Fluorophosphonate and Alkoxy- and Aroxy-fluorophosphine Complexes of Platinum(II) and Palladium(II). Part II.[1] Reactions of Complexes of Tertiary Amines with Alkoxy- and Aroxy-difluorophosphines

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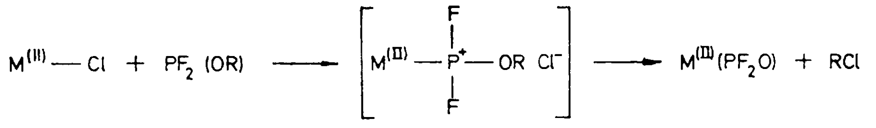
Ionic complexes $[R\cdot L]_2[M(PF_2O)_4]$ [M = Pt or Pd; L = NMe_3, pyridine (py), or PPh_3; R = allyl or Bu^n] and $[R\cdot L]_2[cis\text{-}MCl_2(PF_2O)_2]$ (M = Pt or Pd; L = NMe_3; R = allyl or Bu^n) have been obtained by treating $[MCl_2L_2]$ with $PF_2(OR)$ at room temperature. Similar ionic complexes seem to be formed in the reactions of $PF_2(OR)$ with $[Pt(C_2H_4)L_2]$ and $[Ir(CO)ClL_2]$ (L = PPh_3; R = allyl). The products have been characterized by means of ^1H, ^{13}C, ^{19}F, and ^{31}P n.m.r. and i.r. spectroscopy, and elemental analysis.

In the previous paper[1] we reported the formation of difluorophosphonato-complexes in the reaction of platinum(II) and palladium(II) chloride complexes with alkoxy- and aroxy-difluorophosphines, $PF_2(OR)$, *via* a Michaelis–Arbuzov reaction [equation (1), type (a)].



$$M^{(II)}—Cl + PF_2(OR) \longrightarrow \left[M^{(II)}—\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{P^+}}—OR\ Cl^-\right] \longrightarrow M^{(II)}(PF_2O) + RCl \qquad (1)$$

Also, we observed redistribution of the substituents at phosphorus in $PF_2(OR)$ under the influence of Pt^{II} and Pd^{II} complexes [equation (2), type (b)]. The products

$$PF_2(OR) \xrightarrow{M^{II}} PF(OR)_2, P(OR)_3, PF_3 \qquad (2)$$

of this reaction were obtained either as free ligands or co-ordinated to the metal.[1] Earlier, we reported formation of anionic platinum and palladium difluorophosphonato-complexes $[C_3H_5\cdot L]_2[M(PF_2O)_4]$ [L = PPh_3 or pyridine (py); $C_3H_5 = CH_2{:}CH\cdot CH_2$; M = Pt or Pd].[2] In this paper, further investigations on the reactions of $PF_2(OR)$ with Pt^{II} and Pd^{II} complexes are described, including some other relevant reactions.

RESULTS AND DISCUSSION

Besides the basic reaction types (a) and (b) mentioned above, reactions of type (c) were also observed for $[MCl_2L_2]$ with $PF_2(OR)$, *i.e.* formation of difluorophosphonatometallate anions and phosphonium and ammonium cations resulting from substitution and quaternization of the ligand L by $PF_2(OR)$ [equation (3) (M = Pt or Pd; L = tertiary amine or phosphine; R = C_3H_5 or Bu^n)]. This is also analogous to a Michaelis–Arbuzov reaction, with the ligand L being the nucleophile abstracting the group R from the co-ordinated

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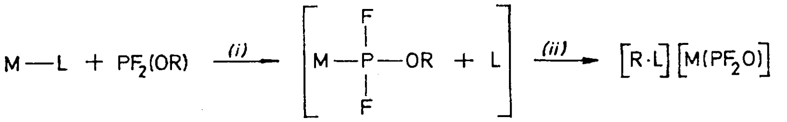
[1] Part I, J. Grosse and R. Schmutzler, preceding paper.

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

phosphine intermediate. Thus, dichlorobis(difluorophosphonato)metallates were obtained at room temperature in benzene as solvent [equation (4)].



$$M{-}L + PF_2(OR) \xrightarrow{(i)} \left[M{-}\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{P}}{-}OR + L \right] \xrightarrow{(ii)} [R{\cdot}L][M(PF_2O)] \quad (3)$$

$$[MCl_2(NMe_3)_2] + 2\ PF_2(OR) \longrightarrow [R{\cdot}NMe_3]_2[cis{-}MCl_2(PF_2O)_2] \quad (4)$$

(I) $M = Pt,\ R = Bu^n$ (II) $M = Pd,\ R = C_3H_5$ or Bu^n

Some other reactions involved combination of reaction types (a) and (c) to give tetrasubstituted difluorophosphonato-complexes, under the same reaction conditions as above [equation (5)]. Formation of allyl chloride was confirmed by i.r. spectroscopy[2] [ν(C–Cl) at 740 and 760 cm^{-1}, identified by comparison with an authentic sample]. In contrast, under the same reaction conditions, $PF_2(OR)$ ($R = Pr^n$ or Bu^n) reacted with $[MCl_2(PPh_3)_2]$ (M = Pt or Pd) to give only the monosubstituted product, *trans*-$[MCl(PPh_3)_2(PF_2O)]$.[1]

$$[MCl_2{\cdot}L_2] + 4\ PF_2(OR) \longrightarrow [R{\cdot}L]_2[M(PF_2O)_4] + 2\ RCl \quad (5)$$

	M	L	R
(III)	Pt	Py	$C_3H_5{}^2$
		Py	Bu^n
		NMe_3	C_3H_5
		PPh_3	$C_3H_5{}^2$
(IV)	Pd	Py	$C_3H_5{}^2$
		PPh_3	$C_3H_5{}^2$

On reaction of $PF_2(OPh)$ with $[PtCl_2(NMe_3)_2]$ substitution of trimethylamine occurred [equation (6)].

$$[PtCl_2(NMe_3)_2] + 2\ PF_2(OPh) \longrightarrow \underset{(V)}{cis\text{-}[PtCl_2\{PF_2(OPh)\}_2]} + 2\ NMe_3 \quad (6)$$

The corresponding palladium complex could not be isolated, even though formation of NMe_3 was observed. On reaction of a large excess of $PF_2(OPh)$ with $[PdCl_2(NMe_3)_2]$ substituent redistribution at phosphorus [reaction type (c)] occurred, with formation of a triphenyl phosphite complex already described in the literature[3,4] [equation (7)]. With $[PtCl_2(NMe_3)_2]$ and excess

$$2\ [PdCl_2(NMe_3)_2] + 6\ PF_2(OPh) \longrightarrow \underset{(VI)}{cis\text{-}[PdCl_2\{P(OPh)_3\}_2]} + 4\ NMe_3 + 4\ PF_3 \quad (7)$$

of $PF_2(OPh)$ a mixture of (V) and at least one more PF-containing species (from ^{19}F and ^{31}P n.m.r. spectra) resulted which could not be isolated or characterized.

The compounds $PF_2(OR)$ were also allowed to react with MCl_2 ($R = C_3H_5$, Bu^n, or Ph; M = Pt or Pd); only in one case could a defined product be isolated, complex (V) already mentioned [equation (8)]. In all the other reactions of $PF_2(OR)$ with MCl_2 oily mixtures were obtained, presumably as a result of combinations of reactions of types (a) and (b) as well as ligand-addition reactions as shown in equation (8); none of the products could be isolated or characterized.

$$PtCl_2 + 2\ PF_2(OPh) \longrightarrow \underset{(V)}{cis\text{-}[PtCl_2\{PF_2(OPh)\}_2]} \quad (8)$$

Some further reactions were conducted with the difluorophosphonato-complexes described in this and the preceding paper.[1] In principle it is possible to substitute the phosphonium and ammonium cations in the difluorophosphonatometallates with simpler cations; thus the sodium salt (VII) was precipitated on reaction of (III; L = py or PPh_3, $R = C_3H_5$) with sodium iodide in acetone [equation (9) (L = py or PPh_3)]. The salt (VII)

$$[C_3H_5{\cdot}L]_2[Pt(PF_2O)_4] + 2NaI \xrightarrow{\text{(acetone)}} \underset{(VII)}{Na_2[Pt(PF_2O)_4]} + 2[C_3H_5{\cdot}L]I \quad (9)$$

is of special interest in the assignment of anionic and cationic i.r. bands for the metallate complexes. Under more vigorous reaction conditions complexes with one or two PF_2O groups reacted further with $PF_2(OR)$ to give more highly substituted derivatives. Such, more vigorous, reaction conditions involve elevated reaction temperatures, longer reaction periods, and, mainly, use of polar reaction media which will promote formation of the ionic Michaelis–Arbuzov intermediate [see reaction type (a)]. Some examples of these reactions include formation of tetrasubstituted metallates [equations (10) (see ref. 1) and (11)].

$$trans\text{-}[PtCl(PEt_3)_2(PF_2O)] + 3\ PF_2(OC_3H_5) \xrightarrow[\text{MeCN}]{80\ ^\circ\text{C}} \underset{(III;\ L = PEt_3,\ R = C_3H_5)}{[C_3H_5{\cdot}PEt_3]_2[Pt(PF_2O)_4]} + C_3H_5Cl \quad (10)$$

$$[C_3H_5{\cdot}NMe_3]_2[cis\text{-}PdCl_2(PF_2O)_2] + 2\ PF_2(OC_3H_5) \xrightarrow[\text{MeCN}]{20\ ^\circ\text{C}} \underset{(IV;\ L = NMe_3,\ R = C_3H_5)}{[C_3H_5{\cdot}NMe_3]_2[Pd(PF_2O)_4]} + 2\ C_3H_5Cl \quad (11)$$

N.M.R. and I.R. Spectra.—The same arguments as previously employed,[1,2] *i.e.* the observed magnitudes of

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[3] N. Ahmad, E. W. Ainscough, T. A. James, and S. D. Robinson, *J.C.S. Dalton*, 1973, 1148.

[4] Ya. M. Kimel'fel'd, E. M. Smirnova, N. I. Pershikova, O. L. Kaliya, O. N. Temkin, and R. M. Flid, *Zhur. strukt. Khim.*, 1972, **13**, 622.

ν(P=O), δ_F, δ_P, $^1J_{Pt-P}$, and $^2J_{Pt-F}$ of the metallate complexes, again suggest that the PF_2O group is bonded to the metal through phosphorus rather than oxygen in the present series of complexes. It has been suggested that only soft acceptors like Pt^{II} and Pd^{II}, according to the definition of Pearson,[5] form *P*-bonded phosphonato-complexes while in other cases *O*-bonded or ionic species are formed.[6]

The presence of the phosphonium and ammonium cations in the complexes has been confirmed by comparison of their ^1H, ^{13}C, and ^{31}P n.m.r. and i.r. data with the parameters of some corresponding ammonium and phosphonium bromides prepared as in equation (12)

$$C_3H_5Br + L \longrightarrow [C_3H_5{\cdot}L]Br \qquad (12)$$

$[L = NMe_3$,[7] py (in analogy with ref. 8), PPh_3,[9] and $PMe_3]$. Allylic stretching frequencies (ν(C=C) at *ca.* 1 640 cm^{-1}) observed for both allyl-ammonium and -phosphonium bromides and for the complexes (Tables 2 and 3) were virtually identical; this suggests that no interaction between the metal and the allylic π system is taking place. For comparison, the salt $[C_3H_5{\cdot}NH_3]_2[PdCl_4]$ exhibits ν(C=C) at 1 646 cm^{-1} and also contains an allyl system which does not interact with the metal.[10] In the i.r. spectra, assignments were attempted for the vibrations ν(M–Cl), ν(M–P), ν(P–F), and ν(P=O) (Tables 2 and 3). Identification of anionic and cationic i.r. bands was facilitated by the availability of separate i.r. spectra of the ions $[C_3H_5{\cdot}L]^+$ (from $[C_3H_5{\cdot}L]Br$) and $[Pt(PF_2O)_4]^{2-}$ [from the sodium salt (VII)].

For the anions $[M(PF_2O)_4]^{2-}$ only single fluorine and phosphorus n.m.r. chemical shifts, δ_F and δ_P (Table 1), were observed due to chemical equivalence of the PF_2O groups. The spectra were however, highly complicated due to second-order effects. Thus phosphorus and fluorine coupling constants cannot be obtained from the spectra. For M = Pt, platinum satellites were observed having corresponding coupling constants ($^1J_{Pt-P}$ 4 015 and $^2J_{Pt-F}$ *ca.* 700 Hz) of the expected magnitudes.[1,2] The n.m.r. spectra of the dichlorobis(difluorophosphonato)metallates (I) and (II) also showed chemically equivalent but magnetically non-equivalent P and F nuclei, with a spin system of type $[AX_2]_2$. The *cis* structures of these salts as well as of complex (V), were derived from i.r. (observation of two metal–chlorine stretching frequencies; Tables 2 and 3) and n.m.r. data (magnitude of $^2J_{P-P}$; Table 1), *cf.* the arguments put forward in the preceding paper.[1] Complex (VI) was identified by comparison of its ^{31}P n.m.r. shift (δ_P −83.2 p.p.m.) and i.r. parameters to literature values.[3,4]

TABLE 1

Fluorine-19 and ^{31}P n.m.r. data

Anion (P)	Cation (P′)	δ_F p.p.m.	$^2J_{Pt-F}$ Hz	δ_P p.p.m.	$^1J_{Pt-P}$ Hz	$\delta_{P'}$ p.p.m.
(I) [a–c] $[cis\text{-}PtCl_2(PF_2O)_2]^{2-}$	$[Bu^n{\cdot}NMe_3]^+$	19.96	1 045	−32.44	6 287	
(II) [a] $[cis\text{-}PdCl_2(PF_2O)_2]^{2-}$	$[C_3H_5{\cdot}NMe_3]^+$	12.4		−58.6		
(II) [a,b,d]	$[Bu^n{\cdot}NMe_3]^+$	12.86		−58.79		
(III) [e] $[Pt(PF_2O)_4]^{2-}$	$[C_3H_5{\cdot}py]^+$	13.8	690	−69.9	3 800 [f]	
(III) [e]	$[Bu^n{\cdot}py]^+$	13.6	684	−69.8	*g*	
(III) [a]	$[C_3H_5{\cdot}NMe_3]^+$	13.4	688	−70.0	*g*	
(III) [h]	$[C_3H_5{\cdot}PPh_3]^+$	13.0	696	−70.4	*g*	−20.8
(VII) [i]	Na^+	*j*	684	−72.7	4 015	
(III) [a]	$[C_3H_5{\cdot}PEt_3]^+$	13.5	683	−70.8	*g*	−37.5
(IV) [e] $[Pd(PF_3O)_4]^{2-}$	$[C_3H_5{\cdot}py]^+$	9.3		−75.4		
(IV) [e]	$[C_3H_5{\cdot}PPh_3]^+$	8.3		−75.2		−20.7
(IV) [c]	$[C_3H_5{\cdot}NMe_3]^+$	9.6		−75.9		
(V) [b,k,l] $[cis\text{-}PtCl_2\{PF_2(OPh)\}_2]$		39.91	640	−69.36	6 182	
(VIII) [e] $[Ir(CO)Cl(PF_2O)_2]^{2-}$	$[C_3H_5{\cdot}PPh_3]^+$	*g*		*g*		*g*
(IX) [e] $[Ir(PF_2O)_3\{PF_2(OC_3H_5)\}]^{2-}$	$[C_3H_5{\cdot}PPh_3]^+$	0.4		*g*		*g*
(X) [k,m] $[Pt(PPh_3)_2\{PF_2(OC_3H_5)\}]$		9.1	992	*g*	*g*	−21.4 [n]
Br^-	$[C_3H_5{\cdot}PPh_3]^+$					−21.1 [h]
Br^-	$[C_3H_5{\cdot}PMe_3]^+$					−25.3 [a]

[a] In MeCN. [b] Spectra from Dr. Murray, University of Bristol. [c] $^2J_{P-P}$ 25.9 Hz. [d] $^2J_{P-P}$ 110.6 Hz. [e] In Me_2CO. [f] Estimated value. [g] Not obtained due to limited solubility. [h] In CH_2Cl_2. [i] In MeOH. [j] Not obtained. [k] In C_6H_6. [l] $^2J_{P-P}$ 18.9 Hz. [m] $^1J_{P-F}$ 1 226 Hz. [n] $\delta_{(PPh_3)}$.

A more detailed n.m.r. study of the difluorophosphonato-complexes described in this and the preceding paper[1] is under way together with a crystal-structure analysis of complex (II; R = Bu^n). ^1H N.m.r. data have also been measured for all the complexes discussed, as well as some ^{13}C n.m.r. spectra. Since these data were only compared with the parameters of the ammonium and phosphonium bromides they are not reported and discussed in detail in this paper.

Reactions of $PF_2(OC_3H_5)$ *with Vaska's Complex,* $[Ir(CO)Cl(PPh_3)_2]$, *and the Ethylene Complex* $[Pt(C_2H_4)(PPh_3)_2]$.—A number of reactions of $PF_2(OC_3H_5)$ with $[Ir(CO)Cl(PPh_3)_2]$ and $[Pt(C_2H_4)(PPh_3)_2]$ were carried out. Characterization of the products was not conclusive, however, since, due to low solubility, satisfactory ^{19}F and ^{31}P n.m.r. spectra could not be obtained. On the basis of elemental analyses, i.r. (Table 3), and, in part, ^1H n.m.r. data, iridium products obtained corresponded to $[C_3H_5{\cdot}PPh_3]_2[Ir(CO)Cl(PF_2O)_2]$, (VIII), and $[C_3H_5{\cdot}PPh_3]_2[Ir(PF_2O)_3\{PF_2(OC_3H_5)\}]$, (IX). Molar ratios of

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[5] R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 581, 643.

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

[7] J. v. Braun and W. Schirrmacher, *Ber.*, 1923, **B56**, 538.

[8] O. Magidson and G. Menschikoff, *Ber.*, 1926, **59**, 1209.

[9] M. Grayson and P. Keough, *J. Amer. Chem. Soc.*, 1960, **82**, 3919.

[10] F. R. Hartley and J. L. Wagner, *J.C.S. Dalton*, 1972, 2282.

$[Ir(CO)Cl(PPh_3)_2]$: $PF_2(OC_3H_5)$ of 1 : 1 and 1 : 7, respectively, were employed. On reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $PF_2(OC_3H_5)$ in a 1 : 1 molar ratio a product of formula $[Pt(PPh_3)_2\{PF_2(OC_3H_5)\}]$, (X), was formed. In this case, again due to low solubility, complete spectroscopic data could not be obtained (Tables 1 and 3). On reaction of excess of $PF_2(OC_3H_5)$ with $[Pt(C_2H_4)(PPh_3)_2]$ complex (III; L = PPh_3, R = C_3H_5) was formed and identified by ^1H, ^{19}F, and ^{31}P n.m.r. and i.r. spectroscopy; the product could not, however, be isolated in a pure state.

TABLE 2

Characteristic i.r. data (cm^{-1})[a] for the platinum complexes and the bromides $[C_3H_5\cdot L]Br$

	Cation	$\nu[C{=}C(C_3H_5)]$	$\nu(P{=}O)$	$\nu(P{-}F)$	$\nu(Pt{-}P)$	$\nu(Pt{-}Cl)$
(I)	$[Bu^n\cdot NMe_3]^+$		1 225vs, 1 215vs	830s, 792vs	430w, 417w, 406 (sh)	310m, 280m
(II)[b]	$[C_3H_5\cdot py]^+$	1 649w	1 248s, 1 212s	810—770[d]	418m, 401m	
(III)[c]	$[Bu^n\cdot py]^+$		1 240—1 210[d]	850—760[d]	415m	
(III)[c]	$[C_3H_5\cdot NMe_3]^+$	1 648w	1 270—1 200[d]	840—770[d]	415s, 405 (sh)	
(III)[c]	$[C_3H_5\cdot PPh_3]^+$	1 638w	1 233vs, 1 184 (sh)	795vs	410m, 396m	
(VII)[c]	Na^+		1 240m, 1 216vs	830vs, 803s, 814vs	425 (sh), 419m, 405 (sh)	
(III)[c]	$[C_3H_5\cdot PEt_3]^+$	1 636w	1 247vs	810vs, 756 (sh)	414m	
(V)	*cis*-$[PtCl_2\{PF_2(OPh)\}_2]$		1 028m,[e] 1 012m,[e] 980s[e]	910—890[d]	403m, 365w	
(X)	$[Pt(PPh_3)_2\{PF_2(OC_3H_5)\}]$	*f*	1 233vs, 1 180s	800—780[d]	410w	
	$[C_3H_5\cdot py]^+$[g]	1 637w				
	$[C_3H_5\cdot NMe_3]^+$[g]	1 645w				
	$[C_3H_5\cdot PPh_3]^+$[g]	1 632m				
	$[C_3H_5\cdot PMe_3]^+$[g]	1 641m				

[a] vs = Very strong, s = strong, m = medium, w = weak, and sh = shoulder. [b] Anion [*cis*-$PtCl_2(PF_2O)_2]^{2-}$. [c] Anion $[Pt(PF_2O)_4]^{2-}$. [d] Very broad intense band, with no fine structure. [e] $\nu(P{-}O)$ or $\nu(C{-}O)$. [f] Not obtained. [g] $[C_3H_5\cdot L]Br$.

TABLE 3

Characteristic i.r. data (cm^{-1}) for the palladium and iridium complexes

	Cation	$\nu[C{=}C(C_3H_5)]$[a]	$\nu(P{=}O)$	$\nu(P{-}F)$	$\nu(M{-}P)$	$\nu(M{-}Cl)$
(II)[b]	$[C_3H_5\cdot NMe_3]^+$	1 647w	1 230vs	820—780[c]	410m, 401m	314m, 284m
(II)[b]	$[Bu^n\cdot NMe_3]^+$		1 240—1 190[c]	825—775	415m, 405m, 397 (sh)	311m, 284m
(IV)[d]	$[C_3H_5\cdot py]^+$	1 650w	1 250—1 190,[c] 1 170 (sh)	830—780[c]	410m	
(IV)[d]	$[C_3H_5\cdot PPh_3]^+$	1 641w	1 228vs, 1 190 (sh)	795—770[c]	409m, 399 (sh)	
(IV)[d]	$[C_3H_5\cdot NMe_3]^+$	1 648w	1 250—1 190[c]	830—760[c]	408m, 399m	
(VIII)[e]	$[C_3H_5\cdot PPh_3]^+$	1 635w	1 215vs	820 (sh), 790vs, 715vs	*f*	*f*
(IX)[g]	$[C_3H_5\cdot PPh_3]^+$	1 642w	1 230s	770—740[c]	380m	

[a] See Table 2 for comparison. [b] Anion [*cis*-$PdCl_2(PF_2O)_2]^{2-}$. [c] Very broad intense band with no fine structure. [d] Anion, $[Pd(PF_2O)_4]^{2-}$. [e] Anion $[Ir(CO)Cl(PF_2O)_2]^{2-}$; $\nu(CO)$ at 2 040 cm^{-1}. [f] No signal obtained; measured between NaCl plates. [g] Anion, $[Ir(PF_2O)_3\{PF_2(OC_3H_5)\}]^{2-}$; measured in MeCN solution.

Conclusions.—By the application of the principle of the Michaelis–Arbuzov reaction to transition-metal chemistry it has been possible to synthesize, under mild conditions, a number of difluorophosphonato-complexes of Pt^{II} and Pd^{II} (see also refs. 1 and 2). The type of product formed is mainly determined by the group R of $PF_2(OR)$ and by the ligand L in the starting complex $[MCl_2L_2]$. No essential differences were observed between the reactivity of the corresponding platinum and palladium derivatives. The reactivity of $PF_2(OR)$ decreases, in complete analogy with the classic Michaelis–Arbuzov reaction,[11] as R changes in the order allyl > alkyl ≫ phenyl. The extent of substitution increases with increasing reaction temperature. The same effect is noted when polar rather than non-polar solvents are employed in the reactions. Most of the reactions described, however, proceed readily at room temperature in benzene.

As far as the ligands L are concerned, in agreement with Pearson's concept of hard and soft acids and bases,[5] amines are more readily substituted and quaternized by $PF_2(OR)$ than phosphines; only co-ordinated PPh_3 is displaced from the metal and quaternized at room temperature by $PF_2(OC_3H_5)$, but not by the less reactive $PF_2(OBu^n)$.[1]

Other phosphine systems, $P(OR)Y_2$ (Y = halogen, aryl, alkyl, OR, *etc.*), are likely to react in a similar way with analogous transition-metal systems; reaction may be limited, however, to soft-acid species because hard-acid systems seem to form oxygen-bonded M–OP complexes.[6] Further studies are required to extend the scope of the synthetic methods to other systems.

EXPERIMENTAL

Most n.m.r. spectra were recorded on Varian HA 60 IL and Jeol C 60 HL spectrometers, some on Bruker HFX 90 and Jeol PFT 100 instruments. [Measurements on the

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

latter instrument were kindly made by Dr. Murray, University of Bristol.] Tetramethylsilane (^1H) and trichlorofluoromethane (^{19}F) were used as internal references, 85% phosphoric acid as external reference (^{31}P) in sealed capillaries. Chemical shifts to low-field of the reference signal are negative, those to high field are positive. The ^{19}F and ^{31}P n.m.r. parameters are believed to be accurate to *ca.* ±7 Hz, unless otherwise indicated. I.r. spectra were recorded as Nujol mulls between KBr or CsI plates on a Beckmann IR 20 A spectrometer, with an accuracy of *ca.* ±5 cm^{-1}. Elemental analyses were by J. Beller, Göttingen, Germany.

TABLE 4

Preparative, melting-point, and analytical data for the platinum, palladium, and iridium complexes and bromide salts $[C_3H_5\cdot L]Br$

Complex	Molar ratio [a]	M.p. (θ_c/°C)	Analysis [b](%)						Formula	*M*
			C	H	P	F	Cl	N		
(I) [c]	1 : 6	*d*	24.8 (25.2)	5.3 (5.4)	9.2 (9.3)		10.1 (10.6)		$C_{14}H_{36}Cl_2F_4N_2O_2P_2Pt$	668.5
(II; R = C_3H_5) [c]	1 : 6	*d*	25.3 (26.3)	5.0 (5.1)	12.1 (11.4)	15.0 (13.9)			$C_{12}H_{28}Cl_2F_4N_2O_2P_2Pd$	547.4
(II; R = Bu^n) [e]	1 : 7	165 (decomp.)	28.9 (29.0)	6.4 (6.3)	10.7 (10.7)		12.2 (12.2)		$C_{14}H_{36}Cl_2F_4N_2O_2P_2Pd$	579.8
(VI; L = py, R = C_3H_5) [f]	1 : 10	*ca.* 200 (decomp.)	24.9 (24.8)	2.6 (2.6)	15.3 (16.0)	18.9 (19.6)	<0.1 (0)	3.5 (3.6)	$C_{16}H_{20}F_8N_2O_4P_4Pt$	775.3
(III; L = py, R = Bu^n) [f]	1 : 6	63	26.6 (26.8)	3.5 (3.5)	15.2 (15.3)	18.8 (18.8)			$C_{18}H_{28}F_8N_2O_4P_4Pt$	807.4
(III; L = NMe_3, R = C_3H_5) [c]	1 : 5	109	19.7 (19.6)	3.8 (3.8)	16.8 (16.9)	20.3 (20.7)			$C_{12}H_{28}F_8N_2O_4P_4Pt$	734.9
(III; L = PPh_3, R = C_3H_5) [f]	1 : 10	*d*	43.5 (44.2)	3.4 (3.5)	16.4 (16.3)	13.4 (13.3)			$C_{42}H_{40}F_8O_4P_6Pt$	1 143.1
(IV; L = py, R = C_3H_5) [f,g]	1 : 10	82	28.0 (28.0)	2.9 (2.9)	17.9 (18.1)	21.9 (22.2)			$C_{16}H_{20}F_8N_2O_4P_4Pd$	686.4
(IV; L = PPh_3, R = C_3H_5) [f]	1 : 12	148	46.2 (48.0)	3.6 (3.8)	17.1 (17.6)	14.2 (14.4)			$C_{42}H_{40}F_8O_4P_6Pd$	1 053.9
(V) [h]	1 : 2	65	24.8 (24.8)	1.9 (1.7)	9.9 (10.7)	12.7 (13.1)	11.8 (12.2)		$C_{12}H_{10}Cl_2F_4O_2P_2Pt$	580.2
(VI) [f,3,4]	1 : 10	180	54.1 (54.2)	3.9 (3.8)	7.6 (7.8)		9.1 (8.9)		$C_{36}H_{30}Cl_2O_6P_2Pd$	797.9
(VII) [e]	*e*	171 (decomp.)	*i*	*i*	*i*	*i*			$F_8Na_2O_4P_4Pt$	581.0
(III; L = PEt_3, R = C_3H_5) [e]	1 : 9	175	25.6 (25.3)	4.9 (4.7)	21.3 (21.8)				$C_{18}H_{40}F_8O_4P_6Pt$	853.5
(IV; L = NMe_2, R = C_3H_5) [e]	1 : 5	85	22.2 (22.3)	4.4 (4.4)	18.8 (19.2)	23.1 (23.5)			$C_{12}H_{28}F_8N_2O_4P_4Pd$	646.7
(VIII) [e]	1 : 1	107 (decomp.)	50.6 (50.0)	4.0 (3.9)	11.4 (12.0)		4.7 (3.4)		$C_{43}H_{40}ClF_4IrO_3P_4$	1 031.7
(IX) [f]	1 : 7	77	43.3 (45.8)	3.8 (3.8)	15.6 (15.9)	12.1 (12.9)			$C_{45}H_{45}F_5IrO_4P_6$	1 179.2
(X) [e]	1 : 1	233	56.0 (55.4)	4.4 (4.4)	10.9 (11.0)				$C_{39}H_{35}F_2OP_3Pt$	845.1
$[C_3H_5\cdot PMe_3]Br$ [e]	*e*	171	36.6 (36.6)	7.1 (7.2)					$C_6H_{14}BrP$	197.1
$[C_3H_5\cdot py]Br$ [j]	*j*	95	48.0 (48.0)	5.1 (5.1)					$C_8H_{10}BrN$	200.1

[a] Of the starting complex to $PF_2(OR)$ as applied in the reaction; all reactions were at room temperature in benzene as solvent. [b] Calculated values are given in parentheses. [c] Prepared as for (II; R = Bu^n) (see text); 30 h reaction time. [d] Not obtained. [e] Preparation described in detail in the Experimental section. [f] Prepared as for (II; R = Bu^n); 7—15 d reaction time. [g] Reaction in acetone as solvent. [h] Prepared in analogy to (II; R = Bu^n) starting from $PtCl_2$ as well as from $[PtCl_2(NMe_3)_2]$. [i] No satisfactory data obtained. [j] Prepared in close analogy to $[C_3H_5\cdot PMe_3]Br$.

Preparation of Compounds.—Solvents and starting materials were dried and purified by standard procedures. The usual precautions were taken to exclude moisture and/or air in all reactions; reactions were carried out in Schlenk tubes under an atmosphere of dry nitrogen or argon.

(a) *Ligands*. The compounds $PF_2(OR)$ (R = C_3H_5, Bu^n, or Ph) [12] and trimethylphosphine, PMe_3,[13] were prepared as described in the literature. A typical procedure for the preparation of allyl-ammonium and -phosphonium bromides, $[C_3H_5\cdot L]Br$ [L = py (following ref. 8), NMe_3,[7] PPh_3,[9] or PMe_3] is given below.

Allyltrimethylphosphonium bromide, $[C_3H_5\cdot PMe_3]Br$. A trimethylphosphine–diethyl ether mixture [600 mg, containing *ca.* 500 mg (7 mmol) of PMe_3] in benzene (20 cm^3) was allowed to react overnight with allyl bromide (1 g, 8 mmol). The resulting colourless precipitate was collected and recrystallized from acetonitrile as colourless needles in almost quantitative yield. Analytical data and the melting point are given in Table 4.

(b) *Complexes*. Platinum and palladium precursors were prepared by literature procedures: $[MCl_2(NMe_3)_2]$ (M = Pt or Pd),[14] $[PdCl_2(py)_2]$,[15] and $[Ir(CO)Cl(PPh_3)_2]$.[16] All other

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complexes were prepared according to ref. 17 and refs. cited therein. A typical procedure is given below for reactions of $[\mathrm{MCl_2L_2}]$ with $\mathrm{PF_2(OR)}$. Complexes prepared in an analogous manner include (III), (IV), and (IX). All these reactions were carried out using an excess of $\mathrm{PF_2(OR)}$. Analytical data, melting points, and further preparative details are summarized in Table 4.

Bis(n-butyltrimethylammonium) cis-*dichlorobis(difluorophosphonato)palladate*(II), $[\mathrm{Bu^n{\cdot}NMe_3}]_2[\text{cis-}\mathrm{PdCl_2(PF_2O)_2}]$ (II; R = $\mathrm{Bu^n}$). The complex *trans*-$[\mathrm{PdCl_2(NMe_3)_2}]$[1] (0.3 g, 1 mmol) was suspended in benzene (3 $\mathrm{cm^3}$) and treated with $\mathrm{PF_2(OBu^n)}$ (1 g, 7 mmol) with magnetic stirring. The reaction was slightly exothermic. A pale yellow oil soon started to separate out. After 30 h of stirring, all volatile components were removed *in vacuo*. The solid product remaining was dissolved in acetonitrile (2 $\mathrm{cm^3}$), and a small amount of insoluble residue was removed by centrifugation. From the clear solution, on addition of acetone (*ca.* 1 $\mathrm{cm^3}$), complex (II; R = $\mathrm{Bu^n}$) crystallized in the cold as colourless needles. The mother liquid was removed with a syringe, and the *crystals* washed with pentane and dried *in vacuo*.

Further preparations are described below.

Disodium tetrakis(difluorophosphonato)platinate(II), $\mathrm{Na_2[Pt(PF_2O)_4]}$ (VII). Complexes (III; L = py or $\mathrm{PPh_3}$, R = $\mathrm{C_3H_5}$) (0.6 g, *ca.* 1 mmol) were dissolved in acetone (2 $\mathrm{cm^3}$) and a saturated solution of NaI (1 g, 6.5 mmol) in acetone was added with magnetic stirring. A colourless solid was precipitated almost immediately. It was collected, washed with acetone (3 $\mathrm{cm^3}$), then acetonitrile and dichloromethane, and dried *in vacuo*. Complex (VII) is soluble in methanol and dimethyl sulphoxide, but could not be recrystallized without decomposition.

Bis(allyltriethylphosphonium) tetrakis(difluorophosphonato)platinate(II), $[\mathrm{C_3H_5{\cdot}PEt_3}]_2[\mathrm{Pt(PF_2O)_4}]$ (III; L = $\mathrm{PEt_3}$, R = $\mathrm{C_3H_5}$). A sample of *trans*-$[\mathrm{PtCl(PEt_3)_2(PF_2O)}]$ (0.3 g, 0.95 mmol), dissolved in acetonitrile, was transferred to a heavy-walled glass tube. After addition of $\mathrm{PF_2(OC_3H_5)}$ (1 g, 8.5 mmol), the tube was sealed *in vacuo* and heated to 80 °C for 2 weeks. All volatile compounds were removed *in vacuo*, and the residue was dissolved in acetonitrile and centrifuged and recrystallized twice from acetone–diethyl ether. The cream product was dried *in vacuo*.

Bis(allyltrimethylammonium) tetrakis(difluorophosphonato)palladate(II), $[\mathrm{C_3H_5{\cdot}NMe_3}]_2[\mathrm{Pd(PF_2O)_4}]$ (IV; L = $\mathrm{NMe_3}$, R = $\mathrm{C_3H_5}$). Complex (II; R = $\mathrm{C_3H_5}$) (0.27 g, 0.5 mmol) in acetonitrile (3 $\mathrm{cm^3}$) was allowed to react with $\mathrm{PF_2(OC_3H_5)}$-(0.3 g, 2.4 mmol) at room temperature. After stirring for 3 d, volatile products were removed *in vacuo* and the oily product was washed with benzene. On drying *in vacuo* the oil crystallized as a colourless powder.

Bis(allyltriphenylphosphonium) carbonylchlorobis(difluorophosphonato)iridate(I), $[\mathrm{C_3H_5{\cdot}PPh_3}]_2[\mathrm{Ir(CO)Cl(PF_2O)_2}]$ (VIII). The complex $[\mathrm{Ir(CO)Cl(PPh_3)_2}]$ (0.415 g, 1.2 mmol) and $\mathrm{PF_2(OC_3H_5)}$ (0.15 g, 1.2 mmol) were allowed to react in benzene. After 30 min the solvent was removed *in vacuo*. The residue was extracted with dichloromethane in order to remove the remaining starting material. The solvent was removed and the solid product was washed with benzene and dried *in vacuo* to give a cream *powder*.

(Alloxydifluorophosphine)bis(triphenylphosphine)platinum, $[\mathrm{Pt(PPh_3)_2\{PF_2(OC_3H_5)\}}]$ (X). The complex $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ (1 g, 1.5 mmol) dissolved in benzene (3 $\mathrm{cm^3}$) was allowed to react with $\mathrm{PF_2(OC_3H_5)}$ (0.17 g, 1.5 mmol) at room temperature. After 30 min of magnetic stirring, the solvent was removed *in vacuo* and the product was obtained as a light yellow *powder*.

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