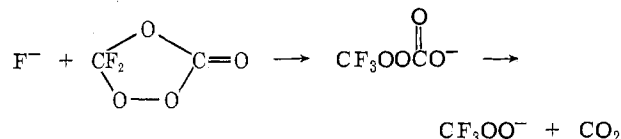


Because of the probable pronounced polarization of the C=O bond, the carbon is electron deficient to the extent that the weaker bases, such as KF, can effectively react. Thus, the isomerization reaction is effected by all bases capable of adding to C=O bonds.

The other potential acid site in II, the CF<sub>2</sub> group, must be susceptible to F<sup>-</sup> attack only in the case where the cation is large as in CsF. This postulate is consistent with the ring opening reactions of perfluoroalkylene oxides where it was shown that only strong F<sup>-</sup> bases such as CsF could cause ring opening.<sup>11</sup> The attacking CsF then leads to an irreversible reaction with the elimination of CO<sub>2</sub>. The postulated peroxide



(11) J. A. Young, *Fluorine Chem. Rev.*, **1**, 370 (1967).

salt, CsOOCF<sub>3</sub>, likely accounts for both III and IV.<sup>12</sup>

It is noteworthy that only isomerization of I or II occurs with KF and disproportionation occurs exclusively with CsF. When a catalytic amount of trimethylamine is used with I, both the isomerization reaction and disproportionation reaction occur suggesting that a transitory quaternary fluoride is of base strength between KF and CsF. This suggestion was not tested directly through the use of a fluoride such as R<sub>4</sub>NF.

**Acknowledgment.**—We are indebted to Dr. J. Muirhead for the <sup>19</sup>F nmr data and Mr. S. Cohz for the mass cracking patterns. We also wish to thank Dr. K. O. Christe for many helpful discussions. This work was supported in part under Contract F04711-C-67-0007 through the Air Force Rocket Propulsion Laboratory, Air Force System Command, Edwards, California.

(12) The salts of CF<sub>3</sub>OOH were shown to be intermediates in the synthesis of III and IV in ref 9.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, MARYGROVE COLLEGE, DETROIT, MICHIGAN 48221, AND THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

## The Synthesis of a Cyclic Fluorodialkylaminophosphine and Its Coordination with Boron Acids. The Formation of a Unique Dialkylaminophosphine Cation

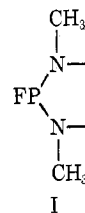
By SUZANNE FLEMING,\* MARY KATHRYN LUPTON,<sup>1</sup> AND KATHLEEN JEKOT<sup>1</sup>

Received November 5, 1971

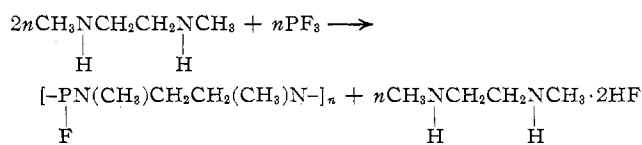
The synthesis of a new cyclic fluorodialkylaminophosphine ligand is reported. It is 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine (I). Nuclear magnetic resonance and infrared techniques have been used to demonstrate that in the borane adduct bonding occurs *via* the phosphorus atom. Trifluoroborane, on the other hand, combines with a nitrogen atom of the base in a 1:1 mole ratio to give the first reported adduct of this type which is stable to fluorine shift and phosphorus-nitrogen bond cleavage. Reaction of I with an excess of trifluoroborane is shown conclusively by nmr techniques to result in the reversible formation of the unique cation-anion system, [CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)NP]<sup>+</sup>[B<sub>2</sub>F<sub>7</sub>]<sup>-</sup>. The cation has also been isolated as the stable [CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)NP]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup> species by the reaction between I and PF<sub>5</sub>.

### Introduction

Compounds of the type F<sub>2</sub>PNR<sub>2</sub> and FP[NR<sub>2</sub>]<sub>2</sub> have been described<sup>2-5</sup> and it has been shown conclusively by X-ray and/or nmr studies that bonding takes place *via* the phosphorus atom when these ligands react with boron hydrides.<sup>2b,5,6</sup> On the other hand, though all available evidence indicates boron-nitrogen bonding in trifluoroborane adducts of these ligands, their instability to halogen shift and P-N bond cleavage have prohibited the structural studies needed to make an unequivocal decision.<sup>2b,5</sup> In the present paper we report the synthesis of the cyclic fluorodialkylaminophosphine 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine, I, and its reactions with B<sub>2</sub>H<sub>6</sub>, BF<sub>3</sub>, and PF<sub>5</sub>.



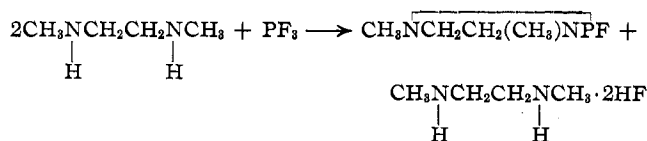
1. **Synthesis of CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)NPF (I).**—The reaction of PF<sub>3</sub> with an excess of (CH<sub>3</sub>)<sub>2</sub>NH yields FP[N(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>.<sup>2b,5</sup> By analogy, it was thought that the reaction of PF<sub>3</sub> with an excess of *N,N'*-dimethylethylenediamine should result in formation of either a polymeric species



or a cyclic fluorodialkylaminophosphine, as follows.

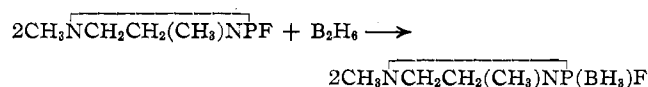
\* Author to whom correspondence should be addressed at Marygrove College.

(1) American Chemical Society Petroleum Research Fund Scholars.  
 (2) (a) H. Noth and H. J. Vetter, *Chem. Ber.*, **96**, 1298 (1963); (b) S. Fleming, Ph.D. Dissertation, University of Michigan, 1963.  
 (3) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).  
 (4) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).  
 (5) S. Fleming and R. W. Parry, *ibid.*, **11**, 1 (1972).  
 (6) M. D. LaPrade and C. E. Nordman, *ibid.*, **8**, 1669 (1969).



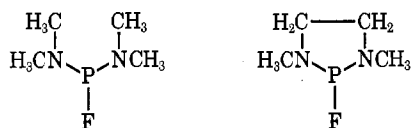
In the present study, no evidence of formation of a polymeric species was found. Rather, the cyclic compound, formed in 59% yield, was identified by its  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{19}\text{F}$  spectra and by its molecular weight as determined by identification of the parent ion in the mass spectrum of the compound. The nmr data, summarized in the Experimental Section, are fully consistent with the cyclic structure proposed for I. It should be noted, however, that a molecular weight determination was necessary to eliminate conclusively a "head to tail" polymeric structure.

**2. Reaction of I with  $\text{B}_2\text{H}_6$ .**—Because of the structural similarity of I to  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$  it was anticipated that reaction of the cyclic ligand with diborane would yield an adduct possessing a B–P bond.<sup>2b,5</sup>



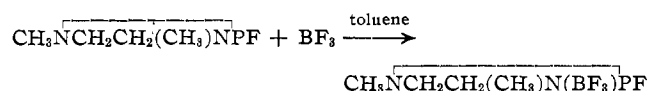
The white crystalline product was identified as the borane adduct by its  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{19}\text{F}$ , and  $^{11}\text{B}$  nmr spectra. The nmr data, summarized in the Experimental Section, indicate retention of the equivalence of the *N*-methyl protons upon adduct formation and the appearance of P–B spin–spin splitting offering unequivocal evidence for P–B bonding. The quintet splitting evidenced in the  $^{11}\text{B}$  spectrum is identical with that of  $\text{F}(\text{BH}_3)\text{P}[\text{N}(\text{CH}_3)_2]_2$ .<sup>2b,5</sup> Confirmatory evidence for the B–P bond is to be found in the infrared data. The appearance of a new, medium-intensity band at  $552\text{ cm}^{-1}$  in the P–B stretching region corresponds well to the  $574$ -,  $586$ -, and  $607\text{-cm}^{-1}$  absorptions of  $\text{F}(\text{BH}_3)\text{P}[\text{N}(\text{CH}_3)_2]_2$ ,  $\text{F}_2(\text{BH}_3)\text{PN}(\text{CH}_3)_2$ , and  $\text{H}_3\text{BPF}_3$ , respectively. In each case these bands have been assigned to the P–B stretching mode.<sup>2b,5,7</sup>

**3. Reaction of I with  $\text{BF}_3$  (1:1 Mole Ratio).**—It was thought that the reaction of trifluoroborane with I might result in formation of a considerably more stable adduct than that formed by the analogous reaction between  $\text{BF}_3$  and  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ .<sup>2b,5</sup> Though the two compounds might be considered structurally similar



the "tying back" of two alkyl groups in the cyclic compound should make the nitrogen atoms sterically more favorable as bonding sites.

Substantiation of this postulate was obtained by direct interaction of I with trifluoroborane in a 1:1 mole ratio



Initially, the complex forms as a viscous, glassy liquid which, under vacuum, slowly crystallizes to a

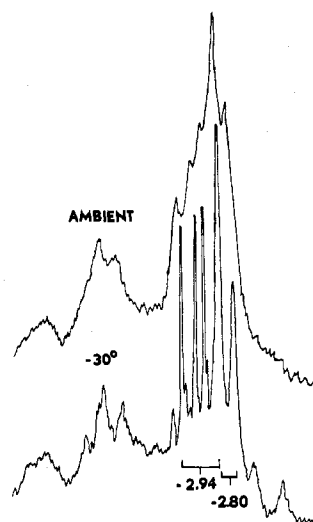


Figure 1.—Proton nmr spectra of  $\text{CH}_3\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{N}(\text{BF}_3)\text{PF}$ .

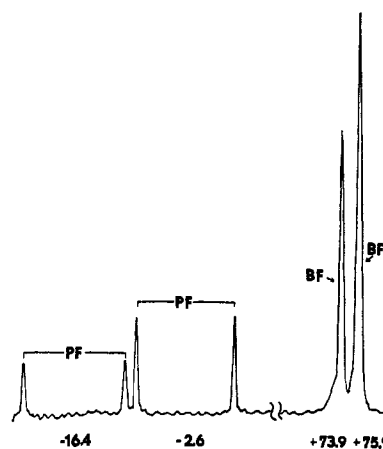


Figure 2.— $^{19}\text{F}$  nmr spectrum of  $\text{CH}_3\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{N}(\text{BF}_3)\text{PF}$ .

sublimable solid. This solid complex is stable indefinitely when held under vacuum at room temperature. There is no evidence, under these conditions, for the P–N bond rupture and halogen shift usually found in such adducts.<sup>2b,5</sup>

The  $^{11}\text{B}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  nmr spectra of the glassy liquid in toluene solution are essentially the same as those of the solution formed from the solid dissolved in methylene chloride. The proton spectra of the dissolved liquid and solid complexes are similar but chemical shift values are substantially different, presumably due to solvent effects. A summary of nmr spectral data for both liquid and solid adducts is given in the Experimental Section.

At ambient temperatures the proton nmr of the crystalline adduct dissolved in  $\text{CHCl}_3$  (Figure 1) is broad and poorly resolved indicating that an exchange process is taking place. The line width of about 40 cps (at 100 MHz) enables an upper limit of approximately  $250\text{ sec}^{-1}$  to be placed on the exchange velocity at room temperature. The low-temperature ( $-30^\circ$ ) proton nmr of the same sample (Figure 1) indicates clearly that at this temperature the six *N*-methyl protons are

no longer equivalent. The broad doublet at  $\delta -2.80$  ppm may be attributed to the protons of the methyl group attached to the coordinated nitrogen, the broadening arising from quadrupole interaction with the boron nucleus. The protons of the methyl group attached to the uncoordinated nitrogen,  $\delta -2.94$  ppm, show the usual splitting by phosphorus and fluorine. The presence of two types of methyl protons in a 1:1 ratio conclusively verifies B-N bonding in this adduct. The other low-intensity peaks in the methyl region of the spectrum may be due to the presence of either an impurity or a second isomer of the 1:1 adduct, the latter being more likely.

The broadening observed at ambient temperatures is most probably due to rapid exchange of a  $\text{BF}_3$  molecule between the two available nitrogen sites in the ligand molecule.

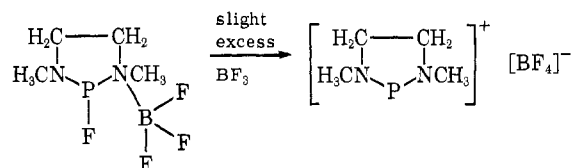
Evidence for the existence of two isomeric forms of  $\text{CH}_3\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{N}(\text{BF}_3)\text{PF}$  appears in the  $^{19}\text{F}$  spectrum of the solid dissolved in  $\text{CH}_2\text{Cl}_2$  (Figure 2). At temperatures from ambient to  $-40^\circ$  the mole ratio of isomers remains approximately 2:1 and the spectrum exhibits no broadening. From ambient temperatures to  $+55^\circ$  the isomer ratio remains nearly the same but the peaks begin to broaden slightly. From  $55$  to  $73^\circ$  broadening becomes more pronounced but rather than one isomer increasing in abundance, the signals for both isomers disappear and a single, very broad, irregular absorption appears at approximately  $+74.7$  ppm. As the sample is cooled, the absorption peaks of the two isomers in a 2:1 ratio reappear.

It is interesting to note that the exchange phenomenon observed in the room-temperature proton nmr of this compound is not evident in the analogous  $^{19}\text{F}$  spectrum (94.1 MHz) since the separation of the two B-F signals of the isomers on the  $^{19}\text{F}$  nmr scale is 205 cps. Thus the exchange rate of  $250 \text{ sec}^{-1}$  observed in the proton spectrum is slow compared to the separation (in frequency units *ca.*  $1290 \text{ sec}^{-1}$ ) of the  $^{19}\text{F}$  signals of the coordinated  $\text{BF}_3$  of the two isomers.

In order to investigate both the nature of the two isomeric forms of  $\text{CH}_3\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{N}(\text{BF}_3)\text{PF}$  and the reversible reaction noted in the temperature study, an nmr titration of I with varying amounts of  $\text{BF}_3$  was designed.

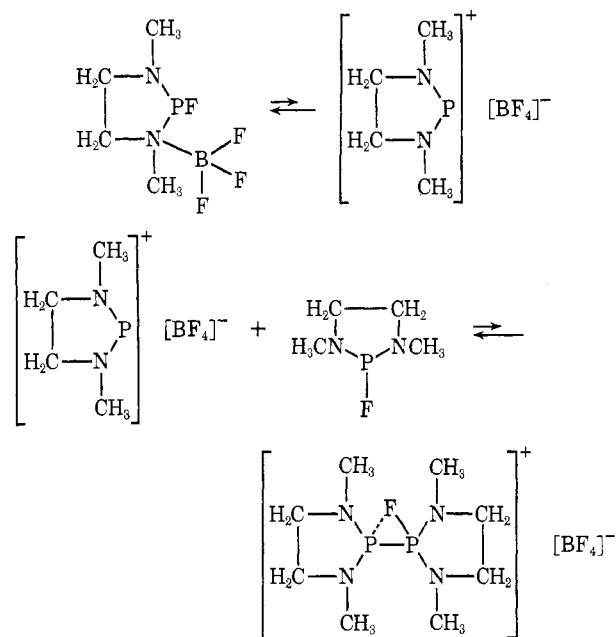
**4. Nmr Titration of I with  $\text{BF}_3$ .**—The  $^{19}\text{F}$  nmr data (see Experimental Section) for those samples in which the mole ratio of trifluoroborane to ligand is less than 1:1 indicate again the presence of two isomers. This evidence eliminates the possibility of one of the isomers being due to a 2:1 adduct. The  $^{19}\text{F}$  absorption,  $\delta_6$ , and the  $^{31}\text{P}$  absorption,  $\delta_2$  (Table II), are identified by their positions as collapsed doublets of excess ligand.

At a mole ratio of 1.03:1.00 a new weak, but sharp  $^{19}\text{F}$  absorption appears at  $+72.0$  ppm. This absorption corresponds to that reported for  $\text{BF}_4^-$ ,<sup>8,9</sup> indicating that in the presence of a slight excess of  $\text{BF}_3$  the following reaction may take place to a limited extent



Though the  $^{31}\text{P}$  nmr did not reveal a new absorption due to the phosphorus-containing cation, perhaps because of its low concentration, the low temperature ( $-30^\circ$ ) proton nmr does exhibit two new doublets centered at  $\delta -2.69$  ppm,  $J_{\text{NCH}_3\text{P}} = 12$  Hz, and  $\delta -3.31$ ,  $J_{\text{CH}_2\text{NP}} = 5$  Hz, and overlapping the *N*-methyl and methylene signals of the 1:1 adduct.

The presence of even trace amounts of such a cation-anion pair in samples one and two could account for the collapse of the  $^{19}\text{F}$  and  $^{31}\text{P}$  signals of the excess ligand by the mechanism



The most interesting feature of the titration, however, is revealed in an examination of the spectral data for the aliquot in which the reaction mixture was stirred for 12 hr under a trifluoroborane pressure of 1 atm. For this sample the  $^{19}\text{F}$  spectrum exhibits only a *single* absorption at  $+66.8$  ppm. The  $^{31}\text{P}$  doublet, located at  $-148$  ppm in the 1:1 adduct, disappears and is replaced by a sharp *singlet* located at  $-274$  ppm. The position of this absorption indicates a highly deshielded phosphorus atom. The proton nmr also exhibits a dramatic change. At room temperature the absorption bands attributable to the *N*-methyl protons and the methylene protons of the 1:1 adduct are broad and poorly resolved (Figure 1). Resolution of the methyl signal indicating two types of methyl protons is obtained at  $-30^\circ$ . On the other hand, the ambient proton spectrum of the sample under discussion consists of a sharp doublet at  $\delta -2.67$  ppm ( $J_{\text{NCH}_3\text{P}} = 11$  Hz) and a second sharp doublet at  $\delta -3.36$  ppm ( $J_{\text{CH}_2\text{NP}} = 5$  Hz), area ratio 6:4. There is no change in the structure of the spectrum as the temperature is lowered to  $-30^\circ$  (Figure 3).

However, when the excess  $\text{BF}_3$  is removed from this sample by pumping under vacuum for several hours, the

(8) R. D. Chambers, H. C. Clark, L. W. Reeves, and C. J. Willis, *Can. J. Chem.*, **39**, 258 (1961).

(9) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 946.

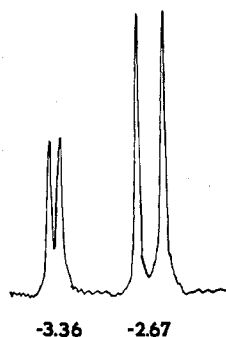
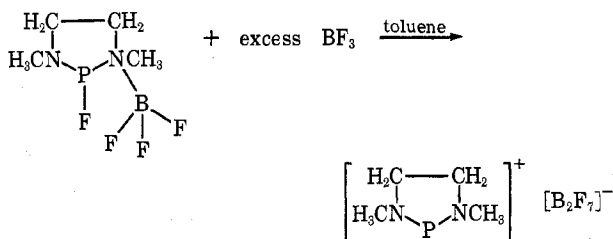


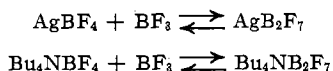
Figure 3.—Proton nmr spectrum of  $[\text{CH}_3\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{NP}]^+[\text{B}_2\text{F}_7]^-$ .

$^{19}\text{F}$  spectrum clearly indicates re-formation of the two isomeric forms of the 1:1 adduct.

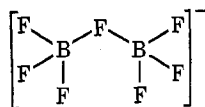
These changes in spectra as the stoichiometric amount of trifluoroborane is increased can be interpreted on the basis of formation of a cation-anion species



The  $\text{B}_2\text{F}_7^-$  anion was first reported by Brownstein and Paasivirta in 1965<sup>10</sup> as a result of equilibrium studies of the systems  $\text{AgBF}_4\text{-BF}_3$  and tetra-*n*-butylammonium fluoroborate- $\text{BF}_3$  in methylene chloride solution



These authors obtained the  $^{19}\text{F}$  nmr spectrum of the first system above under conditions such that the  $\text{AgB}_2\text{F}_7$  ion pair was the predominant species in the sample. They reported a  $^{19}\text{F}$  chemical shift for the  $\text{B}_2\text{F}_7^-$  anion of +67.4 ppm, a value corresponding closely to the shift of +66.8 ppm obtained for sample 5 in this study. On the basis of infrared evidence, the authors suggest a bent, bridged structure for the species



At temperatures as low as  $-103^\circ$  only a single signal was observed in the  $^{19}\text{F}$  spectrum suggesting rapid exchange between nonequivalent fluorines in the complex fluoroborate.

Later studies<sup>11,12</sup> amplified the earlier work but the nature of the cations involved in these equilibria investigations precluded extensive use of nmr to verify

the existence of an ion pair. On the other hand, examination of the nmr data for the system under discussion in this paper unequivocally supports formation of a cyclic cation as well as the  $\text{B}_2\text{F}_7^-$  anion.

In this system the presence of a phosphorus atom bonded to fluorine makes it possible to follow ion-pair formation using  $^{31}\text{P}$ ,  $^{19}\text{F}$ , and  $^1\text{H}$  nmr data. Disappearance of the high-field doublet of the 1:1 adduct ( $\delta -148$  ppm) in the  $^{31}\text{P}$  spectrum of the 1:1 adduct exposed to an excess of  $\text{BF}_3$  and appearance of a singlet at the extremely low value of  $-274$  ppm verifies the removal of the fluorine atom from phosphorus and the formation of a species containing a highly deshielded phosphorus atom. The value of the chemical shift is well below the normally reported range for phosphorus-containing compounds ( $-230$  to  $+450$  ppm).<sup>13</sup>

Further confirmation of the removal of fluorine from phosphorus is found in the  $^{19}\text{F}$  spectrum where the phosphorus-fluorine doublets of the 1:1 adduct disappear when the presence of excess  $\text{BF}_3$  favors ion-pair formation.

An unambiguous interpretation of the proton nmr is easily made if one assumes a cation-anion species. Equivalence of the *N*-methyl groups indicates the removal of coordinated  $\text{BF}_3$  in the presence of excess  $\text{BF}_3$  while doublet splitting of the *N*-methyl signal rather than a doublet of doublets verifies the removal of fluorine from the phosphorus atom. It is interesting to note that the higher order multiplet observed for the methylene protons of the free ligand, the borane adduct, and the trifluoroborane adduct becomes a simple first-order doublet upon removal of fluorine to form the cation.

Though  $^{11}\text{B}$  nmr absorptions were obtained for all samples in the series, little definitive information could be obtained from these data. However, in the samples consisting primarily of the 1:1 adduct (samples 1-4) incipient doublet splitting of the boron signal is observed. The coupling constant is approximately 14 Hz, a value corresponding closely to the  $J_{\text{BF}}$  of 15 Hz reported for  $\text{BF}_3$ .<sup>14</sup> Expansion of this signal revealed an asymmetric four-line multiplet resembling a 1:3:3:1 quartet which will be studied under higher resolution. At present it seems plausible to assume that the splitting of the boron signal is due to the three fluorine atoms. In sample 5 (Table II), on the other hand, no splitting is observed down to  $-10^\circ$  (solution solidifies below this temperature) supporting rapid exchange of fluorines in  $\text{B}_2\text{F}_7^-$ . The very small chemical shift difference between coordinated  $\text{BF}_3$  (+17.8 ppm) and  $\text{B}_2\text{F}_7^-$  (+17.3 ppm) is not unexpected in view of the observation of Phillips, *et al.*,<sup>15</sup> that  $^{11}\text{B}$  resonance signals of coordinated (tetrahedral)  $\text{BF}_3$  lie within a very small range. Since in  $\text{B}_2\text{F}_7^-$  the boron atoms would be expected to be in a tetrahedral environment, the observed difference of 0.5 ppm is reasonable.

**5. Reaction of I with  $\text{PF}_5$ .**—Further confirmation of the tendency of I to form an ionic species was observed in its reaction with  $\text{PF}_5$  in a 1:1 mole ratio

(10) S. Brownstein and J. Paasivirta, *Can. J. Chem.*, **43**, 1645 (1965).

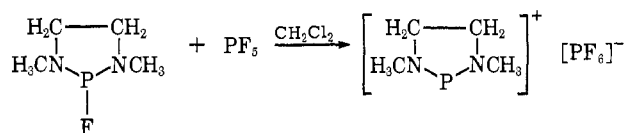
(11) P. J. Burchill, S. Brownstein, and A. M. Eastham, *ibid.*, **45**, 17 (1967).

(12) S. Brownstein, *ibid.*, **45**, 2403 (1967).

(13) J. R. Van Wazer and J. H. Letcher, *Top. Phosphorus Chem.*, **5**, 173 (1967).

(14) J. W. Emsley, *et al.*, ref 9, p 944.

(15) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **81**, 4496 (1959).



Fluorine-19 nmr of the solid, crystalline product in 1,2-dichloroethane exhibits only the doublet signal characteristic of  $\text{PF}_6^-$ . In the  $^{31}\text{P}$  nmr in addition to the characteristic septet of  $\text{PF}_6^-$  located at +144 ppm, one observes the singlet associated with the cation at -264 ppm. The position and intensity of this signal are greatly influenced by choice of solvent, broadening and disappearing almost completely in  $\text{CD}_3\text{CN}$  presumably due to interaction of the basic solvent with the acidic phosphorus of the cation. In  $\text{CD}_3\text{CN}$  the proton nmr consists of a sharp doublet at  $\delta$  -3.10 ppm ( $J_{\text{NCH}_3\text{P}} = 11$  Hz) and a second sharp doublet at  $\delta$  -3.83 ppm ( $J_{\text{CH}_3\text{NP}} = 5$  Hz), area ratio 6:4. Isolation of the cation in a stable species containing the  $\text{PF}_6^-$  anion offers further confirmatory evidence for the presence of the  $\text{B}_2\text{F}_7^-$  anion in the system  $\text{CH}_3\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{NPF}$ -excess  $\text{BF}_3$ .

### Discussion

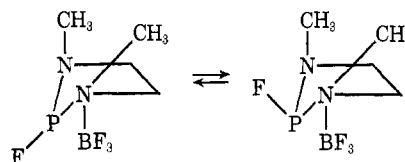
The geometry of  $\text{F}_2\text{PN}(\text{CH}_3)_2$  in the solid state has been determined crystallographically by Morris and Nordman<sup>16</sup> and in the gas phase using electron diffraction techniques by Hollywell, *et al.*<sup>17</sup> The planar  $\text{PN}(\text{C})\text{C}$  configuration and the P-N bond distance of 1.628 Å of the crystallographic study have been interpreted to indicate significant double bonding between N and P enhancing the base strength of the phosphorus atom and concomitantly reducing the base strength of the nitrogen atom. The weak B-N bonded adduct formed between  $\text{BF}_3$  and  $\text{F}_2\text{PN}(\text{CH}_3)_2$  seems to substantiate the postulate of reduced availability of the nitrogen electron pair for adduct formation. In the gas-phase study the P-N bond distance is reported as 1.648 Å and the  $\text{PN}(\text{C})\text{C}$  configuration is distorted from the planar configuration of the solid phase. Though no crystallographic or electron diffraction data are available for  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$ , its similarity to  $\text{F}_2\text{PN}(\text{CH}_3)_2$  in reaction with  $\text{BF}_3$  indicates a structure in which partial double bonding gives rise to a distortion of the normally tetrahedral nitrogen toward planarity. On the other hand, the greatly increased

stability of  $\text{CH}_3\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{N}(\text{BF}_3)\text{PF}$  may be due not only to steric effects but also to the presence of essentially tetrahedral nitrogen atoms possessing available electron pairs. Though no definitive evidence enabling one to determine the stereochemistry of the nitrogen atoms of  $(\text{CH}_3)\text{NCH}_2\text{CH}_2(\text{CH}_3)\text{NPF}$  was obtained during this investigation, the existence of isomers of its 1:1 adduct with  $\text{BF}_3$  can be interpreted without this information.

Three-coordinate nitrogen atoms of five-membered, unstrained heterocyclic compounds should undergo inversion with practically the same ease as analogous open-chain compounds.<sup>18,19</sup> However, the energy bar-

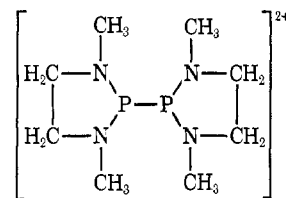
rier to inversion in trisubstituted phosphines has been estimated to be much higher, of the order of 30-60 kcal/mol. Though the inversion rate for  $\text{PH}_3$  is about  $10^6$  cps, doubling the substituent masses to give  $\text{PD}_3$  decreases the inversion rate to about  $10^3$  cps. Substitution of the much heavier fluorine atom and dialkyl-amino groups probably results in an even greater reduction of the inversion rate.<sup>19</sup>

Since four-coordinate nitrogen does not easily invert, the two sets of signals observed in the  $^{19}\text{F}$  nmr may then be assigned to the two invertomers

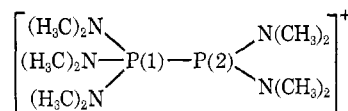


As noted previously, under the conditions employed in this study, no measurable change in the ratio of invertomers was noted over a wide temperature range (-40 to +73°) indicating a relatively large energy barrier to inversion. Recalling that at 73° all  $^{19}\text{F}$  signals due to the invertomers disappear and a single broad peak at about +74 ppm appears, it is tempting to postulate an ionic species as an intermediate in the conversion of one isomer to the other. Further evidence for the ionic species at 73° is found in the  $^{31}\text{P}$  spectrum where the phosphorous-fluorine doublet disappears. Though the  $^{31}\text{P}$  signal for the cation could not be detected, this is not surprising considering the sensitivity of this signal to experimental conditions. In view of the evidence presented for the formation of the  $\text{H}_3\text{CNCH}_2\text{CH}_2(\text{CH}_3)\text{NP}^+$  cation in the presence of excess  $\text{BF}_3$ , the postulate of an ionic intermediate does not seem unreasonable.

The question of dimerization of the cation to form



has been examined. Though this structure cannot be eliminated conclusively, the extremely low value of the  $^{31}\text{P}$  chemical shift (-274 ppm in toluene, -264 ppm in 1,2-dichloroethane) argues against dimerization. In the somewhat analogous structure



Schultz<sup>20</sup> has obtained chemical shift values of -50 and -90 ppm, respectively, for P(1) and P(2). Since P(2) in this diphosphonium ion would be in an environment somewhat similar to the phosphorus atoms of a dimeric structure, the substantially lower chemical shift values obtained indicate a monomeric structure for the new cation.

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## 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 were determined with either a Varian HR-100 (100 MHz) or a Varian Associates HR-60 at 60 MHz. Internal TMS and external TFA,  $B(OCH_3)_3$ , 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 Beckman IR-12. Elemental analyses were performed by Spang Laboratories, Ann Arbor, Mich.

**Materials.**—Commercial  $BF_3$  (Matheson) and  $B_2H_6$  (Callery) were fractionated in the vacuum system before use. Commercial  $PF_3$  (Ozark-Mahoning) and  $N,N'$ -dimethylethylenediamine (Ames) were used without further purification.

**Preparation of I.**—A 10-g (0.114-mol) sample of  $N,N'$ -dimethylethylenediamine was added to a 50-ml reaction flask under dry nitrogen. The gaseous nitrogen was replaced by a controlled flow of phosphorus trifluoride through the stirred amine over a period of 1 hr. After an initial induction period, the reaction proceeds rapidly and exothermically with the formation of solid amine hydrofluoride. Fractionation of the volatile components through traps held at  $-30.6$  and  $-196^\circ$  gave a crude product and unreacted amine in the  $-30.6^\circ$  trap and  $PF_3$  in the  $-196^\circ$  trap. Traces of unreacted amine were removed from the crude product by retreatment with  $PF_3$  and refraction-

ation. The purified  $CH_3NCH_2CH_2(CH_3)NPF$  has a vapor pressure of 4.5 mm at  $23.0^\circ$ ; yield 59% based on amine. Owing to its sensitivity to moisture, the product was handled only in a drybox. *Anal.* Calcd for  $C_4H_{10}N_2PF$ : C, 35.29; H, 7.42; F, 13.96; N, 20.58; P, 22.75; mol wt 136.13. Found: C, 35.40; H, 7.64; F, 14.17; N, 20.77; P, 22.57; mol wt 136 (mass spectral, parent ion). Ir (neat) ( $cm^{-1}$ ):  $\nu(C-H)$  2870 (s, br), 2800 (s);  $\delta^a(CH_3)$  1465 (m), 1440 (m);  $\delta^b(CH_2)$  1365 (vw), 1335 (m); 1250 (sh), 1230 (s), 1210 (s); 1145 (s); 1024 (s), 1003 (sh); 935 (s); 846 (m); 700 (s);  $\nu(P-F)$  650 (s, br); 583 (w);  $\delta(P-F)$  495 (m). The nmr spectra give the following constants:  $^1H$  (neat),  $\delta -3.15$  ppm relative to TMS (complex multiplet,  $CH_2CH_2$ , intensity 4),  $\delta -2.72$  ppm (d,  $J_{HP} = 13$  Hz,  $NCH_3$ , intensity 6), each member of the doublet being a doublet ( $J_{HF} = 3$  Hz);  $^{19}F$  (neat),  $\delta -13.3$  ppm relative to TFA (d,  $J_{FP} = 1055$  Hz,  $FP$  (N)N);  $^{31}P$  (neat),  $\delta -138$  ppm relative to 85%  $H_3PO_4$  (d,  $J_{PF} = 1047$  Hz). The spectra are fully consistent with the proposed structure.

**Preparation of  $H_3CNCH_2CH_2(CH_3)NP(BH_3)F$ .**—In a typical reaction a 2.45-mmol sample of diborane was condensed above a 0.5615-g (4.12-mmol) sample of I in a vacuum-line reaction vessel open to a manometer. The reaction mixture was then warmed to  $0^\circ$ . Rapid decrease of the pressure of diborane indicated strong interaction. The mixture was alternately

TABLE I  
COUPLING CONSTANTS (Hz) AND CHEMICAL SHIFTS (PPM) FOR

Sample	$BF_3$ :ligand	Reaction conditions	$CH_3NCH_2CH_2(CH_3)N(BF_2)PF$	
			Crystalline solid in $CH_2Cl_2$	Glassy liquid in $C_6H_5CH_3$
$^{19}F$ (TFA)	0.326:1.00	Reaction mixture stirred for 0.5 hr	$\delta(BF) +75.5$ ; $\delta_2(PF) -12.7$ ; $J_{F-P} = 1156$ collapsed d of excess free ligand	$\delta(BF) 74.7$ ; $\delta(PF) -2.2$ ; d, $J_{PF} = 1164$
		Reaction mixture stirred for 0.5 hr	$\delta_1(BF) +73.5$ ; $\delta_4(PF) -15.0$ ; $J_{F-P} = 1188$ collapsed d of excess free ligand	$\delta(BF) 72.6$ ; $\delta(PF) -15.9$ ; d, $J_{PF} = 1164$
$^{11}B$ ( $B(OCH_3)_3$ )	0.547:1.00	Reaction mixture stirred for 0.5 hr	$\delta_1(PF) -1.5$ ; $\delta_2(PF) -12.9$ ; $J_{F-P} = 1160$ collapsed d of excess free ligand	$\delta(BF) 72.6$ ; $\delta(PF) -15.9$ ; d, $J_{PF} = 1164$
		Reaction mixture stirred for 0.5 hr	$\delta_1(PF) -1.5$ ; $\delta_2(PF) -12.9$ ; $J_{F-P} = 1160$ collapsed d of excess free ligand	$\delta(BF) 72.6$ ; $\delta(PF) -15.9$ ; d, $J_{PF} = 1164$
$^{31}P$ ( $H_3PO_4$ )	1.00:1.00	Reaction mixture stirred for 0.5 hr	$\delta_1(PF) -1.5$ ; $\delta_2(PF) -12.9$ ; $J_{F-P} = 1160$ collapsed d of excess free ligand	$\delta(BF) 72.6$ ; $\delta(PF) -15.9$ ; d, $J_{PF} = 1164$
		Reaction mixture stirred for 0.5 hr	$\delta_1(PF) -1.5$ ; $\delta_2(PF) -12.9$ ; $J_{F-P} = 1160$ collapsed d of excess free ligand	$\delta(BF) 72.6$ ; $\delta(PF) -15.9$ ; d, $J_{PF} = 1164$
$^1H$ (TMS) <sup>a</sup>	1.03:1.00	Reaction mixture stirred for 0.5 hr	$\delta_1(PF) -1.5$ ; $\delta_2(PF) -12.9$ ; $J_{F-P} = 1160$ collapsed d of excess free ligand	$\delta(BF) 72.6$ ; $\delta(PF) -15.9$ ; d, $J_{PF} = 1164$
		Reaction mixture stirred for 0.5 hr	$\delta_1(PF) -1.5$ ; $\delta_2(PF) -12.9$ ; $J_{F-P} = 1160$ collapsed d of excess free ligand	$\delta(BF) 72.6$ ; $\delta(PF) -15.9$ ; d, $J_{PF} = 1164$

<sup>a</sup>  $CH_2$  proton signals appear in the  $-30^\circ$  spectra as broad complex multiplets in both solid and liquid adducts. d = doublet; q = quartet; br = broad.

Sample	$BF_3$ :ligand	Reaction conditions	$CH_3NCH_2CH_2(CH_3)NPF$ WITH $BF_3$		$^1H$ (TMS)
			$^{31}P$ ( $H_3PO_4$ )	$^{11}B$ ( $B(OCH_3)_3$ )	
1	0.326:1.00	Reaction mixture stirred for 0.5 hr	$\delta_1 -147$ , $J_{PF} = 1112$	$\delta_1 +17.8$ , $J_{BF} = 14.4$	No spectra obtained—overlap of excess free ligand
		Reaction mixture stirred for 0.5 hr	$\delta_2 -139$ ; collapsed d of excess free ligand	$\delta_1 +17.8$ , $J_{BF} = 14.4$ Hz	
2	0.547:1.00	Reaction mixture stirred for 0.5 hr	$\delta_1 -145$ , $J_{PF} = 1142$	$\delta_1 +17.8$ , $J_{BF} = 14.4$ Hz	No spectra obtained—overlap of excess free ligand
		Reaction mixture stirred for 0.5 hr	$\delta_2 -144$ ; collapsed d of excess free ligand	$\delta_1 +17.8$ , $J_{BF} = 14.4$	
3	1.00:1.00	Reaction mixture stirred for 0.5 hr	$\delta_1 -148$ , $J_{PF} = 1169$	$\delta_1 +17.8$ , $J_{BF} = 14.4$	No spectra obtained—overlap of excess free ligand
		Reaction mixture stirred for 0.5 hr	$\delta_2 -144$ ; collapsed d of excess free ligand	$\delta_1 +17.8$ , $J_{BF} = 14.4$	
4	1.03:1.00	Reaction mixture stirred for 0.5 hr	$\delta_1 -147$ , $J_{PF} = 1135$	$\delta_1 +17.7$ , $J_{BF} = 14.2$	Ambient $\delta(NCH_3) -2.69$ br $J_{HF} = 7.5$ $\delta(CH_2) -2.65$ br, $J_{HP} = 8$ $\delta(N(B)CH_3) -2.69$ , $J_{HP} = 12$ $\delta(CH_2) -2.69$ , $J_{HP} = 12$ $\delta(CH_2) -3.31$ , $J_{HP} = 5$ $\delta(CH_2) -2.68$ , $J_{HP} = 11$ $\delta(CH_2) -3.38$ , $J_{HP} = 5$
		Reaction mixture stirred for 0.5 hr	$\delta_2(BF_4^-) +72.0$	$\delta(CH_2) -3.11$ br	
5	Excess $BF_3$	Reaction mixture stirred for 12-14 hr under 1 atm $BF_3$ pressure	$\delta_3 -274$ ; d completely disappears	$\delta_3 +17.3$ ; sp, no splitting	Ambient $\delta(CH_2) -2.67$ , $J_{HP} = 11$ $\delta(CH_2) -3.36$ , $J_{HP} = 5$
		Excess $BF_3$ removed from sample 5 by pumping <i>in vacuo</i> for several hours	$\delta_3(B_2F_7^-) +66.8$	$\delta_3 +12.9$ ; w, dissolved $BF_3$ ? $\delta_1 +17.4$ ; br	
6	Excess $BF_3$ removed	Reaction mixture stirred for 12-14 hr under 1 atm $BF_3$ pressure	$\delta_3(BF_4^-) +71.8$	$\delta_3 +17.3$ ; sp, no splitting	Ambient $\delta(CH_2) -2.67$ , $J_{HP} = 11$ $\delta(CH_2) -3.36$ , $J_{HP} = 5$
		Excess $BF_3$ removed from sample 5 by pumping <i>in vacuo</i> for several hours	$\delta_3(BF_4^-) +71.8$	$\delta_3 +12.9$ ; w, dissolved $BF_3$ ? $\delta_1 +17.4$ ; br	

<sup>a</sup> Coupling constants (Hz) and chemical shifts (ppm). Starred values indicate cation signals.

cooled to  $-196^\circ$  and warmed to  $0^\circ$  for 1 hr and then warmed to room temperature. Excess diborane (0.485 mmol) and a small amount of noncondensable gas were pumped from the reaction mixture. A white, crystalline solid, contaminated by a yellow solid, remained. The air-stable, crystalline solid was purified by dissolving in cyclohexane, filtering under vacuum, and stripping off the solvent. The ratio of Lewis base to diborane was 2.08:1.00 indicating formation of 2 mol of borane adduct. *Anal.* Calcd for  $C_4H_{10}N_2PFBH_3$ : C, 32.03; H, 8.76; B, 7.21; F, 12.67; N, 18.68; P, 20.65. Found: C, 32.06; H, 8.61; B, 7.13; F, 12.56; N, 18.65; P, 20.66. Ir (Kel-F, Nujol mulls) ( $cm^{-1}$ ): Kel-F,  $\nu(C-H)$  2970 (vw), 2930 (m), 2890 (sh), 2860 (m), 2810 (w);  $\nu(B-H)$  2380 (s), 2330 (m), 2220 (w);  $\delta^s(CH_3)$  1475 (sh), 1465 (m), 1440 (w), 1415 (vw);  $\delta^s(CH_3)$  1370 (vw), 1345 (ms); Nujol, 1240 (s); 1200 (s); 1150 (s); 1140 (sh), 1135 (sh), 1120 (sh), 1072 (vw, sh), 1062 (w, sh), 1020 (s), 937 (s); 850 (w), 750 (vs, br);  $\nu(P-F)$  (?) 670 (mw); 552 (m). The nmr spectra are as follows:  $^1H$  (solvent  $CHCl_3$ ),  $\delta$   $-3.25$  ppm relative to TMS (complex multiplet, intensity 4,  $CH_2CH_2$ ),  $\delta$   $-2.76$  ppm (d,  $J_{HP} = 11$  Hz,  $NCH_3$ , intensity 6), each member of the doublet being a doublet ( $J_{HF} = 2.4$  Hz),  $\delta$   $-0.22$  ppm (quartet, 1:1:1:1,  $J_{HB} = 98$  cps,  $H_2B$ );  $^{19}F$  (solvent  $CHCl_3$ ),  $\delta$   $-21.2$  ppm relative to TFA (d,  $J_{FP} = 1150$  Hz,  $FP(N)N$ );  $^{31}P$  (solvent  $CHCl_3$ ),  $\delta$   $-129$  ppm relative to 85%  $H_3PO_4$  (d,  $J_{PP} = 1190$  Hz,  $FP(N)N$ ), signal greatly broadened due to splitting by boron;  $^{11}B$  (solvent  $CHCl_3$ ),  $\delta$   $+61.4$  ppm relative to  $B(OCH_3)_3$  (quintet, 1:4:6:4:1,  $J_{BH} = J_{BP} = 100$  Hz).

**Preparation of  $CH_3NCH_2CH_2(CH_3)N(BF_3)PF_6$ .**—Trifluoroborane, 8.20 mmol, was condensed above a 0.7245-g (5.32-mmol) sample of I dissolved in toluene. The reaction mixture was warmed to  $0^\circ$  and then slowly to room temperature over a 1-hr period. The temperature of the exothermic reaction was moderated by external cooling with a  $0^\circ$  slush bath. The reaction vessel was then warmed to room temperature and the volatile components were fractionated through traps held at  $-30.6$  and  $-196^\circ$ . Trifluoroborane, 2.48 mmol, was recovered from the  $-196^\circ$  trap. The ratio of Lewis acid to Lewis base consumed in the reaction was 1.07:1.00 indicating the formation of a 1:1 adduct.

Initially this adduct is a viscous, glassy liquid which crystallizes upon standing under vacuum for 1–2 days at room temperature. Sublimation of the white, crystalline solid by pumping on under vacuum in a sublimation tube chilled with liquid nitrogen yields an extremely hygroscopic compound of composition  $C_4H_{10}N_2PFBF_3$ . In every run a small amount of liquid did not crystallize. *Anal.* Calcd for  $C_4H_{10}N_2PBF_4$ : C, 23.56; H, 4.95; B, 5.30; F, 37.27; N, 13.74; P, 15.19. Found: C, 23.32; H, 4.81; B, by difference, 5.33; F, 37.11; N, 13.55; P, 14.88. Ir (Kel-F, Nujol mulls) ( $cm^{-1}$ ): Kel-F, 3200 (w, br);  $\nu(C-H)$  2900 (m, br), 2820 (w, sh);  $\delta^s(CH)$  1490 (m), 1475

(m, sh), 1460 (m), 1440 (m);  $\delta^s(CH)$  1365 (w), 1355 (w); Nujol, 1270 (s); 1230 (s);  $\nu(B-F)$  1210 (sh), 1200 (sh), 1185 (sh), 1165 (s), 1140 (s), 1110 (s), 1080 (s, sh); 1030 (s); 1000 (m); 970 (m); 930 (sh), 890 (s); 835 (m); 765 (m, sh), 735 (s); 645 (mw);  $\nu(P-F)$  (?) 605 (m); 540 (mw); 495 (m); 430 (w).

**Nmr Titration.**—In a typical titration run an 11.65-mmol sample of  $C_4H_{10}N_2PF_6$  was condensed with a 4-ml sample of toluene in a reaction tube fitted with a magnetic stirrer and a series of nmr tubes. Consecutive samples of  $BF_3$  were added to the reaction mixture, and aliquots of the resulting solutions were sealed in nmr tubes. Nmr data for the aliquots are reported in Table II.

**Preparation of  $[CH_3NCH_2CH_2(CH_3)NP]^+[PF_6]^-$ .**—A 3.42-mmol sample of  $PF_5$  was frozen in a reaction tube with a 3.00-mmol sample of I in 2 ml of  $CH_2Cl_2$ . The system was then warmed gradually to room temperature. After two such cycles of cooling and warming, excess  $PF_5$  and solvent were stripped off at room temperature. A white, crystalline solid remained in the reaction tube. Due to the difficulty of separating the excess  $PF_5$  from solvent, exact stoichiometry could not be obtained. The new compound owing to its slight sensitivity to moisture was handled in a drybox. It is slightly soluble in  $CH_2Cl_2$  and soluble in 1,2-dichloroethane and  $CH_3CN$ . *Anal.* Calcd for  $C_4H_{10}N_2P_2F_6$ : C, 18.37; H, 3.85; F, 43.50; N, 10.69; P, 23.63. Found: C, 18.50; H, 4.07; F, 43.42, 43.59; N, 10.73; P, 23.65. Ir (Kel-F, Nujol mulls) ( $cm^{-1}$ ): Kel-F,  $\nu(C-H)$  2915 (w), 2840 (w); 1780 (w) (962 + 825);  $\delta^s(CH_3)$  1480 (w), 1430 (w);  $\delta^s(CH_3)$  1375 (w), 1350 (w); Nujol, 1255 (m), 1220 (w), 1206 (w); 1190 (w); 1135 (ms); 1035 (mw), 1010 (w), 962 (mw);  $\nu(PF_6^-)$  825 (s, vbr); 720 (w); 587 (vw);  $\delta(PF_6^-)$  552 (s, sp). The nmr spectra are as follows:  $^1H$  (solvent  $CD_3CN$ ),  $\delta$   $-3.10$  ppm (d,  $J_{HP} = 11$  Hz,  $NCH_3$ , intensity 6),  $\delta$   $-3.83$  (d,  $J_{HP} = 5$  Hz,  $CH_2$ , intensity 4);  $^{19}F$  (solvent 1,2-dichloroethane),  $\delta$   $-6.1$  ppm (d,  $J_{F-P} = 710$  Hz);  $^{31}P$  (solvent 1,2-dichloroethane),  $\delta$   $+144.1$  ppm (septet,  $J_{P-F} = 710$  Hz);  $\delta$   $-264$  ppm. (In  $CD_3CN$  the signal at  $-264$  ppm broadens and is not detectable.)

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## Structure and Dynamics in Metal Tetrahydroborates. II.<sup>1</sup> Vibrational Spectra and Structures of Some Transition Metal and Actinide Tetrahydroborates

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Vibrational spectroscopy allows a reasonably unambiguous distinction to be made between monodentate, bidentate, and tridentate hydrogen-bridged metal-BH<sub>4</sub> interactions for covalent organo-transition metal and -actinide tetrahydroborates. The following compounds have bidentate structures:  $(h^5-C_5H_5)_2Ti(BH_4)_2$ ,  $(h^5-C_5H_5)_2Zr(BH_4)_2$ , and  $(h^5-C_5H_5)_2Zr(H)(BH_4)$ ; the organoactinides  $(h^5-C_5H_5)_3U(BH_4)$  and  $(h^5-C_5H_5)_3Th(BH_4)$  have tridentate geometries. Data on these systems can be understood in terms of analogies with other organometallic systems ( $\pi$ -allyls). The synthesis of  $(h^5-C_5H_5)_3Th(BH_4)$  is also reported.

### Transition metal and actinide tetrahydroborates<sup>3</sup>

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(2) (a) NDEA Predoctoral Fellow, 1970–present; (b) NSF Predoctoral Fellow, 1971–present.

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are of current interest to inorganic and organometallic chemists for a number of reasons. Ideally, studies of any system of molecules should rest upon a firm structural foundation. For metal tetrahydroborates, one of the most significant structural questions concerns the mode by which the BH<sub>4</sub> group is attached