

Figure 7. Cyclic voltammogram at 20 mV s^{-1} of a C/poly-[Fe(5-NH₂-phen)₃]²⁺ ($\Gamma = 2.3 \times 10^{-9} \text{ mol cm}^{-2}$) electrode in the 1.20:1 AlCl₃/BuPyCl melt.

on two other electrodes in the 1.2:1 melt gave values of 1.6×10^{-9} and $1.0 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1/2}$. The electrode of Figure 6A in the neutral melt gave a $D_{\text{ct}}^{1/2}C_{\text{Fe}}$ value of ca. $2 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1/2}$.

These results are more than an order of magnitude smaller than the results obtained in CH₃CN. Since C_{Fe} is unlikely to have changed considerably D_{ct} must be at least 100 times less in the melts than in CH₃CN. This is contrary to the results obtained for poly-[Ru(bpy)₂(vpy)₂]²⁺ in these melts, where $D_{\text{ct}}^{1/2}C_{\text{Ru}}$ is only 2-3 times smaller in the melts than in CH₃CN.⁶⁵

We can offer two reasonable explanations for the slowness of charge transport in poly-[Fe(5-NH₂-phen)₃]²⁺ in the melts. One possibility is that this polymer is heavily cross-linked (see above), and so it cannot absorb enough melt to allow facile movements of the redox centers. Hence, charge transport is limited by a low collision rate between the redox sites. This fits in with the hypothesis that the lower charge-transport rate of poly-[Ru(bpy)₂(vpy)₂]²⁺ in the melt compared to that in CH₃CN is due to a larger degree of swelling (smaller C_{Ru}).⁶⁵ Because the molar volumes of the melts are about 4.5 times that of CH₃CN, it seems reasonable that facile charge transport would require a higher degree of swelling in the melts than in CH₃CN.

A second possible explanation for the slow charge transport in poly-[Fe(5-NH₂-phen)₃]²⁺ in the melts is that adduct formation between AlCl₃ and free nitrogen sites in the polymer reduces the electron-exchange rate between the Fe sites by either steric or electrostatic hinderance. A third explanation, that charge transport is limited by counterion movements, is ruled out by the fact that, although voltammetric peak currents are more than 3 times lower in the melts than in CH₃CN, there is no significant increase in peak separation. Slow counterion movement implies a high resistance in the polymer film and so should result in increased peak separations in cyclic voltammetry. Obviously, further work is required to resolve the correct explanation for the very interesting differences in charging rates observed in this work.

The results shown in Figure 6 show that in the melts relatively thick films of poly-[Fe(5-NH₂-phen)₃]²⁺ exhibit the behavior of a normal redox polymer with slow charge-transport kinetics. There appear to be no significant differences between the results in the neutral and acidic melts. However, the slow charge transport simplifies the voltammetric response in these cases and obscures the details of the electrochemistry. If thinner films and lower scan rates are used, then more complicated behavior is observed.

Figure 7 shows the voltammetry (after break-in) of a $2.3 \times 10^{-9} \text{ mol cm}^{-2}$ film in the 1.2:1 AlCl₃/BuPyCl melt. There are four oxidation waves and four reduction waves, all of different height, in the region of the Fe^{3+/2+} waves. The positions and relative heights of these waves depend on the scan rate and are poorly reproducible. Similar results were also obtained in AlCl₃/ImCl melts. We believe that two major factors are responsible for this behavior, but we have not been able to rationalize the results completely. The oxidation peak at +1.74 V in Figure 7 and the reduction peak at +1.67 V appear to be related to an impurity

in the melt (possibly HCl).⁶⁶ Secondly, adduct formation between AlCl₃ and some of the nitrogen atoms of the substituents of the phenanthroline rings could create a series of Fe sites with significantly different formal potentials.

We have used a spectroelectrochemical experiment similar to that described above for CH₃CN to further investigate the multiple peaks observed in Figure 7. The results were similar to those obtained in CH₃CN, but experimental difficulties prevented sufficiently accurate results from being obtained. Further useful investigation of this system does not seem feasible until methods for preparing purer melts are devised.

One of the reasons for using poly-[Fe(5-NH₂-phen)₃]²⁺ in AlCl₃/RCl melts was to determine if this polymer would be useful for oxygen reduction in these systems. Unfortunately, the formal potential of the polymer in these solvents (ca. +1.3 V) is considerably higher than that of [Fe(phen)₃]²⁺ (1.11 V), on which we based our initial expectations. We could measure no catalytic current for oxygen reduction in acidic melts at poly-[Fe(5-NH₂-phen)₃]²⁺-coated electrodes.

Conclusions

The preparation, electrochemistry, and spectroelectrochemistry of poly-[Fe(5-NH₂-phen)₃]²⁺ in CH₃CN are entirely predictable by analogy with similar polymers. However, its electrochemistry in AlCl₃/RCl molten salts is significantly different from its electrochemistry in CH₃CN and is also different from that of poly-[Ru(bpy)₂(vcpy)₂]²⁺ in these molten salts. The potential shifts, the multiple redox potentials, and the slow charge transport of poly-[Fe(5-NH₂-phen)₃]²⁺ in the molten salts have not been fully explained, but there is good evidence that adduct formation between AlCl₃ and nitrogen-containing groups in the polymer is at least partly responsible. These results are significant because they show that in situ chemical modification of redox polymers can be used to significantly change the electrochemistry and, presumably, the structure of the polymer. Further work of this type, both in molten salts and in more conventional solvents, will greatly increase our understanding of the structure of solvent-swollen redox polymers.

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Synthesis of the Heptahydrobis(trimethylphosphine)tetraboron(1+) Cation

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The triboron complex cation B₃H₆·2P(CH₃)₃⁺ represents the first example of Lewis base attached boron cluster cations, and some novel reactions involving this cation were reported recently.^{2,3} While its reaction chemistry continues to be an intriguing subject of study, the search for other members of the polyboron complex cation family is of natural interest. Several members are known to exist in each of the related, neutral (B_nH_{n+4}·L, L = Lewis base) and anionic (B_nH_{n+5}⁻) boron hydride families.⁴

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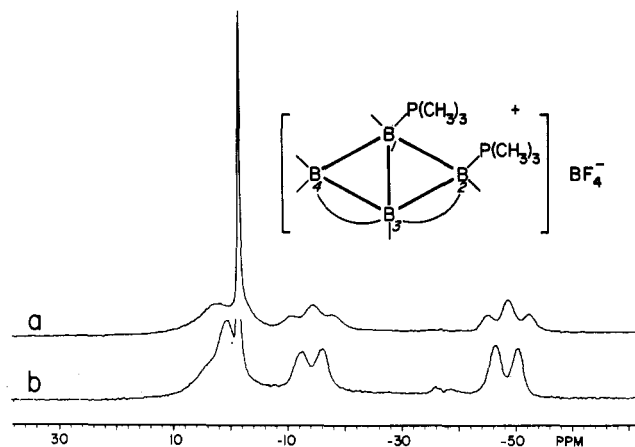


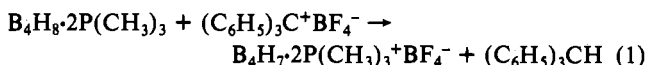
Figure 1. ^{11}B NMR (32.1 MHz) spectra of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$ in CH_2Cl_2 at ambient temperature: (a) normal spectrum; (b) proton-spin-decoupled spectrum.

The above mentioned triboron cation was prepared by the addition of the cationic species BH_2^+ to the neutral borane adduct $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$.¹ Another borane cation of different type, $\text{B}_6\text{H}_{11}^+$, was prepared also by the addition of the H^+ cation to B_6H_{10} .⁵ An alternative approach to the synthesis of a cationic borane species would be the abstraction of a hydride anion (or any anionic species) from an appropriate, neutral borane compound. This method was employed in 1970 by Benjamin and co-workers⁶ for the preparation of the $\text{H}_2\text{BLL}'^+$ cations. They treated the Lewis base adducts of borane(3) with triphenylcarbenium (trityl) cation in the presence of Lewis base L' to successfully synthesize the monoboron complex cations.

The abstraction of the hydride ion would be facilitated if the hydridic character of the hydrogen atoms in the borane compound were enhanced. Boron hydride anions represent the obvious, extreme case where H^- can be abstracted easily. With regard to the neutral borane adducts, one expects that, the stronger the donor property and the larger the number of the Lewis bases involved, the more hydridic the borane hydrogen would be. The hypoh-class tetraborane adduct $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ therefore was chosen for its conversion by means of the hydride abstraction into the tetraboron complex cation. The desired cation formation occurred, and its tetrafluoroborate salt could be isolated.

Results and Discussion

Synthesis and Characterization of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$. When bis(trimethylphosphine)-tetraborane(8) was mixed with trityl tetrafluoroborate in dichloromethane, the following reaction occurred above -80°C :



The reaction was virtually quantitative. After the evaporation of the solvent, the salt of the tetraboron cation could be separated from the solid residue by washing it with toluene. The new compound is soluble in dichloromethane but insoluble in toluene. It is very sensitive to moisture. Once the compound is exposed to the slightest amount of moisture, the $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$ cation is produced from it.

Shown in Figure 1 are the ^{11}B NMR spectra of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$ in dichloromethane at ambient temperature. Also shown in the figure is the structure of the cation, which is proposed on the basis of the observed ^{11}B and ^{31}P NMR spectra. The sharp signal at -1.1 ppm is due to the BF_4^- anion. The multiplet signals at -48.3 and -14.2 ppm unequivocally indicate the presence of

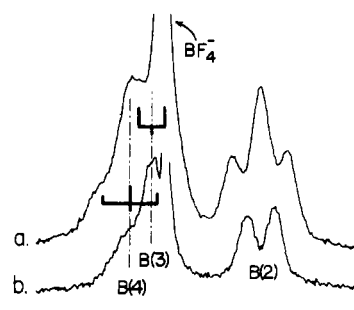
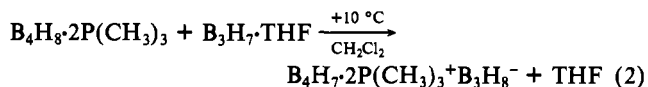


Figure 2. $+10$ to ~ -20 ppm portions of ^{11}B NMR spectra of $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+\text{BF}_4^-$, indicating the multiplet features of the B(3) and B(4) signals: (a) normal spectrum; (b) proton-spin-decoupled spectrum.

two different $\text{B}(\text{H})\text{P}(\text{CH}_3)_3$ moieties in the cation. The more shielded of the two is attributed to the apex boron atom (or the boron atom opposite to the $\text{B}-\text{H}-\text{B}$ bridge bonds).⁸ The broad hump, which centers around $+2$ ppm and partly overlaps with the BF_4^- signal, consists of two signals. In the ^1H -spin-decoupled spectrum (Figure 1b) the feature of two-signal overlap may be discerned. The relative intensity ratio of this hump (excluding the BF_4^- signal) to the other two $\text{B}(\text{H})\text{P}(\text{CH}_3)_3$ signals was measured to be 1.8:1.0:1.0. Shown in Figure 2 is the $+10$ to ~ -20 ppm portion of the spectrum of a separate sample, which was recorded for a closer look at the spectral features in this region. As indicated in the figure, the broad hump consists of a triplet and a doublet (Figure 2a), each of which reduces to a singlet upon irradiation of the sample with the ^1H resonance frequencies (Figure 2b). Thus the cation is of C_1 symmetry, and assignments are made for the four signals as follows: B(1), -48.3 ppm ($J_{\text{BP}} = 126$ Hz, $J_{\text{BH}} = 106$ Hz); B(2), -14.2 ppm ($J_{\text{BP}} = 115$ Hz, $J_{\text{BH}} = 122$ Hz); B(3), $+0.75$ ppm (d, $J_{\text{BH}} \approx 120$ Hz); B(4), $+2.7$ ppm, (t, $J_{\text{BH}} \approx 120$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 121.5 MHz clearly showed two overlapping 1:1:1:1 quartet signals at -6.1 (P(2), $J_{\text{BP}} = 110$ Hz) and -4.6 ppm (P(1), $J_{\text{BP}} = 127$ Hz). Thus, like those of the trio B_3H_8^- , $\text{B}_3\text{H}_7\cdot \text{P}(\text{CH}_3)_3$, and $\text{B}_3\text{H}_6\cdot 2\text{P}(\text{CH}_3)_3^+$, the structures of B_4H_9^- ,⁹ $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3$,² and $\text{B}_4\text{H}_7\cdot 2\text{P}(\text{CH}_3)_3^+$ are closely related. Replacement of H^- by $\text{P}(\text{CH}_3)_3$ at the 1-position of the B_4H_9^- structure, followed by the same replacement at the 2-position of the resulting $\text{B}_4\text{H}_8\cdot \text{P}(\text{CH}_3)_3$, completes the structures of the tetraboron trio.

Octahydrotriborate(1-) Salt of the Tetraboron Cation. Bis(trimethylphosphine)-tetraborane(8) reacted with tetrahydrofuran-triborane(7) to give the B_3H_8^- salt of the tetraboron complex cation.

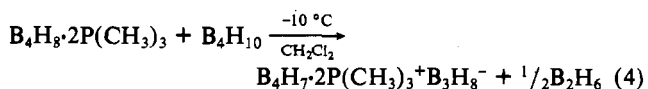


The reaction proceeded at a moderate rate. The B_3H_8^- salt, however, converted slowly at room temperature into the trimethylphosphine adducts of B_4H_8 and B_3H_7 .



This exchange of $\text{P}(\text{CH}_3)_3$ for H^- between the cation and the anion indicates that the hydride abstraction (eq 2) is the process that is kinetically favored over the alternative phosphine abstraction.

Tetraborane(10) reacted with $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ to give the B_3H_8^- salt also.



Here again, the hydride abstraction is the kinetically favored process. This and the above reaction of $\text{B}_3\text{H}_7\cdot \text{THF}$ (eq 2) contrast with the reaction of B_2H_6 with $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$.²

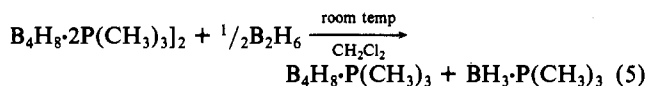
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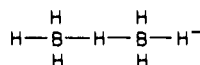
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in which no evidence for the formation of the B_2H_7^- or BH_4^- salt of the $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+$ cation could be found while the reaction was monitored with the use of a ^{11}B NMR spectrometer, starting at -80°C .

Diborane(6) or tetrahydrofuran-borane(3) is capable of abstracting hydride from borane compounds. The reactions of $\text{BH}_3 \cdot \text{N}(\text{CH}_3)_2^-$, $(\text{BH}_3)_2\text{SC}_2\text{H}_5^-$, and $\text{B}_4\text{H}_9 \cdot \text{P}(\text{CH}_3)_3^-$ with B_2H_6 give $\mu\text{-(CH}_3)_2\text{N} \cdot \text{B}_2\text{H}_5$,¹⁰ $\mu\text{-(C}_2\text{H}_5)_2\text{SB}_2\text{H}_5$,¹¹ and $\text{B}_4\text{H}_8 \cdot \text{P}(\text{CH}_3)_3$,¹² respectively, the BH_4^- salt of the Na^+ or K^+ cation being another product in each of the reactions. The formation of the B_2H_7^- anion¹³



offers an example of the significant interaction of the BH_3 acid with the hydridic hydrogens in BH_4^- . Indeed, it would be this type of $\text{B}-\text{H}-\text{B}$ interaction that makes the hydride transfer kinetically favorable over the phosphine transfer in the above reactions (eq 2 and 4). That is, the terminal hydrogen atoms are exposed to the attacking borane acids for the facile interaction. Apparently, the acid strength or the hydride affinity of B_3H_7 and B_4H_{10} is strong enough to effect the hydride transfer to these attacking acids after the intermediates involving the $\text{B}-\text{H}-\text{B}$ bonds are formed, whereas the hydride affinity of B_2H_6 or BH_3 is not high enough to allow the H^- transfer to occur. A similar explanation based on the hydride affinity difference was used to account for the strikingly different behavior between the B_3H_8^- salt of the $\text{B}_3\text{H}_6 \cdot 2\text{P}(\text{CH}_3)_2^+$ cation and the B_2H_7^- salt of the same cation.³

Experimental Section

General Data. Conventional vacuum-line techniques were used throughout for the handling of volatile and air-sensitive compounds. The sources of B_2H_6 , B_4H_{10} , CH_2Cl_2 , and tetrahydrofuran are described elsewhere.² Toluene (reagent grade) was refluxed and stored over CaH_2 . Trityl tetrafluoroborate (Alfa Products) was dried on the vacuum line before use. The NMR spectra were recorded on a Varian XL-100-15 spectrometer operating in the FT mode. A Varian SC-300 spectrometer was used to obtain the ^{13}P NMR spectra. The shifts were expressed with respect to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and 85% orthophosphoric acid. Low-field shifts were taken positive.

Synthesis of $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+ \text{BF}_4^-$. From 0.53 mmol of B_3H_{11} and 1.66 mmol of trimethylphosphine, with the use of a sublimation-sampling apparatus,¹⁴ $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3]_2$ was prepared⁷ and was placed in a 22-mm-o.d. reaction tube equipped with a 24/40 inner joint and a 10-mm-o.d. side tube (for the later introduction of the $\text{C}(\text{C}_6\text{H}_5)_3^+ \text{BF}_4^-$ sample into the reaction tube). The adduct was dissolved in 3.5 mL of CH_2Cl_2 ,

and the solution was frozen at -197°C . A 0.535 mmol sample of $\text{C}(\text{C}_6\text{H}_5)_3^+ \text{BF}_4^-$ was placed above the frozen solution through the side tube under the atmosphere of dry nitrogen gas, the side-tube was sealed off, and the vessel was evacuated. The reaction occurred at -80°C as evidenced by the change of color of the solution from a dark yellow to a pale brown in 10 min. Pieces of solid (the trityl salt) were still seen. The mixture was allowed to warm stepwise to -60 , -45 , -23 , and 0°C and room temperature while it was stirred for 10 min at each of the temperatures. The solution was clear, and no noncondensable gas was found. Then the solvent was pumped out, and the tube containing an off-white solid residue was transferred to a filtration unit. The solid was washed with toluene until nothing could be extracted, and then the remaining solid was washed into another tube with CH_2Cl_2 . Removal of the solvent from the solution by evaporation gave a white solid of $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+ \text{BF}_4^-$. Anal. Calcd for $\text{B}_5\text{C}_6\text{H}_{22}\text{P}_2\text{F}_4$: B, 18.7%. Found: 18.4%.

Reaction of $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3$ with $\text{B}_3\text{H}_7 \cdot \text{THF}$. A 0.54-mmol sample of solid $\text{B}_3\text{H}_7 \cdot \text{THF}$ was prepared¹⁵ in a 19-mm-o.d. tube equipped with a standard taper inner joint, and the adduct was dissolved in 1.5 mL of CH_2Cl_2 . A 0.53-mmol sample of $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3$ was prepared in the same manner as described above, and placed in a 9-mm-o.d. tube equipped with a stopcock and an outer joint. The tube containing the $\text{B}_3\text{H}_7 \cdot \text{THF}$ solution was attached to the 9-mm tube through the joints, the system was evacuated, and the solution was poured onto the $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3$ sample at -80°C . The $\text{B}_3\text{H}_7 \cdot \text{THF}$ that was adhering on the wall was gathered above the solution in the 9-mm tube by cooling the lower end of the tube to -197°C . The mixture was mixed to a uniform solution at -80°C , placed in the cold probe of the NMR spectrometer, and examined for its change, starting at -80°C .

No change could be seen until the temperature was raised to -10°C , where a very weak signal of B_3H_8^- could be detected. At this temperature, the progress of the reaction was very slow. At $+10^\circ\text{C}$ the growth of the B_3H_8^- and $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+$ signals was reasonably fast. At $+20^\circ\text{C}$ the reaction was almost complete in 5 min. At this time the signals of $\text{B}_3\text{H}_7 \cdot \text{P}(\text{CH}_3)_3$ could be detected. The signals of $\text{B}_4\text{H}_8 \cdot \text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_7 \cdot \text{P}(\text{CH}_3)_3$ grew steadily at the expense of the $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+ \text{B}_3\text{H}_8^-$ signals, and 1.5 h later the spectrum showed that the solution contained $\text{B}_4\text{H}_8 \cdot \text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_7 \cdot \text{P}(\text{CH}_3)_3$ in a 1:1 molar ratio, the minor contaminants being B_3H_9 , $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$, $\text{B}_3\text{H}_6 \cdot 2\text{P}(\text{CH}_3)_3^+$, and B_3H_8^- .

Reaction of $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3$ with B_4H_{10} . A 1.1-mmol sample of $\text{B}_4\text{H}_8 \cdot 2\text{P}(\text{CH}_3)_3$ was prepared in a 10-mm-o.d. tube equipped with a stopcock, and the adduct was dissolved in about 2 mL of CH_2Cl_2 . A 1.1-mmol sample of B_4H_{10} was condensed in the tube and was mixed into the solution at -80°C . The change in the solution was monitored on the NMR spectrometer, starting at -80°C .

No change could be detected until the solution was warmed to -20°C where the signals of B_3H_8^- and $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+$ began to appear. At -10°C the reaction was fairly fast, and the B_2H_6 signal grew. At $+20^\circ\text{C}$ the $\text{B}_4\text{H}_7 \cdot 2\text{P}(\text{CH}_3)_3^+ \text{B}_3\text{H}_8^-$ formation was fast and appeared to be completed in a few minutes. At this time the weak signals of $\text{B}_3\text{H}_7 \cdot \text{P}(\text{CH}_3)_3$ and $\text{B}_4\text{H}_8 \cdot \text{P}(\text{CH}_3)_3$ were present in the spectrum of the solution. Minor signals due to B_3H_9 and $\text{BH}_3 \cdot \text{P}(\text{CH}_3)_3$ were detected also.

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Registry No. $\text{B}_4\text{H}_7 \cdot 2[\text{P}(\text{CH}_3)_3]^+ \text{BF}_4^-$, 97042-31-4; $\text{B}_4\text{H}_8 \cdot 2[\text{P}(\text{CH}_3)_3]$, 66750-83-2; $\text{B}_3\text{H}_6 \cdot 2[\text{P}(\text{CH}_3)_3]^+$, 97012-35-6; $\text{B}_3\text{H}_7 \cdot \text{THF}$, 52842-96-3; $\text{B}_4\text{H}_7 \cdot 2[\text{P}(\text{CH}_3)_3]^+ \text{B}_3\text{H}_8^-$, 97012-37-8; $\text{B}_4\text{H}_8 \cdot \text{PMe}_3$, 71749-92-3; $\text{B}_3\text{H}_7 \cdot \text{PMe}_3$, 97012-38-9; B_4H_{10} , 18283-93-7.

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