plex concentration, one will need to make some assumptions about the system. The results obtained should be checked against those from other physical methods to verify the approach used. Some of the considerations given here apply to studies of weak hydrogen bonding[48] and may perhaps apply to some types of metal–ligand complexing in which the equilibria are formally analogous to the types we have been considering.[49]

Acknowledgments. We thank Mr. D. E. Williams and Professor E. L. King for helpful criticisms.

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[48] See, for example, E. Grunwald and W. Coburn, Jr., *J. Am. Chem. Soc.*, **80**, 1322 (1958).

[49] See, for example, E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

Fluorophosphine Ligands. III. Syntheses Involving PF_2I. The Preparation and Characterization of μ-Oxo-bisdifluorophosphine, Cyanodifluorophosphine, and Tetrafluorodiphosphine[1]

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Abstract: Copper(I) salts, CuX, undergo metathesis reactions with PF_2I to give new compounds of the form PF_2X. The new compounds, μ-oxo-bisdifluorophosphine, F_2POPF_2, and cyanodifluorophosphine, F_2PCN, have been prepared in good yield by reactions of PF_2I with Cu_2O and CuCN, respectively. The coupling of two difluorophosphine groups to form F_2PPF_2 can be effected by shaking F_2PI and mercury. The new compounds have been characterized and their nmr and infrared spectra are in complete agreement with the formulas assigned.

Although theoretical arguments have been invoked[2] to show that F_2PPF_2 should be more stable than P_2Cl_4 and comparable in stability to N_2F_4, all attempts to synthesize P_2F_4 by fluorination of P_2Cl_4 or P_2I_4 have given only PF_3 as a major product.[3,4] In this paper a successful synthesis of P_2F_4 is described. The procedure involves the coupling of two PF_2 groups in a reaction somewhat analogous to that used by Bennett, Emeleus, and Hazeldine[5] for the synthesis of the related $(CF_3)_2PP(CF_3)_2$. The equation, using the recently reported[6] PF_2I, is

$$2Hg + 2PF_2I \longrightarrow P_2F_4 + Hg_2I_2$$

When copper was used as the metal in an attempted coupling reaction, small amounts of Cu_2O on the metal surface produced small amounts of F_2POPF_2 but no F_2PPF_2. The subsequent use of Cu_2O as a reagent gave good yields of F_2POPF_2 and suggested the metathesis reaction which is developed herein.

$$CuX + F_2PI \longrightarrow CuI + F_2PX$$

The generality of this process is now being explored. It is already clear that PF_2I is a very useful reagent for the introduction of PF_2 groups and for the synthesis of PF_2X compounds.

μ-Oxo-bisdifluorophosphine, F_2POPF_2

The reaction of Cu_2O and PF_2I gives the highly volatile F_2POPF_2 in yields exceeding 70%.

$$2PF_2I + Cu_2O \longrightarrow F_2POPF_2 + 2CuI$$

The comparable derivative of phosphorus(V), $F_2P(O){-}O{-}P(O)F_2$, has been described[7] as a liquid which boils at 71°. This temperature is significantly higher than the extrapolated boiling point of $-18.3°$ for F_2POPF_2. The latter value is obtained from an extrapolation of the vapor pressure equation

$$\log P_{(\mathrm{mm})} = \frac{-1300}{T} + 7.981$$

The mass spectrum of F_2POPF_2 (Table I) has the expected fragmentation pattern. Since no peaks appear at *m/e* ratio higher than 154 (which is the parent peak for F_2POPF_2), the mass spectrum is consistent with the molecular weight of 154.2 g/mole determined by vapor density.

Decomposition of the pure liquid is slow in clean *glass* tubes; at 25° less than 1% of the sample is decomposed per day. The vapor at lower temperatures and pressures is decomposed more slowly. Adsorbent surfaces like asbestos appear to accelerate the decomposition. A sample in contact with asbestos paper at 25° was 100% decomposed after 1 day. The equation is

$$F_2POPF_2 \longrightarrow PF_3 + (POF)_n$$

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[1] For a communication on this subject, see M. Lustig, J. K. Ruff, and C. B. Colburn, *J. Am. Chem. Soc.*, **88**, 3875 (1966).

[2] R. D. Brown and R. D. Harcourt, *Australian J. Chem.*, **16**, 737 (1963).

[3] (a) A. Finch, *Can. J. Chem.*, **37**, 1793 (1959); (b) G. S. Harris and D. S. Payne, *Quart. Rev.* (London), **15**, 173 (1961).

[4] L. A. Ross, *Dissertation Abstr.*, **23**, 1920 (1962).

[5] F. W. Bennett, H. J. Emeleus, and R. N. Hazeldine, *J. Chem. Soc.*, 1565 (1953).

[6] R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, **5**, 1464 (1966).

[7] (a) V. Wannagat and J. Radamachers, *Z. Anorg. Allgem. Chem.*, **289**, 66 (1957); (b) E. A. Robinson, *Can. J. Chem.*, **40**, 1725 (1962).

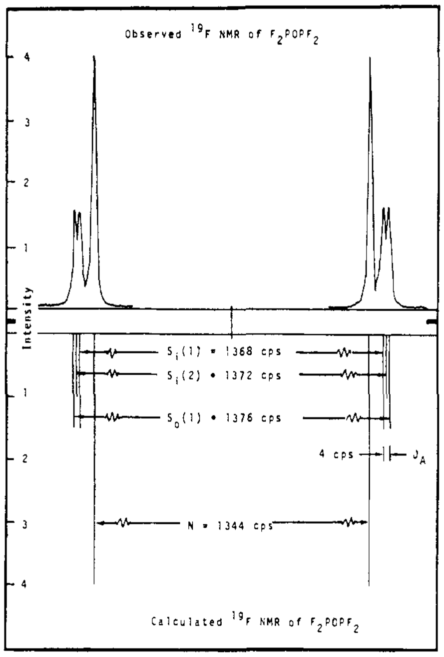

Figure 1. Observed and calculated ^{19}F nmr spectra of F_2POPF_2.

The Infrared Spectrum of F_2POPF_2. Corbridge,[8] after examining a number of compounds containing the P–O–P linkage, assigned absorptions in the 970–870- and 700-cm^{-1} region to the P–O–P modes. The observed band at 976 cm^{-1} listed in Table II for F_2POPF_2 would thus be assignable to the P–O–P asymmetric, stretching motion (ν_{as}) and the band at 682 cm^{-1} to the symmetric P–O–P vibration (ν_s). Such an assignment would be consistent with the assignments made by Griffiths and Burg[9] for the molecule $(CF_3)_2POP(CF_3)_2$. Their values for $(CF_3)_2POP(CF_3)_2$ are ν_{as} POP = 925 and ν_s POP = 715 cm^{-1}.

Table I. Mass Spectra of F_2POPF_2, PF_2CN, and P_2F_4

	F_2POPF_2		PF_2CN		P_2F_4	
m/e	Rel peak ht	Assgn	Rel peak ht	Assgn	Rel peak ht	Assgn
154	20.0	$F_2POPF_2^+$			1.4	$F_2POPF_2^+$
138					29.5	$P_2F_4^+$
135	2.6	F_2POPF^+				
119					10.3	$P_2F_3^+$
95			27.1	PF_2CN^+		
88	2.5	PF_3^+	2.0	PF_3^+	7.8	PF_3^+
85	3.3	PF_2O^+				
76			14.2	$PFCN^+$		
70					3.6	PHF_2^+
69	100.0	PF_2^+	100.0	PF_2^+	100.0	PF_2^+
66	4.3	PFO^+			1.0	PFO^+
57			1.9	PCN^+		
51					3.5	PHF^+
50	16.8	PF^+	17.6	PF^+	26.5	PF^+
47	27.7	PO^+	1.3	PO^+	2.5	PO^+
43			1.8	PC^+		
38			1.4	$PFCN^{2+}$		
31	5.9	P^+	13.3	P^+	12.4	P^+
27			12.6	HCN^+		
26			9.6	CN^+		
25	0.4	PF^{2+}			2.2	PF^{2+}
19	1.2	F^+	1.6	F^+	3.3	F^+
16	0.4	O^+				
15.5	0.3	P^{2+}			1.2	P^{2+}
14			2.5	N^+		

The infrared frequencies of gaseous F_2POPF_2 are compared in Table II with the Raman frequencies of $F_2P(O)$–O–$P(O)F_2$ given by Robinson.[7b] The very intense band in the 1400–1200-cm^{-1} region has been assigned[7b,8] to the terminal PO vibration in $F_2P(O)$–O–$P(O)PF_2$. The *absence* of this band in F_2POPF_2 is thus consistent with the earlier assignment. On the other hand, Robinson's[7b] assignment of absorptions around 700 cm^{-1} in $Cl_2P(O)$–$OP(O)Cl_2$ and $F_2P(O)$–O–$P(O)F_2$ to P–O wagging motion would not be consistent with these observations since P–O wagging modes are precluded in F_2POPF_2. Thus the assignment of the band at 682 cm^{-1} to the symmetric P–O–P stretch would be strongly supported as noted above.

Table II. A Comparison of the Vibrational Spectra of F_2POPF_2 and $F_2P(O)$–O–$P(O)F_2$

Infrared frequencies of $F_2POPF_2(g)$			Raman frequencies of $F_2P(O)$–O–$P(O)F_2(l)$[7]	
cm^{-1} (intensity)	Note[a]	Assgn	cm^{-1} (polarization)	Assgn[7]
			1390 (p)	ν_{PO}
			1370	ν_{PO}
			1270 (dp)	Overtone
1077 (w)		Overtone	1083 (dp)	Overtone
976.1 (vvs)	br	ν_{POP}, asym	987 (dp)	ν_{POP}, asym
863.1 (vvs)	br	ν_{PF}	951 (cp)	ν_{PF}
853 (vvs)			890 (p)	
842 (vvs)			855	
			721 (p)	ω_{PO}
			700	
682 (m)		ν_{POP}, sym		
519 (m)		PF_2 scissors	518	PF_2 scissors
515 (sh)				
			480 (p)	ν_{POP}, sym
460 (w)		ρ_{PF_2}		
			440 (p)	PF_2 scissors
			395	ρ_{PF_2}, ω_{PO} and torsional modes
359 (w)		τ_{PF_2}	362	
			352	
			340	
			295	
			273 (dp)	
			205	
			160 (p)	POP scissors

[a] br = broad.

^{19}F and ^{31}P Nmr Spectra of F_2POPF_2. The high-resolution ^{19}F nmr spectrum of $F_2POPF_2(l)$ is shown in Figure 1; the pattern remained unchanged in appearance from −80 to 37°. The spectrum is best described as "second order" and has been analyzed as a second-order $X_2AA'X_2'$ system using the expressions of Harris.[10] The calculated spectrum is compared with the observed one in Figure 1. From a comparison of the calculated and observed spectra, it is apparent that the doublet separation $S_i(2)$ = 1372 cps remained unresolved in the observed spectrum but did contribute in intensity to the $S_i(1)$ = 1368 and $S_0(1)$ = 1376 cps doublets (Figure 1). Therefore, each member of the doublet of doublets has one-half the *integrated* intensity of each component of the central doublet. The calculations also indicate that another pair of lines of

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(8) D. E. C. Corbridge, *J. Appl. Chem.*, **6**, 456 (1956).

(9) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 3442 (1962).

(10) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

separation $S_0(2) = 4116$ cps would have vanishing intensity. From the parameters of Harris,[10] $L = |J_{PF} - J_{P'OPF}| = 1372$, $N = |J_{PF} + J_{P'OPF}| = 1344$, and $J_A = J_{PP'} = 4$ cps, the following coupling constants were obtained for F_2POPF_2: $J_{PF} = 1358$ cps, $J_{P'OPF} = -14$ cps, and $J_{PP'} = 4$ cps. The analysis assumed that $J_{FPOP'F'} = 0$. The constants J_{PF} and $J_{P'OPF}$ are only relative in sign and rigorously cannot be distinguished; however, J_{PF} certainly must be larger. Also the sign of $J_{PP'}$ is undetermined. The ^{31}P nmr spectrum (Figure 2) is probably amenable to analysis in terms of an $X_2AA'X_2'$ system; however analysis of the phosphorus spectrum has not been completed at this time.

The ^{31}P ($\delta = -111$ ppm, OPA standard) and ^{19}F chemical shifts ($\delta = -39.9$ ppm, TFA standard) of F_2POPF_2(l) are both in good agreement with the corresponding values for PF_3 ($\delta_P = -105$ ppm, $\delta_F = -42.3$ ppm); this agreement is not surprising if F_2POPF_2 is considered as two PF_3 molecules with a bridging oxygen, fluorine's neighbor in the periodic chart, replacing a fluorine atom in each PF_3 unit.

It is appropriate to mention that no elemental analyses for F_2POPF_2 were obtained, but the nmr spectra leave no doubt as to the compound composition. The low-resolution 1:2:1 ^{31}P triplet indicates clearly that two fluorines are bound to each phosphorus, and the basic ^{19}F doublet indicates that a phosphorus is bound to each fluorine. These facts along with the other evidence such as molecular weight values above leave no reasonable doubt as to compound identity.

Cyanodifluorophosphine, PF_2CN

The process for the synthesis of PF_2CN can be described by the equation

$$PF_2I + CuCN \longrightarrow PF_2CN + CuI$$

In contrast to $P(CN)_3$ which is a solid, F_2PCN is a colorless volatile liquid. It is quite unstable, undergoing significant disproportionation in an nmr tube after 1 hr at −20°. Lines for PF_3 were detected in the nmr spectrum and a white solid, presumably $P(CN)_3$, appeared in the tube. The equation consistent with these observations is

$$3PF_2CN \longrightarrow 2PF_3 + P(CN)_3$$

The molecular weight of F_2PCN by vapor density is 97.5 g/mole. The theoretical value is 95 g/mole. The parent peak in the mass spectrum appears at an *m/e* value of 95. A few features of the mass spectrum (Table I) are unexpected, namely the presence of significant peaks of HCN^+ and PO^+ at *m/e* 27 and 47, respectively. Hydrolysis of the F_2PCN by trace amounts of water is suggested, since the infrared spectrum also gave evidence for HCN after the sample had been manipulated repeatedly in the system. The presence of a peak at *m/e* 43 (PC^+) is good evidence that F_2PCN is a true cyanide as opposed to an isocyanide which would be expected to give a peak at *m/e* 45 (PN^+).[11]

^{19}F and ^{31}P Nmr Spectra of F_2PCN. The ^{19}F nmr spectrum of liquid cyanodifluorophosphine at −20° consists of a simple doublet centered 11.7 ppm upfield from trifluoroacetic acid used as an external standard. The doublet splitting of 1267 cps is attributed to first-order spin-spin coupling of the fluorine nuclei with the single phosphorus nucleus. While the fluorine spectrum shows that one phosphorus is present in the molecule, the ^{31}P nmr spectrum clearly establishes the presence of two equivalent fluorines bonded to the phosphorus. The 1:2:1 triplet ($J_{PF} = 1273$ cps) in the ^{31}P nmr is centered 140.8 ppm downfield from orthophosphoric acid.

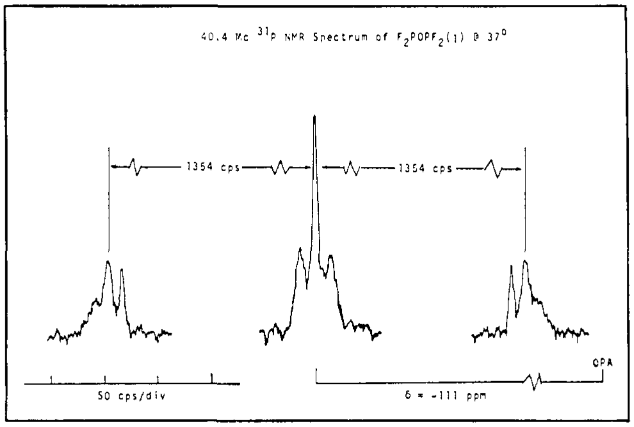

Figure 2. Observed ^{31}P nmr spectrum of F_2POPF_2(l) at 37°.

The Infrared and Raman Spectra of F_2PCN. The infrared bands of PF_2CN are given in Table III and are compared with the frequencies of PF_2Cl which are used as a basis for tentative assignments. In view of the stiff C–N bond, the CN group should approximate a point mass with respect to the rest of the molecule, and one might expect the two spectra to show a number of points of similarity. Experimentally, this prediction is borne out. In the P–F and P–X stretching regions, not only is the pattern of frequencies quite similar but the band shapes also are remarkably alike. The P–Cl bending and wagging motions of PF_2Cl proved unexpectedly weak in the infrared and were not observed under the conditions of the present experiments at the positions they have been reported in the Raman effect.[12] The corresponding P–CN wagging and bending modes likewise were not observed in the present work in the expected region (250–320 cm^{-1})[12,13] although it is possible that they occur below 200 cm^{-1}, the limit of the instrument. Recent work by Miller, *et al.*,[14] on $P(CN)_3$ suggests this may be the case. Although seven of the nine fundamentals have been observed, it is not possible on the basis of the present data to distinguish between the pyramidal C_s model and the planar C_{2v} model since the number of active fundamentals is the same. The pyramidal model is strongly favored on the basis of chemical comparisons. Since the nitrile and isonitrile frequencies fall close together,[15] the vibrational spectrum also cannot be used to distinguish between these two possibilities.

Under high resolution, the C–N stretching vibration of PF_2CN (Figure 3) exhibited fine structure consisting

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[11] Peaks at relative intensity less than 1 were neglected in tabulating the mass spectral data.

[12] M. L. Dewaulle and M. F. Francois, *J. Chim. Phys.*, **46**, 87 (1949).

[13] J. Goubeau, H. Haeberle, and H. Ulmer, *Z. Anorg. Allgem. Chem.*, **311**, 110 (1961).

[14] F. A. Miller, S. G. Frankis, and O. Sala, *Spectrochim. Acta*, **21**, 775 (1965).

[15] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

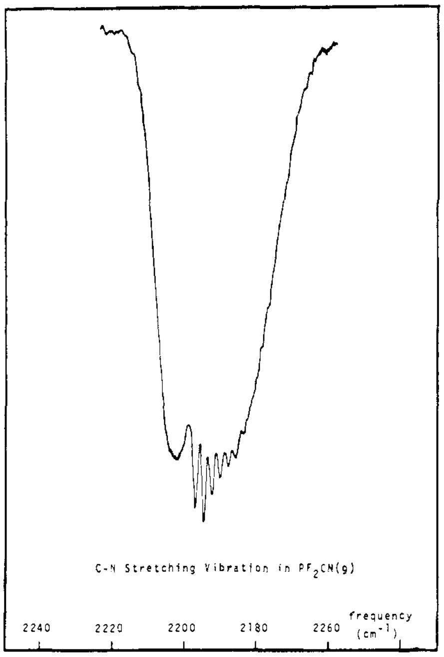

Figure 3. The C–N stretching vibration in PF$_2$CN(g).

of a series of regularly spaced lines having a separation of 2.3 cm^{-1} and degraded in intensity toward low wavelength. This spacing is much too large to be attributed to rotational structure for any reasonable geometry. Calculations of the moments of inertia assuming a pyramidal shape and molecular parameters based on PF$_3$ indicated that PF$_2$CN is an asymmetric top with the axis of least moment (*A* axis) along the C–N bond. Consequently, the C–N stretching band should be an *A*-type band of an asymmetric top having a characteristic strong sharp Q branch.[16] The fine structure therefore is most logically explained as the Q branches associated with "hot" bands, the associated P and R branches being unresolved and contributing to the general high underlying absorption. From a consideration of the number and relative intensities of the subsidiary Q branches, the low-frequency vibration involved is estimated to be approximately 180–200 cm^{-1}.

Table III. A Comparison of the Infrared Spectra of PF$_2$CN and PF$_2$Cl

PF$_2$CN(g)			PF$_2$Cl(g)		
ν, cm^{-1} (intensity)	Note	Assgn	ν, cm^{-1} (intensity)	Note	Assgn
2193.9 (vs)		ν_{CN}			
869.4 (s)		ν_{PF}, sym	864.5 (s)		ν_{PF}, sym
866.6 (vvs)		ν_{PF}, asym	853.5 (vvs)		ν_{PF}, asym
636.4	R		550.3	R	
629.0 (vs)	Q	ν_{PC}, sym	543.7 (vs)	Q	ν_{PCl}, sym
622.1	P		538	P	
549 (w)		δ_{PCN}, sym			
460.5 (w)	. . .^{a}	δ_{PCN}, asym			
			421	R	
			412.2 (m)	Q	δ_{FPF}, sym
			404	P	
344.6 (w)	. . .^{a}	δ_{FPF}, sym			
			302^b		δ_{PCl}, sym^b
			259^b		ω_{PCl}, asym^b

^{a} Indication of P and R branches. ^{b} Not observed in spectra determined on PF$_2$Cl vapor in this study; taken from ref 12.

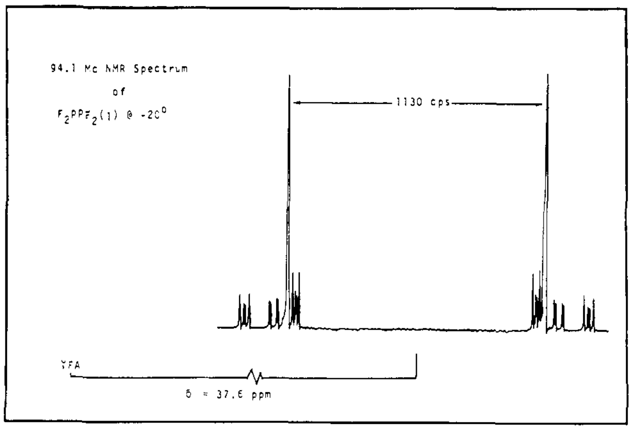

Figure 4. Observed ^{19}F nmr spectrum of F$_2$PPF$_2$(l) at −20°.

Tetrafluorodiphosphine, F$_2$PPF$_2$

The coupling reaction used to prepare F$_2$PPF$_2$ is similar in many ways to that used to prepare F$_2$PH from F$_2$PI, HI, and Hg.[17] A mass balance of products and reactants shows clearly that 2 moles of PF$_2$I react with mercury to form 1 mole of P$_2$F$_4$. The equation is

$$2PF_2I + 2Hg \longrightarrow F_2PPF_2 + Hg_2I_2$$

High yields of P$_2$F$_4$ were obtained when the initial pressure of PF$_2$I was around 50 mm; however, when the initial pressure was raised to 450 mm in a separate experiment, the principal reaction observed was disproportionation of the PF$_2$I in accordance with the equation

$$3PF_2I \longrightarrow 2PF_3 + PI_3$$

After the synthesis of P$_2$F$_4$ from PF$_2$I and Hg, a small amount of F$_2$PN(CH$_3$)$_2$ was observed in that sample of PF$_2$I which was separated from the reaction mixture. The possible catalytic effects of trace quantities of F$_2$PN(CH$_3$)$_2$ in the system are still undefined.

The molecular weight of F$_2$PPF$_2$ as determined by vapor density was 140 g/mole. Theory for F$_2$PPF$_2$ is 138 g/mole. Mass spectral data, recorded in Table I, show the parent P$_2$F$_4^+$ peak at an *m/e* ratio of 138, consistent with the vapor density molecular weight. Other minor peaks attributed to fragments from F$_2$POPF$_2$ and HPF$_2$ were also observed in the spectrum.[11] The existence of the latter molecules in the system is currently ascribed to a hydrolysis reaction resulting from trace amounts of water in the system. The equation consistent with the available data is

$$2P_2F_4 + H_2O \longrightarrow 2PHF_2 + F_2POPF_2$$

However, both detailed stoichiometry and mechanism are still uncertain. This equation is supported, however, by very recent studies[18] of the synthesis of F$_2$PH which

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(16) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1945.

(17) R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, 4, 1339 (1965).

(18) K. W. Morse and R. W. Rudolph, unpublished results, University of Michigan, 1966.

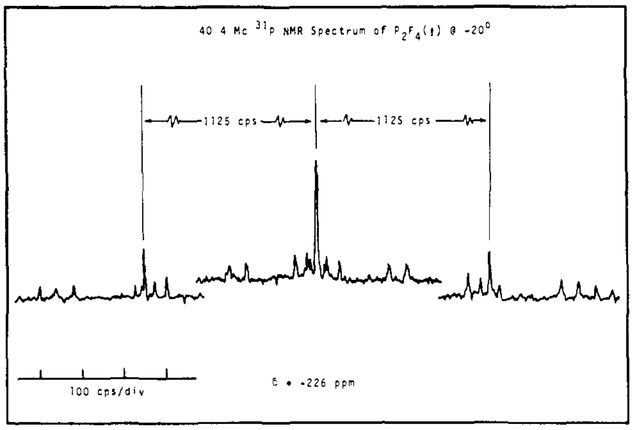

Figure 5. Observed ^{31}P nmr spectrum of F_2PPF_2(l) at −20°.

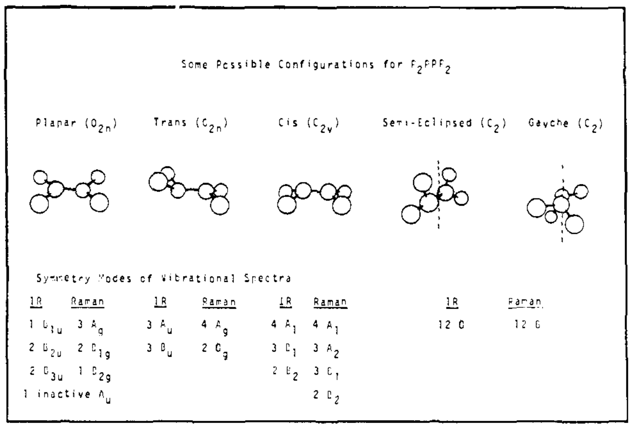

Figure 6. Some possible configurations and their associated symmetry modes for F_2PPF_2.

suggest that P_2F_4 can be easily cleaved by a proton donor such as HI.

$$P_2F_4 + HI \longrightarrow PF_2I + F_2PH$$

In fact, during certain preparations of PHF_2 from PF_2I, HI, and Hg, nmr spectroscopy showed that P_2F_4 was present in the reaction mixture. Thus, the data suggest that P_2F_4 may be a precursor in the synthesis of PHF_2 described earlier.[17]

The ^{19}F and ^{31}P Nmr Spectra of F_2PPF_2. Since both F_2PPF_2 and H_2PPH_2 are composed of nuclei with $I = {}^1/_2$ and are probably isostructural, similarities in their nmr spectra are to be anticipated. The nmr spectrum of H_2PPH_2 is complex and has been interpreted in terms of $X_2AA'X_2'$ pattern.[19] The ^{19}F nmr spectrum of F_2PPF_2(l) has been determined at −20° and is shown in Figure 4. The spectrum is indeed complex as is the ^{31}P nmr spectrum (Figure 5). An analysis of the $X_2AA'X_2'$ spectrum using the methods of Harris[10] predicts only five pairs of lines, yet 13 pairs are observed. The discrepancy can be traced to the fact that Harris has assumed explicitly that $J_{FPP'F'} = 0$. This assumption does not appear to be valid here and a more detailed analysis is required. Thus calculations of the nmr spectra for F_2PPF_2 are still incomplete at this time.

The Infrared and Raman Spectra of F_2PPF_2. A number of configurations may be proposed for the F_2PPF_2 molecule. The most likely possibilities and their respective symmetries are illustrated in Figure 6 together with the number of active infrared and Raman bands predicted for each. The observed infrared and Raman bands of F_2PPF_2 are listed in Table IV. Comparison of the observed and predicted frequencies suggests that tetrafluorodiphosphine quite likely may exist in the *trans* conformation. On inspection of the two spectra, one is immediately struck by their relative simplicity and the small number of bands observed. Barring an unusual number of accidental degeneracies, which does not appear too likely from the appearance of the bands, this weighs against the lower symmetry *cis* (C_{2v}), *gauche* (C_2), and eclipsed (C_2) configurations for which either nine or all twelve fundamentals, respectively, should be active in both the infrared and Raman spectra. Further inspection of the data of Table IV indicates that the mutual exclusion rule indicative of a center of symmetry may be operative. This latter conclusion is not entirely certain since the two spectra were taken with the sample in different physical states, and it is possible, for example, that the Raman band at 825 cm^{-1} and the infrared band centered at about 831 cm^{-1} are the same band with maxima shifted due to medium effects. This pair represents the closest approach to coincidence, however, and over-all, the spectra are quite dissimilar. Both the planar (D_{2h}) and *trans* (C_{2h}) models possess a center of symmetry, and the only evidence pro or con comes from the polarization properties of the Raman bands. The selection rules predict three polarized bands for the former and four for the latter. The qualitative observations of the present work show four bands having depolarization ratios significantly less than 6/7. To this number must be added one of the P–F stretching motions, which undoubtedly has a ratio near the upper limit, for a total of five. If one of the lower bands is assigned as an overtone, the remainder of four agrees with that pre-

Table IV. Vibrational Spectra of P_2F_4[a]

Infrared of P_2F_4(l) cm^{-1} (intensity)	Note	Raman of P_2F_4(l) at −20° ν, cm^{-1} (intensity and polarization)	Tentative assignment
846.9 (vvs)	R		ν_{PF}, asym, out-of-phase
839 (vvs)	P		
833.9 (vvs)	R		ν_{PF}, sym, out-of-phase
827.8 (vvs)	P		
		825 (m, p?)	ν_{PF}, sym, in-phase
		803 (w, sh, dp?)	ν_{PF}, asym, in-phase
		541 (vs, p)	ν_{PP}, sym
		453 (w, dp?)	ω_{PF_2}, sym, in-phase (?)
417.8			PF_2I impurity
412.2 (vw)			
406.8			
		403, (vw, sh, p)	2 × 214 (?)
378.7 (vw)			PF_2I impurity
		377 (s, p)	δ_{PF_2}, sym, in-phase
365 (m)			δ_{PF_2}, sym, out-of-phase
361 (m)			ρ_{PF_2}, asym
		214 (m, p)	ρ_{PF_2}, sym

[a] s = strong, m = medium, w = weak, etc.; p = polarized; sym refers to symmetry of PF_2 groups; in phase and out-of-phase refers to respective motions of the two PF_2 groups.

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[19] (a) R. M. Lynden-Bell, *Trans. Faraday Soc.*, 57, 888 (1961); (b) *Mol. Phys.*, 6, 601 (1963).

dicted for the *trans* model. The spectroscopic evidence clearly favors the *trans* configuration although a more detailed spectroscopic study will be necessary to establish the structure unequivocally.

The Epr Spectrum of F_2PPF_2. Since tetrafluorohydrazine, N_2F_4, is known to yield NF_2 free radicals,[20-22] the epr spectrum of P_2F_4 is of interest. A signal was indeed found for all the samples of P_2F_4 investigated. In the case of the single line observed for neat P_2F_4(l), the *g* value was 2.00129. More complex spectra were observed for gaseous P_2F_4 and for P_2F_4 in CCl_4; the spectra appeared to be the same for the gas and in solution, and fine structure was noted on the high-field line. It should be noted that the signals observed for P_2F_4 were weak, but preliminary data indicate the existence of F_2P radicals. The study is continuing.

Experimental Section

Apparatus. All experiments were conducted in a standard high-vacuum system. Stopcocks were lubricated with Apiezon N.

Materials. Difluoroiodophosphine PF_2I, was prepared as outlined previously.[6] **Cuprous oxide** (Baker and Adamson reagent grade) and **cuprous cyanide** (Baker and Adamson technical grade) were used without further purification.

Preparation of F_2POPF_2. A 40-cc reaction tube equipped with a stopcock was charged with ~0.5 g of Cu_2O (3.5 mmoles). After the tube was attached to the vacuum system and evacuated, PF_2I (1.07 mmoles) was condensed in. The contents of the tube was then allowed to warm to 25° and cooled to −196° five times. Reaction was evidenced by the formation of tan solids. Finally, the volatile products were removed from the vessel by pumping volatiles through a series of traps held at −112, −145, and −196°. It was necessary to heat the reaction tube to ~150° with a hot-air gun to remove the last trace of products. Retained at −112° was 0.05 mmole of an unidentified material; PF_3 (0.04 mmole) was stopped at −196°. The desired F_2POPF_2 (0.39 mmole) corresponding to 73% yield based on the amount of PF_2I taken was recovered from the −145° trap. The X-ray powder photograph of the solids remaining in the tube was consistent with a mixture of CuI and Cu_2O. The preparation was also carried out on a considerably larger scale with somewhat smaller yields.

Properties of F_2POPF_2. The vapor pressure data for F_2POPF_2 are: −83.6° (13.1 mm), −78.5° (19.5 mm), −63.0° (61.0 mm), −50.0° (141.6 mm), −45.0° (190.5 mm); extrapolated bp −18.3°; mp −132.1 to −131.8 in a sealed tube; Trouton's constant 23.3 cal/deg mole.

Preparation of F_2PCN. A 70-cc reaction tube was charged with 1 g (11 mmoles) of CuCN, attached to the vacuum system, and evacuated. After a 1.39-mmole sample of PF_2I had been condensed onto the powder, the system was warmed from −196 to 25°, then refrozen, and rewarmed for five cycles. The volatile products were led through U traps at −95, −126, and −196°. It was necessary to heat the reaction tube to about 150° with a hot-air gun in order to remove the last traces of product. The trap held at −196° contained 0.31 mmole of PF_3; the trap at −126° held an undetermined amount of PF_2I; and the trap at −95° held 0.44 mmole of F_2PCN. This corresponds to a 32% yield based on the amount of F_2PI taken.

Preparation of P_2F_4. Difluoroiodophosphine (2.39 mmoles) was condensed into a 1000-cc bulb (equipped with a stopcock) containing 2 cc of mercury. The bulb and contents were slowly warmed to 25°; the contents were removed from the vacuum system and shaken. A discoloration of the mercury and formation of yellow and gray solids indicated reaction. After 4 hr of shaking, the bulb was attached to the vacuum system and the volatile contents removed by pumping through U tubes maintained at −112, −126, and −196°. The −196° fraction was 0.10 mmole of PF_3 while 0.30 mmole of unreacted PF_2I (containing an undetermined amount of F_2PNMe_2) was retained at −112°. The desired P_2F_4 (0.97 mmole) was held at −126°. This corresponds to a 93% yield based on the amount of PF_2I which reacted.

Spectroscopic Techniques and Notation. The infrared spectra were obtained with a Beckman IR-12 spectrophotometer, the precise vibrational frequencies noted in the text being determined by recording each band at high dispersion. Prior calibration of the spectrometer ensured accuracies of 0.5 cm^{-1} or better in the range used. Sample pressures ranged from 2 to 30 mm in a 75-mm path-length cell equipped with CsI windows.

The Raman spectra were obtained of pure liquid P_2F_4 which was distilled into a 2-mm i.d. capillary tube with a flat end suitable for transmission of the scattered light. Details of the instrumentation used for the Raman spectra are described by Farran.[23]

The ^{31}P and ^{19}F nmr spectra were determined with a Varian HR-100 instrument operating at 94.1 and 40.4 Mc, respectively. The samples were distilled into semimicro nmr tubes as pure liquids and the tubes sealed off under vacuum. Chemical shifts were determined by tube interchange. The standards used were trifluoroacetic acid (TFA) and 85% orthophosphoric acid (OPA). The sweep of the instrument was calibrated with side bands of a known frequency.

Mass spectra were determined at 70 ev on a Consolidated Electrodynamics Model 21-103 B mass spectrometer.

The epr spectra of P_2F_4 were graciously determined by Dr. J. Gendell, University of Michigan, on a Varian instrument. Samples were contained in 3-mm o.d. quartz or Pyrex tubes.

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