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Cleavage of the Ring Trimer $[(CF_3)_2PBH_2]_3$ by Trimethylamine or by Trimethylphosphine: Neutral and Ionic Complex Products and Their Borane(3) Complexes; Evidence for F–P Through-Space NMR Coupling

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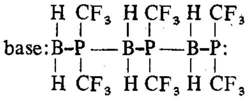
The ring trimer $[(CF_3)_2PBH_2]_3$ is easily cleaved by excess trimethylamine to give nearly equal yields of the sublimable monomer complex $(CH_3)_3N{\cdot}BH_2P(CF_3)_2$ (mp 81 °C) and the ionic oil $[(CH_3)_3N]_2BH_2^+(CF_3)_2PBH_2P(CF_3)_2^-$. The similar but faster trimethylphosphine reaction yields a more volatile monomer complex (mp 48 °C) and an analogous ionic oil. With deficient base, the PBPBP$^-$ anion $(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$ persists as a major product; less persistent, especially in the amine reaction, is the dimer complex (DC) base$\cdot BH_2P(CF_3)_2{\cdot}BH_2P(CF_3)_2$. Yet longer chains are obscure but seem to be favored in the phosphine reaction. In all of these ring-cleavage products, any three-bonded P atom easily forms a BH_3 complex of the nonpolar, nonhydridic type, which HCl attacks at a central BH_2 group rather than at an end BH_3 group. Such complexes are stable at 100 °C but lose BH_3 by action of trimethylamine. The ^{19}F NMR spectrum of the PBPBP$^-$ anion (or either DC) strongly indicates through-space coupling of F in a central $P(CF_3)_2$ group to a three-bonded end-P atom; the same principle seems applicable to the second-order spectrum of the PBP$^-$ anion. Such coupling is lost when a BH_3 complex is formed.

The action of trimethylamine upon the ring trimer $[(CF_3)_2PBH_2]_3$ was explored in our laboratories during 1960 by Dr. Arnold Wittwer, who found that excess amine at 100 °C led to an air-stable product, vacuum sublimable at 80 °C (mp 82 °C) and analyzable by HCl methanolysis to demonstrate the formula $(CH_3)_3N{\cdot}BH_2P(CF_3)_2$. Its molecular weight (by vapor pressure lowering of trimethylamine) seemed to be in the neighborhood of 300, reasonably suggesting a monomer. However, the recoverable yield of this monomer complex was only 49%, and the parallel product was a nonvolatile oil, apparently containing 0.92 amine per monomer unit $(CF_3)_2PBH_2$. At that time there seemed to be no feasible way to obtain satisfactory knowledge of the structural character of this oil, especially since it resisted attempts at analysis by the HCl–methanol method.

Recent resumption of this study with the aid of NMR spectra quickly led to confirmation of the monomer complex $(CH_3)_3N{\cdot}BH_2P(CF_3)_2$, and the analogous $(CH_3)_3P{\cdot}BH_2P(CF_3)_2$ also was made and confirmed. However, the by-product oils seemed to be mixtures having NMR spectra not easily understood, even with the aid of proton decoupling.

With the hope of obtaining a less complicated mixture of such by-products, the attack by trimethylamine was tried at 21 °C and found to be quite extensive after 2 days; and the analogous trimethylphosphine reaction seemed about equally rapid at 0 °C. The resulting oils, after brief heating in vacuo to sublime out the monomer complexes, were pure enough for dependable structural interpretations of their NMR spectra.

The main principle is fairly obvious: when the base opens the $(PB)_3$ ring by donor–acceptor bonding to boron, the initial product must be the open-chain trimer complex



$$\text{base:}\underset{\displaystyle H}{\overset{\displaystyle H}{B}}-\underset{\displaystyle CF_3}{\overset{\displaystyle CF_3}{P}}-\underset{\displaystyle H}{\overset{\displaystyle H}{B}}-\underset{\displaystyle CF_3}{\overset{\displaystyle CF_3}{P}}-\underset{\displaystyle H}{\overset{\displaystyle H}{B}}-\underset{\displaystyle CF_3}{\overset{\displaystyle CF_3}{P}}:$$

Then further base action to cleave B–P bonds would lead to the observable variety of fragments. The exception would be failure to cleave off an end $P(CF_3)_2$ unit, for if the $P(CF_3)_2^-$ anion were formed, it would be expected to decompose to F^- and $(CF_3PCF_2)_2$,[1] which is not observed. Hence the tris(boranium) cation base$\cdot BH_2P(CF_3)_2BH_2P(CF_3)_2BH_2{\cdot}$base$^+$ also would not be present. Then the remaining possibilities would be designated:

monomer complex (MC), base$\cdot BH_2P(CF_3)_2$
boranium cation (BC$^+$), $(\text{base})_2BH_2^+$
bis(phosphinide) anion (PBP$^-$), $(CF_3)_2PBH_2P(CF_3)_2^-$
dimer complex (DC), base$\cdot BH_2P(CF_3)_2{\cdot}BH_2P(CF_3)_2$
bis(boranium) cation (BPB$^+$), base$\cdot BH_2P(CF_3)_2BH_2{\cdot}$base$^+$
tris(phosphinide) anion (PBPBP$^-$),
$(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$
the trimer complex

In fact, the moderate-temperature experiments with excess base, allowed to go to completion, always gave yields of the monomer complex approaching 50% and an oil consisting almost exclusively of BC$^+$ and PBP$^-$. The failure of this ionic "salt" $(\text{base})_2BH_2^+(CF_3)_2PBH_2P(CF_3)_2^-$ to crystallize would be due to poor ion-packing and low lattice energy. Also, its persistence confirms that a chain-terminal B–P bond is not cleaved.

Also fairly persistent was the PBPBP$^-$ anion, the virtual elimination of which required much extra time, especially when the base was trimethylphosphine. Indeed, in one experiment, using a deficient proportion of this base, the PBPBP$^-$ anion was the major fluorine-containing product. In any experiment not completing all possible cleavages, it was the most prevalent intermediate product, and it probably was the chief reason for the deficient consumption of trimethylamine in the Wittwer experiments. If it can be isolated in reasonably pure condition,

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it may become an interesting ligand for chelate bonding of transition elements, for only the end P atoms are ternary.

A less persistent product was the dimer complex, observed best in the trimethylphosphine experiments: $(CH_3)_3P \cdot 2BH_2P(CF_3)_2$. In those experiments the trimer ring was opened far more rapidly than in the amine experiments, allowing this dimer complex to be seen as an early product, before too much of it could be cleaved. The analogous amine dimer complex seems to be destroyed more rapidly by the amine and so is not easily observable.

Most of the products were best observed by their ^{19}F NMR spectra, with important use also of their ^{11}B spectra and some observations of their ^{31}P and ^{1}H spectra. With trimethylphosphine there were some broad upfield ^{19}F signals replacing the trimer spectrum. These may have represented evanescent products such as the trimer complex and the bis(boranium) cation. In the amine experiments, fewer such signals were covered by the more persistent spectrum of the trimer.

Further confirmation of the various products came from a study of their BH_3 complexes. A simple rule emerged: each base molecule which combines with the BH_2 part causes an open $P(CF_3)_2$ unit, to which BH_3 can attach; and in no case is the base molecule removed by BH_3 to make base$\cdot BH_3$. Thus for either the monomer complex base$\cdot BH_2P(CF_3)_2$ or the "salt" $(base)_2BH_2^+(CF_3)_2PBH_2P(CF_3)_2^-$ there would be one open $P(CF_3)_2$ unit (able to hold BH_3) per combined base molecule. Moreover, in the "salt" $(base)_2BH_2^+(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$ the central $P(CF_3)_2$ unit is not available for BH_3 bonding, and accordingly the "deficient" base combination (relative to one per BP monomer unit) leads to an equally "deficient" attachment of BH_3.

These BH_3 complexes are to be classified as nonpolar, for they are not rapidly attacked by HCl at 25 °C, and the $MC \cdot BH_3$'s are almost as volatile as the corresponding MC's. In these ways they are like the BH_3 complexes of CO, PF_3, and the more recently described methoxyphosphines.[2] However, they are far more stable than any of those, for they do not lose BH_3 even during sublimation in vacuo at 80 °C or higher. But they are less stable than such highly polar complexes as $(CH_3)_3N \cdot BH_3$ or $(CH_3)_3P \cdot BH_3$; for example, trimethylamine at 25 °C quickly removes BH_3 from any of them, restoring the original MC or chain anion. What we see here, then, are ligands of the $RP(CF_3)_2$ type, where R is a combined BH_2 group rather than a hydrocarbon type.

It is well recognized that a methyl group on phosphorus strengthens its σ-donor bonding power, and the reason is clearly understood in terms of a wide carbon bonding orbital, which demands 3s character in the C–P bonding, so that the lone-pair electrons of phosphorus have more 3p character, for better donor bonding action.[3] But boron is larger than carbon and so should exert the same effect even more strongly than carbon does. For this reason, we may expect a base$\cdot BH_2P(CF_3)_2$ unit to have fairly good σ-donor bonding power, despite strong electron-withdrawal by the CF_3 groups. Indeed, just this CF_3-group electronegativity makes phosphorus a better π acceptor for B–H bonding electrons. Hence the present BH_3 complexes could have been expected to be fairly stable, in contrast to the nonexistence of analogous BF_3 complexes; and π bonding by B–H electrons would increase the activation energy required for hydridic behavior.

The same B–H to P π bonding, made credible by infrared spectra, helps to explain the stability of the dative-bonded ring in $[(CF_3)_2PBH_2]_3$.[4] However, it may be more important that each BH_2 group enhances the base action of phosphorus toward the other BH_2 group on the same phosphorus atom. Lacking such a base-enhancing effect, the complex $(CF_3)_2PF \cdot BH_3$ is very unstable, and $(CF_3)_2PH \cdot BH_3$ has not been shown to exist.

These BH_3 complexes are slowly reactive to HCl but not at the BH_3 group itself; instead

$$(CH_3)_3N \cdot BH_2P(CF_3)_2 \cdot BH_3 + HCl \rightarrow H_2 + (CH_3)_3N \cdot BHClP(CF_3)_2 \cdot BH_3$$

$$(CH_3)_3N \cdot BH_2P(CF_3)_2 \cdot BH_3 + HCl \rightarrow (CH_3)_3N \cdot BH_2Cl + (CF_3)_2PH + {}^{1}/{}_{2}B_2H_6$$

Here the H_2-forming reaction is like the slow action of HCl upon $(CH_3)_3N \cdot BH_2Cl$, observed in my own experiments some 40 years ago. The second process is a proton–phosphinide cleavage, and the replacement of a B–P by an H–P bond liberates BH_3 (as B_2H_6) because $(CF_3)_2PH \cdot BH_3$ does not hold together.

For the phosphine $MC \cdot BH_3$ a reaction of the first type is far slower, and a cleavage of the second type was not clearly observable at all. The reason for the difference is obscure.

Experimental Methods

All reaction components were handled by modified Stock-type high-vacuum methods. The trimer $[(CF_3)_2PBH_2]_3$ was made either by the original methods[5] or by a more direct procedure employed first by Dr. Wittwer: heating a mixture of diborane and $(CF_3)_2PI$ in a sealed tube at 100 °C. The resulting BI_3 then could be removed from the similarly volatile trimer by the action of water or by brief treatment with trimethylamine at 25 °C. However, the Wittwer method could be hazardous, for when one attempts to sublime out the last traces of the desired trimer by heating the nonvolatile residue in vacuo, a very brisant detonation can occur. In one case, this happened when a 130 °C heat gun was employed; in another, the heavy-wall bomb tube was to be cleaned by acetone at 25 °C, but the first drops of this inflamed on contact with the residue, setting off the explosion. Fortunately, the tube was shielded well enough to prevent any personal injury.

The B–P bond cleavage reactions were performed on weighed samples of the trimer, by means of measured samples of highly purified $(CH_3)_3N$ or $(CH_3)_3P$, at first in 7 mm wide sealed tubes, pointed at the lower end to aid the efficient removal of the liquid product by a long capillary "medicine dropper". At the presumed end of the process, the tube would be opened into the vacuum line by means of a vacuum tube opener, delivering the excess volatile base for measurement. Then the monomer complex would be sublimed into the upper part of the tube, which then would be broken cleanly at the middle, permitting separate weighing of the sublimate and the oily residue.

The early experiments provided most of the pertinent NMR parameters; then it was possible to monitor the course of each cleavage reaction by repeated recordings of the ^{19}F NMR spectra. The Varian XL-100-FT instrument gave just sufficient separation of the components, with some intelligible superpositions. The inert lock solvent C_6D_6 was well absorbed by the products, but too much of it formed a very dilute upper liquid layer. The trimer usually formed another, denser phase, especially in the amine experiments.

For delivery of an MC sublimate from the NMR tube, the receiver was a thin-wall drawn-down tube making a very close fit inside the upper half of the NMR tube. This receiving tube was sealed into the top of the NMR tube by Apiezon wax W and was connected through a standard-taper joint to the vacuum line. Thus the sublimate could be weighed separately from the residue.

The formation of a BH_3 complex usually was managed by attaching the containing NMR tube through an Apiezon W slip-joint to a stopcock jointed to the vacuum line, from which a measured sample of diborane could be condensed into the tube. Then the NMR tube with the stopcock could be removed from the line and shaken or rotated horizontally, for good contact between the diborane and the C_6D_6 solution of the sample. Then the excess diborane could be returned to the line for purification, measurement, and infrared verification.

Although the monomer complexes, the ionic oils, and the BH_3 complexes all seemed unchanged after long exposure to the open air, a dry nitrogen atmosphere was used when convenient.

The Monomer Complexes

Formation and Physical Properties. The action of either $(CH_3)_3N$ or $(CH_3)_3P$ (present in excess) upon the trimer $[(CF_3)_2PBH_2]_3$ usually produced at least a 45% yield of the monomer complex as a crystalline sublimate, along with a nonvolatile oil, the complexity of which depended upon how far short of completion the overall reaction had gone. Lower or higher temperatures had no qualititative effect as the same products were observed at 0 as at 100 °C. Indeed, the higher temperature experiments showed less increase of rate than might have been expected, possibly because the vaporized bases made less effective contact with the nonvolatile intermediates.

The lowest feasible temperature for high-vacuum sublimation of the amine MC was about 60 °C; for the phosphine MC, about 40 °C. In one experiment, 24 mg of the latter was sublimed through the high-vacuum line to a weighing bulb, during 3 days at 25 °C. However, removal of all traces of the MC from the nonvolatile oil could be accomplished only above 80 °C; most conveniently, at 100 °C. Under vacuum conditions, the amine MC melted at 81 °C; the phosphine MC, at 48 °C.

Both of these sublimates proved to be readily soluble in C_6D_6, which therefore was an eminently suitable lock solvent for recording the NMR spectra by means of the XL-100-FT instrument (Table I and accompanying discussion).

The Borane(3) Complexes. A 102.4-mg sample (0.425 mmol) of the MC, $(CH_3)_3N{\cdot}BH_2P(CF_3)_2$, vacuum resublimed in a 4.2-mm i.d. NMR tube, absorbed only 0.173 mmol of B_2H_6 (present in excess) during a few minutes at 60 °C. However, the solution of the mixture in C_6D_6 absorbed more diborane, with observable formation of white crystals, until the total consumed was 0.214 mmol, or 1.01 BH_3 per MC unit.

In a similar experiment, 0.240 mmol of $(CH_3)_3P{\cdot}BH_2P(CF_3)_2$ absorbed 0.25 mmol of BH_3. It was noticed that complete removal of the benzene solvent in vacuo required warming to 50 °C.

In each experiment, the unused diborane was shown by its infrared spectrum to be quite pure; thus the stoichiometry of the adduct formation was dependable. Both adducts sublimed in vacuo with similar ease at 80 °C, and their melting ranges were remarkably similar: 67.5–68.0 °C for the amine compound and 68.5–69.0 °C for the phosphine compound.

The HCl reactions of these BH_3 complexes were slow and none too simple. A 0.170-mmol sample of $(CH_3)_3N{\cdot}BH_2P(CF_3)_2{\cdot}BH_3$, with 0.138 mmol of HCl at 25 °C for 16 h, yielded only 0.084 mmol of H_2. The HCl was wholly consumed, producing 0.020 mmol of B_2H_6 and 0.066 mmol of $(CF_3)_2PH$, both of which were authenticated by their infrared spectra. The nonvolatile residue was only partly soluble in C_6D_6, and the ^{19}F NMR spectrum of the soluble part showed only the MC·BH_3 with 4% MC. It is clear that HCl attacked the MC·BH_3, not by a proton–hydride reaction at the BH_3 group but by cleavage of either the B–H or the B–$P(CF_3)_2$ bond at the BH_2 group. The latter cleavage would yield $(CH_3)_3N{\cdot}BH_2Cl$, which again would have a slow proton–hydride reaction to HCl.

Far slower and qualitatively different was the attack by 0.109 mmol of HCl upon 0.127 mmol of $(CH_3)_3P{\cdot}BH_2P(CF_3)_2{\cdot}BH_3$ during 22 h at 25 °C. The yield of H_2 was only 0.019 mmol, and diborane could not be detected at a sensitivity of 10^{-4} mmol. The recovered HCl amounted to 0.084 mmol (used, 0.025 mmol), and the yield of $(CF_3)_2PH$ was only 0.002 mmol but was easily measured by its very intense C–F stretching spectrum. In this case, then, it appeared that HCl had not cleaved many B–P chain bonds but might have attacked the BH_2 group very slowly; indeed the rate was roughly comparable to that for $(CH_3)_3N{\cdot}BH_2Cl$ under similar conditions. Since the reaction had not gone far, most of the MC·BH_3 remained in the residue; about half of it was converted back to MC by action of $(CH_3)_3P$, and then the ^{19}F NMR spectrum showed both MC and MC·BH_3 in roughly equal amounts.

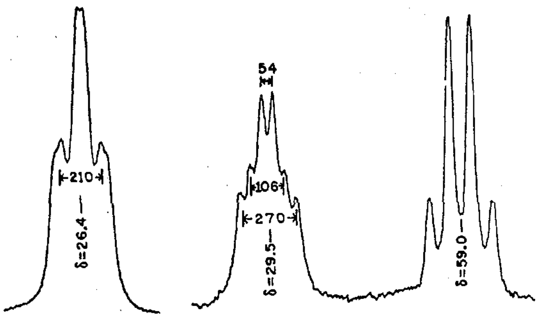


Figure 1. The ^{11}B spectra of $(CH_3)_3NBH_2P(CF_3)_2$ (left) and its BH_3 complex (middle and right).

The removal of BH_3 from such complexes by $(CH_3)_3N$ was fast and quantitative. For example, in the experiment summarized by the equation (with stoichiometry in mmol)

$$\begin{array}{lll}
(CH_3)_3P{\cdot}BH_2P(CF_3)_2{\cdot}BH_3 & + & (CH_3)_3N \rightarrow \\
\quad 0.150 & & 0.181 \\
 & & \underline{-0.030} \\
 & & 0.151 \\
 & & (CH_3)_3N{\cdot}BH_3 + (CH_3)_3P{\cdot}BH_2P(CF_3)_2 \\
 & & \quad (0.150?) \qquad\qquad 0.150
\end{array}$$

the reaction was signaled immediately by transitory melting of the solid but still was allowed 16 h for completion. The recovered amine showed no trace of $(CH_3)_3P$ impurity; indeed, it usually would be assumed that the more strongly attached $(CH_3)_3P$ would not be displaced by $(CH_3)_3N$.

The same kind of experiment was performed several times, with the amine–MC·BH_3 and with the oil–BH_3 complexes; always it was possible to remove the BH_3 quantitatively to recover the MC or the oil or to form the BH_3 complex again quantitatively. With the $PBPBP^-$ anion, of course, unnecessarily long exposure to the amine had to be avoided, lest the chain be cleaved. Most easily, these experiments were monitored by the ^{19}F NMR spectra.

NMR Spectra. All of the results shown in Table I were obtained by means of the Varian XL-100-FT instrument, using the FT mode for all nuclei except boron. Standard offsets were determined for the various chemical shift standard compounds $(CH_3)_4Si$, Cl_3CF, H_3PO_4, and $B(OCH_3)_3$, always with the use of C_6D_6 as the lock-standard solvent. The chemical shifts are reported in terms of the traditional convention: δ is positive upfield of the standard for F, P, and B, but for protons δ is positive downfield of $(CH_3)_4Si$. An upper left superscript number on δ means multiplicity, but this is omitted for complex spectra or broad pseudosinglets. As usual, the coupling constants J are in s^{-1}.

The ^1H and ^{19}F spectra here were simple enough: the methyl groups showed sharp singlets or doublets, and the broad low peaks for protons on boron could be magnified for easy measurement; however, confusion was possible when BH_2 and BH_3 showed some superposition of the broad proton peaks.

The ^{31}P spectra were poorly resolved, but the change of chemical shift due to formation of a BH_3 adduct was quite clear and aided the interpretation of the components of the oils. For $(CH_3)_3N{\cdot}BH_2P(CF_3)_2$ the expected 1:1:1:1 quartet looked like a doublet with two high shoulders, and for its BH_3 complex, only a single broad peak (half-height width 200 s^{-1}) could be seen. The corresponding phosphine MC showed broad absorption with six discernible peaks, evidently representing inexact superposition of the two phosphorus spectra. For its BH_3 complex, the $P(CF_3)_2$ aspect was a broad singlet far downfield (half-height width 300 s^{-1}), but the $(CH_3)_3P$ part was relatively sharp: the outer peaks of the 1:1:1:1 quartet were two-thirds as high as the inner pair.

The boron spectra of the amine MC and its BH_3 complex (Figure 1) clearly show that the formation of the BH_3 complex

Table I. NMR Parameters of the MC's and BH_3 Adducts[a]

		$(CH_3)_3N{\cdot}BH_2P(CF_3)_2$	BH_3 adduct		$(CH_3)_3P{\cdot}BH_2P(CF_3)_2$	BH_3 adduct
^1H	HC $^1\delta$	1.8	1.8	HCP $^2\delta$	0.50	0.53
	HB $^4\delta$	2.1	1.1, 2.2	J	10.5	12.2
	J	104	100, 103	HB $^4\delta$	1.13	1.13
	$H^{13}C$ $^2\delta$	1.8		J	103	97?
	J	141.5				
^{19}F	FCP $^2\delta$	52.0	61.8	FCP $^2\delta$	52.9	63.0
	J	63	58	J	63	60
^{31}P	PB $^4\delta$	2.5	−40.6	P_2B δ	(7)	
	J	54	...	J	?	
				Me_3P δ		7.7
				J		?
				$(CF_3)_2P$ δ		−44.6
^{11}B	BH_2 δ	26.4	29.5	BH_2 $^3\delta$	52.1	54.0
	J	104	(104)	J	103	120
	BP J	30?	(>62)	BP J	60	87
	BH_3 δ	...	59.0	BP′ J	39	68
	BH J		103	δ	...	59.2
	BP J		<20	BH J		104
				BP J		<20

[a] Upper left superscript on δ indicates multiplicity (omitted for complex spectra or broad pseudosinglets). δ in ppm relative to standard (see text); J given in s^{-1}.

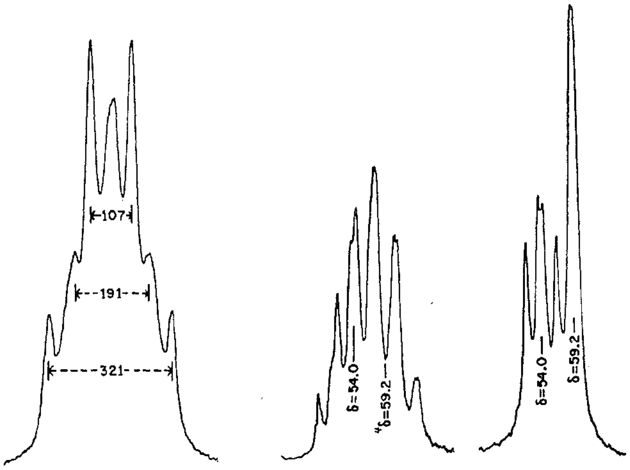


Figure 2. The ^{11}B NMR spectra of $(CH_3)_3PBH_2P(CF_3)_2$ (left) and its BH_3 adduct (central and right). The proton-decoupled spectrum (right) aided interpretation: the large upfield near-singlet ($\delta = 59.2$) represents the BH_3 group, for which J_{BP} is small.

increases the H_2B–P coupling constant, presumably because attaching BH_3 to phosphorus causes its lone-pair (dative bonding) electrons to gain 3p character, thereby assigning more 3s character to the H_2B–P bond.

For the phosphine MC, the boron spectrum (Figure 2) is complicated by two B–P couplings, but computer simulation led to J values which probably are accurate to 2 s^{-1}. For the BH_3 complex, proton decoupling made it possible to recognize that the BH_2 spectrum included two B–P couplings, for which the J values could be estimated by solving the simultaneous equations $J_1 + J_2 = 155$ and $J_1 - J_2 = 20$. The results show that both H_2B–P coupling constants are increased by forming the BH_3 complex.

In sum, then, the NMR spectra of these four compounds left no doubt of the suggested structures.

The Boranium Bis(phosphinides)

The Trimethylamine Product. A relatively clean early experiment employed 368.9 mg of the trimer $[(CF_3)_2PBH_2]_3$ (2.016 mmol of monomer) with 2.654 mmol of $(CH_3)_3N$, in a 7 × 200-mm tube attached through a stopcock to the vacuum line. After 20 h at 0 °C, the reaction had consumed 0.201 mmol of the amine; after 42 h, 0.361 mmol. Now the tube was sealed off and left at 21 °C for 66 h, with occasional shaking. Halfway along, the two liquid phases merged into one. The final consumption of the amine was 1.869 mmol, and 15.9 mg of the trimer could be recovered. Thus the overall empirical formula of the product was $(CF_3)_2PBH_2{\cdot}0.970(CH_3)_3N$. The MC was sublimed off in vacuo and weighed as 216.2 mg (0.898 mmol, representing 46% of the unrecovered trimer); later, the ^{19}F spectrum of the remaining oil showed the MC as an impurity, bringing the actual yield to 49%.

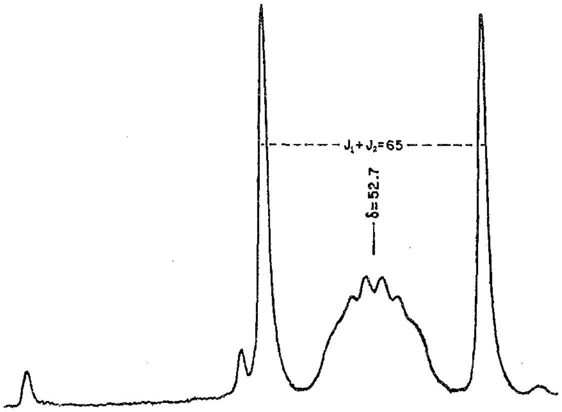


Figure 3. The second-order ^{19}F spectrum of the PBP⁻ anion $(CF_3)_2PBH_2P(CF_3)_2^-$. The small downfield doublet represents the amine MC impurity. The small, broad, upfield peak belongs to the PBPBP⁻ anion. When the $2BH_3$ complex is made, the second-order spectrum is replaced by a simple doublet (cf. Table VI).

This ^{19}F spectrum, shown in Figure 3, identifies the anion $(CF_3)_2PBH_2P(CF_3)_2^-$. Its second-order character would imply that the two $P(CF_3)_2$ groups be magnetically nonequivalent, with long-range F–P coupling. However, there seems to be a discrepancy: the FCPBP coupling would be too small in view of the poor B–P coupling. This discrepancy disappears if F–P through-space coupling is assumed, as discussed later in this paper.

The boron spectrum of this oil is quite clear: the PBP⁻ anion shows a poorly resolved but clear triplet at $\delta = 51.4$ ($J = 104$) and the cation $[(CH_3)_3N]_2BH_2^+$ appears as a better resolved triplet at $\delta = 15.6$ ($J = 119$); lit.[6] for this cation $\delta = 14.5 \pm 0.4$ ($J = 120 \pm 5$).

This oil contained also an impurity whose ^{19}F spectrum consisted of a fairly broad doublet at $\delta = 53.3$ ($J = 64.5$) and a doublet of triplets at $\delta = 60.0$ ($J_1 = 57.0$; $J_2 = 11.0$), later

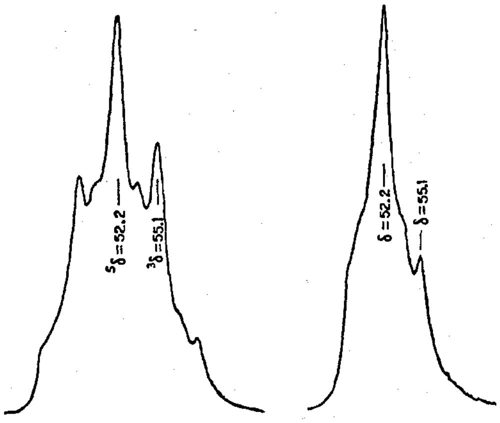


Figure 4. The full (left) and proton-decoupled (right) ^{11}B spectra of the oil $[(CH_3)_3P]_2BH_2^+[(CF_3)_2P]_2BH_2^-$. The probable triplet at $\delta = 55.1$ ($J = 94$ s^{-1}) is attributed to the BH_2 group in the anion $(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$.

understood as the spectrum of the $PBPBP^-$ anion. In an earlier experiment, in which $(CH_3)_3N$ attacked $[(CF_3)_2PBH_2]_3$ during 17 h at 76 °C, this "impurity" accounted for 69% of the total fluorine intensity in the nonvolatile oil, while the PBP^- anion represented only 26%. Clearly, the vapor-phase reaction was far from the "complete" stage (MC and boranium bis(phosphinide)), and the same slowness would account for the failure of the Wittwer experiments to achieve the 1:1 ratio of amine to $(CF_3)_2PBH_2$ monomer.

The Trimethylphosphine Product. A typical experiment began with 1.155 mmol of $(CH_3)_3P$ and 184.2 mg of $[(CF_3)_2PBH_2]_3$ (1.013 mmol of monomer), dissolved in C_6D_6 in a standard 5-mm thin-wall NMR tube. The ^{19}F spectrum of the trimer disappeared rather quickly (in contrast to the slow cleavage by trimethylamine); then the tube was heated for 17 h at 70 °C; with all P–B material in the liquid phase, this treatment almost eliminated all products except the MC and the PBP^+PBP^- ionic oil. The unused $(CH_3)_3P$ now was measured as 0.165 mmol; consumed, 0.990 mmol, or 97.7% of the expected amount. Nearly all of the MC now was sublimed out and the ^{19}F NMR spectrum of the residue consisted almost entirely of the characteristic second-order pattern of the PBP^- anion.

However, the identification of the $[(CH_3)_3P]_2BH_2^+$ cation, requiring the ^{11}B spectrum, was more difficult because of an almost perfect superposition upon the ^{11}B spectrum of the PBP^- anion. Assuming that this anion accounts for half of the total boron intensity in Figure 4, we can substract its size and shape from the full spectrum, and then what remains is a pseudoquintet with $\delta = 52$ and $J = 92$, closely in agreement with the known parameters for the PBP^+ cation.[6] With proton decoupling, the full spectrum collapses to a shouldered peak wherein two B–P couplings cause the shoulders. With subtraction of the proton-decoupled PBP^- anion spectrum, the remainder would look more like a blurred triplet.

NMR-Monitored Cleavages: Longer Chain Products

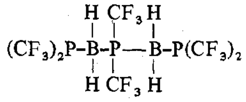
For the observation of the cleavage products at various stages of fragmentation, only the ^{19}F NMR spectra are suitably sharp and distinct. The two bases behaved differently: the trimer ring was opened far more rapidly by trimethylphosphine than by trimethylamine, but the amine cleaved the resulting long-chain products more rapidly. Thus the $PBPBP^-$ anion was more persistent in the phosphine reaction; and the phosphine dimer complex could be identified, but the amine DC remained speculative. Also in the phosphine reaction, the trimer spectrum was soon replaced by four broad humps for long-chain products, whereas in the amine reaction the trimer spectrum persisted and was only moderately confused by probable long-chain products.

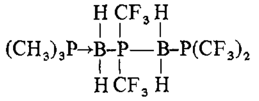
The PBPBP⁻ Anion. The anion $(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$ was identified by the previously mentioned doublet at $\delta = 53.3$ ($J = 64.5$) and the doublet of triplets at $\delta = 60.0$ ($J_1 = 57.0$; $J_2 = 11.0$), appearing in the same 2:1 ratio in all ^{19}F spectra, regardless of total intensity. The downfield doublet obviously represents the end $P(CF_3)_2$ groups, which are far enough apart to be magnetically equivalent, while the upfield doublet of triplets identifies the central $P(CF_3)_2$ unit. Here the F-atom resonances are split first by the central P atom and then by the end P atoms; but the doublet for the end F atoms is not split by the central P atom, nor indeed do we find effective F–C–P–B coupling, other than a slight broadening of the ^{19}F peaks.

The Phosphine DC. The same principle appears in the complex $(CH_3)_3P{\cdot}BH_2P(CF_3)_2{\cdot}BH_2P(CF_3)_2$: a doublet at $\delta = 53.5$ ($J = 66$), not quite superposed upon the downfield doublet of the $PBPBP^-$ anion, is assignable to the end $P(CF_3)_2$ group, whose F atoms evidently do not couple to the central P atom; and a doublet of doublets of $\delta = 60.0$ ($J_1 = 66.0$; $J_2 = 13.4$) identifies the central $P(CF_3)_2$ group, whose F atoms do couple to the end P atom, again without any evident communication through boron.

This doublet of doublets superposes almost perfectly upon the outer members of the $PBPBP^-$ anion doublet of triplets and so can be observed clearly only in the early stages of the phosphine reaction. As the reaction progresses, these triplets appear very unsymmetrical and then become more and more symmetrical as the phosphine DC disappears.

A Through-Space F–P Coupling. It would be difficult to believe that the structures


$$(CF_3)_2P\text{-}\underset{H}{\overset{H}{B}}\text{-}\underset{CF_3}{\overset{CF_3}{P}}\text{—}\underset{H}{\overset{H}{B}}\text{-}P(CF_3)_2$$


$$(CH_3)_3P\rightarrow\underset{H}{\overset{H}{B}}\text{-}\underset{CF_3}{\overset{CF_3}{P}}\text{—}\underset{H}{\overset{H}{B}}\text{-}P(CF_3)_2$$

would permit coupling from the central F atoms through C, P, and B to an end P atom (without splitting by boron), while there is no such coupling from the end F atoms to the central P atoms. The only reasonable explanation for this apparent discrepancy is through-space coupling of the central F to the end P atoms.

It seems to be generally agreed that such through-space interaction can occur only by means of nonbonding electrons, on atoms brought into proximity by the molecular geometry.[7] Thus an end F atom could not have through-space coupling to a quaternary P in either the $PBPBP^-$ anion or the DC, but the central F atoms in either structure could well couple through space with the ternary P in an end $P(CF_3)_2$ group. The adjacency would be governed by five-atom rings having a P–F nonbond proximity, whereas F–F through-space coupling would require a less convenient seven-atom ring geometry with an F–F nonbond.

The same kind of F–P through-space coupling may well occur in the anion $(CF_3)_2PBH_2P(CF_3)_2^-$, for here again the tetrahedral angle at the central B atom would force F to rub against the far P atom in a five-atom ring manner. However, we have here two chemically equivalent sets of F atoms lacking magnetic equivalence, leading to the observed second-order spectrum (Figure 3). With poor coupling through the central B atom, the second-order pattern has some resolution but is still too blurred by the boron quadrupoles for any Harris-type analysis.

It is notable that none of these probable examples of F–P through-space coupling retain such coupling when the BH_3 complexes are made (cf. Table VI). Again, quaternary phosphorus cannot offer the required lone-pair electrons.

The Monitored Cleavage Reactions. For a fairly accurate estimate of the total fluorine intensity of each component at

Table II. Cleavage of $[(CF_3)_2PBH_2]_3$ by $(CH_3)_3P$ in Excess[a]

Time, h	MC[b]	PBP⁻ [b]	PBPBP⁻ [b]	DC[b]	Long chain[b]
0.6	19	3	57	20	1
0.75	25	5	56	14	Nil
1.0	28	7	55	10	
1.5	31	9	54	6	
2.5	34	13	50	3	
4.0	36	16	46	2	
26	40	42	17	0.7	
80	45	45	10	Nil	
173	50	50	Nil		

[a] Trimer: 0.282 mmol expressed as monomer. Base: 0.379 mmol; consumed, 0.282 mmol, as calculated. [b] Numbers indicate percent of total fluorine in this component.

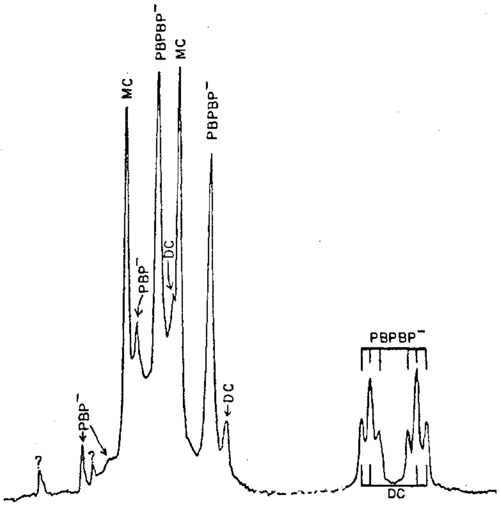


Figure 5. The ^{19}F NMR spectrum of the Table III final mixture. The question marks concern an unidentified small impurity, present at constant intensity throughout the run, and so left out of the fluorine-intensity calculations. The two upfield triplets are not mirror images because the dimer complex (DC, doublet of doublets) has a chemical shift possibly 0.02 ppm different from that of the PBPBP⁻ anion doublet of triplets.

any stage of the cleavage process, a cleanly isolated peak was chosen from the spectrum of each component, and the area of that peak was compared to its height as printed out by the FT computer. The comparison led to a factor whereby the height of the chosen peak could be converted to the relative intensity of the whole spectrum of the pertinent component, at any stage of the process.

Thus, if the conversion factor for the PBP anion is set arbitrarily at 3.00 times the height of an end peak of the second-order spectrum (Figure 3), the factor for the PBPBP⁻ anion is 3.52 times the height of one peak of the downfield doublet. For the phosphine DC, the height of one peak of the downfield doublet is multiplied by 3.17. The one-peak factor for the amine MC is 1.04 and for the broader phosphine MC chosen peak is 1.95. For the trimer, we multiply one peak height by 2.68, and for the four broad, noisy peaks representing long-chain material, we multiply one peak by 10.

The accuracy of this system was tested by measuring the yield of the MC at the end of a run, showing errors not over 5%. Also, the consumption of base was calculated from the NMR-measured quantitities of the products; the total base content was within 4% of the known base consumption.

The results of four such experiments, done with 3.43-mm i.d. NMR tubes and C_6D_6 solvent at 25 °C, are shown in Tables II–V. Here each number (other than time) shows the percent of the total fluorine content represented by the corresponding component. Representative spectra from two experiments with deficient base are shown in Figures 5 and 6. The latter shows the trimer in two liquid phases, in the

Table III. Cleavage of $[(CF_3)_2PBH_2]_3$ by Deficient $(CH_3)_3P$[a]

Time, h	MC[b]	PBP⁻ [b]	PBPBP⁻ [b]	DC[b]	Long chain[b]
0.10	3	Nil	11	16	70
0.25	7	Nil	27	27	39
0.75	11	Nil	43	25	21
0.93	13	Nil	45	23	19
4.9	22	3	52	20	3
22	28	6	54	12	Nil
48	30	6	53	11	
140	32	6	51	11	
451	33	6	52	9	

[a] Trimer: 0.134 mmol of monomer. Base: 0.1205 – 0.013 = 0.1075 mmol; calculated for products, 0.105 mmol. [b] Numbers indicate percent of total fluorine in this component.

Table IV. Cleavage of $[(CF_3)_2PBH_2]_3$ by $(CH_3)_3N$ in Excess[a]

Time, h	MC[b]	PBP⁻ [b]	PBPBP⁻ [b]	Trimer[b]
2.5	8	4	15	73
5	16	5	13	66
11	28	17	18	37
18	34	25	16	25
34	40	36	12	12
66	44	49	5	2
144	45	52	2	1

[a] Trimer: 0.339 mmol of monomer. Base: 0.422 mmol; 0.331 mmol consumed, 0.334 mmol calculated for products. [b] Numbers indicate percent of total fluorine in this component.

Table V. Cleavage of $[(CF_3)_2PBH_2]_3$ by Deficient $(CH_3)_3N$[a]

Time, h	MC[b]	PBP⁻ [b]	PBPBP⁻ [b]	DC?[b]	Trimer[b]
2.5	1	1	15	1	82
8.5	4	10	31	2	53
13	7	18	46	3	26
23	9	27	54	4	6[c]
30	13	33	51	1.4	1.8
47	14	37	47	1	0.4
119	17	44	38	1	Nil
216	18	47	35	Nil	Nil

[a] Trimer: 0.213 mmol of monomer. Base: 0.18 mmol; calculated for products, 0.188 mmol. Solvent: C_6D_6 with equal tetrahydrofuran. [b] Numbers indicate percent of total fluorine in this component. [c] Denser liquid now all dissolved.

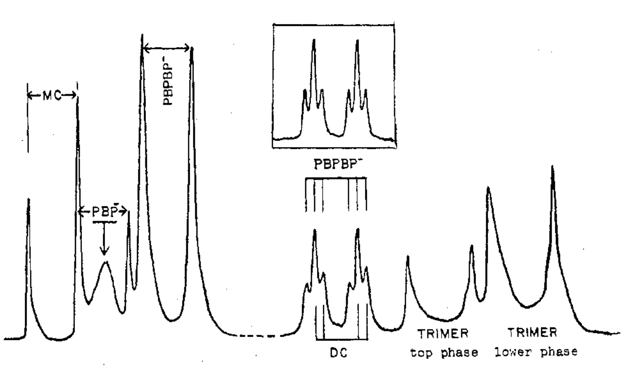


Figure 6. Fluorine NMR spectrum for the 13-h point in the amine-deficient experiment (Table V). The trimer in the top phase has $\delta = 62.1$; lower phase, $\delta = 63.2$ ppm. The difference is ascribed to differing benzene solvation in the two phases, for the same effect occurred without THF. Both trimer spectra have shapes suggesting a second-order effect; the distance between the peaks for each is 84.5 s^{-1}. The inset doublet of triplets was recorded at the end of the run (216 h), showing the disappearance of the presumed dimer complex.

Table VI. Boron and Fluorine NMR Spectra of Ions and Their BH_3 Complexes

	Boron		Fluorine		
Formula	δ	J, s^{-1}	δ	J, s^{-1}	Source of sample
$[(CH_3)_3N]_2BH_2^+$	15.6	118.5	...	...	Fig 3 product (amine oil)
$[(CH_3)_3P]_2BH_2^+$	52.4	92	...	...	Table III product; MC removed
$[(CF_3)_2P]_2BH_2^-$	51.4	104	52.7	"65"	Fig 3 product (second-order ^{19}F)
$[(CF_3)_2PBH_3]_2BH_2^-$	BH_2 55.0	?	62.8	58.5	Fig 3 product + B_2H_6; ^{19}F now a simple doublet, half-height width 7 s^{-1}
	BH_3 58.7	100?			
$[(CF_3)_2PBH_2]_2P(CF_3)_2^-$	55.0	?	53.3	64.5	Table III product; consensus with earlier incomplete $(CH_3)_3P$ expt
			60.0[a]	57.0	
				11.0	
$[(CF_3)_2P(BH_3)BH_2]_2P(CF_3)_2^-$	BH_2 55.4	?	59.2[b]	67	Table III product + B_2H_6
	BH_3 59.0	?	62.5[c]	59	

[a] Doublet of triplets, of total intensity half that of the δ 53.3 doublet. [b] Doublet for central $P(CF_3)_2$ unit; half-height width 18 s^{-1}. [c] Doublet for end $(CF_3)_2PBH_3$ units; half-height width 16 s^{-1}; intensity twice that of *b*.

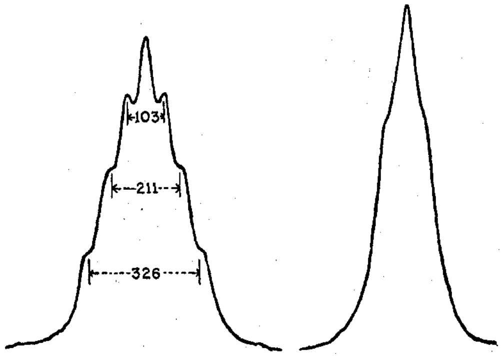


Figure 7. ^{11}B NMR spectrum of $[(CF_3)_2PBH_2]_3$. The full spectrum (left) is consistent with a BH_2 triplet with J = 105 s^{-1}, split further by a BP_2 triplet having J = 52 s^{-1}, confirmed by the proton-decoupled spectrum on the right.

denser of which it was especially concentrated.

This separation of phases meant that the percent of the F assignable to the trimer could not always be accurately judged, for the probe would not always interact with the two phases in a comparable manner. Also, the segregated trimer was less directly exposed to the amine, despite efforts to improve the contact by shaking or horizontal rotation of the tube. In the Table V experiment, therefore, the dissolving of the trimer in the upper phase was improved by tetrahydrofuran, and indeed the trimer was consumed far more rapidly than in a strictly parallel experiment without THF. In that parallel experiment, indeed, the unused trimer still was about 27% after 50 h, and much of the amine had been used up for cleaving the $PBPBP^-$ anion, now assayed as only 7% of the total fluorine.

An outstanding difference between the phosphine-deficient and the amine-deficient experiments was the persistence of the phosphine DC. The presence of an amine DC was reasonably (albeit somewhat speculatively) indicated in the Table V results, but with excess amine (Table IV) there was not the least evidence of its presence. The persistence of the phosphine DC seemed to correlate with the high rate at which the phosphine cleaved the trimer. With deficient phosphine, the trimer cleavage was faster than the subsequent cleavages; and then the remaining phosphine worked on the long-chain material more rapidly than on the dimer complex. Then most of the yet unused phosphine went to cleave the dimer complex, leaving the $PBPBP^-$ anion as a far more persistent component.

The Table V results suggest a way to isolate fairly pure boranium bis(phosphinide): by using deficient amine to cleave the trimer and stopping the reaction at the 2-h point, one could obtain 90% samples of the nonvolatile BPB^+PBPBP^- product by removing the volatiles and subliming out the MC. The same volatiles, reacting further in another tube, would repeat the process for increased yield.

NMR Spectra of the Ions and Their Borane(3) Complexes. Table VI summarizes the ^{11}B and ^{19}F parameters for all ionic products, including the BH_3 complexes. Usually, each assignment was based on the sample containing the largest proportion, or offering the best isolation, of the pertinent ion. In the case of the $PBPBP^-$ anion a consensus was required: the Table III experiment offered the most boron in that form, but in the ^{11}B spectrum a superposition on the PBP^+ cation made it seem too intense; hence the experiment giving Figure 4 aided the assignment. A further argument is that boron here would be expected to appear farther upfield than in the PBP^- anion, since the four-bonded phosphorus in the BH_3 complex of the PBP^- anion had the effect of moving the central BH_2 group farther upfield than in the PBP^- anion itself.

The ^{11}B spectrum of the Table III product showed a small component at δ = 49.4, persisting as δ = 49.6 in the BH_3 complex; the assignment of that "impurity" remains uncertain.

For comparison with Table VI, it is mentioned that the ring trimer $[(CF_3)_2PBH_2]_3$ has the ^{11}B spectrum shown in Figure 7, with a chemical shift of δ = 60.1 ppm upfield of methyl borate. Here, of course, each BH_2 group is between two four-bonded phosphorus atoms.

The ^{19}F second-order spectrum of the PBP^- anion was changed drastically by forming its double-BH_3 complex $[(CF_3)_2PBH_3]_2BH_2^-$. The spectrum of this seems to be a simple doublet with J close to that for other simple doublets for similar compounds. This loss of second-order character is what one would expect if the second-order spectrum of the free PBP^- anion was due to through-space F–P coupling.

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Registry No. $[(CF_3)_2PBH_2]_3$, 65036-27-3; $(CF_3)_2PBH_2$(trimer), 65016-23-1; $(CH_3)_3N$, 75-50-3; $(CH_3)_3P$, 594-09-2; $(CH_3)_3N\cdot BH_2P(CF_3)_2$, 65016-24-2; $(CH_3)_3P\cdot BH_2P(CF_3)_2$, 65016-25-3; B_2H_6, 19287-45-7; $(CH_3)_3N\cdot BH_2P(CF_3)_2\cdot BH_3$, 65016-26-4; $(CH_3)_3P\cdot BH_2P(CF_3)_2\cdot BH_3$, 65016-27-5; $PBP^-[(CH_3)_3N]_2BH_2^+$, 65036-21-7; $PBP^-[(CH_3)_3P]_2BH_2^+$, 65036-22-8; $PBPBP^-$, 65036-23-9; $(CH_3)_3P\cdot BH_2P(CF_3)_2\cdot BH_2P(CF_3)_2$, 65036-24-0; $[(CF_3)_2PBH_3]_2BH_2^-$, 65036-25-1; $[(CF_3)_2P(BH_3)BH_2]_2P(CF_3)_2^-$, 65036-26-2.

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