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Bis(trimethylphosphine)-Diborane(4) as a Reagent for Borane Framework Expansion

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There are few published methods available for systematic, stepwise expansions of lower borane compounds. Earlier, Shore and co-workers developed a method for expanding these types of compounds through insertion of a BH_3 group into borane anions.[1] Later, the same group developed another systematic approach for obtaining higher boranes from lower boron hydride anions.[2] This approach is based on the abstraction of a hydride ion from an anionic boron hydride using boron trihalide. The resulting reactive, neutral borane species is thought to undergo further reaction to yield an expanded borane compound.

Bis(trimethylphosphine)-diborane(4), $B_2H_4{\cdot}2P(CH_3)_3$, is reactive toward electrophiles such as hydrogen chloride, boranes, and certain transition-metal compounds.[3] Noted in several papers is the description that the diborane(4) adduct acts as a reagent for borane framework expansion. See eq 1-3. In these reactions, the diborane(4) adduct splits into $BH_3{\cdot}P(CH_3)_3$ and "$BH{\cdot}P(CH_3)_3$", and the latter combines with the respective borane substrate. On the other hand, we observed that the triborane(7) adducts of trimethylamine and trimethylphosphine *would not* react with $B_2H_4{\cdot}2P(CH_3)_3$.[4] Subsequently, we investigated the reactions of several other lower borane compounds with $B_2H_4{\cdot}2P(CH_3)_3$ to examine if the borane expansion is a general type of reaction. The results are reported in this paper.

$$B_2H_6 + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_3H_7{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 \qquad (1)^{3a}$$

$$B_3H_7{\cdot}THF + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_4H_8{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 + THF \qquad (2)^{3e}$$

$$B_5H_{11} + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_6H_{12}{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 \qquad (3)^{3c}$$

Results

Reactions of Bis(trimethylphosphine)-Diborane(4). (a) With Tetraborane(8) Adducts. The diborane(4) adduct readily reacted with phosphine-tetraborane(8), $B_4H_8{\cdot}PH_3$, at 0 °C in dichloromethane to give trimethylphosphine-pentaborane(9) [$B_5H_9{\cdot}P(CH_3)_3$] and $BH_3{\cdot}P(CH_3)_3$. Equation 4 is appropriate for this reaction. The yield of the pentaborane(9) adduct was 72% as determined by signal intensities of the ^{11}B NMR spectrum of the reaction solution. However, neither the trimethylamine or trimethylphosphine adduct of B_4H_8 reacted with $B_2H_4{\cdot}2P(CH_3)_3$ at room temperature.

$$B_4H_8{\cdot}PH_3 + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_5H_9{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 + BH_3{\cdot}PH_3 \qquad (4)$$

(b) With Trimethylphosphine-Pentaborane(9). The diborane(4) adduct reacted slowly with $B_5H_9{\cdot}P(CH_3)_3$ in dichloromethane at room temperature and yielded a mixture of several borane compounds. Trimethylphosphine-borane(3) and $B_6H_{10}{\cdot}2P(CH_3)_3$ were the two major products as determined by the ^{11}B NMR spectrum. The principal reaction is summarized by eq 5. The spectroscopic yield of $B_6H_{10}{\cdot}2P(CH_3)_3$ was 65%.

$$B_5H_9{\cdot}P(CH_3)_3 + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_6H_{10}{\cdot}2P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 \qquad (5)$$

Discussion

In contrast to the observed expansion of $B_3H_7{\cdot}THF$ and $B_4H_8{\cdot}PH_3$ by $B_2H_4{\cdot}2P(CH_3)_3$ into $B_4H_8{\cdot}P(CH_3)_3$ and $B_5H_9{\cdot}P(CH_3)_3$ (eqs 2 and 4), respectively, the trimethylamine and trimethylphosphine adducts of B_3H_7 and B_4H_8 do not undergo reaction under comparable conditions. Bonding of a strong base, like $N(CH_3)_3$ or $P(CH_3)_3$, to the B_3H_7 and B_4H_8 fragments renders these borane adducts less electrophilic, as compared with $B_3H_7{\cdot}THF$ or $B_4H_8{\cdot}PH_3$, and therefore the reaction with $B_2H_4{\cdot}2P(CH_3)_3$ is thought to be prevented.

Borane acidity generally increases with size of the borane structure.[5] Therefore, although bonded to $P(CH_3)_3$, the B_5H_9 moiety in $B_5H_9{\cdot}P(CH_3)_3$ has sufficient borane acidity, or electrophilicity, to undergo a slow expansion reaction at room temperature (eq 5). In contrast, the reaction of pentaborane(11) is rapid even at -80 °C (eq 3).[3c] Here again, the difference in borane acidity is thought to be largely responsible for the reactivity difference between these two *arachno*-pentaborane compounds.

The borane framework expansion by $B_2H_4{\cdot}2P(CH_3)_3$ appears to be a general type of reaction provided that sufficient electrophilicity is maintained in the reacting borane compound. Trimethylphosphine adducts of larger borane fragments will undergo the aforementioned expansion reaction, because increased borane acidity of large borane fragments overcomes the effect of the strong bases bonded. The observed low yields of $B_5H_9{\cdot}P(CH_3)_3$ and $B_6H_{10}{\cdot}2P(CH_3)_3$ in the above reactions (eqs 4 and 5) are, therefore, in part attributed to the further reactions of the expanded products with $B_2H_4{\cdot}2P(CH_3)_3$ to yield higher borane compounds that have yet to be characterized.

Like $B_2H_4{\cdot}2P(CH_3)_3$, other B_2H_4 adducts are reactive toward electrophilic borane compounds. We have reported the reactions of $B_2H_4{\cdot}2N(CH_3)_3$ and $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ with diborane(6) to form $B_3H_7{\cdot}N(CH_3)_3$ and $B_3H_7{\cdot}P(CH_3)_3$, respectively.[6] The B_2H_4 adducts containing different Lewis bases should exhibit varied degrees of reactivity toward electrophiles depending upon the nature of the Lewis bases involved, and therefore by choosing appropriate Lewis bases in the B_2H_4 adducts, one should be able to control the framework expansion reactions. The study is in progress, and the results will be reported at a future date.

Experimental Section

Equipment and Chemicals. Conventional vacuum-line techniques were used throughout for the handling of volatile and air-sensitive compounds. Air-sensitive solids were handled in nitrogen-filled plastic bags. Our laboratory stock $B_2H_4{\cdot}2P(CH_3)_3$ was prepared from B_5H_9 by the published method[3c] and stored at -50 °C. The other borane adducts used for the reaction studies were prepared by the methods that are described in the respective references. Reagent grade dichloromethane was refluxed and distilled over P_2O_5, stored over molecular sieves in a container, and distilled directly into the vacuum line as needed. The ^{11}B NMR spectra were recorded on a Varian XL-100-15 NMR spectrometer, operating in FT mode, equipped with a variable-temperature control unit and a spin-decoupling device. The ^{11}B chemical shift values for $BH_3{\cdot}P(CH)_3)_3$,[7] $BH_3{\cdot}PH_3$,[8] $BH_3{\cdot}N(CH_3)_3$,[8] $B_2H_4{\cdot}2P(CH_3)_3$,[3b,10] $B_3H_7{\cdot}P(CH_3)_3$,[11] $B_4H_8{\cdot}PH_3$,[12] $B_4H_8{\cdot}P(CH_3)_3$,[3e] $B_4H_8{\cdot}N(CH_3)_3$,[13] $B_5H_9{\cdot}P(CH)_3)_3$,[3c,14] and $B_6H_{10}{\cdot}2P(CH_3)_3$[15] are found in the respective references

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cited, and these were used to identify the components in the reaction mixtures.

Reactions of $B_2H_4{\cdot}2P(CH_3)_3$ with Borane Adducts. (a) With $B_4H_8{\cdot}PH_3$. A sample of $B_4H_8{\cdot}PH_3$[12] was prepared in a 10 mm o.d. Pyrex reaction tube that was equipped with a stopcock and a 10 mm o.d. side arm. A 0.54-mmol sample of B_5H_{11} and 1.41 mmol of PH_3 were used for this preparation. About 2 mL of dichloromethane was condensed into the tube to prepare a clear solution, and then the solution was frozen at −197 °C. Nitrogen gas was admitted into the tube and the side arm cut open to introduce a 0.52-mmol sample of $B_2H_4{\cdot}2P(CH_3)_3$. During this procedure an outward flow of nitrogen gas was maintained through the side arm. The side arm was then resealed, and the tube was reevacuated. The contents of the tube were mixed throughly at −80 °C to give a clear solution. The tube was then placed in the chilled probe of the NMR spectrometer to monitor the reaction starting at −80 °C.

Up to −30 °C no sign of reaction could be detected; the spectrum consisted of the signals of $B_4H_8{\cdot}PH_3$ and $B_2H_4{\cdot}2P(CH_3)_3$. At 0 °C, the signal of $BH_3{\cdot}P(CH_3)_3$ began to appear in the spectrum. In 1 h the signals of $BH_3{\cdot}P(CH_3)_3$ and $B_5H_9{\cdot}P(CH_3)_3$ were strong, and as the tube was allowed to warm to room temperature, the signals of $B_2H_4{\cdot}2P(CH_3)_3$ and $B_4H_8{\cdot}PH_3$ completely disappeared. Minor quantities of several other boron compounds were present in the final solution, identifiable components being $BH_3{\cdot}PH_3$ and B_5H_9.

(b) With $B_4H_8{\cdot}P(CH_3)_3$ and $B_4H_8{\cdot}N(CH_3)_3$. A 0.45-mmol sample of $B_4H_8{\cdot}P(CH_3)_3$[3e] was prepared by the reaction of $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$ with $N(CH_3)_3$ in a reaction tube and was treated with 0.56 mmol of $B_2H_4{\cdot}2P(CH_3)_3$ in a manner similar to that described for the $B_4H_8{\cdot}PH_3$ reaction in part a. The ^{11}B NMR spectrum of the reaction solution indicated there was no significant reaction after 12 h at room temperature; faint signals of $B_3H_7{\cdot}P(CH_3)_3$ and an unidentified borane compound (−18 ppm) were detected.

Similarly, a 0.54-mmol sample of $B_4H_8{\cdot}N(CH_3)_3$[13] was treated with 0.55 mmol of $B_2H_4{\cdot}2P(CH_3)_3$. At 0 °C, a small amount of $BH_3{\cdot}N(CH_3)_3$ formed. However, no further change occurred while the tube was kept at room temperature for 5 h.

(c) With $B_5H_9{\cdot}P(CH_3)_3$. A sample of $B_5H_9{\cdot}P(CH_3)_3$[3c] was prepared by the reaction of B_5H_{11} (0.50 mmol) with $B_2H_4{\cdot}2P(CH_3)_3$ (0.4 mmol). The amount of $B_5H_9{\cdot}P(CH_3)_3$ produced was estimated to be 0.3 mmol on the basis of the amount of B_2H_6 generated from the reaction. This sample was condensed into a reaction tube and treated with 0.4 mmol of $B_2H_4{\cdot}2P(CH_3)_3$ in a manner similar to that described above.

At 0 °C slow change began to occur; the signals of $B_6H_{10}{\cdot}2P(CH_3)_3$ and $BH_3{\cdot}P(CH_3)_3$ were discernible. As the tube was allowed to warm to room temperature, the intensities of the $B_6H_{10}{\cdot}2P(CH_3)_3$ and $BH_3{\cdot}P(CH_3)_3$ signals continued to increase slowly, and in 10 h the signals of $B_5H_9{\cdot}P(CH_3)_3$ had diminished considerably. Weak signals of $B_2H_4{\cdot}2P(CH_3)_3$ and other unidentified boron compounds were present, as determined from the final spectrum.

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Secondary (Polyfluoroalkyl)chloroamines: Precursors to Fluoroazaalkenes

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There are a very large number of fluorinated azaalkenes, and there is an excellent review of synthetic methods for and reported chemistry of these compounds.[1] A facile, nearly quantitative route to azaalkenes provided by the photolysis of $R_fN(CF_2CFXCl)Cl$ ($R_f = CF_3, C_2F_5$; X = Cl, F) has been reported.[2] We now have extended this reaction by taking advantage of recently synthesized precursors to synthesize azaalkenes.

Results and Discussion

Chlorine fluoride can be reacted smoothly with $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ to saturate the carbon–nitrogen double bond and partially fluorinate the compound. Repeated photolysis and reaction with chlorine fluoride provide a high-yield route to $CF_3N{=}CF_2$

$$\mathrm{Cl_2C{=}NCCl_2CCl_2N{=}CCl_2 + ClF \rightarrow \underset{\mathbf{1}}{CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl}}\,[3]$$

$$\mathbf{1} \xrightarrow[-2\mathrm{Cl_2}]{h\nu} \underset{\mathbf{2}}{\mathrm{CF_2ClN{=}CFCF{=}NCF_2Cl}}\,[3]$$

$$\mathbf{2} + \mathrm{2ClF} \rightarrow \underset{\mathbf{3}}{\mathrm{CF_2ClN(Cl)CF_2CF_2N(Cl)CF_2Cl}}$$

$$\mathbf{3} \xrightarrow[-\mathrm{Cl_2}]{h\nu} \underset{\mathbf{4}}{\mathrm{F_2C{=}NCF_2CF_2N{=}CF_2}} + \underset{\mathbf{5}}{\mathrm{CF_2ClN{=}CF_2}}$$

$$\mathbf{4} + \mathrm{2ClF} \rightarrow \underset{\mathbf{6}}{\mathrm{CF_3N(Cl)CF_2CF_2N(Cl)CF_3}}$$

$$\mathbf{6} \xrightarrow[-\mathrm{Cl_2}]{h\nu} \mathrm{CF_3\dot{N}{-}CF_2{-}CF_2{-}\dot{N}CF_3} \rightarrow \underset{\mathbf{7}}{\mathrm{2CF_3N{=}CF_2}}$$

Olefins, such as $CF_2{=}CFCl$, can be inserted into the N—Cl bond of $Cl_2NCF_2CF_2NCl_2$[4] to give a bis(secondary chloroamine)[3] similar to **1**

$$\mathrm{Cl_2NCF_2CF_2NCl_2 + CF_2{=}CFX \rightarrow \underset{\mathbf{8}\ (X = Cl),\ \mathbf{9}\ (X = F)}{CFXClCF_2N(Cl)CF_2CF_2N(Cl)CF_2CFXCl}}$$

$$X = \mathrm{Cl, F}$$

which can be photolyzed to the azaalkenes **10** and **11**

$$\mathbf{8}\text{ or }\mathbf{9} \xrightarrow[-\mathrm{Cl_2}]{h\nu} \underset{\mathbf{10}\ (X = Cl),\ \mathbf{11}\ (X = F)}{\mathrm{2CF_2{=}NCF_2CFXCl}}\,[5]$$

and in the presence of fluoride ion isomerization to **12** and **13** occurs:

$$\mathbf{10}\text{ or }\mathbf{11} \xrightarrow{\mathrm{CsF}} \underset{\mathbf{12}\ (X = Cl),\ \mathbf{13}\ (X = F)}{\mathrm{CF_3N{=}CFCFXCl}}$$

Dechlorofluorination of certain secondary chloroamines with triphenylphosphine also gives rise to azaalkenes:

$$\mathrm{CF_3N(Cl)CF_2CFXCl}\,[2] + \mathrm{Ph_3P} \rightarrow \mathbf{12}\text{ or }\mathbf{13}$$

$$X = \mathrm{Cl, F}$$

Experimental Section

Materials. The reagents $CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl$,[3] $CF_2ClN{=}CFCF{=}NCF_2Cl$,[3] and $Cl_2NCF_2CF_2NCl_2$[4] were prepared according to the literature; $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ was a gift of Dr. E. Klauke (Bayer AG, Laverkusen, FRG). Other chemicals were purchased and used as received: chlorine fluoride (Ozark-Mahoning); $CF_2{=}CF_2$ and $CF_2{=}CFCl$ (PCR); and CsF (American Potash).

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system fitted with a Heise Bourdon tube and Televac thermocouple gauges. Volatile starting materials and products were quantitated by using *PVT* techniques. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform infrared spectrometer with a 10-cm gas cell equipped with KBr windows. ^{19}F

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