Table II. Kinetic Parameters for the Formation and Dissociation of $(NH_3)_5CoC_2O_4Fe^{4+}$

temp, °C	$(k_1K_1 + k_4K_h)$,[a] s^{-1}	$10^{-4}k_3$,[b] $M^{-1}\ s^{-1}$	$10^{-2}k_1$,[c] $M^{-1}\ s^{-1}$	$10^{-3}k_4$,[c] $M^{-1}\ s^{-1}$	$(k_{-1} + k_{-4})$,[d] s^{-1}
20.0	6.15 ± 0.01	2.3 ± 0.1	3.8	2.5	0.75 ± 0.03
25.0	15.3 ± 1.0	3.7 ± 0.4	8.7	4.6	1.0 ± 0.1
30.0	22.1 ± 1.0	5.4 ± 0.4	11.0	4.8	1.4 ± 0.2
$\Delta H^\ddagger$, kcal mol^{-1}		14.5 ± 0.7			10.4 ± 0.6
$\Delta S^\ddagger$, cal $deg^{-1}\ mol^{-1}$		11.0 ± 2.4			−23.5 ± 2.0

[a] As determined from the intercept values of the plots given in Figure 2. [b] Calculated from the slope values of Figure 2 and the known values of K_1 and K_h at the three temperatures. [c] Calculated by assuming $k_1K_1 = k_4K_h$ (see text). [d] Values of $(k_{-1} + k_{-4})$ are averages of the values of the intercepts of k_{obsd} vs. $[Fe^{3+}]_T$ plots of the type given in Figure 1.

$RC_2O_4^+$ from the $Fe(H_2O)_6^{3+}$ species of $\sim 9 \times 10^2\ s^{-1}$ and from the $Fe(H_2O)_5OH^{2+}$ species by $RC_2O_4^+$ and $RC_2O_4H^{2+}$ of $\sim 4 \times 10^4$ and $\sim 5 \times 10^3\ s^{-1}$, respectively. The water-exchange rate constants for $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ are known to be close to 1.6×10^2 and $1.4 \times 10^5\ s^{-1}$, respectively.[6,19] Comparisons of these values with the substitutive rate constants lead to the assignment of the I_a mechanism to our $Fe(H_2O)_6^{3+}$ complexation reaction and of I_d to the two $Fe(H_2O)_5OH^{2+}$ complexations, in total agreement with the conclusions already quoted.[6,17] We were able to determine reasonably precise activation parameters only for the k_3 pathway (see Table II) and these are not substantially different from figures[20] for the reactions of $FeOH^{2+}$ with large anions such as Cl^- and SO_4^{2-}.

It has already been noted that the rate constant for the hydrolysis of the binuclear product complex, k_r, is essentially independent of acidity at each temperature (see Table I and Figure 1). From the form of eq 3, it is obvious that neither k_{-2} nor k_{-3} can contribute perceptibly to the dissociation rate of the complex, so that eq 3 reduces to $k_r = (k_{-1} + k_{-4})$. Furthermore, it is seen that k_{-1} and k_{-4} should be very similar in magnitude, since the transition states for the two reactions must not differ greatly if at all. In fact, any differences in distribution of the hydrolysis products can be expected to be determined at a given acidity of the medium by the very rapid proton transfers governed by K_h and K_1. Experimental confirmation of such an identity is provided by calculations based on the published data[13] concerning the reactions of mono-, di-, and the trichloroacetate species with a aqueous Fe(III), which, as noted above, behave in a manner somewhat similar to our system. Use of these data[21] results in rough estimates at 25 °C for k_{-1} of 12, 17, and 69 s^{-1} and for k_{-4} of 43, 25, and 15 s^{-1}, respectively, for the three chloroacetate species, satisfactorily supporting our conclusion that $k_{-1} \cong k_{-4}$. Our complex $Co(NH_3)_5C_2O_4H^{2+}$ has a p*K* close to that of CH_2ClCO_2H, but our binuclear product $Co(NH_3)_5C_2O_4Fe^{4+}$ has a charge 2 units greater than $CH_2ClCO_2Fe^{2+}$. The rather slow dissociation rate of the binuclear complex ($k_{-1} \cong k_{-4} \cong 0.5\ s^{-1}$ as compared to $k_{-1} \cong k_{-4} \cong 20\ s^{-1}$ for the acetato species) may be taken as evidence that Fe(III) in the binuclear species is chelated by the oxalate moiety. Similar conclusions were reached from consideration of the stability constants of various analogous binuclear complexes[4] and the high catalytic power of Fe^{3+} relative to H^+ in promoting water-for-oxalate substitution at a cobalt(III) center.[2] The activation parameters for $RC_2O_4Fe^{4+}$ dissociation are quite "normal", being similar to those[20] for a series of FeL^{n+} dissociations, with ΔH^* typically in the range 9–15 kcal mol^{-1} and ΔS^* in the range −10 to −30 cal $deg^{-1}\ mol^{-1}$. All in all, one can conclude that $Co(NH_3)_5C_2O_4H^{2+}$ behaves as a conventional ligand in both its association and dissociation reactions involving aqueous Fe(III) species.

Acknowledgment. We are grateful to the John D. and Francis H. Larkin Foundation of the State University of New York at Buffalo for financial support and to Utkal University for a leave of absence to A.C.D.

Registry No. $(NH_3)_5CoC_2O_4^+$, 18443-73-7; $Fe(H_2O)_6^{3+}$, 15377-81-8.

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(19) Another recent measurement of the water-exchange rate of $Fe(H_2O)_6^{3+}$ ion has yielded a value of 167 s^{-1} at 25 °C (Dodgen, H. W.; Liu, Gordon; Hunt, J. P. *Inorg. Chem.* **1981**, *20*, 1002).

(20) Cavasino, F. P. *J. Phys. Chem.* **1968**, *72*, 1378.

(21) Data for k_1, k_4, K_1, K_{HA}, and K_{OH} given in ref 13 and the equality $K_4 = K_1K_{HA}/K_{OH}$ were utilized in this calculation.

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Reaction of Pentaborane(11) with Bis(trimethylphosphine)-Diborane(4)

Mitsuaki Kameda and Goji Kodama*[1]

Received April 16, 1981

Recently we reported[2] that both diborane(6) and tetraborane(10) react with bis(trimethylphosphine)–diborane(4) to give a novel triboron complex cation $B_3H_6[P(CH_3)_3]_2^+$:

$$^3/_2B_2H_6 + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_3H_6[P(CH_3)_3]_2^+B_2H_7^-$$

$$B_4H_{10} + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_3H_6[P(CH_3)_3]_2^+B_3H_8^- \qquad (1)$$

In these reactions, B_2H_6 and B_4H_{10} are cleaved unsymmetrically: $B_2H_6 \rightarrow$ "$BH_2^+ + BH_4^-$" and $B_4H_{10} \rightarrow$ "$BH_2^+ + B_3H_8^-$". The BH_2^+ unit combines with the diborane(4) adduct to give the triboron cation. The BH_4^- anion further reacts with diborane(6) to form the $B_2H_7^-$ anion.

It was of interest to see if the next higher borane, pentaborane(11), would react with $B_2H_4{\cdot}2P(CH_3)_3$ in the manner similar to that observed for diborane(6) and tetraborane(10). The study of the reaction, which is reported in this paper, showed that the reaction pattern of B_5H_{11} was different from that of B_2H_6 or B_4H_{10}; the unsymmetrical cleavage of B_5H_{11} was not effected by $B_2H_4{\cdot}2P(CH_3)_3$.

Results and Discussion

A rapid reaction occurred at −80 °C between B_5H_{11} and $B_2H_4{\cdot}2P(CH_3)_3$ in a 1:1 molar ratio in dichloromethane to give trimethylphosphine–borane(3) and other compounds. As the reaction solution was allowed to warm, the latter products underwent gradual changes. At room temperature the solution contained $(CH_3)_3PBH_3$, $(CH_3)_3PB_5H_9$, B_5H_9, and B_2H_6 as the final reaction products.

As noted earlier, $B_2H_4{\cdot}2P(CH_3)_3$ cleaved both the B_2H_6 and B_4H_{10} molecules unsymmetrically to give the $B_3H_6[P(CH_3)_3]_2^+$ cation and the anion characteristic of unsymmetrical cleavage of that borane.[2] Since it had been known that B_5H_{11}, like B_2H_6[3] and B_4H_{10},[4] undergoes unsymmetrical cleavage with

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(1) To whom correspondence should be addressed.

(2) Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.

(3) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 8.

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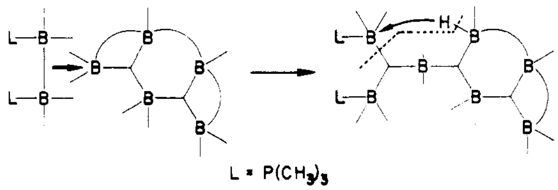
Scheme I



ammonia,[5] it was expected that $B_2H_4\cdot 2P(CH_3)_3$ would interact with B_5H_{11}

$$B_5H_{11} + B_2H_4\cdot 2P(CH_3)_3 \rightarrow B_3H_6[P(CH_3)_3]_2{}^+B_4H_9{}^- \quad (2)$$

No evidence for the formation of the $B_4H_9^-$ anion and the triboron cation could be found. Furthermore, the rapid, initial reaction of B_5H_{11} at −80 °C contrasted with the slow reactions of B_2H_6 and B_4H_{10} at the same temperature.

The observed initial reaction of B_5H_{11} with $B_2H_4\cdot 2P(CH_3)_3$ is reminiscent of the reaction of anhydrous HCl with the diborane(4) adduct in that the reaction which produces $(CH_3)_3PBH_3$ occurs immediately upon mixing at −80 °C.

$$B_2H_4\cdot 2P(CH_3)_3 + HCl \xrightarrow[CH_2Cl_2]{-80\ °C} (CH_3)_3PBH_3 + ClBH_2\cdot P(CH_3)_3{}^{6}$$

Since B_5H_{11} is known to act as a stronger protic acid than B_4H_{10},[7] it seems plausible to regard the initial reaction of B_5H_{11} as a congener of the HCl reaction. Thus,

$$B_2H_4\cdot 2P(CH_3)_3 + B_5H_{11} \rightarrow (CH_3)_3PBH_3 + B_5H_{10}\cdot BH_2\cdot P(CH_3)_3 \quad (3)$$

Subsequently the product $B_5H_{10}\cdot BH_2\cdot P(CH_3)_3$, or $B_6H_{12}\cdot P(CH_3)_3$, decomposes at higher temperatures according to eq 4. The intensity measurements on the ^{11}B NMR signals of

$$B_6H_{12}\cdot P(CH_3)_3 \rightarrow \begin{cases} (CH_3)_3PBH_3 + B_5H_9 \text{ (ca. 25\%)} \\ B_5H_9\cdot P(CH_3)_3 + {}^1/_2B_2H_6 \text{ (ca. 75\%)} \end{cases} \quad (4)$$

the reaction products at various temperatures during the reaction process appeared to support the initial formation of $B_6H_{12}\cdot P(CH_3)_3$ (proposed above). The formation of $B_6H_{12}\cdot P(CH_3)_3$ may be visualized in an alternative manner which, as illustrated in Scheme I, involves the formation of an unstable intermediate (I)[8] as the result of interaction between the B–B bond of $B_2H_4\cdot 2P(CH_3)_3$ as a base[2] and B_5H_{11} as a Lewis acid. Subsequent elimination of $(CH_3)_3PBH_3$ (cleavage at the dotted line) from I would leave $B_6H_{12}\cdot P(CH_3)_3$ behind.

Earlier, Long observed[9] that B_6H_{12} combined with $P(CH_3)_3$ in a 1:1 molar ratio at −95 °C and that the adduct decomposed at higher temperatures to give B_5H_9, B_2H_6, $B_5H_9\cdot P(CH_3)_3$, and $(CH_3)_3PBH_3$. Although the details of characterization of the 1:1 adduct, $B_6H_{12}\cdot P(CH_3)_3$, have yet to be perfected, this observation further supports the process proposed above for the reaction of B_5H_{11} with $B_2H_4\cdot 2(CH_3)_3$, which involves the initial formation of $B_6H_{12}\cdot P(CH_3)_3$ followed by the decomposition of the B_6H_{12} adduct (eq 3 and 4). The ^{11}B NMR spectrum of the supposed $B_6H_{12}\cdot P(CH_3)_3$ observed in this study, or the total spectrum of the initial reaction products less the signal of $(CH_3)_3PBH_3$, appears to consist of two sets of signals. One of the two sets has a common feature with the spectrum that was reported by Long as the spectrum of $B_6H_{12}\cdot P(CH_3)_3$.[10] At higher temperatures the two sets of signals both disappear and are replaced by the signals of the final products. This suggests that $B_6H_{12}\cdot P(CH_3)_3$ possibly exists in two isomeric forms and that each of the two modes of the $B_6H_{12}\cdot P(CH_3)_3$ decomposition described above (eq 4) may represent the decomposition of each of the isomers.

Long and Shore were the first to prepare trimethylphosphine–pentaborane(9), $B_5H_9\cdot P(CH_3)_3$. The characterization of the compound has been described in detail.[9] Additional NMR data for the compound, which were obtained in this study, are appended in the Experimental Section. The data indicated that, at room temperature, four of the nine borane hydrogen atoms form four rigid terminal H–B bonds at the four basal positions of the square-pyramidal boron framework, while the other five hydrogen atoms are undergoing a rapid tautomeric motion below the four basal edges of the pyramid. Attempts to prepare the 1:1 adduct by the direct reaction of B_5H_9 with $P(CH_3)_3$ were unsuccessful. No evidence for the formation of the 1:1 adduct in the reaction of B_5H_9 with $P(CH_3)_3$ could be found in the ^{11}B NMR spectra of the reaction solution. The product that could be detected first was the 1:2 adduct, $B_5H_9\cdot 2P(CH_3)_3$. This contrasted with the reaction of B_6H_{10} with $P(CH_3)_3$ in that the 1:1 adduct, $B_6H_{10}\cdot P(CH_3)_3$, could be detected as the precursor in the 1:2 adduct formation.[11] The formation of $B_5H_9\cdot P(CH_3)_3$ that is reported in this paper would serve as an additional, practical method for the preparation of the compound.

Experimental Section

General Data. Laboratory stock pentaborane(11) was purified according to the procedure described elsewhere.[12] Bis(trimethylphosphine)–diborane(4) was prepared by the reaction of B_5H_9 with $P(CH_3)_3$.[6] Reagent grade dichloromethane was stored over molecular sieves. Standard high-vacuum line techniques were used throughout for the handling of volatile compounds. The ^1H and ^{11}B NMR spectra were recorded on a Varian XL-100-15 instrument operating at 100 and 32.1 MHz, respectively. Chemical shift values for the ^{11}B resonance signals were measured relative to the signal of $BF_3\cdot O(C_2H_5)_2$, high-field shifts being taken as negative.[13] The proton shifts were measured with respect to the resonance signal of proton impurity in CD_2Cl_2 which was taken as δ 5.28.

Reaction of B_5H_{11} with $B_2H_4\cdot 2P(CH_3)_3$. A weighed sample (usually 0.25–0.5 mmol) of $B_2H_4\cdot 2P(CH_3)_3$ was placed in a reaction tube (10-mm o.d. × 25 cm, Pyrex; equipped with a stopcock at the upper end) and was dissolved in about 1.5 mL of CH_2Cl_2. The tube was chilled with liquid nitrogen, and a measured amount of B_5H_{11} was condensed above the frozen solution. The tube was then immersed in a −80 °C bath and shaken gently for mixing of the reactants in the solution. The solution remained clear. The tube was then inserted in the precooled probe of the NMR instrument to record the ^{11}B NMR spectra of the solution at various temperatures beginning at −80 °C. A series of spectra for such a reaction mixture is shown in Figure 1.

At −80 °C the signals of B_5H_{11} or $B_2H_4\cdot 2P(CH_3)_3$ were not present in the spectrum unless one of the reactants was used in excess of a 1:1 molar ratio. The signal of $(CH_3)_3PBH_3$ appeared intensely at −37.2 ± 0.1 ppm. Other signals were very broad at this temperature. Two doublets (^{31}P spin coupled) at −27.6 and −48.0 ppm and two broad featureless signals at −12.9 and −58.7 ppm were seen in the ^1H-spin-decoupled spectrum. It was noted that the area of the strong

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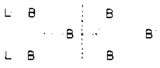
(4) Kodama, G.; Parry, R. W. *Proc. Int. Congr. Pure Appl. Chem.* **1958**, *16*, 483.

(5) Kodama, G.; Dunning, J. E.; Parry, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 3372.

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

(7) Shore, S. G. *Pure Appl. Chem.* **1977**, *49*, 717.

(8) For the reaction of $B_2H_4\cdot 2P(CH_3)_3$ with B_4H_{10}, formation of an intermediate similar to I may be considered (see figure). Subsequent cleavage at the dotted line will result in the $B_3H_6[P(CH_3)_3]_2{}^+B_3H_8{}^-$ salt.



(9) (a) Long, J. R. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1973. (b) Long, J. R.; Shore, S. G., to be submitted for publication.

(10) Reference 9a, p 63.

(11) Kameda, M.; Kodama, G. *Inorg. Chem.* **1981**, *20*, 1072.

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

(13) *J. Organomet. Chem.* **1977**, *131*, C43.

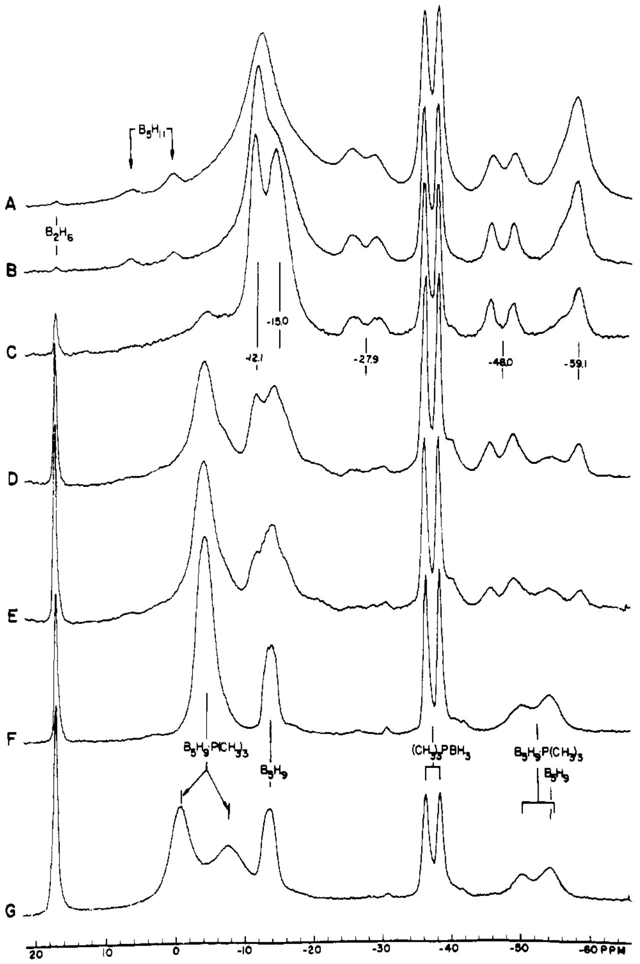
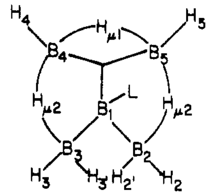


Figure 1. Proton-spin-decoupled ^{11}B NMR spectra of a reaction mixture of B_5H_{11} and $B_2H_4{\cdot}2P(CH_3)_3$, indicating the reaction progress with temperature and time: A, −80 °C; B, −60 °C; C, −40 °C; D and E, −30 °C; F, 0 °C. G was recorded at −60 °C after the mixture was once warmed to 25 °C.

signal at −12.9 ppm was about twice the sum of the areas of the other three signals. As the temperature of the sample was raised to −60 °C and then to −40 °C, the signals became narrower and better resolved. These signals were found at about −7 (s, v br), −12.1 (d, J_{BH} = 118 Hz), −15.0 (s), −27.9 (d, J_{BP} = 112 Hz), −40 (s, severely overlapped with the signal of $(CH_3)_3PBH_3$), −48.0 (d, J_{BP} = 102 Hz), −56.9 (s, br), and −59.1 ppm (d, J_{BH} = 141 Hz). In addition, at −40 °C the signal of B_2H_6 was detectable and at −30 °C the signals of B_5H_9 and $B_5H_9{\cdot}P(CH_3)_3$ became noticeable. These signals of the secondary products grew in at the expense of the signal intensities of the initial products. The intensity of the $(CH_3)_3PBH_3$ signal appeared to increase also as the secondary reaction progressed. The eight signals of the initial products described above may be grouped into two sets of signals. The signals at −27.9 (B–P doublet) and −56.9 ppm belong to one of the sets, and those at −48.0 (B–P doublet) and −59.1 ppm to another set. The pair of signals in each set appeared in an approximately 1:1 intensity ratio and faded away at the same rate, but the intensity ratio between the two pairs varied depending upon the reaction conditions. The signals of the first set disappeared faster than those of the second set. Grouping of the other low-field signals into the two sets was made uncertain by the overlaps of the signals with each other and with the signals of the secondary products (B_5H_9 and $B_5H_9{\cdot}P(CH_3)_3$).[14] The signals of the initial products, except the $(CH_3)_3PBH_3$ signal, disappeared fast above 0 °C. At room temperature only the signals of $(CH_3)_3PBH_3$, $B_5H_9{\cdot}P(CH_3)_3$, B_2H_6, and B_5H_9 were seen in the spectrum. The signal intensity ratio for $B_5H_9{\cdot}P(CH_3)_3/B_5H_9$ ranged from 3 to 4 and the amount of diborane that was produced in the reaction was 0.37–0.42 mol/mol of the reactant when the two reactants were used in a 1:1 molar ratio.

NMR Spectra of $B_5H_9{\cdot}P(CH_3)_3$. A crude sample of $B_5H_9{\cdot}P(CH_3)_3$ was obtained from the solution of the reaction of B_5H_{11} with $B_2H_4{\cdot}2P(CH_3)_3$ by pumping out the volatile components at 0 °C. This was purified in a sublimation-sampling apparatus[12] to prepare an authentic sample solution (CD_2Cl_2 solvent) for the NMR measurements. The sublimation was performed under dynamic vacuum by first circulating ice water through the cold finger until all of the lighter contaminants (e.g., CH_2Cl_2 and $(CH_3)_3PBH_3$) were judged to have been removed and then by passing cold nitrogen gas (ca. −120 °C) through the cold finger. The sublimation apparatus was kept exposed to the ambient atmosphere. A small amount of a viscous yellow liquid residue was left behind. The $B_5H_9{\cdot}P(CH_3)_3$ sample thus prepared contained a small amount (<1 mol %) of $(CH_3)_3PB_3H_7$.

At 25 °C the ^{11}B resonance signals were observed at −4.2 (d, J_{BH} = 120 Hz, $J_{BB} \simeq$ 20 Hz) and −52.6 ppm (d, J_{BP} = 139 Hz) in an intensity ratio 4:1. These values compare with the reported values of −3.8 and −51.5 ppm (d, J_{BP} = 129 Hz), which were recorded at −35 °C.[9] The ^1H resonance signals (^{11}B spin decoupled) for the borane protons were found at 2.39 (d, $^3J_{HP} \simeq$ 12 Hz) and −0.12 ppm (d, $^3J_{HP} \simeq$ 10 Hz) in an intensity ratio about 4:5, and for the methyl protons at 1.38 ppm (d, $^2J_{HP} \simeq$ 12 Hz). At −60 °C the methyl proton signal remained unchanged (1.25 ppm, J_{HP} = 12 Hz), but the borane proton signals appeared at 2.81 ($H_{4,5}$), 2.02 ($H_{2,3}$ or $H_{2',3'}$), 1.73 ($H_{2',3'}$ or $H_{2,3}$), −1.50 ($H_{\mu2}$), and −2.58 ppm ($H_{\mu1}$) in an approximate intensity ratio 2:2:2:2:1. The signals at 2.02 and 1.73 ppm were severely overlapped with each other, and thus the general feature of this low-temperature ^1H resonance spectrum was consistent with that reported.[15] In the ^{11}B spectrum recorded at −60 °C, the low-field signal appeared at two places as a broad doublet (J_{BH} = 150 Hz) at −0.6 ppm ($B_{4,5}$) and a broad hump centered at −7.6 ppm ($B_{2,3}$). The high-field doublet signal remained unchanged. The numbering for the hydrogen and boron atoms is indicated in the figure shown, where L = $P(CH_3)_3$. The assignments were made by using the single-frequency decoupling technique on proton and boron spins.



Reaction of B_5H_9 with $P(CH_3)_3$ in a 1:1 Molar Ratio. About 2 mL of a CH_2Cl_2 solution containing 0.534 mmol of B_5H_9 was prepared in a 10-mm o.d. tube similar to that described earlier and was frozen with liquid nitrogen. Then, a 0.534-mmol sample of $P(CH_3)_3$ was condensed in the tube and the reactants were mixed at −80 °C. The reaction was monitored on the NMR instrument by observing the ^{11}B resonance spectra of the solution. The temperature of the probe was raised at a rate of about 1 °C/min. No sign of reaction could be detected up to −20 °C; the spectra contained only the signals of B_5H_9. At −15 °C the signals of $B_5H_9{\cdot}2P(CH_3)_3$ were discerned, but no additional signal could be detected. A similar experiment with an excess of $P(CH_3)_3$ was performed earlier, whereupon no evidence for the formation of the 1:1 adduct was observed.[6] The reaction of $B_5H_9{\cdot}P(CH_3)_3$ with $P(CH_3)_3$ was run under the similar conditions. The formation of $B_5H_9{\cdot}2P(CH_3)_3$ was complete at *−30 °C.*

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

Registry No. $B_2H_4{\cdot}2P(CH_3)_3$, 39678-68-7; B_5H_{11}, 18433-84-6; $B_5H_9{\cdot}P(CH_3)_3$, 80288-02-4; $(CH_3)_3PBH_3$, 54223-05-1; B_5H_9, 19624-22-7; B_2H_6, 19287-45-7; $P(CH_3)_3$, 594-09-2.

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(14) Long reported[10] the $^{11}B\{^1H\text{–spin decoupled}\}$ NMR spectrum of $B_6H_{12}{\cdot}P(CH_3)_3$ in $CHCl_3/HCF_2Cl$ (−78 °C). The major signals in the spectrum are at −5.7 (s, br), −17.5 (overlap of signals), −39.2 (s), and −47.1 ppm (d, B–P). Three of these signals appear to correspond to the signals in our spectrum at −7, −40, and −48.0 ppm, indicating that perhaps these belong to the second set of signals. It is noted, however, that the −59.1-ppm signal, which is accompanied by the −48.0-ppm signal in our spectrum, is not mentioned in the report.

(15) It was reported[9a] that the borane proton resonance signals for $B_5H_9{\cdot}P(CH_3)_3$ at −65 °C appeared at 4.08, 3.19, −0.1, and −1.2 ppm as converted from the reported τ values. These values are consistently higher by 1.34 ± 0.06 ppm than those found in this work.