Preparation, Structures, and Reactions of some Difluorothiophosphonate and Difluoroselenophosphonate Complexes of Platinum(II)

By **J. Andrew S. Duncan, E. A. V. Ebsworth,* Robert O. Gould, C. Lynn Jones, David W. H. Rankin,** and **John D. Whitelock,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The complexes $[Pt(PEt_3)_2(PF_2Y)X]$ (X = Cl, Br, or I; Y = S or Se) have been prepared by the reaction of *trans*-$[PtH(PEt_3)_2X]$ with $PF_2H(Y)$. The reactions have been studied at low temperatures using ^{31}P and ^{19}F n.m.r. spectroscopy; the formation of $[Pt^{IV}H_2(PEt_3)_2(PF_2Y)X]$ and $[Pt^{II}H(PEt_3)_2(PF_2Y)]$ as intermediates was observed, and a mechanism has been proposed. The complexes $[Pt(PEt_3)_2(PF_2Y)X]$ (X = H, Cl, Br, or I) were also prepared by reaction of $[Pt(PEt_3)_3X][BPh_4]$ with $PF_2H(Y)$: the hydride complexes were stable at room temperature. The *X*-ray crystal structure was obtained for *trans*-$[PtCl(PEt_3)_2(PF_2S)]$. The crystals are orthorhombic, space group *Pbcn*, with $a = 1.1597(2)$, $b = 1.3355(2)$, and $c = 1.3632(3)$ nm. The structure has been solved with 934 diffractometer data and refined with 876 data to $R = 0.034$. The molecules are packed with a two-fold disorder about the Pt–Cl bond, but the two positions of the PF_2S moiety are clearly resolved.

ALTHOUGH many transition-metal complexes are known where PF_2O is bound to the metal,[1] relatively little is known about analogous PF_2S and PF_2Se complexes. A series of PF_2Y complexes [2] was proposed as the products from the reaction of $[Ir(CO)Cl(PPh_3)_2]$ with $PF_2(Y)X$ (Y = S or Se, X = Cl or Br) to give $[Ir(CO)ClX(PF_2Y)(PPh_3)_2]$. These complexes were very insoluble and no n.m.r. data were obtained. The structure was assigned on the basis of vibrational spectra and analyses.

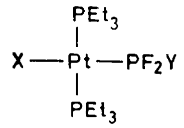
In this paper we report the formation of a series of complexes $[Pt(PEt_3)_2(PF_2Y)X]$ (X = Cl, Br, or I; Y = S or Se) which were formed in the reaction of $[PtH(PEt_3)_2X]$ with $PF_2H(Y)$. The same complexes were formed in the reactions of $[Pt(PEt_3)_3X][BPh_4]$ with $PF_2H(Y)$, with the complexes $[PtH(PEt_3)(PF_2Y)]$ isolated as well.

RESULTS AND DISCUSSION

At room temperature the reactions of $[PtH(PEt_3)_2X]$ with equimolar amounts of $PF_2H(Y)$ gave clear colourless solutions with the evolution of one mole of H_2 for each mole of platinum starting material. These solutions were studied using ^{31}P and ^{19}F n.m.r. spectroscopy. By removing the solvent and recrystallising from benzene, the products were obtained as air-stable crystalline solids. Carbon and hydrogen analyses were obtained.

The n.m.r. spectra were all first order and showed similar patterns for all the products isolated. In a typical ^{31}P spectrum there were two distinct groups of resonances. To low frequency, where resonances due to PEt_3 groups are found, a doublet of triplets was observed, and at high frequency, the PF_2 region, there was a triplet of triplets. The larger triplet coupling was *ca.* 1 100 Hz and is assigned to $^1J(PF)$, confirming the presence of a PF_2 group. The magnitude of the smaller triplet coupling is the same as that of the doublet coupling in the PEt_3 resonance. Both low- and high-frequency resonances showed platinum satellites confirming the presence of a platinum complex containing a PF_2Y and two PEt_3 groups. Analyses indicate that S or Se is retained in the complexes, and, in the ^{19}F spectra of species formed from $PF_2H(Se)$, selenium satellites were detected close to the main resonance.

The presence of halogen bound to Pt in the products was confirmed by analyses, by the sensitivity of the n.m.r. parameters of the products to the halogen in the starting material, and by the absence of any couplings that could be associated with a possible hydride ligand. It follows that the species we have obtained are complexes (1)—(6).



$$X-\overset{\overset{\displaystyle PEt_3}{|}}{\underset{\underset{\displaystyle PEt_3}{|}}{Pt}}-PF_2Y$$

(1) X = Cl, Y = S (4) X = Cl, Y = Se
(2) X = Br, Y = S (5) X = Br, Y = Se
(3) X = I, Y = S (6) X = I, Y = Se

Nuclear magnetic resonance parameters for these complexes are given in Table 1.

At low temperature, ^{31}P and ^{19}F n.m.r. spectra showed that unstable intermediates were formed. The species present depended on the molar ratios of the reactants taken.

(*i*) Pt : $PF_2H(Y)$ = 1 : 1.—For these systems the S and Se behaved similarly, the sulphur reactions being cleaner. No reaction took place until −50 °C; at this temperature three complexes were detected in the ^{31}P spectra. The first, giving a singlet ^{31}P-{^1H} resonance, was identified as $[PtH_2(PEt_3)_2X_2]$.[3] The other two complexes, one of which was only present in small amounts, each showed a doublet pattern with Pt satellites in the PEt_3 region. In the PF_2 region only one resonance was detected, as a triplet of triplets with Pt satellites. The smaller triplet splitting corresponded with the doublet coupling in the stronger of the two observed at low frequency. When proton coupling was retained the peaks in the PF_2 region showed a large additional doublet splitting, which suggested that a *trans* hydride was present. The ^{19}F-{^1H} spectra showed a

TABLE 1

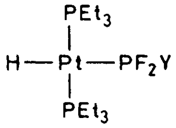
^{31}P and ^{19}F n.m.r. parameters [a]

Complex	(1)	(2)	(3)	(4) [b]	(5)	(6)	(7)	(8) [e]	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16) [c,d]	(17) [e]	(18) [e]	(19) [e]	(20) [e]	(21) [e]
δP/p.p.m.	18.9	15.7	10.7	17.8	14.6	9.5	19.0	18.5	9.1	6.4	2.1	9.2	6.5	2.3	6.8	18.6	17.6	n.r.	n.r.	13.1	8.8
δP′/p.p.m.	132.7	133.7	135.7	137.7	138.4	141.0	222	234.6	162.3	156.2	144.7	n.r.	170	152	148.1	127.6	n.r.	n.r.	n.r.	161.5	144.7
^1J(PtP)/Hz	2 346	2 326	2 305	2 354	2 339	2 302	2 500	2 504	1 634	1 636	1 626	1 632	1 607	1 716	1 533	2 324	2 312	n.r.	n.r.	2 373	3 151
^1J(PtP′)/Hz	5 322	5 337	5 217	5 054	5 039	5 002	3 032	2 827	2 066	2 078	n.r.	n.r.	n.r.	n.r.	1 878	n.r.	n.r.	n.r.	n.r.	n.r.	4 884
^2J(PP′)/Hz	24	22	22	22	22	20	29	29	27	27	27	24	24	24	22	27	27	n.r.	n.r.	27	37
^3J(PF)/Hz	10	10	10	10	10	10	4	5	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	10	9	9	6	6	0
^1J(PF)/Hz	1 162	1 169	1 184	1 181	1 191	1 201	1 199	1 210	1 234	1 231	1 230	1 234	1 236	1 228	1 229	1 147	1 150	1 152	1 176	1 189	1 196
^2J(PH)/Hz							273	273	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.						
δF/p.p.m.	−5.7	−5.2	−5.1	−7.0	−6.9	−6.1	−13.0	−16.0	−11.6	−10.6	−8.8	−15.5	−14.1	−11.9	−10.4	−7.6	−7.8	−7.9	−11.7	−8.4	−13.1
^2J(PtF)/Hz	792	796	772	720	725	699	400	358	240	233	245	210	212	210	187	759	773	780	1 023	640	711
^3J(FH)/Hz							38	34	41	40	40	36	37	36	37						

[a] In CD_2Cl_2 unless stated otherwise. Measurements considered accurate to 1 Hz, 0.1 p.p.m. The label P refers to PEt_3^-, and P′ to PF_2Y^- phosphorus nuclei; n.r. = not resolved. Chemical shifts were measured relative to 70% H_3PO_4 (^{31}P), CCl_3F (^{19}F), or $SeMe_2$ (^{77}Se), taking shifts to high frequency as positive. [b] ^1J(PSe) = 846.4(2) Hz; ^2J(FSe) = 71.3(1) Hz; δ(^{77}Se) = 148.3(1) p.p.m. In the ^{77}Se spectrum the lines were clearly not simple, and it appears that ^2J(SePt) is around 5 Hz. [c] In $CDCl_3$. [d] ^2J($P^{15}N$) = 81 Hz, ^3J($F^{15}N$) = 10 Hz.

doublet of triplets with Pt satellites; each line was further split into a doublet when proton coupling was retained.

The same parameters were obtained no matter which platinum starting material was used, the only difference being observed when Se replaced S in the PF_2 group. We propose that the species are of the form (7) and (8).



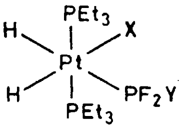
$$\begin{array}{c} PEt_3 \\ | \\ H\text{—}Pt\text{—}PF_2Y \\ | \\ PEt_3 \end{array}$$

(7) Y = S
(8) Y = Se

It appears that ^3J(PF) is too small to be detected at low temperatures.

We suggest that the weak doublet resonances observed at low frequency are due to the PEt_3 resonance of the platinum(IV) six-co-ordinate complexes (9)—(14) formed by oxidative addition of $PF_2H(Y)$ to the platinum starting material. The high-frequency parts of the spectra of these complexes were not observed but in view of the weakness of the PEt_3 resonances this is not surprising.

As the systems were warmed from −50 °C the amount of $[PtH(PEt_3)_2(PF_2Y)]$ present fell and the final products appeared. Loss of HX from complexes (9)—(14) would give the four-co-ordinate platinum(II) complexes (7) and (8) which were observed as the major intermediates. This HX could then add to unreacted starting material to give the other observed intermediates *cis, cis, trans*-$[PtH_2(PEt_3)_2X_2]$. Ultimately loss of H_2 from complexes (9)—(14) would give the final products, complexes (1)—(6). [Further evidence will be mentioned to confirm the existence of complexes (9)—(14).]



(9) X = Cl, Y = S (12) X = Cl, Y = Se
(10) X = Br, Y = S (13) X = Br, Y = Se
(11) X = I, Y = S (14) X = I, Y = Se

Thus the first step involves oxidative addition of $PF_2H(Y)$ to $[PtH(PEt_3)_2X]$ to give the platinum(IV) complexes (9)—(14). These complexes can then undergo reductive elimination in two ways: they can lose HX (step A, which is fast and reversible at low temperature), or they can lose H_2 (step B, which is slower and irreversible and gives the final products).

(*ii*) Pt : $PF_2H(Y)$ = 1 : 4.—The course of reactions with excess of $PF_2H(Y)$ depended on the nature of Y. For reactions with $PF_2H(S)$ the stable intermediates at low temperature were the platinum(IV) complexes $[PtH_2(PEt_3)_2(PF_2S)X]$ with very little else present in solution. However for the PF_2Se systems the stable intermediate at low temperature was observed to be a six-co-ordinate complex of Pt^{IV} whose n.m.r. parameters were the same no matter which platinum starting material was used. The ^{31}P spectrum of this species in the PEt_3 region showed a peak with triplet coupling due to ^2J(PP), which suggests that the intermediate observed here was $[PtH_2(PEt_3)_2(PF_2Se)_2]$: addition of a second $PF_2H(Se)$ molecule must have occurred. No evidence was obtained for the formation of such a species in the PF_2S system. Moreover, the room-temperature spectra of solutions containing $[Pt(PEt_3)_2(PF_2Y)X]$ and excess of $PF_2H(Y)$ did not contain any peaks due to platinum(IV) species, showing that the complexes $[Pt(PEt_3)_2(PF_2Y)X]$ exist in solution in the presence of excess of $PF_2H(Y)$. Therefore further addition does not occur to the halogen-containing species at room temperature.

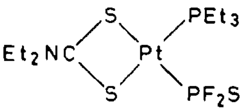
Reactions with $[Pt(PEt_3)_3X][BPh_4]$.—When the reactions of $PF_2H(Y)$ with $[Pt(PEt_3)_3X][BPh_4]$ (X = H, Cl, or I) were studied it was found that the products were again $[Pt(PEt_3)_2(PF_2Y)X]$ with 1 mole of $[PHEt_3][BPh_4]$, identified by ^{31}P n.m.r. parameters and by analysis, as a by-product. Separation of these two compounds proved difficult and analytically pure samples of the PF_2Y complexes were not obtained. However, reaction of $PF_2H(Y)$ with $[PtH(PEt_3)_3][BPh_4]$ gave $[PtH(PEt_3)_2(PF_2Y)]$ as stable complexes at room temperature. The instability of these species in the reactions with $[PtH(PEt_3)_2X]$ must therefore have been due to the presence of some other reagent, which we believe to have been HX.

Some reactions of the complexes (1)—(6) have also been studied. These reactions involved exchange of the halogen for other types of ligands. Two types of ligands were used: the pseudo-halides NCO^-, NCS^-, $NCSe^-$, and CN^-, and some potentially bidentate ligands, $CH_3CO_2^-$, $PhCOS^-$, Et_2NCS^-, and $Me_2PS_2^-$.

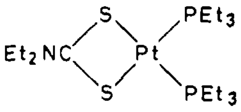
In the reactions with alkali-metal salts of the pseudo-halides MZ, the products obtained showed the expected pattern in the PEt_3 region of the ^{31}P spectrum for $[Pt(PEt_3)_2(PF_2Y)Z]$, but there were no peaks in the PF_2 region. If the ligands NCO^-, NCS^-, $NCSe^-$, and CN^- were bonding to the Pt through N [complexes (16)—(19)], quadrupolar relaxation of ^{14}N might cause the PF_2 signal to be lost. The reaction was carried out with $Ag[^{15}NCO]$ and the spectra all showed sharp PF_2 signals with the additional doublet splitting expected when ^{15}N is *trans* to the PF_2Y group.

For the reactions with bidentate ligands, no reaction took place with sodium acetate. For sodium monothiobenzoate the spectra showed that the halogen had been replaced by PhCOS and that this group was bound through sulphur [complex (20)]. In the reaction with $Et_2NCS_2^-$ two products were obtained. In one, the dithio-ligand had replaced Cl and one PEt_3 group (21), and in the other the PF_2S had been replaced (22). Complex (21) was the major product. For the reactions with

$Me_2PS_2^-$ the products depended on the amount of the ligand added. The results were not clear, but it appeared that with a large excess of $Me_2PS_2^-$ the product obtained contained one PF_2S group, one PEt_3 group, and one $Me_2PS_2^-$ group.



(21)



(22)

Crystal Data and Structure Determination of (1).—$C_{12}H_{30}ClF_2P_3PtS$, $M = 568$, Orthorhombic, $a = 1.1597(2)$, $b = 1.3355(2)$, $c = 1.3632(3)$ nm, $U = 2.111$ nm^3, $D_m = 1.75$, $Z = 4$, $D_c = 1.786$ Mg m^{-3}, Mo-K_α radiation, $\lambda = 71.069$ pm, $\mu(\text{Mo-}K_\alpha) = 7.44$ mm^{-1}, space group *Pbcn* (no. 60) (conditions for reflection: $0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h + k = 2n$).

Cell dimensions and X-ray intensity data were obtained with a Nonius CAD4 diffractomer, using graphite-monochromatised Mo-K_α radiation. The cell dimensions are based on 20 reflections with $\theta = 20°$. Intensity data were collected for one asymmetric unit, 1 300 reflections with $\theta \leqslant 22°$. The structure was solved and refined using the 876 reflections with $I \geqslant 3\sigma(I)$. The data were corrected for absorption. The platinum atoms were shown by the Patterson function to occupy a set of special positions $4c$: $0,y,\frac{1}{4}$, with y *ca.* 0.15. A difference-Fourier synthesis gave the positions of the other non-hydrogen atoms except for the PF_2S group, which is disordered about the two-fold axis. The disorder does appear to be strictly two-fold, and it was possible to refine the structure with these atoms given a site occupancy of $\frac{1}{2}$ on a set of general positions. The structure was refined with hydrogen atoms in fixed, idealised positions (C–H = 110 pm). All atoms were constrained to be isotropic except the platinum and chlorine atoms and the phosphorus atoms of the phosphines. In the last few cycles of full-matrix least-squares refinement, a weighting scheme of the form $w = 120/|F_o|$ for $|F_o| > 120$ and $w = 1.0$ otherwise was used. At convergence, $R = 0.034$ and $R' = 0.043$. Positional parameters for the refined atoms are given in Table 2. The structure factor table, thermal parameters, and the positional parameters for the hydrogen atoms are deposited as Supplementary Publication No. SUP 22998 (9 pp.).* The 'X-Ray '76' computer program system † was used for all crystallographic calculations.

TABLE 2

Fractional co-ordinates ($\times 10^4$) with standard deviations in parentheses for (1)

Atom	x	y	z
Pt	0	1 541(1)	2 500
Cl	0	−232(3)	2 500
S *	−52(10)	3 931(7)	1 435(7)
P(1)	1 904(3)	1 392(2)	1 954(3)
P(2) *	151(7)	3 185(4)	2 652(5)
F(1) *	1 292(15)	3 501(12)	3 167(13)
F(2) *	−641(18)	3 680(15)	3 460(14)
C(1)	1 961(13)	594(11)	867(10)
C(2)	1 275(16)	1 046(14)	26(13)
C(3)	2 746(12)	741(10)	2 869(10)
C(4)	2 860(16)	1 264(14)	3 825(14)
C(5)	2 747(12)	2 490(10)	1 648(10)
C(6)	3 956(16)	2 314(14)	1 211(14)

* These atoms have a site occupancy of 0.5.

The molecular structure is shown in Figure 1, along with the numbering scheme used for the atoms. Only one of the alternative sites for the PF_2S group is shown. Bond lengths, bond angles, and torsion angles are given in Table 3. There was no difficulty in identifying the atoms making up one PF_2S group on the basis of interatomic distances: the bond lengths for P(2) to the symmetry-related sulphur and fluorine atoms are: P(2)–S′, 160; P(2)–F(1)′, 206; and P(2)–F(2)′, 175 pm. The main limitations to the refinement were two close approaches of atoms in the different possible sites: P(2)–P(2)′, 55; S–F(2)′, 88 pm. There does not appear to be any further significant departure from an ordered structure, although the relatively high temperature factors for the carbon atoms ($U = 900$ pm^2 for the methyl carbons and 600 pm^2 for the methylene) suggest a slight further disorder. The co-ordination of the platinum is almost planar, the platinum atom being 7.2 pm out of the plane defined by the ligand atoms. Deviations of *cis* bond angles at platinum from 90° are substantial, as might be

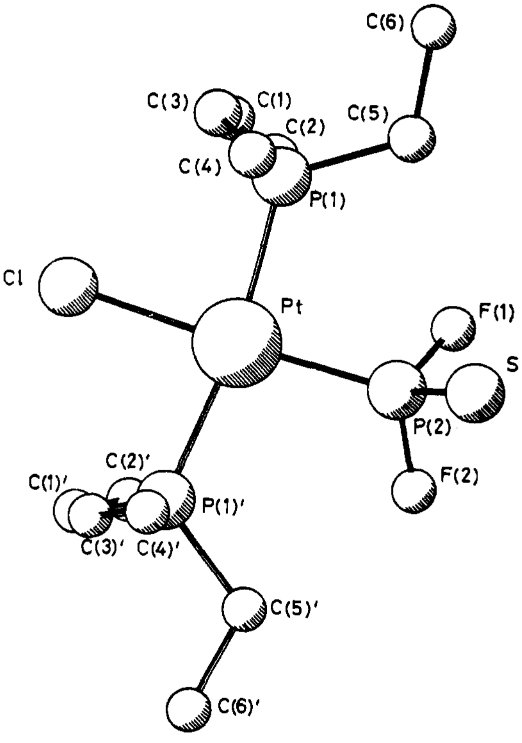


FIGURE 1 View of (1) projected into the co-ordination plane

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

† 'The X-Ray System—Version of March, 1976,' Technical Report TR446, Computer Science Center, University of Maryland, U.S.A.

TABLE 3

Bond lengths (pm), bond angles and torsion angles (°) for (1). Primed atoms are related to unprimed ones by the operation $(-x, y, \frac{1}{2} - z)$

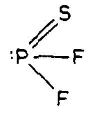
Pt–P(1)	233.8(3)	P(1)–C(1)	182.6(15)
Pt–P(2)	221.3(5)	P(1)–C(3)	180.7(14)
Pt–Cl	236.8(4)	P(1)–C(5)	181.1(14)
P(2)–S	195.0(11)	C(1)–C(2)	152(2)
P(2)–F(1)	155.5(12)	C(3)–C(4)	148(2)
P(2)–F(2)	157.9(18)	C(5)–C(6)	154(2)
Cl–Pt–P(1)	85.1(1)	F(1)–P(2)–F(2)	93.8(10)
Cl–Pt–P(2)	172.9(2)	Pt–P(1)–C(1)	110.0(5)
P(1)–Pt–P(2)	92.3(2)	Pt–P(1)–C(3)	109.3(5)
P(1)–Pt–P(1)′	170.3(1)	Pt–P(1)–C(5)	120.9(5)
P(2)–Pt–P(1)′	97.4(2)	P(1)–C(1)–C(2)	111.2(11)
Pt–P(2)–S	114.7(4)	P(1)–C(3)–C(4)	115.3(11)
Pt–P(2)–F(1)	112.3(7)	P(1)–C(5)–C(6)	117.2(11)
Pt–P(2)–F(2)	115.8(8)	C(1)–P(1)–C(3)	105.0(7)
S–P(2)–F(1)	110.4(8)	C(1)–P(1)–C(5)	105.4(7)
S–P(2)–F(2)	108.0(8)	C(3)–P(1)–C(5)	104.9(7)
Cl–Pt–P(1)–C(1)	53.7(5)		
Cl–Pt–P(1)–C(3)	−61.2(5)		
Cl–Pt–P(1)–C(5)	176.9(5)		
P(2)–Pt–P(1)–C(1)	−132.9(5)		
P(2)–Pt–P(1)–C(3)	112.3(5)		
P(2)–Pt–P(1)–C(5)	−9.6(6)		
P(2)–Pt–P(1)′–C(1)′	−119.7(5)		
P(2)–Pt–P(1)′–C(3)′	125.4(5)		
P(2)–Pt–P(1)′–C(5)′	3.5(6)		
P(1)′–Pt–P(1)–C(1)	52.2(9)		
P(1)′–Pt–P(1)–C(3)	−62.6(9)		
P(1)′–Pt–P(1)–C(5)	175.5(8)		
Cl–Pt–P(2)–S	149.8(13)		
Cl–Pt–P(2)–F(1)	22.8(20)		
Cl–Pt–P(2)–F(2)	−83.4(19)		
P(1)–Pt–P(2)–S	81.8(5)		
P(1)–Pt–P(2)–F(1)	−45.3(8)		
P(1)–Pt–P(2)–F(2)	−151.4(9)		
P(1)′–Pt–P(2)–S	−99.1(5)		
P(1)′–Pt–P(2)–F(1)	133.9(8)		
P(1)′–Pt–P(2)–F(2)	27.7(9)		
Pt–P(1)–C(1)–C(2)	62.0(12)		
Pt–P(1)–C(3)–C(4)	−63.7(12)		
Pt–P(1)–C(5)–C(6)	−175.0(10)		
C(1)–P(1)–C(3)–C(4)	178.3(12)		
C(1)–P(1)–C(5)–C(6)	−49.5(13)		
C(3)–P(1)–C(1)–C(2)	179.6(9)		
C(3)–P(1)–C(5)–C(6)	61.1(13)		
C(5)–P(1)–C(1)–C(2)	−69.9(12)		
C(5)–P(1)–C(3)–C(4)	67.4(13)		

expected from the difference in size of the PF_2S and Cl ligands. The much greater size of P(2)–Pt–P(1)′ than P(2)–Pt–P(1) (5.2°) is related to the fact that at least one of the fluorine atoms must make a close contact with one of the substituents of the phosphines. Even with the obvious distortions of bond angles and torsion angles, especially the very large Pt–P(1)–C(5) and the very small F(1)–P(2)–F(2), there are two very short intramolecular contacts: F(1) $\cdots$ C(5), 299 pm, and F(2) $\cdots$ C(5)′, 292 pm. The estimated F $\cdots$ H contacts are 225 and 221 pm respectively.

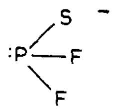
The packing of the molecules is shown in Figure 2, where an arbitrary choice has been made for the orientation of the PF_2S groups. As may be seen, rotating these through 180° about the pseudo-two-fold axis will not alter the contact pattern. There are no intermolecular contacts between non-hydrogen atoms less than 320 pm. It is unlikely that packing considerations will significantly affect the molecular geometry.

Hitchcock *et al.*,[4] in reporting the structure of *cis*-$[PtCl_2(PF_3)(PEt_3)]$ (23), discuss the correlation of Pt–Cl bond lengths with those for Pt–P for various phosphine ligands in the *trans* position. Their predicted value of 234 pm for a Pt–Cl bond *trans* to a Pt–P bond of 221 pm is approximately equal to that found here. The Pt–P bond for the PF_2S group is roughly the mean of the values for Pt–PF_3 (214 pm) and Pt–PEt_3 (227 pm) found in (23),[4] indicating an intermediate π-acceptor ability for the PF_2S group.

Two possible formulations of the PF_2S ligand are I and II (shown below). A distinction between these two



I



II

formulations might be made in terms of the length of the P–S bond. Extreme examples are S=PF_2Br, S=P, 188.1 pm[5] and $GeH_3(SPF_2)$, S–P, 211.5 pm.[6] The value obtained here suggests that there is substantial double-bond character in the P–S bond, which is in the range common for dithiophosphinate complexes. Similar arguments could be applied to the PF_2O ligand in $[PtCl(PF_2O)(PEt_2Ph)_2]$.[7] In this structure, Grosse *et al.* assume a P–O single bond, although its length, 147 pm, is much closer to that found in O=PF_3[5] (144 pm) than to the normal P–O single-bond length of *ca.* 160 pm.[8] Similarly, ^1J(PSe) in (4) is at the low end of the range associated with P=Se and is a good deal larger than in P–Se systems.[9]

EXPERIMENTAL

Nuclear magnetic resonance measurements were made on JEOL FX-60Q (^{31}P) and Varian Associates XL-100 spectrometers, or [for compound (4) in the ^{77}Se region and the high-frequency part of the ^{31}P spectra] a Bruker WH-360 instrument. All manipulations were carried out under vacuum or in a dry nitrogen atmosphere. Platinum-containing starting materials were prepared by standard methods. Solvents were dried and freshly distilled before use.

PF_2HS.—This was prepared by treating $S(PF_2)_2$ with H_2S. The $S(PF_2)_2$ was prepared by treating PF_2Br with $S(SnBu_3)_2$. The $S(SnBu_3)_2$ (10 mmol) was weighed out in a 500-cm^3 flask fitted with a cold finger. This was then attached to the vacuum line and pumped out in order to de-gas the tin compound. The PF_2Br (20 mmol) was then condensed into the flask and the system allowed to warm to room temperature. The best yields were obtained if the two reactants were mixed in the liquid phase. The product was collected by pumping off all the volatile species left in the flask and collecting them at −196 °C. The pure product was collected at −96 °C and any PF_2Br passed into the −196 °C bath.

The $S(PF_2)_2$ (8 mmol) was then measured into a 500-cm^3 flask and the H_2S (16 mmol) condensed in. Allowing the mixture to warm to room temperature yielded PF_2HS. The pure product was collected at −120 °C the mixture having passed through the −96 °C bath to remove any $S(PF_2)_2$ remaining. Any H_2S would carry on into the −196 °C bath.

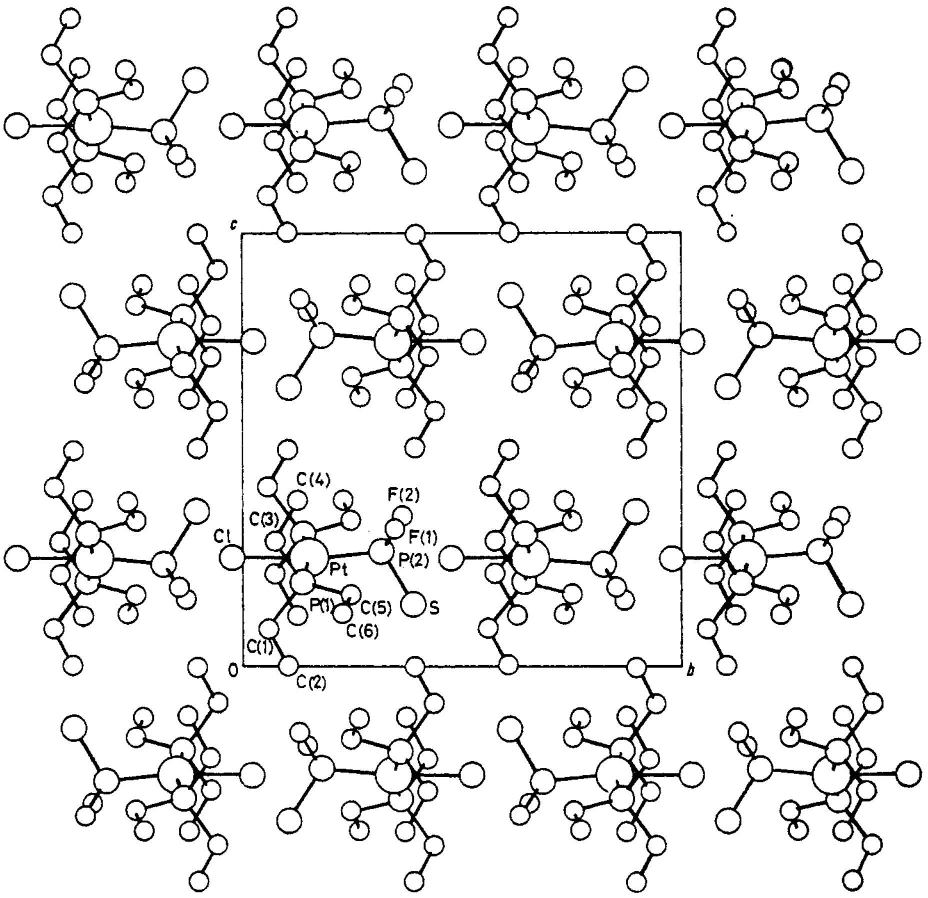


FIGURE 2 Packing diagram for (1) viewed along the *a* axis. Only one of the possible molecular orientations is shown

PF_2HSe.—The PF_2HSe was prepared by treating PF_2Br with H_2Se in the presence of Hg. Mercury (0.6 cm^3) was placed in a 250-cm^3 flask and PF_2Br (3.6 mmol) and H_2Se (3.75 mmol) were added. The system was allowed to warm to room temperature and shaken for 2 h and then left for 24 h The product was collected and purified by passing it through −78 °C and −120 °C baths. The PF_2HSe stopped in the −120 °C bath.

TABLE 4

Analytical and melting point data

	Analysis (%) *		
Complex	C	H	M.p. (θ_c/°C)
(1)	23.3	5.3	122—124
	(25.5)	(5.4)	
(2)	23.4	4.9	122—124
	(23.3)	(4.8)	
(3)	22.0	4.6	128—130
	(21.8)	(4.5)	
(4)	23.2	4.8	140—141
	(23.4)	(4.9)	
(5)	22.1	4.6	135—136
	(21.9)	(4.5)	
(6)	20.6	4.4	128—130
	(20.6)	(4.2)	

* Calculated values are given in parentheses.

Complexes (1)—(6).—These complexes were prepared by treating *trans*-[PtH(PEt$_3$)$_2$X] (X = Cl, Br, or I) with $PF_2H(Y)$ (Y = S or Se). The platinum complex was weighed into a Schlenk tube and the vessel pumped out. The complex was dissolved in CH_2Cl_2 then kept at −196 °C when an equimolar amount of $PF_2H(Y)$ was condensed in. The system was allowed to warm up and H_2 gas was evolved. Removing the solvent gave the product as a white powder. The recrystallisation was carried out from benzene. The C and H analysis figures, melting points, and i.r. spectra were obtained (Table 4).

We thank the S.R.C. for a studentship (to J. D. W.).

[0/1199 *Received*, 29th *July*, 1980]

REFERENCES

[1] J. Grosse and R. Schmutzler, *J. Chem. Soc., Dalton Trans.*, 1976, 405, 412.

[2] C. B. Cockburn, W. E. Hill, and D. W. A. Sharp, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 625.

[3] D. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1973, 854.

[4] P. B. Hitchcock, B. Jacobson, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2043.

[5] D. W. H. Rankin, unpublished work.

[6] E. A. V. Ebsworth, E. K. Macdonald, and D. W. H. Rankin, *Monatsh. Chem.*, 1980, **111**, 221.

[7] J. Grosse, R. Schmutzler, and W. S. Sheldrick, *Acta Crystallogr., Sect. B*, 1974, **30**, 1623.

[8] D. E. J. Arnold and D. W. H. Rankin, *J. Fluorine Chem.*, 1972, **73**, 405.

[9] W. MacFarlane and D. S. Rycroft, *J. Chem. Soc., Chem. Commun.*, 1972, 902; W. MacFarlane and J. A. Nash, *ibid.*, 1969, 913.