would position the interactions assigned to these chlorines in the reverse order, inplying that the difference in bond lengths in this case is of much greater importance in determining interaction frequencies.[21,22]

(21) An alternative approach to the assignment of the lower frequency pair of interactions was suggested by a referee: Cl(1) and Cl(2), having different crystallographic environments, have different average moments of inertia with respect to the principal direction of their field gradient tensors and hence different temperature dependences of their electric field gradients and nqr frequencies. Using the moments of inertia and a detailed calculation on an assembly of quantum mechanical harmonic oscillators the zero-point vibrational contribution to the electric field gradient could be separated out. This was attempted by Ragle[22] using a value for the restoring force constant for 1,2-dichloroethane, a simple and relatively well-understood molecule, and found to be about 1.2% of the value of the coupling constant. For Cl(1) and Cl(2) the splitting amounts to about 3.6% of the

average of the estimated coupling constants and it is unlikely that the difference in their respective zero-point vibrational contributions could even approach 3.6%; thus this alternative approach would not reverse the assignments. Further calculation is not possible without knowledge of the restoring forces in the molecule.

(22) J. L. Ragle, *J. Phys. Chem.*, **63**, 1395 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Difluorothiophosphoryl-μ-thio-difluorophosphine and Difluorophosphoryl-μ-oxo-difluorophosphine. Novel Mixed-Valence Fluorophosphorus Compounds[1]

BY T. L. CHARLTON AND R. G. CAVELL

The compound $F_4P_2S_2$, a moderately stable volatile liquid (bp 85.7°), has been prepared by the reaction of iodothiophosphoryl difluoride with a stoichiometric quantity of mercury and by the reaction of difluorodithiophosphoric acid with dimethylaminodifluorophosphine. The reaction of difluorophosphoric acid with dimethylaminodifluorophosphine gives the considerably less stable oxygen analog $F_4P_2O_2$ (bp 50°). Infrared and nuclear magnetic resonance spectral measurements and chemical studies indicate that the compounds do not have a phosphorus–phosphorus bonded structure but rather the isomeric structure $F_2P(=E)EPF_2$ (E = S, O) with trivalent and pentavalent phosphorus linked by a sulfur- or an oxygen-bridging atom.

Introduction

Many diphosphorus compounds containing a phosphorus–phosphorus bond have been synthesized by coupling halogenophosphorus monomers with active metals.[2–4] We now wish to report successful synthesis of diphosphorus compounds derived from phosphoryl and thiophosphoryl difluoride monomers. These compounds, however, do not possess the phosphorus–phosphorus bonded structure.

Experimental Section

Standard vacuum techniques using Pyrex-glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon N grease. Infrared spectra were measured with a Perkin-Elmer 421 (4000–300 cm^{-1}) dual-grating instrument, mass spectra with an AEI MS-9 double-focusing mass spectrometer, and nuclear magnetic resonance spectra with Varian A 56/60 or HA 100 instruments. All fluorine spectra were measured on 10% solutions of compounds in CCl$_3$F at 56.4 MHz with chemical shifts given relative to CCl$_3$F. Phosphorus spectra were measured on neat samples at 40.5 MHz with chemical shifts given relative to P$_4$O$_6$[5] which was contained within a reference capillary in the sample.

Preparation of Difluorothiophosphoryl-μ-thio-difluorophosphine. (a) From Iodothiophosphoryl Difluoride and Mercury.—In a typical experiment, SPF$_2$I[6] (1.16 g, 5.10 mmol) and a stoichiometric quantity of mercury (0.51 g, 2.56 mmol) were sealed in a 75-cm^3 reaction tube which was vigorously shaken for 1 week at room temperature. Separation of the volatile products gave F$_4$P$_2$S$_2$ (0.49 g, 2.42 mmol, 95% yield based on eq 3) collected at −81°, SPF$_2$H[7] (0.018 g, 0.176 mmol) condensed at −116°, and a trace of (SPF$_2$)$_2$S[8] condensed at −65°. The reaction vessel contained mercuric iodide (1.08 g, 2.38 mmol).

(b) From Difluorodithiophosphoric Acid and Dimethylaminodifluorophosphine.—F$_2$P(S)SH[9] (1.00 g, 7.50 mmol) and F$_2$PN(CH$_3$)$_2$[10] (0.465 g, 4.11 mmol) reacted immediately upon warming to room temperature in a 75-cm^3 tube to form a white solid and a volatile liquid. Separation of the volatile products after 15 min of reaction at room temperature gave F$_2$PSP(S)F$_2$ (0.72 g, 3.57 mmol, 95% yield based on eq 4) collected at −81° and a mixture of PF$_3$ and PF$_2$N(CH$_3$)$_2$ (0.05 g) collected at −196°. A solution of the residual white solid in CH$_3$CN gave ^{1}H and ^{19}F nmr lines corresponding to[11] (CH$_3$)$_2$NH$_2$+S$_2$PF$_2$⁻.

Characterization of Difluorothiophosphoryl-μ-thio-difluorophosphine.—F$_2$PSP(S)F$_2$ was a clear, colorless liquid which was characterized by spectroscopic studies, by vapor density molecular

(1) For a preliminary communication see R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *Chem. Commun.*, 424 (1969).

(2) A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965).

(3) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

(4) M. Lustig, J. K. Ruff, and C. B. Colburn, *ibid.*, **88**, 3875 (1966).

(5) A. C. Chapman, J. Homer, D. J. Mowthorpe, and R. T. Jones, *Chem. Commun.*, 121 (1965).

(6) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **7**, 2195 (1968). A typographical error in Table III of this paper gives the fluorine chemical shift of SPF$_2$I as +11.2 ppm *vs.* CCl$_3$F. It should be −11.2 ppm.

(7) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

(8) T. L. Charlton and R. G. Cavell, unpublished results.

(9) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969); R. W. Mitchell, M. Lustig, F. A. Hartmann, J. K. Ruff, and J. A. Merritt, *J. Am. Chem. Soc.*, **90**, 6329 (1968).

(10) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

(11) R. G. Cavell, *Can. J. Chem.*, **46**, 613 (1968).

weight (calcd for $F_2PSP(S)F_2$: 202.0; found (on two different samples): 199.7 and 200.4), and by chemical reaction with HCl (below). A parent ion was not observed in the mass spectrometer since the compound seemed to react in the inlet system to give $(SPF_2)_2O$ and other products. Vapor pressure data, given in Table I, obey the equation

$$\log P(\text{mm}) = 7.639 - (1708/T) \qquad (1)$$

which gives an extrapolated boiling point of 85.7°, heat of evaporation of 7814 cal/mol, and a Trouton constant of 21.8 eu.

TABLE I
VAPOR PRESSURE DATA

| | $F_2P(S)SPF_2$ | | | $F_2P(O)OPF_2$ | |
| | P, mm | | | P, mm | |
Temp, °C	Obsd	Calcd[a]	Temp, °C	Obsd	Calcd[b]
0.0	24.1	24.5	−36.6	4.4	4.9
5.8[c]	35.5	33.0	−31.4[c]	7.4	7.3
10.7	39.0	42.1	−29.4	8.6	8.5
16.4[c]	57.7	55.3	−21.6[c]	16.3	15.0
20.7	64.7	67.4	−19.4	18.2	17.5
25.9[c]	87.1	85.1	−11.8[c]	30.3	29.1
29.7	97.6	100.3	−9.6	33.4	33.5
35.7[c]	130.6	129.1	−2.4[c]	53.0	52.4
40.0	154.8	153.8	+0.4	60.0	61.9
45.9[c]	194.7	193.1	+10.2	101.8	108.5
50.5	231.3	231.0			

[a] Pressure calculated from eq 1. [b] Pressures calculated from eq 2. [c] Measured with temperature descending from the highest value reached. All other points were measured with ascending temperatures.

Pure samples of $F_2PSP(S)F_2$ could be kept for a few days in sealed tubes at room temperature without appreciable decomposition. After several months at room temperature, however, the sealed tube contained a mixture of PF_3, SPF_2SH, $(SPF_2)_2O$, a light yellow involatile solid, and a nonvolatile colorless liquid. A sample heated to 70° for 2 hr was 90% consumed yielding PF_3 and an unidentified colorless nonvolatile liquid.

Preparation of Difluorophosphoryl-μ-oxo-difluorophosphine.—Reaction of $F_2P(O)OH$[12,13] (1.25 g, 12.21 mmol) with F_2PN-$(CH_3)_2$[10] (0.95 g, 8.40 mmol) at room temperature for 3 min in a 40-cm³ glass tube followed immediately by fractionation of the volatile products in the vacuum system gave PF_3 (0.15 g, 1.76 mmol), $F_2PN(CH_3)_2$ (0.17 g, 1.49 mmol) collected at −116°, the desired $F_2POP(O)F_2$ (0.70 g, 4.10 mmol) collected at −81°, and a small amount of unidentified material trapped at −65°. The residue remaining in the reaction tube was initially a clear colorless liquid which crystallized after standing for about 30 min. A solution of the crystalline residues showed ^1H and ^{19}F nmr resonances corresponding[14] to $(CH_3)_2NH_2^+O_2PF_2^-$.

Difluorophosphoryl-μ-oxo-difluorophosphine was characterized by mass spectroscopy including accurate mass measurement of the parent peak (calcd for $F_4P_2O_2$, m/e 169.9310; obsd m/e 169.9308). The mass spectral cracking pattern is given in Table II, and nmr and ir spectral parameters are given in Tables III and IV. Vapor pressure measurements were less reliable than those obtained on the sulfur analog because of the limited stability of the compound above 0°. The data (Table I) obeyed the equation

$$\log P(\text{mm}) = 8.83 - (1925/T) \qquad (2)$$

(12) Vacuum-distilled commercial (Columbia Organic Chemicals) materials were used without success in initial experiments probably because of the difficulty of separating water and monofluorophosphoric acid by this procedure. Acid of high purity was prepared by hydrogen chloride cleavage of carefully purified difluorophosphoric anhydride[13] prepared from the same batch of commercial acid.

(13) E. A. Robinson, *Can. J. Chem.*, **40**, 1725 (1962).

(14) R. G. Cavell, *ibid.*, **45**, 1309 (1967).

TABLE II
MASS SPECTRUM OF $F_4P_2O_2$

m/e	Intens[a]	Fragment
170	24.7	$F_2POP(O)F_2$[b]
154	1.2	$(F_2P)_2O$
151	2.4	$FPOP(O)F_2$
135	0.8	$FPOPF_2$
104	0.8	OPF_3
101	0.6	O_2PF_2
88	1.3	PF_3
85	3.3	OPF_2
69	57.3	PF_2
66	1.6	OPF
50	2.8	PF
47	3.2	PO

[a] Intensities are expressed relative to the total ionization defined as Σ_n(intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. [b] Identity confirmed by accurate mass measurement.

TABLE III
NUCLEAR MAGNETIC RESONANCE PARAMETERS

| Obsd nucleus | Temp, °C | Chem shift, ppm | Coupling constants, Hz | | | | |
			$^1J_{PF}$	$^2J_{PF_a}$	$^3J_{PF_b}$	$^4J_{FF}$	$^2J_{PP}$
		$F_2P(S)SPF_2$					
^{19}F[a]	+40	13.7	1216.9	...	...	...	...
		60.5	1321.5	...	...	...	...
	−90	14.4	1217.9	15.0	...	5.9	...
		60.8	1319.6	...	22.2	5.9	...
^{31}P[b]	−40	153.2	1209.9	14.3	...	...	68.1
		37.0	1323.6	...	22.5	...	67.6
		$F_2P(O)OPF_2$					
^{19}F[a]	+40[c]	38.3	1396.4	...	...	...	...
		80.0	1032.5	...	...	...	...
^{31}P[b]	+40	122.3	1400	...	...	...	...
		262.2	1031	...	...	...	...

[a] Chemical shift relative to $CFCl_3$. [b] Chemical shift relative to P_4O_6. [c] At −50° pronounced broadening of the peaks was observed. The sample froze at lower temperatures.

giving an extrapolated boiling point of 50°, heat of vaporization of 8800 cal/mol, and Trouton constant of 27 eu.

Decomposition of Difluorophosphoryl-μ-oxo-difluorophosphine. —A sample of the compound (0.17 g, 1.00 mmol) was sealed in a glass tube and warmed to room temperature. Noticeable formation of a white solid was observed within 1 hr and after 18 hr the original liquid was no longer visible. The only volatile product at this point was PF_3 (0.05 g, 0.58 mmol). The white solid material remaining in the reaction vessel was insoluble in $CFCl_3$ and CH_3CN but soluble in dimethyl sulfoxide with apparent reaction. The ^{19}F nmr spectrum of the resultant DMSO solution showed only the resonances due to the $O_2PF_2^-$ ion.[11,14]

Reactions of Difluorothiophosphoryl-μ-thio-difluorophosphine. (a) **With Anhydrous Hydrogen Chloride.**—Hydrogen chloride (0.0140 g, 0.38 mmol) was combined with $F_2PSP(S)F_2$ (0.0806 g, 0.40 mmol) at room temperature for 24 hr. Separation of the volatile products gave SPF_2SH (0.0525 g, 0.39 mmol) and PF_2Cl (0.0405 g, 0.39 mmol). The latter, identified spectroscopically,[15] was contaminated with small traces of HCl and SPF_2H. A trace of unreacted $F_2PSP(S)F_2$ was also recovered.

(b) **With Water.**—Combination of water (0.0153 g, 0.85 mmol) with $F_2PSP(S)F_2$ (0.100 g, 0.495 mmol) in a sealed 10-cm³ tube at room temperature led to a rapid exothermic reaction and the evolution of a gas. Separation of the volatile products

(15) A. Mueller, O. Glemser, and E. Niecke, *Z. Naturforsch.*, **21b**, 732 (1966).

TABLE IV
INFRARED SPECTRA[a]

$F_2P(S)SPF_2$	$F_2P(O)OPF_2$	Assignment
1380 vw	...	
...	1384 s	P=O str
...	1025 vs	P—O—P str[b]
925 s	975 s	}PV—F str
898 s	914 w	
847 s	872 s	}PIII—F str
834 s	...	
731 s	...	P=S str
705 w	724 m	
580 vw		
534 w	505 m	
500 vw		
480 s		
	447 w	
402 vw		
	405 w	
391 vw		
358 w		
350 sh		

[a] All values in cm^{-1}. The abbreviations are: s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] See text.

after 24 hr gave only SPF$_2$SH (0.05 g, 0.37 mmol) and a mixture of SiF$_4$ and PF$_3$ (0.02 g). A nonvolatile clear liquid remained in the reaction tube.

(c) **With Mercury.**—Mercury (0.05 g, 0.26 mmol) was vigorously shaken with F$_2$PSP(S)F$_2$ (0.05 g, 0.26 mmol) in a 10-cm^3 tube at room temperature. The products, after 3 days of reaction, were a mixture of PF$_3$ and SPF$_3$ (0.02 g) and an involatile yellow-green solid.

(d) **With Methyl Mercaptan.**—Reaction of F$_2$PSP(S)F$_2$ (0.073 g, 0.36 mmol) with methyl mercaptan (0.021 g, 0.44 mmol) in a 10-cm^3 tube for 48 hr at room temperature gave SPF$_2$SH (0.034 g, 0.26 mmol) and PF$_3$ (0.030 g, 0.34 mmol), the latter contaminated with traces of SPF$_2$H. A bright orange solid residue and a pale yellow liquid of low volatility remained in the reaction vessel.

(e) **With Methanol.**—F$_2$PSP(S)F$_2$ (0.102 g, 0.51 mmol) was combined with methanol (0.017 g, 0.54 mmol) in a 10-cm^3 reaction tube at temperature for 3 hr. Separation of the volatile products gave SPF$_2$SH (0.07 g, 0.50 mmol) containing a trace of SPF$_2$OCH$_3$ as the $-116°$ condensate and PF$_3$ (0.048 g, 0.54 mmol) containing traces of SPF$_2$H and SPF$_3$ in the $-196°$ trap. A small amount of a light yellow solid residue remained in the reaction vessel.

(f) **With Chlorine.**—Reaction of F$_2$PSP(S)F$_2$ (0.06 g, 0.31 mmol) and chlorine (0.023 g, 0.32 mmol) in a 10-cm^3 reaction tube at room temperature for 48 hr gave SPF$_2$Cl (0.02 g, 0.15 mmol) collected with traces of OPF$_3$ and PF$_3$, unreacted F$_2$PSP-(S)F$_2$ (0.0176 g, 0.087 mmol) collected at $-81°$, and 0.02 g of an unidentified, unstable product which was trapped at $-45°$. A white solid residue remained in the reaction vessel.

(g) **With Hydrothiophosphoryl Difluoride.**—SPF$_2$H (0.07 g, 0.71 mmol) and F$_2$PSP(S)F$_2$ (0.15 g, 0.76 mmol) were combined in a 10-cm^3 reaction tube. Separation of the volatile products after 48 hr at room temperature gave PF$_3$ (0.042 g, 0.48 mmol), SPF$_2$H (0.060 g, 0.59 mmol), and F$_2$PSP(S)F$_2$ (0.035 g, 0.17 mmol). A light yellow solid and nonvolatile liquid remained as residues. The liquid appeared to be of a similar constitution to that obtained from the decomposition of F$_2$PSP(S)F$_2$.

(h) **With Sulfur.**—Excess sulfur was combined with F$_2$PSP-(S)F$_2$ (0.078 g, 0.39 mmol) for 60 hr at room temperature. The only volatile products obtained were F$_2$PSP(S)F$_2$ (0.059 g, 0.29 mmol) and PF$_3$ (0.006 g, 0.07 mmol).

(i) **With Dimethylamine.**—Immediate reaction occurred when F$_2$PSP(S)F$_2$ (0.096 g, 0.475 mmol) and (CH$_3$)$_2$NH (0.046 g, 1.01 mmol) were combined in a 10-cm^3 reaction tube at room temperature. Separation of the volatile products after 48 hr gave
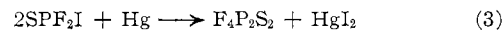
SPF$_2$N(CH$_3$)$_2$ (0.008 g, 0.055 mmol) collected at $-81°$, PF$_2$N-(CH$_3$)$_2$ (0.027 g, 0.24 mmol) collected at $-116°$, and PF$_3$ (0.015 g, 0.17 mmol) trapped at $-196°$. Ir and nmr spectra showed the residue to be a mixture of the salt[11,14] (CH$_3$)$_2$NH$_2$$^+S_2PF_2$$^-$ plus a material having a ^{19}F nmr spectrum similar to that of the adduct formed between SPF$_2$H and trimethylamine described below.

The Reaction of Hydrothiophosphoryl Difluoride with Methylamines.—Combination of equimolar proportions of SPF$_2$H and (CH$_3$)$_3$N resulted in the immediate formation of a white solid. Very small amounts of volatile products (mostly PF$_3$ with traces of H$_2$S and SPF$_2$N(CH$_3$)$_2$) were obtained. Reaction of water or anhydrous HCl with this adduct gave solid products and no significant quantities of volatile materials. The adduct of SPF$_2$H with (CH$_3$)$_3$N dissolved readily in CH$_3$CN at $-35°$ to give a pale yellow solution with lines due to the (CH$_3$)$_3$NH$^+$ ion in the ^{1}H nmr spectrum and a simple doublet ($\phi = 34.0$ ppm $vs.$ CCl$_3$F, $J = 1180$ Hz) in the ^{19}F spectrum. The solution, even when kept at $-35°$ during preparation and subsequent spectral measurements, deposited a yellow precipitate within 15–20 min of preparation with simultaneous disappearance of the doublet in the ^{19}F nmr spectrum.

Dimethylamine reacted with SPF$_2$H in both 1:1 and 2:1 molar ratios to give similar results except that the (CH$_3$)$_2$NH$_2$$^+$ ion appeared in the ^{1}H spectrum.
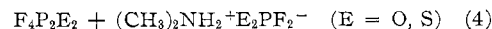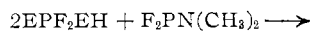
Results and Discussion

Reaction of SPF$_2$I with a *stoichiometric* quantity of mercury gave a good yield of the diphosphorus compound with the formula F$_4$P$_2$S$_2$ (eq 3). Since mercury

$$2SPF_2I + Hg \longrightarrow F_4P_2S_2 + HgI_2 \qquad (3)$$

reacts with the diphosphorus compound, as demonstrated in a separate experiment, to give an intractable solid similar to that obtained previously,[6] excess mercury cannot be used (as is usual in this type of reaction[2-4]) in order to ensure complete consumption of the iodophosphorus compound. This method, which is troubled by the difficulty of separating the product from unreacted SPF$_2$I, is therefore not the most suitable synthesis of this compound.
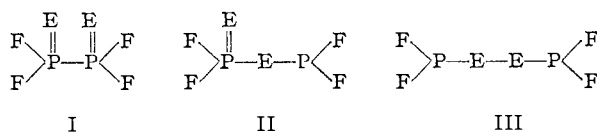
This compound, which proved to be difluorothiophosphoryl-μ-thio-difluorophosphine [F$_2$PSP(S)F$_2$], by means of structural studies described below, was more conveniently synthesized by the smooth reaction of dithiodifluorophosphoric acid (E = S) with dimethylaminodifluorophosphine

$$2EPF_2EH + F_2PN(CH_3)_2 \longrightarrow$$

$$F_4P_2E_2 + (CH_3)_2NH_2{}^+E_2PF_2{}^- \quad (E = O, S) \quad (4)$$

in which the salt of the acid is also obtained. A good yield of the oxygen analog, difluorophosphoryl-μ-oxo-difluorophosphine, F$_2$POP(O)F$_2$, can also be obtained from the analogous reaction with difluorophosphoric acid (eq 4, E = O) provided that the reaction and subsequent separations are executed quickly. This is the only method applicable to the synthesis of the oxygen compound since iodophosphoryl difluoride is unknown.

There are three possible isomeric structures which can be reasonably suggested for these compounds: (a) a structure with a phosphorus–phosphorus bond (I) in which both phosphorus atoms are pentavalent; (b) one with a single sulfur or oxygen bridge between the phosphorus atoms (II) in which the phosphorus atoms are necessarily dissimilar, one being trivalent and one

pentavalent; (c) a dithio or dioxo bridge (III) in which both phosphorus atoms are trivalent.

I   II   III

Although a phosphorus–phosphorus bonded structure (I) might be expected from the coupling reaction and by structural analogy with many known organodiphosphorus compounds,[2] the spectroscopic and chemical evidence (including synthesis by eq 4) favors the mixed-valence structure (II).

Comparison of the gas-phase infrared spectra of the new compounds to those of similar compounds such as $(SPF_2)_2S$,[8] $(SPF_2)_2O$,[8] $(OPF_2)_2O$,[13] and $(PF_2)_2O$[16] indicates several features in support of structure II. The spectrum of $F_2PSP(S)F_2$ shows four bands in the P–F stretching region instead of two observed in the pentavalent compounds $(EPF_2)_2E$. The pair of strong bands at 925 and 898 cm^{-1} can be assigned to pentavalent P–F stretching frequencies in agreement with the 974, 949 cm^{-1} pair observed in $(SPF_2)_2O$[8] and the 952, 923 cm^{-1} pair in $(SPF_2)_2S$.[8] The additional pair of bands of approximately equal intensity at 847 and 834 cm^{-1} does not have a counterpart in the pentavalent molecules, but since *trivalent* fluorophosphorus compounds[17] including $O(PF_2)_2$[16] have strong P–F bands in the 825–860-cm^{-1} region, it seems reasonable to assign this latter pair of bands to trivalent P–F stretching vibrations.

The strong band at 731 cm^{-1} in the spectrum of $F_2PSP(S)F_2$ can be associated with a P=S absorption in keeping with bands at 708 cm^{-1} in $(SPF_2)_2O$ and 703 cm^{-1} in $(SPF_2)_2S$[8] which can also be assigned to this absorption. The band at 480 cm^{-1} in $F_2PSP(S)F_2$ has a counterpart in the spectrum of $(SPF_2)_2S$ at 501 cm^{-1} but no counterpart in the spectrum of $(SPF_2)_2O$.[8] It therefore seems reasonable to assign this band to the P—S—P stretch.

Although infrared spectral measurements on $F_2POP(O)F_2$ were hampered by the instability of the compound and its reactivity with cell windows, some evidence to support the mixed-valence structural isomer (II) was obtained. The strong bands at 1384 and 1025 cm^{-1} may be readily associated with P=O and P—O—P stretching vibrations although the latter may be mixed with some pentavalent P—F stretch component. The presence of a P=O function is however assured and in combination with nmr spectral results this indicates that the compound has structure II.

The nuclear magnetic resonance spectra strongly support structure II for both compounds. At $+40°$, the normal operating temperature of the spectrometer, the ^{19}F spectra of both compounds show two doublets with chemical shifts and coupling constants (Table III) which can reasonably be associated with the presence of a pentavalent, four-coordinate $-P(O)F_2$ or $-P(S)F_2$ and
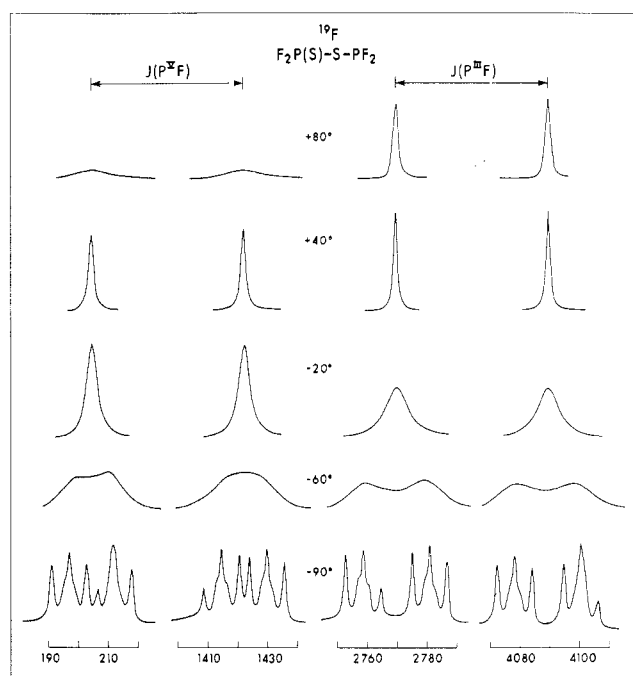
Figure 1.—Temperature dependence of the ^{19}F nmr spectra of difluorothiophosphoryl-μ-thio-difluorophosphine. All spectra were measured under identical sweep width conditions with spectrum amplitudes of 32 ($+80°$), 25 ($+40°$), and 50 (remaining temperatures) with a Varian A56/60 spectrometer.

tricoordinate trivalent $-PF_2$ structural units[17,18] in each molecule.

At lower temperatures all four peaks in the ^{19}F spectrum of $F_2PSP(S)F_2$ (Figure 1) broaden with the peaks assigned to the fluorine attached to trivalent phosphorus atoms broadening at higher temperatures than those which are assigned to fluorine attached to pentavalent phosphorus. Each line eventually splits into a doublet and at the lowest attainable temperature $(-90°)$ each of the individual components of these doublets is further split into a triplet. The low-temperature spectrum is readily assigned to the first-order spectrum expected for a molecule with structure II and it is not compatible with the other isomers. The parameters (Table III) are readily assigned because the two long-range $^3J_{PF}$ coupling constants should be and indeed are different and depend upon the valence of the phosphorus atom to which the observed fluorine is attached whereas long-range $^4J_{FF}$ couplings are necessarily identical in both parts of the spectrum. At high temperatures the pentavalent region of the spectrum collapses while the trivalent region remains relatively sharp. Since decomposition became noticeable at temperatures in excess of $+80°$, this was the highest temperature investigated.

It seems reasonable to suggest that the thermal behavior of the spectra can be attributed to a rapid averaging process such as rotation about the P–S bonds. Complete decoupling of nuclear spins at ordinary
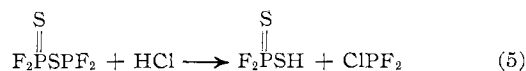
(16) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

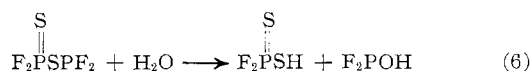(17) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).

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temperatures results in the observation of only directly bonded interactions but at low temperatures less rapid interchange between conformations leads to resolution of the longer range coupling interactions. The different rates of collapse of the trivalent and pentavalent regions of the spectrum may be due to a difference in the rate of rotation about the P(III)–S and P(V)–S bonds since these will not necessarily be identical.

The chemical behavior of $F_2PSP(S)F_2$ agrees with a formulation involving both P(III) and P(V) atoms (structure II). With molar quantities of HCl, nearly quantitative yields of SPF_2SH and PF_2Cl are obtained according to

$$\underset{\|}{\overset{S}{F_2P}}SPF_2 + HCl \longrightarrow \underset{\|}{\overset{S}{F_2P}}SH + ClPF_2 \qquad (5)$$

Water reacts with $F_2PSP(S)F_2$ to form SPF_2SH. By analogy with eq 5 the unknown compound F_2POH would be expected

$$\underset{\|}{\overset{S}{F_2P}}SPF_2 + H_2O \longrightarrow \underset{\|}{\overset{S}{F_2P}}SH + F_2POH \qquad (6)$$

but neither the trivalent compound F_2POH nor its pentavalent isomer $F_2P(O)H$[7] was isolated. The trivalent isomer probably rearranges to the pentavalent form as was proposed in a study[19] of the hydrolysis of phosphorus trifluoride. The thermal instability[7] of $F_2P(O)H$ precludes its isolation under our reaction conditions.

Methanol and methyl mercaptan react with $F_2PSP(S)F_2$ to give principally SPF_2SH and phosphorus trifluoride so it seems reasonable to suggest that the reactions involve preferential cleavage of the P(III)–S bridge bond to give an initial reaction similar to eq 5

$$\underset{\|}{\overset{S}{F_2P}}SPF_2 + CH_3EH \longrightarrow \underset{\|}{\overset{S}{F_2P}}SH + CH_3EPF_2 \quad (E = S, O) \quad (7)$$

In neither case was the expected trivalent fluorophosphine CH_3EPF_2 isolated. The yield of approximately two-thirds molar quantity of PF_3 obtained suggests however that the expected CH_3EPF_2 has decomposed during the reaction. It is also possible that PF_3 arises from decomposition of $F_2PSP(S)F_2$ which is slow for the pure compound at room temperature but perhaps catalyzed by other reagents. Cleavage of the P(V)–S bridge which would result in the formation of $F_2P(S)H$ and $F_2P(S)ECH_3$ does not appear to be an important pathway since only minor amounts of these two compounds were obtained.

The reaction of dimethylamine with $F_2PSP(S)F_2$ appears to involve cleavage of both the P(III)–S and P(V)–S bridge bonds since the salt obtained contains the $S_2PF_2^-$ ion and a species which we have tentatively identified as the SPF_2^- ion. This latter species was first observed in the ^{19}F nmr spectrum of a solution of the solid adduct formed between trimethylamine and SPF_2H. The identity of spectral parameters is however the only basis for the identification. Because of the

instability of the species in solution, complete characterization has not been achieved. The required quantity of $PF_2N(CH_3)_2$ for a reaction similar to eq 7 was obtained but in addition significant quantities of $SPF_2N(CH_3)_2$ and PF_3 were obtained.

Elemental sulfur did not oxidize $F_2PSP(S)F_2$ to any known pentavalent phosphorus derivative such as the bridged compound $(SPF_2)_2S$, which has been prepared by other methods,[8] probably because decomposition of the mixed-valence compound occurred before significant reaction with sulfur. SPF_2H also did not react with $F_2PSP(S)F_2$.

The adoption of mixed-valence bridged isomeric structures (II) by these compounds rather than structures in which equivalence of phosphorus atoms is preserved is rather unexpected. All known organophosphorus analogs of our tetrafluoro compounds, $R_4P_2E_2$ (E = O, S), have the phosphorus–phosphorus bonded structure.[2,20] Organodiphosphorus monosulfides, R_4P_2S, also exist in the isomeric form with a phosphorus–phosphorus bond,[21] which of necessity must be a mixed-valence compound of phosphorus. Exceptions to this general monosulfide structure are the sulfur-bridged structure of $(CF_3)_4P_2S$[22,23] and oxygen-bridged structures[3,4,24] of $(CF_3)_4P_2O$ and F_4P_2O, all of which contain equivalent trivalent phosphorus atoms. The reason for the observed structural preference may be a stabilization of the trivalent state of phosphorus by the strong electron-withdrawing groups such as fluorine or CF_3. If this is so, however, the disulfide structure (III) involving trivalent phosphorus might be predicted.

If *trans* fluorine geometry is considered for structure I of $F_4P_2S_2$ by analogy with the structure of P_2F_4 for which a *trans* configuration is preferred since this minimizes interaction between fluorine atoms on different phosphorus atoms,[25] models quickly demonstrate that the two additional sulfur atoms produce four S–F interactions at the van der Waals distance. In contrast, minimal S–F interactions and a single P–S interaction are the apparent steric features of isomer (II). Even less interatomic interaction might be expected in structure III; however the disulfide or peroxo bridge probably provides a weaker bonding situation than that provided by a phosphorus–sulfur–phosphorus, etc., bridge. The preference of one particular structural isomer is probably a consequence of both electronic and steric contributions to the system.

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