

REACTION OF BIS(TRIMETHYLPHOSPHINE)HEPTAHYDROTETRABORON(1+) CATION WITH TRIMETHYLPHOSPHINEMitsuaki KAMEDA and Goji KODAMA^{1,*}*Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.;**e-mail: ¹ kodama@atlas.chem.utah.edu*Received April 3, 1997
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Dedicated to Professor Jaromir Plesek on the occasion of his 70th birthday in recognition of his outstanding contributions to organic, borane and carborane chemistry.

The reaction of the *arachno*-bis(trimethylphosphine)heptahydrotetraboron(1+) cation, $B_4H_7 \cdot 2 P(CH_3)_3^+$ (**1**), with trimethylphosphine paralleled with that of the isoelectronic *arachno*-trimethylphosphine-tetraborane(8), $B_4H_8 \cdot P(CH_3)_3$ (**2**). Thus, it first gave the *hypho*-tris(trimethylphosphine)heptahydrotetraboron(1+) cation, $B_4H_7 \cdot 3 P(CH_3)_3^+$ (**3**), which further reacted with $P(CH_3)_3$ to finally give cleaved products, the *hypho*-tetrakis(trimethylphosphine)tetrahydrotriboron(1+) cation, $B_3H_4 \cdot 4 P(CH_3)_3^+$ (**4**), and trimethylphosphine-borane(3), $BH_3 \cdot P(CH_3)_3$. The effect of the ionic charges upon the reaction rates was apparent. Thus, the second reaction for **1** was rapid at room temperature while the corresponding reaction for **2** was slow and the negatively charged isoelectronic species, the $B_4H_9 \cdot P(CH_3)_3^-$ anion, did not undergo the second reaction. The above two *hypho* polyboron complex cations, **3** and **4**, were characterized by ¹¹B and ³¹P NMR spectroscopy. Like its isoelectronic counterparts, the cation **3** was highly fluxional; at room temperature the three B–P(CH₃)₃ groups were equivalent on the NMR time scale.

Key words: Tetraborane cation; Triborane cation; Polyborane complex cation.

The bis(trimethylphosphine)heptahydrotetraboron(1+) cation, $B_4H_7 \cdot 2 P(CH_3)_3^+$, was reported in 1985 as a new member of polyborane complex cation¹. The cation belongs to the *arachno* class of borane compounds, having 14 (= 2 × 4 + 6) skeletal electrons, and is isoelectronic with trimethylphosphine-tetraborane(8), $B_4H_8 \cdot P(CH_3)_3$ (ref.²) and nonahydrotetraborate(1–) anion, $B_4H_9^-$ (ref.³). The NMR studies of these three species indicated that the structures are similar to each other, as illustrated in Fig. 1.

The treatment of $B_4H_8 \cdot P(CH_3)_3$ and the $B_4H_9^-$ ion with trimethylphosphine, $P(CH_3)_3$, results in the formation of 1 : 1 adducts, $B_4H_8 \cdot 2 P(CH_3)_3$ (ref.⁴) and the $B_4H_9 \cdot P(CH_3)_3^-$

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ion⁵, respectively. The bis(trimethylphosphine) adduct further reacts with $\text{P}(\text{CH}_3)_3$ to produce $\text{P}(\text{CH}_3)_3$ adducts of BH_3 , B_2H_4 and B_3H_5 fragments⁶, whereas the $\text{B}_4\text{H}_9 \cdot \text{P}(\text{CH}_3)_3^-$ anion does not undergo the further reaction with $\text{P}(\text{CH}_3)_3$. The reaction study of the $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+$ cation, therefore, was undertaken to compare the results with those found for the two isoelectronic counterparts. The results are described in this report.

EXPERIMENTAL

Equipment and Materials

A standard high-vacuum line equipped with Teflon valves was used throughout for the handling of the volatile compounds. Tetraborane(10) B_4H_{10} , pentaborane(11) B_5H_{11} , and $\text{P}(\text{CH}_3)_3$ were our laboratory stock, and were purified by fractional condensation or distillation before use. Dried and distilled reagent grade dichloromethane and tetrahydrofuran had been stored over molecular sieves in glass flasks which were equipped with Teflon valves and o-ring joints, and were distilled directly into reaction vessels on the vacuum line as needed. NMR spectra were recorded on a Varian XL-300 NMR spectrometer, unless stated otherwise. The ¹¹B and ³¹P chemical shift values are expressed relative to the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and 85% orthophosphoric acid signals, respectively.

$\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+ \text{BF}_4^-$: The sample of $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+ \text{BF}_4^-$ salt was prepared for each experiment from B_5H_{11} by the following procedure: B_5H_{11} was first converted into a 1 : 1 mixture of $\text{B}_4\text{H}_8 \cdot 2 \text{P}(\text{CH}_3)_3$ and $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ by the treatment with excess $\text{P}(\text{CH}_3)_3$ (ref.²), $\text{B}_4\text{H}_8 \cdot 2 \text{P}(\text{CH}_3)_3$ was isolated by subliming out $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ from the mixture, and the B_4H_8 adduct was treated with $\text{C}(\text{C}_6\text{H}_5)_3\text{BF}_4^-$ to produce the $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+ \text{BF}_4^-$ salt¹. Then, the product mixture was washed with toluene to isolate pure $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+$ salt. The salt thus obtained was washed with CH_2Cl_2 , as quantitatively as possible, into an appropriate reaction tube. The above entire process was performed on the high-vacuum line. The amount of $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+ \text{BF}_4^-$ that was finally delivered into the reaction tube, therefore, was necessarily smaller than the initially measured amount of B_5H_{11} . Nevertheless, the amount of B_5H_{11} was used as the measure of the amount of the cation in the reaction tube. This procedure was chosen in order to avoid thermal or hydrolytic decomposition of the $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+$ salt, which would have occurred if the samples were weighed in a conventional manner.

$\text{B}_3\text{H}_5 \cdot 3 \text{P}(\text{CH}_3)_3$: This compound was prepared by the reaction of B_5H_{11} with a large excess of $\text{P}(\text{CH}_3)_3$ (ref.⁶). The resulting mixture of $\text{B}_3\text{H}_5 \cdot 3 \text{P}(\text{CH}_3)_3$, $\text{B}_2\text{H}_4 \cdot 2 \text{P}(\text{CH}_3)_3$ and $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ was pumped under a dynamic high vacuum at 0 °C in order to sublime out $\text{B}_2\text{H}_4 \cdot 2 \text{P}(\text{CH}_3)_3$ and $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$. The sample employed for this study was still contaminated with a fair amount of $\text{B}_2\text{H}_4 \cdot 2 \text{P}(\text{CH}_3)_3$.

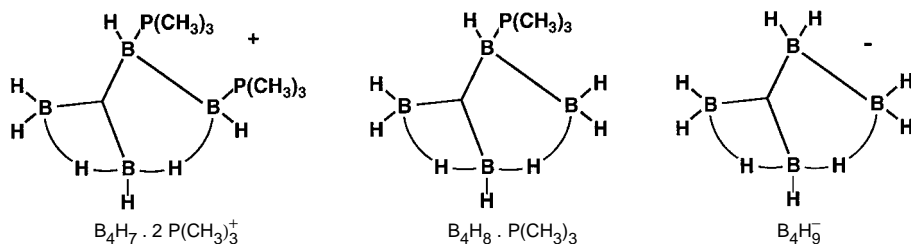


FIG. 1

The three isoelectronic tetraborane species

Procedure

Generally, the reaction mixture was prepared in a 10 mm o.d. Pyrex tube, and the tube was inserted into the 16 mm diameter probe of the NMR instrument to monitor the reaction progress. Details of the procedure were described elsewhere^{1,7}.

Reactions of $B_4H_7 \cdot 2 P(CH_3)_3^+$ with $P(CH_3)_3$: For the reactions in 1 : 1 and 1 : 2 molar ratios, 0.46 and 0.50 mmol samples, respectively, of B_5H_{11} were used to prepare the samples of the $B_4H_7 \cdot 2 P(CH_3)_3^+ BF_4^-$, and they were treated with 0.45 and 1.00 mmol samples, respectively, of $P(CH_3)_3$ in CH_2Cl_2 . For the reaction in which an excess of $P(CH_3)_3$ was employed, a sample of $B_4H_7 \cdot 2 P(CH_3)_3^+$ salt was prepared from a 0.45 mmol sample of B_5H_{11} . The salt sample was first treated with 0.87 mmol of $P(CH_3)_3$ in CH_2Cl_2 , and the volatile components (CH_2Cl_2 and $BH_3 \cdot P(CH_3)_3$) were removed from the reaction vessel at $-10^\circ C$. Then, the residue was redissolved in CH_2Cl_2 , and was further treated with a 0.70 mmol of $P(CH_3)_3$. Finally, the volatiles were pumped out of the reaction tube at $-10^\circ C$, and the residue was washed with cold toluene to remove $BH_3 \cdot P(CH_3)_3$. The white solid thus obtained was dissolved in CD_2Cl_2 for the final spectral investigation.

Reaction of $B_3H_5 \cdot 3 P(CH_3)_3$ with B_4H_{10} : A 0.53 mmol quantity of the $B_3H_5 \cdot 3 P(CH_3)_3$ sample was dissolved in CH_2Cl_2 (2 ml) in a reaction tube, and a 0.53 mmol sample of B_4H_{10} was condensed into the tube at $-19^\circ C$. The tube was gently shaken in a $-80^\circ C$ bath to prepare a uniform solution, and then it was placed in the 12 mm diameter probe of a Varian XL-100-15 NMR spectrometer. At $-80^\circ C$ the signal of the $B_3H_8^-$ ion was detected at -30.2 ppm. At $-40^\circ C$, the reaction was fast, and as the probe temperature was increased to $0^\circ C$ the B_4H_{10} signals disappeared completely. The ^{11}B spectrum of the resulting solution at $0^\circ C$ contained, in addition to the $B_3H_8^-$ signal, two overlapped, strong signals; one at -37.0 ppm and another less strong signal at -39.4 ppm. A broad hump in the range from 0 to -15 ppm was noticeable. Thus, the sample was judged to be a mixture of the $B_3H_8^-$ salts of $B_4H_7 \cdot 3 P(CH_3)_3^+$ and $B_3H_6 \cdot 2 P(CH_3)_3^+$, the contaminant $B_2H_4 \cdot 2 P(CH_3)_3$ being responsible for the formation of the latter cation. [^{11}B shifts for $B_3H_6 \cdot 2 P(CH_3)_3^+$: ref.⁸ -10.5 (br) and -39.0 ppm.]

RESULTS

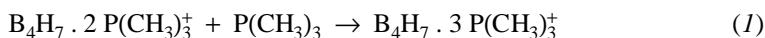
Reaction of $B_4H_7 \cdot 2 P(CH_3)_3^+$ with $P(CH_3)_3$

The tetrafluoroborate salt of the $B_4H_7 \cdot 2 P(CH_3)_3^+$ cation reacted with $P(CH_3)_3$ in dichloromethane at $-95^\circ C$. The reaction was instantaneous upon mixing the two reagents. A series of variable temperature ^{11}B NMR spectra of a reaction mixture are shown in Fig. 2a. This particular reaction mixture contained the $B_4H_7 \cdot 2 P(CH_3)_3^+$ cation and $P(CH_3)_3$ in a 1 : 2 molar ratio. As the probe temperature was increased to $-40^\circ C$, a broad signal centered around -7 ppm became noticeable, and at about $-30^\circ C$ the two signals at -36 and -41 ppm merged together at -37.5 ppm. This coalescence process was reversible with respect to the temperature change. When the temperature was further increased to near $0^\circ C$, the signal of $BH_3 \cdot P(CH_3)_3$ began to show in the spectrum. At $20^\circ C$, the progress of this second reaction was fast; the $BH_3 \cdot P(CH_3)_3$ signal and three signals at -32.3 , -35.3 and -40.9 ppm rapidly developed while the signals from the first reaction product at -6.6 and -37.5 ppm became weak. When the reaction

ceased to proceed at room temperature, the signals from the first product were still present in the spectrum.

Likewise, when the two reactants were mixed in a 1 : 1 molar ratio, the reaction was complete upon mixing at $-95\text{ }^{\circ}\text{C}$. However, when the temperature was increased, the products of second reaction were formed only in very small amounts. On the other hand, when an excess of $\text{P}(\text{CH}_3)_3$ was used, the signals from the first reaction product disappeared completely as the reaction mixture was allowed to warm to $20\text{ }^{\circ}\text{C}$. The BF_4^- signal was present throughout. A white, non-volatile solid was obtained from this reaction mixture. The ^{11}B NMR spectrum of the solid in CD_2Cl_2 is shown in Fig. 2b.

The observation described above indicated that the $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+$ cation underwent two sequential reactions with $\text{P}(\text{CH}_3)_3$, and suggested that the following two equations [Eqs (1) and (2)] were appropriate for the reactions.



The ^{11}B and ^{31}P NMR spectra of the product cations, which are described below in this section, are consistent with the formulas given in the above equations.

The formulation of the first product as $\text{B}_4\text{H}_7 \cdot 3\text{P}(\text{CH}_3)_3^+$ received further support from the reaction study of tris(trimethylphosphine)-triborane(5) [$\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$]. When $\text{B}_3\text{H}_5 \cdot 3\text{P}(\text{CH}_3)_3$ was treated with B_4H_{10} in dichloromethane, a rapid reaction occurred above $-40\text{ }^{\circ}\text{C}$. The ^{11}B NMR spectrum of the resulting solution contained the signals that were assigned to the $\text{B}_4\text{H}_7 \cdot 3\text{P}(\text{CH}_3)_3^+$ cation, as well as the signal from the

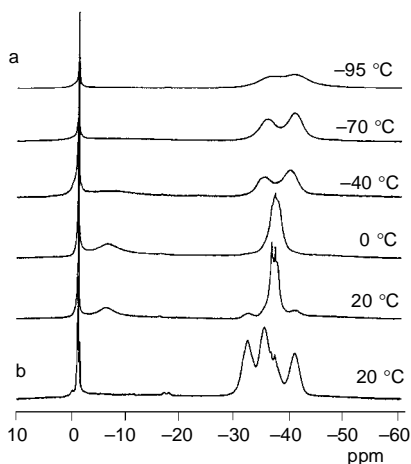
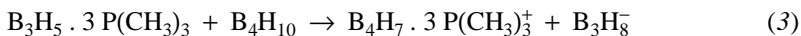
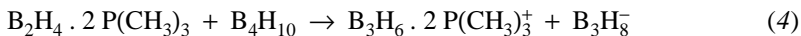


FIG. 2
 a $^{11}\text{B}\{^1\text{H}\}$ (96.2 MHz) NMR spectra of the $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3 + \text{P}(\text{CH}_3)_3$ reaction mixture in CH_2Cl_2 , showing the reaction progress with the temperature increase. b $^{11}\text{B}\{^1\text{H}\}$ (96.2 MHz) NMR spectrum of the final product residue $\text{B}_3\text{H}_4 \cdot 4\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$. Footnote: a) The spectra in a are aligned to the signal of the BF_4^- ion. The BF_4^- signal was at -1.2 ppm above $0\text{ }^{\circ}\text{C}$. b) The extraordinarily low intensity of the BF_4^- signals in the above spectra is due to the use of short acquisition time and zero pulse delay time

$B_3H_8^-$ ion. Thus, the following equation [Eq. (3)] is appropriate for the $B_3H_5 \cdot 3 P(CH_3)_3$ reaction.



This reaction is reminiscent of the well-established reaction of bis(trimethylphosphine)-diborane(4) [$B_2H_4 \cdot 2 P(CH_3)_3$] with B_4H_{10} (ref.⁸), in which the BH_2^+ unit from B_4H_{10} combined with $B_2H_4 \cdot 2 P(CH_3)_3$ to form the $B_3H_6 \cdot 2 P(CH_3)_3^+$ cation [see Eq. (4)].



The formulation for the cationic product in Eq. (2) as $B_3H_4 \cdot 4 P(CH_3)_3^+$ also receives support from a separate experiment⁹ in which another triborane complex cation, $B_3H_4 \cdot 3 P(CH_3)_3^+$, was found to combine with $P(CH_3)_3$ to produce the $B_3H_4 \cdot 4 P(CH_3)_3^+$ cation. The ^{11}B NMR spectra of the two ionic products were identical with each other.

NMR Studies of the New Tetra- and Triborane Cations

$B_4H_7 \cdot 3 P(CH_3)_3^+$ cation. The NMR spectral data for the $B_4H_7 \cdot 3 P(CH_3)_3^+$ cation are summarized in Table I. In Fig. 3, two possible valence bond structures are shown for the low temperature configuration of the cation. As indicated in structure II of the figure, one of the bridge hydrogen bonds is assumed to be changing its position between B1–B4 and B1–B2 rapidly even at the low temperatures to render the B2 and B4 atoms equivalent. The shift value of -6.6 ppm for the B1 signal and its extreme broadness, particularly at low temperatures, are reminiscent of the BH_2 signal observed for the $B_3H_6 \cdot 2 P(CH_3)_3^+$ cation⁸. Knowing that the BH_2 group is bonded to $B_2H_4 \cdot 2 P(CH_3)_3$ through two B–H–B bridge bonds in the triborane cation^{8,10}, structure I and II are thought to be favorable over other possible structures for the tetraborane cation.

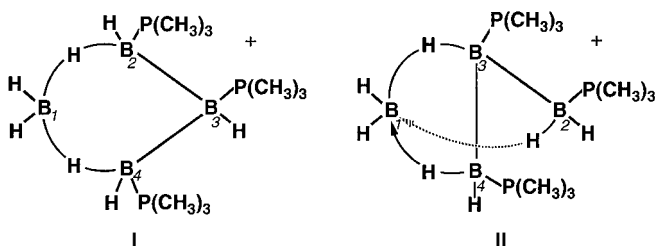


FIG. 3

Possible valence bond structures for the $B_4H_7 \cdot 3 P(CH_3)_3^+$ cation

The highly fluxional behavior of the cation at higher temperatures suggests that, in effect, the B1 atom is tumbling around above (or even on both sides of) a non-rigid trigonal plane formed by the three B–P(CH₃)₃ units while rapidly exchanging the hydrogen atoms, as illustrated in Fig. 4. This fluxional behavior of the cation is compared with those of the isoelectronic counterparts in the Discussion.

B₃H₄ · 4 P(CH₃)₃⁺ cation. The ¹¹B and ³¹P NMR spectral data for the B₃H₄ · 4 P(CH₃)₃⁺ cation are summarized in Table II, and the spectra are shown in Fig. 5. The ¹¹B shift values for B₃H₅ · 3 P(CH₃)₃ (ref.⁶) are also included in the table for comparison. The B2 signal of B₃H₅ · 3 P(CH₃)₃ at –40.5 ppm remains essentially unchanged in the cation, and the B1,3 signal at –34.5 ppm is split into two signals at –32.3 and –35.3 ppm, which are assigned to B1 and B3, respectively, for the following reasons: The ¹¹B shift values for BH₃ · P(CH₃)₃ and BH₂ · 2 P(CH₃)₃⁺ are –37.1 (ref.¹¹) and –33.9 (ref.¹²), respectively. This low-field shift upon replacement of H for P(CH₃)₃ compares favorably with the assignment of the B1 signal, and the value of –35.3 ppm assigned to B3 is well within the range of –35.3 ± 0.6 ppm, which was found for the –BH₂P(CH₃)₃ group among the diborane complex cations¹³.

TABLE I
¹¹B and ³¹P NMR chemical shift data for the B₄H₇ · 3 P(CH₃)₃⁺ cation

Nuclide	T, °C	δ, ppm (intensity)
¹¹ B	–50	–6.8 ^a (1) [BH ₂]; –35.5 ^a (1); –40.7 ^a (2)
	0	–6.6 (1) [BH ₂]; –37.5 (3)
³¹ P	–90	1.19 (1); –1.64 (2)
	–40	–1.07

^a These values are relative to the BF₄[–] signal which was taken as –1.2 ppm, since the position of the BF₃ · O(C₂H₅)₂ signal at the lower temperatures were not recorded. Above 0 °C the BF₄[–] signal appeared at –1.2 ppm relative to the BF₃ · O(C₂H₅)₂ signal.

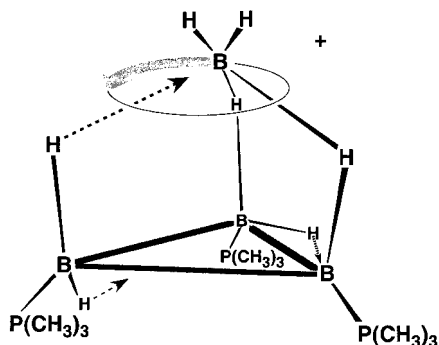


FIG. 4
Migration of the BH₂⁺ group in the B₄H₇ · 3 P(CH₃)₃⁺ cation

Although the ^{31}P signal at -3.6 ppm can readily be assigned to P1 for its relative intensity 2, the assignment for the other two signals is tentative. The ^{11}B NMR spectra in Fig. 5 show that the sample contained $\text{B}_2\text{H}_4 \cdot 2 \text{P}(\text{CH}_3)_3$ and a small quantity of remaining $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$. The origin of the diborane(4) complex will be discussed later in the Discussion.

DISCUSSION

A summary diagram is presented in Fig. 6, indicating the formation routes for the tri- and tetraborane complex cations relevant to this study*. The reactions of the three isoelectronic species, $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+$, $\text{B}_4\text{H}_8 \cdot \text{P}(\text{CH}_3)_3$ and B_4H_5^- are compared in Table III. A feature common to the three species is the facile addition of $\text{P}(\text{CH}_3)_3$ to form *hypho*

TABLE II

^{11}B and ^{31}P NMR shift data for the $\text{B}_3\text{H}_4 \cdot 4 \text{P}(\text{CH}_3)_3^+$ cation
 $\{[\text{P}(\text{CH}_3)_3]_2\text{HB}(1) \cdot \text{B}(2)\text{H}[\text{P}(\text{CH}_3)_3] \cdot \text{B}(3)\text{H}_2[\text{P}(\text{CH}_3)_3]\}^+$

Cation	Nuclide	T , °C	δ , ppm (intensity)
$\text{B}_3\text{H}_4 \cdot 4 \text{P}(\text{CH}_3)_3^+$	^{11}B	26	-32.3 (1) [B1]; -35.3 (1) [B3]; -40.9 (1) [B2]
$\text{B}_3\text{H}_5 \cdot 3 \text{P}(\text{CH}_3)_3$		20	-34.5 (2) [B1,3]; -40.5 (1) [B2]
$\text{B}_3\text{H}_4 \cdot 4 \text{P}(\text{CH}_3)_3^+$	^{31}P	10	2.8 (1) [P2]; 0.0 (1) [P3]; -3.5 (2) [P1]

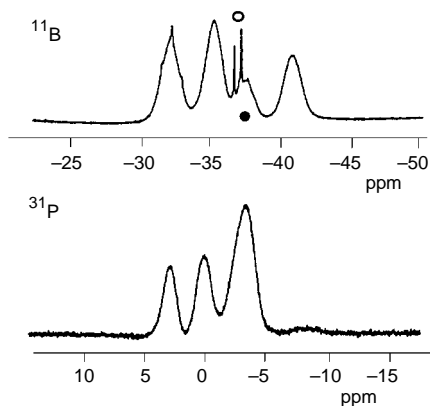


FIG. 5

The $^{11}\text{B}\{^1\text{H}\}$ (128.3 MHz) and $^{31}\text{P}\{^1\text{H}\}$ (121.4 MHz) NMR spectra of the $\text{B}_3\text{H}_4 \cdot 4\text{P}(\text{CH}_3)_3^+$ cation in CD_2Cl_2 at 20°C . The counter-ion was the BF_4^- anion, and its ^{11}B signal was at -1.2 ppm. Impurities: \circ $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$; \bullet $\text{B}_2\text{H}_4 \cdot 2\text{P}(\text{CH}_3)_3$

* In an earlier review presentation, the cleavage products of the $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+$ cation by $\text{P}(\text{CH}_3)_3$ were described to be the $\text{B}_3\text{H}_4 \cdot 3 \text{P}(\text{CH}_3)_3^+$ cation and $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ (ref.¹⁴). It is now clear that the description was in error.

tetraborane complexes. The second reaction that cleaves the tetraborane framework proceeds with different reaction rates. As expected, the charge on the species has an overwhelming effect on the reaction rates. Thus, the reaction of the $B_4H_7 \cdot 3 P(CH_3)_3^+$ cation proceeds rapidly at room temperature, whereas the corresponding reaction for the $B_4H_8 \cdot 2 P(CH_3)_3$ is very slow under comparable conditions⁶. The reaction of the $B_4H_9^-$ anion stops at the formation of $B_4H_9 \cdot P(CH_3)_3^-$ (ref.⁵).

The second reaction for $B_4H_8 \cdot P(CH_3)_3$ proceeded in two different manners as indicated in Table III (ref.⁶). If the same should have occurred for the cation, the following reaction [Eq. (5)] would have been observed in addition to the one given in the table.

TABLE III

The $P(CH_3)_3$ reactions of $B_4H_7 \cdot 2 P(CH_3)_3^+$, $B_4H_8 \cdot 2 P(CH_3)_3$ and $B_4H_9 \cdot P(CH_3)_3^-$

Reaction	Reactant, A:	$B_4H_7 \cdot 2 P(CH_3)_3^+$	$B_4H_8 \cdot P(CH_3)_3$	$B_4H_9^-$
1st	Addition of $P(CH_3)_3$ to A	Fast below $-80^\circ C$	Fast below $-80^\circ C$	Moderate at $-35^\circ C$
	Product, B:	$B_4H_7 \cdot 3 P(CH_3)_3^+$ Isolable at room temperature ^a	$B_4H_8 \cdot 2 P(CH_3)_3$ Stable at room temperature	$B_4H_9 \cdot P(CH_3)_3^-$ Stable below $0^\circ C$ in THF
2nd	Cleavage of B by $P(CH_3)_3$	Fast at room temperature	Slow at room temperature	No reaction at room temperature
	Product, C:	$B_3H_4 \cdot 4 P(CH_3)_3^+$ + $BH_3 \cdot P(CH_3)_3$	$B_3H_5 \cdot 3 P(CH_3)_3$ + $BH_3 \cdot P(CH_3)_3$ and $2 B_2H_4 \cdot 2 P(CH_3)_3$	N.A.

^a Stability depends on the nature of the counter anion.

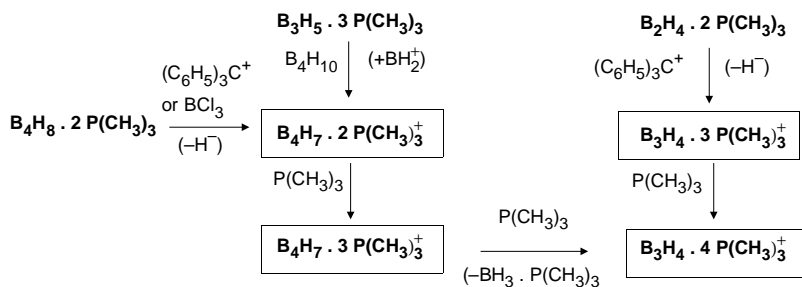
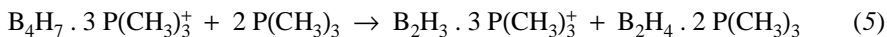


FIG. 6

Formation of the relevant tetra- and triborane complex cations



Indeed, as mentioned earlier, the signal of $\text{B}_2\text{H}_4 \cdot 2 \text{P}(\text{CH}_3)_3$ was seen in the spectrum of the $\text{B}_3\text{H}_4 \cdot 4 \text{P}(\text{CH}_3)_3^+$ sample (Fig. 5). It has not been determined yet whether the $\text{B}_2\text{H}_4 \cdot 2 \text{P}(\text{CH}_3)_3$ was produced from the tetraborane cation according to Eq. (5), or from other impurity sources. Trimethylphosphine-triborane(7) [$\text{B}_3\text{H}_7 \cdot \text{P}(\text{CH}_3)_3$] is a common contaminant in the $\text{B}_4\text{H}_7 \cdot 2 \text{P}(\text{CH}_3)_3^+$ salt due to the very high hydrolytic sensitivity of the cation¹, and it will produce $\text{B}_2\text{H}_4 \cdot 2 \text{P}(\text{CH}_3)_3$ when treated with $\text{P}(\text{CH}_3)_3$ at room temperature². The signals of the yet unknown $\text{B}_2\text{H}_3 \cdot 3 \text{P}(\text{CH}_3)_3^+$ cation, if present in the sample, would be difficult to be identified due to their overlap with the $\text{B}_3\text{H}_4 \cdot 4 \text{P}(\text{CH}_3)_3^+$ signals.

TABLE IV

Isoelectronic series for the *hypho*-triborane and *hypho*-tetraborane complexes

Isoelectronic <i>hypho</i> -B ₃ complex	Isoelectronic <i>hypho</i> -B ₄ complex
$\text{B}_3\text{H}_8^{3-}$	$\text{B}_4\text{H}_{10}^{2-}$
$\text{B}_3\text{H}_7 \cdot \text{P}(\text{CH}_3)_3^{2-}$	$\text{B}_4\text{H}_9 \cdot \text{P}(\text{CH}_3)_3^-$
$\text{B}_2\text{H}_6 \cdot 2 \text{P}(\text{CH}_3)_3^-$	$\text{B}_4\text{H}_8 \cdot 2 \text{P}(\text{CH}_3)_3$
$\text{B}_3\text{H}_5 \cdot 3 \text{P}(\text{CH}_3)_3$	$\text{B}_4\text{H}_7 \cdot 3 \text{P}(\text{CH}_3)_3^+$
$\text{B}_3\text{H}_4 \cdot 4 \text{P}(\text{CH}_3)_3^+$	$\text{B}_4\text{H}_6 \cdot 4 \text{P}(\text{CH}_3)_3^{2+}$
$\text{B}_3\text{H}_3 \cdot 5 \text{P}(\text{CH}_3)_3^{2+}$	

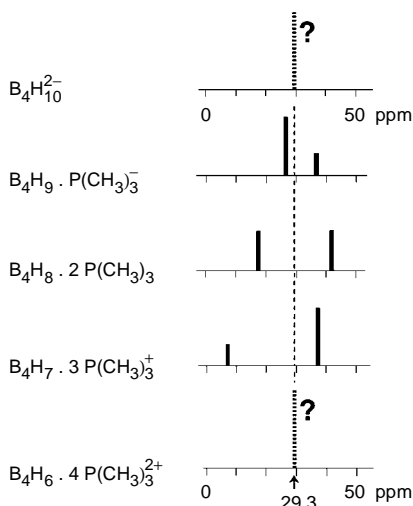


FIG. 7

¹¹B NMR chemical shift positions at high temperature for the series of tetraborane complexes

Isoelectronic series of trimethylphosphine complexes of tri- and tetraborane species are listed in Table IV. Those species that are shown in bold face have been isolated. The knowledge of the stabilities and trends for the known species would be useful for estimating the properties of the unknowns in the series. For example, the $B_4H_{10}^{2-}$ anion would have a reasonable stability to be isolated at a lower temperature. Not too long ago, the $B_5H_{11}^{2-}$ anion was isolated at room temperature¹⁵. Its stability was in line with its isoelectronic counterparts, $B_5H_{10} \cdot P(CH_3)_3$ (ref.¹⁶) and $B_5H_9 \cdot 2 P(CH_3)_3$ (ref.¹⁷).

Earlier in the Results, a remarkable fluxional behavior of the $B_4H_7 \cdot 3 P(CH_3)_3^+$ ion was mentioned. Knowing that its isoelectronic counterparts, $B_4H_8 \cdot 2 P(CH_3)_3$ (ref.²) and $B_4H_9 \cdot P(CH_3)_3^-$ (ref.⁵), are also highly fluxional, the $B_4H_{10}^{2-}$ and $B_4H_6 \cdot 4 P(CH_3)_3^{2+}$ ions too are likely to be fluxional. In Fig. 7, the ¹¹B NMR signal positions are indicated schematically for the series of tetraborane species. Interestingly, the weighted averages of the shift values are -29.8, -29.4 and -28.8 ppm for $B_4H_7 \cdot 3 P(CH_3)_3^+$, $B_4H_8 \cdot 2 P(CH_3)_3$ (ref.²) and $B_4H_9 \cdot P(CH_3)_3^-$ (ref.⁵), respectively, and are all within 0.5 ppm of the averaged value (-29.3 ppm). It is yet to be seen if the coalesced signals of the two unknown ions, $B_4H_{10}^{2-}$ and $B_4H_6 \cdot 4 P(CH_3)_3^{2+}$, appear close to the weighted values.

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