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Reactions of Hexamethylenetetramine with Diborane(6), Triborane(7), Tetraborane(10), and Pentaborane(11)

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The reactions of hexamethylenetetramine with B_2H_6, $THF \cdot B_3H_7$, B_4H_{10}, and B_5H_{11} in chloroform solutions were investigated. The products isolated are $(CH_2)_6N_4 \cdot 4BH_3$, $(CH_2)_6N_4 \cdot 2B_3H_7$, $(CH_2)_6N_4 \cdot 2B_3H_7 \cdot 2BH_3$, and $(CH_2)_6N_4 \cdot B_4H_8$, respectively. Differences and similarities in the properties between the borane adducts of $(CH_2)_6N_4$ and those of trimethylamine are described.

Introduction

The reported borane adducts of hexamethylenetetramine, $(CH_2)_6N_4$, have so far been limited to those of borane(3), namely, $(CH_2)_6N_4 \cdot nBH_3$ ($n = 1-4$)[2,3] and $(CH_2)_6N_4 \cdot 4BF_3$.[4] There have been cases in which solid hexamethylenetetramine was used as a base catalyst to effect the 1,2-isomerization of halopentaborane(9)[5] and to convert pentaborane(11) to higher borane species.[6] Probably, lack of solvents appropriate for the amine in its reactions with boranes[7] could have been a discouraging factor for one to investigate its reactions with boranes in solution phases. On the other hand, the general insolubility of the amine allowed the inherently strongly basic amine to function as a weak base in its solid form, thus making it suitable for the conversion catalyst. The formation of nonaborane(15) from pentaborane(11) in the presence of solid $(CH_2)_6N_4$, which was reported by Burg and Kratzer[6] in 1962, had been of particular interest to us at the time this research was initiated. It was thought that certain intermediates would be first formed by the reaction of the amine with pentaborane(11), and further reactions of the intermediates would lead to the formation of the higher boranes. The identification of any of such intermediate species would then be substantial for the understanding of the conversion reaction. We, therefore, began investigating the reactions of $(CH_2)_6N_4$ with boranes in solution phases in hope of identifying definitive reactions and products of the reactions.

In this paper the products of the hexamethylenetetramine reactions with diborane(6), tetrahydrofuran–triborane(7), tetraborane(10), and pentaborane(11) in chloroform solutions are reported.

Results and Discussion

$(CH_2)_6N_4 \cdot 2B_4H_{10}$. Treatment of a chloroform solution of $(CH_2)_6N_4$ with tetraborane(10) at 0 °C or −45 °C results in the formation of a white precipitate which can be formulated as $(CH_2)_6N_4 \cdot 2B_4H_{10}$. The solid is insoluble in dichloromethane, benzene, and other common hydrocarbon solvents. It dissolves in dioxane and tetrahydrofuran but decomposes to form $(CH_2)_6N_4 \cdot 4BH_3$ in these solvents. The solid is stable enough in air to be handled for its weighing. When heated in vacuo, it decomposes at about 170 °C to a yellowish solid.

By analogy to the reaction of tetraborane(10) with trimethylamine, in which trimethylamine–borane(3) and –triborane(7) form as the products,[8] the solid described above is expected to contain BH_3 and B_3H_7 groups that are coordinated to $(CH_2)_6N_4$. Indeed, a broad absorption at 2040 cm^{-1} in the infrared spectrum of the solid suggests the presence of B_3H_7 group.[9] The ¹H-spin-decoupled ¹¹B NMR spectrum of a chloroform solution saturated with this solid product at 20 °C consists of three resonance signals at −13.1, −14.5, and −23.2 ppm in an intensity ratio of about 2:1:1. The signals at −23.2 and −13.1 ppm are attributed to the B(1) and B(2,3) atoms,

respectively, of the B_3H_7 group and the signal at −14.5 ppm is attributed to the BH_3 group. The ¹¹B NMR spectra of methylamine adducts of triborane(7) have been reported.[10] The pattern of spectral appearance observed here for the B_3H_7 group is consistent with that observed for the methylamine adducts. The results described below suggest a molecular formula $(CH_2)_6N_4 \cdot 2B_3H_7 \cdot 2BH_3$ for this solid and that the solid is not a mixture of $(CH_2)_6N_4 \cdot 4B_3H_7$ and $(CH_2)_6N_4 \cdot 4BH_3$, nor a mixture of $(CH_2)_6N_4 \cdot 3B_3H_7 \cdot BH_3$ and $(CH_2)_6N_4 \cdot B_3H_7 \cdot 3BH_3$.

$(CH_2)_6N_4 \cdot 2B_3H_7$. Treatment of tetrahydrofuran–triborane(7) with $(CH_2)_6N_4$ in chloroform solution at room temperature results in the formation of a white precipitate. Stoichiometry of the reaction and elemental analyses are consistent with the formulation $(CH_2)_6N_4 \cdot 2B_3H_7$ for the solid.

$$(CH_2)_6N_4 + 2THF \cdot B_3H_7 \rightarrow (CH_2)_6N_4 \cdot 2B_3H_7 + 2THF$$
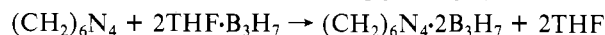
The solid is also insoluble in diethyl ether and dichloromethane but is soluble in liquid sulfur dioxide. The ¹¹B NMR spectrum of a chloroform solution saturated with this adduct at 20 °C consists of two resonance signals at −15.2 and −24.7 ppm in an intensity ratio 2:1. A liquid sulfur dioxide solution of the adduct gave two signals at −14.8 and −24.1 ppm (−10 °C). These data are consistent with the formula given above for the adduct. Like other amine–triboranes(7),[8,11] this compound reacts slowly with trimethylamine at room temperature to give $(CH_3)_3N \cdot BH_3$.

When a clear solution of the triborane(7) adduct in liquid sulfur dioxide is treated with B_2H_6, 1 mol of B_2H_6 is absorbed by 1 mol of the adduct to form a white, SO_2-insoluble solid. The X-ray powder pattern of this solid is identical with that of $(CH_2)_6N_4 \cdot 2B_4H_{10}$ described above. The compound, therefore, is appropriately formulated as $(CH_2)_6N_4 \cdot 2B_3H_7 \cdot 2BH_3$.

$$(CH_2)_6N_4 \cdot 2B_3H_7 + B_2H_6 \rightarrow (CH_2)_6N_4 \cdot 2B_3H_7 \cdot 2BH_3$$
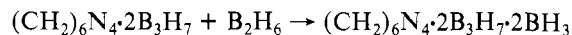
$(CH_2)_6N_4 \cdot B_4H_8$. When a chloroform solution of $(CH_2)_6N_4$ is treated with pentaborane(11) at −23 or −45 °C in a molar ratio of about 2:1 (amine:borane), a reaction slowly proceeds to form two products, one of which is soluble in chloroform and another insoluble. The latter product was identified as a borane(3) adduct of the amine, and the chloroform-soluble solid was characterized as hexamethylenetetramine–tetraborane(8), $(CH_2)_6N_4 \cdot B_4H_8$.

$$5(CH_2)_6N_4 + 4B_5H_{11} \rightarrow$$
$$(CH_2)_6N_4 \cdot 4BH_3 + 4(CH_2)_6N_4 \cdot B_4H_8$$
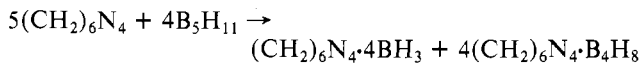
The tetraborane(8) adduct is moderately soluble in dichloromethane and is soluble in diethyl ether and tetrahydrofuran. The compound is inert to trimethylamine. Although examples of symmetrical cleavage of pentaborane(11) by Lewis bases are abundant,[12] the above reaction represents the first definitive example of symmetrical cleavage
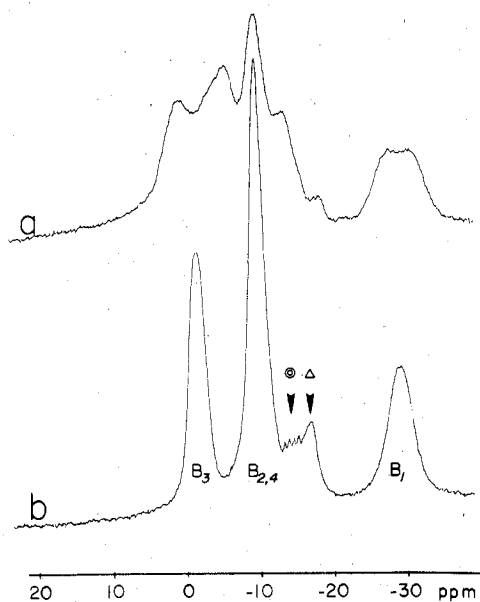
Figure 1. ^{11}B NMR spectra of $(CH_2)_6N_4{\cdot}B_4H_8$ in $CHCl_3$ at 25 °C: (a) normal spectrum; (b) ^{1}H-spin-decoupled spectrum (⊚ and △ = impurities in the sample, B_5H_9 and $(CH_2)_6N_4{\cdot}nBH_3$, respectively).

Table I. NMR Spectral Data for $(CH_2)_6N_4{\cdot}B_4H_8$

	shift, ppm	multiplicity^a	J_{BH}, Hz	assignt
$^{11}B^b$	−1.1	d	132	B(3) (B–H)
	−9.3	t	120	B(2,4) (H–B–H)
	−28.5	d	96	B(1) (B–H)
$^1H\{^{11}B\}^c$	4.40	complex structure		H_C
	2.99	s		H(3)
	2.20	s (overlap of singlets)		H(2,4) and H(1)
	−2.08	s		H_b

^{a} s, singlet; d, doublet; t, triplet. ^{b} 25 °C in $CHCl_3$. ^{c} 0 °C in $CDCl_3/CD_2Cl_2$.

of pentaborane(11) *by an amine base*, and the adduct is the first *amine* adduct of tetraborane(8) ever isolated. The trimethylamine adduct of B_4H_8 was recently isolated as a stable solid and is reported concurrently with this paper.[13]

The ^{11}B and ^{1}H NMR spectra of $(CH_2)_6N_4{\cdot}B_4H_8$ are shown in Figures 1 and 2, and the spectral data are summarized in Table I. The ^{11}B NMR spectrum is consistent with the structure indicated in Figure 3, which is drawn after the reported structure for $(CH_3)_2NPF_2{\cdot}B_4H_8$,[14] and the assignments for the signals are made with reference to the reported NMR spectra of other B_4H_8 adducts.[13,15] The ^{11}B-spin-decoupled ^{1}H NMR spectrum at 0 °C contains three distinctive signals for hydrogen atoms associated with boron atoms (Figure 2b). The assignments for the signals could be made by comparing the spectrum with that of $(CH_3)_3N{\cdot}B_4H_8$.[13] The overall spectral features of the two spectra are similar to each other, but much sharper signals were obtained for $(CH_3)_3$-N$\cdot$B$_4$H$_8$ at lower temperatures. The signals due to H(3) and H(2,4) could unequivocally identified by irradiating the sample with each of the B(3) and B(2,4) resonance frequencies and observing the appearance of ^{1}H resonance signals. The H_b signal is sharpened by irradiating the sample with the B(3) resonance signal, but the effect upon irradiation of the B(2,4) atoms is much less. The same was observed for the trimethylamine adduct. The location of the H(1) signal in the spectrum is uncertain; irradiation of the sample with the B(1) frequency brings about a hump at 1.88 ppm, but the overlap of broad, partially decoupled signals of other hydrogen atoms obscures the identity of the hump. The methylene proton
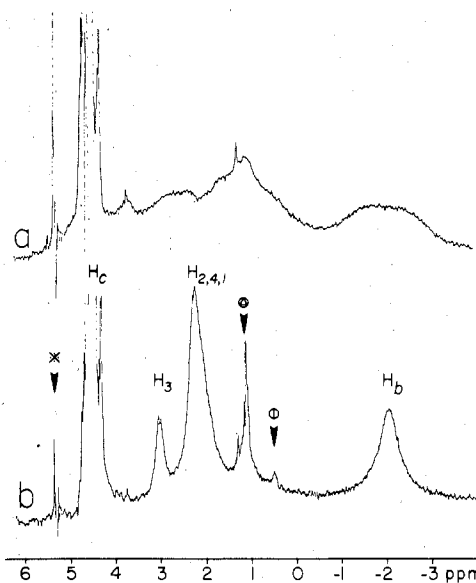

Figure 2. ^{1}H NMR spectra of $(CH_2)_6N_4{\cdot}B_4H_8$ in $CDCl_3/CD_2Cl_2$ at 0 °C: (a) normal spectrum; (b) ^{11}B-spin-decoupled spectrum (✕ = CH_2Cl_2; ⊕ and ⊕ = impurities in the sample).
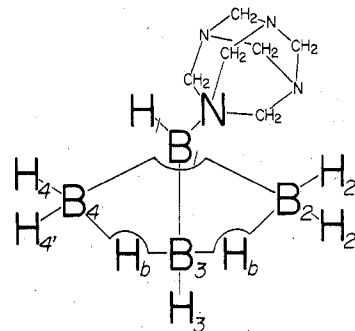

Figure 3. Proposed structure for $(CH_2)_6N_4{\cdot}B_4H_8$.

signal, which appears centered at 4.40 ppm over a 40-Hz range, has a complex structure consisting of at least five peaks. The presence of two methylene environments that would be expected for a monoadduct by assuming free rotation about the B–N bond is not obvious in this spectrum. No unequivocal evidence for the presence of structural isomers, exo form and endo form with respect to the ligand position relative to the V-shaped B_4 framework, could be obtained for $(CH_2)_6N_4{\cdot}B_4H_8$. The existence of such isomers has been reported for the CO and $(CH_3)_2NPF_2$ adducts of tetraborane(8).[16,17]

$(CH_2)_6N_4{\cdot}4BH_3$. Riley and Miller[2] reported a series of borane(3) adducts of $(CH_2)_6N_4$, $(CH_2)_6N_4{\cdot}nBH_3$ where $n =$ 1–4. These adducts were prepared by the reactions of $(CH_2)_6N_4$ and B_2H_6 in benzene; the amine is insoluble in benzene, and therefore the adduct formation was initiated by heating the reaction mixture to 50 °C to produce a slightly soluble precipitate of $(CH_2)_6N_4{\cdot}BH_3$, which was then treated with excess B_2H_6 to obtain $(CH_2)_6N_4{\cdot}4BH_3$. When a chloroform solution of $(CH_2)_6N_4$ is treated with excess B_2H_6, the reaction proceeds smoothly at room temperature, and the product separates as a white solid from the solution.

$$(CH_2)_6N_4 + 2B_2H_6 \rightarrow (CH_2)_6H_4{\cdot}4BH_3$$
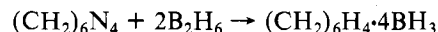
The tetrakis(borane(3)) adduct is moderately soluble in dioxane, tetrahydrofuran, diglyme, and liquid sulfur dioxide and is slightly soluble in chloroform. The compound is insoluble in benzene, toluene, diethyl ether, and dichloromethane. Trimethylamine displaces $(CH_2)_6N_4$ from the adduct to give $(CH_3)_3N{\cdot}BH_3$. The sample of the tetrakis adduct that was prepared in chloroform solution, being of larger particle size,

appears to be more stable than that prepared in benzene. In the paper by Riley and Miller,[2] the solubility of the tetrakis adduct in benzene was left undecided, because an *"apparent solution" of the adduct, which was obtained as the result of the treatment of the* $(CH_2)_6N_4 \cdot BH_3$ *precipitate with* B_2H_6 *in benzene, produced precipitates at all attempts to transfer the "solution".* This observation was reproducible in our laboratory. We, however, conclude that the compound is insoluble in benzene, and the apparent "dissolution" of the adduct is attributed to the fortuitously close refractive index of solid $(CH_2)_6N_4 \cdot 4BH_3$ to that of benzene. An NMR sample containing solid $(CH_2)_6N_4 \cdot BH_3$ in benzene gives a broad [11]B resonance signal (FT, ^{1}H spin decoupled) at about -15 ppm. Upon addition of excess B_2H_6 to the sample, the signal disappears, only the signal of B_2H_6 in excess being detectable and the "solution" being clear.

Unique Properties of Hexamethylenetetramine–Borane Adducts. As described above, in chloroform solution $(CH_2)_6N_4$ reacts with each of B_2H_6, B_4H_{10}, and B_5H_{11} to give symmetrical cleavage products of the boranes. Thus, borane(3), triborane(7), and tetraborane(8) groups are found coordinated to the amine in the products. While, in general, the reaction chemistry of $(CH_2)_6N_4$ with the boranes resembles that of trimethylamine,[8,13,18] behavior unique to $(CH_2)_6N_4$ and its borane adducts was also observed.

Upon reaction with excess B_2H_6 in chloroform, $(CH_2)_6N_4$ combines with up to four BH_3 groups to form slightly soluble $(CH_2)_6N_4 \cdot 4BH_3$ utilizing all four of its basic sites. With excess tetrahydrofuran–triborane(7), however, the amine forms a chloroform-insoluble adduct $(CH_2)_6N_4 \cdot 2B_3H_7$, and the excess $THF \cdot B_3H_7$ is recovered unchanged. The two uncoordinated nitrogen atoms in the adduct molecule would have become weakly basic relative to the nitrogen atoms in the free $(CH_2)_6N_4$ molecule. Yet they are strong enough bases to combine with BH_3, which is a weaker acid than B_3H_7, to form $(CH_2)_6N_4 \cdot 2B_3H_7 \cdot 2BH_3$ in a liquid SO_2 solution. The insolubility of $(CH_2)_6N_4 \cdot 2B_3H_7$ in $CHCl_3$, therefore, appears to be responsible for the selective formation of the bis(triborane(7)) adduct.

In the molecule of $(CH_2)_6N_4 \cdot B_4H_8$, three nitrogen atoms are left uncoordinated. Here again the weakened base strength of the three nitrogen atoms would not be the sole factor for the formation of the mono(tetraborane(8)) adduct. The low solubility of the borane(3) adducts of $(CH_2)_6N_4$ and the high solubility of $(CH_2)_6N_4 \cdot B_4H_8$ in chloroform seem to be the decisive factors that contribute to the selective formation of the mono(tetraborane)adduct. Thus, for example, a species such as $(CH_2)_6N_4 \cdot B_4H_8 \cdot BH_3$, if formed in chloroform, would undergo a reaction with available $(CH_2)_6N_4$ in the solution to give $(CH_2)_6N_4 \cdot B_4H_8$ and $(CH_2)_6N_4 \cdot 4BH_3$:

$$(CH_2)_6N_4 \cdot B_4H_8 \cdot BH_3 + {}^1/_4(CH_2)_6N_4 \rightarrow$$
$$(CH_2)_6N_4 \cdot B_4H_8 + {}^1/_4(CH_2)_6N_4 \cdot 4BH_3$$
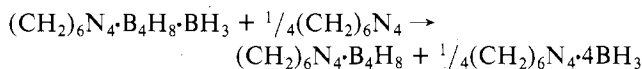
One might expect that more B_4H_8 groups can be added on the $(CH_2)_6N_4 \cdot B_4H_8$ molecule by using excess B_5H_{11} in the reaction with $(CH_2)_6N_4$. The tetraborane(8) adduct $(CH_2)_6N_4 \cdot B_4H_8$, however, reacts readily with B_5H_{11} to give a complex mixture of boron hydride compounds consisting of B_5H_9, B_6H_{10}, $(CH_2)_6N_4 \cdot nBH_3$, and others, and the expected compound could not be isolated. This reaction, however, is thought to be one of the important reactions that may be involved in the formation of higher boranes from B_5H_{11} in the presence of solid $(CH_2)_6N_4$. Further studies on the reactions of amine–tetraborane(8) with boranes are in progress, and the results will be reported at a future date.

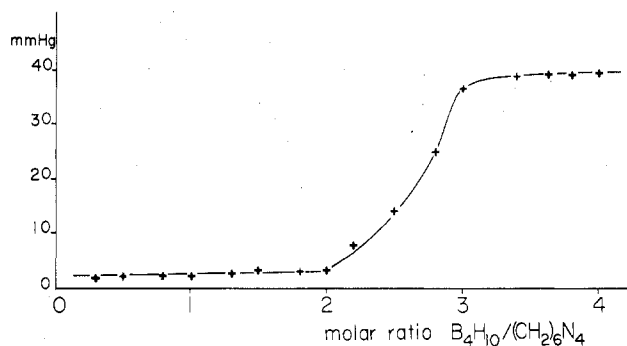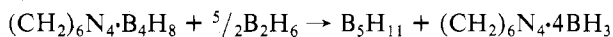The reaction of $(CH_2)_6N_4 \cdot B_4H_8$ with excess B_2H_6 in chloroform produces B_5H_{11}:

$$(CH_2)_6N_4 \cdot B_4H_8 + {}^5/_2B_2H_6 \rightarrow B_5H_{11} + (CH_2)_6N_4 \cdot 4BH_3$$

Figure 4. Tensimetric titration curve for a $(CH_2)_6N_4$–B_4H_{10} system $(-45\ °C)$.

In this reaction a strong acid, B_4H_8, is displaced by a weak acid, BH_3. Apparently the insolubility of $(CH_2)_6N_4 \cdot 4BH_3$ is again responsible for the seemingly paradoxical reaction. Trimethylamine–tetraborane(8) does not react with B_2H_6 under the comparable conditions.

Experimental Section

General Procedure. Conventional vacuum line techniques were used throughout for the handling of volatile compounds. Diborane(6) was either prepared by the reaction of $BF_3 \cdot O(C_2H_5)_2$ with $LiAlH_4$[19] or obtained from a cylinder (Callery Chemical Co.). Tetraborane(10) was either prepared by the high-pressure decomposition of B_2H_6 in a stainless steel cylinder[20] or taken from the laboratory (University of Utah) stock which had been prepared by a hot–cold reactor method.[21] Pentaborane(11) was either prepared by the reaction of B_4H_{10} with B_2H_6 at 100 °C[22] or taken from the laboratory (University of Utah) stock which had been prepared by a hot–cold reactor method.[21] These boranes were fractionated in the vacuum line before use. Hexamethylenetetramine was prepared from reagent grade aqueous ammonia and formalin, and the solid product obtained from the aqueous solution was sublimed in vacuo. Trimethylamine was generated from its hydrochloride by treating it with a concentrated aqueous solution of KOH and was dried over KOH pellets and then over $LiAlH_4$. Sulfur dioxide was generated from Na_2SO_3 (reagent grade) by the addition of concentrated H_2SO_4 and dried over P_4O_{10}. Reagent grade chloroform, tetrahydrofuran, and dichloromethane were stored over P_4O_{10}, $LiAlH_4$, and molecular sieves, respectively, and taken directly into the vacuum line from the containers as needed.

The ^{11}B and ^{1}H NMR spectra were recorded on a Varian XL-100 spectrometer at 32.1 and 100 MHz, respectively. The [11]B signal of $BF_3 \cdot O(C_2H_5)_2$ was used as the reference (zero) for [11]B chemical shifts, upfield being taken as negative. The ^{1}H signal of CH_2Cl_2 was taken at δ 5.28.

Reactions of B_4H_{10} with $(CH_2)_6N_4$. (a) Reaction in $CHCl_3$. A weighed sample of $(CH_2)_6N_4$ was placed in a 22-mm o.d. reaction tube fitted with a 24/40 male joint. The tube was evacuated, and about 3 mL of chloroform was condensed in the tube to prepare a chloroform solution of $(CH_2)_6N_4$. The solution was cooled to -196 °C, and a measured amount of B_4H_{10} was condensed on top of the frozen solution. It was then allowed to melt and warm to 0 °C while being stirred continuously. White turbidity gradually developed in the solution, and in 15 min the formation of the white solid appeared complete. The stirring was continued for a total of 40 min at 0 °C. Volatile components were then distilled out, and the unchanged B_4H_{10} was separated from the solvent by fractional condensation. No noncondensable gas and no B_2H_6 were found. The tube containing the white residue was transferred onto a vacuum line filtration unit,[23] and the solid was washed with fresh portions of chloroform to leach out unchanged $(CH_2)_6N_4$. The reaction data are tabulated in Table II. Shown in Figure 4 is the curve obtained for a tensimetric titration of a $(CH_2)_6N_4$ solution at -45 °C. The solution was stirred at least 15 min at this temperature after each addition of B_4H_{10} before the pressure measurement was made. The vapor pressure of the system approaches that of blank titration (40 mmHg) as the borane/amine ratio exceeds 2/1. The $CHCl_3$-insoluble solid was treated with 6 N HCl in a sealed tube at 150 °C for 50 h, and the resulting solution was analyzed for boron (mannitol method) and nitrogen (Kjeldahl method). Anal. Calcd for $(CH_2)_6N_4 \cdot 2B_4H_{10}$: B, 35.0; N, 22.7. Found: B, 34.2; N, 22.6.

Table II. Reactions of B_4H_{10} with $(CH_2)_6N_4$ in $CHCl_3$

amt charged, mmol		amt recovered, mmol		stoichiometry $B_4H_{10}/$ $(CH_2)_6$- N_4
B_4H_{10}	$(CH_2)_6N_4$	B_4H_{10}	$(CH_2)_6N_4$	
5.26	1.04	3.12	0	2.09
3.08	0.72	1.61	0	2.03
2.91	1.37	0.24	0	1.96

Table III. Reactions of B_2H_6 with $(CH_2)_6N_4$ in $CHCl_3$

amt charged, mmol		amt recovered, mmol		stoichiometry $B_2H_6/$ $(CH_2)_6$- N_4
B_2H_6	$(CH_2)_6N_4$	B_2H_6	$(CH_2)_6N_4$	
3.56	1.36	0.85	0	1.99
0.41	0.20	0	0	2.04
4.26	0.93	2.38	0	2.01
2.67	0.77	1.16	0	1.98

(b) Reaction without the Solvent. A 0.46-mmol sample of $(CH_2)_6N_4$ and a 2.66-mmol sample of B_4H_{10} were sealed in a reaction tube (ca. 30-mL volume) equipped with a break-off tip, and the tube was kept at room temperature for 50 h, during which the amine was always in contact with liquid B_4H_{10}. When the tube was opened, H_2 (0.57 mmol), B_2H_6 (0.37 mmol), B_4H_{10} (1.89 mmol), and B_5H_9 (0.12 mmol) were separated as volatile components. Nonvolatile residue in the tube was leached with chloroform to leave only a small amount of chloroform-insoluble, white solid. The infrared spectrum of the solid indicated the presence of B–H groups (absorption at 2360 and 2480 cm^{-1}). The identity of the solid is unknown. The chloroform-soluble component was $(CH_2)_6N_4$.

Reaction of $THF\cdot B_3H_7$ with $(CH_2)_6N_4$. A sample of $THF\cdot B_3H_7$ was prepared in the 22-mm o.d. reaction tube by treating B_4H_{10} (2.86 mmol) with excess tetrahydrofuran (about 2 mL) and then by pumping out the excess tetrahydrofuran and B_2H_6. A 0.53-mmol quantity of $(CH_2)_6N_4$ was added to the reaction tube that contained the solid $THF\cdot B_3H_7$ sample, the tube was evacuated, and about 3 mL of $CHCl_3$ was condensed in it. When the temperature of the reaction mixture was raised to room temperature, a clear solution resulted from which a white precipitate gradually formed. The mixture was stirred for 3 h at about 10 °C. Volatile components were then distilled out, and the solid residue was washed with fresh $CHCl_3$. The $CHCl_3$-insoluble solid was treated with 6 N HCl in a sealed tube at 150 °C for 24 h, and the resulting solution was analyzed for boron and nitrogen. Anal. Calcd for $(CH_2)_6N_4\cdot2B_3H_7$: H_2 (upon hydrolysis), 73.0 mmol/g; B, 29.6%; N, 25.6%. Found: H_2, 68.7 mmol/g; B, 29.0%; N, 25.4%.
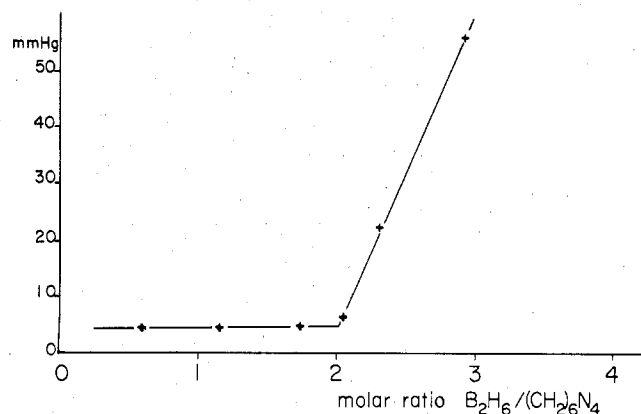
From the wash liquid a solid residue was obtained upon evaporation of the solvent $CHCl_3$. The solid was soluble in tetrahydrofuran and was identified as $THF\cdot B_3H_7$ (1.76 mmol) by its IR spectrum. Thus the reaction stoichiometry ($THF\cdot B_3H_7/(CH_2)_6N_4$) was 2.08. When an excess of $(CH_2)_6N_4$ was mixed with $THF\cdot B_3H_7$ (e.g., 3.50 mmol of $(CH_2)_6N_4$ and 0.41 mmol of $THF\cdot B_3H_7$ in 4 mL of $CHCl_3$) for 10 min at 0 °C, the $CHCl_3$-insoluble product obtained was identical with that described above (IR spectrum and X-ray powder pattern). When, however, such a reaction mixture was allowed to stand for a prolonged period of time (e.g., 4.5 h at room temperature), the $CHCl_3$-insoluble product was different (IR spectrum and X-ray powder pattern) from that of $(CH_2)_6N_4\cdot2B_3H_7$, and noncondensable gas was found in the reaction system, suggesting a certain reaction of the B_3H_7 adduct with the excess amine. When $(CH_2)_6N_4\cdot2B_3H_7$ was treated with excess $N(CH_3)_3$ at –23 °C, $(CH_3)_3N\cdot BH_3$ was separated as a reaction product.

Reaction of $(CH_2)_6N_4\cdot2B_3H_7$ with B_2H_6. A 0.12-mmol quantity of $(CH_2)_6N_4\cdot2B_3H_7$ was dissolved in liquid sulfur dioxide (ca. 3 mL) in a 22-mm o.d. reaction tube, the solution was frozen with liquid nitrogen, and a 0.50-mmol quantity of B_2H_6 was condensed in the tube. When the temperature of the tube was raised to –23 °C, a white precipitate formed in the solution. No noncondensable gas was detected. A 0.37-mmol quantity of diborane was recovered from the reaction system, the reaction stoichiometry $B_2H_6/(CH_2)_6N_4\cdot2B_3H_7$ thus being 1.08. The X-ray powder pattern and IR spectrum of the SO_2-insoluble product was identical with those of $(CH_2)_6N_4\cdot2B_4H_{10}$ that was obtained by the reaction of B_4H_{10} with $(CH_2)_6N_4$ in $CHCl_3$.

Reaction of B_5H_{11} with $(CH_2)_6N_4$. A 93.7-mg quantity (0.67 mmol) of $(CH_2)_6N_4$ was dissolved in ca. 3 mL of $CHCl_3$, and 0.35 mmol of B_5H_{11} was condensed above the frozen solution (–196 °C). The reaction mixture was allowed to warm to –45 °C and was stirred at that temperature for 4.5 h. White turbidity, which developed shortly after the temperature reached –45 °C, became intense and changed to a white precipitate during this period of time. The volatile component was then distilled out and was found to be pure $CHCl_3$, free of any borane compounds. The residue in the reaction tube was washed with $CHCl_3$. The $CHCl_3$-insoluble component was identified as $(CH_2)_6N_4\cdot4BH_3$ (IR spectrum and X-ray powder pattern). The

Figure 5. Tensimetric titration curve for a $(CH_2)_6N_4$–B_2H_6 system (–45 °C).

$CHCl_3$-soluble component was leached with diethyl ether after pumping out the solvent, $CHCl_3$. From the ether solution, a colorless solid was obtained upon removal of the ether by pumping. The solid product was hydrolyzed with 6 N HCl in a sealed tube (95–96 °C, 13 h), and the resulting solution was analyzed for boron. Anal. Calcd for $(CH_2)_6N_4\cdot B_4H_8$: H_2 (upon hydrolysis), 52.2 mmol/g; B, 22.6%. Found: H_2 (upon hydrolysis), 51.2 mmol/g; B, 22.1 and 22.0%.

When the above reaction was run with a mixture of B_5H_{11} and $(CH_2)_6N_4$ in a 1:1 or 3:2 molar ratio, the diethyl ether soluble, nonvolatile product was also obtained. The product was identical with that described above as judged by its IR spectrum. In addition, however, B_2H_6, B_5H_9, B_6H_{10}, and possibly other boranes were detected as the volatile products.

Chemical Properties of $(CH_2)_6H_4\cdot B_4H_8$. (a) Toward $(CH_3)_3N$. A sample of $(CH_2)_6N_4\cdot B_4H_8$ was placed in a reaction tube equipped with a break-off tip, excess $(CH_3)_3N$ was condensed in the tube, and the tube was sealed off. After standing for 24 h at room temperature, the tube was opened, and the volatile component was pumped out. No noncondensable gas or $(CH_3)_3N\cdot BH_3$ was found, and the residual solid was unchanged $(CH_2)_6N_4\cdot B_4H_8$ as identified by its IR spectrum.

(b) Toward B_2H_6. A clear $CHCl_3$ solution of $(CH_2)_6N_4\cdot B_4H_8$ (ca. 0.65 mmol) was prepared in a 10-mm o.d. NMR sample tube, and B_2H_6 (1.8 mmol) was condensed above the frozen solution at –196 °C. The tube was allowed to warm by exposing it to room temperature. As soon as the solution melted, a white solid began to form in the solution. The solution was agitated to ensure good contact with the diborane, and then the excess unchanged B_2H_6 was briefly pumped out at –63 °C. The ^{11}B NMR spectrum of the reaction mixture showed strong signals of B_5H_{11} and a weak signal of B_2H_6. No signals of $(CH_2)_6N_4\cdot B_4H_8$ could be detected.

When $(CH_3)_3NB_4H_8$[13] was treated with B_2H_6 under conditions comparable with that described above for the $(CH_2)_6N_4\cdot B_4H_8$ reaction, no evidence for reaction was detected in the ^{11}B NMR spectrum of the resulting solution.

Preparation of $(CH_2)_6N_4\cdot4BH_3$ in $CHCl_3$. A weighed sample of $(CH_2)_6N_4$ was placed in a reaction tube, the tube was evacuated, and about 3 mL of $CHCl_3$ was condensed in the tube to prepare a solution of the amine. The tube was cooled to –196 °C again, and a measured amount of B_2H_6 was condensed on top of the frozen solution. The tube was then allowed to slowly warm by exposing the tube to room temperature. The solution became turbid as it melted. When the temperature of the solution reached room temperature, the reaction appeared complete. Volatile components were distilled out of the reaction tube, and unchanged diborane was recovered and measured.

No noncondensable gas was found during this whole process. Reaction data are summarized in Table III. The reaction proceeds to completion even at -45 °C. A tensimetric titration curve is presented in Figure 5. Both sets of data support the formation of $(CH_2)_6\cdot N_4\cdot 4BH_3$.

The residue in the reaction tube was washed with $CHCl_3$, and its molecular weight was determined in dioxane solution by observing the melting point lowering, $(CH_3)_3N\cdot BH_3$ being used as the reference compound for the measurement: calcd for $(CH_2)_6N_4\cdot 4BH_3$, 195.2; found, 200.4. Anal. Calcd for $(CH_2)_6N_4\cdot 4BH_3$: B, 22.1; N, 28.7. Found: B, 22.1; N, 28.6.

The diborane reaction product of $(CH_2)_6N_4$ described above was treated with trimethylamine. A 84.2-mg sample of the product (0.43 mmol as $(CH_3)_6N_4\cdot 4BH_3$) was dissolved in ca. 3 mL of dioxane and was treated with 2.04 mmol of $(CH_3)_3N$ at room temperature for 2.5 h. A white precipitate was found in the tube, and 0.29 mmol of $(CH_3)_3N$ and 117.1 mg (1.61 mmol) of $(CH_3)_3N\cdot BH_3$ were separated out from the reaction system. The precipitate was identified as $(CH_2)_6N_4$. In another experiment, a 0.29-mmol sample of solid $(CH_2)_6N_4\cdot 4BH_3$ was sealed in a break-off reaction tube with a 4.32-mmol sample of $(CH_3)_3N$, and the tube was kept at room temperature for 24 h. The volume of the tube had been made small enough so that the liquid amine could always be in contact with the solid amine sample. From this reaction mixture, 3.14 mmol of $(CH_3)_3N$ and 72.8 mg (1.00 mmol) of $(CH_3)_3N\cdot BH_3$ were sublimed out. The remaining solid in the reaction tube was $(CH_2)_6N_4$. The two sets of data presented above are consistent with the reaction $(CH_2)_6N_4\cdot 4BH_3 + 4(CH_3)_3N \rightarrow 4(CH_3)_3N\cdot BH_3 + (CH_2)_6N_4$.

X-ray Powder Pattern and Infrared Absorption Data. X-ray powder patterns were obtained on film strips in a 114.6-mm diameter camera by using Cu Kα radiation. Corrections for film shrinkage were not made. Infrared spectra were recorded on a Hitachi EPI spectrophotometer with NaCl optics. Sample specimens were prepared in KBr disk forms. Absorption maxima listed as follows are wave numbers in cm^{-1} as read on chart papers.

(a) $(CH_2)_6N_4\cdot 2B_3H_7\cdot 2BH_3$. d values: 6.88 (s), 5.53 (s), 3.16 (s), 2.93 (vw), 2.54 (vw), 2.24 (m), 2.08 (vw), 2.02 (vw), 1.87 (vw), 1.68 (w), 1.58 (w). IR data: 3010 (m), 2960 (m), 2920 (m), 2850 (w), 2500 (sh), 2390 (s), 2280 (m), 2040 (w), 1620 (w), 1455 (s), 1255 (s), 1232 (m), 1179 (s), 1100 (m), 1045 (s), 1019 (s), 921 (m), 885 (m), 839 (m).

(b) $(CH_2)_6N_4\cdot 2B_3H_7$. d values: 7.69 (s), 7.08 (s), 6.21 (m), 5.28 (s), 4.57 (s), 4.29 (m), 4.05 (m), 3.87 (m), 2.73 (w), 2.60 (vw), 2.51 (vw), 2.33 (w), 2.20 (vw), 2.08 (vw). IR data: 3030 (m), 2960 (m), 2475 (s), 2350 (sh), 2040 (w), 1450 (s), 1420 (sh), 1320 (m), 1260 (s), 1220 (m), 1160 (s), 1110 (s), 1070 (s), 1030 (s), 1000 (sh), 920 (w), 890 (w).

(c) $(CH_2)_6N_4\cdot B_4H_8$. IR data: 3040 (m), 2970 (m), 2600 (sh), 2530 (m), 2410 (s), 2300 (m), 2040 (w), 1460 (s), 1400 (sh), 1310 (w), 1265 (w), 1239 (m), 1190 (s), 1110 (sh), 1050 (s), 1020 (s), 930 (m), 895 (m), 820 (s), 670 (m), 555 (w), 460 (w).

(d) $(CH_2)_6N_4\cdot 4BH_3$. d values: 5.96 (vs), 4.88 (m), 4.26 (m), 3.81 (m), 3.41 (m), 2.68 (m), 2.54 (m), 2.43 (w), 2.24 (vw), 2.07 (vw), 1.98 (vw), 1.88 (m), 1.83 (vw). IR data: 3010 (w),[24] 2960 (w), 2890 (w), 2385 (s),[24] 2325 (w, sh),[24] 2280 (m),[24] 1620 (w), 1450 (m), 1420 (sh), 1255 (m), 1230 (m), 1180 (s), 1100 (w), 1043 (s), 1018 (s), 921 (w), 880 (w), 860 (w), 838 (w), 805 (m), 650 (w), 460 (w).

Registry No. $(CH_2)_6N_4\cdot 2B_3H_7$, 69765-87-3; $(CH_2)_6N_4\cdot 2B_3H_7\cdot 2BH_3$, 69814-96-6; $(CH_2)_6N_4\cdot B_4H_8$, 69780-69-4; $(CH_2)_6N_4\cdot 4BH_3$, 42976-02-3; $(CH_2)_6N_4$, 100-97-0; B_4H_{10}, 18283-93-7; B_5H_{11}, 18433-84-6; B_2H_6, 19287-45-7; THF$\cdot B_3H_7$, 12544-89-7.

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