this material was not undertaken at this time.

Conclusion

Ferromagnetic coupling, as evidenced by the positive Θ, is observed for those structures possessing $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chains. This has also been observed for other systems.[3] Of the compounds studied, $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ solely has an 1-D chain structure. It also has the greatest Weiss constant, Θ, largest effective moment, and most pronounced field dependence of the susceptibility. $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$ possesses isolated $D^{\bullet+}A_2{}^{2-}D^{\bullet+}$ dimers and has the lowest μ_{eff}; Θ is zero, and there is no field dependence of the susceptibility. This is consistent with one highly anisotropic moment per repeating unit. The α- and β-$[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$ phases possess 1-D $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ strands in one direction and $\cdots$DAAD$\cdots$ units in another direction and its Θ, μ_{eff}, and $M(H)$ are intermediate in value. This is consistent with the presence of one-third of the anions having a singlet ground state.

These results support the necessity of a 1-D $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chain structure for achieving ferromagnetic coupling and ultimately bulk ferromagnetic behavior as observed for $[Fe(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$.[2] With the wide variation of bis- and tris(dithiolates) available[10-12,23] other salts may exhibit stronger ferromagnetic coupling and possibly bulk ferromagnetic behavior. Furthermore, many polymorphs with differing physical properties can easily, albeit sometimes irreproducibly,[22,24] be prepared, and the specific design of structure types, e.g., 1-D $\cdots$DADADA$\cdots$ chains, continues to be an art.[25]

Acknowledgment. A.J.E. and J.S.M. gratefully acknowledge support from the U.S. Department of Energy, Division of Materials Science (Grant No. DE-FG02-86ER45271.A000). We also appreciate the gift of $Ni[S_2C_2(CF_3)_2]_2$ by Dr. S. Freilich and the synthetic assistance supplied by C. Vazquez and D. Wipf as well as the Faraday susceptibility data taken by R. S. McLean (Du Pont CR&DD) and magnetization data taken by K. S. Narayan (Ohio State).

Registry No. **1**·$[Fe(C_5Me_5)_2]^+$ (M = Ni), 122799-70-6; **1**·$[Fe(C_5Me_5)_2]^+$ (M = Pt), 122762-60-1; **1**·$[Bu_4N]^+$ (M = Ni), 55401-12-2; **1**·$[Ph_3PMe]^+$ (M = Pt), 69990-22-3; **2** (M = Ni), 18820-78-5; **2**·$[Fe(C_5Me_5)_2]^+$ (M = Ni), 122722-21-8; $[Fe(C_5Me_5)_2]^+[BF_4]^-$, 100021-51-0; $Fe(C_5Me_5)_2$, 12126-50-0; $[Fe(C_5Me_5)_2]^+[Ni(S_2C_6H_3Me)_2]^-$, 122762-61-2; $[NBu_4][Ni(S_2C_6H_3Me)_2]$, 15492-42-9.

Supplementary Material Available: A summary of the crystallographic data (Table SI), tables of bond angles, least-squares planes, anisotropic thermal parameters, general temperature factors, and bond angles, and stereoviews and labeling diagrams for $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CN)_2]_2\}$, the α- and β-phases of $[Fe(C_5Me_5)_2]\{Pt[S_2C_2(CN)_2]_2\}$, and $[Fe(C_5Me_5)_2]\{Ni[S_2C_2(CF_3)_2]_2\}$ (40 pages); tables of calculated and observed structure factors (44 pages). Ordering information is given on any current masthead page.

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Preparation and Spectroscopic Characterization of Difluorophosphorane, PH_3F_2. ^{31}P NMR Spectrum of Protonated Diphosphine, $P_2H_5{}^+$

Rolf Minkwitz* and Andreas Liedtke

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The preparation of difluorophosphorane, PH_3F_2, from the reaction of diphosphine and hydrogen fluoride is reinvestigated; it has been characterized by multinuclear (^1H, ^{19}F, ^{31}P) NMR spectroscopy. Complete infrared and Raman low-temperature spectra of difluorophosphorane are reported. It reacts with alkali-metal fluorides to give phosphine and hexafluorophosphates(V). On the basis of ^{31}P NMR spectroscopic results, a reaction mechanism for the formation of PH_3F_2 is proposed. The byproducts of the reaction were PH_2F_3, $(PH)_n$, and $P_2H_5{}^+$; the last was observed for the first time. In carbon disulfide solution, diphosphine neither reacts with hydrogen halides to yield protonated diphosphine nor interacts with hydrogen fluoride to form difluorophosphorane.

From its position in the periodic table of the elements phosphorus is an element predestined to form compounds of trigonal-bipyramidal (tbp) structure that are stable and neutral and therefore volatile and isolable. The nonequivalence of axial and equatorial ligands gives rise to interesting preparative aspects[1-3] and offers sensitive tests of bonding theories.[4,5] A basic demand of MO theory is that the axial ligands must be able to take up considerable amounts of negative charge.[6,7] Thus, the electronegativity rule, which was established[8] by experiment, is theoretically verified.

Following the MO concept, in the series of fluorophosphoranes, $PH_{5-n}F_n$ (n = 1–5), difluorophosphorane, PH_3F_2, should lie at the limit of preparatively accessible tbp compounds. Indeed, ab initio calculations[9-13] show that phosphoranes containing less fluorine should be thermodynamically unstable with respect to decomposition to phosphine.

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Table I. NMR Spectra of Fluorophosphoranes Measured at 205 K[a,b]

phosphorane	solvent	$\delta(^1H)$	$\delta(^{19}F_{ax})$	$\delta(^{19}F_{eq})$	$\delta(^{31}P)$	$^1J_{PH}$	$^1J_{PF(ax)}$	$^1J_{PF(eq)}$	$^2J_{F(ax)H}$	$^2J_{F(eq)H}$
PHF_4[c]	SO_2ClF	+7.44[d] dqui	n.m.[e]	n.m.[e]	−45.6 dqui	1089.3	982.2[e]		91.9[e]	
PH_2F_3[f]	SO_2ClF	+6.63 dtd	−22.0 dt	−105.3 d	−19.2 dtt	865.1	816.7	963.3	101.2	36.7
PH_3F_2[g]	HF	+6.51 d, br	n.o.		−62.5 q[h]	752.4	n.o.		n.o.	
	SO_2ClF	+6.28 dt	−73.0 dq		−66.6 qt	732.2	532.1		81.1	

[a] δ in ppm, *J* in Hz. Abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), qui (quintet), sex (sextet), br (broad), n.m. (not measured), n.o. (not observed), *A* (signal area). [b] Literature[2] NMR data of PF_5: $\delta(^{19}F) = -70.7$, $\delta(^{31}P) = -80.3$, $^1J_{PF} = 916–938$. [c] NMR data measured in dimethyl ether: $\delta(^{31}P) = -102$ sex (930 Hz). NMR data measured in diethyl ether: $\delta(^{31}P) = -90.6$, $^1J_{PH} = 1086.6$, $^1J_{PF} = 929.8$. [d] Measured in $CDCl_3$ (215 K). [e] Literature[17] data: $\delta(^{19}F_{ax}) = -27.4$, $\delta(^{19}F_{eq}) = -65.9$, $^1J_{PF(ax)} = 941.0$, $^1J_{PF(eq)} = 1025$, $^2J_{F(ax)H} = 147.5$, $^2J_{F(eq)H} = 36.47$, $^2J_{F(ax)F(eq)} = 87.89$. [f] $^2J_{F(ax)F(eq)}$ was not observed. NMR data obtained in hydrogen fluoride solution: $\delta(^{31}P) = -18$ sex, br (810 Hz). [g] Literature[21] data: $\delta(^1H) = +5.95$ d, $^1J_{PH} = 545$. [h] In addition to signals from PH_4^+ ($A = 2.3$) and PH_3F_2 ($A = 1.0$) the following signals were observed in freshly prepared reaction mixtures: $\delta(^{31}P) = -226.0$ dt (246.2, 204.7 Hz), $A = 0.03$; −89.4 qdt (515.6, 245.8, 20.0 Hz), $A = 0.03$ from $P_2H_5^+HF_2^-$; −19 sex, br (820 Hz), $A = 0.03$ from PH_2F_3.

Whereas the fluorophosphoranes PF_5, PHF_4, and PH_2F_3 have been widely examined[2,14–18] by spectroscopic means and even their gas-phase molecular structures have been determined,[19,20] only very few experimental data are available for difluorophosphorane, which was first detected by mass spectrometry and an incomplete infrared spectrum by Seel and Velleman.[21] In fact, PH_3F_2 is not mentioned as an existant compound in many review articles.[1,2,22] However, a very recent ab initio calculation[13] confirms the reported[21] infrared frequencies.

We have therefore tried to optimize the previously given procedure[21] and to obtain convincing evidence for the existence of PH_3F_2. In addition, NMR data and vibrational frequencies would be expected to give unambiguous structural evidence for this phosphorane. By analogy with the reactions of PF_5, PHF_4, and PH_2F_3,[23–27] PH_3F_2 could serve as a starting material for the unknown monofluorophosphonium cation, PH_3F^+, and the trifluorotrihydridophosphate(V) anion, $PH_3F_3^-$.

Experimental Section

Materials and Apparatus. Standard vacuum-line techniques were used for all manipulations. Hydrogen fluoride was handled in a vacuum line made from stainless steel. The hydrogen halides HF, HCl, HBr, and HI were received from Bayer Co., Leverkusen, FRG, as a gift and purified by standard techniques.[28] Hydrogen fluoride was stored over antimony pentafluoride and freshly distilled prior to use. PH_2F_3 and PHF_4 were prepared by reported[14] procedures. For the preparation of P_2H_4 and precautions regarding its handling refer to ref 29. The mass spectrum of PH_3F_2 was recorded with a Varian MAT CH5 spectrometer. All NMR parameters reported were obtained with a Bruker AM 300 spectrometer at 300.1 MHz (^1H), 282.5 MHz (^{19}F), and 121.5 MHz (^{31}P) with positive shifts being to high frequency of the external standard, TMS (^1H), $CFCl_3$ (^{19}F), and 85% *o*-H_3PO_4 (^{31}P), and a pulse width of 4 μs (^1H), 1.5 μs (^{19}F), and 5 μs (^{31}P). The ^{31}P measurements were made with a relaxation delay of 1.5 s. All NMR spectra were usually obtained in the range 0 to −250 ppm (^{31}P, 2048 scans), +200 to −200 ppm (^{19}F, 2048 scans), and 0 to 11 ppm (^1H, 256 scans). The spectra were then rerecorded for each signal with a smaller spectral width, and the midpoint of the spectrum was set at the signal frequency. By this means a maximum resolution of 0.1 Hz/data point was obtained.

The Raman spectra were obtained on a Coderg T 800 spectrometer equipped with an Ar ion laser (Spectra Physics) operating at 488.0 nm and 400-mW laser power level. The maximum resolution was 1.5 cm^{-1}. The Raman spectrum of $PH_4^+HF_2^-\cdot xHF$ in hydrogen fluoride solution was measured at 195 K with a quartz cell. Phosphine was condensed at 195 K into liquid hydrogen fluoride until the solution became milky. On addition of a small amount of hydrogen fluoride a clear solution of $PH_4^+HF_2^-\cdot xHF$ was obtained.

The infrared spectra were recorded on a Perkin-Elmer Model 580 B spectrometer in the range 4000–200 cm^{-1} with a resolution of 0.8 cm^{-1}. Mixtures of solid difluorophosphorane and $PH_4^+HF_2^-\cdot xHF$ were sublimed with N_2 or Ar as matrix gas onto a cesium iodide window cooled to 10 K. Infrared spectra of pure $PH_4^+HF_2^-\cdot xHF$ were obtained in the same manner for comparison.

All vibrational measurements showed a reproducibility within the range of the maximum resolution.

Reactions of Diphosphine with Hydrogen Halides in Carbon Disulfide Solutions. A 0.1-mL portion of diphosphine, 1.2 mL of carbon disulfide, and 5–20 mmol of the hydrogen halide (HF, HCl, HBr, HI) were condensed at 77 K into a quartz NMR sample tube. After the tubes were sealed, the samples were allowed to slowly warm to 205 K. The products observed by ^{31}P NMR spectroscopy depended on the hydrogen halide employed. While hydrogen fluoride, chloride, and bromide only gave one soluble phosphorus-containing product (PH_4^+, PCl_3, and PBr_3, respectively), the reaction of diphosphine with hydrogen iodide yielded a mixture of PI_3, P_2I_4, PHI_2, PH_4^+, and PH_2I. These compounds could be identified by comparison with published[30,31] NMR data.

Besides, all these reactions gave yellow to orange precipitates.

Preparation of Difluorophosphorane, PH_3F_2. A total of 0.5 mL of diphosphine and 8.0 mL of hydrogen fluoride were condensed into a reaction vessel made of quartz or KEL-F. The reaction mixture was warmed to 195 K, at which temperature a large proportion of the hydrogen fluoride and $PH_4^+HF_2^-\cdot xHF$ could be removed by pumping. On further warming of the sample, a mixture of PH_3F_2 and $PH_4^+HF_2^-\cdot xHF$ could be transferred into a separate container, leaving behind yellow solids. When quartz reaction vessels were employed the yields of difluorophosphorane were higher, on the basis of NMR data. The mass spectrum (70 eV) is summarized as follows [*m/e* (relative intensity) assignment]: 31 (18%) P^+, 32 (100%) PH^+, 33 (28%) PH_2^+, 34 (98%) PH_3^+, 50 (4%) PF^+, 51 (12%) PHF^+, 52 (7%) PH_2F^+, 53 (3%) PH_3F^+, 69 (6%) PF_2^+, 71 (33%) $PH_2F_2^+$.

When the products were passed through or condensed onto alkali-metal fluorides (KF, CsF), phosphine remained as the only volatile product. The resulting solids were slightly yellow. They contained alkali-metal hexafluorophosphates(V), on the basis of their ^{31}P NMR spectra[30] in acetonitrile solution.

Results

Formation and Stability of PH_3F_2. Our results confirm the reported[21] formation of PH_3F_2 in the reaction of diphosphine, P_2H_4, with hydrogen fluoride (eq 1). Contrary to the procedure described by Seel and Velleman[21] we found it advantageous to carry out the reaction at 195 K. Moreover, higher yields of PH_3F_2 could be obtained in quartz vessels, owing to the higher thermal conductivity of quartz glass compared with that of perfluorinated plastics. Furthermore, the recommended[21] absorption of excess

$$P_2H_4 + 4HF \rightarrow PH_3F_2 + PH_4^+HF_2^- \qquad (1)$$

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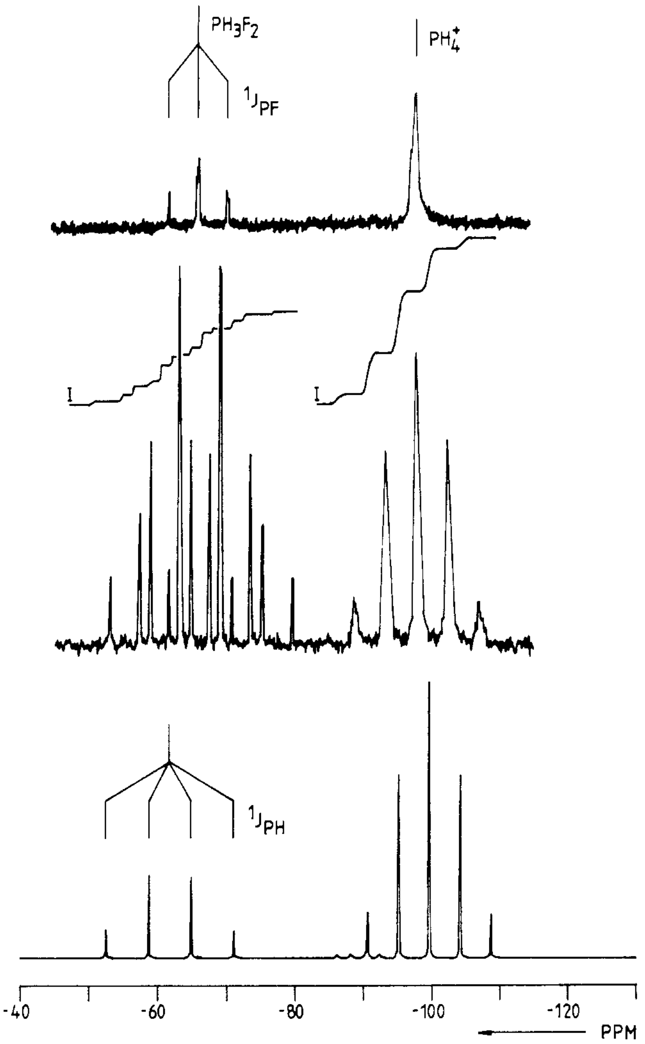

Figure 1. ^{31}P NMR spectra of difluorophosphorane: (a, top) SO_2ClF solvent, ^1H decoupled; (b, middle) SO_2ClF solvent; (c, bottom) HF solvent.

Table II. Vibrational Spectral Data for PH_3, $PH_4^+HF_2^-\cdot xHF$ and PH_3F_2[a]

$PH_3F_2/PH_4^+HF_2^-\cdot xHF$[b]				
IR solid (4 K; sublimed)[e]	Ra liquid (195 K; HF solvent)[f]	PH_3F_2[c] IR gaseous	PH_3F_2[d] ab initio	assgnt
2538 (25)	2540 (8) dp	2500 m	2499 s	$\nu_5(e')$ $(\nu_{as}(PH_3))$
	2486 (100) p		2454[g]	$\nu_1(a_1')$ $(\nu_s(PH_3))$
1287 (4)		1262 w	1285 m	$\nu_3(a_2'')$ $(\gamma(PH_3))$
	1168 (2) dp		1182[g]	$\nu_8(e'')$ $(\rho(PF_2))$
984 sh	975 sh, dp	970 s	954 s	$\nu_6(e')$ $(\delta(PH_3))$
680 (49) br		760 vs	800 vs	$\nu_4(a_2'')$ $(\nu_{as}(PF_2))$
	635 (6) p		603[g]	$\nu_2(a_1')$ $(\nu_s(PF)_2)$
376.5 (58)	390 (5) dp		331 m	$\nu_7(e')$ $(\delta(PF_2))$

[a] Frequencies in cm^{-1}. Abbreviations: p (polarized), dp (depolarized), sh (shoulder), br (broad), v (very), s (strong), m (medium), w (weak). [b] This work; intensities in percent are given in parentheses. [c] Reference 21. [d] Reference 13; calculated infrared intensities are given. [e] Impurities: due to PH_3, 2323 (77), 2318 (82), 1104 (46), 993 (100); due to HF, 3300–3700, 600–800. [f] Impurities: due to PH_4^+, 2530 (14), 2486 (100), 1134 (12), 990 (6); due to $HF_2^-\cdot xHF$, 400–500 (1). [g] Infrared forbidden.

Table III. Comparison of NMR Parameters for PH_3, PH_4^+, P_2H_4, and $P_2H_5^+$[a]

	$H_2PPH_3^+$[b]		related compds for comparison		
	H_2P-	$-PH_3^+$	PH_3[c]	PH_4^+[d]	P_2H_4[e]
$\delta(^{31}P)$	−226.0	−89.4	−238	−99.9	−204.0
$^1J_{PH}$	204.8	515.6	182–188	548.5	186.5
$^1J_{PP}$	246.2	245.8			108.2
$^2J_{PH}$	n.o.[f]	20.0			11.9

[a] δ in ppm, J in Hz. [b] Measured at 205 K; dissolved in HF. [c] References 22 and 30. [d] Data from Table I, footnote *h*. [e] Reference 37. [f] n.o. = not observed.

hydrogen fluoride with potassium fluoride was not possible. Apparently, PH_3F_2 decomposes in contact with alkali-metal fluorides, yielding hexafluorophosphates and phosphine.

We did not succeed in the preparation of pure PH_3F_2 either by using a Stock apparatus for fractional condensation or by pumping off the more volatile impurities, namely phosphine and hydrogen fluoride. The best product mixtures obtained contained PH_3F_2 and $PH_4^+HF_2^-\cdot xHF$ in a ratio of 1:2–2.5 (Table I). From the ^1H NMR results x was about 4–5.

Dilute solutions of PH_3F_2 and $PH_4^+HF_2^-\cdot xHF$ in hydrogen fluoride did not decompose over a 4-week period at 215 K and were stable even at room temperature for 1 h. By contrast, mixtures of solid PH_3F_2–$PH_4^+HF_2^-\cdot xHF$ decomposed quantitatively within 2 weeks at 195 K, yielding yellow solids.

NMR Spectra. The NMR data obtained for PH_3F_2 and the observed side products are listed in Table I. Figures 1 and 2 depict typical ^{31}P NMR spectra. PHF_4 and PH_2F_3 were examined by NMR spectroscopy under similar temperature, solvent, and concentration conditions. This was done to allow a proper comparison of the NMR data; furthermore, not all the NMR data for PH_2F_3 had previously been published.

The NMR signals of PH_4^+ and of the solvents were observed at known[22,32] chemical shifts.

Mass Spectra of PH_3F_2. The mass spectra were recorded at 70 eV (see Experimental Section). No ion fragments resulting from PH_3F_2 could be observed at 16 eV because of the contamination with $PH_4^+HF_2^-\cdot xHF$ and because of decreased spectrometer sensitivity.

Vibrational Spectra. The infrared spectroscopic investigation of vaporized mixtures of PH_3F_2 and $PH_4^+HF_2^-\cdot xHF$ in gas cells caused decomposition of PH_3F_2 at the cell windows (KBr, NaCl). The samples were therefore condensed onto a cesium iodide window, which was cooled to 10 K. Infrared frequencies obtained in this way are listed in Table II. For a reliable assignment of its infrared frequencies, a sample of pure $PH_4^+HF_2^-\cdot xHF$ was investigated by using an identical procedure.

The Raman frequencies of concentrated solutions of product samples (PH_3F_2, $PH_4^+HF_2^-\cdot xHF$) and of pure $PH_4^+HF_2^-\cdot xHF$ dissolved in hydrogen fluoride are also given in Table II. Figures 3 and 4 give representative infrared and Raman spectra for PH_3F_2–$PH_4^+HF_2^-\cdot xHF$ mixtures.

Discussion

Formation and Reactivity of PH_3F_2 and the ^{31}P NMR Spectrum of $P_2H_5^+$. Whereas the P–P bond lengths of P_2H_4 (221.9 pm[33]) and of $P_2(CF_3)_4$ (218.2 pm[34]) differ only insignificantly, P_2H_4 reacts with hydrogen chloride even at −125 °C under P–P bond fission,[35] while $P_2(CF_3)_4$ is stable toward attack by hydrogen chloride up to 300 °C.[36] Therefore, it was assumed that the basicity of a particular diphosphine defines its tendency for P–P bond fission and that the first reaction step is its protonation.[36] The ^{31}P NMR spectra of freshly prepared reaction mixtures of diphosphine and excess hydrogen fluoride revealed weak signals of equal areas at −226 and −89.4 ppm. The observed signal splittings prove that these signals arise from protonated diphosphine, $P_2H_5^+$ (Table I, footnote *h*; Figure 2). In Table III the NMR data obtained for $P_2H_5^+$ are compared with those of similar compounds. The values of $\delta(^{31}P)$ and $^1J_{PH}$ for the PH_3^+

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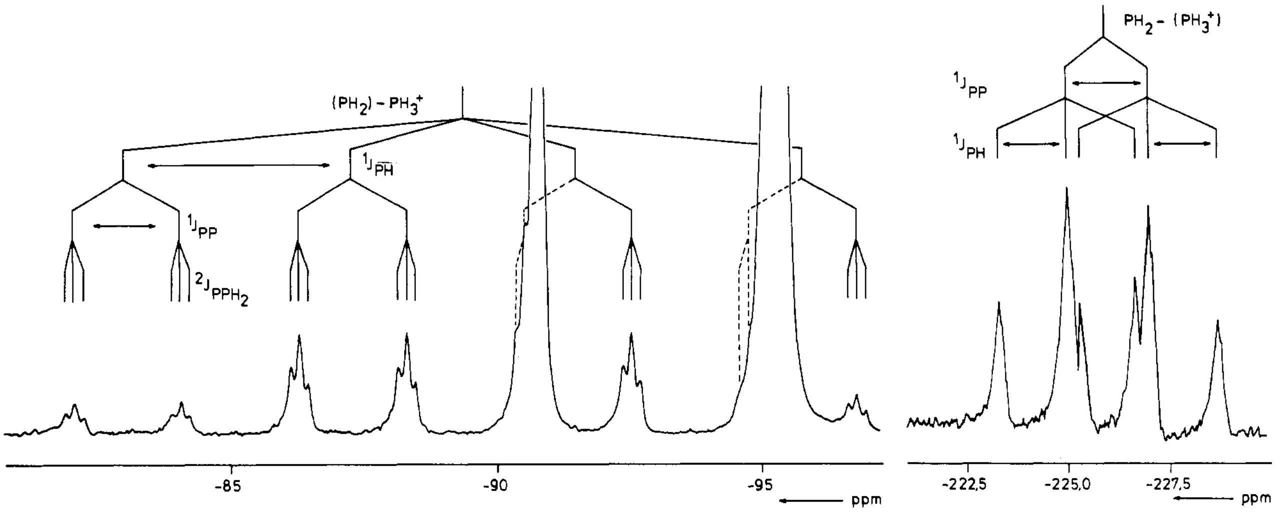


Figure 2. ^{31}P NMR spectra of protonated diphosphine: (a, left) PH_3^+ fragment; (b, right) PH_2 fragment.

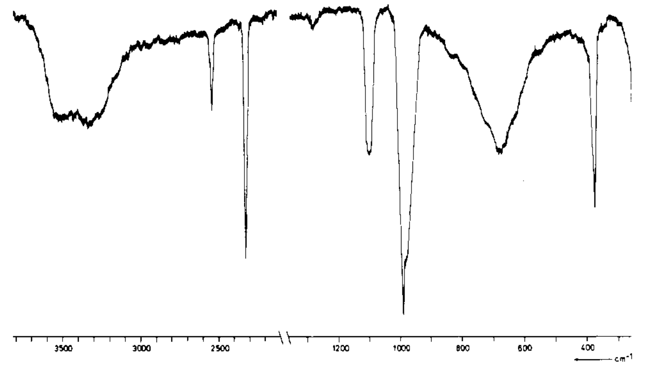


Figure 3. Infrared spectrum of a mixture of difluorophosphorane and phosphine dissolved in hydrogen fluoride.

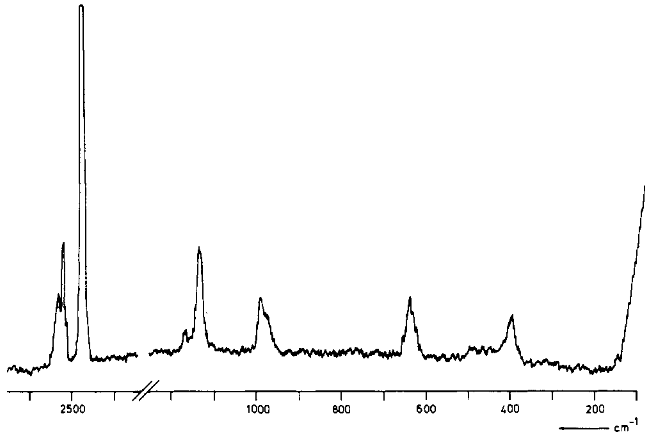
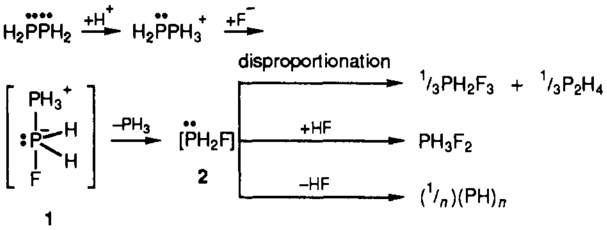


Figure 4. Raman spectrum of a mixture of difluorophosphorane and $PH_4^+HF_2^-$ dissolved in hydrogen fluoride.

fragment of $P_2H_5^+$ closely correspond with the appropriate data for PH_4^+. The greater value of $^1J_{PH}$ in PH_4^+ is caused by the larger electronegativity of the hydrogen ligand (in $H-PH_3^+$) compared with that of the phosphino ligand (in $H_2P-PH_3^+$).[22,27,38] Accordingly, the NMR parameters $\delta(^{31}P)$ and $^1J_{PH}$ for the PH_2 fragment of $P_2H_5^+$ agree with the NMR data for phosphine (Table III). The values of the couplings $^1J_{PP}$ and $^2J_{PH}$ are characteristic for P–P compounds.[39]

Another product detected in very low concentration in the reaction mixtures of diphosphine and hydrogen fluoride was PH_2F_3 (Table I, footnotes *f* and *h*). Its concentration did not increase on storing the solutions at 220 K. In contrast to the report of Seel and Velleman,[21] we did not observe decomposition of PH_3F_2 into PH_2F_3. This is consistent with ab initio calculations.[40] We conclude that PH_2F_3 is a side product of the interaction of diphosphine with hydrogen fluoride. A suitable mechanistic proposal for the reaction of diphosphine and hydrogen fluoride is given in eq 2.



(2)

Whereas the formation of polymeric phosphorus hydrides $(PH)_n$[35] was obvious and $P_2H_5^+$, PH_4^+, PH_2F_3, and PH_3F_2 were detected by NMR spectroscopy (Table I), the formulation of the intermediates **1** and **2** refers to mechanistic concepts that were developed from the investigation of the hydrolysis of esters of phosphoric acid and from the hydrolysis of phosphonium salts.[2] The entering and leaving groups (F^- and PH_3, respectively) occupy axial positions in **1**; in addition, the assumed pseudorotational isomer corresponds to the energetically favored isomer.[41] The disproportionation reaction of **2**, however, is in accordance with a reaction that is well-known[42] for organosubstituted monofluorophosphines.

The reactions of diphosphine with hydrogen halides in carbon disulfide solution did not lead to concentrations of $P_2H_5^+$ detectable by ^{31}P NMR spectroscopy; in particular, the reaction of diphosphine and hydrogen fluoride did not yield detectable amounts of PH_3F_2 in this solvent (see Experimental Section).

The reaction of PH_3F_2 with the Lewis acid SbF_5, yielding $PH_3F^+SbF_6^-$, has been described previously.[27] With the Lewis base F^-, however, no evidence for the $PH_3F_3^-$ anion was observed. Instead its decomposition products (eq 3) were observed.

$$4PH_3F_2 + 4F^- \rightarrow 4[PH_3F_3^-] \rightarrow PF_6^- + 3PH_3 + 3HF_2^- \quad (3)$$

PH_2F_3[24,25] and PHF_4[14,27] react with alkali-metal fluorides with the formation of stable fluorohydridophosphates(V) such as $PH_2F_4^-$ and PHF_5^-. We have found that PHF_4 and the Lewis bases dimethyl ether and diethyl ether react to give coordination compounds, as established by the considerable shift of $\delta(^{31}P)$ to low frequency (Table I, footnote *c*).

NMR Spectra of PH_3F_2. The NMR spectra obtained in SO_2ClF clearly prove that the products contain PH_3F_2 (Table I).

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The ^{31}P NMR spectra of PH_3F_2 are shown in Figure 1. The observed signal splittings indicate a tbp structure for PH_3F_2, with three equivalent protons and two equivalent fluorine ligands (D_{3h} symmetry). The alternative structure—a tetragonal pyramid with four equivalent basal positions and an apical one—is not compatible with the observed spectra and is found only for cyclic phosphoranes.[1-3] No proof for pseudorotation in PH_3F_2 was found within the temperature range 200–250 K, in accordance with the behavior of substituted difluorophosphoranes.[43-47] This finding is attributable to the considerably different apicophilicities of hydrogen and fluorine ligands.[2,4,11]

In a comparison of NMR data for the fluorophosphoranes $PH_{5-n}F_n$ (n = 2–5, Table I), $\delta(^1H)$ increases with increasing n, in accordance with an increase in the diamagnetic contribution to the ^1H shielding. $\delta(^{31}P)$ reveals a trend similar to that obtained for the phosphonium cations $PH_{4-n}F_n^+$ (n = 0–4);[27] i.e., with increasing n it increases to a maximum value but decreases for the highly fluorinated compounds. An extremely low-frequency shift is observed for the fluorine atoms of difluorophosphorane.

Whereas $^1J_{PH}$ of the fluorophosphoranes $PH_{5-n}F_n$ (n = 2–4) is obviously determined by changes of the local P sp^2 hybridization (Table I and ref 48), $^1J_{PF(ax)}$ is assumed to decrease with decreasing electronegativity of the equatorial ligands.[39,45]

Therefore $^1J_{PH}$ and $^1J_{PF(ax)}$ are of similar magnitude for PH_3F_2 ($^1J_{PH}$ = 732.2, $^1J_{PF}$ = 532.1 Hz), $(CH_3)_2PHF_2$ ($^1J_{PH}$ = 733, $^1J_{PF}$ = 535 Hz[43]), and $(CH_3)_3PF_2$ ($^1J_{PF}$ = 530–542 Hz[47]). However, $^1J_{PF(ax)}$ is not a measure of the P–F_{ax} bond strength; for example, although the values of $^1J_{PF}$ of PH_3F_2 and of $P(CH_3)_3F_2$ are almost equal, the following points illustrate the differences in the P–F_{ax} covalent bond strengths:

1. The P–F bond lengths in $P(CH_3)_3F_2$ (168.5 pm[49]) are considerably longer than those estimated for PH_3F_2 (163.4 pm[50]).
2. The P–F stretching modes of $P(CH_3)_3F_2$ ($\nu_{as}(PF_2)$ 670, $\nu_s(PF_2)$ 501 cm^{-1} [51]) reveal frequencies lower than those of PH_3F_2 (Table II).
3. $P(CH_3)_3F_2$ reacts with hydrogen fluoride under P–F bond fission, leading to $P(CH_3)_3F^+HF_2^-$;[47] however, PH_3F_2 does not (see below).

When difluorophosphorane was dissolved in hydrogen fluoride and investigated by means of ^1H and ^{31}P NMR spectroscopy, couplings to fluorine could not be observed (Table I, Figure 1). This finding refers to an intermolecular fluorine exchange, comparable to that observed for $PH_2F_2^+$ salts.[27] However, no reaction leading to $PH_3F^+HF_2^-$ occurs; this, as we have found, would result in a considerable ^{31}P shift to high frequency.[27]

Mass Spectra of PH_3F_2. The mass spectra obtained give additional evidence for the presence of PH_3F_2. The fragment-ion intensities listed in the Experimental Section match with observations made on PH_2F_3 and PHF_4;[15,21] i.e., no peak is found for the molecular ion, and $M^+ - 1$ is of high intensity.

Vibrational Spectra of PH_3F_2. Hitherto, PH_3F_2 had not been fully characterized by means of vibrational spectroscopy.[21] Whereas its NMR spectroscopic investigation was not influenced by the presence of $PH_4^+HF_2^-\cdot xHF$, the infrared and Raman spectra are complex, consisting of several overlapping spectra (Table II, Figures 3 and 4). The spectrum of $PH_4^+HF_2^-\cdot xHF$ is in good agreement with published spectra of other phosphonium halides;[52] the vibrational frequencies of $PH_4^+HF_2^-\cdot xHF$ are, however, shifted to higher frequencies. This observation corresponds to the trend found for the other phosphonium halides, where the vibrations shift to higher frequencies with decreasing size of the anion.[53] When mixtures of PH_3F_2 and $PH_4^+HF_2^-\cdot xHF$ were condensed onto a cesium iodide window using a gas inlet system made from glass, bands resulting from SiF_4[52] at 1032 and 389 cm^{-1} were also observed.

On the basis of NMR spectroscopic findings, PH_3F_2 has D_{3h} symmetry, and eight fundamental vibrational bands should occur:

$$\Gamma_{vib} = 2a_1'(Ra) + 2a_2''(IR) + 3e'(IR, Ra) + e''(Ra) \qquad (4)$$

The vibrational assignments made in Table II correspond to the known experimental values[21] and to ab initio frequencies.[13]

The $\nu_{as}(PH_3)$ vibration is observed in the infrared and Raman spectra at 2538 and 2540 cm^{-1}, respectively. The increase in frequency compared to that found by Seel and Velleman[21] in the gaseous state (2500 cm^{-1}, Table II) is associated with the condensed states. $\nu_s(PH_3)$ is infrared inactive, and in the Raman spectra it is obviously overlapped by ν_1 of PH_4^+. Its frequency of 2486 cm^{-1} is in excellent agreement with the PH stretching frequencies found for PH_2F_3 ($\nu_s(PH_2)$ 2482 cm^{-1} [16]) and PHF_4 (ν(PH) 2482 cm^{-1} [16]). $\nu_{as}(PF_2)$ is obtained as a very broad band at 680 cm^{-1} in the infrared spectra. Compared to other measured[21] and calculated[13] values, it is found at lower frequency. The broadening and low-frequency shift of $\nu_{as}(PF_2)$ can be explained by the assumption that difluorophosphorane and hydrogen fluoride give hydrogen-bridged aggregates even in the gas phase. These hydrogen bridges presumably result from the high negative charge localized on the fluorine ligands.[5,52] $\nu_s(PF_2)$, which is infrared forbidden, is observed as a polarized signal at 635 cm^{-1} in the Raman spectrum of difluorophosphorane. The frequencies of $\gamma(PH_3)$ and $\rho(PF_2)$ are found at 1287 and 1168 cm^{-1}, respectively, in good agreement with ab initio frequencies. $\gamma(PH_3)$ gives rise to a weak band in the infrared spectrum only and corresponds to the frequency reported by Seel and Velleman[21] (Table II). The reported[21] frequency for $\delta(PH_3)$ matches our measurement. We have assigned the $\delta(PF_2)$ vibration to an intense band at 376.5 cm^{-1} in the infrared spectrum, which corresponds to the medium-intense line at 390 cm^{-1} in the Raman spectrum. The large frequency shift results from the different stages of aggregation for the Raman (liquid) and infrared (solid) spectra.

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Registry No. P_2H_4, 13445-50-6; HF, 7664-39-3; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; PH_3F_2, 34278-32-5; PH_4^+, 16749-13-6; PHF_4, 13659-66-0; PH_2F_3, 13659-65-9; $H_2PPH_3^+$, 53290-62-3; PI_3, 13455-01-1; P_2I_4, 13455-00-0; PHI_2, 15177-78-3; PH_2I, 14500-79-9.

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