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Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

Tetraborane(8) Adducts of Strongly Basic Phosphines

MITSUAKI KAMEDA, MAMORU SHIMOI, and GOJI KODAMA*

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Four methods were developed for the preparation of $B_4H_8\cdot P(CH_3)_3$: the removal of one of the trimethylphosphine ligands from $B_4H_8\cdot 2P(CH_3)_3$ by B_2H_6, the hydride removal from $B_4H_9\cdot P(CH_3)_3^-$ by B_2H_6, the boron framework expansion of $B_3H_7\cdot THF$ with the use of $B_2H_4\cdot 2P(CH_3)_3$, and the reaction of $B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^-$ with trimethylamine. The yields were better than 90%. The adduct of tris(dimethylamino)phosphine, $B_4H_8\cdot P[N(CH_3)_2]_3$, was prepared by the hydride removal reaction of $B_4H_9\cdot P[N(CH_3)_2]_3^-$. Two hypho-class bis(base) adducts of B_4H_8 were prepared from the above mono(phosphine) adducts. These were $B_4H_8\cdot P(CH_3)_3\cdot N(CH_3)_3$ and $B_4H_8\cdot P(CH_3)_3\cdot P[N(CH_3)_2]_3$. The former existed in two isomeric forms, each being different from the other in the positions of the two different ligands. These compounds were characterized by their ^{11}B, ^1H, and ^{31}P NMR spectra.

Introduction

Generally, Lewis base adducts of tetraborane(8) (B_4H_8) are prepared by the reactions of pentaborane(11) (B_5H_{11}) with appropriate Lewis bases.[1] These reactions, however, can proceed one step further if the reacting bases are strong, and give bis(base) adducts of B_4H_8. Thus, when B_5H_{11} is treated with $P(CH_3)_3$ in a 1:2 molar ratio, an appreciable amount of the bis(phosphine) adduct is produced along with the mono(phosphine) adduct.[2] The bis(trimethylphosphine) adduct, $B_4H_8\cdot 2P(CH_3)_3$, is stable, and the rate of its formation is fast in the above reaction. Effective separation of $B_4H_8\cdot P(CH_3)_3$ from such a product mixture containing the other phosphine adducts and unchanged B_5H_{11} is difficult and has not been accomplished.

During the course of the boron hydride reaction study in our laboratory, the formation of $B_4H_8\cdot P(CH_3)_3$ was observed in several different reactions. Some of the reactions appeared to give clean mixtures of products from which $B_4H_8\cdot P(CH_3)_3$ could be isolated readily. We, therefore, investigated these reactions for the feasible preparation of $B_4H_8\cdot P(CH_3)_3$. Furthermore, one of these reactions was utilized to prepare $B_4H_8\cdot P[N(CH_3)_2]_3$, a B_4H_8 adduct of another strongly basic phosphine. This paper describes the preparation and Lewis acid behavior of these phosphine adducts.

Results and Discussion

A. $B_4H_8\cdot P(CH_3)_3$. The tetraborane(8) adduct of trimethylphosphine could be obtained in yields better than 90% by the following four reactions:

$$B_4H_8\cdot 2P(CH_3)_3 + {}^1/_2B_2H_6 \rightarrow B_4H_8\cdot P(CH_3)_3 + (CH_3)_3P\cdot BH_3 \tag{1}$$

$$K^+B_4H_9\cdot P(CH_3)_3^- + {}^1/_2B_2H_6 \rightarrow B_4H_8\cdot P(CH_3)_3 + KBH_4 \tag{2}$$

$$B_2H_4\cdot 2P(CH_3)_3 + B_3H_7\cdot THF \rightarrow B_4H_8\cdot P(CH_3)_3 + (CH_3)_3P\cdot BH_3 + THF \tag{3}$$

$$B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^- + N(CH_3)_3 \rightarrow B_4H_8\cdot P(CH_3)_3 + (CH_3)_3P\cdot BH_3 + (CH_3)_3N\cdot BH_3 \tag{4}$$

Reaction 1 amounts to an improvement of the procedure involving the reaction of B_5H_{11} with $P(CH_3)_3$. Pentaborane(11) was converted first, with the use of excess $P(CH_3)_3$, into $B_4H_8\cdot 2P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$,[2] the BH_3 adduct was sublimed out of the mixture, and then one of the $P(CH_3)_3$ groups on the bisadduct was extracted by diborane(6). Thus, the complication due to the presence of unchanged B_5H_{11} in the reaction products could be eliminated. In reaction 2 the hydride ion was abstracted from the $B_4H_9\cdot P(CH_3)_3^-$ ion by diborane(6). The adduct anion, $B_4H_9\cdot P(CH_3)_3^-$,[3] could be prepared by the addition of $P(CH_3)_3$ to the $B_4H_9^-$ ion, which had been prepared by deprotonating B_4H_{10}.[4] In effect, the replacement of H^- in the $B_4H_9^-$ ion by $P(CH_3)_3$ was accomplished via the formation of the hypho-class compound $B_4H_9\cdot P(CH_3)_3^-$ ion. Methods 3 and 4 are based on the novel reaction chemistry of bis(trimethylphosphine)–diborane(4) [$B_2H_4\cdot 2P(CH_3)_3$]. In reaction 3 $B_2H_4\cdot 2P(CH_3)_3$ acted as a reagent for the borane framework expansion; half of the diborane(4)-adduct molecule was added to the triborane unit to form $B_4H_8\cdot P(CH_3)_3$ while another half was converted into $BH_3\cdot P(CH_3)_3$. The $B_3H_8^-$ salt of the triboron cation in reaction 4 was prepared by the reaction of $B_2H_4\cdot 2P(CH_3)_3$ with B_4H_{10}.[5,6] The reaction of this salt with $N(CH_3)_3$ proceeded as indicated in eq 4. The mechanism of the reaction is discussed in a separate paper.[5] Both reactions 3 and 4 proceeded smoothly, and the tetraborane adduct of high purity could be separated from the products in excellent yields. In particular, reaction 4 did not require stoichiometric amounts of the reactants. The use of a slight excess of $N(CH_3)_3$ was not detrimental to the yield and purity of the product. The reaction of $B_3H_6\cdot 2P(CH_3)_3^+B_3H_8^-$ with $P(CH_3)_3$ in a 1:1 molar ratio also gave $B_4H_8\cdot P(CH_3)_3$,[5] but the stoichiometric mixing was necessary or the purity of the product was affected.

$B_4H_8\cdot P(CH_3)_3$ was a stable, sublimable solid at room temperature in the absence of air. The mass spectrum of $B_4H_8\cdot P(CH_3)_3$ showed a major cluster of peaks in the range from *m/e* 119 to 129, which was attributable to a group of $B_4H_{8-n}\cdot P(CH_3)_3^+$ ions. In addition, a cluster of weak peaks appeared at *m/e* 198–204, corresponding to $B_4H_{8-n}\cdot 2P(CH_3)_3^+$ ions. The intensity of this high-mass cluster was 10% of that of the *m/e* 119–129 cluster when 15 eV was used and 23% at 70 eV. No peaks were found between the two clusters. In the mass spectrum of $B_4H_8\cdot 2P(CH_3)_3$, there were two major clusters of peaks centered at *m/e* 175 and 189, between the clusters of $B_4H_{8-n}\cdot 2P(CH_3)_3^+$ and $B_4H_{8-n}\cdot P(CH_3)_3^+$ ions. The high-mass cluster at *m/e* 198–204 in the spectrum of $B_4H_8\cdot P(CH_3)_3$, therefore, was attributed to the $B_4H_{8-n}\cdot 2P(CH_3)_3^+$ ions that were generated in the instrument as a result of the electron impact.

$B_4H_8\cdot P(CH_3)_3$ interacted with strong bases to give bis(base) adducts of B_4H_8 (see section C) but was inert to weak bases such as ethers. It reacted readily with hydrogen chloride at −80 °C in CH_2Cl_2, producing $B_3H_7\cdot P(CH_3)_3$, B_2H_5Cl, B_2H_6, and BCl_3. The ease of reaction was similar to that observed[7]

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[1] See, for example: "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 135.

[2] Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302.

[3] Shimoi, M.; Kodama, G. *Inorg. Chem.* **1983**, *22*, 1542.

[4] Johnson, H. D., II; Shore, S. G. *J. Am. Chem. Soc.* **1970**, *92*, 7586.

[5] Kameda, M.; Kodama, G. *Inorg. Chem.*, following paper in this issue.

[6] Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.

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Table I. NMR Data

		$B_4H_8{\cdot}P(CH_3)_3$			$B_4H_8{\cdot}P[N(CH_3)_2]_3$		
	temp, °C	shift, ppm	coupling const, Hz	assgnt	shift, ppm	coupling const, Hz	assgnt
^{11}B	+25	−51.5	$J_{PB} = 115$	B(1)	−52.7	$J_{PB} = 180$	B(1)
			$J_{HB} = 110$			$J_{HB} = 110$	
		−7.0	$J_{HB} = 122$	B(2,4)	−7.8	$J_{HB} = 120$	B(2,4)
		−1.8	$J_{HB} = 120$	B(3)	−0.7	$J_{HB} = 120$	B(3)
			$J_{BB} = 12$				
		+5.1		B′(3)[a]			
^{31}P	+25	−0.9	$J_{BP} = 118$		+94.0	$J_{BP} = 182$	
^{1}H	0	−2.42		H(μ)	−2.77		H(μ)
		+1.10[b]	$J_{BH} = 110$	H(1)	+0.92	$J_{BH} = 105$	H(1)
		+1.27	$^2J_{PH} = 10.5$	H(C)	+1.71		H(2,4)
		+2.08		H(2,4)	+2.10	$^3J_{PH} = 9$	H(C)
		+2.49		H(3)	(+2.1?)[c]		H(3)

[a] B(3) atom of the isomer. [b] Overlapped with the H(C) signal. [c] Probably buried under the H(C) signal.

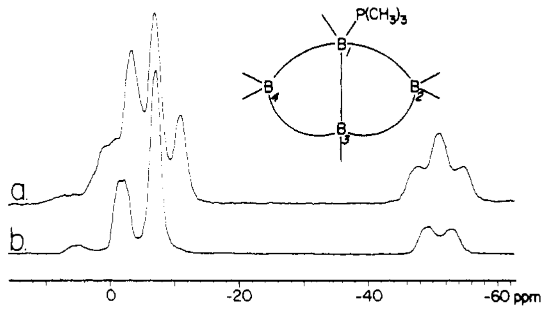

Figure 1. ^{11}B NMR spectra of $B_4H_8{\cdot}P(CH_3)_3$ in dichloromethane-d_2 at +25 °C: (a) normal spectrum; (b) proton-spin-decoupled spectrum. The structure was drawn after the structure of $B_4H_8{\cdot}PF_2N(CH_3)_2$.[16]

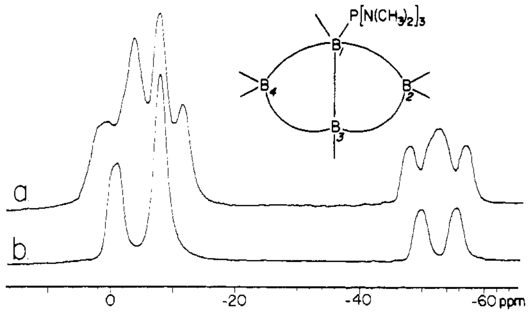

Figure 2. ^{11}B NMR spectra of $B_4H_8{\cdot}P[N(CH_3)_2]_3$ in dichloromethane-d_2 at +25 °C: (a) normal spectrum; (b) proton-spin-decoupled spectrum. The structure was drawn after the structure of $B_4H_8{\cdot}PF_2N(CH_3)_2$.[16]

for the reaction of $B_4H_8{\cdot}N(CH_3)_3$ with HCl in CH_2Cl_2, but the pattern of the products was different in that the chlorotriborane(7) adduct was not produced. The HCl reaction of $B_4H_8{\cdot}P(CH_3)_3$ in tetrahydrofuran gave $B_3H_7{\cdot}P(CH_3)_3$ and $BH_2Cl{\cdot}THF$ and is similar to that of $B_4H_8{\cdot}N(CH_3)_3$.

The ^{11}B NMR spectrum of $B_4H_8{\cdot}P(CH_3)_3$ in dichloromethane-d_2 is shown in Figure 1, and the data are listed in Table I along with those of ^1H and ^{31}P. In addition to the three signals due to B(1), B(2,4), and B(3), a weak signal is seen at +5.1 ppm. This weak signal always appears with the above three signals of $B_4H_8{\cdot}P(CH_3)_3$ in the same relative intensity (about 10% of the B(3) intensity), regardless of the source of the sample and the method of preparation. The signal, therefore, is thought to be due to the B(3) atom of an isomer of $B_4H_8{\cdot}P(CH_3)_3$. The existence of two isomers, exo and endo with respect to the position of the phosphine relative to the bent B_4 framework, was reported for some phosphine adducts of B_4H_8.[8]

B. $B_4H_8{\cdot}P[N(CH_3)_2]_3$. Tris(dimethylamino)phosphine is another strong base, and therefore the reaction of B_5H_{11} with this base will proceed in much the same way as that with trimethylphosphine. Indeed, when the reactants were allowed to react in a 1:2 ratio, a complex mixture of products resulted, and the separation of the mono(phosphine) adduct from it was intractable. The method of hydride replacement for the preparation of $B_4H_8{\cdot}P(CH_3)_3$ (eq 2) was successfully applied to the preparation of $B_4H_8{\cdot}P[N(CH_3)_2]_3$. The appropriate anionic adduct, $B_4H_9{\cdot}P[N(CH_3)_2]_3^-$, for the intended preparation had been unknown, and therefore it was synthesized first.

(i) $K^+B_4H_9{\cdot}P[N(CH_3)_2]_3^-$. Potassium nonahydrotetraborate(1−) ($K^+B_4H_9^-$) reacted with $P[N(CH_3)_2]_3$ in tetrahydrofuran at −35 °C to give the salt of the anionic adduct, $K^+B_4H_9{\cdot}P[N(CH_3)_2]_3^-$. The ^{11}B NMR spectrum of the product in tetrahydrofuran was similar to that of $B_4H_9{\cdot}P(CH_3)_3^-$.[3] Two broad resonance signals were seen at −26.2 and −38.2 ppm in an intensity ratio 3:1.

(ii) $B_4H_8{\cdot}P[N(CH_3)_2]_3$. A tetrahydrofuran solution of $K^+B_4H_9{\cdot}P[N(CH_3)_2]_3^-$ was treated with excess B_2H_6 at low temperatures. The hydride removal reaction proceeded smoothly, and subsequently $B_4H_8{\cdot}P[N(CH_3)_2]_3$ could be separated from the reaction mixture as a stable, nonvolatile solid. The ^{11}B NMR spectrum of this B_4H_8 adduct is shown in Figure 2, and the data are listed in Table I along with those of ^1H and ^{31}P spectra. The data are consistent with those expected from the structure indicated in Figure 2. It is noted that any signal which might be attributable to the other isomer could not be detected.

C. Lewis Base Adducts of $B_4H_8{\cdot}P(CH_3)_3$ and $B_4H_8{\cdot}P[N(CH_3)_2]_3$. The Lewis base adducts of B_4H_8 combine with Lewis bases to give hypho-class bis(base) adducts of B_4H_8. Thus, trimethylamine–tetraborane(8) combines with amines,[7] and $B_4H_8{\cdot}P(CH_3)_3$ further reacts with $P(CH_3)_3$ to give $B_4H_8{\cdot}2P(CH_3)_3$.[2] The dissociative stability of these bis(base) adducts naturally depends upon the base strength of the Lewis bases involved. At room temperature $B_4H_8{\cdot}2N(CH_3)_3$ dissociates completely into $B_4H_8{\cdot}N(CH_3)_3$ and $N(CH_3)_3$,[7] but $B_4H_8{\cdot}2P(CH_3)_3$ can be isolated as a stable solid.[2] In view of the scarcity of the examples of the bis(base) adducts of B_4H_8, particularly the adducts with two different bases, the B_4H_8 adducts obtained here were treated with appropriate bases for the formation of possible base adducts.

(i) $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$. (a) Formation. Trimethylphosphine–tetraborane(8) reacted with trimethylamine in CH_2Cl_2 at −30 °C in a 1:1 molar ratio. The reaction proceeded slowly even at −80 °C. The adduct could be isolated as a white solid at −80 °C. At higher temperatures (above −30 °C) the compound appeared to dissociate into and equilibrate with the

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(7) Dodds, A. R.; Kodama, G. *Inorg. Chem.* **1979**, *18*, 1465.

(8) (a) Odom, J. D.; Zozulin, A. J. *Inorg. Chem.* **1981**, *20*, 3740. (b) Odom, J. D.; Moore, T. F. *Ibid.* **1980**, *19*, 2651. (c) Odom, J. D.; Moore, T. F.; Dawson, W. H.; Garber, A. R.; Stampf, E. J. *Ibid.* **1979**, *18*, 2179.

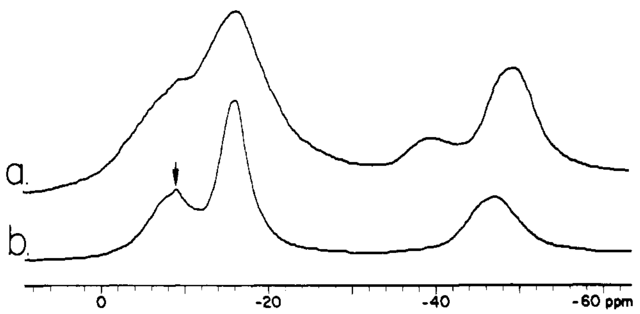
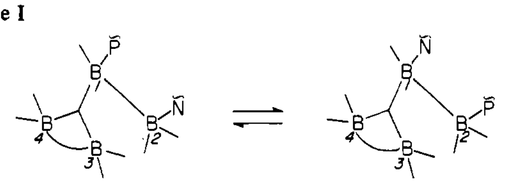


Figure 3. ^{11}B NMR spectra of $B_4H_8 \cdot P(CH_3)_3 \cdot N(CH_3)_3$ in dichloromethane-d_2. A 1-equiv amount of $N(CH_3)_3$ had been added to prevent the dissociation of the bis(base) adduct: (a) -80 °C; (b) -30 °C. The small peak indicated by the arrow is due to $BH_3 \cdot N(CH_3)_3$ impurity.

Scheme I



I II

original two compounds. The same adduct formed also when $B_4H_8 \cdot N(CH_3)_3$ was treated with $P(CH_3)_3$ in CH_2Cl_2. In the mass spectrum of the adduct, the peaks corresponding to $B_4H_{8-n} \cdot P(CH_3)_3 \cdot N(CH_3)_3^+$ were absent. Instead, the highest mass peak was seen at *m/e* 128, corresponding to $B_4H_8 \cdot P(CH_3)_3^+$, and the strong peak of $N(CH_3)_3^+$ appeared.

(b) Nonrigidity of the $B_4H_8 \cdot P(CH_3)_3 \cdot N(CH_3)_3$ Molecule. The ^{11}B NMR spectra of $B_4H_8 \cdot P(CH_3)_3 \cdot N(CH_3)_3$ at -30 and -80 °C are shown in Figure 3. In the -30 °C spectrum the three signals at -8.2, -16.2, and -46.5 ppm are in an intensity ratio 1.0:2.0:1.0 and are assignable to the amine-attached boron (B_N), unligated boron (B_U), and phosphine-attached boron (B_P) atoms, respectively. As the temperature is lowered, the B_P signal broadens and then splits into two signals of different intensities (at -39.3 and -48.9 ppm in a 1:~4 ratio). The course of signal change for the lower field signals (B_N and B_U), such as the splitting of the signals, if any, is obscured by the severe broadening and overlap of the signals and cannot be followed. This temperature dependence of the spectra can be interpreted in terms of a rapid isomerization of the molecules resulting from the fluxional motion of the boron framework similar to that suggested for the molecules of $B_4H_8 \cdot 2P(CH_3)_3$:[2] The molecule can assume two isomeric forms, one with the phosphine attached to the apex position, B(1), and the amine at the basal position, B(2), and another form with the ligand positions interchanged. See Scheme I, in which P̄ and N̄ denote $P(CH_3)_3$ and $N(CH_3)_3$, respectively. The three signals in the higher temperature spectrum thus represent the averaged signals of the B_N, B_U, and B_P atoms resulting from the rapid isomerization of the two forms. At the lower temperatures where the rate of isomerization is sufficiently slow, the signals of each isomer appear separately. As we see in the structures shown in Scheme I, B(1), B(3), and B(4) form a B_3H_7-like moiety and, by the same token, B(2) is in a BH_3-like moiety, and since the ^{11}B NMR shift values for $B_3H_7 \cdot P(CH_3)_3$ and $BH_3 \cdot P(CH_3)_3$ are known to appear at -45.0 and -37.1 ppm, respectively, the two signals for $B_4H_8 \cdot P(CH_3)_3 \cdot N(CH_3)_3$ at -48.9 and -39.0 ppm are attributed to the phosphine-attached boron atoms of isomers I and II, respectively. It is noted that the signal of the phosphine-attached boron of $B_4H_8 \cdot 2P(CH_3)_3$ also splits into two signals of equal intensity at low temperatures (below -10 °C) and that they appear at -47.0 and -37.4 ppm, representing the B(1) and B(2) atoms, respectively. The higher intensity of the -48.9 ppm signal of $B_4H_8 \cdot P(CH_3)_3 \cdot N(CH_3)_3$ indicates that isomer I is more stable than isomer II or the apex position is more favored by $P(CH_3)_3$ than by $N(CH_3)_3$. The above isomerization model would require that the B_N and B_U signals also split at the low temperatures. The overlap of the broad signals prohibited its confirmation in the spectra that were obtained. The interpretation of the ^1H NMR spectra was hampered also by the broadness of the signals (^{11}B-spin-decoupled) and the presence of methyl proton signals at δ 1.16 ($^2J_{HCP} \simeq 12$ Hz) and 2.51. An argument based upon $^1H\{^{11}B\}$ NMR data recorded at a higher magnetic field strength is much desired. However, the observataion described below is consistent with the model considered above. At a higher temperature (about -20 °C) a broad signal showed up at δ 0.75 when the less shielded boron atoms (-8 to -16 ppm) were irradiated. No other H_B signals could be detected unless hidden under the methyl proton signals. Irradiation of the more shielded boron atoms (-46.5 ppm) resulted in the appearance of the signal at the same shift (δ 0.75) with its width somewhat broader than it was before and no other change. At a lower temperature (-80 °C), two broad signals at δ 1.70 and 0.66 were seen in an intensity ratio 1:~5 when the less shielded boron atoms were irradiated. When the more shielded boron atoms were irradiated, the signal at δ 1.70 flattened, and a slight hump developed on the high-field side of the 0.66 ppm signal as a shoulder (δ 0.5). Thus, at the higher temperatures the borane hydrogen atoms appeared all equivalent (δ 0.75), and the three lower temperature signals at δ 1.70, 0.66, and 0.5 might represent the hydrogen atoms attached to B(2) in I, the B(1,3,4) moieties in I and II, and B(2) in II, respectively. The six hydrogen atoms associated with the B(1,3,4) moieties are expected to be undergoing a rapid migration motion within the three-boron framework even at this low temperature, like the hydrogen atoms in $B_3H_7 \cdot N(CH_3)_3$,[9] $B_3H_7 \cdot P(CH_3)_3$[10] and $B_4H_8 \cdot 2P(CH_3)_3$.[2] The ^{31}P NMR spectrum at -30 °C showed a signal with a quartet feature ($J_{BP} \approx 80$ Hz) at +3.1 ppm (OPA standard). At -80 °C the multiplet feature was lost from the signal and the signal was trapezoid shaped, the half-height width being 190 Hz. The expected separation of the peak into two could not be confirmed: Further lowering of the temperature to -90 °C changed the appearance of the signal to a singlet peak (half-height width 150 Hz), the shift being +4.2 ppm. The apparent singlet feature was observed also for the ^{31}P NMR spectrum of $B_4H_8 \cdot 2P(CH_3)_3$,[2] for which the sharpening was thought to be due to the thermal decoupling of the boron spins, and the expected two ^{31}P signals were too close to be resolved. The situation appeared to be the same here.

(ii) $B_4H_8 \cdot P(CH_3)_3 \cdot P[N(CH_3)_2]_3$. $B_4H_8 \cdot P[N(CH_3)_2]_3$ reacted with $P(CH_3)_3$ in a 1:1 molar ratio in dichloromethane. The reaction proceeded slowly at -80 °C but was rapid at -50 °C. Conversely, treatment of $B_4H_8 \cdot P(CH_3)_3$ with $P[N(CH_3)_2]_3$ resulted in the formation of the same compound as that obtained above. The latter reaction, however, was slower than the former even when excess of the reacting base was used, and it was necessary to warm the reaction mixture to room temperature to complete the reaction. At -60 °C no sign of reaction could be detected in its ^{11}B NMR spectrum. The compound could be isolated as a colorless, nonvolatile solid at 0 °C. The solid, however, underwent slow decomposition at room temperature, developing a yellow-brown tinge. It appeared to be more stable in the solution phase.

The ^{11}B NMR spectrum of the compound is shown in Figure 4. The high-field and low-field signals are attributed to the phosphine-attached boron and nonligated boron atoms, respectively. The group of high-field signals may be looked upon

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[9] Dodds, A. R.; Kodama, G. *Inorg. Chem.* **1976**, *15*, 741.

[10] Bishop, V. L.; Kodama, G. *Inorg. Chem.* **1981**, *20*, 2724.

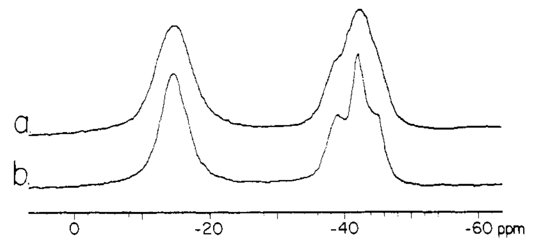

Figure 4. ^{11}B NMR spectra of $B_4H_8{\cdot}P(CH_3)_3{\cdot}P[N(CH_3)_2]_3$ in dichloromethane at 0 °C: (a) normal spectrum; (b) proton-spin-decoupled spectrum.

as an overlap of two doublets. On the basis of this assumption, the two signals are estimated very crudely to be at −41 and −43 ppm with the approximate J_{BP} values of 105 and 85 Hz, respectively. Unlike the B_P signals of $B_4H_8{\cdot}2P(CH_3)_3$[2] and $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$, the appearance of the high-field signals remained unchanged when the sample was cooled to −60 °C, except for the slight broadening of the signals; the nonfluxional nature of the boron atom arrangement in the molecule is suggested. With respect to the hydrogen atoms, however, the fluxional motions appeared to be taking place to varied extents depending upon the temperatures: At 0 °C, in addition to the two doublet signals of methyl protons (δ 2.47, $^3J_{HCNP}$ = 8.8 Hz, and δ 1.16, $^2J_{HCP}$ = 11.4 Hz), a signal showed up at δ 0.51 when the ^{11}B spins were decoupled. At −40 °C this signal became dissymmetric, the peak position being at δ 0.57 with a weak broad hump superimposed on the high-field side of the signal at δ 0.2. Thus, the separation of H atoms into B_3 and B_1 moieties was suggested. Two trapezoid-shaped ^{31}P signals were seen at +102.8 and +1.3 in a 1:1 intensity ratio at −20 °C, representing the $P[N(CH_3)_2]_3$ and $P(CH_3)_3$, which are attached to the boron atoms, respectively. The positions of the two phosphines in the molecule, however, remain undecided, although the fast rate of the adduct formation from $B_4H_8{\cdot}P[N(CH_3)_2]_3$ relative to that from $B_4H_8{\cdot}P(CH_3)_3$ might suggest that $P[N(CH_3)_2]_3$ is at the apex position if the site of the second base attack was assumed to be B(2).

D. Conclusion. Four methods were developed for the preparation of $B_4H_8{\cdot}P(CH_3)_3$. Three of them were novel in that the starting compounds were not B_5H_{11}, which had been almost the exclusive source of B_4H_8 adducts.[11] Tetraborane(10), $THF{\cdot}B_3H_7$, and $B_2H_4{\cdot}2P(CH_3)_3$, and even $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$ were used for the preparataion of the $B_4H_8{\cdot}P(CH_3)_3$. One of the methods that utilized B_4H_{10} was employed successfully to prepare $B_4H_8{\cdot}P[N(CH_3)_2]_3$. The NMR spectra of the $P(CH_3)_3$ and $P[N(CH_3)_2]_3$ adducts indicated that their structures were similar to those of the known B_4H_8 adducts, as illustrated in Figures 1 and 2. Although the presence of two isomeric forms (exo and endo) was noticed for $B_4H_8{\cdot}P(CH_3)_3$, no evidence for the possible two isomeric forms could be found for $B_4H_8{\cdot}P[N(CH_3)_2]_3$. The specific position of the base (exo or endo) in each adduct, however, has yet to be determined.

Two hypho-class B_4H_8 adducts, $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ and $B_4H_8{\cdot}P(CH_3)_3{\cdot}P[N(CH_3)_2]_3$, were prepared. The ^{11}B NMR spectrum of the $N(CH_3)_3$ adduct was interpreted in terms of the positional isomerization of the two different ligands, which was effected by the fluxional nature of the boron atom arrangement in the molecule. Trimethylphosphine favors the apex position, B(1), and $N(CH_3)_3$ the B(2) position in the molecule. The boron atom arrangement in the $P[N(CH_3)_2]_3$ adduct appeared to be rigid. The positions of the two bases in the molecule, however, could not be revealed unequivocally.

The site preference of two different bases should be a general phenomenon in these hypho B_4H_8 adducts and should represent an interesting case since the two sites are at two different borane acid environments; i.e., B(1) and B(2) are in B_3H_7-like and BH_3-like moieties, respectively. Lewis acidity of $B_4H_8{\cdot}L$ (L = Lewis base) toward the second Lewis base L′ to form $B_4H_8{\cdot}L{\cdot}L'$ would be another interesting subject of study, which might be related to the site preference mentioned above.

Experimental Section

General Data. Conventional vacuum-like techniques were used for the handling of volatile compounds. Air- and moisture-sensitive solids were handled in glovebags filled with dry nitrogen gas. Laboratory stock, pure tetraborane(10),[9] pentaborane(11),[7] trimethylphosphine,[12] tris(dimethylamino)phosphine, and $B_2H_4{\cdot}2P(CH_3)_3$[13] were used. Tetrahydrofuran (reagent grade) was stored over $LiAlH_4$, and dichloromethane (reagent grade) and dichloromethane-d_2 (99+%) were stored over molecular sieves. These solvents were transferred directly into the reaction vessel on the vacuum line.

The NMR spectra were recorded on a Varian XL-100-15 spectrometer, operating in the FT mode at 32.1, 40.5, and 100.1 MHz for ^{11}B, ^{31}P, and ^1H, respectively. Chemical shift values were recorded with respect to $BF_3{\cdot}O(C_2H_5)_2$ and 85% orthophosphoric acid for boron and phosphorus, respectively. The shift of proton signals were measured relative to the CH_2Cl_2 signal, which was taken as δ 5.28.

Preparation of $B_4H_8{\cdot}P(CH_3)_3$. (i) From $B_4H_8{\cdot}2P(CH_3)_3$. A 0.508-mmol quantity of B_5H_{11} was used to prepare a sample of $B_4H_8{\cdot}2P(CH_3)_3$[2] in a reaction tube (22-mm o.d., Pyrex). The sample was dissolved in about 2 mL of CH_2Cl_2, diborane(6) (0.552 mmol) was condensed into the tube, and the solution was mixed at −80 °C. Then, the tube was allowed to warm slowly to room temperature and kept there for 1 h while the solution was stirred. The volatile components were then condensed out into a U-trap (it took 12 h to complete this process) and were fractionated through a −10 °C trap. In the reaction tube a tiny droplet of liquid remained. The component that was trapped in the −10 °C trap was $B_4H_8{\cdot}P(CH_3)_3$ and weighed 66.7 mg or 0.498 mmol; yield 98% based on the B_5H_{11} used. A small amount of $B_3H_7{\cdot}P(CH_3)_3$ was detected in the ^{11}B NMR spectrum of the product as the only impurity, and it was estimated to be about 4.7 mol % from its signal intensity.

It is noted that no $B_3H_7{\cdot}P(CH_3)_3$, or a trace of it if any, could be found in the fresh samples of $B_4H_8{\cdot}P(CH_3)_3$. It appeared that the triborane adduct was produced during the process of transfer of the sample. The same was observed for the samples prepared by methods ii–iv.

(ii) From $K^+B_4H_9{\cdot}P(CH_3)_3{}^-$. A 1.403-mmol quantity of B_4H_{10} was allowed to react with potassium hydride (1.37 mmol) in diethyl ether at −80 °C to prepare a sample of $K^+B_4H_9{}^-$ in a 22-mm-o.d. reaction tube. The amount of hydrogen gas evolved (1.070 mmol) was taken as the amount of the $B_4H_9{}^-$ ion produced. The solvent ether was pumped out and was replaced by tetrahydrofuran. Then the solution was treated with $P(CH_3)_3$ (2.072 mmol) according to the reported procedure[3] to prepare a solution containing $K^+B_4H_9{\cdot}P(CH_3)_3{}^-$. A 1.087-mmol quantity of B_2H_6 was condensed into the reaction tube, and the mixture was stirred at −80 °C. The tube was then warmed to −63, −45, −35, −23, and 0 °C and to room temperature in succession. The solution was stirred for 10 min at each temperature. The volatile components were processed in the same manner as in section i, and 126.3 mg (0.992 mmol) of the product was collected; yield 92.7%. An estimated 2.9 mol % amount of $B_3H_7{\cdot}P(CH_3)_3$ was found in the product.

(iii) From $B_3H_7{\cdot}THF$. A sample of $B_3H_7{\cdot}THF$ was prepared[14] in a 22-mm-o.d. reaction tube from a 0.493-mmol quantity of B_4H_{10} and was dissolved in CH_2Cl_2 (ca. 2 mL). A weighed amount of $B_2H_4{\cdot}2P(CH_3)_3$ (0.494 mmol) was added to the tube at −197 °C under an atmosphere of nitrogen gas, and the mixture was allowed to warm slowly under vacuum to room temperature, where it was held for 30 min. The volatile components were processed as in method i, and 58.0 mg (0.455 mmol) of the product was collected; yield 92.3%. An

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estimated 3.0 mol % amount of $B_3H_7{\cdot}P(CH_3)_3$ was found in the product.

(iv) From $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$. A solid sample of $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$ was prepared in a 22-mm-o.d. reaction tube by the reaction of $B_2H_4{\cdot}2P(CH_3)_3$ (0.526 mmol) with B_4H_{10} (0.538 mmol) in CH_2Cl_2[5,6] and was dissolved in a fresh portion (ca. 2 mL) of CH_2Cl_2. A measured amount of $N(CH_3)_3$ (0.519 mmol) was condensed into the tube and mixed into the solution at −80 °C. The tube was allowed to warm slowly to 0 °C, where it was kept for 30 min, and then was held at room temperature for 5 min. The volatile components were processed as in method i, and 65.8 mg (0.517 mmol) of the product was collected; yield 98.2% based on the $B_2H_4{\cdot}2P(CH_3)_3$ used. The $B_3H_7{\cdot}P(CH_3)_3$ contamination in the product was 1.8%.

Preparation of $B_4H_8{\cdot}P[N(CH_3)_2]_3$. A sample of $K^+B_4H_9{}^-$ (0.717 mmol based on the H_2 gas evolved in the preparation) was prepared[4] in a 22-mm-o.d. reaction tube and was dissolved in tetrahydrofuran (ca. 3 mL) at −35 °C. A 0.930-mmol quantity of $P[N(CH_3)_2]_3$ was condensed into the tube and was mixed into the solution at −80 °C. The solution was then stirred at −35 °C for 4 h. At this stage, the solution was slightly turbid due to the limited solubility of $K^+B_4H_9{\cdot}P[N(CH_3)_2]_3{}^-$ in tetrahydrofuran. A measured amount of B_2H_6 (0.993 mmol) was condensed into the tube and mixed into the solution at −80 °C, and the temperature was raised stepwise in the manner similar to that described for the preparation of $B_4H_8{\cdot}P(CH_3)_3$. Excess diborane and tetrahydrofuran were pumped out at −45 °C and finally at 0 °C. Then, a fresh portion of tetrahydrofuran (ca. 3 mL) was added to the tube, and the insoluble solid (KBH_4) was filtered out. From the filtrate containing $B_4H_8{\cdot}P[N(CH_3)_2]_3$ and $BH_3{\cdot}P[N(CH_3)_2]_3$, a crystalline solid of the tetraborane adduct was obtained as the residue when the solvent and the BH_3 adduct were pumped out at room temperature. No impurity could be detected in the ^{11}B and ^{31}P NMR spectra of the compound thus prepared.

Reaction of $B_4H_8{\cdot}P(CH_3)_3$ with $N(CH_3)_3$. The samples of $B_4H_8{\cdot}P(CH_3)_3$ were prepared from $K^+B_4H_9{\cdot}P(CH_3)_3{}^-$ by the procedure that was described earlier. A weighed amount of the $B_4H_8{\cdot}P(CH_3)_3$ sample (0.5–1.5 mmol) was placed in a 10-mm-o.d. tube equipped with a stopcock and dissolved in CH_2Cl_2, and a measured amount of $N(CH_3)_3$ was condensed into the tube. The tube was placed in a −80 °C bath, the solution was agitated by shaking the tube, and then it was placed in the precooled probe of the NMR instrument to monitor the reaction.

The reaction occurred at −80 °C. When an excess of $N(CH_3)_3$ (2–3 mol/mol of $B_4H_8{\cdot}P(CH_3)_3$) was used, the reaction was complete in less than 30 min at −45 °C, the ^{11}B NMR spectrum of the resulting solution being that shown in Figure 3. Removal of volatile components at −80 °C left a white solid as the residue. A CD_2Cl_2 solution of the residue gave a ^{11}B spectrum identical with that in Figure 3, and its ^1H NMR spectrum contained two methyl proton signals from $N(CH_3)_3$ and $P(CH_3)_3$ moieties in a 1:1 intensity ratio. When a solid residue thus obtained was pumped at much higher temperatures (above −30 °C, or 0 to +20 °C for 10 min as was the case when the mass spectrum experiment was performed), the ^{11}B NMR spectrum of the residual solid in CH_2Cl_2 showed the presence of $B_4H_8{\cdot}P(CH_3)_3$. When a CH_2Cl_2 solution of $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ was allowed to stand at room temperature, the adduct underwent slow decomposition, and the signals of $B_4H_8{\cdot}P(CH_3)_3$, $B_4H_8{\cdot}2P(CH_3)_3$, $B_4H_8{\cdot}N(CH_3)_3$, $BH_3{\cdot}P(CH_3)_3$, and $BH_3{\cdot}N(CH_3)_3$ were detected in the sample.

Reaction of $B_4H_8{\cdot}N(CH_3)_3$ with $P(CH_3)_3$. A sample of $B_4H_8{\cdot}N(CH_3)_3$ was prepared from B_5H_{11} (0.549 mmol) via $B_4H_8{\cdot}S(CH_3)_2$ as the intermediate, as reported elsewhere,[7] and was treated with $P(CH_3)_3$ (0.479 mmol) in CH_2Cl_2 at −80 °C. The mixture was then allowed to warm to −25 °C in the probe of the NMR instrument. The ^{11}B spectrum consisted of the signals of $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ and $B_4H_8{\cdot}N(CH_3)_3$, the latter being very weak. As the temperature was raised to 0 and +25 °C, weak signals of $B_4H_8{\cdot}2P(CH_3)_3$ and $B_4H_8{\cdot}P(CH_3)_3$ became detectable in addition to the above two signals. At the same time, the signal of $BH_3{\cdot}N(CH_3)_3$ was growing in slowly.

Formation of $B_4H_8{\cdot}P(CH_3)_3{\cdot}P[N(CH_3)_2]_3$. A sample of $B_4H_8{\cdot}P[N(CH_3)_2]_3$ (0.60 mmol; prepared from $K^+B_4H_9{\cdot}P[N(CH_3)_2]_3{}^-$) was dissolved in CD_2Cl_2, and $P(CH_3)_3$ (0.59 mmol) was mixed into the solution at −80 °C. The reaction tube (a 10-mm-o.d. NMR sample tube equipped with a stopcock) was then placed in the probe of the NMR spectrometer, and the reaction was monitored as the temperature was raised stepwise. The reaction occurred slowly at −80 °C and was fast at −40 to −50 °C. When the complete disappearance of the original mono(phosphine) adduct and the absence of noncondensable gas in the tube were confirmed, the tube was sealed and the ^{31}P and ^1H NMR spectra were recorded. In addition to the ^{31}P signals of the product at 102.8 and 1.3 ppm in a 1:1 ratio, very weak signals of free $P[N(CH_3)_2]_3$ (121.4 ppm; lit.[15] 122 ppm) and free $P(CH_3)_3$ (61.9 ppm; lit.[15] 62 ppm) could be detected.

Likewise, a sample of $B_4H_8{\cdot}P(CH_3)_3$ (0.333 mmol; prepared from $K^+B_4H_9{\cdot}P(CH_3)_3{}^-$) was treated with $P[N(CH_3)_2]_3$ (0.907 mmol) in CH_2Cl_2 (ca. 1.5 mL). The reaction did not proceed with an appreciable rate until the mixture was warmed to −20 °C. The tube was shaken at room temperature to complete the reaction. The ^{11}B NMR spectrum of the solution was identical with the one obtained above. The ^{31}P spectrum contained the strong signal of free $P[N(CH_3)_2]_3$ in addition to the two signals of the bis(base) adduct. The signal of free $P(CH_3)_3$ could not be detected.

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Registry No. $B_4H_8{\cdot}P(CH_3)_3$, 71749-92-3; $B_4H_8{\cdot}2P(CH_3)_3$, 66750-83-2; B_2H_6, 19287-45-7; $K^+B_4H_9{\cdot}P(CH_3)_3{}^-$, 85185-84-8; B_2H_4, 67113-98-8; $B_3H_7{\cdot}THF$, 52842-96-3; $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$, 92219-77-7; $N(CH_3)_3$, 75-50-3; $B_4H_8{\cdot}P[N(CH_3)_2]_2$, 92219-78-8; $K^+B_4H_9{}^-$, 57406-39-0; $P[N(CH_3)_2]_3$, 1608-26-0; $K^+B_4H_9{\cdot}P[N(CH_3)_2]_3{}^-$, 92219-82-4; $B_4H_8{\cdot}N(CH_3)_3$, 69765-82-8; $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$, isomer I, 92219-79-9; $B_4H_8{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$, isomer II, 92219-80-2; $B_4H_8{\cdot}P(CH_3)_3{\cdot}P[N(CH_3)_2]_3$, 92219-81-3.

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