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Isolation and Characterization of Trimethylamine–Tetraborane(8)

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The formerly elusive trimethylamine adduct of tetraborane(8), $(CH_3)_3N{\cdot}B_4H_8$, was prepared by the displacement reaction of alkyl sulfide–tetraborane(8) with trimethylamine. It also could be isolated from the products of pentaborane(11) reaction with trimethylamine. The compound melts at about 40 °C and is stable indefinitely below 0 °C. The trimethylamine adduct forms a bis(trimethylamine) adduct of tetraborane(8), $B_4H_8{\cdot}2N(CH_3)_3$, upon reaction with trimethylamine at low temperatures. Anhydrous hydrogen chloride (or bromide) reacts readily with $(CH_3)_3N{\cdot}B_4H_8$ to give $(CH_3)_3N{\cdot}B_3H_7$ and $H_2BCl{\cdot}$ether (or $H_2BBr{\cdot}$ether) in ether solutions and to give $(CH_3)_3N{\cdot}B_3H_6Cl$ (or $(CH_3)_3N{\cdot}B_3H_6Br$) and B_2H_6 in dichloromethane. Boron-11 and proton NMR spectra of the mono- and bis(trimethylamine) adducts are described.

Introduction

Since the carbon monoxide adduct of tetraborane(8), B_4H_8, was isolated by Burg and Spielman[1] in 1959, a goodly number of fluorophosphine adducts of tetraborane(8) have been reported in the literature.[2] Strangely, however, amine adducts of tetraborane(8) had not been known until Kondo and Kodama isolated hexamethylenetetramine–tetraborane(8)[3] which is reported concurrently with this paper. A representative amine adduct of tetraborane(8), the trimethylamine adduct, would be expected to be obtained by the reaction of pentaborane(11) with trimethylamine as the other B_4H_8 adducts have been prepared in similar manners[1,2] and as trimethylamine is known to cleave diborane(6) and tetraborane(10) to give $(CH_3)_3N{\cdot}BH_3$ and to give $(CH_3)_3N{\cdot}BH_3$ and $(CH_3)_3N{\cdot}B_3H_7$, respectively.[4] The reaction of B_5H_{11} with the amine, however, was reported to give a complex mixture of boron hydride compounds,[5] and the adduct "$(CH_3)_3N{\cdot}B_4H_8$" was assumed to be unstable.[5b,6]

Having found that hexamethyleneteramine–tetraborane(8) is isolable and that thioether–tetraborane(8)[7] is stable at low temperatures in solution phases, we directed our effort to look for direct evidence for the formation of the assumed "$(CH_3)_3N{\cdot}B_4H_8$" and to study the properties of the compound. In this study the compound $(CH_3)_3N{\cdot}B_4H_8$ was isolated as a solid which is fairly stable at room temperature. This paper describes the preparation and characterization of the trimethylamine adduct.

Results and Discussion

A. Isolation of Trimethylamine–Tetraborane(8).

(a) By the Displacement Reaction of $R_2S{\cdot}B_4H_8$ with Trimethylamine. Treatment of a pentaborane(11) solution in dichloromethane with dimethyl or diethyl sulfide (R_2S) at −80 °C gives a solution containing $R_2S{\cdot}BH_3$ and $R_2S{\cdot}B_4H_8$.[7] When this solution is treated with trimethylamine, and then the volatile components are distilled out from the reaction system under vacuum, a colorless crystalline solid remains in the reaction vessel. Elemental analysis of the solid and the stoichiometry of the reaction suggested the solid to be $(CH_3)_3N{\cdot}B_4H_8$. The reactions are appropriately expressed by

$$B_5H_{11} + 2R_2S \rightarrow R_2S{\cdot}BH_3 + R_2S{\cdot}B_4H_8$$

$$R_2S{\cdot}BH_3 + R_2S{\cdot}B_4H_8 + 2N(CH_3)_3 \rightarrow (CH_3)_3N{\cdot}BH_3 + \underline{(CH_3)_3N{\cdot}B_4H_8} + 2R_2S$$

The new compound, $(CH_3)_3N{\cdot}B_4H_8$, can be sublimed for purification at room temperature. The compound thus purified melts at about 40 °C and stays unchanged at room temperature in vacuo over a period of 12 h. At or below 0 °C even the unsublimed solid is indefinitely stable.

(b) By the Direct Symmetrical Cleavage Reaction of Pentaborane(11). The compound $(CH_3)_3N{\cdot}B_4H_8$ can also be prepared by the direct reaction of pentaborane(11) with *excess* trimethylamine in dichloromethane or in the absence of solvent. The reaction can be regarded as the symmetrical cleavage[8] of pentaborane(11) by trimethylamine:

$$B_5H_{11} + 2N(CH_3)_3 \rightarrow (CH_3)_3N{\cdot}BH_3 + \underline{(CH_3)_3N{\cdot}B_4H_8}$$

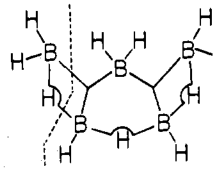

Table I. NMR Spectral Data for $(CH_3)_3N{\cdot}B_4H_8$

	shift,[a] ppm	multiplicity[b]	J, Hz	assignt
^{11}B[d]	1.1	d	130	B(3)
	−8.5	t	116	B(2,4)
	−22.5	d	116	B(1)
$^1H\{^{11}B\}$[e]	3.11	s (q)[c]	133[c]	H(3)
	2.55	s		H_C
	1.99	s		H(2,4) (a or e)
	1.76	s		H(2,4) (e or a)
	1.06(?)	s		H(1)
	−2.04	s		H_b

[a] B: reference $BF_3{\cdot}O(C_2H_5)_2$; downfield taken as positive. H: in δ. [b] s = singlet; d = doublet; t = triplet; q = quartet. [c] Undecoupled spectrum at 25 °C. [d] 0 °C in CD_2Cl_2. [e] −40 °C in CD_2Cl_2.

The tetraborane(8) adduct thus prepared, however, is usually less stable than the one prepared by the base displacement reaction described above. The solid is often slightly yellowish upon isolation and/or decomposes readily upon standing at room temperature.

B. Characterization of $(CH_3)_3N{\cdot}B_4H_8$.

(a) Mass Spectrum. The mass spectrum of the compound gives the high-mass cutoff at m/e 111, which corresponds to the parent molecular ion $(CH_3)_3N^{11}B_4H_8^+$. The observed intensity ratio for the high-cutoff region is not consistent with that expected from the natural isotopic abundance for $(CH_3)_3N{\cdot}B_4H_8^+$ but is in good agreement with that calculated for a mixture of $(CH_3)_3N{\cdot}B_4H_8^+$, $(CH_3)_3N{\cdot}B_4H_6^+$, and $(CH_3)_3N{\cdot}B_4H_4^+$ in a 9.4:89.7:1.0 ratio [m/e (observed intensity, calculated intensity)]: 113 (0.0, 0.0), 112 (0.0, 0.1), 111 (2.2, 2.7), 110 (4.1, 3.4), 109 (25.8, 26.4), 108 (25.4, 24.8), 107 (9.3, 9.3), 106 (1.8, 1.7), 105 (0.0, 0.2), 104 (0.0, 0.0). Similar successive loss of pairs of hydrogen atoms from the parent molecule has been observed in the mass spectra of other boron hydride compounds.[9,10,2e]

(b) ^{11}B NMR Spectra. The ^{11}B NMR spectra of $(CH_3)_3N{\cdot}B_4H_8$ in dichloromethane-d_2 are shown in Figure 1. Each of the spectra consists of three resonance signals in a intensity ratio 1:2:1. The shift values and the assignments are

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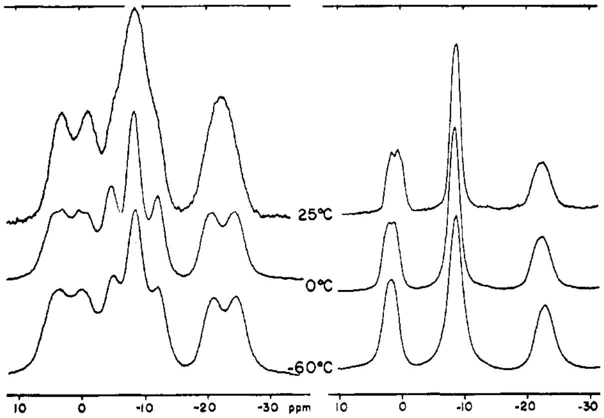


Figure 1. ^{11}B NMR spectra of $(CH_3)_3N{\cdot}B_4H_8$ in CD_2Cl_2: left, normal spectra; right, ^1H-spin-decoupled spectra.

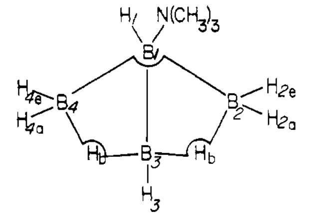


Figure 2. Proposed structure for $(CH_3)_3N{\cdot}B_4H_8$.

summarized in Table I. These assignments are consistent with the structure given in Figure 2, which is drawn after the reported structure of $(CH_3)_2NPF_2{\cdot}B_4H_8$,[11] and are also consistent with the NMR signal assignments of other tetraborane(8) adducts.[2a,c,e,12] The absence of multiplet features from the two high-field signals at 25 °C suggests rapid motion of the hydrogen atoms that are associated with B(1) and B(2,4) atoms. The ^1H NMR spectra described later indicate this point more informatively. The doublet B(3) signal has a further multiplet structure (see Figure 1). The multiplet is considered to be due to the $^{11}B(1)$–$^{11}B(3)$ coupling rather than to the presence of two different isomers (see next subsection), and the coupling constant is estimated to be 31 Hz. This value compares with the value of 24 Hz which is reported for the carbon monoxide adduct of B_4H_8.[13]

(c) ^1H NMR Spectra. Shown in Figure 3 are the ^1H NMR spectra of $(CH_3)_3N{\cdot}B_4H_8$. In the ^{11}B-spin-decoupled spectrum at 25 °C, a sharp signal at 3.11 ppm and a broad signal at 1.9 ppm appear. Also a slight rise of the baseline can be detected in the range from 0 to −4 ppm. The sharp signal is related to the quartet that is discernible in the undecoupled spectrum at the same temperature. The peak separation (134 Hz) of the quartet is in good agreement with the peak separation (135 Hz) of the B(3) doublet signal in the ^{11}B NMR spectrum at 25 °C. The signal at 3.11 ppm, therefore, is assigned to the H(3) atom. When the temperature is lowered, sharp peaks develop at 1.99, 1.76, and −2.04 ppm in the ^{11}B-spin-decoupled spectra (Figure 2e,f). These peaks are assigned to the H(2,4) (equatorial or axial), H(2,4) (axial or equatorial), and H_b (bridged) atoms, respectively. The assignments are confirmed by the ^{11}B single-frequency decoupling experiments. The location of the H(1) signal in the ^1H NMR spectrum is uncertain. When the sample is irradiated (−45 °C) with the B(1) resonance frequency, a broad hump of significant intensity can be detected at 1.06 ppm. While this hump may represent the H(1) signal, its identity is not unequivocal because of the complexity of the spectral appearance at the region due to the overlap of broad H(2,4) and H(3) multiplet peaks.

The presence of two (or possibly three) broad signals in the ^{11}B-spin-decoupled spectrum at 25 °C suggests a hydrogen tautomerism involving H(2), H(4), and H_b atoms, similar to those observed for the $B_4H_9^-$ ion.[14] The H(3) atom is static at 25 °C as indicated by the appearance of well-resolved quartet and doublet signals in the ^1H and ^{11}B NMR spectra, respectively, at 25 °C. This is also the case for the $B_4H_9^-$ ion. The two terminal hydrogen atoms attached to the B(1) and B(3) atoms are thought to be static on the basis of the ^{11}B NMR evidence.[14]

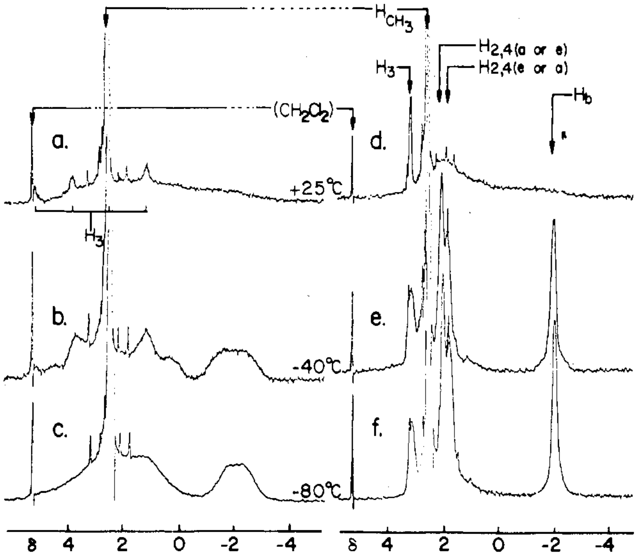


Figure 3. ^1H NMR spectra of $(CH_3)_3N{\cdot}B_4H_8$: left, normal spectra; right, ^{11}B-spin-decoupled spectra.

The tetraborane(8) adducts of $F_2PN(CH_3)_2$ and CO are considered to exist in two isomeric forms,[2c,13] exo and endo, with respect to the position of the ligand relative to the V-shaped B_4 framework. In the crystalline state, $(CH_3)_2NPF_2{\cdot}B_4H_8$ is in the endo form.[11] In this study no evidence was obtained for the presence of the two isomeric species of $(CH_3)_3N{\cdot}B_4H_8$. In the temperature range from −80 to +25 °C, the methyl proton signal is a sharp single peak, and the B(3) signal is a single multiplet peak in our judgement based on the presently available data. At present the absolute conformation of $(CH_3)_3N{\cdot}B_4H_8$ remains unknown.

C. Chemical Properties of $(CH_3)_3N{\cdot}B_4H_8$. (a) Decomposition and the Reaction with B_5H_{11}. On standing at room temperature the colorless, crystalline solid of $(CH_3)_3N{\cdot}B_4H_8$ slowly turns yellow, and the decomposition proceeds further to give a mixture of sticky yellow solid and volatile boron hydride compounds. The onset of decomposition is strongly dependent on the presence of certain impurities in the sample. At the initial stage of decomposition, hexaborane(10), pentaborane(9), trimethylamine–borane(3), and trimethylamine–triborane(7) are identified as the major decomposition products. After a period of prolonged standing (ca. 2 weeks), hydrogen gas, trimethylamine–borane(3), and trimethylamine–triborane(7) were the major volatile components in the system. Nonvolatile components that could be identified were $B_{11}H_{14}^-$ and/or $B_{12}H_{12}^{2-}$.

Undoubtedly the decomposition process is complex, and, at the early stage of the decomposition, it involves yet undefined reactions of the initially produced borane compounds with unchanged $(CH_3)_3N{\cdot}B_4H_8$. The process that follows would be of much complex nature. In dichloromethane solution the decomposition pattern is similar to that of the solid, except that the rate is slower.

Trimethylamine–tetraborane(8) reacts readily with B_5H_{11} at room temperature. Diborane(6), B_5H_9, B_6H_{10}, $(CH_3)_3N{\cdot}B_3H_7$, and $(CH_3)_3NB{\cdot}H_3$ are the products which can be identified at the early stage of the reaction. The further change is again complicated by the complex secondary reactions

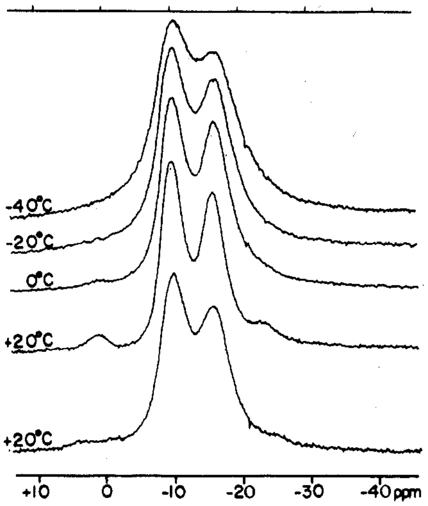


Figure 4. ^{11}B NMR spectra of a sample containing $(CH_3)_3N{\cdot}B_4H_8$ and $(CH_3)_3N$ (1:1.3 mole ratio) in CD_2Cl_2: ^{1}H-spin-decoupled spectra except the bottom one (20 °C) which is a normal spectrum.

similar to those observed in the decomposition of $(CH_3)_3N{\cdot}B_4H_8$.

(b) Behavior toward Bases. The presence of certain bases stabilizes $(CH_3)_3N{\cdot}B_4H_8$. A solution of $(CH_3)_3N{\cdot}B_4H_8$ in a mixture of tetrahydrofuran and dimethyl sulfide remained colorless even after 4 days at room temperature, and the ^{11}B NMR spectrum of the solution indicated that most of the $(CH_3)_3N{\cdot}B_4H_8$ remained unchanged. Small amounts of $(CH_3)_3N{\cdot}BH_3$ and $(CH_3)_3N{\cdot}B_3H_7$ were evidence for slight decomposition. Solutions of $(CH_3)_3N{\cdot}B_4H_8$ in tetrahydrofuran also show no sign of decomposition until after several days at room temperature.

After treatment with excess trimethylamine in a tetrahydrofuran solution at 50 °C for 30 min, the original $(CH_3)_3N{\cdot}B_4H_8$ was recovered unchanged. At temperatures below about −40 °C, a trimethylamine adduct of trimethylamine–tetraborane(8), $B_4H_8{\cdot}2N(CH_3)_3$, can be isolated. The formation and the characterization of the bis(trimethylamine) adduct is described below.

(c) Bis(trimethylamine)–Tetraborane(8). A system containing $(CH_3)_3N{\cdot}B_4H_8$ and $(CH_3)_3N$ can be expressed by the equation which involves the formation of the bis(trimethylamine) adduct:

$$(CH_3)_3N{\cdot}B_4H_8 + (CH_3)_3N \rightleftharpoons B_4H_8{\cdot}2N(CH_3)_3$$

When the temperature is lowered, the equilibrium shifts to the right. Thus, when a solution of $(CH_3)_3N{\cdot}B_4H_8$ in dichloromethane is treated with excess trimethylamine, and then the volatile components are removed by pumping at temperatures below −40 °C, the bis(trimethylamine) adduct is isolated as a white solid. When the temperature is raised to 0 °C, the second trimethylamine is released and can be removed by pumping.

Shown in Figure 4 are the ^{11}B NMR spectra of a system which consists of $(CH_3)_3N{\cdot}B_4H_8$ and $(CH_3)_3N$ in a 1:1.3 molar ratio in dichloromethane. At 20 °C the peaks of $(CH_3)_3N{\cdot}B_4H_8$ at 0.7 and −22.5 ppm are evident with the central peak at −8.5 ppm overlapped by a peak which appears at −10.0 ppm. The peak at −10.0 ppm and a slightly broader peak at −15.9 ppm are attributed to the bis(trimethylamine) adduct. As the temperature is lowered, the signals of the mono(trimethylamine) adduct lose their intensities while the two peaks of the bis(trimethylamine) adduct become broad. The ^{11}B-spin-decoupled ^{1}H NMR spectrum of the same system at 25 °C contains the methyl proton signal at 2.57 ppm as a sharp singlet and the borane proton (H_B) signal at 1.15 ppm as a singlet in an observed intensity ratio about 20:8. The signal due to the free trimethylamine appears at 2.11 ppm. The two trimethylamine groups in $B_4H_8{\cdot}2N(CH_3)_3$ are, therefore, equivalent, and so are the eight borane hydrogen atoms. The H_B signal remains as a singlet even at −70 °C. In the normal spectrum, the H_B signal is extremely broad, lost in the baseline and hardly detectable.

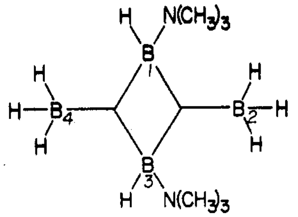


Figure 5. Proposed structure for $B_4H_8{\cdot}2N(CH_3)_3$.

A structure consistent with the above ^{11}B NMR spectrum is shown in Figure 5, which may be regarded as derived from $(CH_3)_3N{\cdot}B_4H_8$ by the coordination of trimethylamine to the most deshielded B(3) boron atom. Such a static structure, however, does not indicate the equivalency of the eight borane hydrogen atoms. Several other tautomeric structures can be drawn on the basis of the above structure. So far, no definitive structural study has been made on any of the known B_4 *hypho*[15] class compounds to draw an analogy for the structure of $B_4H_8{\cdot}2N(CH_3)_3$.

Ammonia, monomethylamine, and dimethylamine also add to $(CH_3)_3N{\cdot}B_4H_8$ to form $B_4H_8{\cdot}2$(amine). Characterization and detailed properties of these new $B_4H_8{\cdot}2$(amine) compounds will be described in a separate report.

(d) Reactions with Anhydrous HCl and HBr. Anhydrous hydrogen chloride cleaves $(CH_3)_3N{\cdot}B_4H_8$ into B_3 and B_1 fragments. In a tetrahydrofuran solution the reaction yields $(CH_3)_3N{\cdot}B_3H_7$ and the tetrahydrofuran adduct of H_2BCl:

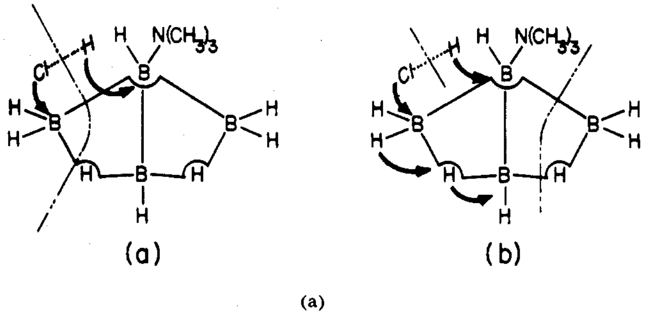
$$(CH_3)_3N{\cdot}B_4H_8 + HCl \xrightarrow[-80\ °C]{\text{in THF}} (CH_3)_3N{\cdot}B_3H_7 + H_2BCl{\cdot}THF$$

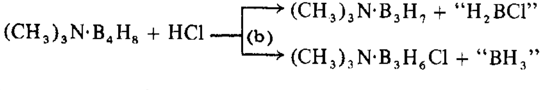
Whereas, in a dichloromethane solution, $(CH_3)_3N{\cdot}B_3H_6Cl$ (trimethylamine–chlorotriborane(7))[16] is produced as the major product and $(CH_3)_3N{\cdot}B_3H_7$ as a minor product. The molar ratio between the two triborane adducts in the product is about 7:3. Diborane(6) and chlorodiborane(6) are also the products in the reaction. The major reaction in dichloromethane can be expressed as

$$(CH_3)_3N{\cdot}B_4H_8 + HCl \xrightarrow[-80\ °C]{\text{in } CH_2Cl_2} (CH_3)_3N{\cdot}B_3H_6Cl + {}^1/_2B_2H_6$$

The reactions of anhydrous HBr with $(CH_3)_3N{\cdot}B_4H_8$ parallel those of HCl described earlier.

These reactions may be generalized and schematically illustrated as shown.





$$(CH_3)_3N{\cdot}B_4H_8 + HCl \begin{cases} \xrightarrow{(a)} (CH_3)_3N{\cdot}B_3H_7 + \text{“}H_2BCl\text{”} \\ \xrightarrow{(b)} (CH_3)_3N{\cdot}B_3H_6Cl + \text{“}BH_3\text{”} \end{cases}$$

In the presence of tetrahydrofuran, the cleavage by scheme

(a) is facilitated by the formation of the stable tetrhydrofuran adduct of H_2BCl. Whereas, in the absence of such a base, the cleavage by scheme (b) that yields B_2H_6 becomes the favorable process, and the cleavage by scheme (a) occurs only to a small extent. The "H_2BCl" which is produced by the latter process would be responsible for the formation of B_2H_5Cl in the reaction.

D. Preparation of $(CH_3)_3N{\cdot}B_4H_8$. The chemical properties of $(CH_3)_3N{\cdot}B_4H_8$ described above clarify why such a representative adduct of B_4H_8 had not been isolated. It has been known that the trimethylamine adduct of triborane(7), $(CH_3)_3N{\cdot}B_3H_7$, decomposes readily when treated with trimethylamine[4b] and that the trimethylamine adduct of pentaborane(9), $B_5H_9{\cdot}2N(CH_3)_3$, also decomposes to give $(CH_3)_3N{\cdot}BH_3$ and other boron hydride compounds.[17] These observations naturally suggested that $B_4H_8{\cdot}N(CH_3)_3$ would be unstable in the presence of trimethylamine. Therefore, one would have avoided the use of excess trimethylamine, or at least tried to limit the molar ratio $N(CH_3)_3$:B_5H_{11} to 2:1, in the reaction with B_5H_{11} for the attempted preparation of $B_4H_8{\cdot}N(CH_3)_3$. It is demonstrated in this study that $(CH_3)_3{\cdot}NB_4H_8$ is reactive to acids including boranes and that the compound is stable to bases. Bases appear to stabilize the compound, presumably by combining with acidic species and thus deactivating the acids. When a deficient amount of trimethylamine is used in the reaction of B_5H_{11} with the amine, the excess of B_5H_{11} reacts with the initially produced $(CH_3)_3N{\cdot}B_4H_8$. Trimethylamine–borane(3), which is produced in the reaction, is also known to decompose B_5H_{11} catalytically.[18] Even when the amine and B_5H_{11} are used in a 2:1 ratio, some of the $(CH_3)_3N{\cdot}B_4H_8$, which is produced at the early stage of the reaction, undergoes complicated side reactions with yet unchanged B_5H_{11} and with some intermediate side products in the reaction system. These side reactions yield a mixture of borane compounds which would further react with $(CH_3)_3N{\cdot}B_4H_8$. Isolation of fragile $(CH_3)_3N{\cdot}B_4H_8$ from such a product mixture would be an extremely difficult task to accomplish, if not impossible. Earlier observations on the reaction systems of B_5H_{11} and $N(CH_3)_3$,[5] which were also reproducible in our laboratory, are thus explainable.

The use of excess $N(CH_3)_3$ forces the symmetrical cleavage reaction of B_5H_{11} to completion and therefore suppresses the formation of undesirable contaminants. However, when an excess of $N(CH_3)_3$ is used in the preparation of $(CH_3)_3N{\cdot}B_4H_8$, a heavy liquid results upon removal of the volatile components by pumping. The liquid consists of $(CH_3)_3N{\cdot}B_4H_8$, $(CH_3)_3N{\cdot}BH_3$, and some trimethylamine which is strongly retained by this particular mixture. The $(CH_3)_3N{\cdot}BH_3$ and the trimethylamine are released very slowly from the liquid at room temperature under the conditions of ordinary dynamic vacuum, and the crystals of $(CH_3)_3N{\cdot}B_4H_8$ slowly grow in the liquid. This process is so slow that often the yellowing of the liqud takes place while the system is being pumped, and then the decomposition of the B_4H_8 adduct proceeds fast, resulting in a yellow residue of complicated composition. It was, therefore, found necessary to efficiently apply high vacuum on the surface of the heavy liquid to separate out the more volatile components rapidly. (See Experimental Section.) Once the more volatile components are separated from the mixture, the less volatile residue left behind is a dry solid of $(CH_3)_3N{\cdot}B_4H_8$.

The purity of B_5H_{11} used in this study might have contributed to the successful isolation of $(CH_3)_3N{\cdot}B_4H_8$. The crude B_5H_{11} as obtained by a hot–cold reactor process was treated with BF_3 in the process of purification. This BF_3 treatment was to remove and/or to deactivate any possible basic contaminants which would accelerate the decomposition of B_5H_{11}. Furthermore, throughout this experimental study the sampling system for B_5H_{11} was strictly separated from other systems in which solvents and basic reagents were handled.

The base displacement reaction of $R_2S{\cdot}B_4H_8$ with $N(CH_3)_3$ is so far the most reliable preparative method for $(CH_3)_3N{\cdot}B_4H_8$. The cleavage reaction of pentaborane(11) with R_2S to yield a mixture of $R_2S{\cdot}B_4H_8$ and $R_2S{\cdot}BH_3$ is clean and complete at low temperatures and so is the displacement reaction with trimethylamine. Thus, $(CH_3)_3N{\cdot}B_4H_8$ produced in the reaction system is kept from coming in contact with B_5H_{11} and other reactive boron hydride compounds throughout the entire reaction process. It is noted, however, that trimethylamine has to be added in an amount sufficient to displace R_2S from both $R_2S{\cdot}B_4H_8$ and $R_2S{\cdot}BH_3$ in the reaction system. The selective displacement of R_2S from $R_2S{\cdot}B_4H_8$, leaving $R_2S{\cdot}BH_3$ intact, which might be expected to proceed on the basis of the strong acidity of B_4H_8 relative to that of BH_3, can not be effected in this system.

Experimental Section

Equipment and Instruments. Standard high-vacuum techniques were used throughout for the handling of volatile compounds. Stopcocks and joints were greased with Apiezon N or M. Reactions were run in 22-mm o.d. Pyrex tubes, each fitted with a 24/40 inner joint, unless otherwise mentioned. The ^{11}B and ^1H NMR spectra were recorded on a Varian XL-100-15 instrument equipped with a spin decoupler (Gyrocode) and with a variable temperature unit, operating at 32.1 and 100 MHz, respectively. Samples for the NMR measurements were either prepared in the sample tubes (5, 10, or 12-mm o.d.) or transferred into the sample tubes within the vacuum system and sealed off. The mass spectra were obtained on an AEI MS-30 mass spectrometer operating in the electron-impact mode at 70 eV.

Chemicals. Pentaborane(11) was prepared from diborane(6) (Callery Chemical Co.) by the hot–cold reactor method under the conditions described previously.[7] The crude sample of B_5H_{11}, which was obtained from the condensate in the reactor, was agitated for a few minutes in an atmosphere of BF_3 at 0 °C. The mixture was first distilled through a −80 °C trap, and the distillate was then distilled at −95 °C. After BF_3 had distilled out, the portions of distillate that followed were monitored by IR spectrometer for the presence of B_4H_{10}. When no B_4H_{10} became detectable in the distillate, the pure sample of B_5H_{11} was collected. The process of distillation at −95 °C is very slow. The B_5H_{11} thus purified had a vapor pressure of 52.5 mmHg at 0 °C.

Trimethylamine was liberated from its hydrochloride (Eastman Kodak Co.) by treatment with a concentrated NaOH solution, dried over KOH pellets, then dried with a small quantity of $LiAlH_4$, and fractionated. Dimethyl and diethyl sulfide, hydrogen chloride, dichloromethane, and tetrahydrofuran were treated before use as described previously.[7]

Preparation of $(CH_3)_3N{\cdot}B_4H_8$ by the Displacement Reaction. In a typical preparation, 1.57 mmol of B_5H_{11}, 3.45 mmol of $(CH_3)_2S$, and 3 mL of CH_2Cl_2 were condensed at −196 °C into a reaction tube and mixed briefly at −80 °C. The resulting solution was allowed to warm once to 0 °C and then was cooled to −196 °C to condense 3.38 mmol of $(CH_3)_3N$ above the solution. The mixture was stirred at −80 °C for 2 min and the resulting colorless solution was warmed to 0 °C. At this temperature the volatile components (solvent, excess $(CH_3)_3N$, $(CH_3)_2S$, and $(CH_3)_3N{\cdot}BH_3$) were slowly pumped out to yield the white crystalline solid product. The last portion of $(CH_3)_3N{\cdot}BH_3$ was sublimed out in 30 min at room temperature. No hydrogen gas formed during the entire process.

Reaction Stoichiometry. When 0.48 mmol of B_5H_{11}, 1.18 mmol of $(CH_3)_2S$, and 1.93 mmol of $(CH_3)_3N$ were used to prepare $(CH_3)_3N{\cdot}B_4H_8$ according to the procedure described above, 0.93 mmol of $(CH_3)_3N$ was recovered unchanged, and 38.1 mg (0.52 mmol) of $(CH_3)_3N{\cdot}BH_3$ was obtained. These data give 2.08 for the reaction ratio $(CH_3)_3N$:B_5H_{11}, 1.08 for the ratio $(CH_3)_3NBH_3$:B_5H_{11}, and therefore a composition $B_4H_8{\cdot}1.0N(CH_3)_3$ for the residue. Anal. Calcd for $(CH_3)_3N{\cdot}B_4H_8$: B, 39.1; N, 12.7. Found: B, 39.2; N, 13.4.

Preparation of $(CH_3)_3N{\cdot}B_4H_8$ by the Cleavage Reaction of B_5H_{11}. A CH_2Cl_2 solution (3 mL) containing 0.74 mmol of B_5H_{11} was prepared in a reaction tube. The solution was stirred at −80 °C, and

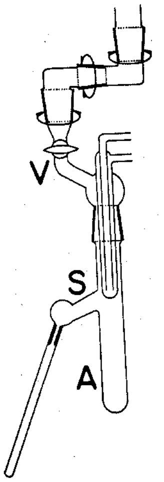


Figure 6. Sublimation-sampling apparatus.

1.97 mmol of $(CH_3)_3N$ was slowly leaked into the reaction tube through the stopcock. Absorption of the amine was complete, and a clear solution resulted. The solution was then allowed to warm to 0 °C, and slow removal of volatile component was started. When most of the volatile components had been removed, a mixture of a crystalline solid and a heavy liquid remained in the tube. As pumping was continued at 0 °C, solid $(CH_3)_3N{\cdot}B_4H_8$ remained in the tube.

The reaction was also run without the solvent. About 5 mL of liquid $(CH_3)_3N$ was condensed onto B_5H_{11} (1.22 mmol) in a reaction tube at −196 °C. A −112 °C bath was placed around the tube, and the mixture was stirred. A white, solid suspension was seen in the liquid amine. As the temperature was raised to −80 °C, the solution began to become clear, and, at the same time, sticky globules formed in the solution. Soon the sticky mass gradually changed to a finely divided white solid to form a milky suspension. The system was kept at −80 °C for 10 h and then allowed to warm to 0 °C, and the volatile components ($N(CH_3)_3$ and $(CH_3)_3N{\cdot}BH_3$) were removed by pumping. The residue behaved similarly to that described above for the reaction in CH_2Cl_2. The final residue was $(CH_3)_3N{\cdot}B_4H_8$.

Prolonged pumping is required to obtain the solid product from the heavy liquid which results upon removal of most of the volatile component. This pumping time can be shortened by chilling a portion of the reaction tube, 4–5 cm above the tube end, with liquid nitrogen cooled glass wool. Amine and $(CH_3)_3N{\cdot}BH_3$ distill out of the heavy liquid rapidly because of the better vacuum thus produced and condense on the cooled portion of the reaction tube, leaving the dry $(CH_3)_3N{\cdot}B_4H_8$ behind.

Preparation of the Authentic $(CH_3)_3N{\cdot}B_4H_8$ Samples for the NMR and Mass Spectrum Measurements. Samples for NMR experiments were prepared by using the apparatus shown in Figure 6. A sample of $(CH_3)_3N{\cdot}B_4H_8$ was prepared by the displacement reaction in the apparatus at the bottom of tube A. A coolant liquid (10 °C) was passed through the cold finger, and tube A was exposed to room temperature while stopcock V was opened to the vacuum pump. Impurities such as $(CH_3)_3N{\cdot}BH_3$, $(CH_3)_3N$, and the solvent distilled out of the apparatus, but $(CH_3)_3N{\cdot}B_4H_8$ slowly sublimed to condense on the cold finger. When a sufficient amount of the tetraborane adduct was collected on the cold finger, the entire apparatus was tilted about the two L-shaped joints so that the side arm (S) was positioned directly below the tip of the cold finger. Then the vapor of the solvent was expanded into the apparatus from the vacuum line through stopcock V. The solvent condensed on the cold finger and dissolved the adduct, and the solution dripped into the side arm and ran into the sample tube. The adduct solution which was adhering on the wall of the side arm was washed down into the sample tube in the usual manner. The NMR sample tube was cooled to −196 °C and sealed off. Samples for mass spectrum measurements were prepared similarly.

Reaction of $(CH_3)_3N{\cdot}B_4H_8$ with $(CH_3)_3N$. A 2.67-mmol quantity of $(CH_3)_3N$ was condensed above a 0.54-mmol sample of $(CH_3)_3N{\cdot}B_4H_8$ at −196 °C. The temperature was raised once to −80 °C and then to −45 °C while the mixture was being stirred. A white suspension, which had resulted, was stirred at −45 °C for 1 h. Removal of excess $(CH_3)_3N$ at −80 °C left a white solid. The mass balance gave a formula $(CH_3)_3N{\cdot}B_4H_8{\cdot}0.96N(CH_3)_3$ for the solid product. When the above product was warmed 0 °C under dynamic vacuum, 0.50 mmol of $(CH_3)_3N$ was released from the solid, and a dry solid of $(CH_3)_3N{\cdot}B_4H_8$ remained in the reaction tube.

Reaction of $(CH_3)_3N{\cdot}B_4H_8$ with HCl and HBr. (a) In Ethers. A tetrahydrofuran solution (3 mL) of $(CH_3)_3N{\cdot}B_4H_8$ (1.14 mmol) was frozen (−196 °C), and anhydrous HCl (1.17 mmol) was condensed above the solution. The mixture was stirred for 20 min at −80 °C. A small amount of hydrogen gas (ca. 0.35 mmol) evolved. The temperature was then raised to room temperature, and the solution was transferred into an NMR sample tube. The ^{11}B NMR spectrum of the sample consisted of resonance peaks of $(CH_3)_3N{\cdot}B_3H_7$ (−18.4 ppm) and $H_2BCl{\cdot}THF$ (+4.1 ppm) in an intensity ratio 3:1 (a 1:1 molar ratio). Weak signals of $(CH_3)_3N{\cdot}B_4H_8$, $(CH_3)_3N{\cdot}BH_3$, and $HBCl_2{\cdot}THF$ were also detected in the spectrum.

A similar treatment of $(CH_3)_3N{\cdot}B_4H_8$ (0.37 mmol) with HCl (0.35 mmol) in diethyl ether (3 mL) resulted in the formation of $(CH_3)_3N{\cdot}B_3H_7$ and $(C_2H_5)_2O{\cdot}BH_2Cl$. Small amounts of $(C_2H_5)_2O{\cdot}BHCl_2$, unchanged $(CH_3)_3N{\cdot}B_4H_8$, and hydrogen gas (0.07 mmol) were also detected. A sample of $(CH_3)_3N{\cdot}B_4H_8$ (0.55 mmol) was treated likewise with HCl (1.10 mmol) in dimethyl sulfide (3 mL). Hydrogen gas (0.09 mmol) was evolved during the treatment. The products identified in the ^{11}B NMR spectrum of the reaction solution were $(CH_3)_3N{\cdot}B_3H_7$, $(CH_3)_2S{\cdot}BH_2Cl$ (−7.4 ppm, t, J_{BH} = 130 Hz), and $(CH_3)_2S{\cdot}BHCl_2$ (+1.7 ppm, d, J_{BH} = 158 Hz). A similar treatment of $(CH_3)_3N{\cdot}B_4H_8$ (0.60 mmol) with HBr (0.80 mmol) in diethyl ether (3 mL) gave $(CH_3)_3N{\cdot}B_3H_7$ and $(C_2H_5)_2O{\cdot}BH_2Br$ (+2.4 ppm, t, J_{BH} = 139 Hz). Hydrogen gas (0.13 mmol) was evolved, and weak signals attributable to $(CH_3)_3N{\cdot}BHBr_2$ and $(CH_3)_3N{\cdot}BH_2Br$ were also detected in the ^{11}B NMR spectrum of the reaction solution.

(b) In Dichloromethane. A dichloromethane solution (3 mL) of $(CH_3)_3N{\cdot}B_4H_8$ (0.94) mmol) was mixed with HCl (1.12 mmol) in a manner similar to that described in (a). The mixture was stirred at −80 °C for 5 min and then warmed to 0 °C for 15 min while stirring. The amount of hydrogen gas evolved during this time was 0.27 mmol. Upon removal of volatile components from the reaction mixture, a white crystalline solid remained in the reaction tube. Fractionation of the volatile components yielded 0.42 mmol of a B_2H_6–B_2H_5Cl mixture. The crystalline solid was dissolved in dichloromethane, and the solution was transferred into an NMR sample tube. The ^{11}B NMR spectrum (^1H spin decoupled) of the sample at 30 °C consisted of the resonance of $(CH_3)_3N{\cdot}B_3H_7$ at −18.4 ppm and three peaks at −7.9, −9.8, and −15.7 ppm. The latter three peaks are attributed to 1-(trimethylamine)-2-chlorotriborane(7), $(CH_3)_3N{\cdot}B_3H_6Cl$, the assignment being B(2), B(3), and B(1), respectively, reading upfield. Weak signals of $(CH_3)_3N{\cdot}BH_2Cl$ and $(CH_3)_3N{\cdot}BHCl_2$ were also detected in the spectrum. On the basis of the intensities of the $(CH_3)_3N{\cdot}B_3H_7$ peak and the B(1) peak of the chlorotriborane, the solid residue was estimated to contain about 70 mol % $(CH_3)_3N{\cdot}B_3H_6Cl$. An attempted separation of the $(CH_3)_3N{\cdot}B_3H_7$ from $(CH_3)_3N{\cdot}B_3H_6Cl$ by vacuum sublimation was unsuccessful. The sublimation of the supposedly more volatile $(CH_3)_3N{\cdot}B_3H_7$ was slow at room temperature, and under these conditions the $(CH_3)_3N{\cdot}B_3H_6Cl$ began to decompose to give a sticky yellow residue.

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Registry No. $(CH_3)_3N{\cdot}B_4H_8$, 69765-82-8; $B_4H_8{\cdot}2N(CH_3)_3$, 69765-84-0; B_5H_{11}, 18433-84-6; $(CH_3)_3N$, 75-50-3; $(CH_3)_3N{\cdot}B_3H_7$, 12076-72-1; HCl, 7647-01-0; HBr, 10035-10-6; $H_2BCl{\cdot}THF$, 55606-72-9; $(CH_3)_2S{\cdot}BH_2Cl$, 63348-81-2; $(CH_3)_2S{\cdot}BHCl_2$, 69765-79-3; $(C_2H_5)_2O{\cdot}BH_2Br$, 69765-80-6; $(CH_3)_3N{\cdot}B_3H_6Cl$, 69765-86-2.

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Reaction of Active Nickel with PF_3, H_3BCO, H_3BPF_3, PH_3, and PF_2H. Preparation of Complexes of the Form $M(L)_4$ and Other Processes

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Gaseous PF_3, initially at 2-atm pressure and *25 °C*, will react with sulfide-activated nickel in 46 h to convert 62% of the original PF_3 to $Ni(PF_3)_4$. Gaseous H_3BCO will react with sulfide-activated nickel to give $Ni(CO)_4$ and B_2H_6 with 87% conversion of H_3BCO under similar conditions. Gaseous F_3PBH_3 (initially at a pressure of 2 atm) will react at 50 °C over 46 h to convert 98% of the original F_3PBH_3 to $Ni(PF_3)_4$ and B_2H_6. When PH_3 was allowed to react with this extremely reactive sulfide-activated nickel, H_2 and unreacted PH_3 were recovered but *no* $Ni(PH_3)_4$ was ever found. Similarly the reaction of PF_2H with sulfide-activated nickel gave *no* tetrakis ligand complex. Rather, only PF_3H_2, PF_3, and unreacted PF_2H were recovered as volatiles. The foregoing observations are interpreted in mechanistic terms involving gas adsorption and hydride and fluoride transfer to the metal. It is postulated that the fluoride coating is removable in the presence of hydrogenic species such as PF_2H, or H_3BPF_3, but is not easily removable when H is not present as in the case of pure PF_3. Reactions of Ni with PF_3 are believed to be inhibited by a nickel fluoride coating. It is suggested that B_2H_6 should promote the formation of PF_3 complexes from PF_3 and active metals.

The molecules of the fluorophosphine series PF_3, PF_2H, PFH_2, PH_3 display interesting stability trends. The second member of the series, PF_2H, known since 1965,[1] is prepared with considerable difficulty while the third member, PFH_2, is still unknown.[2] Base properties of the known members of the series also present some anomalies. For example, PF_3 is fundamentally a π acid, forming stable complexes with transition-metal atoms and their ions.[3–5] The PF_3 complex with BH_3 is of very limited stability[6] while no purely σ complex such as that formed with H^+ is known. In contrast, PH_3 is fundamentally a σ base, forming a stable complex with PH_4^+. The BH_3 complex is roughly comparable in stability to that of F_3PBH_3,[7,8] while no complexes such as $Ni(PH_3)_4$ are known. Timms[9] tried to make $Ni(PH_3)_x$ molecules by the metal-atom technique but obtained only H_2 and undefined solids. He[9] did prepare the mixed complex $Ni(PF_3)_3PH_3$ as a stable compound but $Ni(PF_3)_2(PH_3)_2$ decomposed at room temperature. Another mixed PH_3 complex $Cr(CO)_3(PH_3)_3$ has also been reported.[10]

If PF_2H were to follow smoothly in the series, its BH_3 complex should have a stability comparable to that of PF_3 and to that of PH_3. In actual fact PF_2H forms an unusually stable complex with both BH_3 and B_4H_8.[7,8] Thus PF_2H will displace PF_3 or PH_3 quantitatively from F_3PBH_3 or H_3PBH_3. The reactions of PF_2H with protons and with metal atoms remain largely unexplored. Rudolph found some evidence for the relatively unstable cation $PF_2H_2^+$ and some evidence for $Ni(PF_2H)(CO)_3$, but he was unable to prepare $Ni(PF_2H)_4$ by displacement methods. This paper is concerned with the reactions of active nickel with PF_3, PF_2H, PH_3, F_3PBH_3, and $OCBH_3$. For purposes of comparison the reactions of nickel with CO were examined. The studies were intended to define more precisely the strength of PF_2H as a π-acid ligand. In particular we wanted to know whether PF_2H had anomalously high base strength toward nickel atoms or whether its unusual base strength was limited only to borane acids.

Reactions of CO, PF_3, H_3BCO, and H_3BPF_3 with Bulk Nickel. Although CO reacts readily with active nickel powder at 1 atm of CO pressure and 25 °C, the reaction of PF_3 under comparable conditions is slow and incomplete.[12] Kruck[13] noted that under extreme conditions (pressure 70 atm, $T > 100$ °C) nickel powder could be converted quantitatively to $Ni(PF_3)_4$, but he wrote, "(this) is a further example of the rare direct formation of a nickel(0) complex from metallic nickel and a compound of trivalent phosphorus". Street and Burg[14] using relatively mild conditions and nickel obtained from the pyrolysis of $Ni(CO)_4$ obtained only very small yields of $Ni(PF_3)_4$. Nixon and Sexton[15] were able to get about 38% of the PF_3 in glass tubes (unspecified pressure) to react with active nickel powder at 60 °C. Clearly direct reaction is not usually an effective route for the synthesis of $M(PF_3)_x$ complexes. For purposes of this study it was essential to prepare nickel of unusual activity.

In general, active nickel is produced by the thermal decomposition of nickel oxalate or formate under vacuum.[12,15] In 1946 Gilliland and Blanchard[16b] reported that the activity of such nickel toward CO can be improved by using sulfide activators. In 1963 Heinicke and Harenz[16a] reapplied this

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