figure 2. Possible mechanism for the formation of the AlB_4H_{11} polymer.

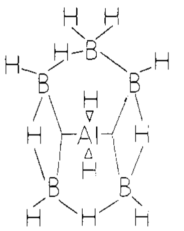

Figure 3. Proposed structure of the AlB_5H_{12} repeating unit.

mentally observed hydrolytic and pyrolytic stability of the AlB_4 unit in these compounds, we propose polymeric structures with a maximum bonding interaction between aluminum and the borane framework. These structures also correlate well with observed chemical properties.

The proposed configuration of polymeric AlB_4H_{11} is illustrated in Figure 1. In the repeating structural unit, the aluminum atom occupies the apex (1) position of a B_5H_{11} framework system and, as such, has maximum bonding overlap with all four boron atoms. The failure for a reaction to occur between AlB_4H_{11} and $(CH_3)_3N$ provides further evidence for the proposed configuration, as symmetrical cleavage, favored by $(CH_3)_3N$, would require rupture of the especially stable AlB_4 unit. Note that a facile reaction occurs between $(CH_3)_3N$ and B_5H_{11},[23,24] indicating that additional chemical stability has been gained in formation of the polymer. Formation of B_4H_{10} in the reaction of AlB_4H_{11} with HCl provides further evidence as to the framework nature. In addition, the presence of BH_2 groups is indicated by two absorption bands in the B–H terminal stretching region of the infrared spectrum. As such, chemical and physical data support a polymeric structure for AlB_4H_{11} in which aluminum is bonded to the borane framework exclusively by symmetrical, closed three-center bonds.

On the basis of the proposed structure for AlB_4H_{11}, it is possible to suggest a mechanism for the formation of this compound. Numerous reactions of $Al(BH_4)_3$ involve an initial reversible loss of B_2H_6 to form $HAl(BH_4)_2$,[27] which probably exists as a hydrogen-bridged dimer. Reaction of this species with B_2H_6 would explain the experimentally observed stoichiometry, in terms of the following overall reaction process:

$$Al(BH_4)_3 \rightarrow HAl(BH_4)_2 + {}^1/_2B_2H_6$$

$$HAl(BH_4)_2 + B_2H_6 \rightarrow AlB_4H_{11} + 2H_2$$

$$\text{Net:} \quad Al(BH_4)_3 + {}^1/_2B_2H_6 \rightarrow AlB_4H_{11} + 2H_2$$

A possible mechanism for this process is shown in Figure 2. As B_2H_6 adds to the $HAl(BH_4)_2$ dimer, Al–B bonds are formed by elimination of bridging hydrogen atoms. The aluminum atom, now effectively acidic, abstracts a bridging hydride from the bound B_2H_6 moiety, resulting in a closure of the AlB_4 unit through formation of symmetrical three center bonds (i.e., through overlap of the two filled Al–B bonding orbitals and the two vacant sp^3 orbitals from the bound B_2H_6 system). Coupling can then occur between these aluminoborane structural units, forming the polymeric arrangement in Figure 1.

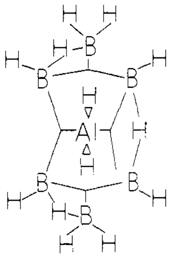

Figure 4. A possible structure of AlB_6H_{13} based on a 3403 B_7H_{13} configuration.

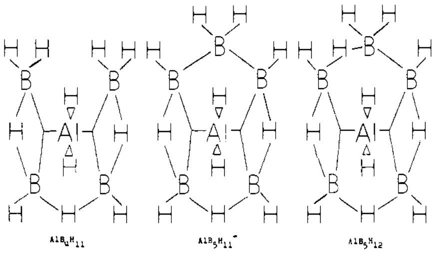

Figure 5. Structural similarities between AlB_4H_{11}, $AlB_5H_{11}^-$, and AlB_5H_{12}.

On the basis of the observed chemical and physical properties of AlB_5H_{12} and AlB_6H_{13}, a similar polymeric configuration is proposed in each case. This is further supported by strong similarities in the infrared spectra of all three aluminoboranes. Suggested structures of the repeating units in these compounds are illustrated in Figures 3 and 4. Note that in each case, the aluminum atom is placed in a BH_2 position to allow for polymerization and is bonded to the borane cage by closed three-center bonds, necessary to explain the observed thermal and hydrolytic stability of the AlB_4 unit in these compounds.

As noted previously, data from the reactions of AlB_5H_{12} with H_2O and gaseous HCl indicate the formation of the dihydroboron cation BH_2^+, in both instances. In the case of the hydrolysis reaction, this can be rationalized in terms of unsymmetrical hydrolytic cleavage of the basal B–B bond[28] (Figure 3). A similar cleavage apparently occurs in the reaction of AlB_5H_{12} with gaseous HCl. In this case, the $BH_2^+AlCl_4^-$ species proposed may possibly be formulated as $BH_2Cl{\cdot}AlCl_3$, although the nonvolatility and thermal stability of the material are suggestive of ionic character.

In addition, the reaction of AlB_4H_{11} with BH_4^- in diglyme can be understood in terms of this structural configuration (Figure 5). Interaction of AlB_4H_{11} with BH_4^- most likely results in the elimination of hydrogen from both BH_4^- and the BH_2 groups on the aluminoborane and closure of the $AlB_5H_{11}^-$ system through formation of boron–boron bonds. AlB_5H_{12} may be generated from this system by formal protonation of one boron–boron bond. Thus, a "4212" B_6H_{12} configuration has been adopted for AlB_5H_{12} to account for these observed chemical properties and to reflect structural restrictions induced upon formation of the polymeric configuration. Although this configuration differs from the accepted structure of B_6H_{12}, it alone can account for the observed physical and chemical properties of AlB_5H_{12}.

Investigations of the reaction between $Al(BH_4)_3$ and B_4H_{10} indicated that this system is much more complex than was previously realized.[11] The observed thermal instability of octahydrotriborate-substituted aluminum compounds suggests that highly stable aluminoborane species such as AlB_6H_{13} and possibly AlB_3H_{10} ($H_2AlB_3H_8$) are the ultimate products of this reaction. Attempts to isolate AlB_3H_{10} from the thermal decomposition of $(BH_4)_2Al(B_3H_8)$ have been unsuccessful thus far. However, the rapid formation of AlB_6H_{13} demonstrates severe steric hindrance in aluminum octahydrotriborates.

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A possible structure of the AlB_6H_{13} repeating unit is illustrated in Figure 4. This arrangement is based upon a "3403" structural model for B_7H_{13}, which is favored over other possible geometries because of the maximum use of closed three-center bonding. Further confirmation of this structure must await a complete characterization, which is complicated by difficulties in preparation of sufficient quantities of B_4H_{10} for the preparative reaction. However, the observed physical properties of AlB_6H_{13} indicate a polymeric species similar to AlB_4H_{11}.

As noted previously, the great thermal stability of the aluminoborane compounds is primarily a result of polymerization. Additional stabilization of the aluminoborane framework may be attributed to a greater bonding overlap made possible by the larger aluminum orbitals. Also, polymerization blocks the apex cage position in such a manner that a decomposition mechanism involving the apex could be kinetically inhibited. Detailed studies of B_5H_{11} and B_6H_{12} pyrolyses might provide evidence for this.

Upon an overall examination of the known compounds of aluminum, hydrogen, and boron, it is evident that a polymeric structural configuration such as that found in $(AlH_3)_x$ is most commonly adopted. Forms such as $Al(B_3H_8)_3$ and $Al(B_4H_9)_3$ would be sterically hindered and unstable with respect to decomposition to a polymeric aluminoborane species with one borane group per aluminum. The existence of $Al(BH_4)_3$ as a volatile, monomeric compound is correlated with the lower steric requirements of the BH_4^- group. As such, $Al(BH_4)_3$, the first covalent metalloborane to be isolated,[29] proves an exception to the general structural trend of aluminoborane compounds.

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Metal Atom Syntheses of Metallaboron Clusters. 2. Synthesis of Cobaltathiaborane and Cobaltadithiaborane Complexes. Crystal and Molecular Structures of 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$ and 7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$

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Abstract: The reactions of cobalt atoms with three different boron hydrides in the presence of cyclopentadiene and various sulfur reagents were examined and found to yield several novel cobaltathiaborane and cobaltadithiaborane complexes. The reaction of pentaborane(9) and cyclopentadiene with cobalt atoms followed by reaction with elemental sulfur yielded 6,8,7,9-$(\eta\text{-}C_5H_5)_2Co_2S_2B_5H_5$ (I), the structure of which was assigned on the basis of the spectroscopic data. If cyclohexene sulfide is used in place of sulfur in the above reaction, improved yields of I are obtained along with a new compound which was identfied as 2,3,6-$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$ (II). The structure of II was established by a single-crystal X-ray determination and has a cage geometry that can best be described as a tricapped trigonal prism missing one equatorial vertex. Although this structure is predicted by electron-counting rules, this is the first time it has been observed for an eight-vertex, $2n + 4$ skeletal electron system. Crystal data for II: space group $P2_1/c$; $Z = 4$, $a = 8.838$ (4) Å, $b = 22.019$ (19) Å, $c = 7.910$ (4) Å, $\beta = 114.96$ (1)°; $V = 1395$ (3) Å^3. The structure was refined by full-matrix least squares to a final R of 0.051 and R_w of 0.049 for the 1233 reflections which had $F_o^2 > 3\sigma(F_o^2)$. The reaction of hexaborane(10) and cyclopentadiene with cobalt atoms followed by reaction with cyclohexene sulfide yielded 7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$ in moderate yields. The structure of II was established by a single-crystal X-ray determination and shown to be consistent with structures observed for other 9-atom, $2n + 6$ skeletal electron systems. Crystal data for III: space group $P2_1/n$; $Z = 4$, $a = 6.862$ (5) Å, $b = 16.703$ (5) Å, $c = 10.037$ (2) Å, $\beta = 100.11$ (1)°; $V = 1132$ (1) Å^3. The structure was refined to a final R of 0.029 and $R_w = 0.034$ for the 1528 reflections which had $F_o^2 > 3\sigma(F_o^2)$. Finally, the reaction of cobalt atoms with cyclopentadiene followed by reaction with decaborane(14) and cyclohexene sulfide was found to yield the previously known compound 1,2-$(\eta\text{-}C_5H_5)CoSB_{10}H_{10}$ in low yield.

Introduction

In 1967 Muetterties[2] was the first to report the synthesis and chemistry of polyhedral boron clusters in which sulfur had been incorporated into the cage system. Since that time several additional thiaboranes and metallathiaboranes have been discovered; however, these have been limited to the larger cage systems which possess sufficient stability to withstand the synthetic conditions normally required for sulfur insertions. Therefore, until the present work, no compounds derived from the smaller boron hydrides have been reported.

We have previously demonstrated the first application of the metal atom technique to the synthesis of metallaborane clusters[3,4] and reported that these unusual reaction conditions have several synthetic advantages. In addition, we have also shown[4,5] that it is possible to use metal atom reactions to incorporate other molecules into these clusters such as the direct insertion of alkynes to form metallacarborane complexes. We have now applied these techniques to the synthesis of various heteroatom metallaboranes complexes and report here our work which has resulted in the synthesis of the first small cage metallathiaborane and metalladithiaborane clusters.

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