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Reactions of Hexahydrobis(trimethylphosphine)triboron(1+) Octahydrotriborate(1–) with Lewis Bases. Novel Formation of Tetraborane(8) Adducts

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Hexahydrobis(trimethylphosphine)triboron(1+) octahydrotriborate(1–), $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$, reacted with Lewis base in a 1:2 molar ratio in dichloromethane to give $B_4H_8\cdot P(CH_3)_3\cdot L$, $BH_3\cdot P(CH_3)_3$, and $BH_3\cdot L$, where $L = N(CH_3)_3$, $P(CH_3)_3$, or $P[N(CH_3)_2]_3$. The bis(base) adduct, $B_4H_8\cdot P(CH_3)_3\cdot L$, further reacted with the $B_3H_8{}^-$ salt, and $B_4H_8\cdot P(CH_3)_3$ was produced. The $B_2H_7{}^-$ salt of the same cation gave $B_2H_4\cdot 2P(CH_3)_3$ and the BH_3 adducts of the reacting base when treated with $N(CH_3)_3$ or $P(CH_3)_3$. A mechanistic consideration was given to account for the difference between the reactions of the $B_3H_8{}^-$ and $B_2H_7{}^-$ salts.

Introduction

In our original report on the triboron complex cation,[1] the reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$ with trimethylamine was described. The reaction produced $B_2H_4\cdot 2P(CH_3)_3$, which was one of the starting compounds for the preparation of the triboron cation:

$$B_2H_4\cdot 2P(CH_3)_3 + {}^3/_2B_2H_6 \rightarrow B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$$

Therefore, it was thought simply that the cation was sensitive toward bases and that it underwent the reverse of the formation reaction.

The $B_3H_8{}^-$ salt of the triboron cation was prepared by the reaction of $B_2H_4\cdot 2P(CH_3)_3$ with tetraborane(10) and was reported in the same report.[1] It was noticed during the course of reaction studies involving the triboron cations that the $B_3H_8{}^-$ salt *did not regenerate* $B_2H_4\cdot 2P(CH_3)_3$ when came into contact with Lewis bases. Instead, adducts of **tetraborane(8)** were produced. In view of the novel formation of the tetraborane(8) adducts, and the strikingly different reaction pattern between the salts of the two different anions, these reactions were investigated in some detail. The results are described in this paper.

Results and Discussion

A. Reactions of $B_3H_6\cdot 2P(CH_3)_3{}^+$ Salts with $P(CH_3)_3$. (i) The $B_3H_8{}^-$ Salt. Treatment of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with $P(CH_3)_3$ in dichloromethane resulted in the formation of the bis(trimethylphosphine) adduct of tetraborane(8). The reaction proceeded smoothly at 0–25 °C and was complete in several minutes.

$$B_3H_6\cdot 2PCH_3)_3{}^+B_3H_8{}^- + 2P(CH_3)_3 \rightarrow B_4H_8\cdot 2P(CH_3)_3 + 2(CH_3)_3P\cdot BH_3 \quad (1)$$

When trimethylphosphine was used in a deficient amount, a secondary reaction proceeded slowly and the bis(phosphine) adduct of B_4H_8 was converted into the mono(phosphine) adduct.

$$B_4H_8\cdot 2P(CH_3)_3 + B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^- \rightarrow 2B_4H_8\cdot P(CH_3)_3 + 2(CH_3)_3P\cdot BH_3 \quad (2)$$

(ii) The $B_2H_7{}^-$ Salt. The reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$ with trimethylamine was reported earlier.[1] The reaction with trimethylphosphine exactly paralleled the reported trimethylamine reaction.

$$B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^- + P(CH_3)_3 \rightarrow B_3H_6\cdot 2P(CH_3)_3{}^+BH_4{}^- + BH_3\cdot P(CH_3)_3 \quad (3)$$

$$B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^- + 3P(CH_3)_3 \rightarrow B_2H_4\cdot 2P(CH_3)_3 + 3BH_3\cdot P(CH_3)_3 \quad (4)$$

The $BH_4{}^-$ salt disproportionated above –40 °C according to the equation

$$3B_3H_6\cdot 2P(CH_3)_3{}^+BH_4{}^- \rightarrow 2B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^- + B_2H_4\cdot 2P(CH_3)_3 \quad (5)$$

Observations supporting the above equations were the formation of $BH_3\cdot P(CH_3)_3$, $BH_4{}^-$, and $B_2H_4\cdot 2P(CH_3)_3$ at low temperatures (below –40 °C) and the disappearance of the $BH_4{}^-$ anion accompanied by the reappearance of the $B_2H_7{}^-$ anion above –40 °C.

B. Reaction of the $B_3H_8{}^-$ Salt with $N(CH_3)_3$ and $P[N(CH_3)_2]_3$. The reaction of the $B_3H_8{}^-$ salt with trimethylamine gave $BH_3\cdot N(CH_3)_3$, $BH_3\cdot P(CH_3)_3$, $B_4H_8\cdot P(CH_3)_3$,[2] and $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$[2] as the products. Likewise, the reaction of the $B_3H_8{}^-$ salt with $P[N(CH_3)_2]_3$ gave $BH_3\cdot P[N(CH_3)_2]_3$, $BH_3\cdot P(CH_3)_3$, and $B_4H_8\cdot P(CH_3)_3\cdot P[N(CH_3)_2]_3$.[2] The adducts of B_2H_4 and B_3H_7 were not produced. In these reactions the pairs of the BH_3 adducts, i.e. $BH_3\cdot P(CH_3)_3$, $BH_3\cdot N(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$, $BH_3\cdot P[N(CH_3)_2]_3$, began to appear at about –40 °C in 1:1 molar ratios. The reactions were faster at 0 °C, but the 1:1 ratio of the two borane(3) adducts in each reaction was maintained. When the salt was allowed to react with $N(CH_3)_3$ in a *1:1* molar ratio, the initially produced $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$ disappeared eventually, and the final products consisted of $B_4H_8\cdot P(CH_3)_3$, $BH_3\cdot P(CH_3)_3$, and $BH_3\cdot N(CH_3)_3$. These observations are combined with those made on the reactions with $P(CH_3)_3$, and the following equations can be written to summarize the reactions of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with Lewis bases:

$$B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^- + 2L \rightarrow BH_3\cdot L + BH_3\cdot P(CH_3)_3 + B_4H_8\cdot P(CH_3)_3\cdot L \quad (6)$$

$$L = P(CH_3)_3,\ N(CH_3)_3,\ \text{or}\ P[N(CH_3)_2]_3$$

$$B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^- + B_4H_8\cdot P(CH_3)_3\cdot L \rightarrow BH_3\cdot L + BH_3\cdot P(CH_3)_3 + 2B_4H_8\cdot P(CH_3)_3 \quad (7)$$

$$L = P(CH_3)_3\ \text{or}\ N(CH_3)_3$$

C. Reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with Tetrahydrofuran. In contrast to the aforementioned reactions with strong bases, the $B_3H_8{}^-$ salt reacted with tetrahydrofuran very slowly in dichloromethane at room temperature. The products were $B_4H_8\cdot P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$. The reaction, however, was faster when the salt was treated with neat tetrahydrofuran, and the formation of the same products was seen at –40 °C. Any precursor to these final products could not be detected.

D. Mechanistic Consideration. Unlike the $B_2H_7{}^-$ anion, the $B_3H_8{}^-$ anion by itself is inert toward these reacting bases under the conditions of the present experiments. However, the cation

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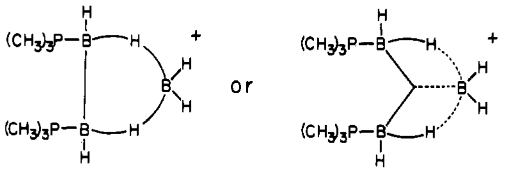
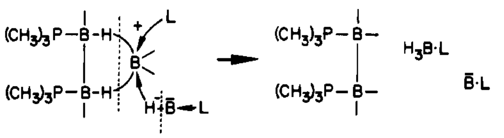


Figure 1. Proposed structure of the $B_3H_6\cdot 2P(CH_3)_3^+$ cation.[1]

Scheme I

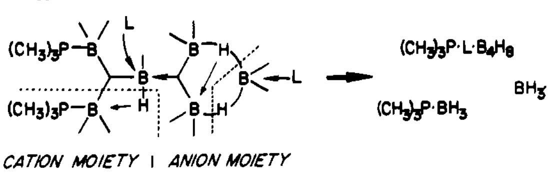


would interact with the base strongly as well as with the anion. In the reactions of the $B_2H_7^-$ salt with the bases, one of the operating mechanisms was thought to be the attack of the base at the unligated BH_2 site of the cation, concerted with the H^- transfer from the anion ($B_2H_7^-$ or BH_4^-) to the BH_2 site. The result is the formation of $BH_3\cdot L$ and $B_2H_4\cdot 2P(CH_3)_3$. See Scheme I where $\bar{B}$ = "B_2H_6". Although this explanation appears to be plausible for the observed reactions of the $B_2H_7^-$ salt, the same does not apply to the reactions of the $B_3H_8^-$ salt because the expected products would be $BH_3\cdot L$, $B_2H_4\cdot 2P(CH_3)_3$, and $B_3H_7\cdot L$ (see Scheme I where $\bar{B}$ = "B_3H_7") but the last two adducts were absent in the products. It was confirmed in this study that $B_2H_4\cdot 2P(CH_3)_3$ and $B_3H_7\cdot L$ (L = $N(CH_3)_3$ or $P(CH_3)_3$) do not react with each other. Therefore, the absence of these two adducts is not due to such a secondary reaction. Possibly, the acid strength of B_3H_7 toward H^- is too strong to allow the facile transfer of H^- from $B_3H_8^-$ to the cation moiety.

Clearly, when the reacting base (L) was strong, 2 mol of the base was consumed by 1 mol of $B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^-$ at the first stage of the reaction (eq 6). Also clear is that two units of BH_3 were eliminated simultaneously as $BH_3\cdot P(CH_3)_3$ and $BH_3\cdot L$ in this first-stage reaction, one of the two L's being combined with the resulting B_4H_8 unit. Since this reaction occurs at the temperatures ranging from −65 to −40 °C, the resulting $BH_3\cdot P(CH_3)_3$ (or one of the two $BH_3\cdot P(CH_3)_3$ units if the reacting base was $P(CH_3)_3$) is more likely to have originated from the cation part: The original B–P bond would be too strong to undergo cleavage for a displacement reaction at these low temperatures.[3]

Apparently, as the result of the interaction of the $B_3H_8^-$ anion with the cation in the presence of the base, a hydrogen atom migrated to one of the phosphine-attached BH_2 sites of the cation moiety and that site was eliminated as $BH_3\cdot P(CH_3)_3$. Another BH_3 unit was removed from the anion moiety as $BH_3\cdot L$ by the second base attack. This mechanism may be visualized as illustrated in Scheme II. The trimethylphosphine–trimethylamine adduct of B_4H_8 thus produced would undergo rearrangement to the more stable, equilibrated state and would dissociate at higher temperatures into $B_4H_8\cdot P(CH_3)_3$ and $N(CH_3)_3$.[2] Therefore, $B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^-$, if present in excess, would further undergo the same reaction with the $N(CH_3)_3$ that had become available, leaving $B_4H_8\cdot P(CH_3)_3$ as the final product (eq 7). The corresponding reaction for $B_4H_8\cdot 2P(CH_3)_3$ is slow even at room temperature because of the dissociative stability of this compound.[4] Tetrahydrofuran appears to stand at the other extreme. Its basicity is not strong enough to effect the facile elimination of $BH_3\cdot P(CH_3)_3$ and $BH_3\cdot$THF and to stay attached to the B_4H_8 moiety in the form of "$B_4H_8\cdot P(CH_3)_3\cdot C_4H_8O$".[2] Therefore, the rate of the reaction is very slow unless

Scheme II



the concentration of tetrahydrofuran is made very high, and the reaction, when it occurs, proceeds to the completion of the second stage (eq 7).

E. Summary. The reactions of $B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^-$ with Lewis bases produced the adducts of tetraborane(8) according to eq 6 and 7. The corresponding reactions of the $B_2H_7^-$ salt of the same cation gave $B_2H_4\cdot 2P(CH_3)_3$ and the BH_3 adducts of the reacting bases. The reluctance of the H^- ion to transfer from $B_3H_8^-$ to the cationic moiety and the facile elimination of $BH_3\cdot P(CH_3)_3$ at an intermediate stage of the reaction were considered to be responsible for the novel formation of the B_4H_8 adducts in the reaction of the $B_3H_8^-$ salt.

Experimental Section

Chemicals and Instruments. Conventional vacuum-line techniques were used throughout for the handling of volatile and air-sensitive compounds. Bis(trimethylphosphine)–diborane(4) was prepared from B_5H_9 and $P(CH_3)_3$ by the method described elsewhere.[5] Diborane(6), which was obtained from Callery Chemical Co., was fractionated on a vacuum line. Laboratory stock B_4H_{10}, which had been prepared by the pyrolysis of B_2H_6, was used. Trimethylamine, trimethylphosphine, and tris(dimethylamino)phosphine were our laboratory stock also. Purities of these compounds were checked by the IR and/or NMR spectra, and no impurities were detected in these samples. Dichloromethane and tetrahydrofuran were of commercial reagent grade and were kept dried over molecular sieves and $LiAlH_4$, respectively. These solvents were distilled directly into the vacuum line from the containers. NMR spectra were recorded on a Varian XL-100-15 spectrometer operating in the FT mode. The shift standard for ^{11}B was $BF_3\cdot O(C_2H_5)_2$. Low-field shifts were taken as positive.

Preparation of the $B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^-$ Samples for the Reaction Studies. A weighed amount of $B_2H_4\cdot 2P(CH_3)_3$ was placed in a tube (10-mm o.d., Pyrex) under at atmosphere of nitrogen through a side arm, which was attached at the upper end of the tube about 1 in. below the stopcock. The side arm was sealed off, and about 2 mL of CH_2Cl_2 was condensed into the tube to prepare a CH_2Cl_2 solution of the diborane(4) adduct. The solution was frozen at −197 °C, and a measured quantity of B_4H_{10} was condensed into the tube. The tube was then allowed to warm to −80 °C to mix the reactants and further to 0 °C, where it was kept for 1 h to complete the reaction. Upon removal of the volatiles from the tube at 0 °C, a white solid was left behind. The solid was $B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^-$ free from any other boron compound as checked by its ^{11}B NMR spectrum. The salt thus prepared was redissolved in about 2 mL of fresh CH_2Cl_2 by condensing the solvent into the tube. A measured amount of the base was condensed into the tube, and the reactants were mixed at −80 °C. Then, the tube was placed in the precooled probe of the NMR spectrometer to record the ^1H-spin-decoupled ^{11}B spectra at various temperatures for the reaction study.

^{11}B Chemical Shifts for Compound Identification. Most of the compounds that were encountered in this study had been known, and their shift values had been reported. Listed below are the values that were used for the identification of the compounds (ppm at ambient temperature unless indicated otherwise): $BH_3\cdot N(CH_3)_3$, −9.0;[6a] $BH_3\cdot P(CH_3)_3$, −37.4;[6b] $BH_3\cdot P[N(CH_3)_2]_3$, −43.0;[6c] $B_2H_4\cdot 2P(CH_3)_3$, −37.5;[5] $B_2H_7^-$, −25.8 (−20 °C);[1,6d] $B_3H_8^-$, −30.5;[6e] $B_3H_6\cdot 2P(CH_3)_3^+$, −10.5, −39.0;[1] $B_3H_7\cdot N(CH_3)_3$, −18.3;[7] $B_3H_7\cdot P(CH_3)_3$, −15.6, −45.0;[8] $B_4H_8\cdot P(CH_3)_3$, −1.0, −6.4, −50.1;[3] $B_4H_8\cdot 2P(CH_3)_3$, −17.1, −41.7 (25 °C) and −17.1, −37.4, −47.0 (−50 °C);[4] $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$, −7.5, −15.8, −45.8.[2]

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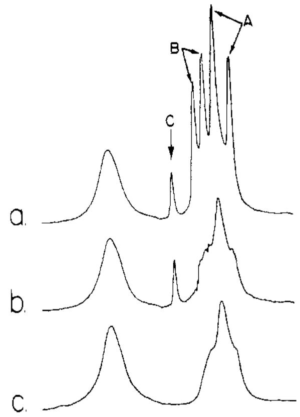

Figure 2. (a) $^{11}B\{^1H\}$ NMR spectrum (25.5 MHz) of the product from the reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with $P[N(CH_3)_2]_3$. A and B indicate the doublet signals of $BH_3\cdot P[N(CH_3)_2]_3$ and $BH_3\cdot P(CH_3)_3$, respectively, and peak C is due to the $B_3H_8{}^-$ ion present in the solution. (b) Resulting spectrum after subtracting from spectrum a the signals of $BH_3\cdot P[N(CH_3)_2]_3$ and $BH_3\cdot P(CH_3)_3$ (1:1). (c) Spectrum of an authentic sample of $B_4H_8\cdot P(CH_3)_3\cdot P[N(CH_3)_2]_3$[2] to compare with spectrum b.

Reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with $P(CH_3)_3$. (i) In a 1:1 Molar Ratio. A CH_2Cl_2 solution containing 0.395 mmol of the salt was treated with a 0.407-mmol quantity of $P(CH_3)_3$. At −40 °C the signal of $(CH_3)_3P\cdot BH_3$ began to appear. At 0 °C the signals of $BH_3\cdot P(CH_3)_3$ and $B_4H_8\cdot 2P(CH_3)_3$ appeared rapidly, and in about 5 min the change appeared to have stopped. The signals of the salt were still seen. These three compounds were present in a 2:1:1 molar ratio ($BH_3\cdot P(CH_3)_3:B_4H_8\cdot 2P(CH_3)_3:B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$). When the mixture was allowed to stand at 25 °C, the signals of $B_4H_8\cdot P(CH_3)_3$ slowly grew in at the expense of the signals of $B_4H_8\cdot 2P(CH_3)_3$ and the $B_3H_8{}^-$ salt. In 3 h the signals of $B_4H_8\cdot P(CH_3)_3$ became strong, and the signals of $B_4H_8\cdot 2P(CH_3)_3$ became very weak, but were still detectable. The solution was clear and colorless.

(ii) In a 1:2 Molar Ratio. A 0.365-mmol sample of the salt was treated with 0.733 mmol of $P(CH_3)_3$ in a CH_2Cl_2 solution. The reaction proceeded in the same manner as in section i. The spectrum of the solution at 25 °C consisted of the signals of $B_4H_8\cdot 2P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$ and contained no signals of $B_4H_8\cdot P(CH_3)_3$ and the $B_3H_8{}^-$ salt. The solution remained clear and colorless.

Reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with $N(CH_3)_3$. (i) In a 1:1 Molar Ratio. A 0.323-mmol sample of the salt in CH_2Cl_2 solution was treated with 0.328 mmol of $N(CH_3)_3$. When the mixture was allowed to warm to −65 °C, the signals of $BH_3\cdot P(CH_3)_3$, $BH_3\cdot N(CH_3)_3$, and $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$ were seen along with the signals of unchanged $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$. The signal of $B_2H_4\cdot 2P(CH_3)_3$ could not be detected. The molar ratio for $BH_3\cdot P(CH_3)_3:BH_3\cdot N(CH_3)_3:B_3H_8{}^-$ was roughly 1:1:1 as judged by the intensities of the signals at −40 °C. At 0 °C the signals of $B_4H_8\cdot P(CH_3)_3$ were growing in rapidly. When the reaction mixture was kept standing at room temperature for 1 h, the signals of $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$ and the $B_3H_8{}^-$ salt had disappeared and the signals of $B_4H_8\cdot P(CH_3)_3$, $BH_3\cdot P(CH_3)_3$, and $BH_3\cdot N(CH_3)_3$ were seen in a 1:1:1 molar ratio. The solution was colorless and clear.

(ii) In a 1:2 Ratio. A CH_2Cl_2 solution containing 0.252 mmol of the salt was treated with 0.504 mmol of $N(CH_3)_3$. The signals of $BH_3\cdot P(CH_3)_3$, $BH_3\cdot N(CH_3)_3$, and ${}_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$ were evident at −30 °C. The signal of the $B_3H_8{}^-$ salt was still present at this temperature. The formation of $B_4H_8\cdot P(CH_3)_3$ became noticeable at −20 °C. The growth of the $B_4H_8\cdot P(CH_3)_3$ signal was fast at 0 °C, and the $B_3H_8{}^-$ salt signal disappeared rapidly. At +20 °C the amounts of $B_4H_8\cdot P(CH_3)_3$ and ${}_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$ were about equal. The solution remained clear and colorless.

Reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with $P[N(CH_3)_2]_3$. A CH_2Cl_2 solution containing 0.547 mmol of the $B_3H_8{}^-$ salt was prepared, and 1.064 mmol of $P[N(CH_3)_2]_3$ was mixed into the solution at −80 °C. At −20 °C the signals of $BH_3\cdot P(CH_3)_3$ and $BH_3\cdot P[N(CH_3)_2]_3$ began to show up in about equal intensities. Above 0 °C the two signals grew more rapidly, the $B_3H_8{}^-$ signal weakened, and a broad signal centered at −14.8 ppm became conspicuous. See Figure 2a. Since this spectrum of the solution containing the final products had such strong signals of $BH_3\cdot P(CH_3)_3$ and $BH_3\cdot P[N(CH_3)_2]_3$, the signals of the phosphine-attached boron atom(s) of the other product(s) could not be identified. Therefore, the subtractions of known signals (those of $BH_3\cdot P(CH_3)_3$ and $BH_3\cdot P[N(CH_3)_2]_3$) were performed on the spectrum of the products with the use of a Varian FT-80A spectrometer. The result indicated that $B_4H_8\cdot P(CH_3)_3\cdot P[N(CH_3)_2]_3$[2] was the product in addition to the two BH_3 adducts. See Figure 2.

Reaction of the $B_3H_8{}^-$ Salt with Tetrahydrofuran (THF). A CH_2Cl_2 solution (2 mL) containing 0.099 mmol of the $B_3H_8{}^-$ salt was treated with 0.286 mmol of THF. No reaction could be detected until the solution had been left standing at room temperature for 5 h. Small amounts of $B_4H_8\cdot P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$ were found as the product. The $B_3H_8{}^-$ salt is only sparingly soluble in THF. It was possible, however, in a separate experiment, to detect the signals of $B_4H_8\cdot P(CH_3)_3$, $BH_3\cdot P(CH_3)_3$, and the $B_3H_8{}^-$ salt at −40 °C for a sample that contained the solid $B_3H_8{}^-$ salt in tetrahydrofuran.

Reactions of the $B_2H_7{}^-$ Salt with $N(CH_3)_3$ and $P(CH_3)_3$. Solutions of the $B_2H_7{}^-$ salt were prepared in 10-mm-o.d. tubes which were similar to that described earlier in this section. A weighed amount of $B_2H_4\cdot 2P(CH_3)_3$ was placed in the tube and dissolved in CH_2Cl_2, and then slight excess B_2H_6 was condensed into the tube. The reactants were mixed at −80 °C, and then the tube was kept at −35 to −23 °C for about 6 h while the solution was agitated occasionally by shaking. The unchanged, excess B_2H_6 could be removed from the mixture by pumping briefly at −80 °C. The solutions of the $B_2H_7{}^-$ salt thus prepared were treated with $N(CH_3)_3$ and $P(CH_3)_3$ for the reaction study.

To a CH_2Cl_2 solution containing 0.289 mmol of the $B_2H_7{}^-$ salt was added 0.292 mmol of $N(CH_3)_3$ at −197 °C. The tube was warmed to −80 °C, and the reactants were mixed. At −65 °C the signals of $BH_3\cdot N(CH_3)_3$, $B_3H_6\cdot 2P(CH_3)_3{}^+$, $B_2H_7{}^-$, and $BH_4{}^-$ were seen clearly. The signal of $B_2H_4\cdot 2P(CH_3)_3$, which was overlapped with the cation signal, was discerned also. As the temperature was raised above −40 °C, the intensity of the $BH_4{}^-$ signal began to decrease, and at the same time the intensity of the $B_2H_7{}^-$ signal increased. At −20 °C the $BH_4{}^-$ signal disappeared in 10 min, and the signals of $BH_3\cdot N(CH_3)_3$, $B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$, and $B_2H_4\cdot 2P(CH_3)_3$ remained in the spectrum. A trace of the $BH_3\cdot P(CH_3)_3$ signal could be detected. Above 0 °C the decomposition of $B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$[1] proceeded slowly, as evidenced by the disappearance of the $B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$ signal accompanied by the appearance of the signals of $BH_3\cdot P(CH_3)_3$ and $B_3H_7\cdot P(CH_3)_3$.

The reaction of the $B_2H_7{}^-$ salt with $P(CH_3)_3$ proceeded similarly to the $N(CH_3)_3$ reaction, except that $BH_3\cdot P(CH_3)_3$ was produced instead of $BH_3\cdot N(CH_3)_3$. The overlap of the signals of $B_2H_4\cdot 2P(CH_3)_3$, $BH_4{}^-$, and $BH_3\cdot P(CH_3)_3$ complicated the analyses of the spectra. However, the sharp signal of $BH_4{}^-$ and the isolated signal of $B_2H_7{}^-$ could be seen distinctly and were used as the guides for the tracking of the reaction sequence.

Treatments of $B_2H_4\cdot 2P(CH_3)_3$ with the B_3H_7 Adducts of $N(CH_3)_3$ and $P(CH_3)_3$. Samples of $B_3H_7\cdot N(CH_3)_3$[7] and $B_3H_7\cdot P(CH_3)_3$[8] (in about 0.5-mmol quantities) were prepared by the reaction of B_4H_{10} with $N(CH_3)_3$ and $P(CH_3)_3$, respectively, in 10-mm-o.d. Pyrex tubes, each of which was equipped with a stopcock and a side arm (10-mm o.d.) as described before. The solid sample of the B_3H_7 adduct was dissolved in CH_2Cl_2 (ca. 2 mL), and an equimolar quantity of $B_2H_4\cdot 2P(CH_3)_3$ was introduced from the side arm into the tube under a stream of nitrogen gas while the solution was frozen at −197 °C. The side arm was sealed off, the tube was evacuated, and the mixture was allowed to warm. The ^{11}B NMR spectra of the solutions contained only the signals of the original compounds and remained unchanged while the solutions were kept at 25 °C for 3 h.

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Registry No. $B_2H_4\cdot 2P(CH_3)_3$, 67113-98-8; B_4H_{10}, 18283-93-7; $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$, 92219-77-7; $P(CH_3)_3$, 594-09-2; $(CH_3)_3P\cdot BH_3$, 1898-77-7; $B_4H_8\cdot 2P(CH_3)_3$, 66750-83-2; $B_4H_8\cdot P(CH_3)_3$, 71749-92-3; $N(CH_3)_3$, 594-09-2; $BH_3\cdot N(CH_3)_3$, 75-22-9; $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$, isomer I, 92219-79-9; $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$, isomer II, 92219-80-2; $P[N(CH_3)_2]_3$, 1608-26-0; $BH_3\cdot P[N(CH_3)_2]_3$, 7319-05-3; $B_4H_8\cdot P(CH_3)_3\cdot P[N(CH_3)_2]_3$, 92219-81-3; B_2H_6, 19287-45-7; $B_3H_6\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$, 92219-83-5; $B_3H_7\cdot P(CH_3)_3$, 12543-29-2; $B_3H_7\cdot N(CH_3)_3$, 57808-48-7.