Fluorophosphonate and Alkoxy- and Aroxy-fluorophosphine Complexes of Platinum(II) and Palladium(II). Part I. Reactions of Complexes of Tertiary Phosphines with Alkoxy- and Aroxy-difluorophosphines

By **Jürgen Grosse** and **Reinhard Schmutzler,*** Lehrstuhl B für Anorganische Chemie der Technischen Universität, D-3300 Braunschweig, Pockelsstrasse 4, Germany

A series of difluorophosphonato-complexes *trans*-[$MClL_2(PF_2O)$] (M = Pt or Pd; L = $PEt_{3-n}Ph_n$; *n* = 0—3) have been prepared *via* a Michaelis–Arbuzov type reaction from [MCl_2L_2] and $PF_2(OR)$ (R = allyl, Pr^n, or Bu^n). Preparation of complexes *cis*-[$MCl_2(PEt_3)\{PF_2(OR)\}$] (M = Pt or Pd; R = Bu^n or Ph) and chloro-bridged binuclear complexes [$\{MCl(PEt_3)(PF_2O)\}_2$] is also reported. Substituent redistribution reactions of $PF_2(OR)$ have been observed under the influence of the transition metal, M. Fluorine-19 and ^{31}P n.m.r., i.r., and, in part, mass-spectroscopic data for the new complexes are reported and discussed in terms of the structures of the products obtained.

ALTHOUGH numerous transition-metal complexes of trifluorophosphine, PF_3, are known,[1] there are only a few examples of those containing the difluorophosphonato-group, $[PF_2O]^-$, which is isoelectronic with PF_3.

Kruck and his co-workers [2-5] obtained a number of $[PF_2O]^-$ derivatives by hydrolysis of the corresponding PF_3 complexes under certain conditions, *e.g.* equation (1). A series of derivatives of PF_2E appear to be

$$2\,[Ni(PF_3)_4] \xrightarrow{Ba[OH]_2} Ba[Ni(PF_3)_3(PF_2O)]_2 \quad (1)$$

formed in oxidative-addition reactions of $P(E)F_2X$ to iridium(I) complexes [equation (2) (L = PPh_3 or

$$[Ir(CO)ClL_2] + P(E)F_2X \longrightarrow [IrCl(CO)(PEF_2)L_2X] \quad (2)$$

$PMePh_2$; E = O or S; X = Cl or Br)].[6] Also, some complexes of type [$Fe(CO)_2(\eta\text{-}C_5H_5)(PEX_2)$] (E = S, X = F; [6] E = O or S, X = CF_3 [7]) are known [equations (3) [6] and (4) [7]].

$$Na[Fe(CO)_2(\eta\text{-}C_5H_5)] + PBrF_2(S) \longrightarrow [Fe(CO)_2(\eta\text{-}C_5H_5)(PF_2S)] + NaBr \quad (3)$$

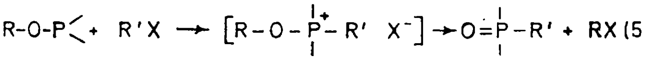
$$[Fe(CO)_2(\eta\text{-}C_5H_5)\{P(CF_3)_2\}] \xrightarrow[S_8(E\,=\,S)]{NO\,(E=O)} [Fe(CO)_2(\eta\text{-}C_5H_5)\{P(CF_3)_2E\}] \quad (4)$$

Recently, we have observed the formation of difluorophosphonato-platinate(II) and -palladate(II) complexes,[8] $[RL]_2[M(PF_2O)_4]$ [R = $CH_2{:}CH{\cdot}CH_2(C_3H_5)$; L = pyridine (py) or PPh_3; M = Pt or Pd] from the reaction of [MCl_2L_2] with allyloxydifluorophosphine, $PF_2(OC_3H_5)$ (see also the following paper). This prompted us to study the reactions of a number of Pt^{II} and Pd^{II} derivatives [MCl_2L_2, MCl_2, and [$\{MCl_2(PEt_3)\}_2$] (M = Pt or Pd; L = tertiary phosphine or amine) with $PF_2(OR)$ (R = C_3H_5, Pr^n, Bu^n, or Ph). This paper describes the reactions of the tertiary phosphine complexes with $PF_2(OR)$ and the following paper is concerned mainly with amine complexes of the two platinum metals.

RESULTS AND DISCUSSION

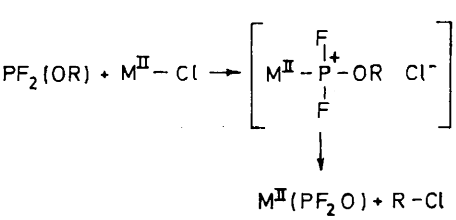
In the reaction of tertiary phosphine complexes of Pt^{II} and Pd^{II} with $PF_2(OR)$ a number of general types of reaction were observed.

Type (*a*): *Michaelis–Arbuzov Reaction*.—The Michaelis–Arbuzov reaction, (5), is common in the chemistry of phosphite esters,[9] where R, R′ = alkyl or alkenyl and X = halogen. In complete analogy with



$$R\text{-}O\text{-}P\langle + R'X \longrightarrow [R-O-\overset{|+}{\underset{|}{P}}-R' \;\; X^-] \longrightarrow O{=}\overset{|}{\underset{|}{P}}-R' + RX \quad (5)$$

this reaction, transition-metal difluorophosphonato-complexes were obtained on treating the appropriate chloride with alkoxydifluorophosphines [equation (6) (M = Pt or Pd; R = C_3H_5, Pr^n, or Bu^n)]. The ionic intermediate in equation (6) is not known, but analogous



$$PF_2(OR) + M^{II}-Cl \longrightarrow \left[M^{II}-\overset{F}{\underset{F}{\overset{|+}{\underset{|}{P}}}}-OR \;\; Cl^- \right] \longrightarrow M^{II}(PF_2O) + R-Cl \quad (6)$$

ionic complexes $[ML_2L'X]Y$ (L = tertiary phosphine or arsine; L′ = tertiary amine, phosphine, or phosphite; X = halogen or H; Y = ClO_4^- or NO_3^-; M = Pt or Pd) have been described in the literature.[10-13] Haines and his co-workers [14-16] have proposed a Michaelis–Arbuzov type mechanism for the formation of POY_2 complexes

[1] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.

[2] Th. Kruck, M. Höfler, K. Bauer, P. Junkes, and K. Glinka, *Chem. Ber.*, 1968, **101**, 3827.

[3] Th. Kruck, *Chimia* (*Switz.*), 1970, **24**, 375.

[4] Th. Kruck, J. Waldmann, M. Höfler, G. Birkenhäger, and Ch. Odenbrett, *Z. anorg. Chem.*, 1973, **402**, 16.

[5] Th. Kruck, H. Jung, M. Höfler, and H. Blume, *Chem. Ber.*, 1974, **107**, 2145.

[6] C. B. Colburn, W. E. Hill, and D. W. A. Sharp, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 625.

[7] (*a*) R. C. Dobbie, P. R. Mason, and R. J. Porter, *J.C.S. Chem. Comm.*, 1972, 612; (*b*) R. C. Dobbie and P. R. Mason, *J.C.S. Dalton*, 1973, 1124; (*c*) M. J. Barrow, G. A. Sim, R. C. Dobbie, and P. R. Mason, *J. Organometallic Chem.*, 1974, **69**, C4.

[8] J. Grosse and R. Schmutzler, *Z. Naturforsch.*, 1973, **B28**, 515.

[9] R. G. Harvey and E. R. De Sombre, in *Topics Phosphorus Chem.*, 1964, **1**, 57.

[10] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3074.

[11] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Canad. J. Chem.*, 1974, **52**, 692.

[12] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, W. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

[13] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1970, 1938.

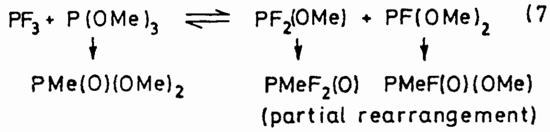
[14] R. J. Haines, I. L. Marais, and C. R. Nolte, *Chem. Comm.*, 1970, 547.

[15] R. J. Haines and C. R. Nolte, *J. Organometallic Chem.*, 1970, **24**, 725.

[16] R. J. Haines, A. L. Du Preez, and I. L. Marais, *J. Organometallic Chem.*, 1971, **28**, 97.

such as $[Mo(CO)_2(\eta\text{-}C_5H_5)(POY_2)\{P(OR)Y_2\}]$ in the reaction of $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ with $P(OR)Y_2$ (Y = Ph or OR; R = alkyl or C_3H_5).

Type (*b*): *Substituent Redistribution at the Phosphorus Atom*.—On interaction of PF_3 with $P(OMe)_3$, redistribution of substituents at phosphorus was observed, followed, to some extent, by a Michaelis–Arbuzov rearrangement, according to equation (7).[17] At room temperature alkoxydifluorophosphines are stable with respect to


(7)

$$\begin{array}{ccc} PF_3 + P(OMe)_3 & \rightleftharpoons & PF_2(OMe) + PF(OMe)_2 \\ \downarrow & & \downarrow \qquad\qquad \downarrow \\ PMe(O)(OMe)_2 & & PMeF_2(O) \quad PMeF(O)(OMe) \\ & & \text{(partial rearrangement)} \end{array} \quad (7)$$

substituent redistribution reactions; during the course of our study, samples were stored unchanged for several months. When such phosphines were allowed to react with Pt^{II} and Pd^{II} derivatives, redistribution reactions resulted in some cases [equation (8) (M = Pt or Pd; R = C_3H_5, Bu^n, or Ph)]. There distribution products were

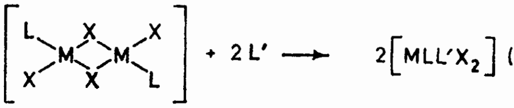
$$PF_2(OR) \xrightarrow{M^{II}} PF(OR)_2,\ P(OR)_3,\ PF_3 \qquad (8)$$

obtained either as free ligands or bonded to the transition metal. Dialkylaminodifluorophosphines have been reported to undergo a similar redistribution reaction, preferably in the presence of $PtCl_2$ and other transition-metal chlorides,[1,18] *e.g.* equation (9). As a consequence

$$2\,PF_2(NR_2) + PtCl_2 \longrightarrow [PtCl_2\{PF_2(NR_2)\}_2] \xrightarrow[-\,2\,PF_3]{2\,PF_2(NR_2)} [PtCl_2\{PF(NR_2)_2\}_2] \qquad (9)$$

of the possible occurrence of reactions of type (b), a number of reactions were carried out employing reactants in a precise molar ratio in order to obtain defined products rather than mixtures.

Type (*c*): *Cleavage of Chloro-bridged Binuclear Complexes*.—Halogen-bridged binuclear complexes $[\{MLX_2\}_2]$ are known to react with a number of ligands L' with cleavage of the halogen bridge to give mononuclear complexes $[MLL'X_2]$, *e.g.* equation (10) (M = Pt or Pd;


(10)

L = tertiary phosphine or phosphite; L' = tertiary phosphite; X = halogen).[19-21] Alkoxyfluorophosphine complexes of platinum and palladium have not previously been described in the literature. We have been able to synthesize a number of alkoxydifluorophosphine complexes of Pt^{II} and Pd^{II} making use of reaction type (c) (reaction of $PF_2(OR)$ with $[\{MCl_2(PEt_3)\}_2]$). In some cases, combinations of reaction types (a)—(c) have been observed.

Difluoro- and Fluoro-phosphonato-complexes, trans-$[MClL_2(PF_2O)]$ *and* trans-$[PdClL_2\{PFO(OR)\}]$.—Difluorophosphonato-complexes, *trans*-$[MClL_2(PF_2O)]$,

$$[MCl_2L_2] + PF_2(OR) \longrightarrow trans\text{-}[MClL_2(PF_2O)] + RCl \qquad (11)$$

	M	L	R
(I)	Pt	PEt_3	C_3H_5 or Bu^n
		PEt_2Ph	C_3H_5 or Bu^n
		$PEtPh_2$	C_3H_5
		PPh_3	Pr^n or Bu^n
	Pd	PEt_3	C_3H_5 or Bu^n
		PEt_2Ph	C_3H_5, Pr^n, or Bu^n
		$PEtPh_2$	C_3H_5 Pr^n, or Bu^n
		PPh_3	Bu^n

were obtained from $[MCl_2L_2]$ and $PF_2(OR)$, according to reaction type (a); most of these reactions proceeded readily and were complete within a few minutes at room temperature, using benzene as solvent. Complex (II; L = PPh_3) crystallized with dichloromethane (1.5 mol CH_2Cl_2 per mol of complex) on recrystallization from that solvent. The complex is isoelectronic with *trans*-$[RhCl(PPh_3)_2(PF_3)]$.[22] Analogous complexes *trans*-$[PtL_2\{PO(OR)_2\}X]$ have been described in the literature [21,23] (L = PEt_3, PBu^n_3, or $AsEt_3$; X = halogen or pseudohalogen; R = Me or Ph).

For M = Pt, complexes (I) were the only products observed, while, for M = Pd, monofluorophosphonato-complexes *trans*-$[PdClL_2\{PFO(OR)\}]$ were formed as by-products according to a combination of reaction types (a) and (b). In contrast to the corresponding difluorophosphonato-complexes, complexes (III) could not be isolated in a pure state from the reaction mixtures. They were not formed in the absence of a large excess of $PF_2(OR)$.

$$[PdCl_2L_2] + 2PF_2(OR) \longrightarrow trans\text{-}[PdClL_2\{PFO(OR)\}] + RCl + PF_3 \qquad (12)$$

Difluorophenoxyphosphine, $PF_2(OPh)$, was unreactive towards $[PtCl_2(PEt_2Ph)_2]$ under the reaction conditions employed (see Experimental section); only at elevated temperature (10 d at 70 °C) and in a polar solvent, were trace amounts of (I; L = PEt_2Ph), together with an unidentified PF-containing product (from the ^{19}F n.m.r. spectrum), formed, with some triphenyl phosphite (from the ^{31}P n.m.r. spectrum). Again the reaction proceeded in accord with type (b). In complete agreement with the classical Michaelis–Arbuzov reaction,[9] the

---

[17] D. H. Brown, K. D. Crosbie, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1969, 872.

[18] J. F. Nixon and M. D. Sexton, *Chem. Comm.*, 1969, 827.

[19] P. Schützenberger and M. Fontaine, *Bull. Soc. chim. France*, 1872, **17**, 482.

[20] M. J. Church and M. J. Mays, *J. Inorg. Nuclear Chem.*, 1971, **33**, 253.

[21] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

[22] D. A. Clement, J. F. Nixon, and M. D. Sexton, *Chem. Comm.*, 1969, 1509.

[23] A. Pidcock and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2080.

reactivity of $PF_2(OR)$ towards $[MCl_2L_2]$ decreases in the order $R = C_3H_5 > \text{alkyl} \gg Ph$. Also, reactions of type (a) proceeded faster in polar than in non-polar solvents as expected because an ionic reaction intermediate is involved.

TABLE 1

Fluorine-19 and ^{31}P n.m.r. data for *trans* complexes $[PtCl(P'Et_{3-n}Ph_n)_2(PF_2O)]$ (I), $[PdCl(P'Et_{3-n}Ph_n)_2(PF_2O)]$ (II), and $[PdCl(P'Et_{3-n}Ph_n)_2\{PFO(OR)\}]$ (III) (n = 0—3; R = C_3H_5 or Bu^n)

	n	R	δ_F	$^1J_{P-F}$	$^2J_{Pt-F}$	$^3J_{P'-F}$	$\delta_{P'}$	$^1J_{Pt-P'}$	δ_P	$^1J_{Pt-P}$	$^2J_{P'-P}$
			p.p.m.		Hz		p.p.m.	Hz	p.p.m.	Hz	
(I) [a]	0		12.4	1 162	1 026	6	−21.4	2 245	−34.4	5 846	28
(I) [a]	1		13.3	1 169	987	8	−18.0	2 500	−34.1	*b*	30
(I) [c,d]	2		11.96	1 175	952	9.8	−20.5	2 449	−34.5	5 821	29.3
(I) [c]	3		15.8	1 179	896	*b*	−23.8	*b*	*b*	*b*	*b*
(II) [a]	0		6.1	1 255		18	−25.3		−63.4		12
(III) [a]	0	Bu^n	9.9	1 170		20	−24.9		−62.7		*e*
(II) [a]	1		6.9	1 250		20	−21.6		−61.8		12
(III) [a,f]	1	C_3H_5	9.8	1 191		23	−21.6		−63.6		*e*
(III) [a,f]	1	Bu^n	10.9	1 187		23	−21.5		−62.5		*e*
(II) [a]	2		6.5	1 266		22	−24.5		−61.2		*b*
(III) [a,f]	2	C_3H_5	9.8	1 193		25	*g*		*g*		*g*
(III) [a,f]	2	Bu^n	13.0	1 183		26	−24.3		−63.2		*e*
(II) [c]	3		9.8	1 262		22	−27.9		−60.6		*b*
(III) [c,f]	3	Bu^n	12.7	1 180		28	*g*		*g*		*g*

[a] In C_6H_6. [b] Not obtained due to limited solubility of sample. [c] In CH_2Cl_2. [d] Spectra measured by Dr. M. Murray, University of Bristol; from $^{31}P\{^1H\}$, $^2J_{P'-P'}$ 391 Hz. [e] $^2J_{P'-P}$ not observed due to broadening of signal because of P–H coupling. [f] Non-isolated by-product. [g] Not obtained due to insufficient concentration of by-product in the mixture.

TABLE 2

Characteristic i.r. bands (cm^{-1})[a] for complexes (I)—(III)

	L	ν(P=O)	ν(P–F) [b]	ν(M–P)	ν(M–Cl)
(I)	PEt_3	1 235vs	803vs, 769vs	421m, 401 (sh)	300m
(I)	PEt_2Ph	1 250s, 1 243vs	800vs, 790vs, 770s	411m, 399 (sh)	305m
(I)	$PEtPh_2$	1 245vs	803vs, 785 (sh)	437 (sh), 417m	309m, 306 (sh)
(I)	PPh_3	1 252vs, 1 221w	820vs, 770 (sh)	440w, 421w	310w, 306 (sh)
(II)	PEt_3	1 245 (sh), 1 233s	790vs, 760vs	410m, 388 (sh)	316m
(III; R = Bu^n) [c]	PEt_3	1 240m, 1 202s	765vs	432m, 416 (sh)	304m
(II)	PEt_2Ph	1 238s	799vs, 788 (sh)	408m, 400 (sh)	309m
(III; R = C_3H_5) [d]	PEt_2Ph	1 206s			
(II)	$PEtPh_2$	1 240s	792s, 765s	424w, 402m	311m
(II)	PPh_3	1 249s	805vs, 750 (sh)	428w, 402m	314m

[a] vs = Very strong, s = strong, m = medium, w = weak, and sh = shoulder. [b] There was no distinction between ν(P–F) and overlapping phosphine bands in some cases. [c] ν(P–O) or ν(C–O) at 1 035s, and 990—965vs cm^{-1}. [d] Mixture with (II; L = PEt_2Ph), all other bands overlapped.

The products were characterized by ^1H, ^{19}F, and ^{31}P n.m.r., and i.r. and mass spectroscopy and elemental analysis. The magnitudes of the chemical shifts, δ_F [2,6,8] and δ_P,[8,21] the platinum–phosphorus coupling constants, $^1J_{Pt-P}$,[21,24] the platinum–fluorine coupling constants, $^2J_{Pt-F}$ (Table 1),[8,25,26] and the P=O stretching frequencies, ν(P=O) (Table 2) [3,4,7,8,23,27] of the difluorophosphonate group, and the comparison of these data with literature values for similar complexes, suggest that the PF_2O ligand is bonded to the metal through phosphorus rather than oxygen. The same is true for the monofluorophosphonato-complexes. The methyl signals in the ^1H n.m.r. spectra of the co-ordinated ethylphosphines, $PEt_{3-n}Ph_n$ (n = 0—2), exhibited a 1 : 4 : 6 : 4 : 1 multiplet structure, characteristic of *trans*-Et–P–M–P–Et systems and arising from 'virtual coupling' of the methyl protons with the *trans*-phosphorus atoms.[10,11,28] The ^{19}F and ^{31}P n.m.r. spectra (Table 1) also clearly indicate the *trans* configuration of the complexes. There is only a single ^{31}P n.m.r. signal assigned to the co-ordinated phosphine ($\delta_{P'}$); the PF_2O phosphorus and fluorine nuclei couple with two equivalent phosphorus nuclei of the phosphine ($^3J_{P'-F}$ and $^2J_{P'-P}$), the magnitude of $^2J_{P'-P}$ also being characteristic of *cis* coupling.[21,24,29-31] On addition of phosphine L to *trans*-$[PdClL_2(PF_2O)]$ (II; L = PEt_2Ph or $PEtPh_2$) in benzene solution, the P′–F coupling collapsed due apparently to rapid exchange between co-ordinated and unco-ordinated phosphine.[32]

$$M{-}L + L' \rightleftharpoons M{-}L' + L \qquad (13)$$

I.r. bands assigned included ν(P=O), ν(P–F), ν(M–P), and ν(M–Cl) (Table 2).

The proposed structure of the complexes, especially in the presence of a metal–phosphorus bond, was fully confirmed by an *X*-ray crystal-structure analysis of

---

[24] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 380.

[25] J. F. Nixon, personal communication to J. G., 1972.

[26] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

[27] J. Chatt and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 2745.

[28] H. C. Clark, K. R. Dixon, and W. J. Jakobs, *J. Amer. Chem. Soc.*, 1968, **90**, 2259.

[29] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1183.

[30] F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1916.

[31] R. J. Goodfellow and B. F. Taylor, *J.C.S. Dalton*, 1974, 1676.

[32] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 4996.

TABLE 3

Mass-spectral data for complexes (I)

	L = PEt_3 at 115 °C		L = PEt_2Ph at 215 °C		L = $PEtPh_2$ at 230 °C		L = PPh_3 at 270 °C	
Assignment [a]	*m/e*	*I* [b]	*m/e*	*I*	*m/e*	*I*	*m/e*	*I*
$[M]^{+}$ [c]	548–557	100.0	644–654	100.0	740–749	100.0	834–845	100.0
$[M - C_2H_4]^{+}$	522–529	31.8	617–623	13.0	713–718	2.9		
$[M$ – Cl or HCl$]^{+}$	514–520	5.2	609–614	4.5	705–710	1.9	802–807	7.4
$[M - PF_2O]^{+}$	463–470	5.9	560–567	14.4	655–663	15.9	751–759	26.7
$[M - PClF_2]^{+}$	444–451	43.3	542–547	16.8	635–643	11.3	733–739	23.6
$[PtL_2(-nH)]^{+}$	425–432	16.7	518–530	7.0	617–626	6.5	715–723	86.4
$[M - PClF_2 - C_2H_4]^{+}$	417–422	5.2	512–518	2.1	609–614	1.2		
$[PtL_2 - C_2H_4]^{+}$	395–405	24.4	490–501	7.9	588–598	6.2		
$[PtL]^{+}$	309–318	8.5	356–366	15.5	405–412	6.0	451–460	35.1
$[PtL - C_2H_4]^{+}$	279–288	5.7	325–339	18.6	376–383	4.8		
$[L{\cdot}PF_2O]^{+}$	203–205	$\geqslant$100	252–254	$\geqslant$100	299–303	$\geqslant$100	347–348	58.4
$[L{\cdot}Cl]^{+}$	153–156	11.6	195–198	25.9	249–252	9.8	297–299	18.8
$[L]^{+}$	118–119	$\geqslant$100	166–167	$\geqslant$100	214–216	$\geqslant$100	262–264	$\geqslant$100

[a] Further fragments observed include: $[M$ – L – Cl or HCl$]^{+}$ (L = PEt_3, $PEtPh_2$, and PPh_3); $[M - PF_2O - HCl - 2\,C_2H_4]^{+}$, $[M - 190]^{+}$ (L = PEt_3, PEt_2Ph, and $PEtPh_2$); $[M - 161]^{+}$ (all L); $[PtL_{1,2} - n\,C_2H_4$ or $-m\,C_6H_6]^{+}$; $[L - n\,C_2H_4 - m\,C_6H_6]^{+}$. [b] Relative to *I* $[M]^{+} = 100$. [c] Parent peak; isotopic intensity pattern in good agreement with theory.

TABLE 4

Mass-spectral data for complex (III; L = PEt_3, R = Bu^n) and mixtures of (II) and (III; R = Bu^n) [a]

	(III; L = PEt_3, R = Bu^n)		*m/e* for (II)–(III; R = Bu^n)			
Assignment [b]	*m/e*	*I* [c]	L = PEt_3	PEt_2Ph	$PEtPh_2$	PPh_3
$[M']^{+}$ [d]	512—524	4.1	514—522	610—619	*e*	807—813
$[M]^{+}$ [d]			454—469	554—566	650—662	*e*
$[M - C_2H_4]^{+}$			438—442	574—580	622—632	
$[M$ – Cl or HCl$]^{+}$			421—434	520—528		714—721
$[PdClL_2]^{+}$	373—384	6.6	374—383	469—479	567—578	659—672
$[M' - PClF(OBu^n)]^{+}$ $[M - PClF_2]^{+}$	356—368	37.0	354—365	450—460	548—556	641—652
$[PdL_2]^{+}$	337—348	100.0	337—348	434—444	530—542	
$[PdL_2 - C_2H_4]^{+}$	307—318	23.7	307—319	404—415	500—509	
$[PdL]^{+}$	220—235	74.0	220—235	269—283	316—327	*ca.* 369
$[PdL - C_2H_4]^{+}$	192—207	49.0	191—201	240—250	289—296	
$[Pd]^{+}$	102—110	*ca.* 5	101—110	101—110	102—107	
$[L{\cdot}PFO(OBu^n)]^{+}$	257—259	25.9	257—261	305—306	352—357	*ca.* 401
$[L{\cdot}PF_2O]^{+}$			203—204	251—252	298—300	*ca.* 353
$[L{\cdot}Cl]^{+}$	153—156	59.3	153—156	201—204	248—252	
$[L]^{+}$	117—120	$\geqslant$100	117—120	165—168	213—217	261—263

[a] Even in pure complexes (II), fragments assigned to the apparently more volatile complexes (III; R = Bu^n) were observed; therefore no relative intensities were obtained and only *m/e* values are given. [b] Further fragments are of the same type as in Table 3; footnote *a*. [c] Relative to *I* $[M]^{+} = 100$. [d] The parent ions for complexes (II) and (III) are $[M]^{+}$ and $[M']^{+}$ respectively; characteristic for complexes (III) are the fragments $[M']^{+}$ and $[L{\cdot}PFO(OBu^n)]^{+}$. [e] Limited volatility, no parent ion observed.

(II; L = PEt_2Ph).[33] The bond lengths Pt–Cl [2.366(6)] and Pt–L [2.322(6) and 2.338(6) Å] are of the same magnitude as in comparable complexes *trans*-$[PtL_2XY]$ (L = tertiary phosphine; X = Cl or Br; Y = H, Cl, Br, EtNC, CO, or SiR_3; see refs. 33—36 and refs. therein). The shorter Pt–PF_2O bond length [2.199(6) Å] can be accounted for as a result of π back bonding from platinum *d* to phosphorus 3*d* orbitals.[33] The P–F bond lengths [1.530(15) and 1.523(15) Å] are virtually the same as in PF_3O [1.524(2) Å], the P–O distance [1.471(17) Å] being slightly larger than in PF_3O [1.346(2) Å].[37] There is also good agreement with P–O bond lengths in related systems, $[Fe(CO)_2(\eta\text{-}C_5H_5)\{P(CF_3)_2O\}]$ [1.478(4)][7c] and $[HgCl\{PO(OEt)_2\}]$ [1.42(07) Å].[38] There is only a slight distortion from the 90° bond angles of an ideal square-planar structure.

---

[33] J. Grosse, R. Schmutzler, and W. S. Sheldrick, *Acta Cryst.*, 1974, **B30**, 1623.

[34] G. G. Mather, A. Pidcock, and G. J. N. Rapsey, *J.C.S. Dalton*, 1973, 2095.

[35] J. S. Field and P. H. Wheatley, *J.C.S. Dalton*, 1974, 702.

[36] B. Jovanovic, L. Manojlovic-Muir, and K. W. Muir, *J.C.S. Dalton*, 1974, 195.

[37] T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, 1971, **10**, 344.

[38] J. Bennett, A. Pidcock, C. R. Waterhouse, P. Coggon, and A. T. McPhail, *J. Chem. Soc.* (*A*), 1970, 2094.

Typical fragment ions, observed in the mass spectra of *trans*-[$MClL_2(PF_2O)$] and assigned by comparison with data for other platinum and palladium complexes,[39-41] included $[M]^+$ (parent peak), $[M - C_2H_4]^+$, $[M - Cl$ or $HCl]^+$, $[M - PF_2O]^+$, $[M - PClF_2]^+$, $[M - Cl - PF_2O (- n\,H)]^+$, $[M - Cl - PF_2O - L(- n\,H)]^+$, $[L{\cdot}PF_2O]^+$, $[L{\cdot}Cl]^+$, and $[L]^+$ (Tables 3 and 4).

The monofluorophosphonato-complexes (III), which could not be isolated from the reaction mixtures, were characterized mainly by ^{19}F and ^{31}P n.m.r. spectroscopy (Table 1) and mass spectroscopy (Table 4). The *trans* configuration is assigned on the same grounds as discussed above. The complex *trans*-[$PdCl(PEt_3)_2\{PFO(OBu^n)\}$], (III; $L = PEt_3$, $R = Bu^n$), was synthesized *via* a different route, and could be isolated in a pure state: the complex *cis*-[$PdCl_2(PEt_3)_2\{PF(OBu^n)\}$], (VI) (preparation, see below), was treated with PEt_3, a Michaelis–Arbuzov reaction being induced through the presence of a neutral donor molecule [equation (14)].

TABLE 5

Fluorine-19 and ^{31}P n.m.r. and i.r. data (cm^{-1}) of the complexes *cis*-[$PtCl_2(P'Et_3)\{PF_2(OR)\}$] (IV), *cis*-[$PdCl_2(P'Et_3)\{PF_2(OR)\}$] (V), and [$PdCl_2(PEt_3)\{PF(OBu^n)\}_2$] (VI)

	R	δ_F	$^1J_{P-F}$	$^2J_{Pt-F}$	$^3J_{P'-F}$	$\delta_{P'}$ [a]	δ_P [a]	$^2J_{P'-P}$	ν(P–O) or ν(C–O) [b]	ν(P–F)	ν(M–P)	ν(M–Cl)
		p.p.m.	Hz			p.p.m.		Hz				
(IV) [c]	Bu^n	40.2	1 183	704	*d*	−19.8	−72.3	21	1 030vs	906 (sh), 885vs 880vs	436w, 406w, 396 (sh)	330m, 305 (sh), 301m
(IV) [e]	Ph	38.7	1 209	717	*d*	−20.8	−69.9	22	1 037s, 698vs	880vs, 910vs	435w, 381w	334m, 299m
(V) [c,f]	Bu^n	36.7	1 270		*d*	(−47.7)		*d*	1 040—1 010 [g]	890—860 [g]	427w, 400m, 380m	335m, 303m
(V) [e]	Ph	35.0	1 277		9	−47.3	−93.7	20	1 038s, 1 008m 965vs	910m, 870vs	438m, 429 (sh)	336m, 301s
(VI) [c]		38.8	1 205		14	−41.6	−99.0	*d*	1 050—955 [g]	893w, 843vs	430w, 415 (sh), 395 (sh)	325m, 298m, 280 (sh)

[a] The constants $^1J_{Pt-P}$ and $^1J_{Pt-P'}$ were not observed due to limited solubility. [b] Not separately assigned; in some cases, there were overlapping phosphine or phenyl bands. [c] In C_6H_6. [d] No coupling observed. [e] In CH_2Cl_2. [f] Unstable in solution (see Results and Discussion section). [g] Extremely broad intense band with no fine structure.

$$cis\text{-}[PdCl_2(PEt_3)\{PF(OBu^n)_2\}] + PEt_3 \longrightarrow trans\text{-}[PdCl(PEt_3)_2\{PFO(OBu^n)\}] + Bu^nCl \quad (14)$$

This reaction is closely related to one [42] dating back to 1896 [equation (15)]. The mass spectrum of (III; $L = PEt_3$, $R = Bu^n$) exhibited most of the fragments that

$$[PdCl_2\{P(OEt)_3\}_2] \xrightarrow[-\,EtCl]{NH_3} [PdCl(NH_3)\{P(OEt)_3\}\{PO(OEt)_2\}] \quad (15)$$

were observed for the PF_2O complexes (Table 4); the similarity of the n.m.r. (Table 1) and mass-spectral data of this complex to those observed for the other complexes (III), which could not be isolated in a pure state, provides further evidence for the nature of the latter.

Reactions of $PF_2(OR)$ *with* [$\{MCl_2(PEt_3)\}_2$] ($R = C_3H_5$, Bu^n, *or* Ph; $M = Pt$ *or* Pd).—On reaction of $PF_2(OR)$ ($R = Bu^n$ or Ph) with [$\{MCl_2(PEt_3)\}_2$] ($M = Pt$ or Pd) in a molar ratio of 2 : 1, the chloro-bridge was cleaved and mononuclear $PF_2(OR)$ complexes *cis*-[$MCl_2(PEt_3)\{PF_2(OR)\}$] were obtained [reaction type (c)]. The reactions proceeded with ease at room temperature in toluene or benzene as solvent. It is worth noting that

$$[\{MCl_2(PEt_3)\}_2] + 2\,PF_2(OR) \longrightarrow 2\,cis\text{-}[MCl_2(PEt_3)\{PF_2(OR)\}] \quad (16)$$

(IV) M = Pt , R = Bu^n or Ph
(V) M = Pd , R = Bu^n or Ph

with pure PF_3 no reaction was observed,[1,43] while $P(OPh)_3$ gave the same type of product.[21] On reaction of excess of $PF_2(OR)$ with [$\{MCl_2(PEt_3)\}_2$], defined products could not be isolated, probably due to competition of reaction types (a)—(c). The only exception was observed in reaction (17), in which a monofluorophosphine complex, (VI), was formed, starting from a difluorophosphine, as a result of a combination of reaction types (b) and (c).

$$[\{PdCl_2(PEt_3)\}_2] + 4\,PF_2(OBu^n) \longrightarrow 2cis\text{-}[PdCl_2(PEt_3)\{PF(OBu^n)_2\}] + 2PF_3 \quad (17)$$

Complexes (IV) and (V) have a *cis* configuration, as demonstrated by i.r. [two separate M–Cl stretching frequencies, ν(M–Cl), being observed] and n.m.r. spectroscopy (Table 5): the magnitudes of the P–P′ coupling constants ($^2J_{P-P'}$ *ca.* 20 Hz) [21,24,29-31] and the Pt–P coupling constant [$^2J_{Pt-P}$ 6 075 Hz, (IV; R = Ph)] [24,44] are typical for *cis* complexes. Complex (V; R = Bu^n) is unstable in solution and decomposes slowly in benzene, and more rapidly in dichloromethane, to give the binuclear difluorophosphonato-complex, (VIII) [equation (18)]. Formation of butyl chloride was confirmed by

$$2\,cis\text{-}[PdCl_2(PEt_3)\{PF_2(OBu^n)\}] \longrightarrow [\{PdCl(PEt_3)(PF_2O)\}_2] + 2\,Bu^nCl \quad (18)$$

^1H n.m.r. spectroscopy. Complex (VIII), and its platinum analogue, (VII), were obtained directly, on reaction of [$\{MCl_2(PEt_3)\}_2$] (M = Pt or Pd) with allyloxydifluorophosphine [reaction types (a) and (c)].

$$[\{MCl_2(PEt_3)\}_2] + 2\,PF_2(OC_3H_5) \longrightarrow [\{MCl(PEt_3)(PF_2O)\}_2] + 2\,C_3H_5Cl \quad (19)$$

---

[39] P. Haake and S. H. Mastin, *J. Amer. Chem. Soc.*, 1971, **93**, 6823.

[40] F. Glockling, T. M. McBride, and R. J. I. Polloch, *Inorg. Chim. Acta*, 1974, **8**, 81.

[41] K. L. Klassen and N. V. Duffy, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2602.

[42] E. Finck, *Compt. rend.*, 1896, *C***123**, 603.

[43] B. T. Heaton, Ph.D. Thesis, University of Sussex, 1967.

[44] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707.

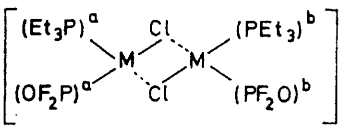
A large number of isomeric structures are possible for complexes [{MLXY}$_2$] (L = neutral ligand, *e.g.* tertiary phosphine or arsine; X and Y = anionic ligand (potentially bridging); M = Pt or Pd).[27,45,46] From a comparison of ^{19}F chemical shifts, δ_F, and P–O stretching frequencies, ν(P=O) (Table 6), with the values found for *trans*-[MClL$_2$(PF$_2$O)], complexes (VII) and (VIII) are considered to contain terminal difluorophosphonate groups. Chatt and Heaton[27] observed distinct ν(PO) values for POR$_2$ complexes of platinum containing terminal [ν(P=O) at 1 103 cm^{-1}] or bridging P–O groups [ν(P–O) at 960—990 cm^{-1} in a M–P–O–M bridged system]. Fluorine atoms of (VII) coupled with only one platinum nucleus each; there was no indication of second-order effects arising from possible phosphonate bridging structures. Thus, complexes (VII) and (VIII) are considered to contain chlorine bridges, which leaves isomers (A) and (B) for discussion.

TABLE 6

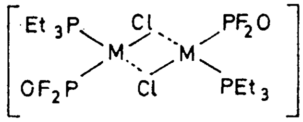
Fluorine-19 and ^{31}P n.m.r.[a] and i.r. data (cm^{-1}) for the binuclear complexes [{PtCl(PEt$_3$)(PF$_2$O)}$_2$] (VII) and [{PdCl(PEt$_3$)(PF$_2$O)}$_2$] (VIII)

	δ_F	$^1J_{P-F}$	$^2J_{Pt-F}$	$^3J_{P'-F}$	δ_P	$^1J_{Pt-P}$	$\delta_{P'}$	$^1J_{Pt-P'}$	$^2J_{P'-P}$	ν(P=O)	ν(P–F)[b]	ν(M–P)	ν(M–Cl)[b]
	p.p.m.	Hz			p.p.m.	Hz	p.p.m.	Hz					
(VII)[c,d]	23.95	1 190	960	10.3	−93.6[e]	6 436	−23.0	3 571.7	26.9	1 267 (sh),	841m,	446m,	330w,
	18.61	1 156	999	*ca.* 0	−1.1[e]	6 445	−22.9	3 779.5	39	1 254m,	820vs,	420w,	310m,
										1 139vs	770s,	402w	303 (sh),
											750m,		270w
											738m		
(VIII)	14.0[c,f]	1 290		12	−46.1		−49.5		15	1 275 (sh),	850—	442m,	336m,
	14.0[h,i]	1 292		7	−46.8		−49.5[j]		15	1 250vs,	810[g]	411m,	310s,
	11.7[d,h]	1 263		13	−47.7[e]		−50.9[j]		24	1 240s,	770—	400m,	270m
	15.8[d,h]	1 275		13	−100.2[e]		−52.3[j]		28	1 170 (sh)	730[g]	387 (sh)	
										1 150vs			

[a] Obtained by Dr. Murray, University of Bristol; ^{31}P{^{1}H}, solvent CH$_2$Cl$_2$. [b] No definite assignment; other bands overlapping.[12] [c] At 20 °C. [d] Sets of signals applying to isomer (A) (see text). [e] It is not quite clear why the differences in δ_P should be so large. [f] Signals applying to an average position due to fast exchange at room temperature [or to isomer (B) ?]. [g] Very broad intense band. [h] Low-temperature spectra: ^{19}F, −60; ^{31}P, −90 °C. [i] Signals applying to isomer (B). [j] Uncertain as to which signal corresponds to which kind of PEt$_3$.



Isomer (A)



Isomer (B)

In the ^{19}F and ^{31}P n.m.r. spectra of the platinum complex, (VII), two separate PF$_2$O and PEt$_3$ resonances of equal intensity were observed, arising from two sets of chemically non-equivalent PF$_2$O and PEt$_3$ groups. The n.m.r. spectra of (VIII) were temperature dependent: at room temperature, broad resonances were observed, while, at low temperatures, signals corresponding to three different kinds of PF$_2$O and PEt$_3$ groups were observed, two of which had the same intensity. In the i.r. spectra, large splittings were found for both P–O and P–F stretching frequencies of (VII) and (VIII) in the solid state. The only reasonable interpretation of these results is that, in the solid state, isomer (A) applies for both complexes. The same should also be true for (VII) in solution, while for (VIII) a rapid equilibrium between isomers (A) and (B) must be assumed, which is slowed down at low temperatures. These arguments only hold on the assumption of non-symmetrical M–Cl bridges, as indicated above, which, in the case of isomer (A), renders the PF$_2$O and PEt$_3$ ligands non-equivalent. For a number of complexes [{MLX$_2$}$_2$] of *trans*-isomer (B), significantly different M–X bridging bond lengths have been observed in *X*-ray crystal-structure investigations (L = AsMe$_3$, PPr$_3$, or SMe$_2$; M = Pt or Pd; X = Cl or Br).[47-50] The same was true for the thio-bridged complex [{PtBr$_2$(SEt$_2$)}$_2$].[47,49] An *X*-ray crystal-structure investigation is in progress to confirm the proposed structure of complex (VII), since no structural data are available for complexes of type (A).

^{1}H n.m.r. spectra were also obtained for all the complexes described in this paper, and are consistent with the proposed structures. Since the amount of information to be gained from such data is limited, they are not included in this paper.

EXPERIMENTAL

Most of the ^{1}H, ^{19}F, and ^{31}P n.m.r. spectra were measured on Varian HA 60 IL and Jeol C 60 HL spectrometers; some were also obtained on a Jeol PFT 100 instrument (courtesy of Dr. Murray, University of Bristol). Tetramethylsilane (^{1}H) and trichlorofluoromethane (^{19}F) were used as internal

---

[45] K. K. Chow, W. Levason, and C. A. McAuliffe in ' Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973, p. 35.

[46] J. G. Verkade and K. J. Coskran in ' Organic Phosphorus Compounds,' vol. 2, eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1973, p. 1.

[47] P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Comm.*, 1968, 31.

[48] S. F. Watkins, *J. Chem. Soc.* (*A*), 1970, 168.

[49] D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc.* (*A*), 1968, 1852.

[50] M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, 1969, **B25**, 1760.

TABLE 7

Preparative, melting-point, and analytical data for complexes (I), (II), and (III; L = PEt_3, R = Bu^n)

	L	$PF_2(OR)$	Molar ratio[a]	M.p. (θ_c/°C)	Analysis[b](%)					Formula	M
					C	H	P	F	Cl		
(I)[c]	PEt_3	C_3H_5, Bu^n	1 : 4—5	109	26.3 (26.1)	5.2 (5.4)	17.1 (16.9)	7.1 (6.9)	6.4 (6.4)	$C_{12}H_{30}ClF_2OP_3Pt$	551.5
(I)[d]	PEt_2Ph	C_3H_5, Bu^n	1 : 5	121	37.2 (37.1)	4.8 (4.7)	14.4 (14.3)	5.7 (5.9)		$C_{20}H_{30}ClF_2OP_3Pt$	648.0
(I)[d]	$PEtPh_2$	C_3H_5	1 : 5	181	45.2 (45.2)	4.1 (4.0)	12.6 (12.5)	5.0 (5.1)		$C_{28}H_{30}ClF_2OP_3Pt$	743.6
(I)	PPh_3	Bu^n [d–f]	1 : 7	267	51.6 (51.4)	3.8 (3.6)	11.0 (11.1)	4.1 (4.2)		$C_{36}H_{30}ClF_2OP_3Pt$	840.2
		Pr^n [d,f,g]	1 : 2								
(II)[d]	PEt_3	C_3H_5, Bu^n	1 : 5—6	92	30.7 (31.1)	6.7 (6.5)	20.1 (20.1)	8.7 (8.2)		$C_{12}H_{30}ClF_2OP_3Pd$	462.9
(II)[d,h]	PEt_2Ph	C_3H_5, Bu^n	1 : 5	145 (decomp.)	43.1 (43.0)	5.4 (5.4)	16.3 (16.6)	6.9 (6.8)		$C_{20}H_{30}ClF_2OP_3Pd$	559.3
		Pr^n [d,g]	1 : 2								
(II)[d,h]	$PEtPh_2$	C_3H_5	1 : 6	164	53.1 (51.3)	4.9 (4.6)	13.9 (14.2)	5.3 (5.8)		$C_{28}H_{30}ClF_2OP_3Pd$	654.9
		Pr^n, Bu^n [d,g]	1 : 2								
(II)[h,i]	PPh_3	Bu^n [f]	1 : 6	>145 (decomp.)	50.0 (51.9)	4.1 (3.7)	10.2 (10.5)		16.3 (16.0)	'$C_{36.5}H_{33}Cl_4F_2OP_3Pd$'	'878.3'
(III; R = Bu^n)[d,j]	PEt_3		1 : 4	32	40.0 (36.9)	7.5 (7.6)	17.8 (17.9)	3.8 (3.7)	7.0 (6.8)	$C_{16}H_{39}ClFO_2P_3Pd$	520.8

[a] Of starting complex to $PF_2(OR)$ employed in the reaction; all reactions were at room temperature in benzene as solvent, unless otherwise stated. [b] Calculated values are given in parentheses. [c] Preparation described in detail in the Experimental section. [d] Prepared applying the same reaction conditions as for (I; L = PEt_3). [e] Reaction temperature 70 °C. [f] Alloxydifluorophosphine reacted to give $[PPh_3(C_3H_5)]_2[M(PF_2O)_4]$ (M = Pt or Pd) (see text, ref. 8, and the following paper) [g] Using dichloromethane as solvent. [h] Formation of by-products (III) which could not be isolated; PF_2O complexes were obtained on extraction of the mixture with methylcyclohexane and recrystallization from that solvent. Formation of the by-products was not observed in absence of a large excess of $PF_2(OR)$. [i] Reaction at 70 °C in acetonitrile; the complex crystallized as a solvent adduct from dichloromethane, with 1.5 mol solvent per mol of complex (see text). [j] Prepared from complex (VI) by adding PEt_3 at room temperature in benzene solution.

TABLE 8

Preparative,[a] melting-point, and analytical data for complexes (IV)—(VIII)

	R	M.p. (θ_c/°C)	Analysis[b](%)					Formula	M
			C	H	P	F	Cl		
(IV)	Bu^n	52	22.6 (22.8)	4.5 (4.7)	11.6 (11.8)	7.9 (7.3)	13.3 (13.5)	$C_{10}H_{24}Cl_2F_2OP_2Pt$	526.3
(IV)	Ph	80	26.6 (24.4)	3.7 (3.7)	11.3 (11.3)		12.9 (13.0)	$C_{12}H_{20}Cl_2F_2OP_2Pt$	546.2
(V)	Bu^n	>100 (decomp.)	[c]	[c]	[c]	[c]	[c]	$C_{10}H_{24}Cl_2F_2OP_2Pd$	437.6
(V)	Ph	83	31.5 (31.5)	4.4 (4.4)	13.5 (13.5)		15.3 (15.5)	$C_{12}H_{20}Cl_2F_2OP_2Pd$	457.3
(VI)[d]		25	33.9 (40.0)	6.7 (6.7)	12.6 (12.5)		13.7 (14.3)	$C_{14}H_{33}Cl_2FO_2P_2Pd$	494.4
(VII)[e]		192	16.7 (16.6)	3.4 (3.5)	14.4 (14.3)	8.9 (8.8)	8.3 (8.2)	$C_{12}H_{30}Cl_2F_4O_2P_4Pt_2$	867.3
(VIII)[f]		153	20.7 (20.9)	4.2 (4.4)	17.7 (18.0)	10.8 (11.0)	10.3 (10.3)	$C_{12}H_{30}Cl_2F_4O_2P_4Pd_2$	689.2

[a] All reactions of $[\{MCl_2(PEt_3)\}_2]$ with $PF_2(OR)$ occurred at 20 °C in benzene or toluene solution as described for (V; R = Ph) in the text, using exact stoicheiometric amounts of reactants (starting complex: $ROPF_2$ = 1 : 2). [b] Calculated values are given in parentheses. [c] No data obtained due to instability (see Results and Discussion section). [d] Obtained by applying a 1 : 6 excess of $PF_2(OBu^n)$; the complex could not be recrystallized, but was obtained in the solid state by pumping off the solvent *in vacuo*. [e] Recrystallized from dichloromethane. [f] The complex could not be recrystallized, but precipitated in a pure state from the reaction mixture (solvent toluene).

references, 85% H_3PO_4, contained in sealed capillaries, as external reference. Chemical shifts to low field of the reference signals are negative, those to high field are positive. The ^{19}F and ^{31}P n.m.r. parameters are accurate to *ca.* ±7 Hz, unless otherwise stated. I.r. spectra were measured on Nujol mulls between KBr or CsI plates, using a Beckmann IR 20 A spectrometer, with an accuracy of ±5 cm^{-1}. Mass spectra were obtained on Varian MAT CH 4 and A.E.I. MS 9 spectrometers at 70 eV.* Elemental analyses were by J. Beller, Göttingen, Germany.

Preparations.—Ligands. The compounds PEt_3,[51] PEt_2Ph,[52] $PEtPh_2$,[52] and $PF_2(OR)$ (R = C_3H_5, Pr^n, Bu^n, or Ph)[53] were prepared as described in the literature.

Complexes. Platinum and palladium precursors were prepared by standard literature methods (see ref. 54 and refs. therein). Solvents and starting materials were dried and purified according to standard literature procedures. The usual precautions regarding the exclusion of air and/or moisture were taken in the reaction of $PF_2(OR)$ with platinum and palladium complexes. All reactions were made in

---

* 1 eV ≈ 1.60×10^{-19} J.

[51] K. Sasse in Houben–Weyl, 'Methoden der Organischen Chemie,' Band 12/1, ed. E. Müller, Georg-Thieme-Verlag, Stuttgart, 1963, p. 33.

[52] L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Zentr.*, 1959, 12037; H. Hoffmann, DAS 1044813, Farbwerke Hoechst, 1957.

[53] R. Schmutzler, *Chem. Ber.*, 1963, **96**, 2435.

[54] F. R. Hartley, *Organometallic Chem. Rev.*, 1970, **A6**, 119.

Schlenk tubes in an atmosphere of dry nitrogen or argon. The following preparations are typical.

trans-*Chloro(difluorophosphonato)bis(triethylphosphine)-platinum*(II), *trans*-[PtCl(PEt$_3$)$_2$(PF$_2$O)] (I; L = PEt$_3$). The complex [PtCl$_2$(PEt$_3$)$_2$] (0.6 g, 1.2 mmol) was suspended in benzene (4 cm^3), and PF$_2$(OC$_3$H$_5$) (0.5 cm^3, *ca.* 4—5 mmol) was added from a syringe, with magnetic stirring, the starting complex being dissolved almost immediately. The Schlenk tube was sealed and, after stirring overnight, all volatile products were removed *in vacuo*. The colourless residue was dissolved in toluene (2 cm^3); and a small amount of a dark residue was removed by centrifugation. After adding a few drops of methylcyclohexane to the then clear solution, complex (I; L = PEt$_3$) crystallized in the cold as colourless needles. The liquid was removed with a syringe, and the *product* washed with a little pentane and dried *in vacuo*.

cis-*Dichloro(difluorophenoxyphosphine)(triethylphosphine)-palladium*(II), *cis*-[PdCl$_2$(PEt$_3$){PF$_2$(OPh)}] (V; R = Ph). To a suspension of [{PdCl$_2$(PEt$_3$)}$_2$] (0.5 g, 0.8 mmol) in toluene (3 cm^3), PF$_2$(OPh) (0.3 g, 1.7 mmol) was added. With magnetic stirring, the starting complex was dissolved within 5 min. After 15 min a small amount of insoluble product was removed by centrifugation. On addition of a few drops of methylcyclohexane to the clear yellow solution the *product* crystallized as yellow needles in the cold. The precipitate was collected as above.

Di-μ-chloro-bis[(difluorophosphonato)(triethylphosphine)-platinum(II)], [{PtCl(PEt$_3$)(PF$_2$O)}$_2$] (VII). Allyloxydifluorophosphine (0.23 g, 1.8 mmol) was added to a suspension of [{PtCl$_2$(PEt$_3$)}$_2$] (0.69 g, 0.9 mmol) in benzene (3 cm^3). After 20 min of magnetic stirring, a white solid precipitated from the clear solution. The precipitate was collected and recrystallized twice from dichloromethane. Complex (VII) was obtained as colourless prisms.

All other reactions of [MCl$_2$L$_2$] and [{MCl$_2$L}$_2$] with PF$_2$(OR) were made in a similar manner. Preparative details, melting points, and analytical data for the products are summarized in Tables 7 and 8.

We thank Dr. R. Schwarz, Degussa A.G., Wolfgang bei Hanau, Germany for generous supplies of platinum and palladium compounds, and Fonds der Chemischen Industrie, Frankfurt am Main, Germany, and Deutsche Forschungsgemeinschaft for support (to J. G.).

[5/631 *Received, 4th April,* 1975]