Preparation and Properties of Difluorophosphino-derivatives of Phosphorus(III) Hydroxy-compounds †

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Phosphorus(III) acid reacts rapidly with $S(PF_2)_2$ to give $PHO(OPF_2)_2$, and then more slowly to give $P(OPF_2)_3$. The latter has been isolated, and characterised by n.m.r., vibrational, mass, and u.v. photoelectron spectroscopy. Diphenyl- and dimethyl-phosphites react with $S(PF_2)_2$ to give $P(OPh)_2(OPF_2)$ and $P(OMe)_2(OPF_2)$. The latter has been isolated, and fully characterised spectroscopically. It reacts rapidly with diborane to give a monoborane adduct, and more slowly to give a bis(monoborane) adduct. Reactions of $S(PF_2)_2$ with hypophosphorous acid and with diphenylphosphine oxide are also described.

The reaction of $S(PF_2)_2$ with hydroxy-compounds has been shown to be of fairly general applicability to the preparation of compounds containing the OPF_2 group.[1] In particular, the syntheses of difluorophosphino-derivatives of orthophosphoric acid and other phosphorus(v) hydroxy-compounds have been described.[2] These compounds have potential as mono-, bi-, and tri-dentate ligands. In this paper we describe an extension of this work to reactions of compounds of the type $PHOR_2$, which can react to give phosphorus(III) products, $P(OPF_2)R_2$. These products may also be useful ligands, and have one more donor site, at the central phosphorus atom, than the phosphorus(v) compounds.

Results and Discussion

Reactions of $PHO(OH)_2$ *with* $S(PF_2)_2$.—The reaction of $S(PF_2)_2$ with phosphorous acid was of particular interest, as the acid is thought to exist in two tautomeric forms, (1a) and

(1a) (1b)

(1b).[3] The equilibrium lies heavily to the left and species (1b) is not observed in the n.m.r. spectra of this compound. However, the equilibrium is rapid at room temperature, and in solution in D_2O there is rapid incorporation of deuterium into all three hydrogen positions.

On mixing two or more moles of $S(PF_2)_2$ with one of phosphorous acid, there was a rapid reaction to give the bis(difluorophosphino) ester [equation (1)]. This product then

$$PHO(OH)_2 + 2S(PF_2)_2 \longrightarrow PHO(OPF_2)_2 + 2PF_2HS \quad (1)$$

either disproportionated fairly quickly [equation (2)], or reacted further, if more $S(PF_2)_2$ was present [equation (3)].

$$3PHO(OPF_2)_2 \longrightarrow PHO(OH)_2 + 2P(OPF_2)_3 \quad (2)$$

$$PHO(OPF_2)_2 + S(PF_2)_2 \longrightarrow P(OPF_2)_3 + PF_2HS \quad (3)$$

The initial product could not be isolated, as further reaction always occurred, but highly concentrated solutions could be obtained by reaction of excess $S(PF_2)_2$ with phosphorous acid at room temperature, and then cooling the mixture to *ca.* 210 K. The product was characterised by its n.m.r. spectra. The ^1H spectrum, and the ^{31}P resonances due to the P^V nucleus, were first order, and the parameters (Table 1) agree well with those observed for similar phosphorus(v) compounds.[2] The other ^{31}P resonances are also effectively first order, but as the central phosphorus atom is a prochiral centre, having H, O, and two OPF_2 substituents, the chemical shifts of the two fluorine nuclei in each PF_2 group differ (by 0.88 p.p.m.), $^2J(FF)$ is observed, and the ^{19}F spectrum is therefore a series of AB sub-spectra. Analysis of all the spectra gave parameters listed in Table 1, and confirm the identity of the product.

The second stage of the reaction [equation (3)] could involve replacement of the remaining proton by a PF_2 group to give $PO(OPF_2)_2(PF_2)$, followed by rearrangement, or the rearrangement step could take place first, with $P(OH)(OPF_2)_2$ being the intermediate. We are unable to distinguish between these two mechanisms.

The product, tris(difluorophosphino) phosphite, was isolated, and characterised by n.m.r., vibrational, photoelectron, and mass spectroscopy. The ^{31}P n.m.r. spectrum shows two types of phosphorus to be present. One gives rise to a wide triplet [$^1J(PF)$], further split into doublets [$^2J(PP)$], and then into a complex second-order pattern, due to coupling between magnetically non-equivalent PF_2 groups. The central part of this triplet lies close to the other resonance, which is a septet [$^3J(PF)$] of quartets [$^2J(PP)$]. The internal chemical shift, $^2J(PP)$, and $^3J(PF)$ are all temperature dependent, with the result that the general appearance of the spectrum changes markedly [Figure 1(*a*) and (*b*)]. Similar temperature dependence of coupling, most notably $^2J(PP)$, has been observed in the related compounds $NH(PF_2)_2$,[4] $S(PF_2)_2$, and $Se(PF_2)_2$.[5] The ^{19}F n.m.r. spectrum is essentially a doublet [$^1J(PF)$] of doublets [$^3J(PF)$], but each line is further split into a complex second-order pattern [Figure 1(*c*)], due to long-range couplings between the PF_2 groups. This pattern, which is very similar to that observed for $PO(OPF_2)_3$,[2] has not been analysed in detail. The measured parameters are listed in Table 1. It should be noted that the value of $^1J(PF)$ is really $^1J(PF) + 2\ ^5J(PF')$ but that this should approximate to $^1J(PF)$ as $^5J(PF')$ should be small. The observed splitting patterns, second order and first order, and the magnitudes of the chemical shifts and coupling constants, all support the proposed formulation.

Details of the vibrational spectra of $P(OPF_2)_3$ are given in Table 2. The spectra might be expected to be similar to those of $PO(OPF_2)_3$, without the stretching mode (*ca.* 1 400 cm^{-1}) and deformations associated with the extra oxygen atom. The spectra do contain bands in the regions associated with asym-

† *Non-S.I. units employed:* mmHg ≈ 13.6 × 9.8 Pa, eV ≈ 1.60 × 10^{-19} J.

Table 1. N.m.r. parameters [a]

	$P'(OPF_2)_3$	$P'HO(OPF_2)_2$	$P'(OMe)_2(OPF_2)$	$P'(OPh)_2(OPF_2)$
$\delta(^{31}P)$/p.p.m.	112.3	108	104.8	114.1
$\delta(^{31}P')$/p.p.m.	110.0	−13	120.7	121.3
$\delta(^{19}F)$/p.p.m.	−37.3	−39.8 [b]	−36.9	−38.2
$\delta(^{1}H)$/p.p.m.		7.47	3.62	n.s.
$\delta(^{13}C)$/p.p.m.			49.8	n.s.
$^{1}J(^{31}P^{19}F)$/Hz	1 349 [c]	1 375	1 322	1 335
$^{1}J(^{31}P^{1}H)$/Hz		803		
$^{2}J(^{31}P^{31}P')$/Hz	0.8 [d]	13	4.5	1.5
$^{2}J(^{31}P'^{13}C)$/Hz			7.1	n.s.
$^{2}J(^{19}F^{19}F)$/Hz		17.5		
$^{3}J(^{31}P'^{19}F)$/Hz	17.9 [e]	12	12.7	11.7
$^{3}J(^{31}P'^{1}H)$/Hz			10.4	n.s.
$^{6}J(^{19}F^{1}H)$/Hz			0.2	

[a] Spectra were recorded at room temperature (300 K) for solutions in CCl_3D or CCl_2D_2. Chemical shifts are to high frequency of external $SiMe_4$ (^{1}H and ^{13}C), CCl_3F (^{19}F), or 85% H_3PO_4 (^{31}P); n.s. = not studied. [b] Mean value: difference of chemical shifts of geminal fluorine nuclei, 0.46 p.p.m. [c] $^{1}J(PF) + 2^{5}J(PF)$. [d] 2.7 Hz at 215 K; <0.1 Hz at 341 K. [e] 19.2 Hz at 215 K; 17.4 Hz at 341 K.

Table 2. Vibrational spectra (cm^{-1}) of $P(OPF_2)_3$

Gas	Liquid	Solid		
I.r.	Raman	I.r.	Raman	Assignment
1 018s	1 017w,dp	1 004m	1 001w	ν_{asym}(POP)
			966w	
910vs	900w,dp	902s	916w	
			896w	
830vs	847s,p	848m	845m	$\nu(PF_2)$
			806m	
	817m,dp	791vs	786m	
			770w	
740w	737w,p	740w	706w	ν_{sym}(POP)
675m		701m	689w	
	657vs,p	683w	650s	
650m		657w	630s	
		630m		
515m	523m,dp	530w	526m	Deformations
		513m	514w	
450m	446w,p	466w	463w	
		448w		
360vw	396m,p	401w	403m	
320w	326w,dp	381w		
	261w,dp	360w	277w	
		339w		
	206m,dp	318w	216m	

Abbreviations used: w = weak, m = medium, s = strong, v = very, p = polarised, and dp = depolarised.

Table 3. Mass spectrum of $P(OPF_2)_3$

m/e	Relative abundance	Assignment
286	11	$[P(OPF_2)_3]^+$
201	61	$[P(OPF_2)_2]^+$
154	22	$[O(PF_2)_2]^+$
135	61	$[P_2F_3O]^+$
113	13	$[P_2FO_2]^+$
85	9	$[PF_2O]^+$
69	100	$[PF_2]^+$
66	11	$[PFO]^+$
50	11	$[PF]^+$
47	66	$[PO]^+$

Metastable ions *m/e*	Assignment
143.3 weak	$[P(OPF_2)_3]^+ \longrightarrow PF_2O + [P(OPF_2)_2]^+$
90.7 weak	$[P(OPF_2)_2]^+ \longrightarrow PFO + [P_2F_3O]^+$
63.5 weak	$[P(OPF_2)_2]^+ \longrightarrow PF_3 + [P_2FO_2]^+$
16.4 weak	$[P_2F_3O]^+ \longrightarrow PF_3 + [PO]^+$
16.2 weak	$[P_2F_4O]^+ \longrightarrow PF_3O + [PF]^+$

metric and symmetric stretching vibrations of POP units,[6] and with stretches of PF_2 groups, but they are much more complicated than the phosphate spectra, possibly indicating that the molecular symmetry is lower, or that several conformers are present. It was not possible to obtain the solid in a crystalline form, suggesting that there are no strong intermolecular forces in the solid phase.

The He(I) photoelectron spectrum of $P(OPF_2)_3$ was recorded, and is shown in Figure 2. It is very similar to that of $O(PF_2)_2$,[7] except that there is one extra band at 10.55 eV. This is tentatively assigned to the lone-pair orbital of the central phosphorus atom, and the next two bands, at 11.57 and 12.28 eV, are assigned to the remaining oxygen and phosphorus lone-pair orbitals, although there is uncertainty about the ordering of the equivalent bands for $O(PF_2)_2$.[7] The P–O bonding orbitals contribute to the peak with a maximum intensity at 14.13 eV, and the remaining large series of peaks is due to ionisation from fluorine lone-pair and P–F bonding orbitals.

Details of the mass spectrum of $P(OPF_2)_3$ are given in Table 3. The ion giving a strong peak at *m/e* 201 is linked by metastable peaks to the molecular ion, and is formed by loss of PF_2O. This ion fragments by loss of PFO or PF_3, both processes involving migration of fluorine. Thus the breakdown route exactly parallels that observed for $PO(OPF_2)_3$.[2] The most prominent peaks can be assigned to $[PF_2]^+$, $[PO]^+$, and $[P_2F_3O]^+$, which are also very prominent in spectra of $PO(OPF_2)_3$ and $PFO(OPF_2)_2$.[2]

$P(OMe)_2(OPF_2)$ and $P(OPh)_2(OPF_2)$.—The reactions of dimethyl and diphenyl phosphite with $S(PF_2)_2$ proceeded rapidly and cleanly at room temperature, being essentially complete within 10 min [equation (4)]. The reaction was only studied with methyl and phenyl substituents, but there is no

$$PHO(OR)_2 + S(PF_2)_2 \longrightarrow P(OPF_2)(OR)_2 + PF_2HS \quad (R = Me \text{ or } Ph) \quad (4)$$

reason to suppose that it does not provide a general route to compounds of the type $P(OPF_2)(OR)_2$. The methyl derivative was isolated, and characterised by its n.m.r., vibrational and mass spectra: the phenyl derivative was identified by its n.m.r. spectra only.

The ^{1}H, ^{13}C, ^{19}F, and ^{31}P n.m.r. spectra of $P(OMe)_2(OPF_2)$

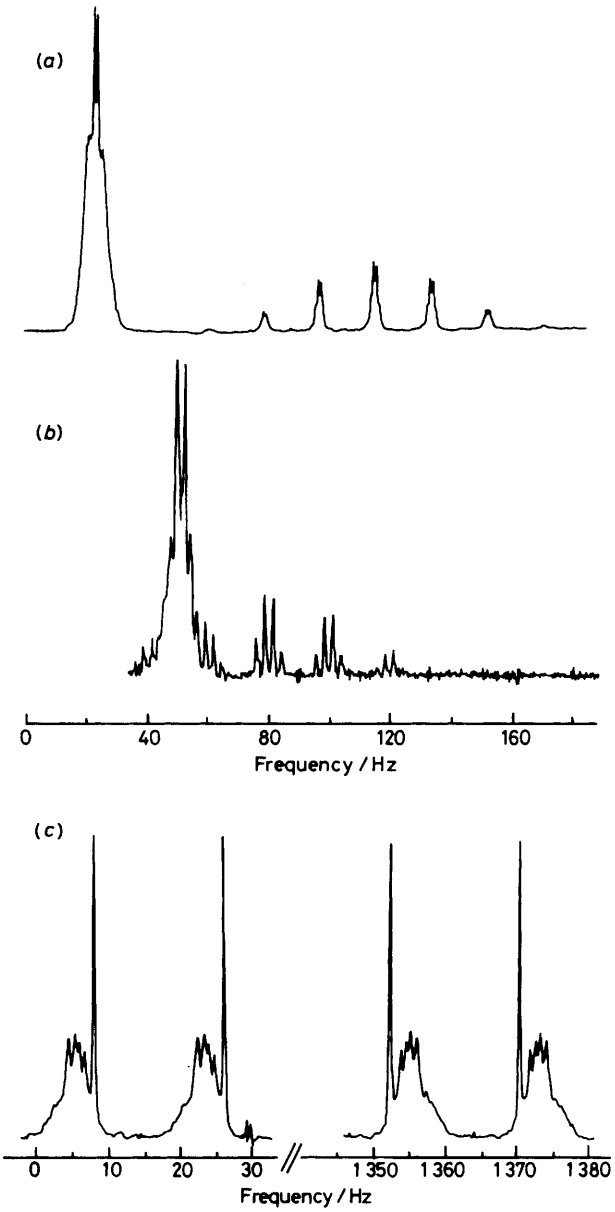


Figure 1. N.m.r. spectra of $P(OPF_2)_3$: (*a*) central section of high-resolution ^{31}P spectrum at 301 K; (*b*) the same section of the ^{31}P spectrum at 215 K; (*c*) high-resolution ^{19}F spectrum

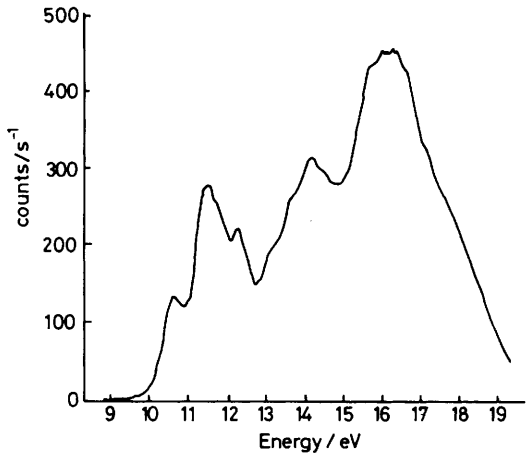


Figure 2. He(I) u.v. photoelectron spectrum of $P(OPF_2)_3$

Table 4. Vibrational spectra (cm^{-1}) of $P(OMe)_2(OPF_2)$

Gas I.r.	Liquid Raman	Solid I.r.	Assignment
3 010m	2 882m,p	3 007w	$\nu(CH_3)$
2 960m	2 827m,p	2 895w	
2 920w		2 881m	
2 855m		2 824w	
1 467w	1 460m,dp	1 465m	$\delta(CH_3)$
		1 255w	
1 185m		1 187m	ν(POP), ν(CO)
1 040vs	1 060m,p	1 050s	
		1 015vs	
940vs	1 025w,p	930vs	
825vs	820m,dp	808vs	$\nu(PF_2)$
770s	770vs,p	775vs	
700w	706m,p	700w	
600m	600w	600s	
520w	518m	525m	
440w	490w	470w	
	440w	430w	
		410w	
	380w	370m	
	278w	330w	

For abbreviations used see Table 2.

were recorded: the parameters, listed in Table 1, are entirely consistent with the proposed formulation. Most notable is the observation of the six-bond $^{19}F-^{1}H$ coupling, in the highest resolution ^{19}F spectra. Only ^{19}F and ^{31}P spectra were recorded for $P(OPh)_2(OPF_2)$, and the parameters are also given in Table 1. Generally the parameter values are very similar to those for the methyl compound, but $^2J(PP')$ is only 1.5 Hz, compared to 4.5 Hz. However, the $P^{III}-O-P^{III}$ couplings are always small, as in $O(PF_2)_2$,[6] whereas in similar compounds in which the intervening atom is sulphur,[8] selenium,[5] or nitrogen [4] the equivalent couplings are large (several hundred Hz) and markedly temperature dependent.

Vibrational spectra of $P(OMe)_2(OPF_2)$ in gas, liquid, and solid phases are described in Table 4. The absence of a band in the region 1 300—1 400 cm^{-1} indicates that possible isomers with $P^V=O$ groups are not present. Full assignment of spectra for such a complicated molecule, with low symmetry, and many atoms of comparable mass, is not possible, but the main bands above 700 cm^{-1} fall in the regions associated with vibrations of methyl and PF_2 groups, and stretching vibrations of P–O–P units and C–O bonds.

Details of the mass spectrum of $P(OMe)_2(OPF_2)$ are given in Table 5. The spectrum supports the suggested formulation, and shows that fragmentation of the molecular ion occurs primarily by loss of PF_2O, followed by CH_2O or OMe_2. A second route involves initial loss of OMe, followed by PFO and then MeF, leaving the $[PO]^+$ ion seen so often with similar compounds.

Reactions of $PH_2O(OH)$ *with* $S(PF_2)_2$.—Since phosphorous acid reacted cleanly with $S(PF_2)_2$ to give $P(OPF_2)_3$, as described above, the reaction of hypophosphorous acid, $PH_2O(OH)$, was also investigated. A rapid reaction occurred at room temperature, giving an inhomogeneous orange-yellow solid material. The only product observed in ^{19}F and ^{31}P n.m.r. spectra was $O(PF_2)_2$, and it would appear that extensive decomposition had occurred.

Table 5. Mass spectrum of $P(OMe)_2(OPF_2)$

m/e	Relative abundance	Assignment
178	3	$[P(OMe)_2(OPF_2)]^+$
147	6	$[P(OMe)(OPF_2)]^+$
97	2	$[PFO(OMe)]^+$
94	2	$[PO_2(OMe)]^+$
93	100	$[P(OMe)_2]^+$
81	34	$[PF(OMe)]^+$
69	12	$[PF_2]^+$
63	18	$[PH(OMe)]^+$
62	4	$[P(OMe)]^+$
47	22	$[PO]^+$
45	3	$[C_2H_5O]^+$
31	3	$[P]^+$, $[MeO]^+$
29	3	$[HCO]^+$, $[C_2H_5]^+$
15	12	$[CH_3]^+$

Metastable ions

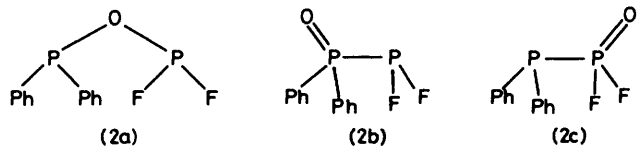
m/e	Assignment
48.6 strong	$[P(OMe)_2(OPF_2)]^+ \longrightarrow PF_2O + [P(OMe)_2]^+$
44.6 strong	$[P(OMe)(OPF_2)]^+ \longrightarrow PFO + [PF(OMe)]^\bullet$
42.7 weak	$[P(OMe)_2]^+ \longrightarrow CH_2O + [PH(OMe)]^+$
27.3 weak	$[PF(OMe)]^+ \longrightarrow MeF + [PO]^+$
23.8 weak	$[P(OMe)_2]^+ \longrightarrow OMe_2 + [PO]^+$

Reaction of $PH(O)Ph_2$ *with* $S(PF_2)_2$.—After preliminary investigations using n.m.r. spectrsocopy, this reaction was carried out on a preparative scale. After removal of the volatile fractions [PF_2HS and excess $S(PF_2)_2$] the major product was a white, microcrystalline solid. Attempts to purify this solid were never totally successful, and the evidence for its identity therefore comes mainly from ^{31}P and ^{19}F n.m.r. spectroscopy.

A reaction analogous to those reported above for phosphites was expected [equation (5)]. There are, however, three

$$PH(O)Ph_2 + S(PF_2)_2 \longrightarrow PPh_2(OPF_2) + PF_2HS \quad (5)$$

possible isomers of the product, one (2a) having a P–O–P linkage between two phosphorus(III) atoms and two (2b and 2c) having P–P bonds, linking phosphorus(III) and phosphorus(V) atoms. The three forms have the same n.m.r. spin



systems, and in the absence of other spectroscopic data, can be distinguished only by consideration of the magnitudes of the n.m.r. parameters. The ^{31}P spectrum at 24.1 MHz was second order, but consisted essentially of a wide triplet of doublets, assigned to a PF_2 group, and a doublet of triplets. The ^{19}F spectrum also showed second-order features, but was basically a wide doublet of doublets. The spectra were analysed as arising from an $[ABX_2]$ spin system, giving $\delta(A)$ 114.0, $\delta(B)$ −2.3, and $\delta(X)$ −35.6 p.p.m., $J(AX)$ −1 274, $J(BX)$ −23, and $J(AB)$ ±366 Hz. The parameters are not consistent with those expected for any of the three isomers. The PP coupling, 366 Hz, is similar to those recorded for many compounds with P–P bonds,[9] and is much greater than two-bond PP couplings observed in other P^{III}–O–P^{III} compounds.[6]

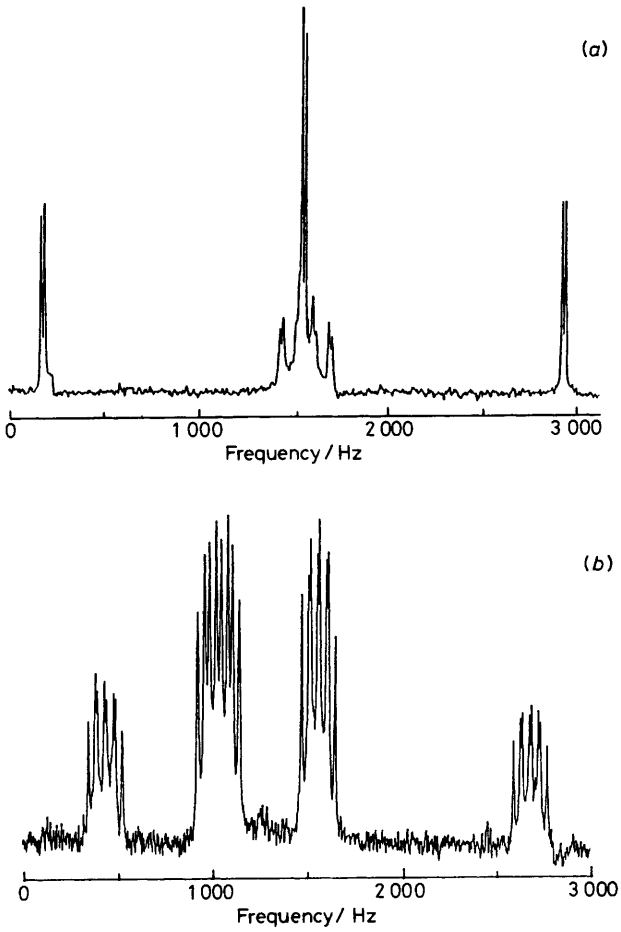


Figure 3. Low-resolution ^{31}P n.m.r. spectra of (*a*) $BH_3 \cdot P(OMe)_2(OPF_2)$ and (*b*) $BH_3 \cdot P(OMe)_2(OPF_2 \cdot BH_3)$

This seems to rule out isomer (2a), the one expected by analogy with the other reactions described in this paper. However, the ^{31}P and ^{19}F chemical shifts in difluorodiphosphines are typically around 290 and −80 p.p.m. respectively, compared with 114 and −35 p.p.m., for this compound. Thus isomer (2b) is also ruled out, and (2c) is also excluded, as the ^{31}P chemical shift and $J(PF)$ for the PF_2O group are well outside the expected range. The chemical shifts also rule out possible P–S–P linked systems. On balance, we prefer isomer (2a), as all the parameters except $J(PP)$ are very close to the expected values. It is unfortunate that the compound could not be obtained in a pure enough form to check the proposed formulation by other spectroscopic means. In the absence of this confirmation it is pointless to speculate on the factors leading to the unexpected PP coupling. However, it should be noted that two-bond PP couplings with intervening atoms other than oxygen are both large, and very variable.[4,5,8]

Reactions of $P(OMe)_2(OPF_2)$ *with* B_2H_6.—When $P(OMe)_2(OPF_2)$ was treated with B_2H_6, in the ratio 2 : 1, a reaction occurred within a few minutes at room temperature, giving a 1 : 1 monoborane adduct. The product was characterised by ^1H, ^{11}B, ^{19}F, and ^{31}P n.m.r. spectroscopy, and was shown to be the isomer in which the borane is co-ordinated to the di(methoxy)phosphine. In particular, the ^{31}P spectrum, depicted in Figure 3(*a*), shows that there is a free PF_2 group, with coupling to a second phosphorus nucleus. This second nucleus

Table 6. N.m.r. parameters of BH_3 adducts of $P(OMe)_2(OPF_2)$ *

	$BH_3{\cdot}P'(OMe)_2(OPF_2{\cdot}B'H'_3)$	$BH_3{\cdot}P'(OMe)_2(OPF_2)$
$\delta(^1HC)$/p.p.m.	3.91	3.83
$\delta(^1HB)$/p.p.m.	0.63	0.6
$\delta(^1H'B')$/p.p.m.	0.75	
$\delta(^{11}B)$/p.p.m.	−61.8	−61.1
$\delta(^{11}B')$/p.p.m.	−62.3	
$\delta(^{19}F)$/p.p.m.	−52	−38.8
$\delta(^{31}P)$/p.p.m.	100.7	111.3
$\delta(^{31}P')$/p.p.m.	116.3	111.0
$^1J(^{31}P^{19}F)$/Hz	1 342	1 366
$^1J(^{11}B^1H)$/Hz	97	99
$^1J(^{11}B'^1H')$/Hz	104	
$^1J(^{31}P'^{11}B)$/Hz	73	86
$^1J(^{31}P^{11}B')$/Hz	56	
$^2J(^{31}P^{31}P')$/Hz	44	16
$^2J(^{31}P'^1H)$/Hz	19	18
$^2J(^{31}P^1H')$/Hz	20	
$^3J(^{31}P'^1H)$/Hz	12	11.5
$^3J(^{19}F^1H')$/Hz	16.6	

* Spectra were recorded for solutions in CCl_3D at room temperature (300 K). Chemical shifts are to high frequency of external $SiMe_4$ (^1H), $B(OMe)_3$ (^{11}B), CCl_3F (^{19}F), or 85% H_3PO_4 (^{31}P).

shows a broad 1 : 1 : 1 : 1 quartet pattern, due to coupling to ^{11}B. The ^{19}F spectrum is a simple doublet.

In the presence of excess B_2H_6, this first product reacted further, over a period of several days, to give the bis(monoborane) adduct, $BH_3{\cdot}P(OMe)_2(OPF_2{\cdot}BH_3)$. This reaction was unexpected, as $O(PF_2)_2$ forms only a monoborane adduct.[10] Again, the product was characterised by ^1H, ^{11}B, ^{19}F, and ^{31}P n.m.r. spectra. The ^{11}B spectrum had two sets of resonances, clearly establishing the presence of two types of BH_3 group, and this was confirmed by observing the ^1H spectrum with ^{11}B decoupling. The ^{31}P spectrum, shown in Figure 3(*b*), clearly shows two different sets of phosphorus resonances. One is a triplet [^1J(PF)] of 1 : 1 : 1 : 1 quartets [^1J(PB)] of doublets [^2J(PP)], while the second is a doublet [^2J(PP)] of 1 : 1 : 1 : 1 quartets [^1J(PB)]. All the parameters for the borane adducts are listed in Table 6; the values obtained agree well with those reported for related compounds, such as $O(PF_2)_2{\cdot}BH_3$ [10] and $PF_2(OMe){\cdot}BH_3$.[11]

Reactions of $P(OPF_2)_3$ *with* B_2H_6.—The reaction of $P(OPF_2)_3$ with B_2H_6 was investigated. Under all conditions studied extensive decomposition occurred, and no useful products were observed. The major reaction products were $O(PF_2)_2$ and an unidentified yellow solid.

Experimental

All volatile materials were handled using a Pyrex glass vacuum line fitted with Sovirel greaseless taps. Bis(difluorophosphino) sulphide was prepared by the exchange reaction of bis(tributylstannyl) sulphide with bromodifluorophosphine.[12] Other reagents were prepared by standard methods.

N.m.r. spectra were recorded on Varian XL100 (^{19}F and ^{31}P), JEOL FX60Q (^{31}P), Bruker WH360 (^{11}B), and Varian HA100 (^1H) spectrometers. Mass spectra were obtained using an A.E.I. MS902 spectrometer, with an ionising voltage of 70 eV, and u.v. photoelectron spectra using a Perkin-Elmer PS16 spectrometer with He(I) (21.22 eV) excitation. Vibrational spectra were recorded on a Perkin-Elmer 557 i.r. spectrometer, operating with KBr or CsI optics in the range 4 000—200 cm^{-1}, and on a Cary 83 Raman spectrometer, with 488 nm argon-ion laser excitation.

Samples for n.m.r. study were prepared by distilling measured amounts (typically 0.2 mmol) of volatile compounds into 5-mm n.m.r. tubes containing *ca.* 0.5 cm^3 of solvent, and weighed amounts of any involatile reagents. The tubes were then sealed.

Preparation of $P(OPF_2)_3$.—An excess of $S(PF_2)_2$ (10 mmol) was condensed into a glass ampoule (250 cm^3) containing $PHO(OH)_2$ (2.0 mmol). The mixture was warmed to room temperature, and reaction was evident by effervescence, and the disappearance of the solid material. After 4 h the volatile products were removed, and separated by fractional condensation *in vacuo*. Tris(difluorophosphino) phosphite (1.9 mmol, 95%) was obtained as the fraction volatile at 250 K but retained at 209 K. The product had a melting point of 165 K, and a vapour pressure of 20 mmHg at 273 K.

Preparation of $P(OMe)_2(OPF_2)$.—The compound $S(PF_2)_2$ (3.0 mmol) was condensed into a glass ampoule (250 cm^3) containing dimethyl phosphite (2.0 mmol), and the mixture was warmed to room temperature for 90 min. Volatile products were removed, and separated by fraction condensation. Difluorophosphino dimethyl phosphite (1.7 mmol, 85%) was retained in a trap held at 228 K. The melting point of the product was 129 K, and its vapour pressure at 273 K was 9 mmHg.

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