quencies and Raman intensities agree well with the experimentally obtained data and assignments for **2** reported by Gillespie and Morton.[2] The experimental infrared spectrum of Cl_2F^+, which was assigned to the symmetric form by Christe and Sawodny,[1] is incompatible with the calculated IR spectrum for **1**. The Cl–F bond strength in **2** is predicted as 41.6 kcal/mol, significantly higher than in **1** (21.2 kcal/mol) but lower than in diatomic ClF (59.4 kcal/mol) and ClF^+ (68.4 kcal/mol). The Cl–Cl bond in **2** is quite strong (63.3 kcal/mol), even stronger than in Cl_2 (58.0 kcal/mol) but weaker than in Cl_2^+ (90.1 kcal/mol).

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Formation of Amine, Phosphine, and Thioether Adducts of Chlorotriborane(7)

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The chlorotriborane(7) (B_3H_6Cl) adduct of $N(CH_3)_3$ was formed by the reaction of $B_4H_8\cdot N(CH_3)_3$ with HCl in dichloromethane or with $HgCl_2$ in chloroform. The reaction of $B_3H_7\cdot N(CH_3)_3$ with BCl_3 in dichloromethane was found to be a better preparative method for $B_3H_6Cl\cdot N(CH_3)_3$. The BCl_3 treatment was employed to convert the $N(CH_3)_2H$, $N(CH_3)H_2$, NH_3, and $S(CH_3)_2$ adducts of B_3H_7 into the corresponding adducts of B_3H_6Cl. In contrast, $B_3H_7\cdot P(CH_3)_3$ and $B_3H_7\cdot PH_3$ are inert to BCl_3. The B_3H_6Cl adducts of $P(CH_3)_3$ and PH_3 could be obtained by treating the B_3H_7 adducts with a mixture of HCl and BCl_3 in dichloromethane. The ^{11}B and ^1H NMR spectra of these B_3H_6Cl adducts showed that their structures were described as 1-(Lewis base)-2-chlorotriborane(7).

Introduction

In an earlier report from this laboratory, the formation of trimethylamine–chlorotriborane(7) was mentioned briefly.[1] The compound was formed when $B_4H_8\cdot N(CH_3)_3$ was treated with hydrogen chloride in dichloromethane. In literature prior to that time, the $B_3H_7Cl^-$ and $B_3H_7Br^-$ anions were the only halogenated derivatives of B_3H_7 adducts that were reported.[2] Subsequently, preparative studies of the neutral chlorotriborane adducts were pursued.[3]

In recent years, Morris and co-workers developed the chemistry of the above halogenated triborohydride anions and reported several new triborohyride anions, including pseudohalogen derivatives.[4] The reaction chemistry of the $B_3H_8^-$ derivatives is of interest, since a variety of new borane derivatives are expected to be synthesized from these compounds. The corresponding derivatives of the neutral B_3H_7 adducts are throught to have different reactivities due to the absence of the negative charge, and they too may serve as the starting compounds for the syntheses of new boron hydride compounds. In this paper, the results of our preparative studies of chlorotriborane(7) adducts are described.

Results

(A) Trimethylamine–Chlorotriborane(7). (a) Formation of $B_3H_6Cl\cdot N(CH_3)_3$. Trimethylamine–chlorotriborane(7) was formed in the rections given in eqs 1–4. The reaction of $B_4H_8\cdot N(CH_3)_3$

$$B_4H_8\cdot N(CH_3)_3 + HCl \xrightarrow[\text{in } CH_2Cl_2]{} B_3H_6Cl\cdot N(CH_3)_3 + \tfrac{1}{2}B_2H_6\text{[1a]} \tag{1}$$

$$B_3H_7\cdot N(CH_3)_3 + BCl_3 \xrightarrow[\text{in } CH_2Cl_2]{} B_3H_6Cl\cdot N(CH_3)_3 + \text{“}BHCl_2\text{”} \tag{2}$$

$$B_3H_7\cdot N(CH_3)_3 + HCl \xrightarrow[\text{in } CH_2Cl_2]{BCl_3} B_3H_6Cl\cdot N(CH_3)_3 + H_2 \tag{3}$$

$$B_4H_8\cdot N(CH_3)_3 + 2HgCl_2 \xrightarrow[\text{in } CHCl_3]{} B_3H_6Cl\cdot N(CH_3)_3 + Hg_2Cl_2 + \text{“}H_2BCl\text{”} \tag{4}$$

with HCl was accompanied by another reaction (eq 5) that yielded

$$B_4H_8\cdot N(CH_3)_3 + HCl \xrightarrow[\text{in } CH_2Cl_2]{} B_3H_7\cdot N(CH_3)_3 + \text{“}BH_2Cl\text{”} \tag{5}$$

$B_3H_7\cdot N(CH_3)_3$.[1a] Thus, a mixture of $B_3H_7\cdot N(CH_3)_3$ and $B_3H_6Cl\cdot N(CH_3)_3$ (ca. 3:7 molar ratio) was obtained. Hydrogen bromide reacted with $B_4H_8\cdot N(CH_3)_3$ in a manner similar to the HCl reaction (eqs 1 and 5), and $B_3H_6Br\cdot N(CH_3)_3$ and $B_3H_7\cdot N(CH_3)_3$ were produced.

The reaction expressed in eq 2 is currently the best method for the preparation of $B_3H_6Cl\cdot N(CH_3)_3$. The reaction proceeded to near completion at −80 °C. Performing the reaction at higher temperatures (−40 to −23 °C) with excess BCl_3 ensured the complete conversion of $B_3H_7\cdot N(CH_3)_3$ to $B_3H_6Cl\cdot N(CH_3)_3$. Equation 3 could also be used for the $B_3H_6Cl\cdot N(CH_3)_3$ preparation; the reaction was completed at −80 °C within a short period of time. The chlorotriborane(7) adduct was also formed in the slow reaction of $B_3H_7\cdot N(CH_3)_3$ with hydrogen chloride, in the absence of BCl_3, in CH_2Cl_2 at room temperature. However, many other boron hydride compounds were formed as the side products. In tetrahydrofuran, $B_3H_7\cdot N(CH_3)_3$ was practically inert to HCl.[5]

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Table I. ^{11}B and ^{1}H NMR Spectral Data for Methylamine Adducts of Chlorotriborane(7) in CH_2Cl_2 at 25 °C[a]

	B_1	B_2	B_3	H_C	H_B	H_N
$B_3H_6Cl\cdot N(CH_3)_3$	-15.7	-7.9	-9.8	2.60 (s)[b]	2.07[b]	
$B_3H_6Cl\cdot (CH_3)_2NH$	-20.9	-3.4	-8.2	2.54 (d)[c]	2.03	3.90
$B_3H_6Cl\cdot CH_3NH_2$	-25.3	-2.2	-5.9	2.50 (t)[d]	2.05	3.89
$B_3H_6Cl\cdot NH_3$	-30.0	+1.2	-5.1		2.16	4.43

[a] Shifts in ppm from $BF_3\cdot O(C_2H_5)_2$ for ^{11}B and from TMS for ^{1}H. [b] At 20 °C. [c] J_{HCNH} = 6.2 Hz. [d] J_{HCNH} = 6.2 Hz.

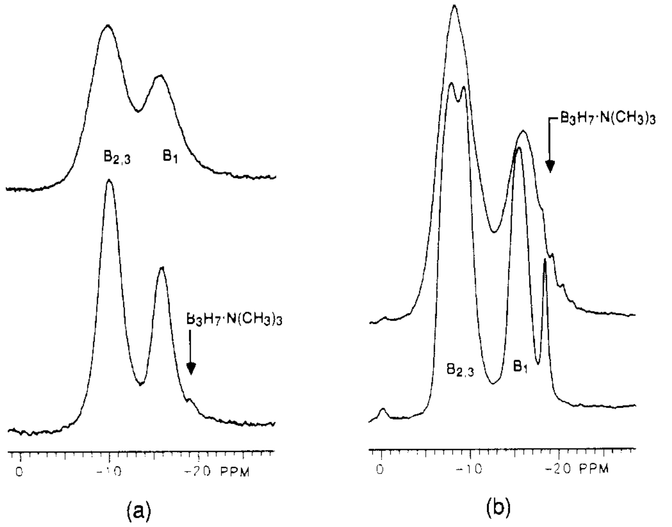

Figure 1. ^{11}B NMR (32.1-MHz) spectra of $B_3H_6Cl\cdot N(CH_3)_3$ in CH_2Cl_2: (a) -40 °C; (b) +30 °C. The upper spectra are normal; the lower spectra are proton spin decoupled.

The reaction of $B_4H_8\cdot N(CH_3)_3$ with $HgCl_2$ in chloroform is shown by the idealized equation (4). The trimethylamine adduct of B_3H_6Cl was produced as the major product, the side products being $BHCl_2\cdot N(CH_3)_3$, $BH_2Cl\cdot N(CH_3)_3$, $B_3H_7\cdot N(CH_3)_3$, B_5H_9, and B_6H_{10}. When this reaction was run in tetrahydrofuran, $B_3H_6Cl\cdot N(CH_3)_3$ was not found in the products.

The trimethylamine adduct of B_3H_6Cl was a white solid that decomposed slowly at room temperature to form a yellow oily liquid. The adduct was sensitive to Lewis bases, and therefore the use of basic solvent should be avoided for the preparation of this compound.

(b) Mass and NMR Spectra of $B_3H_6Cl\cdot N(CH_3)_3$. A sample of $B_3H_6Cl\cdot N(CH_3)_3$ containing a small amount of $B_3H_7\cdot N(CH_3)_3$ showed the high mass cutoff at *m/z* 133, the center of the cluster of peaks being at *m/z* 131 [*m/z* (relative intensity): 133 (2.8), 132 (2.1), 131 (11.8), 130 (6.7), 129 (2.1)]. The calculated mass for $^{11}B_3H_6{}^{37}Cl\cdot N(^{12}CH_3)_3$ is 135. The pattern of the observed mass distribution suggested that successive loss of hydrogen atoms occurred within the instrument, as has been observed for other borane compounds.[1a,6]

In Figure 1, the ^{11}B NMR spectra of $B_3H_6Cl\cdot N(CH_3)_3$ at -40 and +30 °C are shown. The spectrum at +30 °C shows the contamination of $B_3H_7\cdot N(CH_3)_3$ due to the decomposition of $B_3H_6Cl\cdot N(CH_3)_3$. The presence of three signals at -15.7, -9.8, and -7.9 ppm suggests that the compound is 1-trimethylamine–2-chlorotriborane(7). See Figure 2, where L = $N(CH_3)_3$. The B_2 signal shifted toward the high field as the temperature was lowered.[7] Thus, the B_2 and B_3 signals appeared as a single broad signal at -40 °C with its peak position at -11.0 ppm. The $^{1}H\{^{11}B\}$ NMR spectrum of the compound at -40 °C showed two singlet signals at 2.12 (H_B) and 2.67 (H_C), indicating a rapid tautomeric migration of the borane hydrogen atoms.

(B) Trimethylphosphine–Chlorotriborane(7). (a) Formation of $B_3H_6Cl\cdot P(CH_3)_3$. The trimethylphosphine adduct of B_3H_7 was practically inert to BCl_3, even at room temperature. A mixture of $B_3H_7\cdot P(CH_3)_3$ and HCl in CH_2Cl_2 gave off hydrogen gas *very slowly* at -80 °C, but no $B_3H_6Cl\cdot P(CH_3)_3$ was found in the reaction mixture. The chlorotriborane(7) adduct could successfully be prepared by treating $B_3H_7\cdot P(CH_3)_3$ with HCl at -80 °C *in the presence of BCl_3* (eq 6).

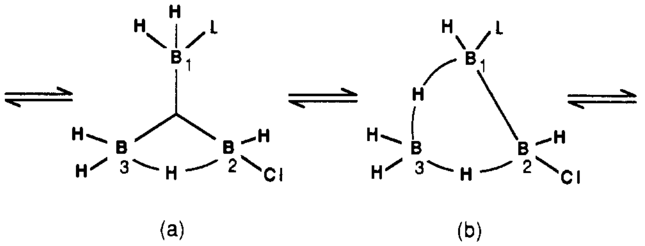

Figure 2. Structures proposed for the Lewis base (L) adducts of B_3H_6Cl.

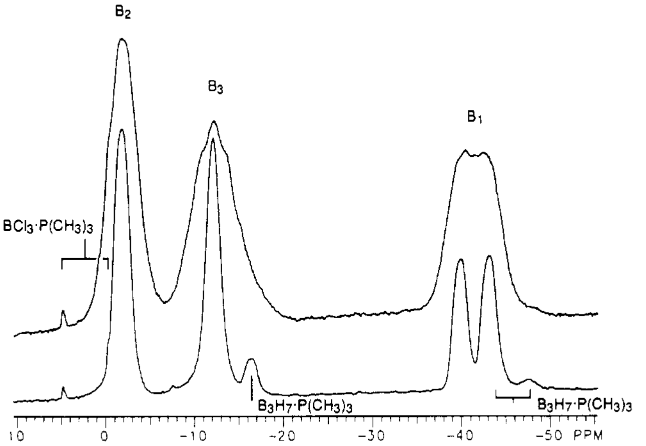

Figure 3. ^{11}B NMR (32.1-MHz) spectra of $B_3H_6Cl\cdot P(CH_3)_3$ in CH_2Cl_2 at +25 °C. The upper spectrum is normal; the lower spectrum is proton spin decoupled.

$$B_3H_7\cdot P(CH_3)_3 + HCl \xrightarrow[\text{in } CH_2Cl_2]{BCl_3} B_3H_6Cl\cdot P(CH_3)_3 + H_2 \qquad (6)$$

(b) Mass and NMR Spectra of $B_3H_6Cl\cdot P(CH_3)_3$. The mass spectrum of $B_3H_6Cl\cdot P(CH_3)_3$ showed the highest mass cutoff at *m/z* 151, the center of the cluster being *m/z* 148 [*m/z* (relative intensity): 151 (1.8), 150 (7.0), 149 (14.3), 148 (36.6), 147 (28.3), 146 (7.9), 145 (1.7), 144 (2.5)]. Apparently, the successive loss of hydrogen atoms occurred for this compound also.

The ^{11}B NMR spectra of a $B_3H_6Cl\cdot P(CH_3)_3$ solution in CH_2Cl_2 at +25 °C is shown in Figure 3. The compound can be described as 1-trimethylphosphine–2-chlorotriborane(7), and the signals at -41.3 (J_{PB} = 102 Hz), -12.1, and -1.9 ppm are assigned to the B_1, B_3, and B_2 atoms, respectively. The $^{1}H\{^{11}B\}$ NMR spectrum of $B_3H_6Cl\cdot P(CH_3)_3$ at +25 °C showed two doublet signals at 1.37 ppm (H_C; J_{HCP} = 12 Hz) and 1.62 ppm (H_B; J_{HBP} = 5.5 Hz). At -90 °C, the H_B signal remained as a single doublet.

(C) Chlorination of Other Lewis Base Adducts of Triborane(7). (a) Formation of the $N(CH_3)_2H$, $N(CH_3)H_2$, and NH_3 Adducts of B_3H_6Cl. The $(CH_3)_2NH$, CH_3NH_2, and NH_3 adducts of B_3H_7 produced corresponding amine adducts of chlorotriborane(7) when treated with BCl_3. The NMR data for these adducts are listed in Table I. Generally, the spectral features observed for these compounds are the same as that of $B_3H_6Cl\cdot N(CH_3)_3$. The stability in CH_2Cl_2 decreased from the $N(CH_3)_3$ adduct to the NH_3 adduct. The amine adducts of $BHCl_2$ and B_3H_7 were slowly produced, and B_5H_9, B_4H_{10}, and B_2H_6 were found among the decomposition

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(7) The upfield movement of the peaks of $BH_2Cl\cdot N(CH_3)_3$ and $BHCl_2\cdot N(CH_3)_3$ with a decrease in temperature paralleled that observed for the B_2 signal.

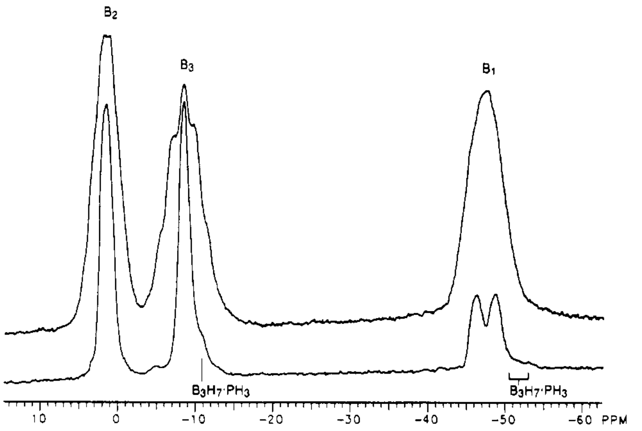


Figure 4. ^{11}B NMR (32.1-MHz) spectra of $B_3H_6Cl{\cdot}PH_3$ in CH_2Cl_2 at +25 °C. The upper spectrum is normal; the lower spectrum is proton spin decoupled.

products when these solutions were aged (ca. 50 h) at room temperature.

(b) Formation of $B_3H_6Cl{\cdot}S(CH_3)_2$. The $S(CH_3)_2$ adduct of B_3H_7 reacted with BCl_3 to give $B_3H_6Cl{\cdot}S(CH_3)_2$. The chlorotriborane adduct was characterized by its ^{11}B NMR spectrum, which gave signals at -26.6 (B_1), -7.9 (B_3), and +1.8 (B_2) ppm [cf. -30.9 (B_1) and -11.7 ppm ($B_{2,3}$) for $B_3H_7{\cdot}S(CH_3)_2$[8]].

(c) Formation of $B_3H_6Cl{\cdot}PH_3$. The phosphine (PH_3) adduct of B_3H_7 did not react with HCl or with BCl_3, in CH_2Cl_2, even at room temperature. However, as in the case of $B_3H_7{\cdot}P(CH_3)_3$, when treated with a mixture of HCl and BCl_3 in CH_2Cl_2, it was converted to $B_3H_6Cl{\cdot}PH_3$. The ^{11}B spectrum of $B_3H_6Cl{\cdot}PH_3$ at +25 °C showed the resonance signals at -47.2 (J_{BP} = 80 Hz) (B_1), -8.3 (B_3), and +1.7 (B_2) ppm (Figure 4). At -60 °C, doublet and quartet features appeared on the B_2 and B_1 signals, respectively. In the $^1H\{^{11}B\}$ spectrum that was recorded at -60 °C, the borane hydrogen signal appeared as a broad hump centered at +1.82 ppm. At -100 °C, the signal was split into four signals at +3.43 (H_{B2}), +2.39 (H_{B3}), +1.25 (H_{B1}), and +0.13 (H_μ) ppm in a 1:2:2:1 intensity ratio. The signal for the PH_3 hydrogen atoms appeared at +4.63 ppm (d, J_{HP} = 412.5 Hz). These observations suggested that structure a in Figure 2 was appropriate for the low-temperature static structure.

Discussion

The HCl and HCl/BCl_3 Reaction. The anionic adducts of triborane(7) are known to readily react with hydrogen chloride to give chloro derivatives of the anions according to the following equation, where X = H,[2] Cl, NCS, NCO, $NCBH_3$,[4b] and NCSe:[9]

$$B_3H_7{\cdot}X^- + HCl \rightarrow B_3H_6Cl{\cdot}X^- + H_2 \tag{7}$$

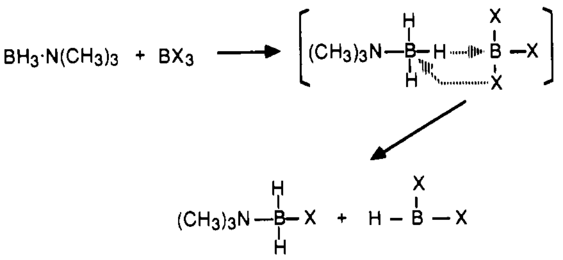
On the other hand, neutral adducts of triborane(7) give off hydrogen gas very slowly when treated with hydrogen chloride, even though a rapid exchange of hydrogen atoms occurs between the borane adducts and HCl.[5] Apparently, both the hydridic character of borane hydrogen atoms and the proton-donor activity of the reacting acid determine the ease of hydrogen gas elimination. Thus, H_2 elimination was effected when the proton-donor activity of HCl was enhanced by the addition of BCl_3. Furthermore, the reaction of $B_3H_7{\cdot}PH_3$ with HCl in the presence of BCl_3 was slower than that of $B_3H_7{\cdot}P(CH_3)_3$; the borane hydrogen atoms in the adduct of a weak base are less hydridic than those in a strong-base adduct.

The BCl_3 Reaction. Nöth and Beyer reported the halogenation of $BH_3{\cdot}N(CH_3)_3$ with boron trihalide.[10]

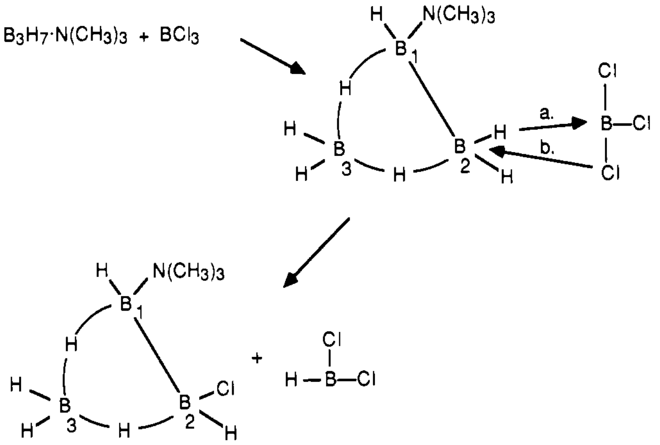
$$BH_3{\cdot}N(CH_3)_3 + BX_3 \rightarrow BH_3{\cdot}N(CH_3)_3 + \text{“}BH_2X\text{”} \tag{8}$$

This H-X exchange reaction appeared to proceed without rupturing the B-N bond. The proposed mechanism[10] is illustrated in Scheme I.

Scheme I



Scheme II



This mechanism can conveniently be applied to the observed formation of the amine adducts of chlorotriborane(7). As illustrated in Scheme II, the first step of the exchange process is thought to be the coordination of the amine adduct to BCl_3 through the B_2-H→BCl_3 bond formation (step a in the scheme). This is followed by the back-coordination B-Cl→B_2 (step b), which is accompanied by the cleavage of the B_2-H and B-Cl bonds to yield $B_3H_6Cl{\cdot}N(CH_3)_3$ and "BCl_2H". The "BCl_2H" may further chlorinate $B_3H_7{\cdot}N(CH_3)_3$ or disproportionate to B_2H_6, B_2H_5Cl, and BCl_3. The B_3H_7 adducts of amines and dimethyl sulfide are converted to the corresponding B_3H_6Cl adducts, presumably by the same mechanism.

In spite of the facile chlorination of the amine adducts of triborane(7) described above, the $B_3H_8^-$ anion (tetramethylammonium salt) did not give the $B_3H_7Cl^-$ anion when treated with BCl_3 in CH_2Cl_2. Tetraborane(10) was the main constituent of the product mixture, other identifiable minor components being B_5H_9, B_6H_{10}, and $HBCl_3^-$.[3a] This mixture gradually changed, in a period of 3 weeks, to a mixture containing pentaborane(9) as the major component.[3a] Apparently, as the BH hydrogen atom coordinated to BCl_3 (step a in Scheme II), H^- transfer occurred to form the $HBCl_3^-$ ion, leaving behind the reactive B_3H_7 group, which underwent further reactions to form B_4H_{10}. Shore and co-workers developed a convenient method for the preparation of B_4H_{10}, in which the solid $B_3H_8^-$ salt was treated with boron trihalides.[11]

The PH_3 or $P(CH_3)_3$ adduct of B_3H_7 was not chlorinated by BCl_3; no reaction occurred. Interestingly, the base strength of the coordinated ligand does not appear to be the single factor that determines the reactivity of the triborane(7) adducts toward BCl_3. The base strength of $N(CH_3)_3$ toward boranes is stronger than that of phosphine (PH_3), but is weaker than that of $(PCH_3)_3$.[6,12] However, neither of the B_3H_7 adducts of these two phosphines reacted with BCl_3. Further studies are needed to elucidate this

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seemingly anomalous behavior of the phosphine adducts.

The $HgCl_2$ Reaction. Mercuric chloride has been used to chlorinate the Lewis base adducts of borane(3).[13] Application of this method to chlorinate $B_3H_7{\cdot}N(CH_3)_3$ for the preparation of $B_3H_6Cl{\cdot}N(CH_3)_3$ was not successful.[3a] However, the treatment of $B_4H_8{\cdot}N(CH_3)_3$ with $HgCl_2$ gave $B_3H_6Cl{\cdot}N(CH_3)_3$ (eq 4). No evidence for the formation of the chlorinated tetraborane(8) adduct, $B_4H_7Cl{\cdot}N(CH_3)_3$, could be found. Both B–B and B–H bonds appeared to undergo cleavages to the same extent by the $HgCl_2$ oxidation, and therefore the tetraborane structure was converted to the chlorotriborane(7) and chloroborane(3) adducts. Improvement of the yield of $B_3H_6Cl{\cdot}N(CH_3)_3$ in the $HgCl_2$ reaction was not pursued.

Fluxional Behavior of the Chlorotriborane(7) Adducts. The molecules of triborane(7) adducts are fluxional with respect to the tautomeric migration of hydrogen atoms around the three-boron framework. The adducts of strong bases such as $B_3H_7{\cdot}N(CH_3)_3$,[14] $B_3H_7{\cdot}P(CH_3)_3$,[6] and $B_3H_8^-$ [15] show the rapid fluxional motion even at considerably low temperatures (below −80 °C). On the other hand, the fluxional motion of the adducts of weak bases such as $B_3H_7{\cdot}PH_3$[6] and $B_3H_7{\cdot}CO$[16] slows down at low temperatures.

The replacement of a hydrogen atom on the B_3H_7 unit by a chlorine atom appeared to have little effect on the ease of the hydrogen atom migration. In the case of $B_3H_6Cl{\cdot}PH_3$, the fluxionality seemed to be increased slightly. The ^{11}B NMR spectrum (32.1 MHz) of the parent adduct $B_3H_7{\cdot}PH_3$ showed the static structure at −50 °C,[6] whereas the static structure for $B_3H_6Cl{\cdot}PH_3$ was not observed until the solution was cooled to −60 °C. Further experimental studies of the substituent effects on the fluxionality of a variety of triborane derivatives would be of interest. A theoretical study on the fluxionality of triborane adducts was reported by Brown and Lipscomb.[17]

Experimental Section

Chemicals, Equipment, and General Procedure. Standard vacuum-line techniques were used throughout for the handling of the volatile compounds. Air-sensitive solids were handled in plastic bags filled with dry nitrogen gas. Tetraborane(10) was our laboratory stock.[14] Boron trichloride and anhydrous HCl (Matheson Gas Products) were purified by fractional condensation before use. The B_3H_7 adducts of $N(CH_3)_3$,[14] $P(CH_3)_3$,[6] PH_3,[6] and $S(CH_3)_2$[8] were prepared by the reported procedures. Tetrahydrofuran, CH_2Cl_2, and $S(CH_3)_2$ were refluxed over $LiAlH_4$, P_4O_{10}, and CaH_2, respectively, and stored over molecular sieves in containers fitted with Teflon valves. These liquids were distilled directly into the vacuum line as needed. The ^{11}B and ^1H NMR spectra were recorded on a Varian XL-100-15 spectrometer. Generally, the B_3H_7 adducts were prepared in 10-mm-o.d. Pyrex tubes, unless otherwise stated. Each of the tubes was equipped with a stopcock or a Teflon valve. The adducts were then dissolved in the solvents, and then the other reactants were condensed into the tubes at −197 °C. The tubes were shaken in cold baths to mix the contents and were placed in the cold probe of the NMR instrument to monitor the reaction progresses.

Reaction of $B_4H_8{\cdot}N(CH_3)_3$ with HCl. This reaction that gave $B_3H_6Cl{\cdot}N(CH_3)_3$ was described in the earlier report.[1a]

Reaction of $B_4H_8{\cdot}N(CH_3)_3$ with HBr. A 1.06-mmol sample of $B_4H_8{\cdot}N(CH_3)_3$, prepared[1a] in a 22-mm-o.d. Pyrex tube, was treated with 1.03 mmol of HBr in 3 mL of CH_2Cl_2 at −100 °C. A 0.34-mmol quantity of hydrogen gas was produced immediately. When the solution was warmed to −80 °C and then to 0 °C while being stirred, only a trace of additional hydrogen gas was evolved. Volatile components were condensed out from the reaction tube, first at 0 °C and finally at room temperature. A white solid residue, containing about 70% $B_3H_6Br{\cdot}N(CH_3)_3$, was obtained in the reaction tube. Other compounds present in the solid were $B_3H_7{\cdot}N(CH_3)_3$ and $BH_2Br{\cdot}N(CH_3)_3$ (−2.2 ppm, t, J_{BH} = 126 Hz). Fractionation of the volatile components yielded 0.22 mmol of B_2H_6 (IR).

The trimethylamine adduct of bromotriborane(7) was characterized by its ^{11}B NMR spectrum, which showed signals at −20.3, −13.7, and −6.9 ppm. Thus, the structure of this bromo derivative may be represented by that in Figure 2, in which Br is attached to the B_2 atom. The three signals are tentatively assigned to B_1, B_2, and B_3 atoms, respectively.[18] The ^1H NMR signals were seen at 2.09 (H_B) and 2.63 (H_C) ppm. The H_B signal remained as a singlet at −40 °C.

Reaction of $B_3H_7{\cdot}N(CH_3)_3$ with BCl_3 [Preparation of $B_3H_6Cl{\cdot}N(CH_3)_3$]. A 0.71-mmol sample of $B_3H_7{\cdot}N(CH_3)_3$ was dissolved in 2 mL of CH_2Cl_2, and the mixture was treated with a 0.81-mmol sample of BCl_3 at −80 °C for 10 min. The ^{11}B NMR spectrum of this solution showed the presence of $B_3H_6Cl{\cdot}N(CH_3)_3$ and $B_3H_7{\cdot}N(CH_3)_3$ in an approximately 10:1 molar ratio. When the volatile components were removed from the tube by pumpimg at 0 °C, a white crystalline solid resulted. The solid was dissolved in a fresh, 2-mL portion of CH_2Cl_2, a 0.89-mmol sample of BCl_3 was condensed into the tube, and the mixture was agitated in a −80 °C bath. The NMR spectrum at −40 °C showed that the amount of $B_3H_7{\cdot}N(CH_3)_3$ was considerably less than before (<5%). When the solution was warmed to −23 °C, the $B_3H_7{\cdot}N(CH_3)_3$ signal became barely detectable within 30 min. When volatile components were removed from this reaction mixture at 0 °C and the resulting solid was redissolved in a fresh portion of CH_2Cl_2, the $B_3H_7{\cdot}N(CH_3)_3$ signal reappeared. For the mass spectrum analysis, a solid sample was sealed in a capillary tube, and then the capillary was introduced directly into the probe of the instrument.

Reaction of $B_3H_7{\cdot}N(CH_3)_3$ with HCl/BCl_3. A 1.2-mmol sample of $B_3H_7{\cdot}N(CH_3)_3$ was treated with samples of HCl (2.96 mmol) and BCl_3 (0.31 mmol) in 2 mL of CH_2Cl_2 at −80 °C. Within 15 min, 0.72 mmol of hydrogen gas was produced. Then, an additional 0.32-mmol sample of BCl_3 was condensed into the tube, and the mixture was allowed to react for 15 min at −80 °C. A total of 0.88 mmol of hydrogen gas was collected. No further hydrogen gas evolution was observed. Volatile components were removed from the reaction tube at room temperature, were fractionated, and were found to contain HCl and BCl_3 (IR). The residue was dissolved in a fresh portion of CH_2Cl_2. The ^{11}B NMR spectrum of the solution was that of $B_3H_6Cl{\cdot}N(CH_3)_3$ containing about 3% $B_3H_7{\cdot}N(CH_3)_3$.

Reaction of $B_4H_8{\cdot}N(CH_3)_3$ with $HgCl_2$. A 0.77-mmol sample of $B_4H_8{\cdot}N(CH_3)_3$, prepared[1a] in a 22-mm-o.d. Pyrex tube, was mixed with a 0.84-mmol sample of $HgCl_2$. The mixture was shaken with 5 mL of $CHCl_3$ at −63 °C. The solid reagents gradually dissolved, and a gray solid suspension formed as the reaction solution was warmed to 0 °C. The solution was held at 0 °C for 1 h and then warmed to room temperature for 15 min while being stirred. During this reaction, 0.08 mmol of hydrogen gas was evolved. Following storage at −80 °C for 38 h, the reaction mixture was filtered. The $CHCl_3$-insoluble gray solid (112 mg) was identified as Hg_2Cl_2 contaminated by Hg. When about half of the volatile components were removed from the clear filtrate by pumping, 0.19 mmol of a mixture of B_2H_6, chlorodiboranes, and HCl (IR) was separated. The ^{11}B NMR spectrum of the remaining filtrate at ambient temperature showed signals of $B_3H_6Cl{\cdot}N(CH_3)_3$ (the major component), $BHCl_2{\cdot}N(CH_3)_3$, $B_3H_7{\cdot}N(CH_3)_3$, and small amounts of $BH_2Cl{\cdot}N(CH_3)_3$, B_6H_{10}, and B_5H_9.

Reaction of $B_3H_7{\cdot}P(CH_3)_3$ with HCl/BCl_3 [Preparation of $B_3H_6Cl{\cdot}P(CH_3)_3$]. A 0.63-mmol sample of $B_3H_7{\cdot}P(CH_3)_3$ was treated with BCl_3 (0.73 mmol) and HCl (0.77 mmol) in 2 mL of CH_2Cl_2 at −80 °C. A rapid gas evolution was observed, and within 5 min a 0.59-mmol quantity of hydrogen gas was collected. The volatile components in the tube were then pumped at −80 °C and found to be CH_2Cl_2, BCl_3, and small amounts of mono- and dichlorodiboranes (IR). The residue was $B_3H_6Cl{\cdot}P(CH_3)_3$ contaminated with small amounts of $B_3H_7{\cdot}P(CH_3)_3$ and $BCl_3{\cdot}P(CH_3)_3$ (Figure 3). A small portion of this product was used for the mass spectral measurement.

In another experiment, where $B_3H_7{\cdot}P(CH_3)_3$, BCl_3, and HCl were used in 1.47-, 1.56-, and 1.71-mmol quantities, respectively, a 1.48-mmol quantity of hydrogen gas was given off within 5 min at −80 °C. When the reaction mixture was allowed to warm to room temperature, hydrogen gas evolution started again. The resulting solution contained only a small amount of $B_3H_6Cl{\cdot}P(CH_3)_3$, other components being diborane, chlorodiboranes, BCl_3, and some unidentified boron compounds.

Reaction of $B_3H_7{\cdot}P(CH_3)_3$ with HCl. A 1.10-mmol sample of $B_3H_7{\cdot}P(CH_3)_3$ was treated with a 2.91-mmol sample of HCl in 2 mL of CH_2Cl_2 at −80 °C. A 0.28-mmol quantity of hydrogen gas was evolved within 3.5 h. Volatile components were then pumped out from the

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(18) The choice between the −13.7 and −6.9 ppm signals for the bromine-bonded boron atom (B_2) may be uncertain. The reasons for assigning the −13.7 ppm signal to B_2 are as follows: (1) The substituent effect of bromine on the ^{11}B chemical shift of boron atoms in many halogenated boron hydride compounds is consistently less than that of chlorine, and (2) the relatively small downfield shift of the −13.7 ppm signal with increasing temperature parallels that observed for $BH_2Br{\cdot}N(CH_3)_3$, which was present in the system.

mixture at −23 °C. The residue in the tube was $B_3H_7{\cdot}P(CH_3)_3$ contaminated with a small amount of $BH_2Cl{\cdot}P(CH_3)_3$ (^{11}B NMR).

Reaction of $B_3H_7{\cdot}P(CH_3)_3$ with BCl_3. A solution containing 0.76 mmol of $B_3H_7{\cdot}P(CH_3)_3$ in about 2 mL of CH_2Cl_2 was treated with a 0.92-mmol sample of BCl_3 at −80 °C for 2 h. No change was observed (^{11}B NMR). The mixture was allowed to warm slowly to room temperature, and then the volatile components were removed by pumping. Small amounts of chlorodiboranes were found in the volatile components (IR). The solid residue was $B_3H_7{\cdot}P(CH_3)_3$, and no $B_3H_6Cl{\cdot}P(CH_3)_3$ was found (^{11}B NMR).

Formation of $B_3H_6Cl{\cdot}(CH_3)_2NH$, $B_3H_6Cl{\cdot}CH_3NH_2$, and $B_3H_6Cl{\cdot}NH_3$. The chlorotriborane(7) adducts of dimethylamine, methylamine, and ammonia were prepared by the same procedure that was employed for the preparation of $B_3H_6Cl{\cdot}N(CH_3)_3$. In a typical reaction, a 1.36-mmol sample of $B_3H_7{\cdot}N(CH_3)_2H$, prepared in a 22-mm-o.d. Pyrex tube, was treated with a 0.75-mmol sample of BCl_3 in 3 mL of CH_2Cl_2 at −80 °C for 10 min. The resulting clear colorless solution was then warmed to 0 °C for 10 min while being stirred. Fractionation of the volatile components from the reaction tube at 0 °C yielded 0.20 mmol of B_2H_6. The resulting white solid product mixture contained $B_3H_6Cl{\cdot}(CH_3)_2NH$ (ca. 90%, ^{11}B NMR).

Formation of $B_3H_6Cl{\cdot}S(CH_3)_2$. A 0.62-mmol sample of $B_3H_7{\cdot}S(CH_3)_2$ was mixed with a 0.34-mmol sample of BCl_3 and 3 mL of CH_2Cl_2 at −80 °C, and the solution was allowed to warm to 0 °C. Then, volatile components were removed by pumping. The clear colorless liquid residue consisted of $B_3H_6Cl{\cdot}S(CH_3)_2$ (ca. 80%), $B_3H_7{\cdot}S(CH_3)_2$, $BHCl_2{\cdot}S(CH_3)_2$, and a small amount of $BHCl_2{\cdot}THF$ (^{11}B NMR).

Reactions of $B_3H_7{\cdot}PH_3$. (a) With HCl. A sample of about 1 mmol of $B_3H_7{\cdot}PH_3$ was mixed with a 1.78-mmol sample of HCl in 2 mL of CH_2Cl_2 at −80 °C. After the solution was allowed to stand for 2 h at −80 °C, no hydrogen gas was found in the tube, and a 1.76-mmol quantity of HCl was recovered from the mixture.

(b) With BCl_3. A 1.2-mmol smple of $B_3H_7{\cdot}PH_3$ was mixed with a 1.24-mmol sample of BCl_3 in 2 mL of CH_2Cl_2. The mixture was kept at −23 °C for 15 min. The ^{11}B NMR spectrum of the solution at −23 °C showed that no reaction had occurred.

(c) With HCl/BCl_3. [Formation of $B_3H_6Cl{\cdot}PH_3$]. To the mixture of $B_3H_7{\cdot}PH_3$ and BCl_3 in (b) above was added a 2.45-mmol sample of HCl. As the mixture was allowed to warm to room temperature, 1.06 mmol of hydrogen gas was evolved. When the volatile components were removed from the reaction mixture at 0 °C, a clear liquid remained in the tube. The ^{11}B NMR spectrum of this liquid in CH_2Cl_2 is shown in Figure 4.

In a separate experiment, a 1.0-mmol sample of $B_3H_7{\cdot}PH_3$ was treated with a mixture of HCl (2.22 mmol) and a BCl_3 (1.97 mmol) in CH_2Cl_2 at −80 °C. A 0.22-mmol quantity of hydrogen gas was evolved within a period of 0.5 h, and after an additional 0.5 h, a total of 0.33 mmol of hydrogen gas was collected. Then, volatile components were pumped out at −80 °C. The ^{11}B NMR spectrum of the residue in CH_2Cl_2 showed that it was a mixture of $B_3H_6Cl{\cdot}PH_3$ and $B_3H_7{\cdot}PH_3$ in a molar ratio of approximately 2:3.

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Electrochemistry of Cyanocopper Thiomolybdates and Thiotungstates: Redox-Based Interconversion of Species

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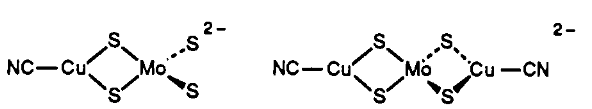
$[MoS_4]^{2-}$ and its 1:1 and 1:2 CuCN adducts $[(CN)CuS_2MoS_2]^{2-}$ and $[(CN)CuS_2MoS_2Cu(CN)]^{2-}$ each exhibit electrochemically reversible one-electron reductions in MeCN at fast scan rates (>500 mV s^{-1}). At lower scan rates, the reduced adduct species are unstable to dissociation of CuCN, leading to interconversion of the three anions. The tungsten analogues show similar properties.

Introduction

Rich structural chemistries have emerged from the interaction of the thiomolybdate ligand $[MoS_4]^{2-}$ with metal fragments.[2,3] Those involving iron and copper are well developed, interest being driven by the bioinorganic importance of FeMoS and CuMoS aggregates.

$[MoS_4]^{2-}$ forms 1:1 and 1:2 adducts with CuCN:[4]



These anions are expected to be redox-active as a number of the related adducts formed with a variety of metal fragments undergo reduction processes.[5] While those reduced species can sometimes be trapped and studied,[5-7] they are invariably unstable on longer time scales and the nature of the subsequent chemical reactions is unknown.

Previous examination of $[MoS_4]^{2-}$ electrochemistry has shown complicated behavior (e.g. refs 8, 9). Conditions have been found in the present work for observation of a chemically and electrochemically reversible, one-electron reduction of $[MoS_4]^{2-}$ in MeCN. This has allowed a detailed examination of the electrochemistry of the CuCN adducts mentioned above and of their tungsten analogues. $[MoS_4]^{2-}$, $[(CN)CuS_2MoS_2]^{2-}$, and $[(CN)CuS_2MoS_2Cu(CN)]^{2-}$ each exhibit diffusion-controlled reversible one-electron reductions in MeCN at fast scan rates (>500 mV s^{-1}). However, at slower scan rates, the reduced adduct species are unstable to dissociation of CuCN, leading to interconversion of the three anions.

Experimental Section

Abbreviations and parameter symbols are given in ref 10.

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(10) Abbreviations: thf, tetrahydrofuran; SHE, standard hydrogen electrode; Fc^+/Fc, ferrocenium/ferrocene; $E_{1/2}{}^r$, reversible half-wave potential; E_p, peak potential; ΔE_p, peak-to-peak separation; v, scan rate; i_L, limiting current; i_p, peak current; i_{pr}, reduction peak current; i_{po}, oxidation peak current; ω, rotation frequency; n, electrons per molecule.

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