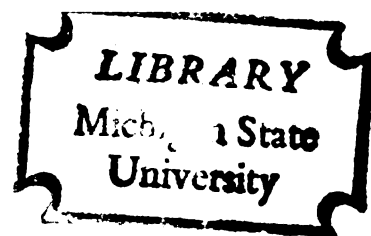


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THE INTERACTIONS OF  
DIMETHYLAMINOTETRAFLUOROPHOSPHORANE WITH  
AMMONIA AND HYDROGEN CHLORIDE : ATTEMPTED  
SYNTHESIS OF PHOSPHINOFLUOROARSINES,  
DIMETHYLAMINOPHOSPHINE, AND  
DIFLUOROAMINOPHOSPHINE

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*Thesis*



## ABSTRACT

THE INTERACTIONS OF DIMETHYLAMINOTETRAFLUOROPHOSPHORANE WITH AMMONIA AND HYDROGEN CHLORIDE: ATTEMPTED SYNTHESIS OF PHOSPHINOFLUOROARSINES, DIMETHYLAMINOPHOSPHINE, AND DIFLUOROAMINOPHOSPHINE

By

Edward Robert Falardeau

The interactions of dimethylaminotetrafluorophosphorane with hydrogen chloride and ammonia were investigated. The product of the reaction in which hydrogen chloride was used was tentatively identified as  $\text{PF}_4\text{Cl}\cdot\text{NH}(\text{CH}_3)_2$  by the use of nmr spectral and stoichiometric data. The interaction of  $\text{PF}_4\text{N}(\text{CH}_3)_2$  with ammonia produced diaminotrifluorophosphorane which was identified by the use of nmr spectral data.

The syntheses of phosphino fluoroarsines were attempted in two ways: first, by allowing phosphine to interact with arsenic trifluoride in the presence of a tertiary amine; second, by allowing arsenic trifluoride to interact with  $\text{LiAl}(\text{PH}_2)_4$ . Neither method was successful.

The synthesis of dimethylaminophosphine by reduction of dimethylaminodichlorophosphine with  $\text{LiH}$ ,  $\text{LiAlH}_4$ , and  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  was attempted. There was no reaction when  $\text{LiH}$  was used. The results obtained from reactions in which  $\text{LiAlH}_4$  and  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  were employed suggest the formation of an aluminium-amine complex.

The synthesis of difluoroaminophosphine was attempted by allowing phosphine to interact with tetrafluorohydrazine. The spectral data obtained on the compounds which resulted from this reaction could not be unequivocally interpreted.

THE INTERACTIONS OF DIMETHYLAMINOTETRAFLUOROPHOSPHORANE WITH  
AMMONIA AND HYDROGEN CHLORIDE: ATTEMPTED SYNTHESIS OF  
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DIFLUOROAMINOPHOSPHINE

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## INTRODUCTION

Many workers have examined the physical and chemical properties of aminophosphines. Some of the results have been rationalized by suggesting that the N-P bond arises from hybridized atomic orbitals forming a sigma molecular orbital. The bond is supplemented by additional pi molecular orbitals which arise from the delocalization of the lone pair of electrons on nitrogen into the empty d orbitals of phosphorous. Although the number of papers<sup>1-10</sup> which have employed multiple bond formation involving d orbitals to rationalize experimental results is large, there have been few systematic attacks in which conclusive evidence as to the consequences and extent of (p→d)π bonding has been obtained.

Experiments can not establish whether d orbitals are really used because the bonding models employed are primitive. A (p→d)π bond model is useful, however, because it enables many of the observed properties of aminophosphines to be brought into a coherent scheme.

In this thesis a report on the attempted synthesis of a number of compounds containing the N-P or the As-P bond is presented. It was hoped to use the data obtained to establish a descriptive framework which would delineate the extent to which d orbital participation could be used to predict the physical and chemical properties of these compounds. The syntheses which were attempted are: first, the synthesis of the mixed aminodialkylaminofluorophosphorane, aminodimethylaminotrifluorophosphorane, ((CH<sub>3</sub>)<sub>2</sub>NPF<sub>3</sub>NH<sub>2</sub>), by allowing

dimethylaminotetrafluorophosphorane,  $\text{PF}_4\text{N}(\text{CH}_3)_2$ , to interact with ammonia; second, the synthesis of the previously reported chlorotetrafluorophosphorane,<sup>28,31,33</sup>  $\text{PF}_4\text{Cl}$ , by allowing dimethylaminotetrafluorophosphorane to interact with hydrogen chloride; third, the synthesis of phosphinofluoroarsines,  $\text{AsF}_x(\text{PH}_2)_{3-x}$ , by allowing  $\text{LiAl}(\text{PH}_2)_4$  to interact with arsenic trifluoride or by allowing arsenic trifluoride to interact with phosphine in the presence of a tertiary amine; fourth, the synthesis of dimethylaminophosphine,  $\text{PH}_2\text{N}(\text{CH}_3)_2$ , by allowing dimethylaminodihalophosphine,  $\text{PX}_2\text{N}(\text{CH}_3)_2$ , to interact with several reducing agents; fifth, preparation of difluoroaminophosphine,  $\text{PH}_2\text{NF}_2$ , by allowing phosphine to interact with tetrafluorohydrazine in the presence of light.

## Experimental

### A. General

Standard high vacuum techniques were employed throughout. Proton and fluorine nmr spectra were obtained on a Varian Model 56/60 nuclear magnetic spectrometer operating at both ambient and low temperatures. Phosphorous nmr spectra were obtained on a Varian DP-60 nuclear magnetic spectrometer. Tetramethylsilane, fluorotrichloromethane, and trimethoxyphosphine were used as external standards by the use of the tube interchange technique for the  $H^1$ ,  $F^{19}$ , and  $P^{31}$  nmr respectively. The ir spectra were obtained on a Perkin-Elmer 301 spectrophotometer. A gas cell with a 7.5 cm path length and KBr or AgCl windows was employed for volatile samples. Mass spectra were obtained on RMU-6 Hitachi mass spectrometer. The gas phase reactions were carried out in a manner previously described.<sup>28,33</sup> The reaction conditions, the amounts used, and the observations obtained for reactions in which the gas phase was employed are summarized (Table 1).

### B. The Interaction of Dimethylaminotetrafluorophosphorane with Anhydrous Hydrogen Chloride

Samples of anhydrous hydrogen chloride (Matheson Co.) were purified by distillation in vacuo through traps held at  $-78^\circ$ ,  $-78^\circ$ , and  $-196^\circ$ . Samples of  $PF_4N(CH_3)_2$  were purified by distillation in vacuo through traps held at  $-45^\circ$ ,  $-78^\circ$ , and  $-196^\circ$ . The nmr spectral data obtained on  $PF_4N(CH_3)_2$  was identical to that previously described.<sup>32</sup> The vapor pressure at  $0^\circ$  was found to be 42.0 mm (literature value, 44.3 mm).<sup>32</sup>

Table 1  
Reactants, Conditions, and Observations  
for the Gas Phase Reactions

Reactants	mmol	Time	Temp	Observations
PF <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	2.9	30 sec	23°	immediate formation of finely divided white solid
HCl	5.6			
PF <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	3.6	5 min	23°	clear liquid deposited in droplets on sides of reaction bulb
NH <sub>3</sub>	7.6			
AsF <sub>3</sub>	3.0	12 hr	23°	mirror-like brown coating formed on sides of reaction bulb over a 12 hr period
PH <sub>3</sub>	6.0			
AsF <sub>3</sub>	3.0	20 sec	23°	immediate formation of brownish-white cloud
N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	5.0			
PH <sub>3</sub>	6.0			
AsF <sub>3</sub>	5.0	20 sec	23°	immediate formation of brownish-white cloud, brownish droplets were deposited on the walls of the reaction bulb
N(CH <sub>3</sub> ) <sub>3</sub>	5.1			
PH <sub>3</sub>	6.0			

Dimethylaminotetrafluorophosphorane and anhydrous hydrogen chloride were allowed to interact in the gas phase (Table 1). The volatile products were distilled in vacuo through traps held at 0°, -78°, and -196°. No volatile materials could be recovered from the 0° or -78° traps. The contents of the -196° trap were shown to be unreacted HCl with traces of  $\text{POF}_3$  and  $\text{SiF}_4$  by the characteristic ir spectra of these compounds.<sup>30,31</sup> The contents of the -196° trap were then distilled in vacuo through traps held at -78°, -127°, and -196°. The contents of the -78° and -127° traps combined was less than 0.1 mmol of volatile materials. The -196° trap held 2.1 mmol of unreacted HCl. This indicated an approximate 1:1 reaction of HCl with  $\text{PF}_4\text{N}(\text{CH}_3)_2$ .

The nonvolatile materials in the reaction bulb were investigated. Approximately 3 ml of acetone was condensed into the bulb. The bulb was removed from the vacuum line and allowed to warm to room temperature. The contents of the bulb were then transferred to a nmr tube. The sample was a clear yellow liquid. The  $\text{H}^1$ ,  $\text{F}^{19}$ , and  $\text{P}^{31}$  nmr spectra of the sample were obtained (Figures 1, 2, 3). These results are presented and discussed in a subsequent portion of this paper.

#### C. The Interaction of Dimethylaminotetrafluorophosphorane with Ammonia

Ammonia (Matheson Co.) was dried over sodium prior to use at -60°. Dimethylaminotetrafluorophosphorane was purified as previously described.<sup>32</sup> A gas phase reaction (Table 1) resulted in some volatile products. These were distilled in vacuo through traps held at -45° and -196°. All of the volatile products remained in the -45° trap. These products were solid at 23°. The  $\text{H}^1$  and  $\text{F}^{19}$  nmr spectral data obtained on these products was identical to that previously described for diaminotri-fluorophosphorane.<sup>29</sup>

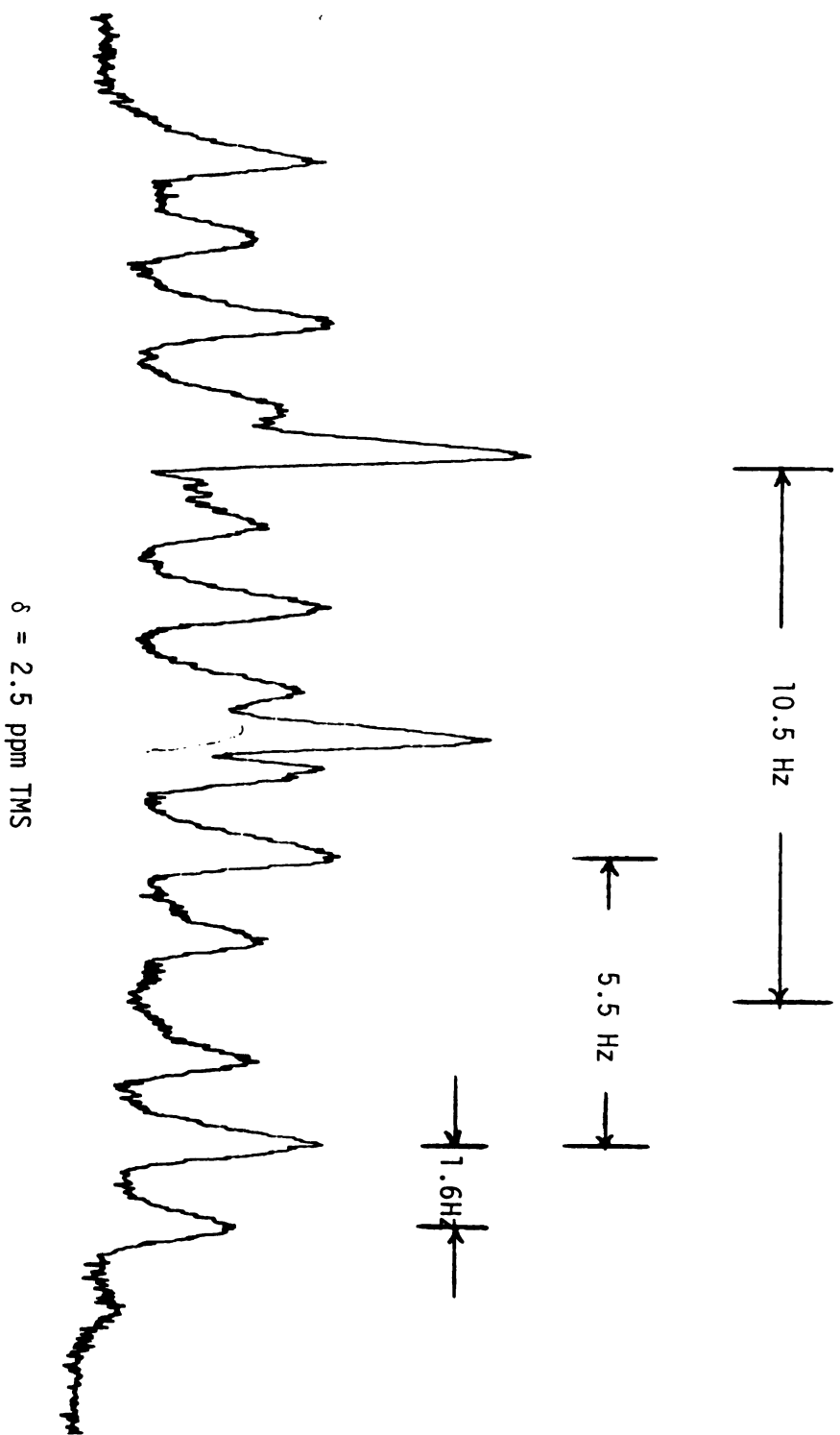
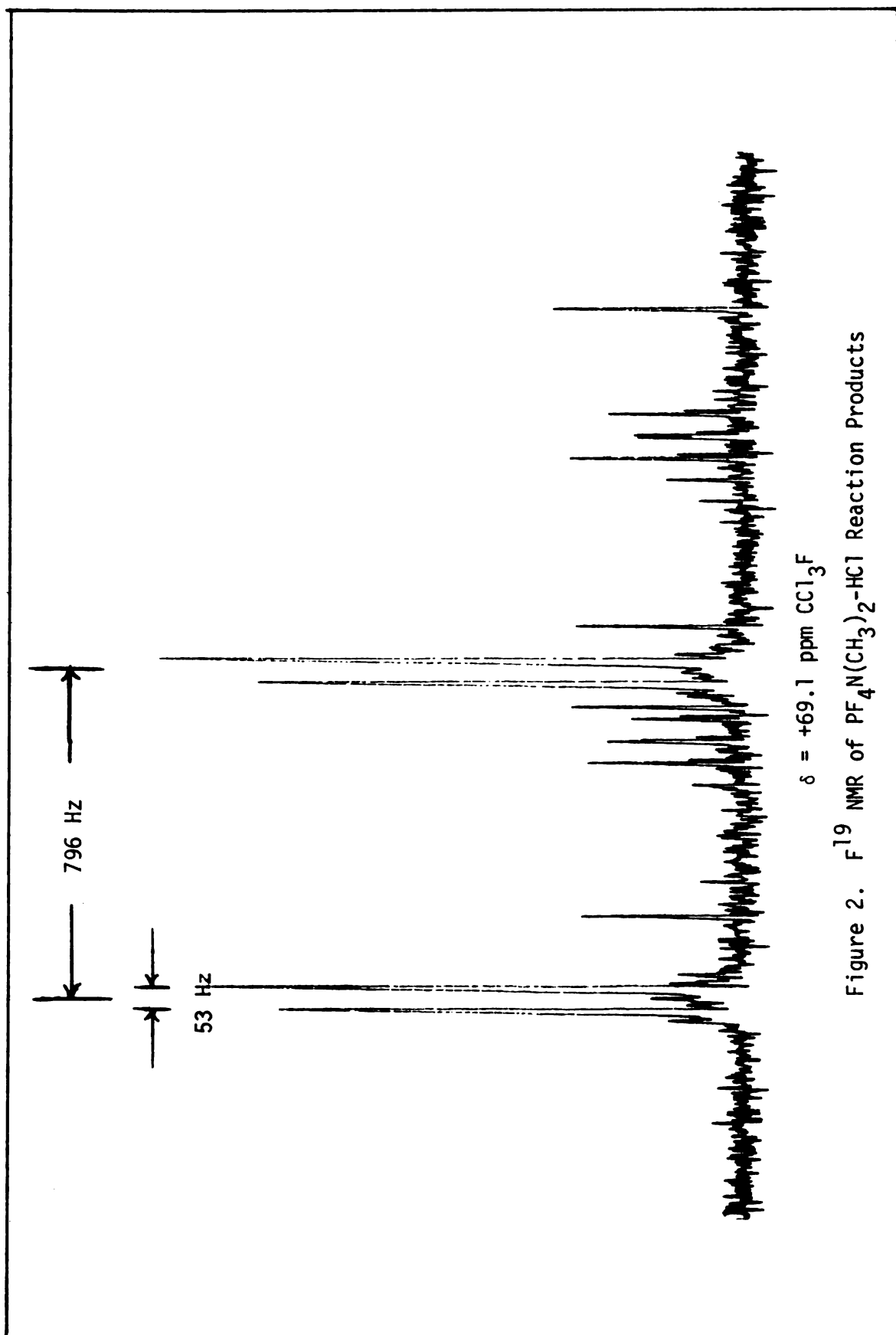
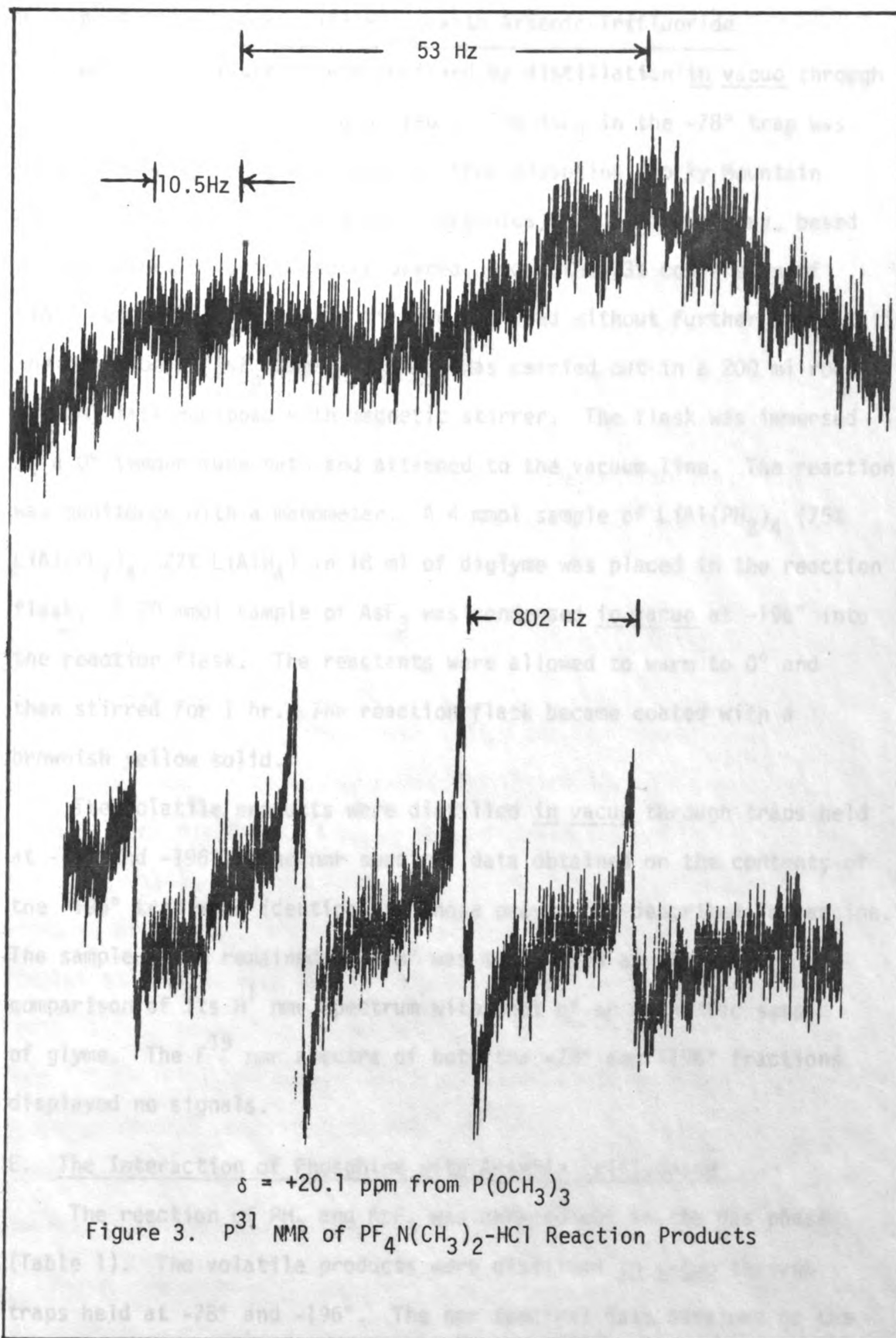


Figure 1.  $^1\text{H}$  NMR of  $\text{PF}_4\text{N}(\text{CH}_3)_2\cdot\text{HCl}$  Reaction Products





#### D. The Interaction of $\text{LiAl}(\text{PH}_2)_4$ with Arsenic Trifluoride

Arsenic trifluoride was purified by distillation in vacuo through traps held at  $-45^\circ$ ,  $-78^\circ$ , and  $-196^\circ$ . The  $\text{AsF}_3$  in the  $-78^\circ$  trap was used. The  $\text{LiAl}(\text{PH}_2)_4$  was prepared from phosphine (Rocky Mountain Research Co.) and  $\text{LiAlH}_4$  (Alpha Inorganics).<sup>16</sup> Stoichiometry, based on the amount of phosphine recovered, indicated 73% conversion of  $\text{LiAlH}_4$  to  $\text{LiAl}(\text{PH}_2)_4$ . This mixture was used without further purification. The reaction of  $\text{AsF}_3$  and  $\text{LiAl}(\text{PH}_2)_4$  was carried out in a 200 ml round bottom flask equipped with magnetic stirrer. The flask was immersed in a  $0^\circ$  temperature bath and attached to the vacuum line. The reaction was monitored with a manometer. A 4 mmol sample of  $\text{LiAl}(\text{PH}_2)_4$  (75%  $\text{LiAl}(\text{PH}_2)_4$ , 27%  $\text{LiAlH}_4$ ) in 18 ml of diglyme was placed in the reaction flask. A 20 mmol sample of  $\text{AsF}_3$  was condensed in vacuo at  $-196^\circ$  into the reaction flask. The reactants were allowed to warm to  $0^\circ$  and then stirred for 1 hr. The reaction flask became coated with a brownish yellow solid.

The volatile products were distilled in vacuo through traps held at  $-78^\circ$  and  $-196^\circ$ . The nmr spectral data obtained on the contents of the  $-196^\circ$  trap were identical to those previously described for arsine.<sup>38</sup> The sample which remained at  $-78^\circ$  was identified as diglyme by comparison of its  $^1\text{H}$  nmr spectrum with that of an authentic sample of glyme. The  $^{19}\text{F}$  nmr spectra of both the  $-78^\circ$  and  $-196^\circ$  fractions displayed no signals.

#### E. The Interaction of Phosphine with Arsenic Trifluoride

The reaction of  $\text{PH}_3$  and  $\text{AsF}_3$  was carried out in the gas phase (Table 1). The volatile products were distilled in vacuo through traps held at  $-78^\circ$  and  $-196^\circ$ . The nmr spectral data obtained on the sample held at  $-78^\circ$  were identical to that of an authentic sample of

AsF<sub>3</sub>. The nmr spectral data obtained on the contents of the -196° trap were identical to that of an authentic sample of PH<sub>3</sub>.

F. The Interaction of Phosphine with Arsenic Trifluoride in the Presence of Triethylamine

Triethylamine was dried over sodium at 23° for 24 hr prior to use. A gas phase reaction was employed (Table 1). The volatile products were distilled in vacuo through traps held at -45°, -78°, and -196°. The nmr spectral data obtained on the -78° sample was identical to that of authentic samples of AsF<sub>3</sub> and N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>. The nmr spectral data of the -196° sample was identical to that of an authentic sample of PH<sub>3</sub>. The nonvolatile material left in the reaction bulb was not investigated.

G. The Interaction of Phosphine with Arsenic Trifluoride in the Presence of Trimethylamine

Trimethylamine was dried over sodium at -60° for 48 hr prior to use. A gas phase reaction was employed (Table 1). The volatile products were distilled in vacuo through traps held at -45°, -78°, and -196°. The -45° trap held a liquid which exhibited a vapor pressure of 8 mm at 23°. The F<sup>19</sup> nmr spectrum consisted of a broad singlet at +53 ppm from CCl<sub>3</sub>F. The H<sup>1</sup> nmr spectrum consisted of a broad singlet at +1.7 ppm from TMS. The sample melted fairly uniformly from 13° to 15°. The compound was purified by another distillation in vacuo through traps held at -45° and -196°. The melting point was found to be 10° to 12°. Anal, Found: C, 23.11, 21.43; H, 5.62, 5.28. The mass spectral data is summarized in Table 2.

H. The Interaction of Dimethylaminodifluorophosphine with Lithium Hydride

LiH (Metal Hydrides Inc.) was used without further purification. Dimethylaminodifluorophosphine was prepared and purified as previously

Table 2  
Mass Spectral Data of  $\text{AsF}_3\text{-N(CH}_3)_3$  Reaction Products

m/e	Relative Intensity	Assignment
155	1	?
96	9.1	?
81	40.5	?
66	1	?
59	29	$\text{N(CH}_3)_3^+$
58	80	$\text{N(CH}_3)_2\text{CH}_2^+$
56	2	?
47	8	?
42	20	$\text{N(CH}_3)_2^+$
30	15	$\text{NCH}_3^+$
15	9	$\text{CH}_3^+$

described.<sup>20</sup> A 24 mmol sample of LiH was placed in a 200 ml round bottom flask which was equipped with a magnetic stirrer. The flask was connected to the vacuum line and a 12 mmol sample of  $\text{PF}_2\text{N}(\text{CH}_3)_2$  were condensed into the flask in vacuo at  $-196^\circ$ . The reactants were allowed to warm to  $23^\circ$  and stirred for 3 hr. No evidence of reaction was observed in the flask. The nmr spectral data obtained on the volatile products of the reaction were identical to that of an authentic sample of the reactants,  $\text{PF}_2\text{N}(\text{CH}_3)_2$  and diglyme.

#### I. The Interaction of Lithium Hydride with Dimethylaminodichlorophosphine

Dimethylaminodichlorophosphine was prepared by reaction of phosphorous trichloride with dimethylamine.<sup>20</sup> It was purified by distillation in vacuo through traps held at  $-45^\circ$  and  $-196^\circ$ . The fraction held in the  $-45^\circ$  trap was used.

A 100 mmol sample of LiH in approximately 10 ml of di-n-butyl ether was placed in a two necked 200 ml round bottom flask. The flask was attached by means of an adapter equipped with a stopcock to the vacuum system. A 50 mmol sample of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  was placed in a 50 ml bulb equipped with a stopcock. The storage bulb was attached to the reaction flask by means of an adapter which was fitted with a sintered glass disc. The reaction flask was evacuated and cooled to  $-78^\circ$ . The stopcock which connected the storage bulb and the reaction flask was slowly opened. The  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  then dripped through the filter at a slow rate. After 1 hr all of the  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  had been added and no visible reaction had taken place. The reaction system was then allowed to warm to room temperature over a period of 2 hr. The nmr spectral data of the volatile materials were identical to that of authentic samples of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  and di-n-butyl ether which indicated that no reaction took place.

J. The Interaction of Lithium Tetrahydroaluminate with Dimethylamino-dichlorophosphine

$\text{LiAlH}_4$  (Alpha Inorganics) was used without further purification. Dimethylaminodichlorophosphine was prepared and purified as previously described.<sup>20</sup> The reaction equipment and procedure were the same as those described in section I. After the reaction was allowed to proceed for 1 hr, the volatile products were distilled in vacuo through traps held at  $-78^\circ$  and  $-196^\circ$ . The nmr spectral data obtained on the volatile products were identical to that of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  and di-n-butyl ether. This reaction was attempted several times with and without solvent and at temperatures ranging from  $-78^\circ$  to  $23^\circ$ . In every attempt a yellow nonvolatile solid remained in the reaction flask after the volatile materials were removed. The volatile materials were always identified as  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  and solvent.

K. The Interaction of Dimethylaminodichlorophosphine with "Redal"

"Redal" (Aldrich Chemical Co.) is a 70% solution of sodium dihydro-bis(2-methoxyethoxy)aluminate,  $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ , in benzene.  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  was prepared and purified as previously described.<sup>20</sup>

A 60 mmol sample of Redal was placed in a 200 ml flask. The flask was attached to the vacuum line and a 57 mmol sample of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  was distilled in vacuo into the flask. The reaction mixture was allowed to warm to  $0^\circ$  and was stirred constantly. After the mixture warmed a violent reaction took place and a gas was liberated. The gas could not be condensed at  $-196^\circ$ . Yellow solid was present everywhere in the reaction system.

The volatile products were distilled in vacuo through traps held at  $-45^\circ$ ,  $-78^\circ$ , and  $-196^\circ$ . The nmr spectral data of the contents of

the  $-45^{\circ}$  trap were identical to that of authentic samples of benzene and  $\text{PCl}_2\text{N}(\text{CH}_3)_2$ . The  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  was present in extremely small amounts.

Due to the violence of the reaction another procedure<sup>20</sup> was tried. A 60 mmol sample of Redal, diluted 50% by volume with toluene, was placed in a dropping funnel which was attached to a 500 ml three necked flask. A 60 mmol sample of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  was placed in the reaction flask and the other two necks were fitted with a stirrer and a dry ice condenser. The Redal-toluene mixture was added dropwise over a period of 2 hr. The nitrogen flow rate through the system was adjusted to about 20 cc/min. When a drop of Redal hit the  $\text{PCl}_2\text{N}(\text{CH}_3)_2$ , a white cloud formed, and the pressure of the system decreased. The reaction mixture turned yellow and thickened. After the addition of "Redal" was complete, the reaction flask was allowed to warm to room temperature. The dry ice condenser was replaced by a connection to a U-trap held at  $-78^{\circ}$ . The volatile products were carried into the U-trap by the nitrogen stream. The nmr spectral data obtained on the contents of the U-trap were identical to that of authentic samples of benzene and toluene. A large amount of yellow nonvolatile solid remained in the reaction flask. The solid was insoluble in pentane and carbon disulfide. In water it formed a gel. The solid dissolved in methylene chloride to give a clear yellow solution. The  $^1\text{H}$  nmr of the solid dissolved in  $\text{CH}_2\text{Cl}_2$  is shown in Figure 4.

#### L. The Interaction of Tetrafluorohydrazine with Phosphine

Tetrafluorohydrazine (Air Products) and  $\text{PH}_3$  (Rocky Mountain Research) were used without further purification. The reaction was carried out in the gas phase in a 500 ml reaction bulb.

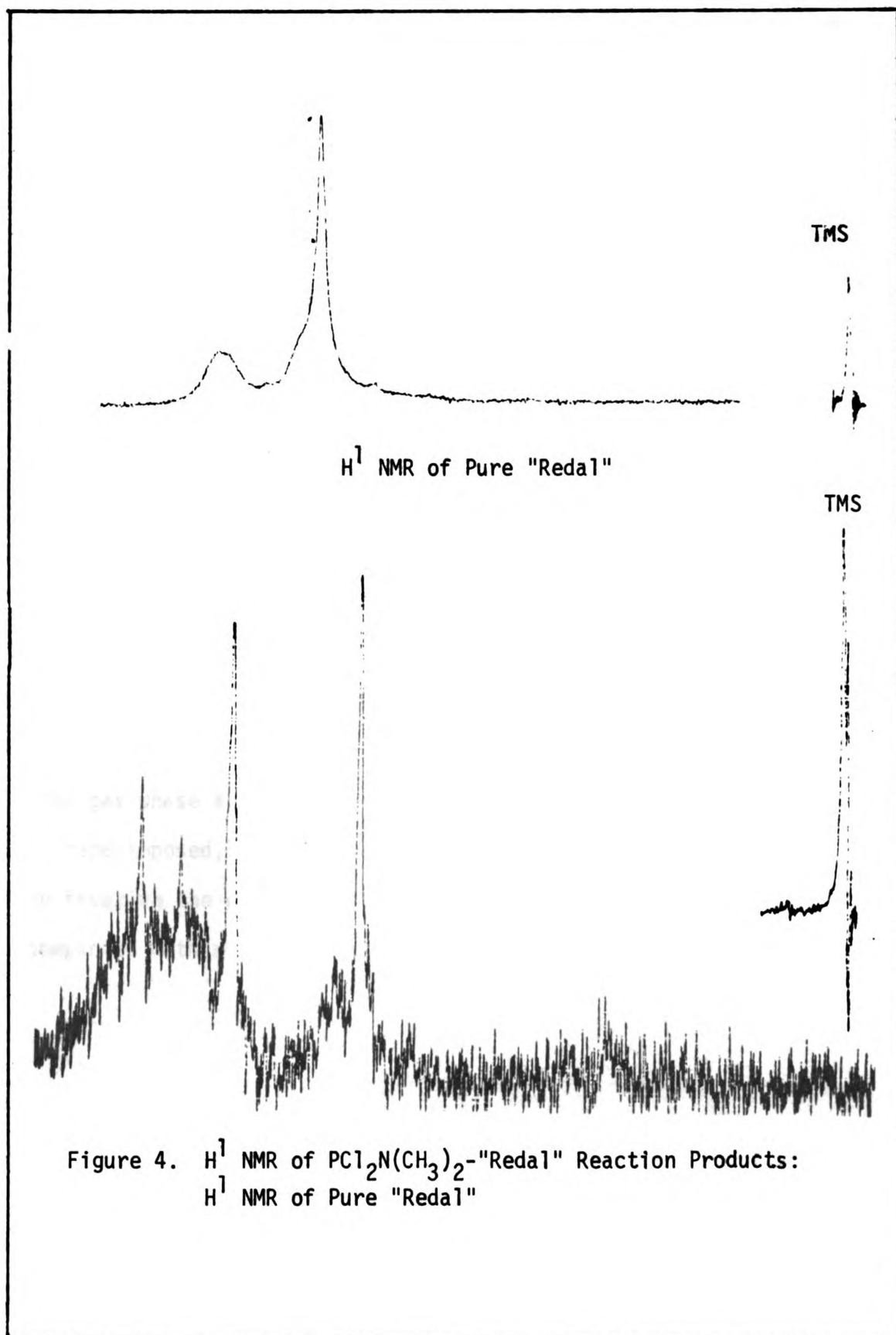


Figure 4.  $^1\text{H}$  NMR of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$ - "Redal" Reaction Products:  
 $^1\text{H}$  NMR of Pure "Redal"

In a typical reaction a 4 mmol sample of phosphine and a 4 mmol sample of tetrafluorohydrazine were condensed in vacuo at  $-196^{\circ}$  into the reaction bulb. The bulb was then removed from the vacuum system and placed behind an explosion shield in a fume hood. The reactants were allowed to warm to  $23^{\circ}$  and irradiated at intervals with an ultra-violet light source. Total irradiation was 310 min over a period of 50 hr. The inner surface of the reaction bulb turned light green during the course of the reaction. At the end of 50 hr, the reaction bulb was reconnected to the vacuum system and the entire contents transferred to a nmr tube. The  $H^1$  nmr, obtained at  $-100^{\circ}$ , exhibited two doublets of approximate 2:1 areas. The larger doublet was identified as phosphine by comparison of the chemical shift and coupling constant with an authentic sample of phosphine. The smaller doublet ( $\delta = -0.5 \pm 0.2$  ppm from  $PH_3$ ,  $J_{P-H} = 177 \pm 2$  Hz) was not identified. The  $F^{19}$  nmr spectra consisted of a broad singlet at +4.7 ppm from  $CCl_3F$ ;  $N_2F_4$  lit. 4.7 ppm from  $CCl_3F$ .<sup>21</sup> The ir spectra in the gas phase at 20 mm pressure showed the spectra of  $PH_3$  and  $N_2F_4$  superimposed.<sup>21</sup> The mass spectral data is summarized in Table 3. Upon freezing the reaction mixture to  $-196^{\circ}$  a violent explosion accompanied with a loud report occurred.

Table 3  
Mass Spectrum of  $\text{PH}_3\text{-N}_2\text{F}_4$  Reaction

m/e	Relative Intensity	Assignment
104	1	$\text{N}_2\text{F}_4^+$
88	3	$\text{PF}_3^+$
85	5	$\text{PH}_2\text{NF}_2^+$ or $\text{N}_2\text{F}_3^+$
69	4	$\text{PF}_2^+$
66	2	$\text{PH}_2\text{NF}^+$ or $\text{N}_2\text{F}_2^+$
53	12	$\text{NF}_2\text{H}^+$
52	110	$\text{NF}_2^+$
47	3	$\text{PH}_2\text{N}^+$ or $\text{N}_2\text{F}^+$
46	3	$\text{PHN}^+$
34	125	$\text{PH}_3^+$
33	180	$\text{PH}_2^+$ , $\text{NF}^+$
32	120	$\text{PH}^+$
31	80	$\text{P}^+$
28	62	$\text{N}_2^+$



## DISCUSSION

### A. Reactions of $\text{PF}_4\text{N}(\text{CH}_3)_2$ with $\text{HCl}$ and $\text{NH}_3$

#### 1. Reaction with $\text{HCl}$

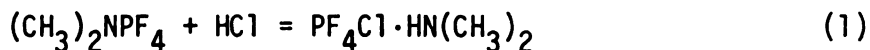
The reaction between dimethylaminotetrafluorophosphorane and anhydrous hydrogen chloride has been reported to yield chlorotetrafluorophosphorane,  $\text{PF}_4\text{Cl}$ , and  $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ <sup>28,33</sup> as products. In the present investigation the reaction was carried out under identical conditions to those previously described.<sup>28,33</sup> Hydrogen chloride was the only volatile product. The reaction stoichiometry suggested that one mole of  $\text{HCl}$  reacted with one mole of  $\text{PF}_4\text{N}(\text{CH}_3)_2$ . The nonvolatile products of the reaction were investigated by the use of nmr spectroscopy. These data suggest that an adduct,  $\text{PF}_4\text{Cl} \cdot \text{HN}(\text{CH}_3)_2$ , was formed when  $\text{HCl}$  and  $\text{PF}_4\text{N}(\text{CH}_3)_2$  were allowed to interact.

In the following discussion of the nmr data the methyl protons are referred to as the B protons and the other proton as the A proton. The  $^1\text{H}$  nmr spectrum (Figure 1) showed a quintet or triplet of doublets of doublets at  $\delta = +2.5$  ppm from TMS. The splitting can be rationalized as the signal split into a doublet,  $J_{\text{P}-\text{H}_\text{B}} = 10.5$  Hz, each member of which is further split into a doublet,  $J_{\text{H}_\text{A}-\text{H}_\text{B}} = 5.5$  Hz, which in turn is split by the fluorines into a triplet or quintets,  $J_{\text{F}-\text{H}_\text{B}} = 1.6$  Hz. A signal that could be attributed to the A proton was not observed. The fact that the samples were dilute and that the A proton was attached to a nucleus with a large quadrupole moment suggests that the signal was too weak and broad to be observed.

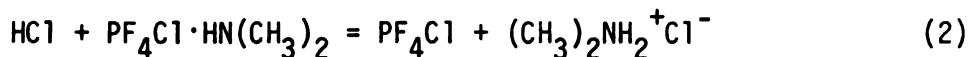
The  $F^{19}$  nmr spectrum (Figure 2) showed a doublet of doublets at  $\delta = +69.1$  ppm from  $CCl_3F$ . The splitting can be rationalized as the signal split into a doublet,  $J_{P-F} = 796$  Hz, each member of which is further split into a doublet,  $J_{H_A-F} = 53$  Hz. Splitting due to the methyl protons was not observed.

The  $P^{31}$  nmr spectrum showed a quintet each member of which was split into a doublet further split into at least a quintet or a septet with the outer two members unresolved at  $\delta = +201$  ppm from  $P(OCH_3)_3$ . The spectrum can be rationalized as the four equivalent fluorines splitting the signal into quintets,  $J_{P-F} = 802$  Hz, each member of which is further split by the A proton into a doublet,  $J_{P-H_A} = 53$  Hz, each member of which is split by the B protons into a septet,  $J_{P-H_B} = 10.5$  Hz.

The magnitude of the P-F coupling constant and the  $P^{31}$  chemical shift are characteristic of tetrafluorophosphorane compounds.<sup>32</sup> The interpretation of the nmr data supports the formation of  $PF_4Cl \cdot HN(CH_3)_2$ . However, these results are equivocal because the compound was impure and attempts to purify the compound failed. Impurities present in the nmr spectra could not be identified but were less than 20% when compared to characterized absorptions. Other workers have shown that the reaction between  $PF_4N(CH_3)_2$  and HCl does not always yield  $PF_4Cl$  and  $(CH_3)_2NH_2^+Cl^-$ .<sup>40,18</sup> On the basis of results obtained in this study, it can be suggested that the first step in the reaction may be described by equation 1.



This adduct will, under conditions not fully understood, spontaneously decompose according to equation 2.





## 2. Reaction with $\text{NH}_3$

The first amino or mixed amino-dialkylamino derivatives of phosphorous pentafluoride were reported in 1970. Roesky and Lustig prepared diaminotrifluorophosphorane,  $\text{PF}_3(\text{NH}_2)_2$ , from the interaction of  $\text{PF}_5$  with  $\text{NH}_3$ .<sup>29</sup> Their results differed from an earlier investigation of the  $\text{PF}_5\text{-NH}_3$  system which reported the formation of various solids of general composition  $x\text{PF}_5\text{-yNH}_3$  where  $5 \leq x, y \leq 1$ .<sup>35</sup> We attempted to prepare a mixed amino-dialkylamino trifluorophosphorane,  $\text{H}_2\text{NPF}_3\text{N}(\text{CH}_3)_2$ , by the interaction of  $\text{PF}_4\text{N}(\text{CH}_3)_2$  and  $\text{NH}_3$ . The nmr spectral data indicated  $\text{PF}_3(\text{NH}_2)_2$  to be the major product. The formation of  $\text{PF}_3(\text{NH}_2)_2$  indicates that this compound is more stable than either  $\text{PF}_4\text{NH}_2$  or  $\text{H}_2\text{NPF}_3\text{N}(\text{CH}_3)_2$ .

## B. Attempted Synthesis of Phosphinofluoroarsines

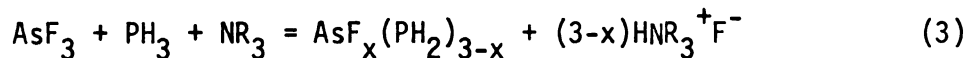
### 1. Interaction of $\text{LiAl}(\text{PH}_2)_4$ with $\text{AsF}_3$

Norman used  $\text{LiAl}(\text{PH}_2)_4$  to prepare phosphinosilanes.<sup>13</sup> This suggested that  $\text{LiAl}(\text{PH}_2)_4$  could interact with  $\text{AsF}_3$  to produce phosphinofluoroarsines. The only volatile product obtained was arsine. The formation of arsine can be attributed to the interaction of  $\text{AsF}_3$  with the impurity,  $\text{LiAlH}_4$ , which was present in the reaction system.<sup>25</sup> No  $\text{AsF}_3$  or  $\text{PH}_3$  remained at the end of the reaction. This indicated that all of the fluorine and phosphorous were tied up as nonvolatile brown solids. If the formation of phosphinofluoroarsines had taken place, they probably would have been volatile. No attempt to identify the solid was made.

### 2. Interaction of $\text{AsF}_3$ , $\text{PH}_3$ and $\text{NR}_3$

The formation of ionic amine-hydrogen halides is a strong driving force in many reactions.<sup>34</sup> Thus, syntheses directed at producing

phosphinofluoroarsines by use of reaction mixtures of  $\text{AsF}_3$ ,  $\text{NR}_3$ , and  $\text{PH}_3$  were attempted. This reaction was expected to proceed in a manner similar to that summarized by equation 3.



The tertiary amines were employed in this reaction to scavenge the HF which would form (equation 4).



It was found that when a mixture of  $\text{AsF}_3$  and  $\text{N}(\text{CH}_3)_3$  were allowed to interact with  $\text{PH}_3$  for 20 sec in the gas phase, a brownish white cloud formed. When the volatile products were removed by distillation in vacuo, a slightly volatile liquid (vp = 8mm; mp = 10-13) and unreacted  $\text{PH}_3$  were obtained. Although samples of the liquid obtained in several different runs melted over a constant, relatively narrow, temperature range, attempts to obtain consistent elemental analysis were unsuccessful. The  $\text{H}^1$  nmr spectrum of the liquid consisted of a broad singlet at +1.7 ppm from TMS. The  $\text{F}^{19}$  nmr spectrum of the liquid consisted of a broad singlet at +53 ppm from  $\text{CCl}_3\text{F}$ . The interpretation of the mass spectral data suggested that the predominate ions in the fragmentation pattern arose from  $\text{N}(\text{CH}_3)_3$ . The liquid can not be unequivocally identified. However, the mass spectral data suggests the presence of a  $\text{N}(\text{CH}_3)_3$  group. Also, interpretation of the  $\text{F}^{19}$  nmr spectrum indicates fluorine(s) to be in a magnetic environment similar to those of the fluorines in  $\text{AsF}_3$  ( $\text{AsF}_3$ , broad singlet at  $\delta = 52.5$  ppm from  $\text{Cl}_3\text{F}$ , liquid, broad singlet at  $\delta = +53$  ppm from  $\text{CCl}_3\text{F}$ ). Since  $\text{AsF}_3$  and  $\text{N}(\text{CH}_3)_3$  do not react in the gas phase, further investigation to ascertain the role of phosphine in the reaction and to establish the identity of the liquid is needed.

C. Attempted Synthesis of  $\text{PH}_2\text{N}(\text{CH}_3)_2$  by Reduction of  $\text{PX}_2\text{N}(\text{CH}_3)_2$

Alkyl phosphines,<sup>11,12,16</sup> aryl<sup>11</sup> phosphines, phosphinosilanes,<sup>13,14,15</sup> and phosphinogermanes<sup>14</sup> have been prepared and characterized by a number of workers. Recently iodophosphine, the first monohalophosphine known, was prepared.<sup>39</sup> However, no preparations for aminophosphines,  $\text{R}_2\text{NPH}_2$ , have been reported. Alkyl and aryl phosphines have been synthesized by the action of the dihydrophosphide ion,  $\text{PH}_2^-$ , on alkyl or aryl iodides.<sup>11,12</sup> Various  $\text{PH}_2^-$  donating compounds have been employed. The first  $\text{PH}_2^-$  species used was tetrasodium diphosphide. Later potassium dihydrophosphide<sup>11</sup> and  $\text{LiAl}(\text{PH}_2)_4$  were used.<sup>12,16</sup> Also, alkyl phosphines have been prepared by reduction of alkyl-dichlorophosphine with  $\text{LiAlH}_4$ .<sup>12</sup> Consideration of these reactions suggested that dimethylaminodichlorophosphine could be reduced to dimethylaminophosphine by the use of an appropriate reducing agent.

No reaction occurred between  $\text{LiH}$  and either  $\text{PF}_2\text{N}(\text{CH}_3)_2$  or  $\text{PCl}_2\text{N}(\text{CH}_3)_2$ . In the reaction of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  with  $\text{LiAlH}_4$  the predicted products might be  $\text{PH}_2\text{N}(\text{CH}_3)_2$ , or if  $\text{LiAlH}_4$  broke the P-N bond,  $\text{PH}_3$ . Neither process took place. A yellow nonvolatile solid was the major product. The reduction of  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  with "Redal" also produced an unidentified yellow solid. The similarity of the  $^1\text{H}$  nmr spectrum of the solid dissolved in  $\text{CH}_2\text{Cl}_2$  to the spectra of "Redal" (Figure 4) suggests that an aluminium complex similar to that of "Redal" was formed. However, in any case the desired reaction to produce  $\text{PH}_2\text{N}(\text{CH}_3)_2$  does not take place when  $\text{PCl}_2\text{N}(\text{CH}_3)_2$  and either  $\text{LiAlH}_4$  or "Redal" are allowed to interact.

#### D. Attempted Preparation of $\text{PH}_2\text{NF}_2$

Difluoroaminodifluorophosphine,  $\text{PF}_2\text{NF}_2$ , was recently prepared from the gas phase interaction of  $\text{PF}_2\text{I}$  and  $\text{N}_2\text{F}_4$ .<sup>22</sup> Tetrafluorohydrazine is known to form stable  $\text{NF}_2$  radicals.<sup>23</sup> This property has been exploited by other workers in the preparations of ethyldifluoroamine and methyldifluoroamine.<sup>23</sup>

Phosphine, when irradiated with uv light, decomposes to red phosphorous and hydrogen. A free radical process has been proposed for this decomposition which suggests that the  $\text{PH}_2$  radical is the chain carrier. Later studies of the  $\text{PH}_3$  decomposition and also of the  $\text{PH}_3\text{-O}_2$  system support this view.<sup>27</sup>

The willingness of  $\text{N}_2\text{F}_4$  to undergo free radical reactions and the evidence of  $\text{PH}_2$  radical formation prompted the investigation of the  $\text{PH}_3\text{ N}_2\text{F}_4$  reaction system. It was hoped the formation of  $\text{PH}_2\text{NF}_2$  would result. The interpretation of the  $\text{H}^1$  nmr spectrum of the reaction products indicates proton(s) attached to phosphorous in a compound other than phosphine. This was concluded by the similarity of the coupling constant and chemical shift to those of phosphine. The mass spectral data of the sample can be interpreted in two ways, as indicated by the dual assignments of  $m/e = 85$  and  $66$  (Table 3). Reported mass spectral data for  $\text{N}_2\text{F}_4$  in most cases do not indicate  $m/e$  values greater than the  $\text{NF}_2^+$  ion,  $m/e = 52$ .<sup>21</sup> However, Colburn reported peaks at  $m/e = 104, 85$  and  $66$  to be present in low relative abundance.<sup>26</sup> The gas phase ir gave the spectrum expected for a mixture of  $\text{PH}_3$  and  $\text{N}_2\text{F}_4$ . The violent explosion of a mixture of  $\text{PH}_3$  and  $\text{N}_2\text{F}_4$  when cooled to  $-196^\circ$  indicated a definite sensitivity to thermal shock not possessed by either  $\text{PH}_3$  or  $\text{N}_2\text{F}_4$ . The interpretation of the  $\text{H}^1$  nmr spectra and the explosive nature of the mixture indicate the

the formation of a new compound. Unfortunately, the difficulty in the interpretation of the mass spectral data, and the equivocal results of the ir leave the identity of the compound open to speculation. Further investigation of the reaction system is required to make any positive identification of products.

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