captions. C_6D_6 was used in all cases both for the lock signal as well as for attainment of optimal homogeneity. $LiAlH_4$ was purchased from Hans Heinrich Hütte, Langelsheim, West Germany, and recrystallized from ether solvents. Standard solutions in THF were prepared and analysed for H^-, Al, and Li, showing >99% purity. Diborane solutions in THF were prepared from $NaBH_4$ and BF_3 in diglyme, and the diborane generated was dissolved in THF at −40 °C. The solutions were analysed for H^- and B and also checked by ^{11}B NMR for any impurities of $(RO)_2BH$. AlH_3 was prepared from $LiAlH_4$ and HCl in ether according to a procedure developed by Suchy,[24] and the AlH_3 isolated was dissolved in THF. Analysis gave the correct Al:H^- ratio. The solutions contained only traces of Cl^- (<10^{-3} mol).

The solutions used for the NMR studies were prepared under dry nitrogen by the syringe technique, and, after thorough mixing at −20 °C, transfered into dry-nitrogen-filled 10 mm o.d. NMR tubes. They were kept at −78 °C. Ten minutes were allowed for each sample to achieve the new equilibrium temperature before recordings were taken.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for a grant to purchase the Bruker WP 200 NMR spectrometer and to the Metallgesellschaft AG for support of this work.

Registry No. AlH_3, 7784-21-6; BH_3, 13283-31-3; $LiAlH_4$, 16853-85-3; H_2AlBH_4, 45632-34-6; $HAl(BH_4)_2$, 19766-57-5; $Al(BH_4)_3$, 13771-22-7; $Li[H_2Al(BH_4)_2]$, 76334-13-9; $Li[HAl(BH_4)_3]$, 76334-14-0; $Li[Al(BH_4)_4]$, 41561-04-0; $LiBH_4$, 16949-15-8; $B_2H_7^-$, 27380-11-6; $C_4H_9OAl(BH_4)_2$, 12340-67-9; $H_3B{\cdot}THF$, 14044-65-6; THF, 109-99-9.

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[24] H. Suchy, Thesis, University of Munich, Munich, 1966.

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

Formation of the 1:1 Phosphine Adducts of Hexaborane(10)

MITSUAKI KAMEDA[1] and GOJI KODAMA*

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The formation of trimethylphosphine–hexaborane(10) in the reaction of hexaborane(10) with trimethylphosphine was confirmed. The compound is stable below −20 °C in dichloromethane or in tetrahydrofuran and reacts with trimethylphosphine to give bis(trimethylphosphine)–hexaborane(10). Triphenylphosphine adds to hexaborane(10) likewise to form $B_6H_{10}{\cdot}P(C_6H_5)_3$. On the basis of the ^{11}B and ^1H NMR spectra, a $B_5H_8^-$ derivative structure is proposed for the 1:1 adducts. A mechanism for the conversion of the pyramid-shaped B_6H_{10} framework to the belt-shaped structure of $B_6H_{10}{\cdot}2P(CH_3)_3$ is discussed.

Introduction

The reaction of hexaborane(10) with trimethylphosphine in a 1:2 molar ratio results in the formation of a molecular adduct $B_6H_{10}{\cdot}2P(CH_3)_3$.[2,3] The structural study of the compound by Shore and his co-workers[2] has revealed that pyramidal boron framework of B_6H_{10} is changed to a belt-shaped arrangement in the adduct:

In 1965 Williams and Gerhart[4] reported that B_6H_{10} reacts with triphenylphosphine in a 1:1 molar ratio to give an air-stable compound $B_6H_{10}{\cdot}P(C_6H_5)_3$. A conflicting result, however, was reported later,[2,3] and the identity of the compound has been obscured. Another monoligand adduct of hexaborane(10), $B_6H_{10}{\cdot}PF_2N(CH_3)_3$, was reported by Lory and Ritter[5] in 1970 as a product of the reaction of pentaborane(9) with $PF_2N(CH_3)_2$. No structural information was available on these 1:1 adducts of B_6H_{10}. It was of interest to us to investigate the formation of $B_6H_{10}{\cdot}P(CH_3)_3$ as a precursor of the 1:2 adduct and thus to gain some clue as to the rearrangement of the borane framework from B_6H_{10} to the bis ligand adduct. The formation of two 1:1 adducts, $B_6H_{10}{\cdot}P(CH_3)_3$ and $B_6H_{10}{\cdot}P(C_6H_5)_3$, is confirmed and is reported in this paper.

Results and Discussion

Hexaborane(10) reacts with trimethylphosphine at low temperatures to form a 1:1 molecular adduct $B_6H_{10}{\cdot}P(CH_3)_3$. The compound is unstable above −20 °C and undergoes an irreversible change to give as yet unidentified compounds. Trimethylphosphine adds to the 1:1 complex above −70 °C and the bis(trimethylphosphine) adduct, $B_6H_{10}{\cdot}2P(CH_3)_3$, is produced (eq 1 and 2). The ^{11}B NMR spectra of $B_6H_{10}{\cdot}P(CH_3)_3$ are shown in Figure 1, and the spectral data are summarized in Table I. The general features of the ^{11}B and ^1H spectra at −80 °C are the same as those of −30 °C. The NMR data are consistent with the structure proposed for the compound in Figure 2b.[6] The assignments for the NMR

$$B_6H_{10} + P(CH_3)_3 \rightarrow B_6H_{10}{\cdot}P(CH_3)_3 \tag{1}$$

$$B_6H_{10}{\cdot}P(CH_3)_3 + P(CH_3)_3 \rightarrow B_6H_{10}{\cdot}2P(CH_3)_3 \tag{2}$$

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[1] On leave from Kawamura Junior College, Tokyo, Japan.

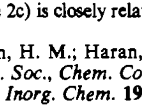
[2] Mangion, M.; Hertz, R. K.; Denniston, M. L.; Long, J. R.; Clayton, W. R.; Shore, S. G. *J. Am. Chem. Soc.* **1976**, *98*, 449.

[3] Denniston, M. L. Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1970. Brubaker, G. L.; Denniston, M. L.; Shore, S. G.; Carter, J. C.; Swicker, F. *J. Am. Chem. Soc.* **1970**, *92*, 7216.

[4] Williams, R. E.; Gerhardt, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 3513.

[5] Lory, E. R.; Ritter, D. M. *Inorg. Chem.* **1970**, *9*, 1847.

[6] The structure



is also consistent with the general features of the observed NMR spectra. The attachment of the H_2BL unit to the apex boron atoms bears some resemblance to that observed for the structure of $B_5H_9{\cdot}TMED$[7] (TMED = *N,N'*-tetramethylethylenediamine) and to that proposed for $B_4H_8{\cdot}2PMe_3$[8] and $B_4H_8{\cdot}TMED$.[9] This structure, however, is considered unlikely for the following reasons: (i) a large spin–spin coupling, which would be expected between the rigidly two-center bonded boron atoms,[10] is not observed: (ii) a tautomeric motion of the three bridge hydrogen atoms[11] is not observed; (iii) the structure of the isoelectronic sister compound $B_6H_{11}^-$[12] (Figure 2c) is closely related to that shown in Figure 2b.

[7] Alcock, N. W.; Colquhoun, H. M.; Haran, G.; Sawyer, J. F.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1977**, 368.

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

[9] Colquhoun, H. M. *J. Chem. Res. Synop.* **1978**, 451.

[10] Astheimer, R. J.; Plotkin, J. S.; Sneddon, L. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1108. Kroner, J.; Wrackmeyer, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2283.

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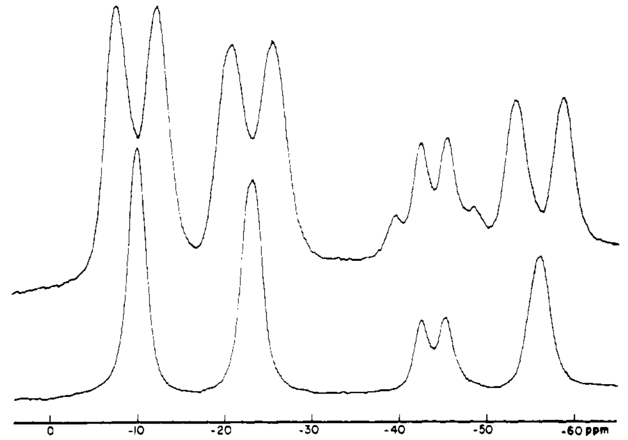


Figure 1. ^{11}B NMR spectra of $B_6H_{10}{\cdot}P(CH_3)_3$ in tetrahydrofuran at −30 °C: upper, normal spectrum; lower, proton-spin-decoupled spectrum.

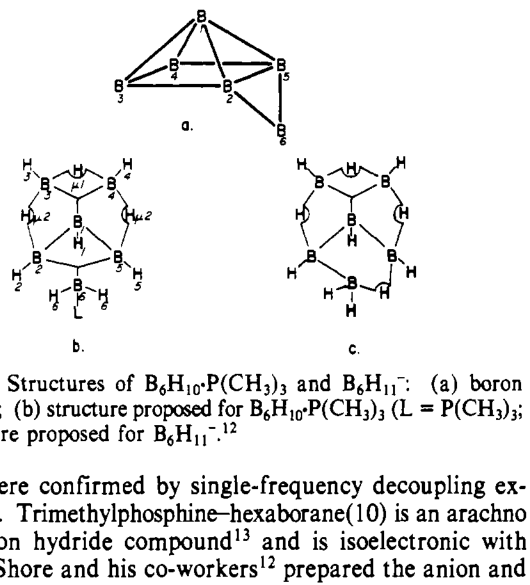
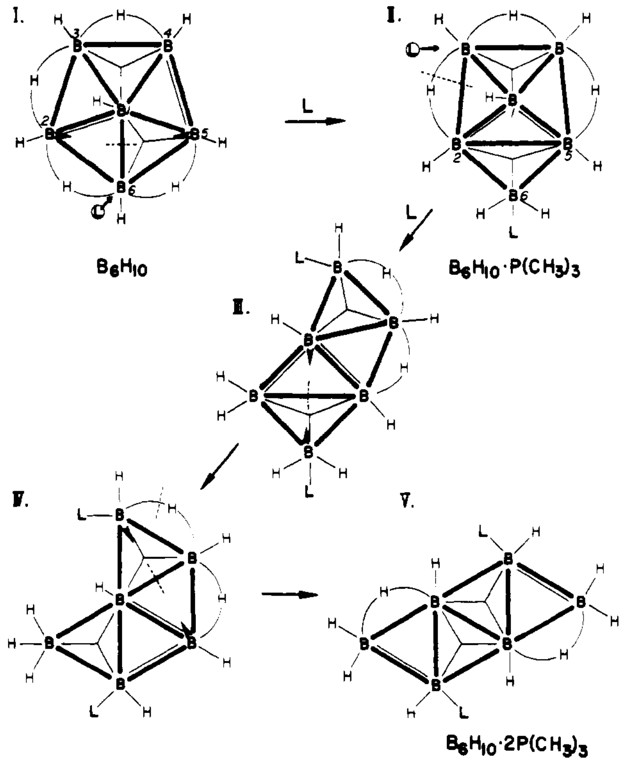


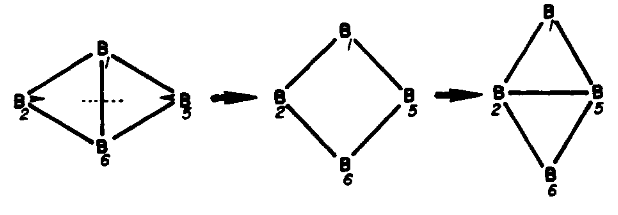
Figure 2. Structures of $B_6H_{10}{\cdot}P(CH_3)_3$ and $B_6H_{11}^-$: (a) boron framework; (b) structure proposed for $B_6H_{10}{\cdot}P(CH_3)_3$ ($L = P(CH_3)_3$); (c) structure proposed for $B_6H_{11}^-$.[12]

signals were confirmed by single-frequency decoupling experiments. Trimethylphosphine–hexaborane(10) is an arachno class boron hydride compound[13] and is isoelectronic with $B_6H_{11}^-$. Shore and his co-workers[12] prepared the anion and proposed a structure for the anion on the basis of their NMR study. The structure is indicated in Figure 2c. The phosphine adduct and the anion can both be regarded as derivatives of $B_5H_8^-$ in that $BH_2P(CH_3)_3^+$ or BH_3 group has been placed as a bridge at the basal B–B bond position of the pyramid-shaped $B_5H_8^-$ ion. The modes of bridging, however, are apparently different from each other. In the phosphine adduct the two hydrogen atoms of the $BH_2P(CH_3)_3$ group are terminally bonded to the boron atom as evidenced by the pseudoquartet structure of the $^{11}B(6)$ NMR signal, whereas in the $B_6H_{11}^-$ anion one of the hydrogen atoms in the BH_3 group is bridging to a neighboring boron atom and the three hydrogen atoms exchange their positions rapidly at −25 °C.[12]

Scheme I



The formation of $B_6H_{10}{\cdot}P(CH_3)_3$ may be visualized as the result of B(apex)–B(base) bond cleavage by the phosphine attack at the basal boron atom of hexaborane(10). See step I to II in Scheme I.[14] It is noted that, in this process of transformation, the boron atom framework consisting of B(1), B(2), B(5), and B(6) appears to have undergone a change similar to the diamond–square–diamond (d–s–d) rearrangement which has been proposed[15] for the isomerization of polyhedral borane and carborane compounds:



Since the monophosphine adduct is the precursor of the bis(phosphine) adduct, the formation of the belt-shaped structure of the bis adduct may be understood as that involves another phosphine attack at a basal boron atom of $B_6H_{10}{\cdot}P(CH_3)_3$ accompanied by a series of the d–s–d (or pseudo-d–s–d) rearrangements, which are indicated in Scheme I (steps III to IV and IV to V).

As mentioned earlier in this section, the 1:1 adduct undergoes a change at higher temperatures. The characterization of the final products is yet to be completed. It is noted, however, that $(CH_3)_3PBH_3$, B_6H_{10}, and $B_6H_{10}{\cdot}2P(CH_3)_3$ are not produced by the change. The major component (ca. 90%) of the products can be identified by its room-temperature ^{11}B NMR signals which appear at 6.9 (BH_3 quartet), −0.9 (br s), and −35.7 ppm (BP d) in an intensity ratio 1:2:1. In addition, there may be an extremely broad signal centered at about +7 ppm. Treatment of this product with trimethylphosphine results in the formation of $B_6H_{10}{\cdot}2P(CH_3)_3$. It is therefore, tempting to speculate that the compound is an isomer or dimer

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(11) This kind of hydrogen atom tautomerism is common among boron hydride compounds. Typical examples are LB_3H_7, $B_3H_8^-$, and B_6H_{10}, all of these compounds have a B–B bond adjacent to B–H–B bonds at the peripheral sites. (See, for example: Shore, S. G. "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 3.)

(12) Remmel, R. J.; Johnson, H. D., II; Jaworiwsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395.

(13) The framework electron count for $B_6H_{10}{\cdot}P(CH_3)_3$ is 18 or $2n + 6$ where $n = 6$, and therefore the compound belongs to the arachno class. See: Muetterties, E. L. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed; Academic Press: New York, 1975; Chapter 1.

(14) The framework of each structure is indicated with bold lines. A possible valence-bond structure is drawn with thin lines in each of the frameworks.

(15) Lipscomb, W. N. *Science (Washington, D.C.)* **1966**, *153*, 373. Kaczmarczyk, A.; Dobrott, R. D.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 729.

Table I. NMR Data for $B_6H_{10}{\cdot}P(CH_3)_3$ and $B_6H_{10}{\cdot}P(C_6H_5)_3$

	^{11}B				$^{1}H^{c}$		
	$B_6H_{10}{\cdot}P(CH_3)_3$		$B_6H_{10}{\cdot}P(C_6H_5)_3$				
	shift,[a] ppm	J_{BH}, Hz	shift, ppm	J_{BH}, Hz		$B_6H_{10}{\cdot}P(CH_3)_3$ shift (δ)	$B_6H_{10}{\cdot}P(C_6H_5)_3$ shift (δ)
B(2,5)	−10.5	146	−9.1	140	H(2,5)	2.48	2.58
B(3,4)	−23.1	151	−20.0	155	H(3,4)	1.84	1.93
B(6)	−44.2	103 (84[e])	−42.3	ca. 100[b] (80[e])	H(6)	1.2[d]	2.03 (15[f])
B(1)	−56.3	172	−54.1	170	H(1)	−0.18	−0.19
					H(μ2)	−1.81	−1.82
					H(μ1)	−3.23	−3.52

[a] $BF_3{\cdot}O(C_2H_5)_2$ standard. A negative sign denotes more shielding. [b] Uncertain due to the broadness of the signal. [c] Only the borane proton resonances are listed. The methyl proton signal appears at δ 1.33 (J_{HCP} = 11 Hz). The phenyl proton signals are at δ 7.1–7.5. [d] Overlapped with the methyl proton signal. [e] J_{BP} value. [f] J_{HBP} value.

of $B_6H_{10}{\cdot}P(CH_3)_3$. The exact nature of the compound will be reported upon completion of the study.

Treatment of B_6H_{10} with triphenylphosphine at low temperatures (−50 to −10°C) in chloroform results in the formation of a 1:1 adduct. The ^{11}B NMR spectrum of the product is almost identical with that of $B_6H_{10}{\cdot}P(CH_3)_3$, the only difference being a small downfield shift for each signal of the triphenylphosphine adduct. See Table I. Apparently the structures of the two adducts are similar to each other. At about −10 °C a white solid begins to separate out from the solution, the signals of the 1:1 adduct fade away, and the signals of B_6H_{10} begin to grow. The nature of the white insoluble solid was not investigated. This change, however, may be attributed in part to the disproportionation of $B_6H_{10}{\cdot}P(C_6H_5)_3$ to $B_6H_{10}{\cdot}2P(C_6H_5)_3$ and B_6H_{10}. The insolubility of $B_6H_{10}{\cdot}2P(C_6H_5)_3$[3] may be largely responsible for the disproportionation.

Experimental Section

Volatile compounds were handled on high-vacuum lines. Laboratory stock B_6H_{10}, which had been prepared by literature methods,[16] was used. Trimethylphosphine used was our laboratory stock.[17] These compounds were handled in a grease-free system which was constructed with Teflon valves and O-ring joints. NMR spectra were recorded on a Varian XL-100 spectrometer, operating frequencies being 100 and 32.1 MHz for ^1H and ^{11}B, respectively. The shifts for the proton resonance signals were measured with reference to the CH_2Cl_2 signal, the shift of which was taken as δ 5.28. The standard for the ^{11}B resonance shifts was $BF_3{\cdot}O(C_2H_5)_2$, and the shifts toward lower field were taken as positive.

Reaction of B_6H_{10} with $P(CH_3)_3$. A measured amount of B_6H_{10} (usually in a 0.15–0.4 mmol quantity) was dissolved in dichloromethane (2–4 mL) in a 10 mm o.d. × 20 cm Pyrex tube equipped with a stopcock. Then a measured amount of $P(CH_3)_3$ was condensed above the frozen solution (−196 °C). The reactants were mixed by shaking the tube gently in a −80 °C slush bath. The tube was then inserted in the probe of the NMR spectrometer, and the ^{11}B spectra of the solution were recorded starting at −80 °C.

(a) Mixing Ratio 1:1 (in Molar Ratio). The reaction solution was turbid at −80 °C, but it became clear when warmed to −20 °C. The ^{11}B NMR spectrum at −80 °C consisted of a set of four signals, which is shown in Figure 1, and the signals of B_6H_{10}.[18] (The set of four signals will be referred as signal 1 hereafter in this paper.) The amounts of the two species in the solution were comparable to each other. As the temperature was raised, the B_6H_{10} signal became weaker and at −20 °C its intensity was less than 5% of the total signal intensity. Above −20 °C the spectrum became complex due to the appearance of several other signals and signal 1 gradually disappeared. This change was irreversible with respect to the temperature. When tetrahydrofuran was used as the solvent, the pattern of the signal 1 growth was the same as described above for the dichloromethane solution. The solubility of the white solid appeared greater in tetrahydrofuran than in dichloromethane. In one of the experiments the reaction mixture containing the 1:1 adduct and a small amount of B_6H_{10} was distilled at −45 °C under vacuum in an attempt to isolate the product, $B_6H_{10}{\cdot}P(CH_3)_3$. No phosphine was distilled out, and a white solid was obtained as the residue. The solid was redissolved in dichloromethane, and the solution was examined on the NMR instrument at −50 °C. (The sample was never warmed above −45 °C.) The ^{11}B NMR spectrum indicated that about 40% of the 1:1 adduct had been changed to something else which appeared to be identical with the species that was produced by the thermal transformation of the 1:1 adduct above −20 °C.

(b) Mixing Ratio 1:2 [B_6H_{10}:2$P(CH_3)_3$]. A white solid formed upon the mixing at −80 °C. The solid dissolved to give a clear solution when the solution was warmed to 0 °C. In the −80 °C spectrum only signal 1 could be seen, and the B_6H_{10} signal could not be detected. At −70 °C the signals of $B_6H_{10}{\cdot}2P(CH_3)_3$ were discerned. The growth of the $B_6H_{10}{\cdot}2P(CH_3)_3$ signals was slow even at −20 °C but was rapid at 0 °C and signal 1 disappeared from the spectrum.

Reaction of B_6H_{10} with $P(C_6H_5)_3$. A 0.156 mmol sample of $P(C_6H_5)_3$ was dissolved in about 1.4 mL of chloroform in a 10 mm o.d. Pyrex tube equipped with a stopcock. The solution was cooled to −63 °C, and then a 0.166 mmol quantity of B_6H_{10} vapor was expanded slowly into the tube through the stopcock while the solution was agitated gently. A slightly turbid solution resulted. The tube was placed in the probe of the NMR instrument, and the spectra were obtained starting at −40 °C. In addition to the signals listed in Table I, fairly strong signals of B_6H_{10} were seen in the −40 °C spectrum. As the temperature was raised, the B_6H_{10} signal intensity increased, and at +20 °C, the signal of the 1:1 adduct was no longer detectable. At this stage a considerable amount of white solid was seen in the sample.

NMR Assignments. A solution of $B_6H_{10}{\cdot}P(CH_3)_3$ was prepared in a standard 10 mm o.d. NMR sample tube by mixing B_6H_{10} and $P(CH_3)_3$ in a 1:1 molar ratio as described above in the reaction section, and the tube was sealed off. Deuterated dichloromethane (99+% D) was used as the solvent and the temperature of the measurement was −30 °C. A sample of $B_6H_{10}{\cdot}P(C_6H_5)_3$ in $CDCl_3$ (99.8% D) was prepared likewise, and its spectra were recorded at −40 °C. These sample solutions had been made dilute enough to give clear solutions at the temperatures of the measurements. The results are summarized in Table I. The assignments were made and confirmed by use of the single-frequency decoupling technique on proton and boron spins together with relative intensities of the decoupled signals.

Acknowledgment. The authors gratefully acknowledge support of this work by the U.S. Army Research Office through Grant DAAG 29-79-C-0129.

Registry No. B_6H_{10}, 23777-80-2; $P(CH_3)_3$, 594-09-2; $P(C_6H_5)_3$, 603-35-0; $B_6H_{10}{\cdot}P(CH_3)_3$, 76334-16-2; $B_6H_{10}{\cdot}P(C_6H_5)_3$, 76334-17-3; $B_6H_{10}{\cdot}ZP(CH_3)_3$, 57034-29-4.

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(16) Johnson, H. D., II; Brice, V. T.; Shore, S. G. *Inorg. Chem.* **1973**, *12*, 689. Geanangel, R. A.; Johnson, H. D.; II; Shore, S. G. *Inorg. Chem.* **1971**, *10*, 2363.

(17) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288.

(18) The observed chemical shifts of the B_6H_{10} signals are +14.3 ppm (J_{BH} = 158 Hz) for the basal boron atoms and −51.8 ppm (J_{BH} = 160 Hz) for the apical boron atom. Literature values are +14.1 and −51.8 ppm (Brice, V. T.; Johnson, H. D., II; Shore, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 6629) and +15.0 and −51.2 ppm (Onak, T. P.; Landesman, J.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533).