

The routine analysis of complex NMR spectra is one of the most powerful methods for accurately obtaining spin–spin coupling constants. In many spin systems, particularly simple systems with symmetry, the solution to the analysis is not unique and one must be aware of uncertainties and ambiguities inherent in the analysis before concrete assignments are made.

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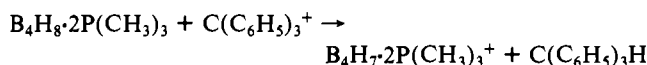
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Reactions of Trimethylphosphine–Pentaboranes with Trityl Cation. Formation of Octahydrobis(trimethylphosphine)pentaboron(1+) and Octahydro(trimethylphosphine)pentaboron(1+) Cations

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Earlier, we reported the synthesis of the heptahydrobis(trimethylphosphine)tetraboron(1+) cation, $B_4H_7\cdot 2P(CH_3)_3^+$.¹ This cation was prepared by abstracting a hydride ion from $B_4H_8\cdot 2P(CH_3)_3$ with the use of triphenylcarbenium (trityl) cation.



This method of hydride abstraction should be applicable to the preparation of other polyboron complex cations. However, the ease of hydride abstraction must be dependent upon the hydridic nature of the borane hydrogens on the substrate borane compound. As the borane structure becomes larger, the borane hydrogen atoms are expected to become less hydridic.² Furthermore, the hydridic character of borane hydrogen atoms should be influenced by the number of the trimethylphosphines that are attached to the borane framework. It was, therefore, of interest to test the reaction on other higher borane compounds containing different numbers of trimethylphosphines. Synthesizing new polyboron cations was of interest by itself. In particular, the structures of these cations were of interest. The above tetraboron cation is isoelectronic and isostructural with $B_4H_8\cdot P(CH_3)_3$ and $B_4H_9^-$ as $B_3H_6\cdot 2P(CH_3)_3^+$, $B_3H_7\cdot P(CH_3)_3$, and $B_3H_8^-$ are isoelectronic and isostructural with each other.³ The generality of this isoelectronic–isostructural feature had yet to be tested. This paper describes the results of these tests, which were performed on trimethylphosphine adducts of pentaborane(9).

Results and Discussion

A. Reaction of Bis(trimethylphosphine)–Pentaborane(9) with Trityl Cation. The adduct $B_5H_9\cdot 2P(CH_3)_3$ reacted with trityl tetrafluoroborate or hexafluorophosphate in dichloromethane at $-80^\circ C$ to give the $B_5H_8\cdot 2P(CH_3)_3^+$ cation. The BF_4^- salt of this cation was reasonably stable at room temperature, but the PF_6^- salt decomposed rapidly above $0^\circ C$.

NMR Spectra. The NMR data for the $B_5H_8\cdot 2P(CH_3)_3^+$ cation are listed in Table I. The ^{11}B spectra shown in Figure 1 immediately indicate that the molecule is of C_1 symmetry and that the -49.4 ppm signal is due to the apex boron atom⁴ to which one of the phosphines is attached. The triplet feature of the -14.3 ppm signal (due to the other phosphine-attached boron atom) and the two doublet signals at 0.3 and 6.9 ppm suggest the structure of the cation to be that shown in Figure 1. The assignments were

Table I. NMR Shift Data for the $B_5H_8\cdot 2P(CH_3)_3^+$ Cation

temp, °C	shift in ppm, assign (<i>J</i> in Hz, J_{XY}) [rel intens]
^{11}B +20	-49.4 , B_1 (143 , J_{BP}) [1]; -14.3 , B_2 (103 , J_{BP}) [1]; -9.7 , B_5 [1]; $+0.3$, B_3 (12.5 , J_{BH}) [1]; 6.9 , B_4 (128 , J_{BH}) [1]
1H -10	-1.84 , $H_{\mu(3,4)}$ [1]; -1.21 , $H_{\mu(4,5)}$ [1]; -0.75 , $H_{\mu(2,3)}$ [1]; 1.87 , H_2 [1]; 1.93 , H_5 [1]; 2.44 , H_5 [1]; 3.21 , H_3 [1]; 3.46 , H_4 [1]; 1.36 , $H_{C(1)}$ (11.9 , $^2J_{HP}$) [9]; 1.56 , $H_{C(2)}$ (12.8 , $^2J_{HP}$) [9]
^{31}P +20	-2.3 , P_1 (146 , J_{PB}) [1]; -5.3 , P_2 [1]

Table II. NMR Shift Data for the $B_5H_8\cdot P(CH_3)_3^+$ Cation

temp, °C	shift in ppm, assign (<i>J</i> in Hz, J_{XY}) [rel intens]
^{11}B -20	-48.6 , B_1 (220 , J_{BP}) [1]; -11.2 , $B_{2,3,4,5}$ (172 , J_{BH}) [4]
1H -10	-1.54 , H_{μ} [4]; 2.86 , H_t (168 , J_{HB}) [4]; 1.74 , H_C (13 , $^2J_{HP}$; 3 , $^3J_{PB}$) [9]
^{31}P -10	-9.5 (215 , J_{PB})

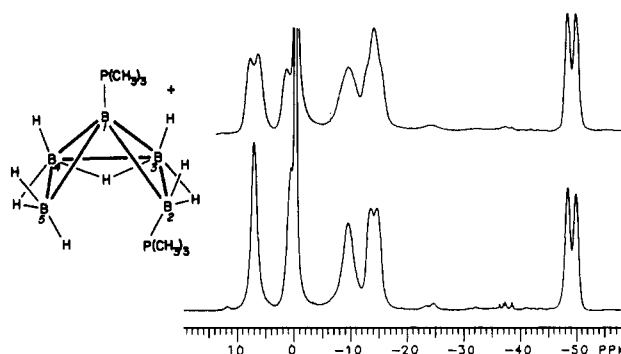


Figure 1. Left: Structure proposed for $B_5H_8\cdot 2P(CH_3)_3^+$. Position of the basal phosphine (endo or exo) is uncertain. Right: 96.2-MHz ^{11}B NMR spectra of the cation (BF_4^- salt, $+20^\circ C$, CD_2Cl_2 solvent). The upper spectrum is normal; the lower spectrum is proton spin decoupled. The truncated tall peak at -0.4 ppm is due to BF_4^- .

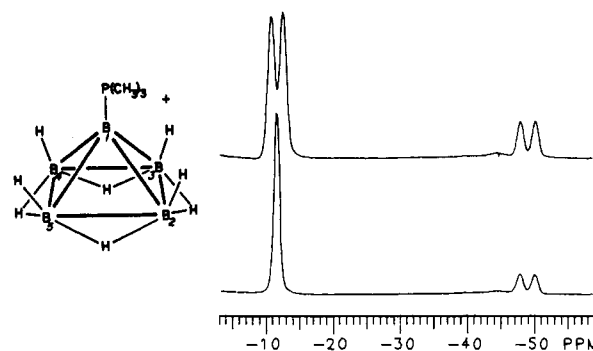


Figure 2. Left: Structure proposed for $B_5H_8\cdot P(CH_3)_3^+$. Right: 96.2-MHz ^{11}B NMR spectra of the cation (BF_4^- salt, $-20^\circ C$, CD_2Cl_2 solvent). The upper spectrum is normal; the lower spectrum is proton-spin decoupled.

based on the 1H spectra obtained by the selective decoupling of boron spins.

B. Reaction of Trimethylphosphine–Pentaborane(9) with Trityl Cation. A 1:1 mixture of $B_5H_9\cdot P(CH_3)_3$ and trityl tetrafluoroborate in dichloromethane remained unchanged at $-80^\circ C$. At $-30^\circ C$, however, a rapid reaction occurred and the $B_5H_8\cdot P(CH_3)_3^+$ cation was produced. The BF_4^- salt of this cation was fairly stable at room temperature. When trityl hexafluorophosphate was used, the pentaboron cation could not be obtained. Apparently, the PF_6^- ion was involved in the reaction. Thus, even at $-80^\circ C$ $B_5H_9\cdot P(CH_3)_3$ was consumed and various boron compounds were produced. These compounds included BF_4^- , $BF_3\cdot P(CH_3)_3$, B_5H_9 , $BH_3\cdot P(CH_3)_3$, and other unidentified species.

NMR Spectra. The data are listed in Table II. The ^{11}B spectra shown in Figure 2 suggest that the molecule is of C_4 symmetry. The spectral data are consistent with the structure illustrated in

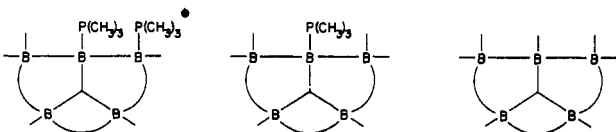
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Figure 2. The extremely large value of J_{BP} (220 Hz) is noteworthy.

C. Pentaborane(9) and Trityl Tetrafluoroborate. Pentaborane(9) did not react with trityl tetrafluoroborate in dichloromethane at room temperature.

D. Conclusion. The reactions described above demonstrated that the attachment of electron-donating trimethylphosphine to pentaborane enhances the hydridic behavior of the borane hydrogen atoms: The ease of hydride abstraction by the trityl cation increases with the number of trimethylphosphines attached to pentaborane.

The new polyboron complex cation $B_5H_8 \cdot 2P(CH_3)_3^+$ is isostructural with its isoelectronic, neutral and anionic counterparts $B_5H_9 \cdot P(CH_3)_3^{5,6}$ and $B_5H_{10}^{-7}$.



Thus, the isoelectronic–isostructural feature observed for the triboron and tetraboron trios is now extended to the pentaboron trio. It is noted that, among $B_5H_9 \cdot 2P(CH_3)_3^+$, $B_5H_9 \cdot P(CH_3)_3$, and $B_5H_{10}^{-}$, the anion is most fluxional with respect to its borane hydrogen atom migration^{6,7} and the cation is least fluxional. The same trend has been observed for the corresponding trios of tri- and tetraboron.^{1,3} The other new cation, $B_5H_8 \cdot P(CH_3)_3^+$, belongs to a new family of polyboron complex cations with the general formula $B_nH_{n+3} \cdot P(CH_3)_3^+$, and it is isostructural also with its isoelectronic, neutral counterpart B_5H_9 .

Two different salts of the trityl cation were used in this study. The BF_4^- salt yielded reasonably stable salts of the pentaboron cations, but the PF_6^- salt did not. Whenever the PF_6^- salt was used, BF_4^- and $BF_3 \cdot P(CH_3)_3$ were formed. The interaction of the PF_6^- ion with borane species is an interesting subject of a separate study, and the results will be reported at a later date upon completion of the study.

Experimental Section

General Information. Conventional vacuum-line techniques were used throughout for the handling of air-sensitive, volatile compounds. Nitrogen gas filled, plastic bags were used for the transfer of air-sensitive solids. Pentaborane(9) (Callery Chemical Co.) was fractionated and treated with trimethylphosphine (laboratory stock, prepared by a literature method⁸) to prepare the samples of $B_5H_9 \cdot 2P(CH_3)_3$.⁹ The sample of $B_5H_9 \cdot P(CH_3)_3$ was prepared from B_5H_{11} and $B_2H_4 \cdot 2P(CH_3)_3$ by the method described previously.⁶ The BF_4^- and PF_6^- salts of the trityl cation (Aldrich Chemical Co. and Alfa Products) were recrystallized from dichloromethane. The NMR spectra were recorded on a Varian XL-100 or XL-300 spectrometer. Chemical shifts for ^{11}B and ^{31}P resonances were recorded with reference to the $BF_3 \cdot O(C_2H_5)_2$ and 85% orthophosphoric acid signals, respectively. For 1H resonances, the shift of dichloromethane was taken to be at 5.28 ppm. The reactions of the pentaborane compounds with the trityl salts were performed in 10-mm-o.d. Pyrex tubes. The tubes containing reaction mixtures were placed in the probe of the NMR instrument to monitor the reactions.

Reaction of $B_5H_9 \cdot 2P(CH_3)_3$ with Trityl Cation. A 0.49-mmol sample of $B_5H_9 \cdot 2P(CH_3)_3$ was dissolved in about 2 mL of CH_2Cl_2 in the reaction tube, and a 0.61-mmol sample of $C(C_6H_5)_3^+BF_4^-$ was added in the tube

above the frozen solution. As the reaction mixture was agitated by shaking the tube in a $-80^\circ C$ bath, the dark yellow color of the trityl cation changed rapidly to a faint yellow. At this stage the original $B_5H_9 \cdot 2P(CH_3)_3$ had been completely converted into the $B_5H_8 \cdot 2P(CH_3)_3^+$ cation. As the tube was allowed to warm to room temperature, a clear, straw yellow solution resulted. At this point the solution did not contain any boron compound other than the BF_4^- salt of the pentaboron cation. The volatile components were evaporated under vacuum, and the resulting pale yellow residue was washed with toluene and then leached with CH_2Cl_2 . By evaporation of the solvent from the leachate, a white solid of the $B_5H_8 \cdot 2P(CH_3)_3^+BF_4^-$ salt was obtained. The solid was contaminated slightly with small amounts of decomposition products, which were produced during the isolation process. The reaction with $C(C_6H_5)_3^+PF_6^-$ (1:1 molar ratio, 0.46 mmol of each reactant) proceeded similarly. However, the formation of BF_4^- was observed at higher temperatures (about $-20^\circ C$) and was fast above $0^\circ C$.

Reaction of $B_5H_9 \cdot P(CH_3)_3$ with Trityl Cation. A 0.59-mmol sample of $B_5H_9 \cdot P(CH_3)_3$ and 0.64 mmol of $C(C_6H_5)_3^+BF_4^-$ were mixed in about 2 mL of CH_2Cl_2 in a reaction tube. At $-80^\circ C$ most of the trityl salt remained undissolved, and the solution was dark yellow. When the mixture was allowed to warm to $-30^\circ C$ and agitated by shaking, the trityl salt quickly disappeared and the solution became pale yellow and turbid. At this point $B_5H_9 \cdot P(CH_3)_3$ had been converted into the $B_5H_8 \cdot P(CH_3)_3^+$ cation. As the tube was allowed to warm to room temperature, the solution became clear. To isolate the $B_5H_8 \cdot P(CH_3)_3^+BF_4^-$ salt, this solution was treated in the same manner as the $B_5H_9 \cdot 2P(CH_3)_3^+$ cation solution. (See above.) During this isolation process, however, a small portion of the salt decomposed; thus, the product was contaminated. It was noted that as the salt was freed from triphenylmethane, its solubility in CH_2Cl_2 decreased markedly.

Mixtures of B_5H_9 and Trityl Salt. Approximately 0.84-mmol samples of $C(C_6H_5)_3^+BF_4^-$ were mixed with B_5H_9 in 1:2 and 2:1 molar ratios in 2-mL portions of CH_2Cl_2 . When allowed to warm to room temperature, the reaction mixtures were dark brownish yellow. The ^{11}B NMR spectra of these solutions contained only the signals of B_5H_9 and BF_4^- and were found to be unchanged when examined 2 days later.

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Reactivity of $[Cu(TIM)]^{2+}$ with Pyridine: Formation Constants Determined by Cyclic Voltammetry

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Recently we reported the unusual reactivity of $[Cu(TIM)]^{2+}$ ($TIM = 2,3,9,10$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane-1,3,8,10-tetraene) with chloride ion in methylene chloride¹ (Figure 1). The formation constant in methylene chloride of the 1:1 adduct was $2 \times 10^7 M^{-1}$, a value which indicates that the reaction had proceeded far to the right. The method used to determine this very large constant was a modified version of a cyclic voltammetric simulation program, reported by Philp and co-workers.²

In this study we examine the reactivity of $[Cu(TIM)]^{2+}$ with pyridine in methylene chloride. The formation constants for this case were considerably smaller than with chloride ion and were determined by conventional electrochemical and spectral techniques. We also demonstrate the usefulness of the cyclic voltammetric simulation technique for formation constant determi-

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(7) Shore and co-workers reported that the ^{11}B NMR spectrum of $B_5H_{10}^-$ consisted of two doublets (-13.2 ppm, $J_{BH} = 162$ Hz; -52.0 ppm, $J_{BH} = 175$ Hz) in the area ratio 4:1 [Rommel, R. J.; Johnson, H. D., II; Jaworinsky, I. S.; Shore, S. J. *Am. Chem. Soc.* **1975**, *97*, 5395]. Our values [Jock, C. P.; Kodama, G., unpublished results] obtained for KB_5H_{10} in dimethyl ether at $-80^\circ C$ were -14.3 ($J_{BH} = 165$ Hz) and -53.6 ppm ($J_{BH} = 170$ Hz) and were comparable to Shore's. (The spectrum is deceptively similar to that of B_5H_9 !) The doublet feature of the low-field signal and therefore the equivalency of the four basal B–H units in $B_5H_{10}^-$ suggest that the three bridge hydrogens and two endo terminal hydrogens are undergoing rapid migration even at $-80^\circ C$.

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