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Formation and Properties of Dimethyl Sulfide–Tetraborane(8). Base-Induced Dynamic Behavior of Tetraborane(8) Adducts

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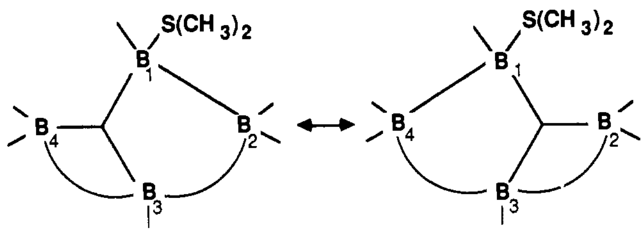
Dimethyl sulfide–tetraborane(8) [$B_4H_8{\cdot}S(CH_3)_2$] was produced from the reaction of B_5H_{11} with $S(CH_3)_2$ and was isolated as a liquid at −23 °C. The compound was unstable at room temperature but showed an increased stability in $S(CH_3)_2$. An unstable adduct $B_5H_{11}{\cdot}S(CH_3)_2$ was identified at −95 °C as a precursor of $B_4H_8{\cdot}S(CH_3)_2$. The ^{11}B NMR spectra of $B_4H_8{\cdot}S(CH_3)_2$ in $S(CH_3)_2$ showed that the B_3 and $B_{2,4}$ signals were coalesced at room temperature, indicating that a rapid internal exchange motion was induced by the solvent $S(CH_3)_2$. The diethyl sulfide, tetrahydrothiophene, and trimethylphosphine adducts of B_4H_8 showed the same coalescence in alkyl sulfides at higher temperatures. A possible mechanism was proposed for the induced dynamic behavior of these B_4H_8 adducts. The B_3 and $B_{2,4}$ signals of $B_4H_8{\cdot}N(CH_3)_3$ did not coalesce when the adduct was dissolved in dialkyl sulfides. The position of the ligand (exo or endo) with respect to the bent B_4H_8 framework might be responsible for the different behavior of the amine adduct.

Introduction

The reaction of pentaborane(11) with dimethyl sulfide was known to produce dimethyl sulfide–tetraborane(8) [$B_4H_8{\cdot}S(CH_3)_2$; shown in the following diagram].[1]



However, the compound had not been isolated. Recently, dimethyl sulfide–triborane(7), $B_3H_7{\cdot}S(CH_3)_2$, was isolated and was found to be a liquid that was stable at room temperature.[2] This triborane adduct underwent a slow change to form pentaborane(9) and $BH_3{\cdot}S(CH_3)_2$ when dissolved in dimethyl sulfide.[2] Furthermore, it underwent a facile cleavage reaction with trimethylamine at −80 °C to give $B_2H_4{\cdot}2N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$.[3] These interesting findings, which followed the isolation of $B_3H_7{\cdot}S(CH_3)_2$, prompted us to undertake a similar investigation for the dimethyl sulfide adduct of B_4H_8. The results are reported in this paper.

Results

Formation and Isolation of $B_4H_8{\cdot}S(CH_3)_2$. When pentaborane(11) and excess $S(CH_3)_2$ were mixed in dichloromethane at −80 °C, $B_4H_8{\cdot}S(CH_3)_2$ formed immediately according to

$$B_5H_{11} + 2S(CH_3)_2 \rightarrow B_4H_8{\cdot}S(CH_3)_2 + BH_3{\cdot}S(CH_3)_2 \qquad (1)$$

The B_4H_8 adduct was isolated as a colorless liquid by pumping out the solvent and $BH_3{\cdot}S(CH_3)_2$ from the reaction mixture at −23 °C. This tetraborane(8) adduct was unstable at room temperature. However, the compound appeared to be more stable when placed in dimethyl sulfide; a solution of $B_4H_8{\cdot}S(CH_3)_2$ in $S(CH_3)_2$ did not show any change at all when it was kept standing at room temperature for 1 h.

Table I. ^{11}B NMR Data for Dialkyl Sulfide–Tetraborane(8) Adducts and Related Borane Adducts

compd	solvent	*T*, °C	shift, ppm B_1	$B_{2,4}$	B_3	BH_3 adduct	shift, ppm
$B_4H_8{\cdot}S(CH_3)_2$	CH_2Cl_2	+20	−33.6	−7.6	+1.8		
$B_4H_8{\cdot}S(CH_3)_2$	$S(CH_3)_2$	−80	−34.2	−6.9	+1.8	$BH_3{\cdot}S(CH_3)_2$	−22.1
$B_4H_8{\cdot}S(C_2H_5)_2$	$S(C_2H_5)_2$	−60	−36.8	−7.0	+1.3	$BH_3{\cdot}S(C_2H_5)_2$	−24.3
$B_4H_8{\cdot}S(CH_2)_4$	$S(CH_2)_4$	−60	−33.5	−7.1	+1.7	$BH_3{\cdot}S(CH_2)_4$	−21.6
$B_4H_8{\cdot}P(CH_3)_3$[a]	CH_2Cl_2	+25	−51.5	−7.0	−1.8		
$B_4H_8{\cdot}N(CH_3)_3$[b]	CH_2Cl_2	+25	−22.5	−8.5	+1.1		

[a] Reference 4b. [b] Reference 4a.

The formation of $B_4H_8{\cdot}S(CH_3)_2$ from B_5H_{11} and $S(CH_3)_2$ (eq 1) was preceded by the formation of an unstable 1:1 adduct, $B_5H_{11}{\cdot}S(CH_3)_2$. This precursor was characterized by its ^{11}B NMR signals at −4.2, −19.3, and −48.8 ppm with an intensity ratio of 3:1:1. Although a mixture of B_5H_{11} and $S(CH_3)_2$ in a 1:2 or 1:excess (>2) molar ratio produced $B_4H_8{\cdot}S(CH_3)_2$ and $BH_3{\cdot}S(CH_3)_2$ instantaneously at −80 °C, the signals of $B_5H_{11}{\cdot}S(CH_3)_2$ were detectable at −95 °C along with the signals of the other products. On the other hand, if a *1-equiv* quantity of $S(CH_3)_2$ was added *slowly* into a *dilute* solution of B_5H_{11} in CH_2Cl_2 at *−95 °C* while the solution was *constantly agitated*, the signals of the 1:1 adduct were observed clearly along with the signals of B_5H_{11}, as shown in Figure 1. The compound decomposed slowly at −90 °C to form $B_4H_8{\cdot}S(CH_3)_2$. At −60 °C, the decomposition was fast; the $B_4H_8{\cdot}S(CH_3)_2$ signals became intense, and the signal of B_2H_6 appeared. These reactions are summarized by the equations

$$B_5H_{11} + S(CH_3)_2 \xrightleftharpoons[\text{in } CH_2Cl_2]{\text{below } -95\ ^\circ C} B_5H_{11}{\cdot}S(CH_3)_2 \qquad (2)$$

$$B_5H_{11}{\cdot}S(CH_3)_2 + S(CH_3)_2 \xrightarrow[\text{in } CH_2Cl_2]{\text{above } -90\ ^\circ C} B_4H_8{\cdot}S(CH_3)_2 + BH_3{\cdot}S(CH_3)_2 \qquad (3)$$

$$B_5H_{11}{\cdot}S(CH_3)_2 \xrightarrow[\text{in } CH_2Cl_2]{\text{above } -90\ ^\circ C} B_4H_8{\cdot}S(CH_3)_2 + \tfrac{1}{2}B_2H_6 \qquad (4)$$

^{11}B NMR Spectra of $B_4H_8{\cdot}S(CH_3)_2$. (a) In CH_2Cl_2. The ^{11}B NMR data are listed in Table I. The assignment for the signals of $B_4H_8{\cdot}S(CH_3)_2$ was made with reference to the spectra of known B_4H_8 adducts.[4,5] The pattern of the spectrum remained unchanged in the temperature range from −80 to +20 °C. Unlike some of the adducts of B_4H_8,[4b,5] this compound appeared to exist in only one isomeric form (exo or endo form according to the position of the ligand with respect to the hinge-shaped structure of the B_4 framework); that is, only one B_3 signal could be seen. The B_3 signals of the two isomers usually appear separated in the

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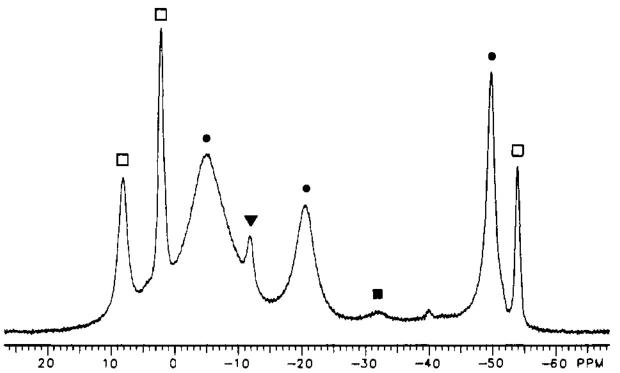

Figure 1. $^{11}B\{^1H\}$ NMR spectrum (96.2 MHz) of a CH_2Cl_2 solution containing B_5H_{11} and $S(CH_3)_2$ in a 1:1 molar ratio at −95 °C, indicating the formation of $B_5H_{11}\cdot S(CH_3)_2$: (●) signals of $B_5H_{11}\cdot S(CH_3)_2$; (□) signals of B_5H_{11}; (■) B_1 signal of $B_4H_8\cdot S(CH_3)_2$; (▼) impurity B_5H_9.

Table II. Coalescence Temperatures[a] of the B_{2-4} Signals[b]

compd	solvent	*T*, °C	shift, ppm
$B_4H_8\cdot S(CH_3)_2$	$S(CH_3)_2$	∼+15	−5.3
$B_4H_8\cdot S(C_2H_5)_2$	$S(C_2H_5)_2$	∼+45	−5.4
$B_4H_8\cdot S(CH_2)_4$	$S(CH_2)_4$	∼+25	−4.0
$B_4H_8\cdot P(CH_3)_3$	$S(CH_3)_2$	∼+25	−6.4
$B_4H_8\cdot P(CH_3)_3$	$S(CH_2)_4$	∼+30	−6.7
$B_4H_8\cdot N(CH_3)_3$	$S(CH_3)_2$	*c*	*c*
$B_4H_8\cdot N(CH_3)_3$	$S(CH_2)_4$	∼+60[d]	−4.0

[a] The temperature at which the appearance of the signal became single and symmetrical. [b] The observe frequency; 25.5 MHz. [c] No coalescence occurred up to +30 °C. [d] The observe frequency; 96.2 MHz.

spectrum if two isomers coexist in the solution.

(b) In $S(CH_3)_2$. Below −10 °C, the spectra of $B_4H_8\cdot S(CH_3)_2$ in $S(CH_3)_2$ showed the same three-signal pattern as those in CH_2Cl_2. However, as the temperature was raised, the B_3 and $B_{2,4}$ signals began to broaden, and at +20 °C, the two signals were coalesced. This change was reversible with respect to the temperature variation.

Base-Induced Dynamic Behavior of B_4H_8 Adducts. Apparently, the coalescence of the B_3 and $B_{2,4}$ signals in $S(CH_3)_2$, described above, was due to a rapid internal exchange motion of the $B_4H_8\cdot S(CH_3)_2$ molecule, which was induced by the solvent $S(CH_3)_2$. Therefore, several other B_4H_8 adducts were tested for the same effect. The results are presented in Table II. The diethyl sulfide $[S(C_2H_5)_2]$ and tetrahydrothiophene $[S(CH_2)_4]$ adducts of B_4H_8 were prepared by a process which was similar to that employed for the $B_4H_8\cdot S(CH_3)_2$ preparation. Complete removal of the BH_3 adducts of the respective sulfides from the product mixtures proved difficult to accomplish. Therefore, the coalescence temperatures were determined in the presence of the BH_3 adducts in the sample solutions. The presence of $BH_3\cdot S(CH_3)_2$ in a $S(CH_3)_2$ solution of $B_4H_8\cdot S(CH_3)_2$ did not alter the temperature of the B_3 and $B_{2,4}$ signal coalescence.

Discussion

Decomposition of Dialkyl Sulfide Adducts of B_4H_8 in Dialkyl Sulfides. The dialkyl sulfide adducts of B_4H_8 decompose at room temperature to give a complex mixture of borane compounds. The major components of the decomposition products are $BH_3\cdot SR_2$, B_6H_{10}, and B_5H_9. Although the adducts gain stability in dialkyl sulfide solutions, they too undergo slow changes. However, the products are B_5H_9, B_6H_{10}, and $BH_3\cdot SR_2$, and no other compounds are produced in significant amounts. The rates of formation of these borane compounds are slower by 1 order of magnitude than that of B_5H_9 formation from $B_3H_7\cdot S(CH_3)_2$ in $S(CH_3)_2$, which was reported recently.[2]

The formation of B_5H_9 from $B_3H_7\cdot S(CH_3)_2$ was considered to be the result of the cleavage of $B_3H_7\cdot S(CH_3)_2$ by $S(CH_3)_2$ to form $BH_3\cdot S(CH_3)_2$ and short-lived "$B_2H_4\cdot 2S(CH_3)_2$", followed by the framework expansion reaction of $B_3H_7\cdot S(CH_3)_2$ with "$B_2H_4\cdot 2S(CH_3)_2$".[2] A similar interpretation may be used to explain the

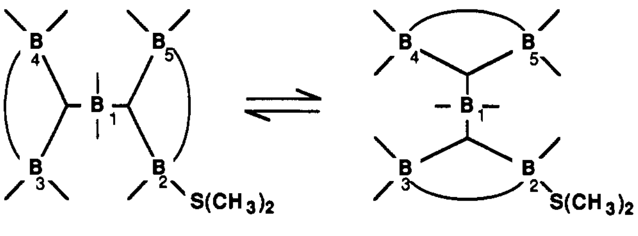

Figure 2. Proposed structure for $B_5H_{11}\cdot S(CH_3)_2$.

formation of B_5H_9 and B_6H_{10} from the B_4H_8 adducts in alkyl sulfides (SR_2), as indicated by eqs 5–8. As for the formation

$$B_4H_8\cdot SR_2 + 3SR_2 \rightarrow 2\text{“}B_2H_4\cdot 2SR_2\text{”} \qquad (5)$$

$$B_4H_8\cdot SR_2 + \text{“}B_2H_4\cdot 2SR_2\text{”} \rightarrow B_5H_9 + BH_3\cdot SR_2 + 2SR_2 \qquad (6)$$

$$B_4H_8\cdot SR_2 + 3SR_2 \rightarrow \text{“}B_3H_5\cdot 3SR_2\text{”} + BH_3\cdot SR_2 \qquad (7)$$

$$2\text{“}B_3H_5\cdot 3SR_2\text{”} \rightarrow B_6H_{10} + 6SR_2 \qquad (8)$$

of B_6H_{10}, another type of cleavage (eq 7), which is followed by the dimerization of "$B_3H_5\cdot 3SR_2$" (eq 8), is thought to be responsible.

When $B_4H_8\cdot P(CH_3)_3$ is treated with excess $P(CH_3)_3$, the B_4H_8 moiety is cleaved in two ways, which correspond to eqs 5 and 7, and $B_2H_4\cdot 2P(CH_3)_3$, $B_3H_5\cdot 3P(CH_3)_3$, and $BH_3\cdot P(CH_3)_3$ are produced.[6] The cleavage reaction of $B_4H_8\cdot P(CH_3)_3$ is slower than that of $B_3H_7\cdot P(CH_3)_3$ by $P(CH_3)_3$. Similarly, the cleavage of $B_4H_8\cdot SR_2$ (eqs 5 and 7) would be slower than that of $B_3H_7\cdot SR_2$. The B_3H_5 adduct of $P(CH_3)_3$ dimerizes to form $B_6H_{10}\cdot 2P(CH_3)_3$ when subjected to vacuum at room temperature.[7] Since dialkyl sulfides are weaker bases than $P(CH_3)_3$, "$B_3H_5\cdot 3SR_2$" would readily dimerize to give B_6H_{10}.

Properties of $B_5H_{11}\cdot S(CH_3)_2$. Recently, the formation of an unstable PH_3 adduct of pentaborane(11), $B_5H_{11}\cdot PH_3$, was reported.[8] The NMR signals of the PH_3 adduct appeared at −6.7, −39.4, and −48.6 ppm in a 3:1:1 intensity ratio, and these signals correspond to the three signals that were found in this work for $B_5H_{11}\cdot S(CH_3)_2$ at −4.2, −19.3, and −48.8 ppm, respectively. Accordingly, the structure shown in Figure 2 is proposed for the $S(CH_3)_2$ adduct after the proposed structure of $B_5H_{11}\cdot PH_3$. The ^{11}B shift value for the ligand-bonded boron atom is shifted considerably from −39.4 ppm for $B_5H_{11}\cdot PH_3$ to −19.3 ppm for $B_5H_{11}\cdot S(CH_3)_2$. This large shift difference is consistent with that which was observed between the ^{11}B shift values of $BH_3\cdot PH_3$ (−42.8 ppm)[9] and $BH_3\cdot S(CH_3)_2$ (−20.2 ppm).[10]

Due to the presence of protonic hydrogen atoms on the ligand PH_3, $B_5H_{11}\cdot PH_3$ decomposed in a complex manner.[8] In contrast, further changes of the $B_5H_{11}\cdot S(CH_3)_2$ were tractable. That is, as long as $S(CH_3)_2$ was present in the solution, $B_5H_{11}\cdot S(CH_3)_2$ reacted with the $S(CH_3)_2$ (eq 3), and when the free $S(CH_3)_2$ had been depleted in the solution, the decomposition (eq 4) occurred.

Base-Induced Dynamic Behaviors. (a) $B_4H_8\cdot S(CH_3)_2$ in $S(CH_3)_2$. Certain Lewis base adducts of B_4H_8 are known to combine with another molecule of Lewis bases to form bis(base) adducts of B_4H_8. Thus, reactions 9–12 have been reported. The B_4H_8

$$B_4H_8\cdot P[N(CH_3)_2]_3 + P(CH_3)_3 \rightarrow B_4H_8\cdot P[N(CH_3)_2]_3\cdot P(CH_3)_3{}^{4b} \qquad (9)$$

$$B_4H_8\cdot P(CH_3)_3 + P(CH_3)_3 \rightarrow B_4H_8\cdot 2P(CH_3)_3{}^{4b} \qquad (10)$$

$$B_4H_8\cdot P(CH_3)_3 + N(CH_3)_3 \rightleftharpoons B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3{}^{4b} \qquad (11)$$

$$B_4H_8\cdot N(CH_3)_3 + N(CH_3)_3 \rightleftharpoons B_4H_8\cdot 2N(CH_3)_3{}^{4a} \qquad (12)$$

adducts of strong Lewis bases $P[N(CH_3)_2]_3$ and $P(CH_3)_3$ form

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(6) (a) Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302. (b) A very slow reaction of $B_4H_8\cdot 2P(CH_3)_3$ with $P(CH_3)_3$ was noted in ref 6a. The products were thought to be $BH_3\cdot P(CH_3)_3$ and $B_2H_4\cdot 2P(CH_3)_3$. Later work revealed that the products contained $B_3H_5\cdot 3P(CH_3)_3$ also: Kameda, M.; Kodama, G. *Inorg. Chem.*, submitted for publication.

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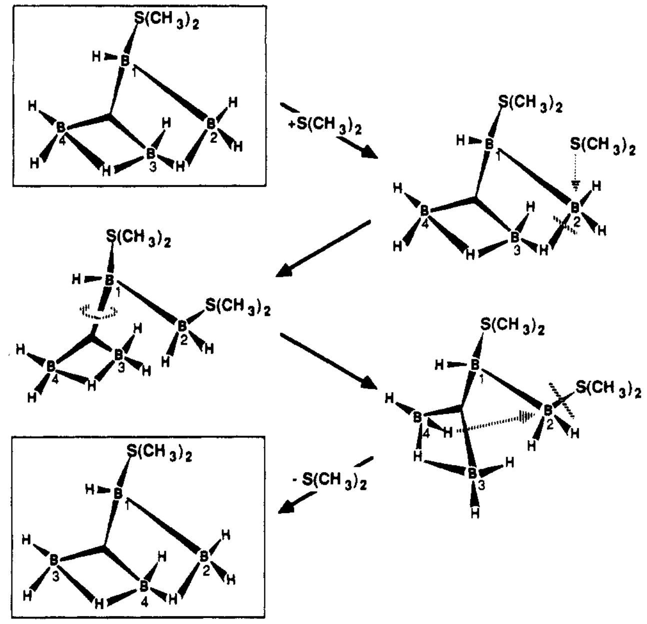
Scheme I



stable bis(base) adducts with the strong Lewis bases (eqs 9 and 10). As the participating Lewis bases become weaker, the resulting bis(base) adducts appear to become progressively less stable (eqs 11 and 12). Thus, $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ dissociates at −30 °C, and $B_4H_8{\cdot}2N(CH_3)_3$ is isolable only below −40 °C. The B_4H_8 adduct of the weak base PH_3, $B_4H_8{\cdot}PH_3$, does not form the bis(base) adduct $B_4H_8{\cdot}2PH_3$.[8]

Dimethyl sulfide is a stronger base that PH_3, but is a weaker base than $N(CH_3)_3$. Therefore, the extent of interaction of $B_4H_8{\cdot}S(CH_3)_2$ with $S(CH_3)_2$ is expected to be between that of $B_4H_8{\cdot}PH_3$ with PH_3 and that of $B_4H_8{\cdot}N(CH_3)_3$ with $N(CH_3)_3$. On the basis of this base strength consideration, a process, shown in Scheme I, is proposed to explain the observed equivalency of the B_3 and $B_{2,4}$ atoms of the $B_4H_8{\cdot}S(CH_3)_2$ molecule at the higher temperatures. The proposed process is tantamount to a rapid, endothermic equilibrium, shown by eq 13.

$$B_4H_8{\cdot}S(CH_3)_2 + S(CH_3)_2 \rightleftharpoons \text{“}B_4H_8{\cdot}2S(CH_3)_2\text{”} \quad (13)$$

The ease of formation of a bis(base) adduct is influenced by the electrophilicity of the mono(base) adduct and the nucleophilicity of the reacting base. When the dialkyl sulfide (SR_2) in the reaction (eq 13) is a weaker base than $S(CH_3)_2$, the electrophilicity of the mono(base) adduct ($B_4H_8{\cdot}SR_2$) would be greater than that of $B_4H_8{\cdot}S(CH_3)_2$, but this stronger electrophile, $B_4H_8{\cdot}SR_2$, interacts with the weaker base SR_2 in order to form the bis(adduct) "$B_4H_8{\cdot}2SR_2$". Consequently, the order of coalescence temperatures is not necessarily parallel with the order of the base strength of the sulfides. The observed coalescence temperatures increase in the order of $S(CH_3)_2 < S(CH_2)_4 < S(C_2H_5)_2$. The reported orders of base strength for dialkyl sulfides are $S(CH_3)_2 \approx S(C_2H_5)_2 > S(CH_2)_4$ toward BH_3[11] and $S(CH_3)_2 > S(CH_2)_4 > S(C_2H_5)_2$ toward BCl_3.[12]

Both $B_4H_8{\cdot}2P(CH_3)_3$ and $B_4H_8{\cdot}2N(CH_3)_3$ are fluxional. The fluxional motion of $B_4H_8{\cdot}2P(CH_3)_3$ is slow at low temperatures on the NMR time scale, and therefore the signals of the two phosphine-bonded boron atoms are coalesced only above 0 °C.[4b] Whereas, the fluxional motion of $B_4H_8{\cdot}2N(CH_3)_3$ appears to be fast, the two amine-bonded boron atoms are seen to be equivalent even at −80 °C.[13] A simple extrapolation of this fluxionality trend to the B_4H_8 adduct of a weaker base, $S(CH_3)_2$, suggests that the same type of fluxional motion for "$B_4H_8{\cdot}2S(CH_3)_2$" would be faster than that of $B_4H_8{\cdot}2N(CH_3)_3$. Apparently, however, the equilibrium shown in eq 13 is faster than the fluxional motion, and therefore only the coalescence of the B_3 and $B_{2,4}$ signals is observed. Should the relative rates of these two processes be reversed, the four boron atoms would appear all equivalent. A Lewis base that would bring about such an effect may exist, and is being sought.

(b) $B_4H_8{\cdot}P(CH_3)_3$ in Dialkyl Sulfides. The mechanistic model proposed in (a) above for the equivalency of the B_3 and $B_{2,4}$ atoms suggests that a similar dynamic behavior may be induced in $B_4H_8{\cdot}P(CH_3)_3$ when it is dissolved in $S(CH_3)_2$. The coalescence is expected to occur at a higher temperature than which was observed for $B_4H_8{\cdot}S(CH_3)_2$ in $S(CH_3)_2$, since the electron density on the B_4H_8 moiety would be higher in $B_4H_8{\cdot}P(CH_3)_3$ than in $B_4H_8{\cdot}S(CH_3)_2$. The observed data that are listed in Table I are consistent with this conjecture.

Trimethylphosphine–tetraborane(8) exists in two isomeric forms, exo and endo isomers;[4b] the ^{11}B NMR spectrum of $B_4H_8{\cdot}P(CH_3)_3$ consists of two sets of signals. In the spectrum, although the B_1 and $B_{2,4}$ signals of the two isomers are severely overlapped, the B_3 signals of the two isomers appear separated from each other at −1.8 and +5.1 ppm. The population ratio of the two isomers is approximately 4:1 at 20 °C. At present, no evidence is available to decide which one of the exo and endo isomers is the more abundant species. Interestingly, the B_3 signal of the minor isomer at +5.1 ppm remained unchanged while the B_3 and $B_{2,4}$ signals of the major isomer coalesced. The uncoalesced $B_{2,4}$ signal of the minor isomer could not be identified clearly due to its overlap with the coalesced signal of the major isomer.

(c) $B_4H_8{\cdot}N(CH_3)_3$ in Dialkyl Sulfides. Since $N(CH_3)_3$ is a weaker base than $P(CH_3)_3$, the B_3 and $B_{2,4}$ atom sites of the $B_4H_8{\cdot}N(CH_3)_3$ molecule are expected to be more reactive toward nucleophiles than the corresponding sites in $B_4H_8{\cdot}P(CH_3)_3$. Therefore, $B_4H_8{\cdot}N(CH_3)_3$ dissolved in dialkyl sulfides was expected to show the coalescence of the B_3 and $B_{2,4}$ signals at temperatures lower than those for $B_4H_8{\cdot}P(CH_3)_3$. Contrary to this expectation, the coalescence did not occur even when the solutions were heated to the temperatures of the $B_4H_8{\cdot}P(CH_3)_3$ coalescence. Instead, when the tetrahydrothiophene solution of $B_4H_8{\cdot}N(CH_3)_3$ was further heated to about +60 °C, a new signal appeared at −4.0 ppm in the spectrum of $B_4H_8{\cdot}N(CH_3)_3$ (see Figure 3). This change is reversible with respect to the temperature variation.

Currently, no unequivocal explanation can be offered for the different behavior of $B_4H_8{\cdot}N(CH_3)_3$ in the dialkyl sulfides. However, the noncoalescence that was observed for one of the $B_4H_8{\cdot}P(CH_3)_3$ isomers may be related to the observed behavior of $B_4H_8{\cdot}N(CH_3)_3$. That is, the trimethylamine adduct, which appears to exist in only one isomeric form at +20 °C, may have the same conformation as the inactive (or minor) isomer of $B_4H_8{\cdot}P(CH_3)_3$. As the temperature is increased, the other isomer of $B_4H_8{\cdot}N(CH_3)_3$ is produced in the solution by a slow equilibrium, and its already coalesced B_{2-4} signal appears at −4.0 ppm. Hopefully, the results of X-ray structural studies of these B_4H_8 adducts, which are being initiated, will provide a clearer answer.[14]

Experimental Section

Chemicals and Equipment. Conventional vacuum-like techniques were used throughout for the handling of volatile, air-sensitive compounds. Dimethyl and diethyl sulfides and tetrahydrothiophene (Kodak Laboratory and Research Products) were refluxed and distilled over calcium hydride and stored over molecular sieves. Laboratory stock pentaborane(11),[4a] trimethylphosphine,[4b] trimethylamine,[3] and dichloromethane[4b] were used. A Varian FT-80A NMR spectrometer was used routinely for the ^{11}B NMR spectral acquisitions unless otherwise stated.

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(11) Coyle, T. D.; Kaesz, H. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1959**, *81*, 2089.

(12) Morris, H. L.; Kulevsky, N. I.; Tamres, M.; Searles, S., Jr. *Inorg. Chem.* **1966**, *5*, 124.

(13) The $^{11}B\{^1H\}$ (96.2 MHz) NMR spectrum of $B_4H_8{\cdot}2N(CH_3)_3$ in $N(CH_3)_3$ at −80 °C showed two clearly separated signals at −9.0 and −13.3 ppm (uncorrected) in a 1:1 intensity ratio. The details will be reported elsewhere along with other related observations.

(14) In the $B_4H_9^-$ ion, the endo B_1–H hydrogen atom appears to undergo a rapid tautomeric motion while the exo B_1–H bond is rigid.[15] Accordingly, in Scheme I, the exo isomer of the B_4H_8 adduct is chosen to be the species that undergoes the rapid motion. However, this choice is by no means definitive.

(15) Remmel, R. J.; Johnson, H D., II; Jaworiwsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395.

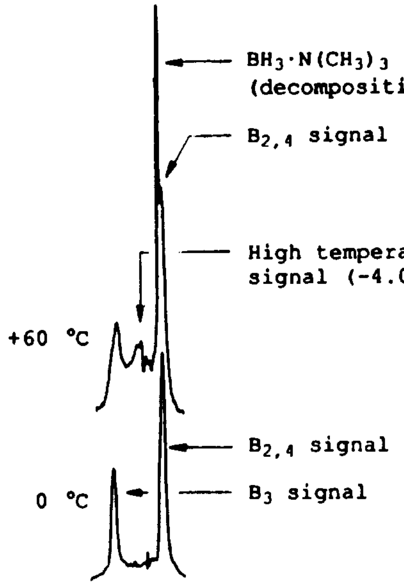

Figure 3. Portion of the $^{11}B\{^1H\}$ NMR spectrum (96.2 MHz) of $B_4H_8·N(CH_3)_3$ showing the growth of the −4.0 ppm signal at the higher temperatures.

The diethyl etherate of boron trifluoride was used as the external standard for the ^{11}B shift values.

Isolation of $B_4H_8·S(CH_3)_2$. A 0.453-mmol sample of B_5H_{11} was taken in a 9 mm o.d. Pyrex tube equipped with a Teflon valve and was dissolved in about a 2-mL sample of CH_2Cl_2. The solution was frozen at −197 °C, and a 0.983-mmol sample of $S(CH_3)_2$ was condensed into the tube. The tube was placed in a −80 °C bath, shaken to mix the contents thoroughly, and then placed in the cooled probe of the NMR spectrometer. The ^{11}B NMR spectrum of the solution contained only the signals of $BH_3·S(CH_3)_2$ and $B_4H_8·S(CH_3)_2$.

The tube was then placed in a −23 °C bath, and the volatile components were pumped out from the tube through a −63 °C trap into a −197 °C trap. From time to time, the liquid residue in the reaction tube was dissolved in a fresh, small portion of CH_2Cl_2 to record the ^{11}B NMR spectrum of the solution at −30 °C. A total pumping time of 30 h was required to remove $BH_3·S(CH_3)_2$ completely from the product mixture. When the CH_2Cl_2 solution containing pure $B_4H_8·S(CH_3)_2$ was kept at room temperature for a few minutes, the signal of $BH_3·S(CH_3)_2$ became detectable.

Formation of $B_5H_{11}·S(CH_3)_2$. A 0.150-mmol sample of B_5H_{11} was taken in a 14 mm o.d. Pyrex tube equipped with a vertical-shape Teflon valve (VNMR valve, product of J. Young Scientific Glassware) and was dissolved in a 2.0-mL sample of CH_2Cl_2. Then, the tube was placed in a −95 °C bath, and a 0.160-mmol sample of $S(CH_3)_2$ was slowly introduced over the B_5H_{11} solution, during which the solution was constantly agitated by shaking the tube in the bath. Then, the tube was inserted into the probe of a Varian XL-300 NMR spectrometer. The probe had been cooled to −100 °C prior to the insertion of the reaction tube. The spectrum obtained at −95 °C is shown in Figure 1. The probe temperature was increased to −80 °C and then to −60 °C in a stepwise fashion to record the spectra of the solution.

Sample Solutions for the Variable-Temperature NMR Studies. (a) $B_4H_8·S(CH_3)_2$. The sample of $B_4H_8·S(CH_3)_2$, which was prepared as described earlier in this section, was dissolved in a 2-mL sample of $S(CH_3)_2$. In a separate experiment, a 0.451 mmol sample of B_5H_{11} was dissolved in a 2-mL sample of $S(CH_3)_2$ at −80 °C. The formation of $B_4H_8·S(CH_3)_2$ and $BH_3·S(CH_3)_2$ was complete at this temperature. The $B_4H_8·S(CH_3)_2$ signals of these two solutions showed identical changes with respect to the temperature variation.

(b) $B_4H_8·S(C_2H_5)_2$ and $B_4H_8·S(CH_2)_4$. The sample solution of $B_4H_8·S(C_2H_5)_2$ was prepared in a 9 mm o.d. Pyrex tube by dissolving a 0.573-mmol sample of B_5H_{11} in a 2-mL sample of $S(C_2H_5)_2$ at −80 °C and raising the temperature slowly to −60°C. The sample solution of $B_4H_8·S(CH_2)_4$ was prepared similarly by dissolving a 0.516-mmol sample of B_5H_{11} in a 2-mL sample of $S(CH_2)_4$.

(c) $B_4H_8·P(CH_3)_3$. A 0.51-mmol sample of $B_4H_8·P(CH_3)_3$, prepared in a 9 mm o.d. Pyrex tube by treating $B_4H_8·2P(CH_3)_3$ with B_2H_6,[4b] was dissolved in a 1.5-mL sample of $S(CH_3)_2$. Another 0.52-mmol sample of $B_4H_8·P(CH_3)_3$, which was similarly prepared, was dissolved in a 2-mL sample of $S(CH_2)_4$.

(d) $B_4H_8·N(CH_3)_3$. A 0.68-mmol sample of $B_4H_8·N(CH_3)_3$, prepared in a 9 mm o.d. Pyrex tube by the literature method,[4a] was dissolved in a 1.5-mL sample of $S(CH_3)_2$. After the completion of the measurements, the solvent $S(CH_3)_2$ was pumped out completely from the tube, and the remaining $B_4H_8·N(CH_3)_3$ was dissolved in a 1.7-mL sample of $S(CH_2)_4$.

The ^{11}B NMR spectra of these sample solutions were recorded on the FT-80A spectrometer. The spectra of the $S(CH_2)_4$ solution of $B_4H_8·N(CH_3)_3$ were also recorded on a Varian XL-300 spectrometer, so that the high-temperature signal at −4.0 ppm could be observed well-separated from the B_3 and $B_{2,4}$ signals, as shown in Figure 3. At +60 °C, decompositions of $B_4H_8·N(CH_3)_3$ proceeded at an appreciable rate. However, the appearance–disappearance of the −4.0 ppm signal was reversible with respect to the temperature variation.

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$Me_3Al·NH_3$ Formation and Pyrolytic Methane Loss: Thermodynamics, Kinetics, and Mechanism

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The thermodynamics, kinetics, and mechanism of the reactions $Me_3Al + NH_3 \rightarrow Me_3Al·NH_3 \xrightarrow{\Delta} {}^1/_3(Me_2AlNH_2)_3 + CH_4$ in homogeneous solution were investigated by solution calorimetry, DSC, and ^{1}H NMR rate measurements. The enthalpy for complex formation from NH_3 and monomeric Me_3Al in benzene was −93 kJ/mol. The observed ΔH for methane loss from the complex was −82.2 kcal/mol. Methane loss from $Me_3Al·NH_3$ was catalyzed by excess Me_3Al monomer or monomeric Me_2AlNH_2 in equilibrium with $(Me_2AlNH_2)_2$ and $(Me_2AlNH_2)_3$. A mechanism for the Me_2AlNH_2-catalyzed reaction involving formation of the methyl-bridged intermediate $(\mu\text{-}Me)(Me_2AlNH_2)(Me_2Al·NH_3)$ and subsequent loss of CH_4 by proton transfer was proposed. The enthalpy of activation for the autocatalytic reaction was 92.8 kJ/mol. A deuterium isotope effect of 8.8 was measured for this reaction. A similar mechanism was proposed for the Me_3Al-catalyzed reaction, involving formation of an analogous methyl-bridged species $(\mu\text{-}Me)(Me_3Al)(Me_2Al·NH_3)$, which apparently loses CH_4 and closes to metastable $(\mu\text{-}NH_2)(\mu\text{-}Me)Al_2Me_4$. This slowly disproportionates to $(Me_3Al)_2$ and $(Me_2AlNH_2)_3$; the autocatalytic path is thus slowed. ΔH^*, for the Me_3Al-catalyzed pathway was 113 kJ/mol. The deuterium isotope effect was 5.5.

Introduction

A general route to nonoxide ceramic materials is the pyrolytic decomposition of a suitable organometallic precursor. While this approach has received considerable attention, the mechanisms of the underlying organometallic thermal elimination reactions have not. The elucidation of these reactions may prove important for the optimization of such ceramic generation processes; it is also essential for a full fundamental understanding of the chemistry

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