Preparation and Chemical and Spectroscopic Properties of Bis(difluorophosphino) Selenide

By **David E. J. Arnold, Ernest R. Cromie, and David W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Bis(difluorophosphino) selenide has been prepared by the exchange reactions of $PBrF_2$ and $PClF_2$ with $Se(SiH_3)_2$ and $Se(SnBu_3)_2$. It has been characterised by vibrational, mass, n.m.r., and photoelectron spectroscopy. Spectroscopic results have also been obtained for bis(difluorophosphino) sulphide, prepared by analogous methods. Both compounds react with Brønsted acids to give PF_2HSe or PF_2HS, and a difluorophosphine derivative of the acid. Basic properties are shown by the reactions with diborane, which give the monoborane adducts, and by the displacement of norbornadiene from $[Mo(C_7H_8)(CO)_4]$. The latter reaction illustrates the potential usefulness of these compounds as chelating bidentate ligands. With chlorine the selenide gives PCl_3F_2 and $PClF_2Se$.

ALTHOUGH bis(difluorophosphino) ether, $O(PF_2)_2$, has been known for some time [1] and has been well studied, the preparation of its sulphur analogue has only recently been reported,[2] and the selenium analogue has not yet been described. The n.m.r. spectra of the sulphur compound, and in particular the remarkable variation of $^1J(PP)$ with temperature, have been commented on,[3] and we have published an account of some exchange reactions leading to the sulphide and selenide,[4] but the compounds were not isolated and only n.m.r. parameters were reported. In our subsequent work we have been able to prepare and isolate both compounds, and to study their properties, and here we present our findings. Although the sulphide has been prepared before,[2] we include our results as they differ in some details from those reported earlier, and also to enable a comparison to be made of the members of the series $O(PF_2)_2$, $S(PF_2)_2$, and $Se(PF_2)_2$.

RESULTS AND DISCUSSION

Our study [4] of the exchange reactions of disilyl sulphide and selenide with bromodifluorophosphine showed that, although replacement of silyl by difluorophosphino-groups was possible, the process was slow and incomplete under the conditions used. Various other possible routes to the fluorophosphine derivatives were therefore investigated. Hydrogen selenide failed to react with aminodifluorophosphine and (dimethylamino)difluorophosphine. Chlorodifluorophosphine did not react with sodium selenide. Similarly, attempts to dehydrofluorinate mixtures of trifluorophosphine and H_2Se were unsuccessful. Hydrogen selenide did react with tris(difluorophosphino)amine, but the products were the secondary amine and difluorophosphine selenide only [equation (1)].[5] Chlorodifluorophosphine, methanethiol, and trimethylamine are known to give difluoro(methylthio)phosphine,[6] but the analogous reaction with H_2Se did not give rise to any new fluorophosphine: trimethylammonium selenide was formed, rather than ammonium halides.

$$N(PF_2)_3 + SeH_2 \longrightarrow NH(PF_2)_2 + PF_2HSe \quad (1)$$

The exchange reaction was then reinvestigated, and it was found that reaction of $PBrF_2$ and disilyl sulphide or selenide, or $PClF_2$ and $S(SiH_3)_2$, could be used to obtain pure samples of the fluorophosphine–Group 6 derivatives [equations (2) and (3)]. The reactions were slow, particularly for the sulphide, and it was necessary to replace the silyl halide–difluorohalogenophosphine mixture with fresh difluorohalogenophosphine several times for completion of reaction. When the mixture was warmed to >209 (Y = Se) or 273 K (Y = S) before completion of the reaction, silyl fluoride and yellow solid, the composition of which was not investigated, were formed. This was probably due to decomposition of the mixed intermediate [equation (4)]. In each preparation by this route the product was contaminated with a small amount of PF_2HY, identified by i.r. spectroscopy. This is believed to be due to trace amounts of impurities in the starting materials (HX in the difluorohalogenophosphines or H_2Y in the silyl compounds) or to water on the surface of the reaction vessel, interacting with the reaction product, although no attempt was made to identify the impurity.

$$Y(SiH_3)_2 + PF_2X \longrightarrow H_3SiYPF_2 + SiH_3X \quad (2)$$

$$H_3SiYPF_2 + PF_2X \longrightarrow Y(PF_2)_2 + SiH_3X \quad (3)$$

$$H_3SiYPF_2 \longrightarrow SiFH_3 + \frac{1}{n}(\text{-}Y\text{-}PF\text{-})_n \quad (4)$$

Finally, $PBrF_2$ was found to react with bis(tributylstannyl) sulphide and selenide to give the desired products. This method was very clean and rapid, and gave a mixture from which the products could be separated very easily by fractional condensation [equation (5)].

$$Y(SnBu_3)_2 + 2PBrF_2 \longrightarrow Y(PF_2)_2 + 2SnBrBu_3 \quad (5)$$

This method is the same as that used by Bockerman and Parry [2] to prepare the sulphide.

Mass Spectra.—Details of the mass spectra of $S(PF_2)_2$ and $Se(PF_2)_2$ are given in Table 1. These show that the breakdown routes for the two compounds are extremely similar. One important process involves loss of PF_3

---

[1] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729.

[2] G. N. Bockerman and R. W. Parry, *J. Fluorine Chem.*, 1976, **7**, 1.

[3] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

[4] D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 2518.

[5] D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1975 889.

[6] R. Foester and K. Cohn, *Inorg. Chem.*, 1972, **11**, 2590.

TABLE 1

Mass spectra of $S(PF_2)_2$ and $Se(PF_2)_2$ *

$S(PF_2)_2$		$Se(PF_2)_2$		
m/e	Relative abundance	*m/e*	Relative abundance	Assignment
172/170	37	214—220	69	$[Y(PF_2)_2]^+$
101	9	145—151	28	$[Y(PF_2)]^+$
88	5	88	7	$[PF_3]^+$
84/82	100	126—132	64	$[Y(PF)]^+$
69	97	69	100	$[PF_2]^+$
63	12	107—113	20	$[YP]^+$
50	7	50	12	$[PF]^+$
32	2	76—82	35	Y^+
31	1	31	2	P^+
metastable				
39.5	very strong	77.6/75.9	strong	$[Y(PF_2)_2]^+ \longrightarrow PF_3 + [Y(PF)]^+$

* Ionising voltage, 70 eV.

from the parent ion [equation (6)]. The existence of strong $[Y(PF_2)]^+$ ions and $[PF_2]^+$ ions implies that an

$$[Y(PF_2)_2]^+ \longrightarrow PF_3 + [Y(PF)]^+ \qquad (6)$$

alternative breakdown route (7) involves initial breaking of a P–Y bond. There is no evidence for any P–F bond cleavage in the parent ion. In this respect these compounds differ from $O(PF_2)_2$.[1]

$$[Y(PF_2)_2]^+ \longrightarrow PF_2 + [Y(PF_2)]^+ \qquad (7)$$

Vibrational Spectra.—Positions of lines observed in the i.r. spectra of $S(PF_2)_2$ and $Se(PF_2)_2$ in the gas and solid phases, and isolated in an argon matrix at 8 K, and in the Raman spectra of liquid and solid phases are given in Tables 2 and 3. The matrix spectra were run in the <500 cm^{-1} region for the purpose of intensifying and observing low-frequency bands. Assignment of vibrational modes to particular frequencies is exceptionally difficult in these cases, as all the bands are at fairly low frequencies, and the concept of group frequencies is unlikely to be helpful as there are no very light atoms. Preliminary results of our studies of the structures of these molecules by electron diffraction indicate that they have C_{2v} symmetry, or are not greatly distorted from that symmetry, and on that basis we make provisional assignments.

TABLE 2

Vibrational spectra (cm^{-1}) of $S(PF_2)_2$

I.r.			Raman		
Gas	Solid	Argon matrix *	Liquid	Solid	Assignment
			855w, p	860m	$\nu(PF)$
840vs, br	810vs, br		835w, p (?)	844m	
			820w, dp (?)	814m	
				791m	
	618m		631w, p	621w	
579m	570m		580s, p	571s	$\nu_{sym}(PSP)$
	524w			558s	$\delta(PF_2)$
	514w		515m, p		
498m	507w		490vw, dp (?)		
	462w			454m	
447ms	436s	444m	444m, dp	434m	$\nu_{asym}(PSP)$
407w					$\omega(PF_2)$
401w		407m	408s, p	402m	
	376m	380m			
319m	318m	322m	318vw, dp (?)	319w	$\rho(PF_2)$
				253m	
			237s, p	234s	$\delta(PSP)$
		130w	125s, dp	133s	$\tau(PF_2)$

s = Strong, m = medium, w = weak, br = broad, p = polarised, dp = depolarised, v = very, sh = shoulder.

* Not studied at >500 cm^{-1}.

TABLE 3

Vibrational spectra (cm^{-1}) of $Se(PF_2)_2$

I.r.			Raman		
Gas	Solid	Argon matrix *	Liquid	Solid	Assignment
850vs			845vw, p (?)	840w	$\nu(PF)$
833 (sh)	800vs, br		820vw, dp	810w	
599m	612w		580vw		
486m	518s		515vvw, p (?)		$\delta(PF_2)$
			482m, p	476s	
443m	433ms	443m	445vw, dp		$\nu_{sym}(PSeP)$
			428m, p		
	405m	402m			$\omega(PF_2)$
	399m		393m, p	395m	
368ms, br		365m	365m, dp	355s	$\nu_{asym}(PSeP)$
		321m			
		292m			
		274m	255w, dp	256m	$\rho(PF_2)$
			215s, p	215s	$\delta(PSeP)$
			95m, dp		$\tau(PF_2)$

* Not studied at >500 cm^{-1}.

The vibrational modes can be classified as in Table 4, although considerable mixing is to be expected. Of the five a_1 modes, that at highest frequency will be a P–F stretching vibration, while the lowest-frequency mode will be the P–Y–P bend at 237 (S) or 215 cm^{-1} (Se).

TABLE 4

Vibrational modes of $Y(PF_2)_2$, point group C_{2v}

	a_1	a_2	b_1	b_2
P–F stretch	/	/	/	/
P–Y stretch	/			/
PF_2 scissors	/			/
PF_2 rock		/	/	
PF_2 wag	/			/
PF_2 torsion		/	/	
PYP bend	/			

Three other polarised Raman bands must therefore correspond to the remaining a_1 modes. We assign those at 515 (S) and 482 cm^{-1} (Se) and 408 (S) and 393 cm^{-1} (Se) to deformations of the PF_2 groups, leaving a band which shifts from 580 cm^{-1} in the sulphide to 428 cm^{-1} in the selenide as the symmetric skeletal stretch. We do not observe polarised Raman bands reported[2] for $S(PF_2)_2$ at 795 and 173 cm^{-1}, although the earlier results were obtained with a sample at 213 K, whereas 298 K was the temperature for the present study. The absence of these two bands supports the C_{2v} assignment, there now being only five polarised bands in the spectra of both sulphide and selenide.

The b_2 vibrations of the PF_2 groups are assumed to lie close to their a_1 analogues, while the asymmetric skeletal stretches are taken to be the strong i.r. absorptions at 447 (S) and 368 cm^{-1} (Se). The relatively large separation of symmetric and antisymmetric skeletal stretches in the compounds compared with trimethylsilyl sulphide and selenide[7] is not surprising, as the fluorophosphine groups do not have the axial symmetry of the trimethylsilyl groups. The average P–S and P–Se frequencies agree reasonably well with those reported for $Y[P(CF_3)_2]_2$.[8]

The a_2 and b_1 classes both contain a P–F stretch and a rock and torsion of the PF_2 groups. The latter must, by a process of elimination, be assigned to the bands at *ca.* 320 and 130 cm^{-1} (S) and 260 and 95 cm^{-1} (Se). These bands are somewhat higher than expected and it may be that the torsions are at lower frequency, and unobserved. If so, some higher frequency bands must be reassigned.

N.M.R. Spectra.—The spectra of samples of $S(PF_2)_2$ and $Se(PF_2)_2$ prepared as described in this work were entirely consistent with results reported earlier.[2-4] The availability of concentrated solutions enabled us to measure $^1J(^{77}Se-^{31}P)$ in $Se(PF_2)_2$ as 365 Hz. This value has been incorrectly quoted.[9]

Photoelectron Spectra.—Observed vertical ionisation potentials are given in Table 5. As there is only one band below 14.5 eV in the spectrum of the sulphide,* this must include both phosphorus lone-pair levels and a sulphur electron-pair level. For a C_{2v} molecule, these have symmetry a_1, b_1, and b_2, so this overlap of bands is feasible. Assuming that the phosphorus lone-pair levels also overlap in the oxygen and selenium compounds, we would assign the larger of the two bands observed in each case to the phosphorus levels, and the smaller to the oxygen or selenium lone-pair level. However, $O(PF_2)_2$ does not have C_{2v} symmetry,[10] and assignment in this case is complicated by the possibility of a P–O bonding orbital being higher in energy than the P–S or P–Se orbitals. The assignment given in Table 5 for the oxygen compound is therefore very tentative: we have taken into account work on other Group 6 derivatives.[11,12]

TABLE 5

Photoelectron spectra of $Y(PF_2)_2$

Vertical ionisation potential ±0.1 eV			
$O(PF_2)_2$ [a]	$S(PF_2)_2$	$Se(PF_2)_2$	Assignment [b]
11.2	10.8	10.2	Y lone pair
12.4	10.8	10.7	P lone pair
14.2	14.5	14.1	P–Y bonding
ca. 16.5	16.0	15.9	F lone pair
17—19	17—18.5	17—18.5	P–F bonding

[a] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940. [b] See text.

Reactions of $Se(PF_2)_2$ *with Protonic Species.*—The usefulness of $Se(PF_2)_2$ as a synthetic intermediate was investigated by studying reactions leading to P–Se bond cleavage. The results of these studies are summarised in the Scheme.

It seems, from our observations, that $Se(PF_2)_2$ reacts with compounds having an acidic hydrogen atom, the initial process being cleavage of a phosphorus–selenium bond [equation (8)]. The subsequent fate of the PF_2X

$$Se(PF_2)_2 + H{-}X \longrightarrow PF_2HSe + PF_2X \quad (8)$$

depends on X. For X = Cl, Br, NH_2, OMe, or SMe, no further change occurs; for X = SH or SeH, rearrangement of $PF_2(YH)$ to PF_2HY is assumed to take place, without the phosphorus(III) intermediate being observed. In other cases there is decomposition of the product, or further reaction, as with the metal carbonyl systems. The expected products $[M(CO)_5(PF_2)]$ are not observed, but PF_2H and solids with the appearance of $[M_2(CO)_{10}]$ are formed, probably by reaction (9) (M = Mn or Re).

$$[M(CO)_5(PF_2)] + [MH(CO)_5] \longrightarrow PF_2H + [M_2(CO)_{10}] \quad (9)$$

---

* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[7] H. Bürger, U. Goetze, and W. Sawodny, *Spectrochim. Acta*, 1968, **A24**, 2003.

[8] R. C. Dobbie, M. J. Hopkinson, and B. P. Straughan, *J. Mol. Structure*, 1974, **23**, 141.

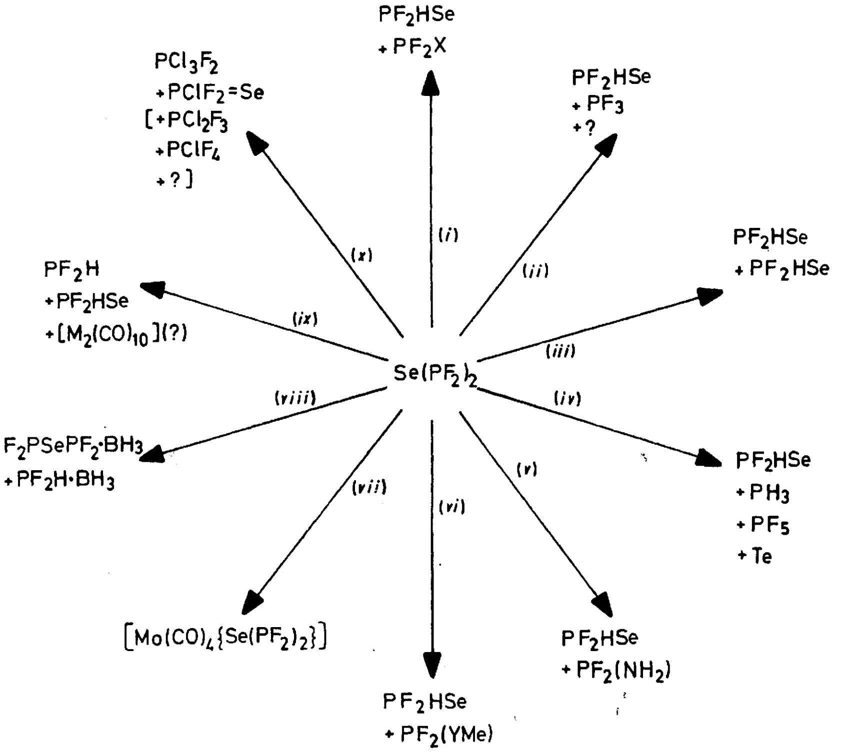
[9] D. W. W. Anderson, E. A. V. Ebsworth, G. D. Meikle, and D. W. H. Rankin, *Mol. Phys.*, 1973, **25**, 381.

[10] D. E. J. Arnold and D. W. H. Rankin, *J. Fluorine Chem.*, 1973, **2**, 405; Hsuikang Yu Yow, R. W. Rudolph, and L. S. Bartell, *J. Mol. Structure*, 1975, **28**, 205.

[11] C. R. Brundle and D. W. Turner, *Proc. Roy. Soc. London*, 1968, **A307**, 27.

[12] S. Cradock and R. A. Whiteford, *J.C.S. Faraday II*, 1972, 281.

Reactions of $S(PF_2)_2$ have not been studied so extensively, but those that have indicate that its chemical properties are very similar to those of the selenide.



SCHEME Reactions of $Se(PF_2)_2$. (*i*) HX (X = Cl or Br); (*ii*) H_2O; (*iii*) H_2Y (Y = S or Se); (*iv*) TeH_2; (*v*) NH_3; (*vi*) MeYH (Y = O or S); (*vii*) $[Mo(C_7H_8)(CO)_4]$; (*viii*) B_2H_6; (*ix*) $[MH(CO)_5]$ (M = Mn or Re); (*x*) Cl_2

Reaction of $Se(PF_2)_2$ *with Chlorine.*—The reaction with chlorine seems to involve an initial cleavage of a P–Se bond, followed by conversion of both products into phosphorus(V) derivatives, one by rearrangement and one by addition of another mol of chlorine [equation (10)]. Disproportionation of the PCl_3F_2 also takes place,

$$Se(PF_2)_2 \xrightarrow{Cl_2} PClF_2 + SeCl(PF_2) \xrightarrow{Cl_2} PCl_3F_2 + PClF_2Se \quad (10)$$

and PCl_2F_3, $PClF_4$, and small amounts of PF_5 and PCl_4F were also observed. The compound $PClF_2Se$, which has not previously been reported, has an exceptionally large [9,13,14] coupling constant, $^1J(^{77}Se–^{31}P)$ 1 200 Hz. Other n.m.r. parameters are: $\delta(^{19}F)$ −2.4 p.p.m.; $\delta(^{31}P)$ +46.5 p.p.m.; $^2J(^{77}Se–^{19}F)$ 165 Hz; $^1J(^{31}P–^{19}F)$ 1 304 Hz. The reaction with chlorine is therefore similar to that reported [15] for $Se[P(CF_3)_2]_2$ except that in that case the $SeCl[P(CF_3)_2]$ formed loses selenium rather than rearranging to the phosphorus(V) form.

Donor Reactions of $S(PF_2)_2$ *and* $Se(PF_2)_2$.—Bis(difluorophosphino) sulphide and selenide both reacted with diborane at 200 K to give adducts containing only one BH_3 group, even in the presence of excess of B_2H_6. In this respect they behave in the same way as the analogous oxygen compound.[16] The sulphide complex has been reported to react further with B_2H_6 at room temperature to give the bis(borane) adduct of a disulphide. However, the selenide complex is stable, over a period of several days, at room temperature, although we did not try to isolate it, as n.m.r. spectra showed that at least two other products were present, one being $PF_2H{\cdot}$

TABLE 6

N.m.r. parameters of $F'_2P'YPF_2{\cdot}BH_3$

	Y	
	S [a]	Se [b]
$\delta(^{31}P)$/p.p.m.	182.1	193.2
$\delta(^{31}P')$/p.p.m.	200.8	228.0
$\delta(^{19}F)$/p.p.m.	−56.6	−55.2
$\delta(^{19}F')$/p.p.m.	−57.8	−59.2
$\delta(^{11}B)$ [c]/p.p.m.	−56.8	N.o.
$\delta(^{1}H)$/p.p.m.	1.29	N.o.
$^1J(^{31}P–^{19}F)$/Hz	1 267	1 277
$^1J(^{31}P'–^{19}F')$/Hz	1 336	1 320
$^2J(^{31}P–^{31}P')$/Hz	68	44
$^1J(^{31}P–^{11}B)$/Hz	N.o. [d]	22
$^2J(^{19}F–^{1}H)$/Hz	19	21
$^1J(^{11}B–^{1}H)$/Hz	107	N.o.
$^2J(^{31}P–^{1}H)$/Hz	12	N.o.

N.o. = Not observed; other coupling constants were not observed.

[a] At 223 K. [b] At 298 K. [c] Relative to $B(OMe)_3$. [d] Broad lines.

---

[13] W. J. Stec, A. Okruszek, B. Uznánski, and J. Michalski, *Phosphorus*, 1972, **2**, 97.

[14] W. MacFarlane and D. S. Rycroft, *J.C.S. Chem. Comm.*, 1972, 902.

[15] R. C. Dobbie and M. J. Hopkinson, *J. Fluorine Chem.*, 1974, **3**, 367.

[16] L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, 1968, **7**, 1005.

BH_3, the other at present unidentified. N.m.r. parameters of the two borane adducts are given in Table 6.

Although they behaved only as unidentate donors to borane, the sulphide and selenide both underwent displacement reactions with tetracarbonyl(η-norbornadiene)molybdenum to give monomeric products of the form $[Mo(PF_2)_2Y(CO)_4]$. Typical $\{A[X]_2\}_2$ n.m.r. spectra were observed, and analysed by the method of Harris and Woplin [17] to give the parameters listed in Table 7. Spectra were obtained at room temperature, but samples decomposed over 10—20 h.

TABLE 7

N.m.r. parameters of $[Mo(PF_2)_2Y(CO)_4]$

	Y	
	S	Se
$\delta(^{31}P)$/p.p.m.	156.3	147.8
$\delta(^{19}F)$/p.p.m.	-27.6	-20.6
$^{1}J(^{31}P-^{19}F)$/Hz	$-1\,299$	$-1\,292$
$^{3}J(^{31}P-^{19}F')$/Hz	$+47$	$+48$
$^{2}J(^{31}P-^{31}P')$/Hz	82	106
$^{4}J(^{19}F-^{19}F')$/Hz	7.5	7.7
$^{4}J(^{19}F-^{19}F'')$/Hz	0.0	0.7
$^{1}J(^{31}P-^{77}Se)$/Hz		N.o.
$^{2}J(^{19}F-^{77}Se)$/Hz		27

EXPERIMENTAL

All the volatile compounds were handled on a conventional Pyrex-glass vacuum line fitted with Sovirel greaseless taps. Chloro- and bromo-difluorophosphine were prepared from hydrogen chloride and bromide and (dimethylamino)-difluorophosphine.[18] Disilyl sulphide and selenide were made from silyl bromide and an appropriate alkali-metal salt.[19] Bis(tributylstannyl) sulphide was prepared from tributyltin chloride and sodium sulphide in aqueous solution,[20] and bis(tributylstannyl) selenide was made from $SnClBu_3$, hydrogen selenide, and trimethylamine. Purities were checked spectroscopically.

Infrared spectra were obtained in the range 200—4 000 cm^{-1} using a Perkin-Elmer 225 grating spectrometer and gas or solid cells with CsI windows. Spectra of samples in argon matrices (ratio 800 : 1, 8 K) were run on a Beckmann-RIIC FS720 interferometer modified to accept an Air Products 'Displex' closed-cycle helium-cooled matrix-isolation apparatus. For Raman spectra a Cary 83 spectrometer, with 488-nm argon-ion laser excitation, was used. Samples were contained in a liquid-nitrogen-cooled cell (solids) or a capillary closed with a greaseless tap (liquids).

For other spectra the following instruments were used: Varian Associates XL100 n.m.r. spectrometer, operating at 94 (^{19}F) or 40.5 MHz (^{31}P); A.E.I. MS902 mass spectrometer, with an ionising voltage of 70 eV; Perkin-Elmer PS16 u.v. photoelectron spectrometer with He(I) (21.22 eV) excitation.

Preparation of Bis(difluorophosphino) Sulphide.—From $S(SiH_3)_2$. Disilyl sulphide (7.2 mmol) and $PBrF_2$ (16.0 mmol) were condensed into a glass vessel (300 cm^3) fitted with a greaseless tap. After 2 h at 209 K and 17 h at 195 K the material volatile at 195 K was removed, and shown by its i.r. spectrum to be a mixture of $SiBrH_3$ and $PBrF_2$. The mixture was returned with more $PBrF_2$ (16.0 mmol), and allowed to react at 209 (28) and 195 K (63 h). The products volatile at 195 K were removed: the residue was shown to be $S(PF_2)_2$, but still containing SiH_3 groups. More $PBrF_2$ (5.0 mmol) was added, and allowed to react at 195 (29), 209 (16), and 273 K (5 h). Finally, after removal of the more volatile fraction, $PBrF_2$ (10 mmol) was added and the reaction proceeded at 273 K for 10 h. Fractional condensation *in vacuo* yielded $S(PF_2)_2$ [3.8 mmol, 54% based on $S(SiH_3)_2$ taken: *M* 169 (calc. for F_4P_2S: 170)] as the fraction retained at 195 K. Other products were $SiBrH_3$, PF_2HS, $SiFH_3$, and some yellow solid which remained in the reaction vessel.

From $S(SnBu_3)_2$. Bromodifluorophosphine (31 mmol) was condensed on to $S(SnBu_3)_2$ (9.18 g, *ca.* 15 mmol) in a glass reaction vessel (250 cm^3). On warming to room temperature for 2 min a reaction took place. Fractional condensation yielded $S(PF_2)_2$ (13.2 mmol, 88%) which was retained at 177 K but passed a trap held at 250 K, and a mixture of PF_3 and excess of $PBrF_2$, volatile at 177 K. A longer reaction time resulted in a greatly increased yield of trifluorophosphine: trace amounts of moisture lead to formation of PF_2HS and $O(PF_2)_2$; insufficient $PBrF_2$ caused a lowering of the yield of $S(PF_2)_2$, presumably due to the formation of $(F_2P)SSnBu_3$.

Preparation of Bis(difluorophosphino) Selenide.—From $Se(SiH_3)_2$. Bromodifluorophosphine (47 mmol) and $Se(SiH_3)_2$ (8.6 mmol) were allowed to react in a glass vessel (300 cm^3) for 5 h at 209 K and 84 h at 195 K. The material volatile at this temperature was replaced by $PBrF_2$ (10 mmol), which was allowed to react at 209 (22) and 195 K (27 h). The volatile portion was again replaced with fresh $PBrF_2$ (4.5 mmol), and the reaction was allowed to continue for 7 h. Fractional condensation *in vacuo* then yielded $Se(PF_2)_2$ [7.1 mmol, 83% based on $Se(SiH_3)_2$ taken: *M* 212 (calc. for F_4P_2Se: 217)] as the component retained at 195 K. Other products were $SiBrH_3$, $SiFH_3$, PF_2HSe [present as an impurity in the $Se(PF_2)_2$], and an involatile yellow solid.

From $Se(SnBu_3)_2$. Bromodifluorophosphine (7 mmol) was condensed on to $Se(SnBu_3)_2$ (2.0 g, *ca.* 3 mmol) in a glass ampoule (50 cm^3). The reagents were warmed to room temperature, mixed, and the volatile products were then immediately removed. This required pumping on the involatile tin residues for up to 1 h in order to remove all the required product. Fractionation yielded $Se(PF_2)_2$ (2.1 mmol, 70%), retained at 177 K, volatile at 228 K.

Reactions of $Se(PF_2)_2$.—(i) *With* HCl, HBr, *and* HCN. Equimolar quantities of $Se(PF_2)_2$ and HX were warmed together to room temperature in a small glass ampoule. Fractionation of the reaction products yielded PF_2X and PF_2HSe (X = Cl or Br) or unchanged starting materials (X = CN).

(*ii*) *With* NH_3, PH_3, *and* AsH_3. The compounds $Se(PF_2)_2$ (0.3 mmol) and ZH_3 (0.1—0.2 mmol) were warmed together to room temperature in a mixture of C_6D_6, CCl_3H, and CCl_3F as solvent in an n.m.r. tube. Ammonia reacted rapidly to give $PF_2(NH_2)$, PF_2HSe, and a trace amount of PF_3; PH_3 and AsH_3 did not react at all, even after several days. In a separate experiment, $PF_2(NH_2)$ was found not to react further with $Se(PF_2)_2$.

(*iii*) *With* H_2O, H_2S, H_2Se, *and* H_2Te. The compounds

---

[17] R. K. Harris and J. R. Woplin, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 44.

[18] J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Synth.*, 1967, **10**, 147.

[19] S. Cradock E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1969, 1628.

[20] Société anon. des manufactures des glaces et produits chimiques de Saint-Gobain, Chauny & Cirey, B.P. 792,309 (*Chem. Abs.*, 1958, **52**, 17805).

$Se(PF_2)_2$ (0.2 mmol) and H_2Y (0.2 mmol) were allowed to react in an n.m.r. tube in a mixture of $SiMe_4$, C_6D_6, and CCl_3F. In each case, PF_2HSe was rapidly and quantitatively formed, together with PF_3 ($Y = O$), PF_2HS ($Y = S$), or PH_3,PF_5 and solid Te ($Y = Te$). The reactions with H_2Se and H_2Te were followed at low temperature, but the intermediates PF_2HSe and PF_2HTe were not observed.

(*iv*) *With* MeOH *and* MeSH. The compound $Se(PF_2)_2$ (0.2 mmol) was allowed to react with MeYH (0.2 mmol) in an n.m.r. tube with a mixture of C_6D_6 and CCl_3H as solvent. The reactions proceeded rapidly and quantitatively giving $PF_2H{\cdot}Se$ and $YPF_2(YMe)$.

(*v*) *With* $[MnH(CO)_5]$ *and* $[ReH(CO)_5]$. Approximately equimolar quantities of $Se(PF_2)_2$ and $[MH(CO)_5]$ were allowed to react at room temperature in an n.m.r. tube, with a mixture of $SiMe_4$ and C_6D_6 as solvent. Difluorophosphine and PF_2HSe were identified as reaction products by n.m.r. spectroscopy. In each case a solid material was precipitated, this being yellow in the manganese reaction and white in the rhenium reaction. These solids resembled samples of the metal carbonyls, but were not isolated and identified conclusively.

(*vi*) *With* Cl_2. The compounds $Se(PF_2)_2$ (0.3 mmol) and Cl_2 (0.6 mmol) were warmed to room temperature in a mixture of $SiMe_4$ and C_6D_6 in an n.m.r. tube. The solution rapidly became deep yellow and a dark precipitate was formed. The soluble reaction products were identified by their n.m.r. parameters.

(*vii*) *With* B_2H_6. The compounds $Y(PF_2)_2$ (0.3 mmol) and B_2H_6 (0.3 or 0.9 mmol) were allowed to react together in an n.m.r. tube with CCl_3D as solvent. Reaction took place immediately on warming to 223 (S) or 298 K ($Y = Se$), giving $F_2PYPF_2{\cdot}BH_3$.

(*viii*) *With* $[Mo(C_7H_8)(CO)_4]$. The compound $Y(PF_2)_2$ (0.3 mmol) and $[Mo(C_7H_8)(CO)_4]$ (0.3 mmol) were allowed to react together in an n.m.r. tube with C_6H_6 as solvent. The reactions took *ca.* 15 min to reach completion at room temperature giving $[Mo(PF_2)_2Y(CO)_4]$ ($Y = S$ or Se).

We thank Dr. S. Cradock for his assistance in obtaining photoelectron spectra, Dr. A. J. Hinchcliffe for the spectra of matrix-isolated species, and Mr. E. K. Macdonald for giving us permission to include results of his experiments involving bis(difluorophosphino) sulphide and diborane or tetracarbonyl(η-norbornadiene)molybdenum.

[7/475 *Received*, 18*th March*, 1977]