

that the electron-transfer process coupled with the adjustment in atomic positions to produce NO₂ or NO and the *cis*-Mo^{VI}O₂²⁺ moiety should be very fast because of the overlap of the d_{xy} orbital of Mo(V) with the π* orbital of nitrate or nitrite.⁷ If the same overlap were reasonably considered in the present d¹ system, the electron transfer itself and the accompanying bond break to liberate NO should be very fast as compared with the k_f process. The second-order rate constant k_o/[NO₂⁻] is smaller than k_f for the substitution reaction with NCS⁻, despite the stronger basicity of NO₂⁻ than of NCS⁻. The activation parameters are also different from those of the substitution reactions of eq 1. It is generally understood that the substitution reaction between aqua ligand and nitrite and vice versa involve the break of an N-O bond rather than the metal-oxygen bond accompanied by a different activation enthalpy than that for other reactions with a metal-oxygen bond break.⁸

Formation of the Binuclear Complex. The equilibrium and kinetic studies were made at pH 4.9, where a significant amount of [V^{VO}O₂(nta)]²⁻ is dissociated.⁹ Hence the k_f and

k_b values, the equilibrium constants, and the activation parameters in Table I should involve rather large experimental errors (e.g., the virtual concentration of [V^{VO}O₂(nta)]²⁻ in Figure 7 should be less than those expressed on the abscissa). Equilibrium studies at 25-45 °C gave ΔH° and ΔS° values ca. -20 kJ mol⁻¹ and -40 J mol⁻¹ K⁻¹, respectively. These values might involve large experimental errors and do not agree with those calculated kinetically. Nevertheless, the negative ΔH° value reflects the stabilization brought about by the mixed-valence state in the V₂O₃³⁺ moiety. The k_f values are of the same order with those for the anation of NCS⁻ and N₃⁻ to [V^{IV}O(nta)(H₂O)]⁻. Thus we tend to reckon the formation reaction of the binuclear complex as the replacement of the aqua ligand in [V^{IV}O(nta)(H₂O)]⁻ by [V^{VO}O₂(nta)]²⁻. The substitution reaction must be followed by a rapid electron exchange within the V₂O₃³⁺ core to give equal states of the two vanadium ions.

Registry No. Ba[VO(nta)H₂O]₂, 73711-57-6; K[VO(nta)H₂O], 72268-05-4; Na[VO(nta)H₂O], 73711-58-7; K₂[VO₂(nta)], 73636-51-8; (NH₄)₃[V₂O₃(nta)₂], 73728-22-0; [VO(pmda)H₂O], 12348-25-3; NO₂⁻, 14797-65-0; NCS⁻, 302-04-5; N₃⁻, 14343-69-2.

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A Cleavage Reaction of Pentaborane(9). Formation of a New Hypo Triborane Adduct

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The reaction of pentaborane(9) with excess trimethylphosphine proceeds to form B₃H₉·2P(CH₃)₃ and then to give a mixture of B₂H₄·2P(CH₃)₃ and a new hypo class compound tris(trimethylphosphine)-triborane(5), B₃H₅·3P(CH₃)₃. At room temperature under vacuum, the phosphine adduct of diborane(4) sublimes out of the mixture and the triborane(5) adduct converts to B₆H₁₀·2P(CH₃)₃. The yield of B₂H₄·2P(CH₃)₃ based upon the pentaborane(9) used is about 110%. Reactions of B₃H₉·TMED (TMED = *N,N,N',N'*-tetramethylethylenediamine) and B₃H₉·diphos (diphos = 1,2-bis(dimethylphosphino)ethane) with excess trimethylphosphine give B₃H₉·2P(CH₃)₃ first and then the same cleavage reaction follows. The cleavage of pentaborane(9) is compared with that reported for the reaction of B₃H₉ with PF₂N(CH₃)₂. The boron-11 NMR data for the borane adducts encountered in this study are appended.

Introduction

Pentaborane(9) reacts with bases in many different ways. Certain phosphines and amines are known to form molecular addition compounds, such as B₃H₉(phosphine)₂² and B₅H₉(amine)₂,^{2a,3} under appropriate conditions of the reactions. Deprotonation of pentaborane(9) by strong bases to give octahydropentaborate(1-) ion (B₅H₈⁻) is another type of reaction that has been established.⁴ The framework of B₃H₉ is cleaved by many bases as observed in the reaction of ammonia to give B₃H₉·2NH₃,⁵ which has been formulated as H₂B-

(NH₃)₂⁺B₄H₇⁻ and in the reaction of trimethylamine^{3b} to give trimethylamine-borane(3) and a solid of a formula (CH₃)₃NB₄H₆. Many bases undergo complex reactions with B₅H₉ under various conditions to give a variety of degraded borane compounds.⁶ Among these, reactions which yield diborane(4) adducts were reported by Lory and Ritter⁷ and by Hertz, Denniston, and Shore.⁸ The former authors presented evidence for the cleavage of B₃H₉ by (dimethylamino)difluorophosphine (PF₂N(CH₃)₂) to give B₂H₄·2PF₂N(CH₃)₂ and B₃H₅·2PF₂N(CH₃)₂, and the latter utilized the B₂H₄ adduct formation for the preparation of B₂H₄·2P(CH₃)₃. In this paper we report evidence for the stoichiometric cleavage of B₅H₉ by trimethylphosphine to give B₂H₄·2P(CH₃)₃ and B₃H₅·3P(CH₃)₃.

Results and Discussion

A. Reaction of B₅H₉ with Excess P(CH₃)₃. When pentaborane(9) is treated with a large excess of trimethylphosphine

(1) On leave from Kawamura Junior College, Tokyo, Japan.

(2) (a) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1973**, 179. (b) Fratini, A. V.; Sullivan, G. W.; Denniston, M. L.; Hertz, R. K.; Shore, S. G. *J. Am. Chem. Soc.* **1974**, *96*, 3013. (c) Alcock, N. W.; Colquhoun, H. M.; Haran, G.; Sawyer, J. F.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1977**, 368.

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(7) Lory, E. R.; Ritter, D. M. *Inorg. Chem.* **1970**, *9*, 1847.

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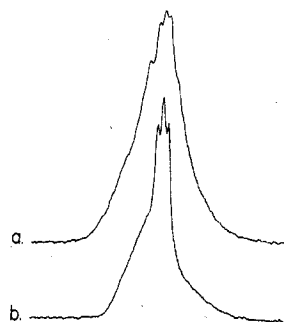
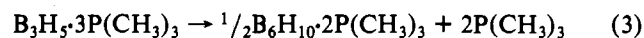
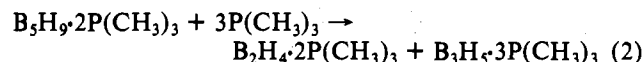


Figure 1. ^{11}B NMR spectra of the reaction product, $\text{B}_5\text{H}_9 + \text{excess P}(\text{CH}_3)_3$ (20 °C; solvent acetonitrile): (a) normal spectrum; (b) proton-spin decoupled spectrum.

in acetonitrile, a reaction slowly proceeds at about -20 °C to form $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$. Trimethylphosphine reacts further with the bis(phosphine) adduct of B_5H_9 at 0 °C or above to cleave the pentaborane framework; the ^{11}B NMR spectrum of the resulting solution consists of the resonance signal of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ at -37.5 ppm⁸ [$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ standard, high field shifts being taken negative] and broad signals overlapped with the signal of the B_2H_4 adduct. See Figure 1. The same change also occurs in dichloromethane or in trimethylphosphine as the solvent. In the latter solvent the reaction proceeds considerably fast. When volatile components are removed by pumping from the resulting solution at -23 or 0 °C, a white solid of an overall composition $\text{B}_5\text{H}_9 \cdot 5\text{P}(\text{CH}_3)_3$ remains in the reaction vessel. The result of vapor pressure depression measurements on the product in liquid trimethylphosphine definitely indicated that B_5H_9 had been cleaved into two fragments by the reaction. The proton-spin decoupled ^{31}P NMR spectrum of a CH_2Cl_2 solution of the solid residue " $\text{B}_5\text{H}_9 \cdot 5\text{P}(\text{CH}_3)_3$ " showed that the signals appear as a dissymmetric broad band in a range of ± 2 ppm centered at 2.0 ppm (85% orthophosphoric acid standard) and that only a small amount of free $\text{P}(\text{CH}_3)_3$ is present in the solution. Since one of the two species in the " $\text{B}_5\text{H}_9 \cdot 5\text{P}(\text{CH}_3)_3$ " is known to be $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$, the other species would have to be $\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$.

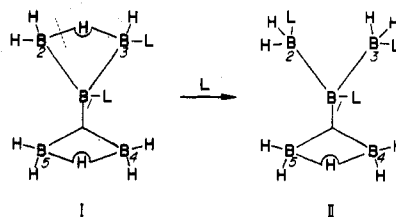
Upon further pumping on the solid residue at room temperature, $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ slowly sublimates out, and a nonsublimable residue is left behind. During this process of separation, $\text{P}(\text{CH}_3)_3$ is given off and the final total reaction stoichiometry approaches to $\text{P}(\text{CH}_3)_3/\text{B}_5\text{H}_9 = 3$. The final residue was identified as bis(trimethylphosphine)-hexaborane(10), $\text{B}_6\text{H}_{10} \cdot 2\text{P}(\text{CH}_3)_3$.⁹ Appropriate equations for these reactions are given (eq 1-3). It is noted that tri-



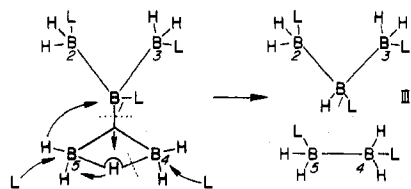
methylphosphine-borane(3) is not produced in these reactions, and only a trace of it, if any, could be detected during the process of the $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ sublimation.

B. Yield of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$. The yield of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ in the process described in section A is about 110% on the basis of the equations presented [(1) and (2)]. The excess yield may be due to a side reaction between the $\text{B}_6\text{H}_{10} \cdot 2\text{P}(\text{CH}_3)_3$ produced and the $\text{P}(\text{CH}_3)_3$ released during the process of the sublimation and/or due to some side reactions during the dimerization process of the B_3H_5 units. In a separate experiment the formation of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ in the reaction of

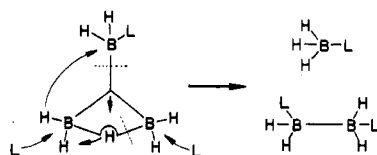
Scheme I



Scheme II



Scheme III



$\text{B}_6\text{H}_{10} \cdot 2\text{P}(\text{CH}_3)_3$ (or B_6H_{10}) with excess $\text{P}(\text{CH}_3)_3$ was confirmed by observing the ^{11}B NMR spectra of the reaction solution. The cleavage pattern of hexaborane(10) is another topic of interest, but the study is yet to be completed. The above findings immediately suggest the use of excess $\text{P}(\text{CH}_3)_3$ for the preparation of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ from B_5H_9 to improve the yield by 55% over that reported previously.⁸ The unchanged excess phosphine can be recovered.

C. Cleavage of Pentaborane(9). Borane compounds are classified into closo, nido, arachno, and hypho classes according to the skeletal electron counts of the compounds.¹⁰ The numbers of the skeletal electrons for compounds belonging to each of these classes are $2n + 2$, $2n + 4$, $2n + 6$, and $2n + 8$, respectively, n being the number of boron atoms. Addition of a Lewis base to a borane compound results in the formation of a compound that belongs to the next higher class. Thus, the addition of $\text{P}(\text{CH}_3)_3$ to an arachno B_4 compound, $\text{B}_4\text{H}_8\text{P}(\text{CH}_3)_3$,¹¹ gives a hypho B_4 compound, $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3$.¹¹ Likewise, a hypothetical compound tris(trimethylphosphine)-pentaborane(9), if formed by the addition of $\text{P}(\text{CH}_3)_3$ to a hypho compound $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$, would be a compound which belongs to a new class next higher to hypho. The structure for the compound may even be considered, by extrapolating the structural pattern change that has been observed on going from closo to hypho,^{10,12} to be II in Scheme I, where $\text{L} = \text{P}(\text{CH}_3)_3$.

In this study, however, no evidence was found for the formation of the tris(phosphine) adduct of B_5H_9 or any other intermediate species; the ^{11}B NMR spectra of the reaction solutions showed the disappearance of the $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$ signals^{2b} accompanied by the appearance of the final signals (Figure 1) and no other signals have ever been detected during the course of the entire process. The tris(phosphine) adduct, however, may still be involved in the reaction as a short-lived

(10) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Williams, R. E. *Ibid.* **1976**, *18*, 67. Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. Rudolph, R. W.; Thompson, D. A. *Inorg. Chem.* **1974**, *13*, 2779.

(11) Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302.

(12) It is noted that, as the structures of B_4 -hypho^{11,13} and B_5 -hypho^{2b,c} compounds indicate, the lower borane compounds assume progressively more branched structures going from arachno to hypho class. The limiting structures would be those of saturated hydrocarbons.

(13) Colquhoun, H. M. *J. Chem. Res. Synop.* **1978**, 451.

(9) Mangion, M.; Hertz, R. K.; Denniston, M. L.; Long, J. R.; Clayton, W. R.; Shore, S. G. *J. Am. Chem. Soc.* **1976**, *88*, 449.

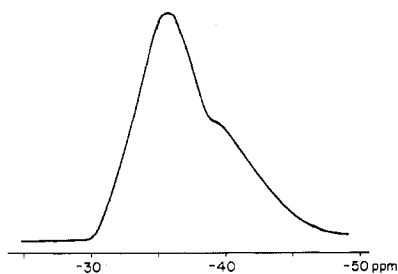
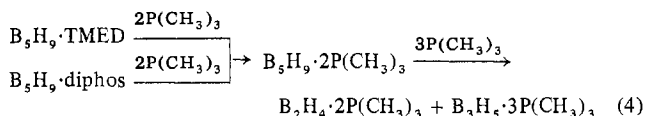


Figure 2. ^{11}B NMR spectrum (proton-spin decoupled) for $\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$.

intermediate, and the cleavage may occur, as indicated in Scheme II, by the addition of phosphines to the unligated boron atoms, which is concerted with migration of the hydrogen atoms and the B(4)–B(5) bond formation. It is noted that the same pattern of cleavage can be visualized for the reaction of $(\text{CH}_3)_3\text{P} \cdot \text{B}_3\text{H}_7$ with $\text{P}(\text{CH}_3)_3$ ¹¹ to produce $(\text{C}-\text{H}_3)_3\text{P} \cdot \text{BH}_3$ and $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ as indicated in Scheme III.¹⁴

Relevant to the idea of the possible formation of the new class of B_5 compounds, the reactions of $\text{B}_5\text{H}_9 \cdot \text{TMED}^{3c}$ (TMED = *N,N,N',N'*-tetramethylethylenediamine) and $\text{B}_5\text{H}_9 \cdot \text{diphos}^{2c}$ (diphos = 1,2-bis(diphenylphosphino)ethane) were investigated. Again no evidence for the formation of $\text{B}_5\text{H}_9 \cdot \text{TMED} \cdot \text{P}(\text{CH}_3)_3$ or $\text{B}_5\text{H}_9 \cdot \text{diphos} \cdot \text{P}(\text{CH}_3)_3$ could be found in the ^{11}B NMR spectra of the reaction solution. Displacement of the base (TMED or diphos) by $\text{P}(\text{CH}_3)_3$ occurs first to form $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$, and then the cleavage reaction follows to give the mixture of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$ (eq 4).

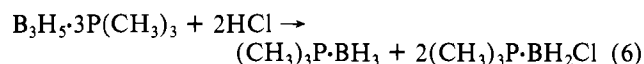
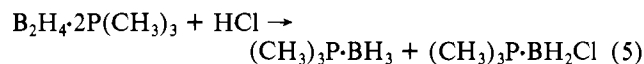


Savory and Wallbridge reported^{2a} that the reaction of $\text{B}_5\text{H}_9 \cdot 2\text{N}(\text{CH}_3)_3$ with $\text{P}(\text{CH}_3)_3$ also results in the displacement of the $\text{N}(\text{CH}_3)_3$ by $\text{P}(\text{CH}_3)_3$ to give $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$.

D. Tris(trimethylphosphine)–Triborane(5). The isolation of the compound $\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$ has not been accomplished, but the formation of the compound as the result of the B_5H_9 cleavage by $\text{P}(\text{CH}_3)_3$ has been demonstrated in this study. The compound is indefinitely stable at -23°C and is stable even at room temperature in liquid $\text{P}(\text{CH}_3)_3$. When placed under a condition of dynamic vacuum above 0°C , the compound gives off $\text{P}(\text{CH}_3)_3$ and changes to $\text{B}_6\text{H}_{10} \cdot 2\text{P}(\text{CH}_3)_3$. Evidence for the formation of $\text{B}_3\text{H}_5 \cdot 2\text{P}(\text{CH}_3)_3$ or $\text{B}_6\text{H}_{10} \cdot \text{P}(\text{CH}_3)_3$ was not found. In the paper⁷ which describes the reaction of B_5H_9 with (dimethylamino)difluorophosphine, $\text{PF}_2\text{N}(\text{CH}_3)_2$, Lory and Ritter reported mass spectral evidence for the formation of $\text{B}_6\text{H}_{10} \cdot \text{PF}_2\text{N}(\text{CH}_3)_2$ and proposed the formation of $\text{B}_3\text{H}_5 \cdot 2\text{PF}_2\text{N}(\text{CH}_3)_2$ as the precursor of the hexaborane adduct. We now see a certain parallel between the two B_5H_9 reactions, one with $\text{PF}_2\text{N}(\text{CH}_3)_2$ and another with $\text{P}(\text{CH}_3)_3$. The differences that we have observed are attributable to the difference in base strength of the two phosphines. Trimethylphosphine is known to be a much stronger base toward boranes than $\text{PF}_2\text{N}(\text{CH}_3)_2$.¹⁵ Thus, $\text{P}(\text{CH}_3)_3$ reacts faster with B_5H_9 and adds to B_3H_5 and B_6H_{10} more tightly than $\text{PF}_2\text{N}(\text{CH}_3)_2$. It was therefore possible to obtain more definitive stoichiometry for the $\text{P}(\text{CH}_3)_3$ reaction than for the $\text{PF}_2\text{N}(\text{CH}_3)_2$ reaction.

The tris(trimethylphosphine) adduct of B_3H_5 represents the first example of B_3 hypophosphite class compounds. Structure III in Scheme II is thought to be appropriate for the adduct. Shown in Figure 2 as the ^{11}B NMR spectrum for $\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$ is a residual spectrum that was obtained by graphically subtracting the signal of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ (Figure 4b) from the spectrum of the 1:1 mixture of the B_2H_4 and B_3H_5 adducts (Figure 1b) after the signal intensity ratio between the two spectra was adjusted to 2:5. Two signals centered at -36.5 and -39.0 ppm are evident in the figure and are attributed to the B(2,3) and B(1) atoms, respectively.

Treatment of the mixture of $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$ in CH_2Cl_2 with anhydrous hydrogen chloride results in the formation of $(\text{CH}_3)_3\text{P} \cdot \text{BH}_3$ and $(\text{CH}_3)_3\text{P} \cdot \text{BH}_2\text{Cl}$ in a 2:3 molar ratio. When $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$ is treated similarly with anhydrous HCl, the B_2H_4 adduct is cleaved to give $(\text{CH}_3)_3\text{P} \cdot \text{BH}_3$ and $(\text{CH}_3)_3\text{P} \cdot \text{BH}_2\text{Cl}$ in a 1:1 molar ratio. Equations 5 and 6 are therefore appropriate. These reactions proceed



readily at -80°C . Thus, the sensitiveness of the B_2H_4 and B_3H_5 adducts toward the acid contrasts with the inertness of the adducts toward the phosphine base.

Experimental Section

General Data. Standard high-vacuum techniques were used throughout for the handling of volatile compounds. Stopcocks and joints were greased with Apiezon N or M, unless otherwise mentioned. The solid borane adducts were handled in a clear plastic bag filled with nitrogen gas.

Pentaborane(9), obtained from Callery Chemical Co., was purified by fractional condensation on a vacuum line. Trimethylphosphine was prepared by the method described by Jolly.¹⁶ The preparation, however, was performed with a 0.5-mol quantity of PH_3 in a 2-L, three-necked flask equipped with a Lew magnetic stirrer (Scientific Glass Apparatus Co.). (Such a scale-up is not recommended in the literature, but no difficulty was met during the performance of the preparation.) Crude trimethylphosphine was distilled through a 70 cm long, vacuum-jacketed column, which had been packed with glass beads, under the atmosphere of nitrogen gas at 1-atm pressure. The very middle portion of the distillate was specially saved and used for the vapor pressure depression experiment. Dichloromethane and acetonitrile (commercial reagents) were stored over molecular sieves and were distilled from the container into the vacuum line as needed. Bis(diphenylphosphino)ethane–pentaborane(9)^{2c} and tetramethylethylenediamine–pentaborane(9)^{3c} were prepared by the methods in the literature. The ^{11}B and ^{31}P NMR spectra were recorded on a Varian XL-100-15 instrument operating at 32.1 and 40.5 Hz, respectively.

Reactions of B_5H_9 with $\text{P}(\text{CH}_3)_3$. A 0.542 mmol sample of B_5H_9 was taken in a reaction tube (10 mm o.d. \times 250 mm long Pyrex glass) equipped with a stopcock, and 16.9 mmol of $\text{P}(\text{CH}_3)_3$ was condensed in the tube at -196°C . The mixture became a uniform, gelatinous solid as it was agitated by shaking at -80°C . Then, as the tube was allowed to warm to -35°C , the mixture became fluid and turbid. The solution became clear when allowed to warm to room temperature. The ^{11}B NMR spectra of the clear solution at room temperature was identical with that shown in Figure 1. No noncondensable gas was found in the reaction tube, and the solution remained clear and colorless at room temperature.

The progress of the reaction in CH_2Cl_2 was monitored by observing the ^{11}B NMR spectra of a reaction mixture. A CH_2Cl_2 solution (1.5 mL) containing 0.466 mmol of B_5H_9 was prepared in a 10-mm o.d. Pyrex reaction tube. It was cooled to -35°C , and a 2.919 mmol sample of $\text{P}(\text{CH}_3)_3$ [$\text{P}(\text{CH}_3)_3/\text{B}_5\text{H}_9 = 6.3$] was admitted slowly into the tube through the stopcock while the solution was being agitated by gentle shaking. $\text{P}(\text{CH}_3)_3$ was absorbed by the solution, but it was

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Table I. Stoichiometry of the Reaction of Pentaborane(9) with Trimethylphosphine

reactants (solvent CH ₃ CN)			products					
amt of B ₅ H ₉ , mmol	amt of P(CH ₃) ₃ , mmol	P(CH ₃) ₃ /B ₅ H ₉	before sublimation			after sublimation		
			amt of P(CH ₃) ₃ recovered, mmol (T, °C)	amt of P(CH ₃) ₃ unrecovered, mmol	P(CH ₃) ₃ /B ₅ H ₉	amt of B ₂ H ₄ ·2P(CH ₃) ₃ , mmol (yield, %)	amt of P(CH ₃) ₃ released, mmol	overall P(CH ₃) ₃ /B ₅ H ₉
0.61	3.75	6.14	0.59 (0)	3.16	5.2	0.649 (106)	1.35	2.96
1.07	6.60	6.17	1.44 (0)	5.16	4.82	1.23 (115)	2.02	2.93
1.02	6.44	6.31	1.46 (0)	4.98	4.88	1.30 (127)	1.69	3.22
1.13	6.84	6.05	1.45 (0)	5.39	4.77	1.34 (119)	1.79	3.19
3.17	19.01	6.00	2.21 (0)	16.80	5.30	3.72 (117)		
2.36	14.07	5.96				2.99 (127)		
2.12	12.94	6.05				2.33 (110)		
0.464	2.95	6.36	0.47 (0)	2.48	5.3			
0.589	3.81	6.47	1.13 (0)	2.68	4.55	0.587 (100)	0.74	3.29
12.65	73.28	5.79	6.80 (0)	66.48	5.26	14.39 (114)	25.85	3.21
0.152	34.40 ^a	226.3	33.63 (-23)	0.77	5.1			
0.508	25.07 ^a	49.35	22.49 (-23)	2.58	5.08			
0.389	12.61 ^a	32.42	10.62 (-23)	1.99	5.11			

^a P(CH₃)₃ was used as the solvent, and the reaction was run in a grease-free system.

necessary to condense the last bit of the P(CH₃)₃ sample by cooling the tube with liquid nitrogen. The mixture was then allowed to warm to -40 °C and placed in the probe of the NMR instrument. At -20 °C the signals of B₅H₉·2P(CH₃)₃ began to grow in the spectrum, and the appearance of the B₂H₄·2P(CH₃)₃ signal followed. The slow growth of these signals is accompanied by the weakening of the B₅H₉ signal intensity. When the temperature was raised to 0 °C after the sample had stood at -20 °C for 20 min, the intensity of the B₂H₄·2P(CH₃)₃ signal increased considerably, but the signals of the B₅H₉ and B₅H₉·2P(CH₃)₃ were still present. It took 50 min at 20 °C for the B₅H₉ signal to disappear and an additional 60 min for the B₅H₉·2P(CH₃)₃ signal to disappear completely. The final spectrum was identical with that shown in Figure 1. In a CH₃CN solution the reaction proceeded similarly to give the final spectrum which is shown in Figure 1.

Stoichiometry of the Reaction. Generally the reaction mixtures were stirred at -35 °C for 15 min and then at room temperature for 2¹/₄ h. Volatile components were then pumped out from the reaction mixture at -23 or 0 °C. A white solid remained in the reaction vessel. When P(CH₃)₃ was used as the solvent, the recovered phosphine was weighed to find the reaction stoichiometry. When CH₂Cl₂ or CH₃CN was used as the solvent, the entire volatile fraction was treated with anhydrous HCl and the weight of the (CH₃)₃PH⁺Cl⁻ was determined. The reaction data are summarized in Table I. A sample of the white solid which was obtained as a residue in the reaction vessel was dissolved in CH₂Cl₂, and its ³¹P{¹H} NMR spectrum was examined. The spectrum consisted of a dissymmetric broad band centered at 2.0 ppm and a very weak signal at -62.9 ppm.¹⁷ The high-field signal is due to free P(CH₃)₃, and its intensity was estimated to be about 1% of the total low-field signal intensity. The ³¹P signal of B₂H₄·2P(CH₃)₃ was found to appear at 2.8 ppm during this study (lit.⁸ 3.2 ppm) and therefore must constitute a part of the broad band at 2.0 ppm.

Sublimation of B₂H₄·2P(CH₃)₃. The solid residue of composition B₅H₉·5P(CH₃)₃ was transferred into a sublimation-sampling apparatus similar to that described elsewhere,¹⁸ the apparatus was evacuated, and the cold finger was cooled to -196 °C while the tube containing the residue was exposed to room temperature. The B₂H₄ adduct condensed on the cold finger along with the P(CH₃)₃ which was given off by the residue during the slow process of this sublimation. The condensate was washed into a weighing tube which was attached to the side of the apparatus, and the two components in the condensate were separated to determine the amount of each. The nonvolatile residue was identified as B₆H₁₀·2P(CH₃)₃ by its ¹¹B NMR spectrum⁹

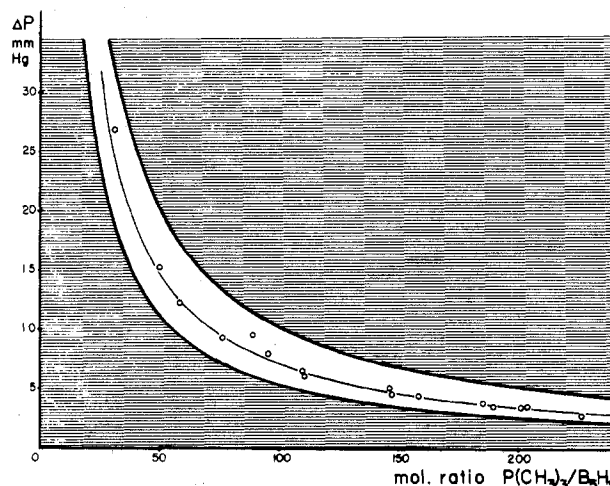


Figure 3. Vapor pressure depression of trimethylphosphine solutions of pentaborane(9).

in CH₂Cl₂. The B₆H₁₀·2P(CH₃)₃ sample was contaminated with minor quantities of impurities including B₂H₄·2P(CH₃)₃. The reaction data are summarized in Table I.

For a larger scale preparation of B₂H₄·2P(CH₃)₃, a 12.6-mmol quantity of B₅H₉ was dissolved in 5 mL of CH₃CN in a 100-mL round-bottom flask equipped with a ground joint and a 73.3-mmol sample of P(CH₃)₃ was condensed in the flask. The mixture was stirred briefly at -35 °C and then at room temperature for 2 h. The flask was then pumped first at 0 °C to remove the solvent and the excess P(CH₃)₃ and further at room temperature through a -196 °C trap which was attached very close to the flask. The B₂H₄ adduct and P(CH₃)₃ condensed in the trap and the P(CH₃)₃ was separated from the adduct later. The yield of B₂H₄·2P(CH₃)₃ was 14.4 mmol (2.56 g) or 113.8% on the basis of B₅H₉ used.

Vapor Pressure Depression Measurements. A U-shaped differential manometer was used to measure the pressure difference between a system containing pure liquid P(CH₃)₃ and another system containing a P(CH₃)₃ solution of B₅H₉. Mercury was used as the manometric fluid. The vapor pressure of the pure P(CH₃)₃ was read directly on a mercury manometer attached to the solvent system. Only Teflon valves and Viton O-ring joints were used for the apparatus including sample-measuring devices to avoid the presence of stopcock grease in contact with the phosphine vapor. (Absorption of trimethylphosphine by stopcock grease is a serious problem for the quantitative handling of the compound.) The entire setup was connected to a vacuum line.

A B₅H₉ solution of a known concentration in P(CH₃)₃ was prepared directly in the solution cell of the apparatus in a manner similar to that described in a foregoing section. The solution and solvent cells were then thermostated at 18 °C. The vapor pressure of the solvent

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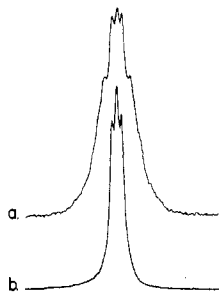


Figure 4. ^{11}B NMR spectra of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ (20 °C; solvent acetonitrile): (a) normal spectrum; (b) proton-spin decoupled spectrum.

at the controlled temperature was 347.8 mmHg. A set of data at different concentrations was obtained by further additions of $\text{P}(\text{CH}_3)_3$ to the solution or removals of $\text{P}(\text{CH}_3)_3$ from the solution. Two sets of data thus obtained are plotted in Figure 3. In the figure, the experimental values are compared with the values that were calculated by Raoult's law for certain hypothetical modes of B_5H_9 cleavage. The upper curve represents an extreme case in which B_5H_9 has been cleaved in $\text{P}(\text{CH}_3)_3$ to form $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ and two other "unligated borane species". If the latter two species were combined with $\text{P}(\text{CH}_3)_3$, the points for ΔP should appear above the curve. The lower curve is for another extreme case where B_5H_9 has been converted to $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ and " $\text{B}_6\text{H}_{10}\cdot 6\text{P}(\text{CH}_3)_3$ ". The middle curve represents values calculated for the formation of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$ in a 1:1 molar ratio. Clearly the experimental values (circles in the figure) are consistent with the cleavage of B_5H_9 into two fragments. As a check of the ideality of trimethylphosphine solutions, the molecular weight of $(\text{CH}_3)_3\text{PBH}_3$ was determined on the same apparatus in a concentration range 0.02–0.06 [$(\text{CH}_3)_3\text{PBH}_3/\text{P}(\text{CH}_3)_3$] (or 20–8 mmHg range of ΔP): calcd for $(\text{CH}_3)_3\text{PBH}_3$, 89.9; found, 90.2 \pm 0.2.

Reactions of $\text{B}_5\text{H}_9\cdot\text{TMED}$ and $\text{B}_5\text{H}_9\cdot\text{diphos}$ with $\text{P}(\text{CH}_3)_3$. A solution containing 0.41 mmol of $\text{B}_5\text{H}_9\cdot\text{TMED}$ in 1.5 mL of CH_3CN was prepared in a 10-mm o.d. Pyrex sample tube equipped with a stopcock. A 0.45-mmol quantity of $\text{P}(\text{CH}_3)_3$ was condensed in the tube at -196 °C, and then the mixture was allowed to warm to -35 °C. The solution became turbid as it was stirred by gentle shaking at -35 °C but became clear when warmed to room temperature. The tube was placed in the probe of the NMR instrument, and the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum was recorded at 20 °C. The spectrum indicated the presence of $\text{B}_5\text{H}_9\cdot\text{TMED}$ ^{3c} and $\text{B}_5\text{H}_9\cdot 2\text{P}(\text{CH}_3)_3$ ^{2b} in the solution.

When $\text{B}_5\text{H}_9\cdot\text{TMED}$ and $\text{P}(\text{CH}_3)_3$ were mixed in a 1:3 molar ratio in a manner similar to that for the 1:1 mixture, the solution gave a spectrum consisting of the $\text{B}_5\text{H}_9\cdot 2\text{P}(\text{CH}_3)_3$ signals and the $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ signal. (The $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$ signal is not easily identifiable in the presence of other overlapping signals.) No signals of $\text{B}_5\text{H}_9\cdot\text{TMED}$ appeared in the spectrum. Further, two more solutions were prepared by mixing $\text{B}_5\text{H}_9\cdot\text{TMED}$ and $\text{P}(\text{CH}_3)_3$ in 1:8.4 and 1:11.5 molar ratios, and the spectra of the solutions were recorded at 20 °C. The spectra were identical with that shown in Figure 1 and contained no other signals.

The reaction of $\text{B}_5\text{H}_9\cdot\text{diphos}$ with $\text{P}(\text{CH}_3)_3$ was studied in the same manner as described for the $\text{B}_5\text{H}_9\cdot\text{TMED}$ reaction. Tetrahydrofuran was used as the solvent. When $\text{B}_5\text{H}_9\cdot\text{diphos}$ and $\text{P}(\text{CH}_3)_3$ were mixed in a 1:3.3 molar ratio, $\text{B}_5\text{H}_9\cdot 2\text{P}(\text{CH}_3)_3$ and a small amount of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$

were found in the resulting solution at 20 °C. When the mixing ratio was 1:8.5, $\text{B}_5\text{H}_9\cdot 2\text{P}(\text{CH}_3)_3$ and $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ (and probably $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$) were the boron compounds in the solution immediately after the solution was warmed to 10 °C. One hour later, the spectrum of the solution was identical with that shown in Figure 1.

Reaction of " $\text{B}_5\text{H}_9\cdot 5\text{P}(\text{CH}_3)_3$ " with HCl. A 0.389-mmol quantity of B_5H_9 was treated with a large excess of $\text{P}(\text{CH}_3)_3$ in a manner similar to that described earlier in this section to obtain the solid " $\text{B}_5\text{H}_9\cdot 5\text{P}(\text{CH}_3)_3$ ". The solid was dissolved in CH_2Cl_2 (1.5 mL), and the solution was treated with 1.17 mmol of anhydrous HCl at -80 °C. A white solid formed immediately. The mixture was allowed to warm slowly to room temperature. No noncondensable gas evolved and some of the white solid still remained at room temperature. More CH_2Cl_2 (1.5 mL) was added to dissolve the solid, and the ^{11}B NMR spectrum of the resulting clear solution was examined. Two signals due to $(\text{CH}_3)_3\text{P}\cdot\text{BH}_3$ and $(\text{CH}_3)_3\text{P}\cdot\text{BH}_2\text{Cl}$ were observed at -37.0 and -18.1 ppm in a 2:2.94 intensity ratio, and no other signals could be detected in the spectrum.

Reaction of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ with HCl. A 0.368-mmol quantity of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ (product from the $\text{B}_5\text{H}_9\cdot\text{P}(\text{CH}_3)_3$ reaction) was placed in a 10-mm o.d. reaction tube and dissolved in CH_2Cl_2 (1.5 mL). A 0.402-mmol quantity of anhydrous HCl was condensed in the tube, and the tube was placed in the probe of the NMR instrument to record the ^{11}B spectra starting at -80 °C. At -80 °C the reaction was already complete; the signals of $(\text{CH}_3)_3\text{P}\cdot\text{BH}_3$ and $(\text{CH}_3)_3\text{P}\cdot\text{BH}_2\text{Cl}$ were observed in a 1:1 intensity ratio, and no other signals were detected.

^{11}B NMR Shift Data for Some of the Borane Adducts. Chemical shift values observed for some of the borane adducts in our laboratory during the course of this study are listed and compared below with those reported in the literature. The literature values have been adjusted by using the following scale and are indicated in parentheses: $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2 = 0$ and $\text{B}(\text{OCH}_3)_3 = +18.1$ ppm.¹⁹

$\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$: solvent, CH_3CN , CH_2Cl_2 , tetrahydrofuran; temperature, 25 to -40 °C; shift, $\delta = -37.5 \pm 0.2$ (-37.4).⁸ The proton-spin decoupled spectrum at ambient temperature is of an XAA'X' type. See Figure 4. The separation between the two outer peaks is 43 Hz.

$\text{B}_5\text{H}_9\cdot 2\text{P}(\text{CH}_3)_3$: solvent, CH_2Cl_2 , CH_3CN ; temperature, 20 °C; shift, $\delta = -19.8$ (-19.6),^{2b} -25.4 (-25.2), -32.4 (-31.8), -56.1 (-55.7). The signal at -32.4 ppm in the proton-spin decoupled spectrum is a doublet at 20 °C; $J_{\text{BP}} = 125$ Hz.

$\text{B}_5\text{H}_9\cdot\text{TMED}$: solvent, CH_3CN ; temperature, 20 °C; shift $\delta = +18.7$ ($+18.1$),^{3c} -3.7 (-4.2), -12.4 (-12.0), -55.2 (-55.4).

$\text{B}_5\text{H}_9\cdot\text{diphos}$: solvent, tetrahydrofuran; temperature, 20 °C; shift, $\delta = -18.3$, -28.8 , -57.1 ; intensity ratio, 3:1:1 in the order presented.

$\text{B}_6\text{H}_{10}\cdot 2\text{P}(\text{CH}_3)_3$: solvent, CH_2Cl_2 ; temperature, 20 °C; shift, $\delta = -2.1$ (d, $J_{\text{BH}} = 112$ Hz) (-2.5),⁹ -19.9 (q, $J_{\text{BH}} = 75$ Hz) (-19.4), -51.5 (t, $J_{\text{BH}} \approx J_{\text{BP}} = 112$ Hz) (-50.2).

$(\text{CH}_3)_3\text{P}\cdot\text{BH}_2\text{Cl}$: solvent, CH_2Cl_2 ; temperature, 20 °C; shift, -18.1 ($J_{\text{BH}} = 115$ Hz, $J_{\text{BP}} = 85$ Hz).

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Registry No. B_5H_9 , 19624-22-7; $\text{P}(\text{CH}_3)_3$, 594-09-2; $\text{B}_5\text{H}_9\cdot 2\text{P}(\text{CH}_3)_3$, 39661-74-0; $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$, 67113-98-8; $\text{B}_6\text{H}_{10}\cdot 2\text{P}(\text{CH}_3)_3$, 57034-29-4; $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$, 73636-27-8; $\text{B}_5\text{H}_9\cdot\text{TMED}$, 53965-74-5; $\text{B}_5\text{H}_9\cdot\text{diphos}$, 73636-28-9; $(\text{CH}_3)_3\text{P}\cdot\text{BH}_3$, 35527-73-2; $(\text{CH}_3)_3\text{P}\cdot\text{BH}_2\text{Cl}$, 64160-46-9.