

TABLE I
 BORON HALIDE ADDUCTS OF CYCLOPOLYPHOSPHINES

Compd no.	Compd	Analysis ^a							
		Calcd, %				Found, %			
		C	H	P	X ^b	C	H	P	X ^b
I	(C ₆ H ₅ P) ₃ ·BF ₃	55.14	3.86	23.70	17.30	54.16	4.58	24.59	...
II	(C ₆ H ₅ P) ₃ ·BCl ₃	48.98	3.43	21.05	24.10	49.25	3.50	20.97	24.04
III	(C ₆ H ₅ P) ₃ ·2BBr ₃	26.19	1.83	11.26	58.10	26.63	4.65	11.50	58.96
IV	(C ₂ H ₅ P) ₂ ·BF ₃	25.47	5.73	32.85	35.95	25.85	5.92	33.25	...
V	(C ₂ H ₅ P) ₂ ·BCl ₃	20.25	4.25	25.30	44.86	20.15	4.52
VI	(C ₂ H ₅ P) ₂ ·BBr ₃	12.96	2.72	16.71	67.61	13.22	3.03	16.46	...
VII	(n-C ₃ H ₇ P) ₂ ·BF ₃	33.34	6.53	28.67	31.46	33.71	6.68	29.00	...
VIII	(n-C ₃ H ₇ P) ₂ ·BCl ₃	23.34	5.31	23.34	48.01	22.91	5.65
IX	(n-C ₃ H ₇ P) ₂ ·BBr ₃	18.08	3.54	15.54	60.13	17.70	3.83
X	(n-C ₄ H ₉ P) ₂ ·BF ₃	39.35	7.43	25.38	27.84	31.98	8.04	23.86	...
XI	(n-C ₄ H ₉ P) ₂ ·BCl ₃	32.73	6.18	21.11	39.98	32.42	6.29	...	35.87
XII	(n-C ₄ H ₉ P) ₂ ·BBr ₃	22.51	4.25	14.52	58.72	22.45	4.36	14.25	...

^a All analyses performed by Alfred Bernhardt, Mülheim, Ruhr, Germany. ^b X = F, Cl, or Br.

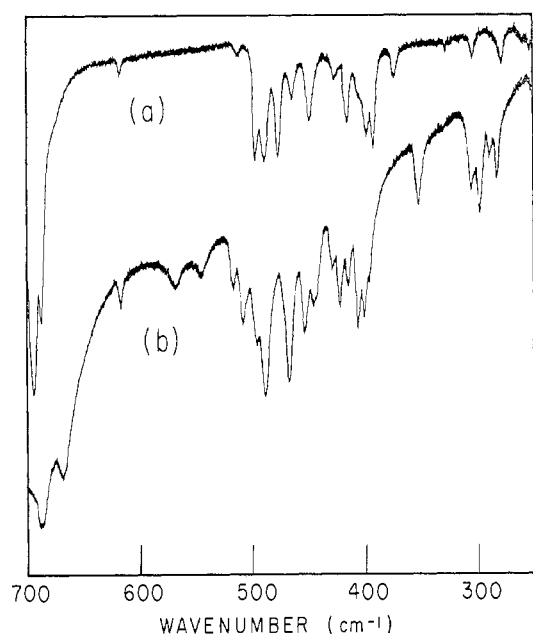


Figure 1.—Infrared spectra of (a) (C₆H₅P)₃ and (b) (C₆H₅P)₃·BCl₃ in the 250–700-cm⁻¹ range.

boron halides. As noted in the Experimental Section these adducts do not precipitate from solution yet, once isolated by evaporation of the solvent, are reactive with or insoluble in common solvents. It is therefore possible that the adducts as formed in solution are different from those which we isolated.

The intractable nature of the adducts limited us to indirect structural evidence. The general similarity of the infrared spectra of the cyclopolyposphines and their boron halide reaction products (see Figure 1 for a comparison of (C₆H₅P)₃ and (C₆H₅P)₃·BCl₃) would suggest that the phosphorus rings are intact.⁹ The infrared spectra of I, II, and III show the characteristic mono-substituted benzene frequencies *v* and *f* in the 680–747 cm⁻¹ range,¹⁰ indicating that the BX₃ molecules are

(9) R. L. Amster, W. A. Henderson, and N. B. Colthup, *Can. J. Chem.*, **42**, 2577 (1964), have identified the asymmetric ring stretch near 500 cm⁻¹ in the phenyl-P rings. R. L. Amster, N. B. Colthup, and W. A. Henderson, *Spectrochim. Acta*, **19**, 1841 (1963), found that this frequency lies in the range 465–490 cm⁻¹ in the alkyl-P rings. The symmetric ring stretch occurred at 390–410 cm⁻¹ in the alkyl-P rings.

(10) For assignments and notation, see D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

most likely associated with the phosphorus atoms in these compounds. Frequencies which could be assigned to tetrahedrally bonded BX₃ groups¹¹ were also found in some of the spectra. In the others, these were probably obscured by the phenyl or alkyl group modes.

One structural interpretation is that the compounds involve phenyl- or alkyl-substituted polyphosphine rings coordinated to the appropriate number of BX₃ groups. If the alkyl-substituted compounds IV–XII do involve phosphorus rings, then the molecular formulas might be twice the empirical formulas shown in Table I. Likewise, the molecular formulas of the phenyl-substituted adducts I, II, and III might also be twice their empirical formulas since there appears to be no evidence for the existence of a three-membered phosphorus ring. However, higher degrees of polymerization or mixtures of polymers cannot be excluded on the basis of the present evidence.

Acknowledgment.—The authors wish to acknowledge the financial support of the Robert A. Welch Foundation (Grant F-135) and the National Institutes of Health (Grant GM 12437-02).

(11) R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964) and references therein.

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Fluorophosphine Ligands. II. The Preparation and Characterization of Difluoroiodophosphine

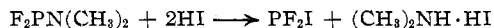
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Although difluoroiodophosphine was previously described as unstable and difficult to characterize,¹ it has now been obtained in pure form and characterized unequivocally.

(1) R. G. Caveil, *J. Chem. Soc.*, 1992 (1964).

Difluoroiodophosphine was obtained in 94% yield from the action of hydrogen iodide on dimethylamino-difluorophosphine according to the equation²



As was indicated by the preparation of PF_2H from PF_2I , Hg , and HI ,³ the PF_2I molecule is a reactive species and should prove useful in introducing the PF_2 moiety into a number of new substances. In particular, we have employed it in the preparation of $\text{F}_2\text{-POPF}_2$, PF_2CN , and P_2F_4 .⁴

Experimental Section

Hydrogen iodide was prepared as outlined in the literature⁵ by the reaction of iodine and 1,2,3,4-tetrahydronaphthalene. Dimethylaminodifluorophosphine was obtained in a manner similar to that described by Schmutzler⁶ by the fluorination of dimethylaminodichlorophosphine with NaF in a suspension of tetramethylene sulfone.

In a typical experiment difluoroiodophosphine, PF_2I , was prepared by separately condensing 6.38 mmoles of $\text{F}_2\text{PN}(\text{CH}_3)_2$ and 12.76 mmoles of HI into a 500-ml reaction bulb equipped with a stopcock. The bulb was then allowed to warm slowly to 25°. Reaction was indicated by the formation of clouds of pale red-yellow solids. The bulb was allowed to stand at 25° for 15 min after the clouds had settled; then the volatile products were separated by fractional condensation (-126, -196°). The desired difluoroiodophosphine (5.98 mmole) was retained at -126° while PF_2 (0.25 mmole) passed through the -126° trap and was held at -196°. It is desirable to use exact stoichiometric amounts of HI and $\text{F}_2\text{PN}(\text{CH}_3)_2$ if pure PF_2I is desired since it is difficult to separate PF_2I and $\text{F}_2\text{PN}(\text{CH}_3)_2$. If either reagent is to be used in excess, a slight excess of HI would be preferred since it eliminates all of the F_2PNR_2 . On the other hand, a sizable excess of HI in liquid F_2PI gives discoloration of product indicating decomposition. Moderate excess of HI seemed to have no effect in the gas phase.

Characterization

The formula PF_2I is supported unequivocally by the vapor density molecular weight (calcd for PF_2I : 195.9 g/mole; obsd: 192.9 g/mole), the elemental analysis (Calcd for PF_2I : P, 15.81; F, 19.39; I, 64.78. Found: P, 15.37; F, 18.09; I, 64.34), and the mass spectrum shown in Table I.

The mass spectrum is consistent with the vapor density molecular weight and shows a fragmentation pattern characteristic of PF_2I ; however, it should be noted that several other minor peaks⁷ were actually observed in the mass spectrum but not noted in Table I. The extraneous peaks could be attributed to impurities which probably resulted from the reaction of PF_2I and trace amounts of water in the vacuum system or to traces of $\text{F}_2\text{PN}(\text{CH}_3)_2$ in the sample of PF_2I .

(2) This unique method for the preparation of pure halodifluorophosphines was developed independently by: (a) Sr. M. A. Fleming, Doctoral Dissertation, University of Michigan, 1961; (b) W. Mahler, private communication, E. I. du Pont de Nemours and Co., Wilmington, Del., 1961; (c) R. G. Cavell.¹ The prototype reaction for the preparation of $(\text{CH}_3)_2\text{PCI}$ from $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2$ and HCl was first described by A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).

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

(4) A complete characterization of these species will appear in a future publication.

(5) C. J. Hoffman and E. A. Heintz, *Inorg. Syn.*, **7**, 180 (1963).

(6) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

(7) The additional peaks typically occurred at m/e values of: 154, $\text{F}_2\text{POPF}_2^+$; 113, $\text{F}_2\text{PN}(\text{CH}_3)_2^+$; 112, $\text{F}_2\text{PN}(\text{CH}_3)\text{CH}_2^+$; 104, PF_3O^+ ; 94, $\text{FPN}(\text{CH}_3)_2^+$; 85, F_2PO^+ ; 66, PFO^+ ; 47, PO^+ ; 44, $\text{N}(\text{CH}_3)_2^+$, all with a relative intensity below 4.

TABLE I
MASS SPECTRUM OF PF_2I^a

m/e	Relative peak height	Assignment
196	100	PF_2I^+
177	15	PFI^+
158	6	PI^+
127	71	I^+
88	1	PF_3^+
69	60	PF_2^+
63.5	4	I^{2+}
50	29	PF^+
31	11	P^+
19	3	F^+

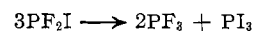
^a Obtained at 70 ev on a Consolidated Electroynamics Model 21-103 B mass spectrometer.

Vapor pressure data for PF_2I (-63.5°, 5.0 mm; -45.6°, 19.8 mm; -31.2°, 48.3 mm; -22.9°, 74.5 mm; 0°, 240.1 mm) are summarized by the equation $\log p$ (mm) = -1514/T + 7.929. The Trouton constant is 23.09 cal deg⁻¹ mole⁻¹; bp 26.7° (extrapolated from vapor pressure equation); and mp -93.8 to -93.3° (sealed tube).

The infrared spectrum (4000-200 cm⁻¹) of PF_2I vapor displays the expected absorptions (cm⁻¹, tentative assignments included in parentheses): 850.4 s (ν_s PF); 845.3 vs (ν_{as} PF); 411.8 m (δ_s PFP); 378.5 m (ν_s PI).⁸ The other two motions expected for PF_2I (δ_s PF_2I and ω_{as} PF_2) may fall below 200 cm⁻¹, the limit of our spectrometer. The corresponding motions in PI_3 have been assigned to absorptions at 111 and 79 cm⁻¹, respectively;⁹ however, because of the difference in the mass of fluorine and iodine, the vibrations probably occur at higher frequencies for PF_2I and may indeed be accidentally degenerate with other modes.

The phosphorus and fluorine nmr spectra of PF_2I display the expected spin-spin splitting patterns with P-F coupling somewhat smaller than in PF_3 ($J_{\text{PF}} = 1441$ cps).¹⁰ The 1:2:1 triplet ($J_{\text{PF}} = 1337$ cps) centered 242.2 ppm downfield from H_3PO_4 in the ³¹P nmr spectrum of PF_2I shows that two equivalent fluorines are directly bonded to phosphorus; the doublet ($J_{\text{PF}} = 1340$ cps) displayed 31.9 ppm downfield from CF_3COOH in the ¹⁹F nmr spectrum further indicates that the fluorine nuclei are bonded to a single phosphorus atom.

Since PF_2I reacts with mercury, their contact should be avoided. The vapor is reasonably stable, but the rate of disproportionation according to the equation



is enhanced by higher pressures; i.e., when $p_0 = 37$ mm, it is ca. 1% decomposed after 1 day at 25° and ca. 19% decomposed after 9 days, but when $p_0 = 280$ mm, it is ca. 6% decomposed after 1 day and ca. 87% decomposed after 8 days all at 25°.

Acknowledgment.—Partial support of this work

(8) vs, very strong; s, strong; m, medium.

(9) H. Stammreich, R. Forneris, and Y. Tavares, *J. Chem. Phys.*, **25**, 580 (1956).

(10) E. L. Muettterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **6**, 244 (1962).

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The Atomic Parameters in the Lanthanum Trifluoride Structure¹

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Crystals of LaF₃ exhibit a structure which is typical of numerous trifluorides of lanthanide and actinide elements. In 1931 Oftedal² suggested a structure, based on a study of crystals of the mineral tysonite, with the assumption that the space group is P6₃/mcm, but with atomic coordinates which correspond almost to the symmetry P6₃/mmc with a smaller unit cell. The evidence for the larger cell is the presence of weak reflections which may easily escape detection in powder diagrams. Schlyter³ failed to see these reflections with tysonite crystals, but Templeton and Dauben⁴ found them with a synthetic crystal of CeF₃. The atomic positions given by Oftedal give lanthanum a peculiar coordination geometry with five nearest neighbors and six more neighbors at a greater distance.

We were prompted to study LaF₃ again by the availability of excellent synthetic crystals and recent interest in the spectroscopic properties of ions in this structure. When we had nearly finished the determination of the structure, we learned that Mansmann⁵ had independently reached the same conclusions concerning the symmetry and assignment of atoms to point sets, without reporting atomic coordinates.

We conclude that Oftedal's cell is correct and that his coordinates for La are quite accurate, but that the crystals are trigonal rather than hexagonal. Because of his failure to recognize this point symmetry, Oftedal did not consider the correct space group, and he misplaced most of the F atoms. In our structure, each La is on a twofold axis and has nine neighbors (a normal number) at nearly equal distances.

Experimental Section

A large crystal of lanthanum trifluoride, purported to be 99.999% pure, was sent to us by Dr. Kenneth Lee of Varian

Associates in Palo Alto, Calif. A fragment of this crystal about 0.1 to 0.2 mm in size was glued to the end of a Pyrex fiber with the hexagonal axis parallel to the fiber axis. The crystal was dipped into liquid nitrogen rapidly several times in an attempt to diminish extinction effects by increasing the mosaic spread by thermal shock, but no effect was observed in the intensities before and after the treatment. Diffraction angles and intensities were measured with an Eulerian cradle goniostat equipped with a scintillation counter using Mo K α radiation ($\lambda(K\alpha_1)$ 0.70926 Å). The cell dimensions measured at 22° are $a = 7.185 \pm 0.001$ and $c = 7.351 \pm 0.001$ Å, in excellent agreement with the values reported by Swanson, *et al.*⁶ The density calculated with 6 molecules per cell is 5.938 g/ml.

The diffraction intensities correspond to Laue symmetry $\bar{3}m1$, but there are clear violations of symmetry 6/mmm and 6/m; *i.e.*, $I(hkl) = I(h+k, -k, l)$, but $I(hkl) \neq I(-k, h+k, l)$. Thus, the crystals are trigonal rather than hexagonal (in the strict sense). The failure of previous workers to recognize the lower symmetry may be the result of twinning in their specimens or the result of low accuracy of intensities estimated from films.

We failed to detect any pyroelectric effect when a large crystal fragment, suspended on a thread, was dipped into liquid nitrogen; when withdrawn, the crystal showed no attraction for the side of the dewar. The systematic absences, $(h0l)$ absent if $l = 2n + 1$, correspond to space groups P3c1 and P $\bar{3}$ c1. We conclude that the crystals are centric because a reasonable structure is found in space group P $\bar{3}$ c1 (D_{3d}⁴), No. 165 in the "International Tables."⁷

The intensity measurements included 914 independent reflections (all positive hkl with $2\theta < 90^\circ$) of which 63 were recorded as zero. The data were corrected for the Lorentz-polarization effects. The absorption factor μ was estimated to be ~ 200 cm⁻¹, and the μR for the crystal was estimated to be ~ 2 . The data were not corrected for absorption. An empirical extinction correction was made based on an approximation suggested by Zachariasen⁸ where $F_c \approx F_o(1.0 + CJ)$, where F is the scaled structure factor, J is the raw observed intensity, and C is an adjustable constant.

The structure given by Oftedal² can be fitted to space group P $\bar{3}$ c1 by assigning the atoms to point sets as listed in Table I. Prior to the extinction correction, we attempted to refine this structure with a full-matrix, least-squares program, with trial-and-error displacements of various atoms to break the higher symmetry. The first set of refinements went poorly; *i.e.*, the R factor, $R = \sum |F_o| - |F_c| / \sum |F_o|$, stayed high (~ 0.15) and the temperature factor for the twofold fluorine "blew up." Different trial structures and the use of a noncentric space group (P3c1) gave even worse results. We observed what appeared to be severe extinction effects, and, by deleting some low-angle data which included some of the larger intensities, definite improvement in the refinement resulted. A plot of F_o/F_c (observed and calculated structure factors) *vs.* the intensities showed a very definite extinction-type correlation. From this plot a value for C in the extinction correction was obtained, and then it was adjusted in the least-squares refinement. The extinction was so severe that the two most intense reflections were observed to be one-eighth of their calculated values. In the final refinements the anomalous dispersion factors for La³⁺ were included ($\Delta f' = -0.4$, $\Delta f'' = 2.9$ electrons).⁹ An anisotropic temperature factor of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ was applied to lanthanum, with suitable constraints because of the twofold axis, and an isotropic temperature factor of the form $\exp[-(B \sin^2 \theta / \lambda^2)]$ was applied to each fluorine. The five most intense reflections and seven of the reflections with the worst

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) I. Oftedal, *Z. Physik. Chem.*, **B13**, 190 (1931).

(3) K. Schlyter, *Arkiv Kemi*, **5**, 73 (1953).

(4) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 4560 (1953).

(5) M. Mansmann, *Z. Anorg. Allgem. Chem.*, **331**, 98 (1964).

(6) H. E. Swanson, N. T. Gilfrich, and M. I. Cook, "Standard X-Ray Diffraction Patterns," National Bureau of Standards Circular 539, Vol. 7, U. S. Government Printing Office, Washington, D. C., 1957, p 21.

(7) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England, 1952, p 271.

(8) W. H. Zachariasen, *Acta Cryst.*, **16**, 1142 (1963).

(9) D. T. Cromer, *ibid.*, **18**, 17 (1965).