Inorg. Chem. **1997,** *36,* 4369−4371

Synthesis of the Tris(trimethylphosphine)tetrahydrotriboron(1+) Cation

Mitsuaki Kameda and Goji Kodama*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received May 1, 1997[⊗]

Details of the reaction of $B_2H_4[P(CH_3)_3]_2$ with the $C(C_6H_5)_3^+$ cation for the synthesis of the $B_3H_4[P(CH_3)_3]_3^+$ cation are described. The reaction was thought to proceed through the formation of the "$B_2H_3P[(CH_3)_3]_2^{+}$" cation followed by the cluster expansion reaction with $B_2H_4[P(CH_3)_3]_2$. The triborane complex cation was fluxional with respect to the migration of the four borane hydrogen atoms. The ^{11}B, ^{31}P, and ^1H NMR chemical shifts were determined at low and high temperatures. The ^{11}B, ^{31}P, and ^{19}F NMR data for $BF_3P(CH_3)_3$, a byproduct in the above reaction, were also reported.

Introduction

The formation of the *arachno*-triborane complex cation with the formula $B_3H_6[P(CH_3)_3]_2^+$ was reported earlier from this laboratory as the first example of "polyborane complex cations".[1] The trimethylphosphine adduct of triborane(7), $B_3H_7P(CH_3)_3$, and the $B_3H_8^-$ anion are formally isoelectronic/isosteric with the triborane complex cation and are related to the cation by successive replacements of $P(CH_3)_3$ for H^-. On the other hand, if *two hydrogen atoms* in the $B_3H_6[P(CH_3)_3]_2^+$ cation are replaced by one $P(CH_3)_3$ unit, another *arachno*-class triborane complex cation, $B_3H_4[P(CH_3)_3]_3^+$, will result. The formal isoelectronic/isosteric species for this cation are $B_3H_5[P(CH_3)_3]_2$, $B_3H_6P(CH_3)_3^-$, and $B_3H_7^{2-}$. None of these four triborane species were known to exist although several transition-metal derivatives of the $B_3H_7^{2-}$ ion, such as $[Pt(\eta^3\text{-}B_3H_7)(PR_3)_2]$,[2a] $[Ir(\eta^3\text{-}B_3H_7)(CO)(PPh_3)_2]$,[2b] and $[Fe_2(B_3H_7)(CO)_6]$,[2c] had been isolated. Therefore, as a part of the polyborane complex cation studies, the $B_3H_4[P(CH_3)_3]_3^+$ cation was synthesized. Details of the formation and characterization of the triborane complex cation are described in this paper.

Results

Formation of the $B_3H_4[P(CH_3)_3]_3^+$ Cation. When $B_2H_4[P(CH_3)_3]_2$ and triphenylcarbenium tetrafluoroborate, $C(C_6H_5)_3^+BF_4^-$, were mixed in dichloromethane at −80 °C, a slow reaction occurred as evidenced by the color change of the solution from dark yellow to faint yellow. Shown in Figure 1 are the proton-spin-decoupled ^{11}B NMR spectra of a reaction mixture consisting of the two reactants in a 1:1 molar ratio. At low temperatures, in addition to the signal from the BF_4^- ion at −1.1 ppm, three signals at −33.6, −37.0 (doublet), and −41.3 ppm are seen in a 2:1:1 intensity ratio. The −37 ppm signal is due to (trimethylphosphine)borane(3) $BH_3P(CH_3)_3$. See Figure **1A**. As the temperature of the mixture was increased to about −35 °C, the two signals at −33.6 and −41.3 ppm coalesced into a single signal at −36.2 ppm as shown in Figure 1B. This process of coalescence was reversible with respect to the temperature change.

The above described observation was reproduced also for a reaction mixture with a 2:1 ratio of reactants $[B_2H_4[P(CH_3)_3]_2/C(C_6H_5)_3^+]$. When a larger excess of $B_2H_4[P(CH_3)_3]_2$ was used, unchanged $B_2H_4[P(CH_3)_3]_2$ was identified in the product mixture. No noncondensable gas was produced in these reactions. From each of these reaction mixtures a toluene-insoluble, white solid was able to be separated. The ^{11}B NMR spectrum of the solid in CD_2Cl_2 showed the signal of the BF_4^- ion and the characteristic signal at −36.2 ppm that split into two signals at the low temperatures. See Figure 2, A1 and A2.

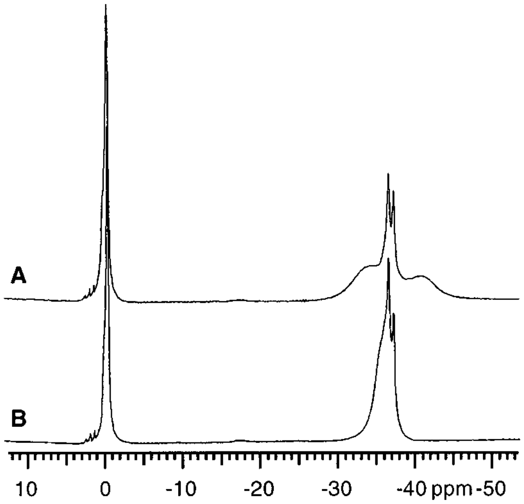

Figure 1. $^{11}B\{^1H\}$ NMR spectra for the mixture of $B_2H_4[P(CH_3)_3]_2$ and $C(C_6H_5)_3^+BF_4^-$ in a 1:1 molar ratio: solvent, CH_2Cl_2; (A) −50 °C, (B) 0 °C.

The observation described above suggested that the reaction of $B_2H_4[P(CH_3)_3]_2$ with the $C(C_6H_5)_3^+$ cation could be expressed by the following equation:

$$2B_2H_4[P(CH_3)_3]_2 + C(C_6H_5)_3^+ \rightarrow B_3H_4[P(CH_3)_3]_3^+ + HC(C_6H_5)_3 + BH_3P(CH_3)_3 \quad (1)$$

The ^{31}P and ^1H NMR spectral data, which are summarized in Table 1, are consistent with the formula assigned to the cation.

When a large excess of $C(C_6H_5)_3^+BF_4^-$ was used for the reaction with $B_2H_4[P(CH_3)_3]_2$, $BH_3P(CH_3)_3$ was not found in the product although the triborane cation was produced. See the Discussion section.

Discussion

The *arachno*-triborane cation $B_3H_4[P(CH_3)_3]_3^+$ that was identified in this study is isoelectronic/isosteric with the yet

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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S0020-1669(97)00519-3 CCC: $14.00

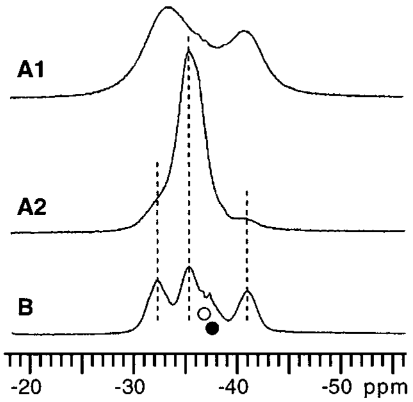

Figure 2. (A) $^{11}B\{^1H\}$ NMR spectra of the $B_3H_4[P(CH_3)_3]_3^+$ cation in CD_2Cl_2: A1, −40 °C; A2, 0 °C. (B) $^{11}B\{^1H\}$ NMR spectra of the $B_3H_4[P(CH_3)_3]_4^+$ cation in CD_2Cl_2 at +20 °C, showing the presence of this cation in the sample of the $B_3H_4[P(CH_3)_3]_3^+$ salt. The signals indicated by ○ and ● are due to $BH_3P(CH_3)_3$ and $B_2H_4[P(CH_3)_3]_2$ impurities, respectively.

unknown $B_3H_7^{2-}$ ion. As a member of polyborane complex cations, it belongs to the $B_nH_{n+1}L_3^+$ series. Presently, the $B_2H_3L_3^+$ cations[3] are the only known members of this series besides the triboron cation that is described here.

The formation of the $B_3H_4[P(CH_3)_3]_3^+$ cation from the reaction of $B_2H_4[P(CH_3)_3]_2$ with the $C(C_6H_5)_3^+$ cation is thought to proceed through the formation of the "$B_2H_3[P(CH_3)_3]_2^{+}$" cation (hydride abstraction; eq 2) followed by the reaction of the "$B_2H_3[P(CH_3)_3]_2^{+}$" cation with $B_2H_4[P(CH_3)_3]_2$ (cluster expansion;[4] eq 3). In order for the cluster expansion reaction to successfully proceed, the reacting species ("expandee") has to be *properly* electrophilic.[5] Having a vacant orbital, the positively charged "$B_2H_3[P(CH_3)_3]_2^{+}$" ion readily undergoes the expansion reaction with $B_2H_4[P(CH_3)_3]_2$, whereas, although positively charged and quite reactive to Lewis bases, the $B_3H_4[P(CH_3)_3]_3^+$ cation does not undergo the reaction with $B_2H_4[P(CH_3)_3]_2$. When a large excess of the $C(C_6H_5)_3^+$ cation was used, the $BH_3P(CH_3)_3$ that was produced by the expansion reaction further reacted with the $C(C_6H_5)_3^+$ cation to form at low temperatures another cationic species, which was tentatively identified as the $B_2H_5[P(CH_3)_3]_2^+$ cation. This intriguing reaction will be described elsewhere.

$$B_2H_4[P(CH_3)_3]_2 + C(C_6H_5)_3^+ \rightarrow \text{"}B_2H_3[P(CH_3)_3]_2^{+}\text{"} + HC(C_6H_5)_3 \quad (2)$$

$$B_2H_4[P(CH_3)_3]_2 + \text{"}B_2H_3[P(CH_3)_3]_2^{+}\text{"} \rightarrow B_3H_4[P(CH_3)_3]_3^+ + BH_3P(CH_3)_3 \quad (3)$$

The compound $B_3H_4[P(CH_3)_3]_3^+BF_4^-$ was reasonably stable; when the 1:1 reaction mixture was kept at 0 °C for a few hours, spectrum B in Figure 1 remained unchanged. However, after the washing of the product mixtures with dried toluene to remove $BH_3P(CH_3)_3$ and $B_2H_4[P(CH_3)_3]_2$, the resulting $B_3H_4[P(CH_3)_3]_3^+$ salt was often found to be contaminated with the *hypo*-$B_3H_4[P(CH_3)_3]_4^+$ cation.[6] See spectra A2 and B in Figure 2. The amount of this impurity was always small and varied from one run to another. The formation of this cation was attributed to the opening of the B−H−B bond in the $B_3H_4[P(CH_3)_3]_3^+$ cation by the reaction with $P(CH_3)_3$ which was liberated as a result of hydrolysis of the moisture-sensitive $B_3H_4[P(CH_3)_3]_3^+$ cation. See Scheme 1. A small and varied amount of moisture was thought to be introduced, inadvertently, into the sample tube during the processes of the taper-joint insertion and/or the tube transfer. See the Experimental Section.

An alternative, logical method for the preparation of the $B_3H_4[P(CH_3)_3]_3^+$ cation would be the abstraction of hydride (H^-) from the neutral $P(CH_3)_3$ adduct of triborane(5), $B_3H_5[P(CH_3)_3]_3$. However, preparing a pure sample of the triborane adduct has been difficult. The diborane(4) adduct, $B_2H_4[P(CH_3)_3]_2$, is the contaminant in a fair amount in the sample. Therefore, although such a $B_3H_5[P(CH_3)_3]_3$ sample reacted with the $C(C_6H_5)_3^+$ cation, a conclusion could not be drawn with regard to the reaction of $B_3H_5[P(CH_3)_3]_3$. See the Experimental Section. This situation now appears to be converse; a pure sample of $B_3H_5[P(CH_3)_3]_3$ may be prepared from a pure sample of the $B_3H_4[P(CH_3)_3]_3^+$ salt by the addition of H^-.

Earlier, the *arachno*-$B_4H_7[P(CH_3)_3]_2^+$ cation was thought to be cleaved by $P(CH_3)_3$ to produce the $B_3H_4[P(CH_3)_3]_3^+$ cation and $BH_3P(CH_3)_3$ when treated in a 1:2 molar ratio.[7] However, the notion was proved to be in error; when treated with $P(CH_3)_3$, the *arachno*-tetraboron cation formed the *hypho*-$B_4H_7[P(CH_3)_3]_3^+$ cation, which was then cleaved into the $B_3H_4[P(CH_3)_3]_4^+$ cation and $BH_3P(CH_3)_3$.[6] The *hypho*-$B_4H_7[P(CH_3)_3]_3^+$ cation was fluxional and gave low- and high-temperature ^{11}B NMR signals that were quite similar to those from the $B_3H_4[P(CH_3)_3]_3^+$ cation.

Experimental Section

Equipment and Materials. Volatile chemicals were manipulated in a conventional high-vacuum line, and air- and moisture-sensitive solids were handled in an atmosphere of dry nitrogen gas. Bis(trimethylphosphine)diborane(4), $B_2H_4[P(CH_3)_3]_2$, was our laboratory stock which had been prepared by the reaction of B_5H_9 with $P(CH_3)_3$.[8] Sources of $C(C_6H_5)_3^+BF_4^-$ and the solvents were described elsewhere.[9]

NMR spectra were recorded on a Varian XL-300 NMR spectrometer unless stated otherwise. Chemical shift scales are based on $BF_3O(C_2H_5)_2$, 85% *o*-phosphoric acid, $Si(CH_3)_4$, and $CFCl_3$ as the standards for ^{11}B, ^{31}P, ^1H, and ^{19}F, respectively.

Reactions of $B_2H_4[P(CH_3)_3]_2$ with $C(C_6H_5)_3^+BF_4^-$. The procedures for monitoring reactions were similar to those described earlier for the reactions in which $C(C_6H_5)_3^+$ salts were employed.[9c] Always, a 2 mL solution of $B_2H_4[P(CH_3)_3]_2$ in CH_2Cl_2 was prepared first in a 10 mm o.d. Pyrex reaction tube, and then the $C(C_6H_5)_3^+$ salt was added into the tube.

$B_2H_4[P(CH_3)_3]_2$ and $C(C_6H_5)_3^+BF_4^-$ in a 1:1 Molar Ratio. A 0.50 mmol sample of $B_2H_4[P(CH_3)_3]_2$ and a 0.50 mmol sample of $C(C_6H_5)_3^+BF_4^-$ were employed. After the recording of NMR spectra was completed, the tube was opened and a ₸24/40 inner joint with an extension tube was sealed at the top of the tube while the reaction solution was cooled with liquid nitrogen and protected by an atmosphere of dry nitrogen gas. The solvent CH_2Cl_2 was pumped out from the tube at −45 °C, and then $BH_3P(CH_3)_3$ was sublimed out at −10 °C. Then, the tube was attached to a vacuum-line filtration unit through the ₸24/40 joint, and the residue in the tube was washed with cold toluene. The toluene-insoluble solid that remained on the filter frit was washed with CH_2Cl_2 into a 10 mm o.d. NMR sample tube, which was then sealed off for the NMR spectral investigation.

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(5) The number of observed cluster expansion reactions involving $B_2H_4[P(CH_3)_3]_2$ is still limited,[4] and presently it is difficult to unequivocally predict whether an electrophile undergoes the expansion reaction with the B_2H_4 adduct. Detailed energetic and mechanistic studies are needed for better understanding and utilization of this unique cluster expansion reaction.

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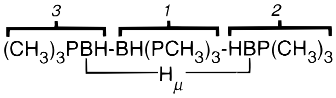
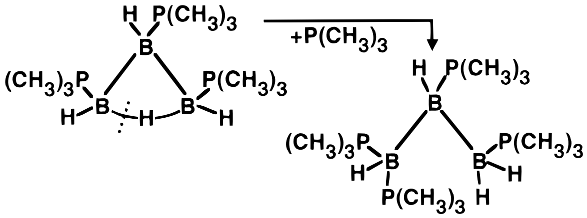
Table 1. NMR Chemical Shift Data for the $B_3H_4[P(CH_3)_3]_3^+$ Cation



$$\underbrace{\overbrace{(CH_3)_3PBH}^{3}\text{-}\overbrace{BH(PCH_3)_3}^{1}\text{-}\overbrace{HBP(CH_3)_3}^{2}}_{H_\mu}$$

	temp, °C	shifts, ppm					
^{11}B (96.2 MHz)	−60	−33.6 ($B_{2,3}$)		−41.3 (B_1)			
	20		−36.2 ($B_{1,2,3}$)				
^{31}P (121.4 MHz)	−55	1.1 (P_1)		−3.8 ($P_{2,3}$)			
	10		−2.4 ($P_{1,2,3}$)				
^{1}H (299.9 MHz)	−100	+0.17 ($H_{B2,3}$)	−0.64 (H_{B1})	−2.19 ($H_{B\mu}$)	1.42 ($H_{C2,3}$) $J_{PH} = 12$ Hz		1.30 (H_{C1}) $J_{PH} = 11$ Hz
	−55		−0.51 (H_B)			1.39 (H_C) $J_{PH} \approx 8$ Hz	

Scheme 1



Note. In the reaction described above, small amounts of BF_3 and $BF_3P(CH_3)_3$ were found after the reaction mixture was allowed to warm to 20 °C. The amount of BF_3 isolated from the mixture was 0.06 mmol. A slight downfield shift of the BF_4^- signal in the room temperature spectrum was due to the presence of BF_3 in the sample; the shift was restored to the normal value of −1.1 ppm when the BF_3 was removed. The signal from $BF_3P(CH_3)_3$ was seen at the lowfield side of the BF_4^- signal. See Figure 1. The NMR shift values for $BF_3P(CH_3)_3$ were determined to be as follows. Shifts in ppm, CH_2Cl_2 solvent: ^{11}B (−45 °C), +0.7 ppm ($J_{FB} = 52$ Hz, $J_{PB} = 180$ Hz); ^{31}P (−55 °C), −28.1 ppm ($J_{BP} = 181$ Hz, $J_{FP} = 229$ Hz); ^{19}F (+20 °C), −137 ppm ($J_{PF} = 230$ Hz, $J_{BF} = 51$ Hz) [lit:[10] ^{11}B, 0 ppm; ^{19}F, −139 ppm].

Reactions with Varied Reactant Ratios. Other reactions with varied reactant ratios were carried out in a manner similar to that described above for the 1:1 mixture. The amounts of reactants employed were as follows. $B_2H_4[P(CH_3)_3]_2/C(C_6H_5)_3^+BF_4^-$ in mmol: 0.26:0.35, 1.11:0.53, 0.76:0.15, 0.16:0.62. The observed results were summarized in the Results section. The last reaction mixture, in which the $C(C_6H_5)_3^+$ cation was used in a large excess, gave the two ^{11}B signals of the $B_3H_4[P(CH_3)_3]_3^+$ cation at −33.6 and −41.3 ppm and a signal at −25.5 ppm (br, wk). This spectral feature remained unchanged from −80 to −40 °C. The signal of $BH_3P(CH_3)_3$ was absent throughout. At 0 °C the −25.5 ppm signal was gone, and the spectrum consisted of the coalesced signal of the triborane cation at −36.1 ppm, a signal at −21.3 ppm (br, wk), and a weak doublet signal at −44.1 ppm ($J_{PB} = 96.5$ Hz).

When the hexafluorophosphate salt of the $C(C_6H_5)_3^+$ cation was used instead of the BF_4^- salt, the result was essentially the same except that the thermal stability of the $B_3H_4[P(CH_3)_3]_3^+PF_6^-$ salt at room temperature appeared to be lower than that of the BF_4^- salt.

Reaction of $B_3H_5[P(CH_3)_3]_3$ with $C(C_6H_5)_3^+BF_4^-$. A 0.54 mmol sample of pentaborane(11) was treated with a large excess of $P(CH_3)_3$ in a 12 mm o.d. tube to first prepare a mixture of $BH_3P(CH_3)_3$, $B_2H_4[P(CH_3)_3]_2$, and $B_3H_5[P(CH_3)_3]_3$. The estimated amount of $B_3H_5[P(CH_3)_3]_3$ in the product mixture was 0.4 mmol.[11] The mixture was pumped under a dynamic high vacuum at 0 °C for 37 h in order to sublime out the BH_3 and B_2H_4 adducts, leaving the $B_3H_5[P(CH_3)_3]_3$ behind. The final residue was found to still contain a small but fair amount of $B_2H_4[P(CH_3)_3]_2$ in addition to a very small amount of $B_6H_{10}[P(CH_3)_3]_2$.[8] This sample of $B_3H_5[P(CH_3)_3]_3$ was dissolved in 2 mL of CH_2Cl_2, and a 0.59 mmol sample of $C(C_6H_5)_3^+BF_4^-$ was mixed into the solution at −95 °C. As the temperature was increased to −60 °C, the signal of $BH_3P(CH_3)_3$ became discernible at the middle of two overlapped broad signals. A further increase of temperature resulted in the narrowing of the broad signals, and at 20 °C a shoulder peak was detected on each side of the $BH_3P(CH_3)_3$ signal, one at −35.0 and another at −40.2 ppm. There appeared to be another signal at around −36.3 ppm overlapped with the $BH_3P(CH_3)_3$ signal. It is noted that the above shift values of −35.0 and −40.2 ppm compared with the values of −34.5 and −40.5 ppm reported for $B_3H_5[P(CH_3)_3]_3$,[11] and the overlapped signal at −36.3 was probably due to the $B_3H_4[P(CH_3)_3]_3^+$ cation.

Acknowledgment. This work was financially supported, in part, by the U.S. Army Research Office through Grant 29-85-K-0034. The authors are grateful for the support.

IC9705195

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