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The Coordination of Fluorodialkylaminophosphines with Boron Acids. The Formation of Boron-Phosphorus and Boron-Nitrogen Bonds

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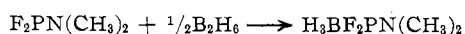
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Nuclear magnetic resonance, infrared, and chemical techniques have been used to demonstrate that borane fragments combine with the phosphorus atom in bases of the type $F_xP\{N(CH_3)_2\}_{3-x}$ to give relatively stable adducts. On the other hand, trifluoroborane combines with the nitrogen of the base to give a complex which decomposes easily by fluorine shift to produce $[F_2BN(CH_3)_2]_2$ and PF_3 . Trimethylborane reacts readily with $F_xP\{N(CH_3)_2\}_{3-x}$ to give unstable adducts which easily dissociate to give the starting materials. Evidence for an initial B-P bond in the trimethylborane adduct of $FP\{N(CH_3)_2\}_2$ is presented. The compound $H_7B_3F_2P\{N(CH_3)_2\}$ can be made from the reaction of $F_2P\{N(CH_3)_2\}$ and tetraborane by a symmetrical cleavage process involving tetraborane; the compound contains a B-P bond.

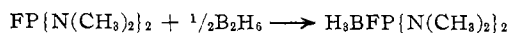
Several addition compounds of the dialkylaminofluorophosphines $F_xP\{N(CH_3)_2\}_{3-x}$ with boron acids have been reported. This paper is concerned with a systematic examination of the evidence for determining bonding site and with the physical and chemical consequence of donor-acceptor bond formation at each site in the dialkylaminofluorophosphines.

Reactions of $F_xP\{N(CH_3)_2\}_{3-x}$ with Diborane

1. The Borane Addition Compounds.—The compounds $H_3BF_2PN(CH_3)_2$ and $H_3BFP\{N(CH_3)_2\}_2$ were first prepared in this laboratory by Kodama¹ using the reaction between neat F_3PBH_3 and $NH(CH_3)_2$ at -78° . The related compound $H_3BFP\{N(CH_3)_2\}_2$ was obtained from the same reaction at 25° . The existence of a P-B bond in the product was suggested by the method of synthesis. The same compounds can, however, be obtained by the direct reaction between $F_2PN(CH_3)_2$ or $FP\{N(CH_3)_2\}_2$ and diborane where a free choice of base site is available. The appropriate equations are



and



The clear liquids $H_3BF_2PN(CH_3)_2$ and $H_3BFP\{N(CH_3)_2\}_2$ are stable indefinitely under vacuum at -78° and undergo no detectable decomposition when held at room temperature for several days. Upon exposure to moist air they hydrolyze slowly. Although a direct extrapolation of base strengths from the known behavior of PF_3 and $N(CH_3)_3$ would suggest that bonding through nitrogen would be favored, the data shown

below provide unequivocal evidence for the boron-phosphorus bond.

2. Nuclear Magnetic Resonance Data for $H_3BF_2PN(CH_3)_2$ and $H_3BFP\{N(CH_3)_2\}_2$.—Proton, fluorine-19, phosphorus-31, and boron-11 nmr spectra for both $H_3BF_2PN(CH_3)_2$ and $H_3BFP\{N(CH_3)_2\}_2$ are summarized in the Experimental Section. Of particular interest is the ^{11}B spectrum of $H_3BF_2PN(CH_3)_2$ in which each member of the ^{11}B quartet is split into a doublet by direct coupling with phosphorus, $J_{P-B} = 79 \pm 1$ Hz. Because of unusual overlap of peaks, the quintet in the spectrum of $H_3BFP\{N(CH_3)_2\}_2$ is somewhat more difficult to assign, but its essential similarity to the $H_3BF_2PN(CH_3)_2$ spectrum is indicated by the fork diagram in Figure 1. The existence of the B-P bond in $H_3BF_2P\{N(CH_3)_2\}$ and $H_3BFP\{N(CH_3)_2\}_2$ is also confirmed by the ^{31}P spectrum in which each member of the original phosphorus signal is split by the attached borons, $J_{P-N} = 80 \pm 1$ Hz.

3. Infrared Spectra of $H_3BF_2PN(CH_3)_2$ and $H_3BFP\{N(CH_3)_2\}_2$.—The infrared spectra of both $H_3BF_2PN(CH_3)_2$ and $H_3BFP\{N(CH_3)_2\}_2$ provide strong confirmatory evidence for a B-P bond. In 1958 Braunscholtz, Ebsworth, Mann, and Sheppard² assigned a small peak in the region at $2760-2820\text{ cm}^{-1}$ to a C-H symmetric stretching vibration of the N- CH_3 group. This band appears, as long as the nitrogen contains a free electron pair, but shifts to significantly higher frequencies (above 2900 cm^{-1}) upon coordination of the free electron pair. The generality of the observation has also been supported by many additional observations in this laboratory. An application of these arguments to borane adducts of dialkylaminofluorophosphines indicates that the nitrogen atoms remain uncoordinated. For F_2-

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(1) G. Kodama and R. W. Parry, *Inorg. Chem.*, **4**, 410 (1965).

(2) J. T. Braunscholtz, E. A. V. Ebsworth, J. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 2780 (1958).

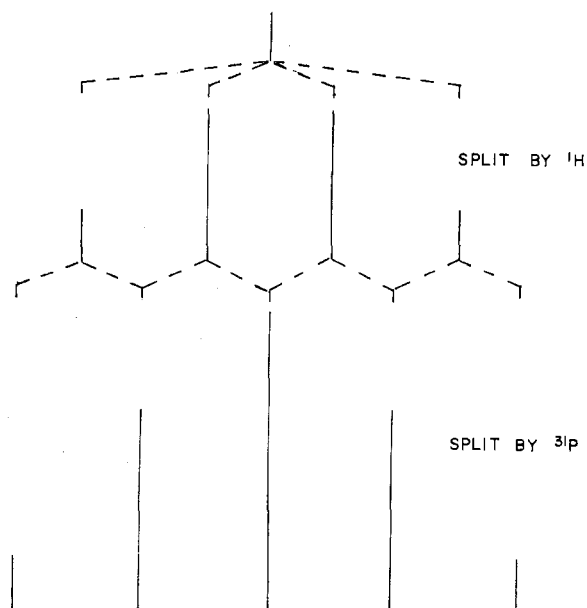


Figure 1.— ^{11}B coupling scheme for $\text{H}_3\text{BFP}\{\text{N}(\text{CH}_3)_2\}_2$.

$\text{PN}(\text{CH}_3)_2$ the band in question appears at 2808 cm^{-1} in the free liquid ligand and at 2810 cm^{-1} after formation of the liquid $\text{H}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ complex. Similar evidence is available for $\text{H}_3\text{BFP}\{\text{N}(\text{CH}_3)_2\}_2$ which shows a band for the liquid phase at 2810 cm^{-1} . For the free ligand the band is at 2790 cm^{-1} , but the difference is not large enough to imply coordination through the nitrogen. (It should be noted here that the appearance of the band at 2810 cm^{-1} in the compound $\text{H}_3\text{BFP}\{\text{N}(\text{CH}_3)_2\}_2$ does not demand a phosphorus-boron bond; it demands only a nitrogen atom with a free electron pair. Since only one nitrogen atom could be coordinated to the borane group, the free pair must always be present.)

An additional infrared argument is available. In the case of both borane addition compounds a new, medium-intensity band appears in the infrared spectrum at 586 cm^{-1} for $\text{H}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ and at 574 cm^{-1} for $\text{H}_3\text{BFP}\{\text{N}(\text{CH}_3)_2\}_2$. This band has been assigned as a P-B stretching mode. The comparable absorption in H_3BPF_3 appears at 607 cm^{-1} .³

Reactions of $\text{F}_x\text{P}\{(\text{CH}_3)_2\}_{3-x}$ with Trifluoroborane

1. The Trifluoroborane Addition Compound.—The compound $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ was prepared independently by Cavell^{4a} and by Fleming^{4b} using a direct reaction between $\text{F}_2\text{PN}(\text{CH}_3)_2$ and trifluoroborane.

The white crystalline solid, $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$, exhibits a dissociation vapor pressure of 56 mm at 24° . An infrared spectrum indicates that the vapor is predominantly a mixture of $\text{F}_2\text{PN}(\text{CH}_3)_2$ and trifluoroborane. A molecular weight determination of the vapor gives a value of 95 indicating approximately 5% association in the vapor phase. This dissociation is reversible, the adduct exhibiting no vapor pressure upon cooling to -78° . Evidence as developed below establishes the existence of a B-N bond in $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$.

2. Nuclear Magnetic Resonance Data for $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$.—Proton, fluorine-19, phosphorus-31, and boron-

11 nmr spectra in benzene for $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ are summarized in the Experimental Section. Of particular interest are the boron-11 and phosphorus-31 spectra. At ambient temperatures no splitting by boron of the sharp ^{31}P triplet is observed, nor is splitting of the ^{11}B signal by phosphorus noted. The possibility that a rapid BF_3 -exchange process would produce a time-averaged signal was minimized by low-temperature studies of the ^{11}B spectrum. At temperatures between -10 and -50° the signal broadened only slightly and exhibited irregularities due to partial freezing of the solution. In a study completed very recently in this laboratory, Michael Thomas has shown that a system containing 1 mol of $\text{F}_2\text{PN}(\text{CH}_3)_2$ and 3 mol of BF_3 gives a saturated solution at -111° containing liquid BF_3 as solvent. The ^{11}B nmr of this system at -111° shows distinct, broad singlets for free and coordinated BF_3 . Thus rapid exchange is eliminated at this temperature and the lack of B-P coupling argues strongly against a B-P bond. Details will be published elsewhere. No doublet splitting by phosphorus was ever observed. If a B-P bond existed in the compound, B-P coupling would be expected to appear as the temperature was reduced, and the exchange rate was slowed.

3. Infrared Spectrum of $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$.—The previously cited criterion of Braunholtz, Ebsworth, Mann, and Sheppard² suggests a boron-nitrogen bond in $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$. The infrared spectrum of the ligand $(\text{CH}_3)_2\text{NPF}_2$ in CCl_4 solution has three significant absorptions in the C-H stretching region. A strong band appears at 2920 cm^{-1} and two medium bands appear at 2655 and 2815 cm^{-1} . In the boron trifluoride adduct $\text{F}_3\text{B}\cdot\text{F}_2\text{PN}(\text{CH}_3)_2$ the strong band appears at 2940 cm^{-1} and the medium band appears at 2900 cm^{-1} , but the band corresponding to the 2815-cm^{-1} absorption is absent. Absence of this band is in accord with previous observations which show that dative-bond formation causes the 2815-cm^{-1} band to shift to much higher frequencies.

Examination of the spectrum of solid $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$, isotopically enriched with ^{10}B , shows a medium-intensity band at 654 cm^{-1} which correlates well with the absorption at 696 cm^{-1} for $\text{F}_3^{10}\text{BN}(\text{CH}_3)_3$ which was assigned by Amster⁵ to the symmetric $\text{F}_3^{10}\text{B-N}$ stretching mode. Only one puzzling feature exists in the infrared data for $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$. Farran⁶ suggested that increases in the P-F stretching frequency may be correlated with the formation of a B-P bond. LaPrade and Nordman⁷ added support to this postulate when their X-ray study showed a shortening of the P-F linkage after formation of the borane adduct. Solid $\text{F}_2\text{PN}(\text{CH}_3)_2$ has a strong band at 764 cm^{-1} which has been assigned as the asymmetric P-F stretching frequency and a medium-intensity band at 728 cm^{-1} which was assigned as the symmetric P-F stretching mode. The asymmetric P-F stretching vibration, appearing at 764 cm^{-1} in the free ligand, appears at 880 cm^{-1} in the boron trifluoride complex. In solid $(\text{CH}_3)_2\text{NPF}_2\text{BF}_3$, the symmetric P-F stretching mode, appearing at 728 cm^{-1} in the free ligand, appears at 827 cm^{-1} . We interpret these observations as an indi-

(5) R. Amster, Ph.D. Dissertation, Laboratory of Professor R. C. Taylor, University of Michigan, 1961.

(6) C. F. Farran, Ph.D. Dissertation, Laboratory of Professor R. C. Taylor, University of Michigan, 1966.

(7) M. D. LaPrade and C. E. Nordman, *Inorg. Chem.*, **8**, 1669 (1969).

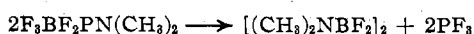
(3) R. C. Taylor and T. C. Bissot, *J. Chem. Phys.*, **25**, 780 (1956).

(4) (a) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964). (b) S. Fleming, Ph.D. Dissertation, University of Michigan, 1963.

cation that complex formation at either the phosphorus atom or the nitrogen atom causes an increase in the P-F stretching frequency. This interpretation is not too difficult to accept in view of the fact that use of the lone pair of electrons on nitrogen for formation of a bond to BF_3 would render these electrons incapable of forming a double bond with phosphorus. Removal of a double bond to phosphorus could thus cause marked changes in the F-P bond (*i.e.*, greater PF double bond?), even though the primary coordination was on nitrogen.

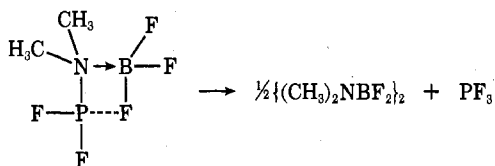
Chemical Characteristics of the Trifluoroborane Adducts of $\text{F}_x\text{P}\{\text{N}(\text{CH}_3)_2\}_{2-x}$

An examination of the chemistry of $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ offers strong evidence supporting the existence of a boron-nitrogen bond. If the crystalline adduct is stored at -78° , no appreciable decomposition occurs. However, if $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ is held at room temperature for 1 day, the following reaction occurs



Trifluorophosphine was identified by its infrared spectrum. Elemental analysis established the empirical formula $(\text{H}_3\text{C})_2\text{NBF}_2$ for the second reaction product. Similar fluoride shifts involving formation of $(\text{H}_3\text{C})_2\text{NBF}_2$ in the reactions of certain compounds of electron donor elements with BF_3 have been observed.⁸⁻¹⁰

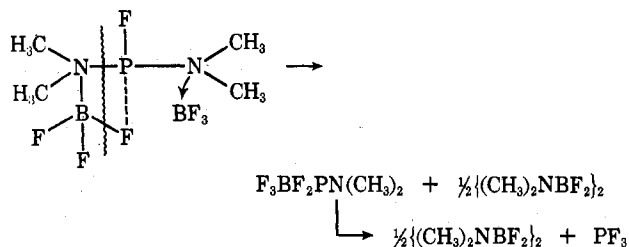
The transfer reaction can be understood easily in terms of a structure involving a B-N bond and interaction of a BF_3 fluorine atom with the phosphorus nucleus. The intermediate and the equation are



Significantly, trifluoroborane reacts with $\text{PF}\{\text{N}(\text{CH}_3)_2\}_2$ in a 2:1 mole ratio, implying bond formation to both nitrogen atoms. However, the diadduct could *not* be isolated since upon warming to room temperature the following reaction occurs



Again, the transfer reaction is easily explained if one assumes B-N bonding.



Reactions of $\text{F}_x\text{P}\{\text{N}(\text{CH}_3)_2\}_{3-x}$ with Trimethylborane

When trimethylborane is condensed with $\text{F}_2\text{PN}(\text{CH}_3)_2$ in a 1:1 mole ratio and warmed to -78° , a solid adduct forms. However, experimental difficulties were such that no physical data to determine structure were obtained.

With $\text{FP}\{\text{N}(\text{CH}_3)_2\}_2$ a solid 1:1 adduct formed at -78° and melted to a colorless liquid near room temperature. This liquid exhibited a dissociation pressure of 9 mm at 25° .

Nuclear Magnetic Resonance Data for $(\text{H}_3\text{C})_3\text{BFP}\{\text{N}(\text{CH}_3)_2\}_2$.—Proton, fluorine-19, and boron-11 nmr data for the trimethylborane adduct of $\text{FP}\{\text{N}(\text{CH}_3)_2\}_2$ are summarized in the Experimental Section.

Evidence for a boron-phosphorus bond is to be found in an examination of the proton and fluorine-19 spectra. The *N*-methyl proton signal is a doublet of doublets similar in appearance to the signal of uncoordinated $\text{FP}\{\text{N}(\text{CH}_3)_2\}_2$. If coordination occurs through a nitrogen atom, one would expect to observe two *N*-methyl signals.

The fluorine-19 resonance signal provides further evidence for a B-P bond. Each member of the doublet can be resolved into a septet of relative intensities 1.0:2.2:3.6:4.0:3.6:2.2:1.0, with a coupling constant of about 2-3 Hz (Figure 2). This pattern cannot arise

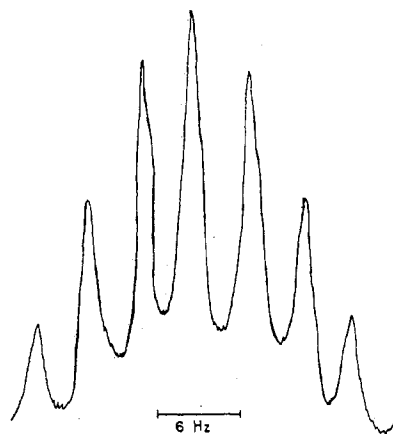


Figure 2.—High-resolution spectrum of one member of the ^{19}F doublet of $(\text{H}_3\text{C})_3\text{BFP}\{\text{N}(\text{CH}_3)_2\}_2$; $J_{\text{FPNCH}} = 2-3$ Hz.

from the protons of the methyl groups attached to boron since ten bands with a doublet at the maximum would be expected for such an interaction. Splitting by the protons of one $(\text{CH}_3)_2\text{N}$ group would result in a septet but the relative intensities would be 1:6:15:20:15:6:1. However, if the trimethylborane is attached to the phosphorus atom and all of the *N*-methyl groups are equivalent, then 13 peaks of relative intensities 1:12:66:220:495:792:924:792:495:220:66:12:1 would be expected. If one assumes that the observed signal corresponds to the seven central peaks, then very nearly perfect correspondence of intensities is observed, 1.00:2.25:3.60:4.20:3.60:2.25:1.00.

In spite of the above evidence, the ^{11}B signal shows no splitting by phosphorus. The signal is considerably broadened, the width of the absorption band indicating that any unresolved P-B coupling must be less than about 65 Hz.

A similar situation has been observed for $(\text{CH}_3)_3\text{BP}(\text{CH}_3)_3$, a compound in which only a phosphorus bonding site is available for the trimethylborane. Here also, no splitting of the ^{11}B signal by phosphorus is observed.¹¹

(8) A. A. Burg and J. Banus, *J. Amer. Chem. Soc.*, **76**, 3903 (1954).

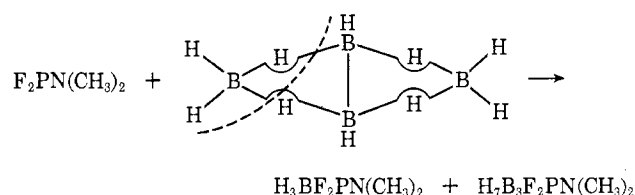
(9) H. Becher, *Z. Anorg. Allg. Chem.*, **288**, 236 (1956).

(10) S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, **79**, 2447 (1957).

(11) C. W. Heitsch, *Inorg. Chem.*, **7**, 1019 (1965).

Reaction of B_3H_{10} with $F_2PN(CH_3)_2$.
Formation of $H_7B_3F_2PN(CH_3)_2$

The reaction of $F_2PN(CH_3)_2$ with tetraborane in a 2:1 mole ratio yields the stable $H_7B_3F_2PN(CH_3)_2$ by symmetrical cleavage of the bridge bonds¹²



Though no nmr data were obtained for this compound in this study, evidence for boron-phosphorus bonding is to be found in the infrared data. The 2808- cm^{-1} band of the liquid ligand, previously mentioned, shifts to 2833 cm^{-1} in the B_3H_7 adduct. This shift is so small that the retention of a free electron pair on nitrogen is indicated. This fact forces the conclusion that a P-B bond exists.¹³

Further, in the region of P-B stretching frequencies (500-600 cm^{-1}) bands are found at 592 and 542 cm^{-1} . The 542- cm^{-1} absorption is assigned to the boron-phosphorus stretching mode since in $H_3BF_2PN(CH_3)_2$ the analogous band is found at 586 cm^{-1} .

An additional argument for the presence of a B-P bond in $H_7B_3F_2PN(CH_3)_2$ is to be found in a comparison of the infrared spectrum of $H_3B_4F_2PN(CH_3)_2$ with that of $H_7B_3F_2PN(CH_3)_2$. The two spectra are essentially identical (Table I). The similarity is strongly indica-

TABLE I

A COMPARISON OF THE INFRARED SPECTRA OF $H_7B_3F_2PN(CH_3)_2$ AND $H_3B_4F_2PN(CH_3)_2$ (LIQUID FILM). EVIDENCE FOR A B-P BOND IN $H_7B_3F_2PN(CH_3)_2$

$H_7B_3F_2PN(CH_3)_2$	$H_3B_4F_2PN(CH_3)_2$	$H_7B_3F_2PN(CH_3)_2$	$H_3B_4F_2PN(CH_3)_2$
2945 mw	2955 m	1172 s	1182 s
2875 sh, w	2840 sh, w	1160 sh, ms	
2833 sh, w	2830 sh, w	1072 m	1077 s
2525 s	2525 s	1010 s	1019 s
2461 s	2460 s	960 w	974 w
2320 w	2332 w	900 sh, ms	899 br, s
2020 br, w	1912 br, m	867 br, s	870 br, s
1576 br, w	1518 br, m	825 sh, m	821 sh, w
1489 m	1485 ms		790 mw
1456 m	1450 ms		779 mw
	1438 sh, m	755 m	
1320 s	1328 s	725 m	724 sh, m
	1272 mw	660 vw	710 ms

tive of similar structures for the two adducts and the latter compound has been shown by crystallography⁷ to possess a B-P bond.¹⁴

Discussion

A possible explanation for the preferential bonding of borane fragments to the phosphorus atoms of $F_2PN(CH_3)_2$ and $FP[N(CH_3)_2]_2$ and of trifluoroborane

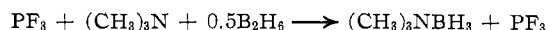
(12) A description of this same reaction by E. R. Lory and D. M. Ritter, *Inorg. Chem.*, **10**, 939 (1971), appeared after this paper was submitted.

(13) An nmr study completed in this laboratory by R. T. Paine, a report of which has been submitted for publication, and a very recent paper by E. R. Lory and D. M. Ritter, *Inorg. Chem.*, **10**, 939 (1971), confirm the P-B bond.

(14) This argument has been confirmed by recent nmr studies of R. T. Paine, Ph.D. Dissertation, University of Michigan, 1970, who reported a B-P coupling constant of 103 Hz. Data to be published. Spectrum also reported independently by E. R. Lory, Ph.D. Dissertation, University of Washington, Seattle, Wash., 1969.

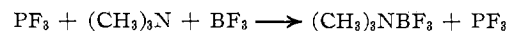
to the nitrogen atoms seems to be worthy of consideration.

If 1 mol of PF_3 and 1 mol of $(CH_3)_3N$ are mixed with 0.5 mol of B_2H_6 at -196° and subsequently warmed to 25° , the following reaction occurs¹⁵



Since trimethylamine readily displaces PF_3 from F_3-PBH_3 to form $(CH_3)_3NBH_3$, the above reaction is not unexpected.

Similarly, if a reaction mixture of BF_3 , $(CH_3)_3N$, and PF_3 in a 1:1:1 molar ratio is warmed to 25° , trimethylamine is found to react preferentially with trifluoroborane.



Since in both of these cases B-N bonds are formed in preference to B-P bonds, it would seem that *N*-methyl bases bind both BH_3 and BF_3 more strongly than do fluorophosphine bases. However, in the single molecule $F_2PN(CH_3)_2$ an apparent reversal of base site occurs in coordination with borane fragments.

A model which can account for bonding through phosphorus in these cases depends upon a knowledge of the structure of $F_2PN(CH_3)_2$. The geometry of this compound in the solid state was determined by Morris and Nordman¹⁶ using X-ray diffraction. Since the infrared spectra of solid and gaseous $F_2PN(CH_3)_2$ are almost identical except for the greater resolution found in the solid spectrum, no major change in geometry on passing from solid to gaseous phase is indicated. The P-N-C configuration of solid $F_2PN(CH_3)_2$ is planar with the P-N bond distance being 1.628 Å, a length considerably less than the usually quoted value of 1.77 Å for a single P-N bond.¹⁷ This planar geometry and shortened bond length suggest significant double bonding between N and P leading to an enhancement of the base strength of the phosphorus atom and a concomitant reduction of the base strength of the nitrogen atom. However, since BF_3 still bonds preferentially to nitrogen in $F_2PN(CH_3)_2$, factors other than the increased base strength of phosphorus must also be influential in the determination of bonding site.

Bonding of other atoms to phosphorus is strongly field dependent. The widely dispersed free electron pair of phosphorus will bind to another atom if that atom has a strong enough positive field to draw the phosphorus atom electrons into a bonding region. In the system under discussion, the effectiveness of the boron kernel in generating a large positive field depends upon its penetration into the lone electron pair of phosphorus. In turn, such penetration of the boron kernel toward the phosphorus nucleus is directly related to deformation of the groups attached to the boron kernel, that is, a movement of these groups backward away from the B-P bond. If the deformation energy of the boron unit is moderate (BH_3), coordination to phosphorus is observed. On the other hand, if the deformation energy of the boron unit is large (*i.e.*, BF_3), the formation of a B-P bond will be prevented in spite of the increased base strength of a phosphorus atom for

(15) R. W. Parry and T. C. Bissot, *J. Amer. Chem. Soc.*, **78**, 1524 (1956).

(16) E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

(17) E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Crystallogr.*, **6**, 621 (1953).

an acid at short distances. In this way we rationalize the formation of a weak B-N bond.

Though the crystal structure of $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ has not yet been determined, it is reasonable to assume an even greater enhancement of the base strength of the phosphorus atom. In this case, although the deformation energy of trimethylborane is considerably greater than that of BH_3 , this effect seems to be at least partially compensated by the increased base strength of phosphorus resulting in a P-B bond. This observation would also suggest that, though in general BF_3 and $(\text{CH}_3)_3\text{B}$ are relatively similar in coordinating properties, the deformation energy of trimethylborane is somewhat less than that of BF_3 . One would have to know with certainty the bonding site in the unstable $(\text{CH}_3)_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ to assess more conclusively the effects of enhanced base strength and deformation energy in trimethylborane complexes of phosphorus-nitrogen bases, but the current evidence points to a conclusion which we had not anticipated, based on the known chemistry of $(\text{CH}_3)_3\text{B}$ and F_3B .

Experimental Section

General Techniques.—Standard high-vacuum techniques were used throughout. Boron, fluorine, and phosphorus nmr spectra were determined with a Varian Associates HR-100 nmr spectrometer at 32.1, 94.4, and 40.4 MHz, respectively. Proton nmr spectra were determined with a Varian Associates HR-60 nmr instrument at 60 MHz. Internal TMS and external TFA, $\text{B}(\text{OCH}_3)_3$, and 85% H_3PO_4 served as references for ^1H , ^{19}F , ^{11}B , and ^{31}P spectra, respectively. Infrared spectra were determined with a Perkin-Elmer Model 21 spectrometer.

Material.—Commercial BF_3 (Matheson), B_2H_6 (Callery), and $(\text{CH}_3)_2\text{NH}$ (Matheson) were fractionated in the vacuum system before use.^{4a} Commercial PF_3 (Ozark-Mahoning) was used without further purification.

Preparation of $\text{F}_2\text{PN}(\text{CH}_3)_2$.—A 4.31-mmol sample of PF_3 was frozen (-196°) with a 4.93-mmol sample of $(\text{CH}_3)_2\text{NH}$ then allowed to warm to 25° where reaction took place. An 84% yield of $\text{F}_2\text{PN}(\text{CH}_3)_2$ was retained in the -95° trap during fractionation.

Preparation of $\text{H}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$.—In a typical reaction 10.0 mmol of $\text{F}_2\text{PN}(\text{CH}_3)_2$ and 6.24 mmol of B_2H_6 were condensed together in a reaction tube. The mixture was warmed to room temperature, allowed to stand for 1 hr, and fractionated (see ref 4 for details). The compound was identical with that reported by Kodama and Parry¹ for $\text{H}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$. Ir spectrum (gas, 12 mm) in cm^{-1} : 3014 (vw), 2945 (m, $\nu_{\text{C-H}}$), 2885 (w, sh), 2820 (w, $\nu_{\text{s, C-H}}$), 2620 (vw, br, 2×1320), 2440 (s, $\nu_{\text{B-H}}$), 2375 (w, $\nu_{\text{B-H}}$), 2245 (vw, 2×1121), 1490-1470 (sh, δ_{CH_3}), 1463 (m), 1320 (ms, $\delta_{\text{s, CH}_3}$), 1187 (m, ρ_{CH_3}), 1121 (w, δ_{BH_2}), 1071 (m, $\nu_{\text{C-N}}$ and/or δ_{BH_2}), 1010 (vs, $\nu_{\text{s, (H}_3\text{C})_2\text{NPF}}$), 891-873 (vs, br, $\nu_{\text{s, P-F}}$, ρ_{BH_2}), 753 (s, $\nu_{\text{s, P-F}}$), 701 (w, $\nu_{\text{s, N-PF}_2}$), 586 (mw, $\nu_{\text{P-B}}$), 441 (vw, br, δ_{PF_2}) [ν = stretching mode, δ = deformation, ρ = rocking, s = symmetric, a = asymmetric]. Nmr spectra: ^1H (neat), δ 2.78 ppm^{1b} (d, $J_{\text{HP}} = 11$ Hz, CH_3); each member of a doublet is a triplet ($J_{\text{HF}} = 3$ Hz), δ 0.55 ppm (q, $J_{\text{HB}} = 100$ Hz, BH_3) each member of a quartet is a quartet (q, $J_{\text{HP}} = J_{\text{HF}} = 18$ Hz); ^{19}F (neat), δ -4.3 ppm relative to trifluoroacetic acid (d, $J_{\text{F-P}} = 1166$ Hz); each member of a doublet is a quartet of intensities 1:2.78:2.78:1 ($J_{\text{HF}} = 17$ Hz, F_2PBH_3); ^{11}B (neat), δ 61.4 ppm relative to $\text{B}(\text{OCH}_3)_3$ (q, $J_{\text{B-H}} = 100$ Hz, BH_3); each member of a quartet is a doublet ($J_{\text{B-P}} = 79$ Hz); ^{31}P (neat), δ = -130 ppm relative to 85% H_3PO_4 (t, 2:2:1, $J_{\text{PF}} = 1170$ Hz); each member of a triplet is a quartet (q, $J_{\text{P-B}} = 80$ Hz) [s = singlet; d = doublet; t = triplet; q = quartet].

Preparation of $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$.—A 1.20-mmol sample of BF_3 was frozen in a reaction tube with a 1.62-mmol sample of $\text{F}_2\text{PN}(\text{CH}_3)_2$ at -196° . The system was then warmed gradually to room temperature.^{4b} After fractionation of volatile components

at -64° , a white solid was obtained which was sublimed at -23° . Ir spectrum of $\text{F}_3^{10}\text{BF}_2\text{PN}(\text{CH}_3)_2$ (solid film, -196°) in cm^{-1} : 2907 (vw, $\nu_{\text{C-H}}$), 1507 (vw), 1497 (vw), 1485 (w), 1473 (w, δ_{CH_3}), 1466 (vw), 1457 (vw, δ_{CH_3}), 1242 (m, $\delta_{\text{s, CH}_3}$), 1216 (m, ρ_{CH_3}), 1201 (s, ρ_{CH_3}), 1189 (s, $\nu_{\text{s, }^{10}\text{B-F}}$), 1162 (m, $\nu_{\text{s, C-N}}$), 1152 (mw, sh, $\nu_{\text{s, }^{11}\text{B-F}}$), 1010 (w, $\nu_{\text{s, (CH}_3)_2\text{N-P}}$), 921 (s, $\nu_{\text{s, }^{10}\text{B-F}}$), 908 (w, $\nu_{\text{s, }^{11}\text{B-F}}$), 884 (s, $\nu_{\text{s, P-F}}$), 853 (s, 2×416), 830 (s, $\nu_{\text{s, PF}}$), 699 (s, $\nu_{\text{s, N-P-F}_2}$), 654 (m, $\nu_{\text{s, F}_2\text{BN}}$), 562 (ms, $\delta_{\text{s, BF}_2}$), 511 (vw), 480 (m, $\delta_{\text{s, PF}_2}$), 445 (mw), 416 (vw). Nmr spectra: ^1H (C_6H_6 solution), δ 2.44 ppm relative to TMS (d, $J_{\text{HP}} = 7$ Hz, $\text{N}(\text{CH}_3)_2$); ^{19}F , δ 71.9 ppm relative to TFA (s, BF_3), δ -0.1 (d, $J_{\text{FP}} = 1325$ Hz, F_2P); ^{11}B (C_6H_6 solution), δ 16.9 ppm relative to $\text{B}(\text{OCH}_3)_3$ (s, BF_3); ^{31}P (C_6H_6 solution), δ -140 ppm relative to 85% H_3PO_4 (t, $J_{\text{P-F}} = 1350$ Hz, PF_2).

The Reaction of $\text{F}_2\text{PN}(\text{CH}_3)_2$ with $\text{B}(\text{CH}_3)_3$.—A 1.99-mmol sample of $(\text{CH}_3)_3\text{B}$ was condensed with 1.20 mmol of $\text{F}_2\text{PN}(\text{CH}_3)_2$ in a reaction vessel. The reaction vessel was then warmed to -78° and held there for 5 hr. At the end of this period a -128° slush was substituted and excess $(\text{CH}_3)_3\text{B}$ (0.79 mmol) was distilled into a trap cooled with liquid nitrogen. The 1:1 adduct was observed visually to be a solid at -78° . However, extensive dissociation takes place as the solid is warmed to room temperature. The melting point is in the vicinity of -45° . Dissociation seems to be irreversible in the sense that the entire system must be cooled with liquid nitrogen and then held at -78° for several hours in order to re-form the complex.

Preparation of $\text{FP}[\text{N}(\text{CH}_3)_2]_2$.—In a typical reaction a 20-mmol sample of PF_3 and 75-mmol quantity of $(\text{CH}_3)_2\text{NH}$ were condensed in a heavy-walled Pyrex tube equipped with a break-off tip. The sealed tube was held at room temperature for 2 weeks. Fractionation of the resulting mixture through traps held at -23° , -95° , and -198° yielded a pure sample of $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ retained in the -23° trap, a mixture of $\text{F}_2\text{PN}(\text{CH}_3)_2$ and $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ in the -95° trap, and excess $(\text{CH}_3)_2\text{NH}$ in the -196° trap. Clear liquid $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ is stable under vacuum at room temperature for several days. Contact with fluorinated stopcock greases causes immediate decomposition to form a bright orange solid. The vapor pressure of the liquid over the range 0 – 46° can be expressed by the equation

$$\log P_{\text{mm}} = -\frac{2006.7}{T} + 7.9085$$

Observed vapor pressures (mm) at several temperatures are recorded below [as T ($^\circ\text{K}$), P (mm)]. The corresponding values calculated from the above equation are given in parentheses: 0.0, 3.6 (3.7); 12.8, 7.7 (7.8); 17.8, 10.2 (10.3); 21.1, 12.3 (12.3); 23.7, 14.3 (14.1); 27.0, 16.9 (16.8); 33.0, 23.2 (22.9); 39.9, 31.8 (31.6); 42.3, 34.7 (35.3); 46.1, 41.7 (42.0). $\Delta H_{\text{vap}} = 9182$ cal/mol; mp -89 to -90° , bp 125.9° . Anal. Calcd for $\text{C}_4\text{H}_{12}\text{N}_2\text{PF}$: N, 20.3; P, 22.4; mol wt, 138.13. Found: N, 21.2; P, 22.9; mol wt by freezing point depression in benzene, 135. Ir spectrum (gas, 8 mm) in cm^{-1} : 2882 (s, $\nu_{\text{C-H}}$), 2842 (sh), 2795 (m, $\nu_{\text{s, C-H}}$), 1504 (w), 1494 (w), 1485 (w), 1479 (w), 1469 (mw, br), 1463 (m, δ_{CH_3}), 1453 (mw), 1448 (w), 1434 (vw), 1280 (m, $\delta_{\text{s, CH}_3}$), 1199 (m), 1164 (mw, sh, ρ_{CH_3}), 1057 (mw, $\nu_{\text{s, C-N}}$), 985-973 (s, $\nu_{\text{s, (CH}_3)_2\text{N-P}}$), 949 (vs), 745 (s, $\nu_{\text{s, P-F}}$), 677 (s, $\nu_{\text{s, N-PNF}}$), 496 (w, br, $\delta_{\text{P-F}}$), 403 (w, br, $\delta_{\text{(CH}_3)_2\text{N}}$). The nmr spectra are as follows: ^1H (neat), δ 2.53 ppm relative to TMS (d, $J_{\text{HP}} = 9$ Hz, $(\text{CH}_3)_2\text{NP}$); each member of a doublet is a doublet ($J_{\text{HF}} = 3$ Hz, $(\text{H}_3\text{C})_2\text{NPF}$); ^{19}F (neat), δ 22.3 ppm relative to TFA (d, $J_{\text{F-P}} = 1045$ Hz, $\text{FP}(\text{NR}_2)_2$); each member of a doublet is a septet of relative intensities 1.00:2.07:3.11:3.66:3.11:2.07:1.00; the calculated relative intensities of the seven central peaks of thirteen (12 H atoms) are 1.00:2.25:3.60:4.20:3.60:2.25:1.00 ($J_{\text{F-H}} = 3$ Hz, $\text{FP}[\text{N}(\text{CH}_3)_2]_2$); ^{31}P (neat), δ -153 ppm relative to 85% H_3PO_4 (d, $J_{\text{P-F}} = 1100$ Hz, $\text{PF}[\text{N}(\text{CH}_3)_2]_2$).

Preparation of $\text{H}_3\text{BFP}[\text{N}(\text{CH}_3)_2]_2$.—In a typical reaction 0.52 mmol of $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ and 0.165 mmol of B_2H_6 were condensed in a reaction tube and allowed to warm to room temperature. The reaction was instantaneous with traces of noncondensable gas formed. The mixture was fractionated (see ref 4 for details). The ratio of Lewis base to Lewis acid consumed was 1.84:1 or higher. Anal. Calcd for $\text{H}_3\text{BFP}[\text{N}(\text{CH}_3)_2]_2$: C, 31.61; H, 9.95; N, 18.44. Found: C, 31.84; H, 10.11; N, 18.30. Ir spectrum (neat), in cm^{-1} : 2991 (sh, $\nu_{\text{C-H}}$), 2924 (m), 2855 (sh), 2810 (w, $\nu_{\text{s, C-H}}$), 2389 (s, $\nu_{\text{s, B-H}}$), 2249 (vw, $\nu_{\text{B-H}}$), 2134 (vvw, 2×1068), 1489-1475 (br, sh, δ_{CH_3}), 1460 (m, δ_{CH_3}), 1416 (vvw, 2×706), 1310 (ms, $\delta_{\text{s, CH}_3}$), 1194-1167 (m, br, ρ_{CH_3} and/or δ_{BH_3}),

(18) Conventions from IUPAC International Bulletin No. 4, Appendices on Tentative Nomenclature, Symbols, Units, and Standards, 1970. Signals downfield from tetramethylsilane are reported as positive.

1134 (w, ρ_{CH_3} and/or δ_{BH_3}), 1068 (m, $\nu_{\text{C-N}}$ and/or δ_{BH_3}), 998–973 (s, $\nu_{\text{C-N}}$), 821 (s, $\nu_{\text{C-F}}$), 775 (ms, ρ_{BH_3} or $\nu_{\text{P-F}}$), 750 (s), 706 (mw, $\nu_{\text{N}_2\text{-P-F}}$), 685 (w, $\nu_{\text{N}_2\text{-P-F}}$), 574 (w, $\nu_{\text{P-B}}$). The nmr spectra give the following constants: ^1H (neat), δ 2.63 ppm relative to TMS (d, $J_{\text{HF}} = 9$ Hz, $\text{N}(\text{CH}_3)_2$); member of a doublet is a doublet ($J_{\text{HF}} = 3$ Hz); δ 0.33 ppm (q, $J_{\text{HB}} = 100$ Hz, H_3B); ^{19}F (neat), δ 12.88 ppm relative to TFA (d, $J_{\text{F-P}} = 1070$ Hz, $\text{FP}(\text{NR}_2)_2$); ^{31}P (neat), δ -133 ppm relative to 85% H_3PO_4 (d, $J_{\text{P-F}} = 1075$ Hz, $\text{PF}(\text{NR}_2)_2$); each member of a doublet is a quartet ($J_{\text{PB}} = 80$ Hz); ^{11}B (neat), δ 60.5 ppm relative to $\text{B}(\text{OCH}_3)_3$ (quintet, 1:4:6:4:1, $J_{\text{BH}} = 98$ Hz, $J_{\text{BP}} = 86$ Hz, H_3BP).

The Reaction of $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ with BF_3 .—In a typical reaction BF_3 (5.54 mmol) was condensed with $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ (1.74 mmol). The tube, open to a blowout manometer, was allowed to warm slowly to room temperature. After three such cycles, the volatile products were distilled from the reaction vessel at -23° through a trap at -95° into a trap at -196° . The reaction vessel was gradually warmed from -23 to 0° ; then the distillation was terminated. Boron trifluoride (2.44 mmol) was trapped at -196° while $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ (1.34 mmol) was retained in the trap at -95° . The ratio of BF_3 to $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ was 1.78:1.00. Since the amount of $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$ was low by 0.4 mmol, one can assume the presence of up to 0.4 mmol of PF_3 in the BF_3 . Such an assumption could alter the stoichiometry to give a ratio of BF_3 to $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ of 2.00:1.00.

Preparation of $(\text{H}_3\text{C})_3\text{BFP}[\text{N}(\text{CH}_3)_2]_2$.—Trimethylborane (2.02 mmol) was condensed with $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ (0.87 mmol) in a reaction vessel open to a blowout manometer. The vessel was warmed stepwise from -196 to -78° using appropriate constant-temperature baths. After 5 hr at -78° the reaction tube was first cooled to -196° and then warmed to -126° . Excess $(\text{H}_3\text{C})_3\text{B}$ (1.96 mmol) was removed by distillation from the reaction vessel at -126° to a trap held at -196° . The ratio of $(\text{H}_3\text{C})_3\text{B}$ consumed to $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ used was 0.99:1.00. The addition compound, retained in the reaction vessel, was a white crystalline solid melting to a colorless liquid near room temperature. It exhibited a dissociation pressure of about 9 mm at 25° . An infrared spectrum of the vapor showed only the absorption peaks for free $(\text{CH}_3)_3\text{B}$ and free $[(\text{CH}_3)_2\text{N}]_2\text{PF}$.

Attempts to purify the new adduct by distillation *in vacuo* from the reaction vessel held at room temperature resulted in an irreversible dissociation of the addition compound into its components. Only by cooling to -196° and repetition of the stepwise warming process could the adduct be re-formed. Once formed, the new compound, $[(\text{CH}_3)_2\text{N}]_2\text{PF}(\text{CH}_3)_3$, seemed fairly stable at room temperature as long as no distillation was attempted.

The irreversible decomposition occurring upon distillation prevented obtaining any significant infrared data using the low-temperature cell. The nmr spectra can be summarized as follows: ^1H (neat), δ 2.67 ppm (d, $J_{\text{H-P}} = 7$ Hz, $(\text{H}_3\text{C})_2\text{NP}$); each member of the doublet was also a doublet ($J_{\text{H-F}} = 3$ Hz, $(\text{H}_3\text{C})_2\text{NPF}$); δ -0.18 ppm (s, $\text{H}_3\text{C})_3\text{B}$); ^{19}F (neat), δ 30.2 ppm relative to TFA (d, $J_{\text{PF}} = 1133$ Hz, $\text{FP}(\text{NR}_2)_2$); each member of a doublet is a septet (1:2:2:3:6:4:0:3:6:2:2:1, $J_{\text{FP}[\text{N}(\text{CH}_3)_2]_2} = 2$ -3 Hz); ^{11}B (neat), δ 24.3 ppm relative to $\text{B}(\text{OCH}_3)_3$.

Preparation of $\text{H}_7\text{B}_3\text{F}_2\text{PN}(\text{CH}_3)_3$.—A 4.97-mmol sample of B_4H_{10} was frozen into a reaction tube with $(\text{CH}_3)_2\text{NPF}_2$ (9.35 mmol). The reactants were alternately warmed to room temperature and chilled with liquid nitrogen over a period of 0.5 hr while the reactants were being stirred with a magnetic jump stirrer. The reaction system was then held at 25° for 1 hr and finally fractionated (0° for reaction vessel, -45 , -78 , -196°) while stirring was continued. The compound $(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$ was retained at -78° while the product in the reaction vessel was identified as $(\text{CH}_3)_2\text{NPF}_2\text{B}_3\text{H}_7$. It has a vapor pressure of about 1 mm at 26° . *Anal.* Calcd for $(\text{CH}_3)_2\text{NPF}_2\text{B}_3\text{H}_7$: C, 15.74; H, 8.59; N, 9.18. Found: C, 16.04, 16.11; H, 8.67, 8.74; N, 8.92. The infrared spectrum is compared to that of $(\text{CH}_3)_2\text{NPF}_2\text{B}_4\text{H}_8$ in Table I. The similarity between the two is striking and confirms the B-P bond.

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Transition Metal Hydroborate Complexes. IV.¹ Cyanotrihydroborate Complexes of the Group Ib Metals

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The synthesis of several copper(I) and silver(I) compounds containing tertiary group V donor ligands and a coordinated cyanotrihydroborate or cyanotriphenylborate anion is reported. Complexes of general formula $\text{L}_3\text{M}(\text{NCBR}_3)$ are shown by physical measurements to contain metal-nitrogen bonds, both in the solid state and in chlorinated hydrocarbon solvents. In acetonitrile solution $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cu}(\text{NCBH}_3)$ is a weak electrolyte, as determined from conductivity studies. The relative extent of dissociation of hydroborate and chloride ligands from triphenylphosphine-coordinated copper(I) ions in acetonitrile is found to be $\text{B}_3\text{H}_8^- \sim \text{H}_3\text{BCN}^- > \text{BH}_4^- \sim \text{Cl}^-$. The cyanotrihydroboratotrakis(triphenylphosphine)silver(I) compound is more highly ionized. From its infrared spectrum, the complex of empirical formula $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{NCBH}_3)$ is concluded to be a dimer, with bridging cyanotrihydroborate ligands coordinated to form both Cu-NCBH₃ and Cu-HBH₂CN type linkages.

Introduction

As discussed previously,² the chemical reactivity of small, reducing hydroborate anions toward copper(I) complexes depends upon the stereochemical environment of the copper atom and the choice of hydroborate ligand. Thus sodium borohydride will decompose a

solution containing a 3:1 triphenylarsine:copper(I) ratio, but borohydride-tris(triphenylphosphine)-copper(I) solutions are stable,^{2,3} and cesium octahydrotriborate forms the crystalline complex $[(\text{C}_6\text{H}_5)_3\text{As}]_2\text{Cu}(\text{B}_3\text{H}_8)$.² The preparation and characterization of coinage metal derivatives of the larger borane anions have also been reported.^{4,5}

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