greatly to the computer programming that made this project possible. Our research was generously supported by National Science Foundation Grant DMR 7681083 to the Materials Science Center at Cornell University.

Appendix I

Extended Hückel parameters for all atoms used appear in Table IV. Ligand and metal H_{ii} and metal exponents are from previous work,[28] except that As and Sb H_{ii} are set equal to P H_{ii}. Ligand exponents are from Clementi and Roetti.[29]

For L = P, S, and Cl, Fe–L = 2.26 Å and Rh–L = 2.36 Å. Other Fe–L distances were 2.38 (As) and 2.60 Å (Sb). L–H distances were 1.43 (P), 1.33 (S), 1.52 (As), and 1.78 Å (Sb). All M–H distances were 1.57 Å. P–P = 2.24 Å in three-dimensional marcasite.

All these distances were kept constant during distortion; only the angle θ was varied. Special values of θ were 73.36 (uniform contraction), 97.5 (uniform expansion), 70.56 (θ_1), and 101.96° (θ_2) for the pairing distortion.

Appendix II

A special points set is a set of k points of size n, designed to give the best value for average properties of the solid for a given n. Our sets were adapted from a standard reference;[10b] the optimal size n was obtained by comparing sets of different size. For one-dimensional problems we used the three-point set $\{(^1/_{12}, ^3/_{12}, ^5/_{12})\}$. A three-point anisotropic set $\{(^1/_4, ^1/_4, k_z)\ k_z = {}^1/_{12}, {}^3/_{12}, {}^5/_{12}\}$ and a twelve-point more isotropic set $\{(^1/_8, ^1/_8, k_z), (^1/_8, ^3/_8, k_z), (^3/_8, ^1/_8, k_z), (^3/_8, ^3/_8, k_z)\ k_z = {}^1/_{12}, {}^3/_{12}, {}^5/_{12}\}$ were used for orthorhombic marcasite.

Registry No. Marcasite, 1317-66-4; arsenopyrite, 1303-18-0.

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Reaction of Tetraborane(10) with Trimethylphosphine in Tetrahydrofuran

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When tetraborane(10) was treated with trimethylphosphine in a 1:1 molar ratio in tetrahydrofuran at −90 to −70 °C, $(CH_3)_3P\cdot BH_3$, $THF\cdot B_3H_7$, and $H_2B(THF)_2{}^+B_3H_8{}^-$ were produced. The formation of $(CH_3)_3P\cdot B_3H_7$ was minimal. The same reaction was performed in dimethyl ether, diethyl ether, and dichloromethane, and the patterns of product distribution were compared with each other. The previously proposed mechanism for the B_4H_{10} cleavage reactions was used to explain the observed results by taking the effects of concentrations and strength of the reacting bases into consideration. This mechanistic model explained also the results of the reactions of B_4H_{10} with trimethylamine and phosphine in tetrahydrofuran. The values of 4 ± 1 and 0.41 ± 0.02 were obtained as the equilibrium constants for $(CH_3)_3P\cdot BH_3 + THF\cdot B_3H_7 \rightleftharpoons THF\cdot BH_3 + (CH_3)_3P\cdot B_3H_7$ at 25 °C and $H_3P\cdot BH_3 + THF\cdot B_3H_7 \rightleftharpoons THF\cdot BH_3 + H_3P\cdot B_3H_7$ at 0 °C, respectively.

Introduction

The cleavage reactions of tetraborane(10) B_4H_{10} with Lewis bases have been classified into two categories:[1] symmetrical cleavage

$$B_4H_{10} + 2L \rightarrow L\cdot BH_3 + L\cdot B_3H_7$$

and unsymmetrical cleavage

$$B_4H_{10} + 2L' \rightarrow H_2BL'_2{}^+ + B_3H_8{}^-$$

where L and L′ represent Lewis bases. Many examples of these reactions have appeared in the literature.[2] However, the cases in which B_4H_{10} are reacting with two different bases, such as "B_4H_{10} + L(1) + L(2)", have not been reported.

Recently, we described the reaction of B_4H_{10} with trimethylphosphine *in tetrahydrofuran* as an observation in connection with the characterization of a new anion $B_4H_9P(CH_3)_3{}^-$.[3] The products in the reaction were **"$(CH_3)_3P\cdot BH_3$ and $THF\cdot B_3H_7$"**, and were **not "$(CH_3)_3P\cdot B_3H_7$ and $THF\cdot BH_3$"**. The latter pair of adducts would be the products that one would normally expect on the basis of the acid–base strength of the species involved. This finding prompted us to investigate the reaction in more detail in efforts to find the factors that determine the "anomalous" product formation.

Results and Discussion

A. Reactions of Trimethylphosphine with $H_2B(THF)_2{}^+B_3H_8{}^-$ and with "$THF\cdot BH_3$ + $THF\cdot B_3H_7$". Trimethylphosphine, $P(CH_3)_3$, is a much stronger base than tetrahydrofuran,[4] and therefore the rate and extent of reaction of tetraborane(10) with trimethylphosphine are expected to be greater than those with tetrahydrofuran. However, when the reaction of tetraborane(10) with trimethylphosphine is performed in tetrahydrofuran as the solvent, due to the predominant concentration of tetrahydrofuran in the reaction mixture, B_4H_{10} will react with both $P(CH_3)_3$ and tetrahydrofuran, and the products of the tetrahydrofuran reaction will further react with $P(CH_3)_3$. The reactions of the B_4H_{10}–tetrahydrofuran reaction products with $P(CH_3)_3$, therefore, were investigated first.

Earlier, Schaeffer, Tebbe, and Phillips[5] found that B_4H_{10} reacted with tetrahydrofuran at −68 to −53 °C to form $H_2B(THF)_2{}^+B_3H_8{}^-$, which at higher temperatures (above −24 °C) changed into a 1:1 mixture of $THF\cdot BH_3$ and $THF\cdot B_3H_7$. We reinvestigated the reactions using a larger quantity of tetrahydrofuran than that in the earlier study and found that the formation of $H_2B(THF)_2{}^+B_3H_8{}^-$ slowly proceeded to completion even at −80 °C.

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0020-1669/83/1322-3300$01.50/0

$$B_4H_{10} + 2\text{THF} \xrightarrow[\text{THF}]{-80\ ^\circ\text{C}} H_2B(\text{THF})_2{}^+B_3H_8{}^- \qquad (1)$$

The conversion of the $B_3H_8^-$ salt into the mixture of $THF\cdot BH_3$ and $THF\cdot B_3H_7$ occurred only above −30 °C, and the rate of the conversion was slow even at 0 °C.

$$H_2B(\text{THF})_2{}^+B_3H_8{}^- \xrightarrow[\text{THF}]{-30\ ^\circ\text{C}} \text{THF}\cdot BH_3 + \text{THF}\cdot B_3H_7 \qquad (2)$$

When a tetrahydrofuran solution containing only $H_2B(THF)_2{}^+B_3H_8{}^-$ was treated with $P(CH_3)_3$ in a 1:1 molar ratio, the $B_3H_8^-$ salt remained unchanged as long as the mixture was kept at −80 °C. At higher temperatures (−60 to −40 °C) a reaction occurred, and **$(CH_3)_3P\cdot BH_3$ and $THF\cdot B_3H_7$** were produced. At much higher temperatures (−10 to +25 °C), in addition to the two borane adducts, the $H_2B[P(CH_3)_3]_2{}^+$ cation and $THF\cdot BH_3$ were found among the products. These observations are summarized by eq 3–5. The decomposition of $H_2B(THF)_2{}^+B_3H_8{}^-$ (eq 2) also occurred at the higher temperatures.

$$H_2B(\text{THF})_2{}^+B_3H_8{}^- + P(CH_3)_3 \xrightarrow[\text{THF}]{-80\ ^\circ\text{C}} \text{no reaction} \qquad (3)$$

$$H_2B(\text{THF})_2{}^+B_3H_8{}^- + P(CH_3)_3 \xrightarrow[\text{THF}]{\text{above } -60\ ^\circ\text{C}} (CH_3)_3P\cdot BH_3 + \text{THF}\cdot B_3H_7 + \text{THF} \qquad (4)$$

$$H_2B(\text{THF})_2{}^+B_3H_8{}^- + 2P(CH_3)_3 \xrightarrow[\text{THF}]{\text{above } -10\ ^\circ\text{C}} H_2B[P(CH_3)_3]_2{}^+B_3H_8{}^- + 2\text{THF} \qquad (5)$$

When a tetrahydrofuran solution containing $THF\cdot BH_3$ and $THF\cdot B_3H_7$ was treated with a 1-equiv quantity of $P(CH_3)_3$ at −80 °C, a rapid, clean reaction occurred. **Trimethylphosphine–borane(3) and $THF\cdot B_3H_7$** were the products.

$$\text{THF}\cdot BH_3 + \text{THF}\cdot B_3H_7 + P(CH_3)_3 \xrightarrow[\text{THF}]{-80\ ^\circ\text{C}} (CH_3)_3P\cdot BH_3 + \text{THF}\cdot B_3H_7 + \text{THF} \qquad (6)$$

The resulting solution was stable at room temperature and no change could be detected during a period of several days. Upon longer standing at room temperature, however, the solution was producing $THF\cdot BH_3$ and $(CH_3)_3P\cdot B_3H_7$ slowly. Alternatively, a 1:1 mixture of $THF\cdot BH_3$ and $(CH_3)_3P\cdot B_3H_7$ in tetrahydrofuran slowly produced $(CH_3)_3P\cdot BH_3$ and $THF\cdot B_3H_7$ at room temperature.

$$(CH_3)_3P\cdot BH_3 + \text{THF}\cdot B_3H_7 \rightleftharpoons \text{THF}\cdot BH_3 + (CH_3)_3P\cdot B_3H_7 \qquad (7)$$

The equilibrium constant for eq 7 was estimated to be in the range 3–5.

The selective formation of $(CH_3)_3P\cdot BH_3$ shown in eq 6 as well as in eq 4 is the result that one would not readily predict on the basis of the acid–base strength of the species[1c,4,6] involved in the reaction. Triborane(7) is a stronger acid than borane(3). Therefore, the formation of $(CH_3)_3P\cdot B_3H_7$ would be the preferred process if the stability of the final products dictated the course of reaction. Apparently, the ease of tetrahydrofuran displacement by $P(CH_3)_3$ was the primary factor that determined the products in the reaction concerned. Trimethylphosphine could displace tetrahydrofuran easily from $THF\cdot BH_3$, but not from $THF\cdot B_3H_7$ because of the stronger O–B bond in the latter adduct. Once $(CH_3)_3P\cdot BH_3$ had been formed, breaking the B–P bond would be difficult because of the strength of the bond. That $THF\cdot BH_3$ dissociates readily at room temperature whereas $(CH_3)_3P\cdot BH_3$ does not and that both $THF\cdot B_3H_7$ and $(CH_3)_3P\cdot B_3H_7$ are isolable solids at room temperature and no evidence for a rapid dissociation of $THF\cdot B_3H_7$ could be found in its room-temperature ^{11}B NMR spectrum[7] are known and demonstrate the relative stability of these adducts. The formation of the same pair of adducts "$(CH_3)_3P\cdot BH_3 + THF\cdot B_3H_7$" in eq 4 may be preceded by the conversion of the $B_3H_8^-$ salt into the tetrahydrofuran adducts of BH_3 and B_3H_7 as in eq 2 or by the displacement of tetrahydrofuran from the $H_2B(THF)_2{}^+$ ion by $P(CH_3)_3$ to give $H_2B\cdot THF\cdot P(CH_3)_3{}^+$ which then eliminates tetrahydrofuran for hydride ion from $B_3H_8^-$ ion. The latter process appears more likely than the former, since the reaction in eq 2 was observable only above −30 °C and since $H_2B[P(CH_3)_3]_2{}^+$ was found in the products at the higher temperatures (eq 5). The choice, however, is not unequivocal.

B. Reaction of B_4H_{10} with $P(CH_3)_3$ (1:1 Molar Ratio) in CH_2Cl_2. The reaction of B_4H_{10} with $P(CH_3)_3$ in the absence of tetrahydrofuran was investigated. Comparison of the result with that of the reaction in tetrahydrofuran should be informative for analyzing the processes that are occurring in the latter reaction. When the two reactants were mixed at −80 °C in dichloromethane, $(CH_3)_3P\cdot BH_3$, $(CH_3)_3P\cdot B_3H_7$, and a small amount of $B_4H_9^-$ ion were produced immediately. Unchanged B_4H_{10} was present also. The $B_4H_9^-$ ion disappeared slowly at this temperature and the resulting solution contained B_4H_{10}, $(CH_3)_3P\cdot BH_3$, and $(CH_3)_3P\cdot B_3H_7$ in a 1:1:1 molar ratio. A very small amount of $B_3H_8^-$ ion could be detected in the solution. When the solution was allowed to warm to room temperature, a slow change occurred as evidenced by the formation of several compounds including B_5H_9, $B_3H_8^-$, B_2H_6, and other unidentified species.

The initial formation of $B_4H_9^-$ ion in the above reaction would be the result of deprotonation of B_4H_{10} by $P(CH_3)_3$. A similar deprotonation of B_4H_{10} by ammonia has been established:[8]

$$B_4H_{10} + P(CH_3)_3 \xrightleftharpoons{-80\ ^\circ\text{C}} (CH_3)_3PH^+ + B_4H_9{}^- \qquad (8)$$

The symmetrical cleavage of B_4H_{10} also occurred rapidly at −80 °C:

$$B_4H_{10} + 2P(CH_3)_3 \xrightarrow[CH_2Cl_2]{-80\ ^\circ\text{C}} (CH_3)_3P\cdot BH_3 + (CH_3)_3P\cdot B_3H_7 \qquad (9)$$

The reverse reaction of eq 8 would have provided free $P(CH_3)_3$, which further reacted with B_4H_{10} according to eq 9. Thus, the overall reaction was the symmetrical cleavage of B_4H_{10} by $P(CH_3)_3$.

The stronger acid strength of B_3H_7 relative to that of BH_3 may imply that $P(CH_3)_3$ would remove the B_3H_7 portion from B_4H_{10} ("$B_3H_7\cdot BH_3$") by forming $(CH_3)_3P\cdot B_3H_7$ and liberating B_2H_6 and that B_4H_{10} would undergo a metathetical reaction with $(CH_3)_3P\cdot BH_3$ to give $(CH_3)_3P\cdot B_3H_7$ and B_2H_6. No evidence, however, for the diborane formation could be found at the low temperature where the symmetrical cleavage was complete. The excess B_4H_{10} remained unchanged in the presence of $(CH_3)_3P\cdot BH_3$ at that temperature. Diborane(6) was produced when the mixture was warmed to room temperature. The reaction that produced B_2H_6, however, was complex in that other products were formed simultaneously, and it is as yet undefined.

C. Reaction of B_4H_{10} with $P(CH_3)_3$ (1:1 Molar Ratio) in Tetrahydrofuran. The result of this reaction at low temperatures was described in an earlier paper.[3] In short, the initial, fast reaction at −90 °C was the deprotonation of B_4H_{10} (eq 8). At −70 °C, $B_3H_8^-$ ion, **$(CH_3)_3P\cdot BH_3$, and $THF\cdot B_3H_7$** were produced fast at the expense of $B_4H_9^-$ and B_4H_{10}. After the latter two species had disappeared, no further reaction occurred

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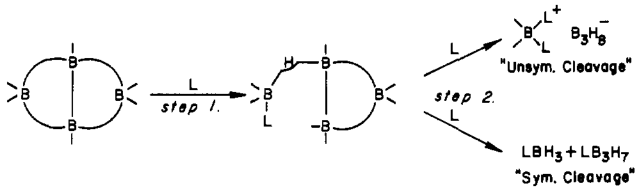
Scheme I



although free $P(CH_3)_3$ was still present in the solution. Apparently, B_4H_{10} had undergone reactions with tetrahydrofuran and $P(CH_3)_3$ in two different ways:

$$B_4H_{10} + 2THF \xrightarrow[THF]{-70\ °C} H_2B(THF)_2{}^+B_3H_8{}^- \quad (1)$$

$$B_4H_{10} + P(CH_3)_3 + THF \xrightarrow[THF]{-70\ °C} (CH_3)_3P{\cdot}BH_3 + THF{\cdot}B_3H_7 \quad (10)$$

No $(CH_3)_3P{\cdot}B_3H_7$, or a very small amount if any of it, could be detected in the solution. Tetraborane(10) was cleaved symmetrically by $P(CH_3)_3$ and tetrahydrofuran (eq 10). When the temperature of the solution was raised above −60 °C, the reaction of $H_2B(THF)_2{}^+B_3H_8{}^-$ with $P(CH_3)_3$ occurred according to eq 4.

Earlier, as an extension of a mechanism proposed for the reactions of diborane(6) with bases,[9] a mechanism was suggested for the reactions of B_4H_{10} with bases.[2b,5,10] In the mechanism, an unstable, reactive adduct is formed at the first step of the reaction between B_4H_{10} and the reacting base. The intermediate then undergoes the second-step reaction with the base to give the final products. See Scheme I.

We saw that the reaction of B_4H_{10} with $P(CH_3)_3$ (eq 9) is much faster than that with tetrahydrofuran (eq 1). In the reaction of current concern, however, there was 40 times more tetrahydrofuran than $P(CH_3)_3$. Therefore, the participation of tetrahydrofuran in the reaction would be appreciable. The reaction of B_4H_{10} with tetrahydrofuran produces $H_2B(THF)_2{}^+B_3H_8{}^-$ by way of the intermediate "$THF{\cdot}B_4H_{10}$". The $B_3H_8{}^-$ salt, once formed, is inert to $P(CH_3)_3$ (eq 3) under the conditions of the reaction. The intermediate "$THF{\cdot}B_4H_{10}$" would react with $P(CH_3)_3$ also. The probable process of the $P(CH_3)_3$ reaction is the displacement of tetrahydrofuran from the intermediate by $P(CH_3)_3$ to form "$(CH_3)_3P{\cdot}B_4H_{10}$", as tetrahydrofuran in $THF{\cdot}BH_3$ was displaced readily by $P(CH_3)_3$ at the low temperature and $(CH_3)_3P{\cdot}BH_3$ was produced. The intermediate "$(CH_3)_3P{\cdot}B_4H_{10}$" would also be formed by the direct reaction of B_4H_{10} with $P(CH_3)_3$, and it would undergo fast reactions with the bases present in the solution. In this second step of the mechanism, the reaction with tetrahydrofuran predominates because of its overwhelming concentration. The net result is that shown in eq 10. Once formed, $THF{\cdot}B_3H_7$ is inert to $P(CH_3)_3$ at the low temperature. As the reaction progresses, the ratio $THF{:}P(CH_3)_3$ in the solution increases, and thus the concentration effect is enhanced further. In our reaction of B_4H_{10} with $P(CH_3)_3$ in tetrahydrofuran, the formation of $(CH_3)_3P{\cdot}BH_3$ was faster than the formation of $B_3H_8{}^-$ ion *at the early stage of the reaction*, but it slowed down soon while the slow formation of $B_3H_8{}^-$ ion continued. Furthermore, when the reaction was performed with the use of a limited amount of tetrahydrofuran ($THF{:}P(CH_3)_3 \simeq 3$) in dichloromethane as the solvent, $(CH_3)_3P{\cdot}B_3H_7$ was produced in a considerable amount along with $(CH_3)_3P{\cdot}BH_3$. The amount of $THF{\cdot}B_3H_7$ produced was correspondingly small, and the formation of $B_3H_8{}^-$ ion was slow. These observations are in accord with interpretation presented above. The seemingly anomalous symmetrical cleavage of B_4H_{10} is thus explainable with the use of the mechanistic model proposed earlier by taking the concentration effect of the reacting bases into consideration.

D. Reactions of B_4H_{10} with $P(CH_3)_3$ (1:1 Molar Ratio) in Dimethyl Ether and in Diethyl Ether. An explanation was developed in the foregoing section for the selective formation of $(CH_3)_3P{\cdot}BH_3$ and $THF{\cdot}B_3H_7$ in the reaction of B_4H_{10} with $P(CH_3)_3$ in tetrahydrofuran. The model suggests that the formation of $(CH_3)_3P{\cdot}B_3H_7$ would be augmented if a more weakly basic solvent was used in place of tetrahydrofuran to counterbalance the concentration effect. When dimethyl ether was used as the solvent, $(CH_3)_3P{\cdot}BH_3$, $(CH_3)_3P{\cdot}B_3H_7$, $(CH_3)_2O{\cdot}B_3H_7$, $(CH_3)_2O{\cdot}BH_3$, and $B_3H_8{}^-$ ion were produced at −80 °C. The molar ratio $(CH_3)_3P{\cdot}B_3H_7{:}(CH_3)_3P{\cdot}BH_3$ was about 0.2 and the ratio $B_3H_8{}^-{:}(CH_3)_3P{\cdot}BH_3$ was about 0.1. Corresponding values for the reaction in tetrahydrofuran were <0.05 and 0.3, respectively, indicating that the effect of solvent basicity on the product distribution is significant. Furthermore, the reaction in diethyl ether produced $(CH_3)_3P{\cdot}B_3H_7$ and $(CH_3)_3P{\cdot}BH_3$ in a 0.6:1.0 molar ratio, and no $B_3H_8{}^-$ ion. Noted in the reaction was the formation of $(C_2H_5)_2O{\cdot}B_3H_7$. Since B_4H_{10} is known to be inert to diethyl ether at low temperatures and it reacts only slowly with the ether at room temperature, the presence of $P(CH_3)_3$ in the solution must be responsible for the formation of the ether adduct of triborane(7). Thus the second step reaction of the B_4H_{10} cleavage process appears to be sensitive even to a weakly basic ligand such as diethyl ether.

E. Reactions of B_4H_{10} with $N(CH_3)_3$ and with PH_3 (1:1 Ratios) in Tetrahydrofuran. To further test the applicability of the mechanistic model presented earlier, reactions of B_4H_{10} with $N(CH_3)_3$ and with PH_3 were examined. When B_4H_{10} and $N(CH_3)_3$ were mixed in tetrahydrofuran at −80 °C, $B_4H_9{}^-$ and $B_3H_8{}^-$ ions were formed first as the major products. The $B_4H_9{}^-$ ion slowly converted into $B_3H_8{}^-$ ion, $(CH_3)_3N{\cdot}BH_3$, and $THF{\cdot}B_3H_7$. Thus, the pattern of the reaction was largely the same as that of the $P(CH_3)_3$ reaction.

$$B_4H_{10} + N(CH_3)_3 \xrightleftharpoons{-80\ °C} (CH_3)_3NH^+B_4H_9{}^- \quad (11)$$

$$B_4H_{10} + 2THF \xrightarrow{-80\ °C} H_2B(THF)_2{}^+B_3H_8{}^- \quad (1)$$

$$B_4H_{10} + N(CH_3)_3 + THF \xrightarrow{-80\ °C} (CH_3)_3N{\cdot}BH_3 + THF{\cdot}B_3H_7 \quad (12)$$

The $B_3H_8{}^-$ salt ($H_2B(THF)_2{}^+B_3H_8{}^-$) is inert to $N(CH_3)_3$ in tetrahydrofuran up to about −40 °C. The unsymmetrical cleavage (eq 1) proceeded more extensively than the symmetrical cleavage (eq 12), whereas the situation was reverse in the reaction involving $P(CH_3)_3$. This difference in the extent of the two types of reactions is attributable to the relative base strength of $P(CH_3)_3$ and $N(CH_3)_3$. Trimethylamine is a weaker base than $P(CH_3)_3$ toward boranes.[4]

Phosphine, PH_3, is a much weaker base than $P(CH_3)_3$ and $N(CH_3)_3$ toward boranes[4] and is a poorer proton acceptor than the two bases.[11] When B_4H_{10} and PH_3 were mixed in a 1:1 molar ratio in tetrahydrofuran at low temperatures (−80 to −50 °C), only the unsymmetrical cleavage of B_4H_{10} by tetrahydrofuran (eq 1) occurred. Phosphine appeared too weak a base to undergo the first-step reaction of the mechanism. No evidence for the deprotonation of B_4H_{10} could be seen either. As the temperature was raised slowly, $H_3P{\cdot}BH_3$, $THF{\cdot}BH_3$, and $THF{\cdot}B_3H_7$ began to appear at −30 to −20 °C, which corresponded to the decomposition temperature of

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$H_2B(THF)_2{}^+B_2H_8{}^-$ in tetrahydrofuran (eq 2). Phosphine–triborane(7), $H_3P{\cdot}B_3H_7$, was not produced until the solution was warmed to 0 °C. In a separate experiment, $H_2B(THF)_2{}^+B_3H_8{}^-$ was treated with PH_3 in a tetrahydrofuran solution. The pattern of product formation was the same as described above. When a 1:1 mixture of $THF{\cdot}BH_3$ and $THF{\cdot}B_3H_7$ was treated with 1 equiv of PH_3 in tetrahydrofuran, $H_3P{\cdot}BH_3$ began to form at –60 °C. However, in this reaction also, $H_3P{\cdot}B_3H_7$ did not appear until the solution was warmed to 0 °C.

$$THF{\cdot}BH_3 + THF{\cdot}B_3H_7 + PH_3 \xrightarrow{-60\ ^\circ C} H_3P{\cdot}BH_3 + THF{\cdot}B_3H_7 + THF \quad (13)$$

Here again, the strong dative O–B bond in $THF{\cdot}B_3H_7$ appeared to prevent the displacement of tetrahydrofuran from the adduct at the low temperature. At 0 °C an equilibrium was reached slowly.

$$H_3P{\cdot}BH_3 + THF{\cdot}B_3H_7 \rightleftharpoons THF{\cdot}BH_3 + H_3P{\cdot}B_3H_7 \quad (14)$$

A value of 0.41 ± 0.02 was obtained for the equilibrium constant of eq 14 at 0 °C.

F. Summary. The results of this study indicated that the reaction of B_4H_{10} with $P(CH_3)_3$ in tetrahydrofuran can be generalized as a special case of the same reaction in ether solutions. Generally, $(CH_3)_3P{\cdot}BH_3$, $(CH_3)_3P{\cdot}B_3H_7$, ether$\cdot B_3H_7$, and $H_2B(ether)_2{}^+B_3H_8{}^-$ are the products of the reactions in these solutions at –90 to –70 °C. Trimethylphosphine–borane(3) is always the major product. The extent of the ether participation in the reaction depends upon the base strength of the ether. In strongly basic ethers (e.g. tetrahydrofuran), the formation of the ether adduct of B_3H_7 is enhanced and that of $(CH_3)_3P{\cdot}B_3H_7$ is suppressed. This situation is reversed in weakly basic ethers (e.g. diethyl ether), and a considerable amount of $(CH_3)_3P{\cdot}B_3H_7$ is produced. The formation of $H_2B(ether)_2{}^+B_3H_8{}^-$ also parallels the base strength of the ethers.

The previously proposed mechanism for the cleavage reactions of B_4H_{10} was used to explain the observed reactions by taking the effects of relative base strength and concentrations of the reacting bases into consideration. The first step of the reaction proceeds much faster with $P(CH_3)_3$ than with the solvent ether despite of the low concentration of the phosphine in the reaction system. Once $P(CH_3)_3$ has been attached to one of the boron atoms of B_4H_{10}, the P–B bond remains connected and this moiety becomes $(CH_3)_3P{\cdot}BH_3$ through the second-step reaction. Thus, $(CH_3)_3P{\cdot}BH_3$ is found as the major product of the cleavage reaction. The second step of the mechanism is fast, and therefore the participation of the solvent ether becomes significant due to its high concentration in the reaction system. Here again, more strongly basic ethers participate more extensively in the reaction. Thus, the formation of $(CH_3)_3P{\cdot}B_3H_7$ becomes minimal when tetrahydrofuran is used as the solvent, and the result is the cleavage of B_4H_{10} by two different bases. The above mechanistic model also explains the reactions of B_4H_{10} with $N(CH_3)_3$ and PH_3 in tetrahydrofuran.

Experimental Section

A. Chemicals and Apparatus. Conventional vacuum-line techniques were used for the handling of volatile compounds. Tetraborane(10) used was our laboratory stock[12] or was prepared by the hydrolysis of laboratory stock B_5H_{11}.[13,14] Trimethylphosphine and phosphine were also laboratory stock[6] that had been prepared by the literature methods. Trimethylamine and dimethyl ether from cylinders (Matheson Gas Products) were fractionated on the vacuum line. Reagent grade tetrahydrofuran and diethyl ether were stored over $LiAlH_4$, and dichloromethane was stored over molecular sieves. These solvents were distilled from the containers directly into the vacuum line as needed.

A Varian XL-100 NMR spectrometer was used for the ^{11}B NMR spectrum recording. The instrument was operated at 32.1 MHz in the FT mode and was equipped with a temperature-control unit and a ^1H-spin-decoupling unit. Shifts were measured with respect to the $BF_3{\cdot}O(C_2H_5)_2$ signal.

B. Reaction Studies. 1. General Procedures. Ten-millimeter-o.d. Pyrex tubes, each equipped with a stopcock, were used as the reaction vessels. The reaction mixture was prepared by condensing the solvent and the reactants in the tube at –197 °C and by shaking the tube in a cold bath (–95 or –80 °C) to obtain a uniform solution. Then, the tube was placed in the cold probe of the NMR instrument for recording of the ^{11}B resonance spectra. When the reactions of B_4H_{10} with bases, i.e. $P(CH_3)_3$, $N(CH_3)_3$, and PH_3, were performed, first the solution of the base was prepared, and then B_4H_{10} was condensed above the frozen solution. This procedure was taken in order to avoid the contact of B_4H_{10} with a high concentration of the base, which would occur if the procedure was reversed. Usually, about 2.0 mL of solvent and a 0.5-mmol quantity of B_4H_{10} were used for each reaction. Compounds in the reaction solutions were identified by their ^{11}B shift values.[15]

2. Preparation of $H_2B(THF)_2{}^+B_3H_8{}^-$ and "$THF{\cdot}BH_3 + THF{\cdot}B_3H_7$" Solutions in Tetrahydrofuran. A measured amount of B_4H_{10} (ca. 0.5 mmol) was dissolved in 1.5–1.8 mL of tetrahydrofuran at –80 °C, and the solution was kept at –63 °C for 3 h. The ^{11}B NMR spectrum of the solution indicated that the conversion of B_4H_{10} into $H_2B(THF)_2{}^+B_3H_8{}^-$ was complete. The solutions thus prepared were treated with the reacting bases ($P(CH_3)_3$, $N(CH_3)_3$, and PH_3), and the changes were monitored by the ^{11}B NMR spectra of the solutions as the temperature was raised from –80 °C.

To prepare the solution of "$THF{\cdot}BH_3 + THF{\cdot}B_3H_7$" in tetrahydrofuran, B_4H_{10} and tetrahydrofuran were mixed in the same manner as that described above, and the solution was kept at 0 °C for 4 h. The complete conversion of B_4H_{10} into the two adducts was confirmed by the ^{11}B NMR spectrum of the solution. The solution was treated with the base ($P(CH_3)_3$, $N(CH_3)_3$, or PH_3), and the reaction was monitored likewise.

3. Product Distributions in the Reactions of B_4H_{10} with $P(CH_3)_3$. a. In Tetrahydrofuran. Reactants: B_4H_{10}, 0.448 mmol; $P(CH_3)_3$, 0.461 mmol; THF, 2.0 mL. Products: $(CH_3)_3P{\cdot}BH_3$:$THF{\cdot}B_3H_7$:$H_2B(THF)_2{}^+B_3H_8{}^-$, 1:1:0.3 (–70 °C). Above –20 °C, $B_3H_8{}^-$ disappeared and $THF{\cdot}BH_3$ grew in.

b. In Tetrahydrofuran/Dichloromethane. Reactants: B_4H_{10}, 0.470 mmol; $P(CH_3)_3$, 0.455 mmol; THF, 1.23 mmol; CH_2Cl_2, 1.5 mL. Products: $(CH_3)_3P{\cdot}BH_3$:$(CH_3)_3P{\cdot}B_3H_7$:$THF{\cdot}B_3H_7$:$B_3H_8{}^-$:B_4H_{10}:$THF{\cdot}BH_3$, 1.00:0.57:0.52:0.32:0.03:0.00 (–80 °C), 1.00:0.63:0.87:0.08:0.00:0.18 (+25 °C).

c. In Dichloromethane. Reactants: B_4H_{10}, 0.456 mmol; $P(CH_3)_3$, 0.435 mmol; CH_2Cl_2, 1.5 mL. Products: B_4H_{10}:$(CH_3)_3P{\cdot}BH_3$:$(CH_3)_3P{\cdot}B_3H_7$, 1:1:1 (–80 °C).

d. In Dimethyl Ether. Reactants: B_4H_{10}, 0.534 mmol; $P(CH_3)_3$, 0.527 mmol; $(CH_3)_2O$, 2.0 mL. Products: $(CH_3)_3P{\cdot}BH_3$:$(CH_3)_3P{\cdot}B_3H_7$:$(CH_3)_2O{\cdot}B_3H_7$:$B_3H_8{}^-$:B_4H_{10}:$(CH_3)_2O{\cdot}BH_3$, 1.00:0.20:0.98:0.12:0.02:0.31 (–80 °C), 1.00:0.18:0.88:0.08:0.0:0.22 (–40 °C). A weak signal of an unidentified species at +26.1 ppm (d, J_{BH} = 165 Hz) was seen.

e. In Diethyl Ether. Reactants: B_4H_{10}, 0.465 mmol; $P(CH_3)_3$, 0.451 mmol; $(C_2H_5)_2O$, 2.2 mL. Products: $(CH_3)_3P{\cdot}BH_3$:$(CH_3)_3P{\cdot}B_3H_7$:$(C_2H_5)_2O{\cdot}B_3H_7$:B_4H_{10}:B_2H_6, 1.00:0.56:0.40:0.46:0.13 (+20 °C). The formation of $(CH_3)_3P{\cdot}BH_3$ and $(CH_3)_3P{\cdot}B_3H_7$ was observed at –90 °C. The reaction proceeded slowly below –30 °C, but rapidly above –20 °C. The B_2H_6 signal was not present in the 0 °C spectrum in which the signal of $(C_2H_5)_2O{\cdot}B_3H_7$ was strong. At

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(15) The ^{11}B shift values for most of the compounds that appeared in this study were found conveniently in ref 16. Listed below are the compounds, the values of which were found elsewhere as indicated: $B_4H_9{}^-$,[8] $H_2B(THF)_2{}^+$,[17] $THF{\cdot}B_3H_7$,[7] $(C_2H_5)_2O{\cdot}B_3H_7$,[7] $(CH_3)_2O{\cdot}B_3H_7$,[18] $(CH_3)_3P{\cdot}B_3H_7$,[6] $H_3P{\cdot}B_3H_7$,[6] $(CH_3)_3N{\cdot}B_3H_7$.[12]

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(18) Found in this study: –6.9 ($B_{2,3}$) and –9.9 (B_1) ppm at –40 °C in dimethyl ether.

+20 °C the B_2H_6 signal was growing in slowly.

C. Equilibrium Studies. 1. $(CH_3)_3P{\cdot}BH_3$ + THF·B_3H_7 $\rightleftharpoons$ THF·BH_3 + $(CH_3)_3P{\cdot}B_3H_7$. The reaction solution in section B.3.a was allowed to stand at room temperature (about 25 °C), and its ^{11}B NMR spectra were recorded from time to time. Another tube containing 0.485 mmol of $(CH_3)_3P{\cdot}B_3H_7$ and 0.261 mmol of B_2H_6 in 1.8 mL of tetrahydrofuran was prepared, and the spectra of its contents were recorded likewise. The intensities of the four species in the title reaction were measured on each spectrum and were used to find the value of $[THF{\cdot}BH_3][(CH_3)_3P{\cdot}B_3H_7]/[(CH_3)_3P{\cdot}BH_3][THF{\cdot}B_3H_7]$ at the time of the spectrum recording. The values for the two samples slowly converged to a value of 4 ± 1 in a period of 8 months. The signals of B_2H_6 and B_5H_9 and a signal of an unidentified species at +26 ppm were present in the final spectra. The solutions were clear and colorless.

2. $H_3P{\cdot}BH_3$ + THF·B_3H_7 $\rightleftharpoons$ THF·BH_3 + $H_3P{\cdot}B_3H_7$. The solutions, which were used for the studies of reactions of $H_2B(THF)_2{}^+B_3H_8{}^-$, "THF·$BH_3$ + THF·B_3H_7", and B_4H_{10} with PH_3, were stored at 0 °C for 67 h. The equilibrium appeared to have been reached within 24 h. The values of $[THF{\cdot}BH_3][H_3P{\cdot}B_3H_7]/[H_3P{\cdot}BH_3][THF{\cdot}B_3H_7]$ for the three samples were 0.43, 0.42, and 0.38; average 0.41 ± 0.02. Prolonged standing (ca. 1 month) of the sample solutions at room temperature resulted in the formation of a white precipitate. Various identified (THF·B_3H_7, B_2H_6, and B_5H_9) and unidentified signals were seen in the ^{11}B spectra of these deteriorated samples, and no signals of $H_3P{\cdot}BH_3$ and $H_3P{\cdot}B_3H_7$ were found.

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Registry No. $H_2B(THF)_2{}^+B_3H_8{}^-$, 55669-45-9; THF·$BH_3$, 14044-65-6; THF·$B_3H_7$, 52842-96-3; B_4H_{10}, 18283-93-7; $(CH_3)_3P{\cdot}BH_3$, 35527-73-2; $(CH_3)_3P{\cdot}B_3H_7$, 12543-29-2; $(CH_3)_2O{\cdot}B_3H_7$, 12347-17-0; $(CH_3)_2O{\cdot}BH_3$, 13292-86-9; $(C_2H_5)_2O{\cdot}B_3H_7$, 52842-97-4; $P(CH_3)_3$, 594-09-2; CH_2Cl_2, 75-09-2; $(CH_3)_2O$, 115-10-6; $(C_2H_5)_2O$, 60-29-7; THF, 109-99-9.

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Kinetics of the Reduction of the Tetrahydroxoargentate(III) Ion by Arsenite

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The reaction of $Ag(OH)_4{}^-$ with arsenite ion to give Ag(I) and arsenate in strong base was studied by stopped-flow spectrophotometry. The reaction was found to fit a second-order rate law in which all three arsenite species present, $H_2AsO_3{}^-$, $HAsO_3{}^{2-}$, and $AsO_3{}^{3-}$, participate. Second-order rate constants for the three paths at 25 °C and $\mu = 1.2$ M are respectively $k_1 = (6.2 \pm 1.0) \times 10^3\ M^{-1}\ s^{-1}$, $k_2 = (3.7 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$, and $k_3 = (1.8 \pm 0.5) \times 10^4\ M^{-1}\ s^{-1}$. In order to evaluate the activation parameters, the temperature dependence of the deprotonation of arsenite by $[OH^-]$ was studied. The equilibrium parameters are ΔH_2(for $H_2AsO_3{}^- + OH^- \rightleftarrows HAsO_3{}^-$) = 5 ± 1 kcal/mol and ΔH_3(for $HAsO_3{}^{2-} + OH^- \rightleftarrows AsO_3{}^{3-}$) = −2 ± 7 kcal/mol ($\mu = 1$ M). The redox reaction appears to proceed by a one-step oxygen atom transfer. Two kinetically indistinguishable mechanisms are discussed: one involving initial attack of an As(III) oxygen at an axial silver(III) site and the other involving initial interaction between the arsenic and a bound hydroxyl. Differences in activation parameters are indicative of a larger barrier to redox for $AsO_3{}^{3-}$ compared to those for the other two arsenite species. The dependence of the reaction rate on ionic strength supports the formulation of the Ag(III) species as the mononegatively charged ion $Ag(OH)_4{}^-$.

Introduction

The complex $Ag(OH)_4{}^-$ is a square-planar d^8 system that is conveniently prepared by the electrochemical oxidation of a silver-foil anode in NaOH solution.[1-3] The complex is metastable and has a half-life of about 1 1/2 h in 1.2 M NaOH at room temperature. The lifetime of the complex and the maximum concentration obtainable depend on the OH^- concentration.[1,2]

Kinetic studies of the oxidation of arsenite by transition-metal complexes in alkaline media have been carried out for a limited number of systems such as $Fe(CN)_6{}^{3-}$,[4] $Mo(CN)_8{}^{3-}$,[5] $W(CN)_8{}^{3-}$,[6] and $Pt(Cl)_6{}^{2-}$.[7] The pH ranges employed for all these studies are such that the monoanion $H_2AsO_3{}^-$ is the predominant form of As(III). The reaction rates for the above-mentioned complexes all show a linear dependence on base concentration, which is accounted for by a mechanism in which the dianion is the reactive species. The rates of reduction of these complexes are many orders of magnitude less than that of $Ag(OH)_4{}^-$, which can react readily by an inner-sphere mechanism.

In their Raman study of the structure of arsenite ions in basic solution, Loehr and Plane[8] noted that at no $[OH^-]$ does $HAsO_3{}^{2-}$ exist unaccompanied by significant fractions of $H_2AsO_3{}^-$ and/or $AsO_3{}^{3-}$. A recent report on the third dissociation constant of arsenous acid indicates that it has a p*K* value only 0.5 unit greater than that of the second dissociation constant.[9] The present kinetic study supports the presence of three stoichiometrically significant arsenite species in the range $0.1 \le [OH^-] \le 1.2$ M.

Experimental Section

Reagents. The chemicals used were all of reagent grade. $Ag(OH)_4{}^-$ solutions were prepared as previously described[3] by using doubly

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