Fluoro-complexes of Platinum Metals

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Metathetical reactions of AgF with chloro-complexes give the fluoro-complexes $[PtF(PEt_3)_3][BF_4]$, *trans*-$[PtF(PEt_3)_2(PPh_3)][ClO_4]$, *trans*-$[PtF(PEt_3)_2\{P(OPh)_3\}][ClO_4]$, $[PtF(PPh_3)_3][BF_4]$, $[PtF(PMe_2Ph)_3][BF_4]$, $[PdF(PEt_3)_3][BF_4]$, *trans*-$[RhF(CO)(PPh_3)_2]$, and *trans*-$[IrF(CO)(PPh_3)_2]$. These products are fully characterised by ^{19}F and ^{31}P n.m.r. spectroscopy, and ^{31}P n.m.r. parameters are also reported for the chloro-complexes $[PtCl(PEt_3)_3][BF_4]$, *trans*-$[PtCl(PEt_3)_2(PPh_3)][ClO_4]$, *trans*-$[PtCl(PEt_3)_2\{P(OPh)_3\}][ClO_4]$, and $[PtCl(PPh_3)_3][BF_4]$. The results suggest that the Pt–F bonding orbital has only small contributions from the Pt 6*s* and F 2*s* orbitals. The *trans* influence of fluorine in these complexes is usually slightly greater than that of chlorine and the Pt–F bond is probably stronger than corresponding Pt–Cl bonds. Hydrolysis of the platinum fluorides yields hydroxo-bridged complexes, $[Pt_2(OH)_2(PR_3)_4]^{2+}$, and reaction of these products with excess of tertiary phosphine gives platinum hydrides, $[PtH(PR_3)_3]^+$. Reaction of $[Pt(PPh_3)_4]$ with excess of anhydrous HF yields $[PtF(PPh_3)_3][H_nF_{n+1}]$ ($n \sim 2$—3).

THE platinum metals in their d^8 oxidation states (*i.e.* Pd^{II}, Pt^{II}, Rh^{I}, and Ir^{I}) are generally regarded as 'soft' (class B) acids and are consequently not expected to form stable complexes with 'hard' bases such as fluoride.[1] Thus the only known binary fluoride[2] for this group is PdF_2 and the first reported complex fluoride was $[PtF_2(PPh_3)_2]$ in 1965.[3] This latter product has since been reformulated[4] as $[PtF(PPh_3)_3][HF_2]$ and several other complexes have been reported, namely $[PtF(PMePh_2)_3]^+$,[4] $[M_2F_2(PPh_3)_4]^{2+}$ (M = Pd or Pt),[4] $[PtCl(F)(PEt_3)_2]$,[5] $[PtX(F)(PPh_3)_2]$ (X = Cl or Br),[4] and $[MF(CO)(PPh_3)_2]$ (M = Rh or Ir).[6,7] All these formulations rely mainly on analytical data and conductance measurements and we considered it desirable to obtain more direct evidence for the presence of metal–fluorine bonds in these complexes. Some of our results have been reported in a preliminary communication[8] and during the progress of our work an *X*-ray structure determination for the complex $[PtF\{CH(CF_3)_2\}(PPh_3)_2]$ was described.[9]

RESULTS AND DISCUSSION

Synthesis and Reactivity of Complexes.—The fluoro-complexes listed in the Table were all prepared by metathetical reaction of silver(I) fluoride with the corresponding chloro-complexes. Most reactions used a suspension of AgF in acetone and under these conditions we obtained yields of 60—80% and did not experience difficulties arising from formation of AgCl·AgF double salts. This has been cited previously as a disadvantage attendant on the use of AgF as a fluorinating agent.[10] Of the products, $[PtF(PEt_3)_3][BF_4]$ is by far the most easily obtained and the most stable. Once isolated, it is stable to normal laboratory procedures provided reasonable care is exercised regarding the moisture content of solvents. Prolonged exposure to halogenated solvents is probably unwise. The other complexes show varying degrees of sensitivity to hydrolysis and halogenated solvents and in some instances (see Experimental section) are difficult to crystallise. In general, however, the most rigorously anhydrous procedures are not required for these complexes.

The products of hydrolysis of the platinum complexes are the known[11] hydroxo-bridged species $[Pt_2(OH)_2(PR_3)_4]^{2+}$, and the reaction appears to be inhibited by the presence of excess of phosphine. This is particularly evident for $[PtF(PPh_3)_3][BF_4]$, the most easily hydrolysed of the fluoro-complexes, where the initial product of fluorination was often deficient in triphenylphosphine, and addition of excess of PPh_3 during reaction and recrystallisation both yielded a stoicheiometric product and prevented hydrolysis. During some of our hydrolysis experiments salts containing hydrido-platinum cations of the type $[PtH(PR_3)_3]^+$ were isolated. We were subsequently able to show that this is due to an unusual reaction of the hydroxo-bridged species with free tertiary phosphine [equation (1), R = Et or Ph]. This reaction

$$[Pt_2(OH)_2(PR_3)_4]^{2+} + 4PPh_3 \xrightarrow{120^\circ C} 2[PtH(PR_3)_2(PPh_3)]^+ + 2POPh_3 \quad (1)$$

gives an interesting insight into the action of PPh_3 as a reducing agent in other circumstances. For example, in

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[7] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1973, 1370.

[8] K. R. Dixon and J. J. McFarland, *J.C.S. Chem. Comm.*, 1972, 1274.

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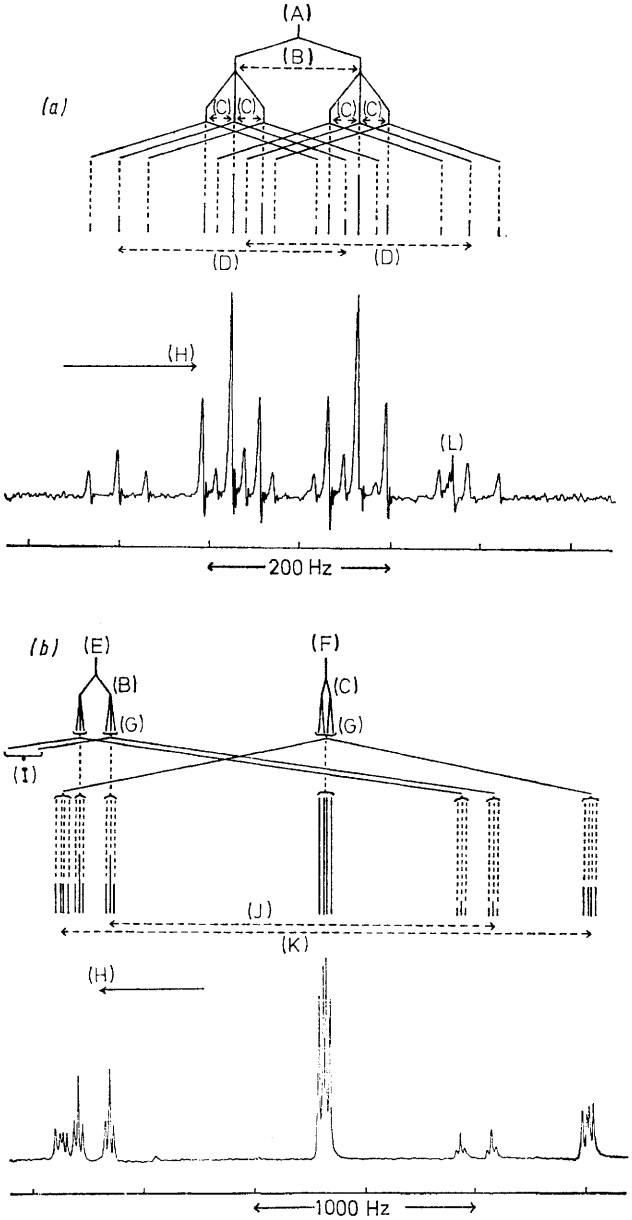
the well known[12] synthesis of $[Pt(PPh_3)_4]$ we could postulate the series of reactions (2).

$$[L_nPt^{II}(OH)_2] \xrightarrow[-2POPh_3]{+2PPh_3} [L_nPt^{II}H_2] \xrightarrow{-H_2} [L_nPt^0] \qquad (2)$$

Characterisation of Complexes.—Satisfactory carbon and hydrogen analyses were obtained as detailed in the Experimental section, but, in common with other authors,[7,13] we did not find fluorine analyses to be a reliable guide to the formulation of these complexes. The conductance measurements (Experimental section), which are typical of 1 : 1 electroytes[14] for the platinum, complexes and show the rhodium and iridium complexes to be non-electroytes, are consistent with the presence of bound fluorine, but the characterisation of the complexes rests primarily on the n.m.r. evidence. The ^{19}F and ^{31}P n.m.r. spectra of $[PtF(PEt_3)_3][BF_4]$ are shown in the Figure, together with the first-order analysis. The sidebands due to coupling with ^{195}Pt (33.8% abundant, $I = \frac{1}{2}$) in the ^{19}F spectrum are clear proof of the presence of a platinum–fluorine bond and the remainder of the spectra unambiguously establish the square-planar structure. The other complexes gave similar first-order spectra and the results are summarised in the Table. In our preliminary communication[8] we were unable to assign ^1J(Pt–F) in $[PtF(PPh_3)_3][BF_4]$ because of the apparently weak and asymmetric nature of the ^{195}Pt sidebands. Subsequent results have shown that these problems were due to a lack of resolution in our early spectra; ^1J(Pt–F) in this complex is much smaller than in the other platinum complexes and the resulting overlapping of bands makes the analysis difficult if resolution is poor.

Reaction of $[Pt(PPh_3)_4]$ *with* HF.—The product of this reaction was originally formulated as $[PtF_2(PPh_3)_2]$[3] and later as $[PtF(PPh_3)_3][HF_2]$.[4] In view of this disagreement, it was of interest to re-examine the product once we had determined the n.m.r. parameters for the $[PtF(PPh_3)_3]^+$ cation. The previous workers used liquid hydrogen fluoride in open polyethylene vessels, whereas most of our experiments were conducted in Teflon bottles connected to a stainless-steel vacuum system. However, we did obtain essentially the same products in polyethylene vessels exposed to the atmosphere and even aqueous HF seemed to give the same compound, although in this case it was impossible to crystallise. ^{19}F N.m.r. spectra of all these products, recorded in polyethylene tubes, showed the typical highfield resonances of the $[PtF(PPh_3)_3]^+$ cation and, in addition, a singlet resonance at +168 p.p.m. from CCl_3F (integrated intensity *ca.* 3.5 relative to fluorine on platinum). When glass n.m.r. tubes were used the +168 p.p.m. resonance was replaced by those characteristic of boron and silicon fluoro-anions. This resonance is therefore assigned to an anionic species, $[H_nF_{n+1}]^-$ (n *ca.* 2—3), and in support of this the ^1H n.m.r. spectrum showed a singlet at τ −2.53, indicating the presence of highly acidic protons. On exposure to moist air, the sharp resonance at τ −2.53 was replaced by a broad band at τ 4.2.



^{19}F (*a*) and ^{31}P (*b*) N.m.r. spectra of $[PtF(PEt_3)_3][BF_4]$ recorded at 56.4 and 40.5 MHz respectively: (A), δ_F; (B), ^2J(P–F) (*trans*); (C), ^2J(P–F) (*cis*); (D), ^1J(Pt–F); (E), δ_P (*trans* to F); (F), δ_P (*cis* to F); (G), ^2J(P–P); (H), direction of increasing magnetic field; (I), high-field ^{195}Pt sidebands omitted for clarity; (J), $\frac{1}{2}$ ^1J(Pt–P) (*trans* to F); (K), ^1J(Pt–P) (*cis* to F); and (L), sideband due to lock signal

Clearly the formulation $[PtF(PPh_3)_3][HF_2]$ is essentially correct, but the product normally contains excess

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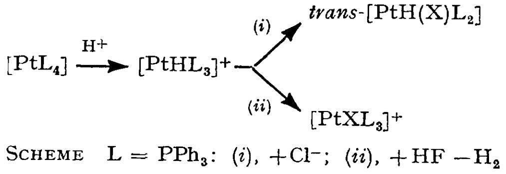
of HF hydrogen bonded to the anion. This explains the i.r. spectrum of the product which, as noted previously,[4] does not show the intense and characteristic spectrum of the $[HF_2]^-$ ion.[15] Our samples showed only broad absorption at *ca.* 1 800s and 2 450vw cm^{-1} in addition to the expected PPh_3 absorptions, and bands of this type have been assigned previously to solvated $[HF_2]^-$ both in HF solutions [16] and in various other donor solvents.[17] They are, therefore, consistent with the anionic species $[H_nF_{n+1}]^-$ postulated above.

N.m.r. data

	^{19}F Spectrum [a]					^{31}P Spectrum [a]					
				^2J(P–F)			*trans* to F or Cl		*cis* to F or Cl		
Complex	Solvent [b]	δ	^1J(M–F)	*trans*	*cis*	Solvent [b]	δ	^1J(M–P)	δ	^1J(M–P)	^2J(P–P)
$[PtF(PEt_3)_3][BF_4]$	Me_2CO	252	250	140	31.6	Me_2CO	141.6	3 455	115.8	2 382	19
trans-$[PtF(PEt_3)_2\{(PPh_3)\}$-$[ClO_4]$	$CHCl_3$	260	215	158	29.7	Me_2CO	141.0	3 762	119.3	2 336	19
trans-$[PtF(PEt_3)_2$-$\{P(OPh)_3\}][ClO_4]$	$CHCl_3$	266	197	246	29.5	Me_2CO	82.9	6 243	110.9	2 146	23
$[PtF(PPh_3)_3][BF_4]$ [c]	Me_2CO	232	65.7	139	38.9	Me_2CO	138.2	3 696	114.7	2 650	19
$[PtF(PMe_2Ph)_3][BF_4]$	Me_2CO	257	230	150	34.3			Not recorded			
$[PdF(PEt_3)_3][BF_4]$	$CHCl_3$	255		160	28.8			Not recorded			
trans-$[RhF(CO)(PPh_3)_2]$	$CHCl_3$	271	55.0		22.0	$CHCl_3$			115.1	136	
trans-$[IrF(CO)(PPh_3)_2]$	CH_2Cl_2	254			30.0			Not recorded			
$[PtCl(PEt_3)_3][BF_4]$						CH_2Cl_2	130.7	3 474	122.2	2 261	19
trans-$[PtCl(PEt_3)_2(PPh_3)]$-$[ClO_4]$						CH_2Cl_2	131.0	3 813	127.6	2 192	21
trans-$[PtCl(PEt_3)_2$-$\{P(OPh)_3\}][ClO_4]$						CH_2Cl_2	73.5	6 335	117.5	2 043	24
$[PtCl(PPh_3)_3][BF_4]$ [d]						CH_2Cl_2	128.0	3 643	117.3	2 482	19

[a] Chemical shifts (δ) in p.p.m. upfield from $CFCl_3$ or $P(OMe)_3$ as external references. Coupling constants (*J*) in Hz. See Experimental section for comments on accuracy of parameters. [b] Or the deuteriated analogues. [c] The complex $[PtF(PPh_3)_3][H_nF_{n+1}]$ had a similar cation spectrum. The anion spectrum is described in the Discussion section. [d] B. R. Steele and A. Pidcock, unpublished work.



SCHEME L = PPh_3: (*i*), $+Cl^-$; (*ii*), $+HF - H_2$

The formation of $[PtF(PPh_3)_3]^+$ in this reaction contrasts strongly with the reported [18] reactions of HCl with $[Pt(PPh_3)_4]$ to form hydride species $\{[PtH(PPh_3)_3]^+$ in ethanol and *trans*-$[PtH(Cl)(PPh_3)_2]$ in benzene$\}$. In view of the reactions [18] of $[Pt(PPh_3)_4]$ with acids having essentially non-co-ordinating anions (*e.g.* $HClO_4$ and HBF_4) to yield $[PtH(PPh_3)_3]^+$ salts, it seems likely that the initial reaction in all these cases is protonation of the platinum complex as in the Scheme. Other routes based on initial oxidative addition to form *trans*-$[PtH(X)L_2]$ cannot be completely excluded, but the comments below apply equally to these alternative mechanisms. Detection of the liberated hydrogen is a difficult experiment in the presence of a large excess of HF and, while we obtained some mass-spectroscopic evidence for the formation of H_2, a definite conclusion was not possible. Further reaction of the protonated species could occur either by attack of protons on the co-ordinated hydride or by an oxidative-addition–reductive-elimination mechanism and precedents are available for both types of process in the reactions of *trans*-$[PtH(Cl)(PEt_3)_2]$ with HBF_4 [19] or HCl.[20] The difference between the HF and HCl reactions is most likely due to the use of HF as the reaction solvent, whereas the HCl reactions were carried out with essentially stoicheiometric quantities of acid.[18] The large excess of HF and the highly acidic character of this solvent would favour the conversion of $[PtHL_3]^+$ into $[PtXL_3]^+$ by either mechanism.

trans *Influence of Fluoride.*—The data for ^1J(Pt–P) (*trans* to X) in corresponding fluoro- and chloro-complexes (Table) show that, in all cases except $[PtX(PPh_3)_3]^+$, the *trans* influence of fluoride is slightly greater than that of chloride. The exception, $[PtF(PPh_3)_3]^+$, also has an anomalously low ^1J(Pt–F), indicative of unusually weak Pt–F bonding (see below). The general F > Cl result is unusual in that previous results [21] for Group 4—6 ligands show the *trans*-influence order Period 2 > Period 1. Whilst it is difficult to make quantitative comparisons because of the wide variety of ligand types involved, the previous results [21] also tend to support the idea that the difference is maximised in

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[19] K. R. Dixon and D. J. Hawke, *Canad. J. Chem.*, 1971, **49**, 3252.

[20] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 854.

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

Group 5, thus $Si > C,P \gg N,S > O,Cl < F$. It is generally accepted that the order of *trans* influence for ligands containing these atoms is $Si > C > P > S > N > Cl > O$, the sequence being determined primarily by electronegativity but modified by the ability of these elements to form strong covalent bonds.[21] In the absence of sufficient data for Pt–X bonds, some indication of this bonding ability may be obtained from C–X bonds.[*] The differences, $E(C–C) - E(C–Si)$, $E(C–N) - E(C–P)$, *etc.*, are 55, 21, 64, and 158 kJ mol^{-1} for Groups 4, 5, 6, and 7 respectively,[22] whereas the electronegativity differences, $X_C - X_{Si}$, *etc.*,[23] show a relatively small steady increase, 0.76, 1.01, 1.06, and 1.27. This suggests that the series $Si > C,P \gg N,S > O,Cl < F$ may be a reflection of covalent bond strengths. Thus the *trans* influence for Period 2 elements is normally greater than that for Period 1 elements because of electronegativity effects; the difference is maximised in Group 5 because bonds to phosphorus are stronger relative to bonds involving nitrogen than is the case in the other Groups. In Group 7 the reverse situation occurs, with bonds to chlorine being unusually weak relative to those involving fluorine.

Magnitudes of Coupling Constants.—In general the ^1J(M–P) coupling constants have the expected [24] magnitudes, being small *trans* to P, large *trans* to Cl or F, and following the sequence $P(OPh)_3 > PPh_3 > PEt_3$. The small value for *trans*-$[RhF(CO)(PPh_3)_2]$ is similar to that observed [25] in the corresponding chloro-complex [^1J(Rh–P) 129 Hz] and may be attributed mainly to the very small magnetogyric ratio of rhodium (−0.176, *cf.* 1.20 for Pt).[24] The chemical shifts observed for the bound floride are also worthy of note since, with the exception of the values reported [26] for the $[PtF_6]^{2-}$ ion, they are the highest field shifts observed for diamagnetic fluorine compounds,[27] a situation very similar to that observed for ^1H shifts in transition-metal hydrido-complexes.

The couplings to fluorine are less straightforward. As an indication of the magnitudes to be expected we note that ^2J(Pt–F) and ^3J(P–F) (*trans*) in the $[Pt(CF_3)(PMe_2Ph)_3]^+$ cation are both *ca.* 10 times larger than ^2J(Pt–H) and ^3J(P–H) (*trans*) in $[PtMe(PMe_2Ph)_3]^+$. These couplings have been assumed to be dominated by Fermi-contact interactions and the difference in magnitude is thus due mainly to the large difference in $|\psi_{ns}(0)|^2$ for hydrogen and fluorine.[28,29] Although recent calculations [30] have shown that orbital contributions cannot always be neglected in couplings involving fluorine, the assumption of dominance of the Fermi-contact interaction for these complexes still seems well justified by the linear correlations, with zero intercepts, observed between ^2J(Pt–H) and ^2J(Pt–F) in the above Me and CF_3 complexes.[29] Coupling constants ^1J(Pt–H) and ^2J(P–H) (*trans*) in $[PtH(PR_3)_3]^+$ species are generally *ca.* 800 and 160 Hz respectively.[31] Assuming similar ratios to those observed in the Me and CF_3 complexes, this would predict magnitudes of *ca.* 8 000 and 1 600 Hz, respectively, for ^1J(Pt–F) and ^2J(P–F) (*trans*) in $[PtF(PR_3)_3]^+$ species. Some explanation of the very small observed values is therefore necessary.

In view of the above arguments it is relatively unlikely that fortuitous cancellation of orbital and Fermi-contact interations is responsible for the small coupling constants, although this possibility cannot be completely excluded. It is more probable that small values for α^2_{Pt} and α^2_{F} (the *s* characters of the orbitals forming the bonding combination) in the Fermi-contact term are responsible, the former being reduced by polarisation of the bonding orbital towards the electronegative fluorine and the latter by the large energy separation between the fluorine 2*s* and 2*p* orbitals. Since we find a greater *trans* influence for fluoride than for chloride, whereas electronegativity would predict the reverse order (see discussion above), it is likely that the Pt–F bond is stronger than the Pt–Cl in our complexes. The crystal-structure determination [9] of *cis*-$[PtF\{CH(CF_3)_2\}(PPh_3)_2]$ shows a Pt–F bond length (203 pm) equal to the sum of covalent radii for *dsp* ^{2} platinum (131 pm) and fluorine (72 pm). Thus the Pt–F bond *trans* to phosphorus is not of unusual length and our n.m.r. results can be taken to indicate the general type of bonding to be expected for low-valent fluorides of the platinum metals.

The coupling constant ^1J(Pt–F) in $[PtF(PPh_3)_3][BF_4]$ is only 65.7 Hz, even smaller than the values for the other platinum fluoro-complexes. This is indicative of an unusually weak Pt–F bond, a view which is supported by the facile hydrolysis and reduced *trans* influence of fluoride in this complex. The effect is most likely steric in origin, the bulky PPh_3 groups causing a distortion of the co-ordination geometry around platinum, either towards a lengthening of the Pt–F bond or possibly towards a tetrahedral geometry. It has recently been proposed that a simple relation exists between bond lengths and coupling constants in platinum–phosphorus complexes.[32] If the very limited data

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[*] X–H and X–Halogen bond energies show similar trends (see ref. 22) and, although the extension to Pt is far from rigorous, it is only necessary that the relative Group to Group trends persist, irrespective, for example, of whether the bond from Pt to a given Period 1 element is actually weaker or stronger than that to the Period 2 element in the same Group.

[22] W. E. Dasent, 'Inorganic Energetics,' Penguin Books, Harmondsworth, 1970, p. 105.

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[30] A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, 1971, **55**, 950.

[31] T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, 1974, **13**, 846.

[32] G. G. Mather, A. Pidcock, and (the late) G. J. N. Rapsey, *J.C.S. Dalton*, 1973, 2095.

available {$[PtF_6]^{2-}$ ^1J(Pt–F) 2 082 Hz,[26] bond length 191 pm;[33] Pt–F *trans* to tertiary phosphine ^1J(Pt–F) *ca.* 230 Hz, bond length 203 pm[9]} may be taken as an indication that ^1J(Pt–F) is very sensitive to bond length, then a bond-length variation of only 1—3 pm would suffice to explain the difference in ^1J(Pt–F) between $[PtF(PEt_3)_3]^+$ and $[PtF(PPh_3)_3]^+$.

EXPERIMENTAL

Data relating to the characterisation of the complexes are given in the Tables. Microanalyses were by D. L. McGillivray of this department or by Schwartzkopf Microanalytical Laboratory, New York. I.r. spectra were recorded from 4 000 to 250 cm^{-1} with accuracy ±3 cm^{-1} on a Beckman IR20 spectrophotometer calibrated against polystyrene film and water vapour. Solid samples were examined as Nujol mulls between caesium iodide plates. ^{19}F N.m.r. spectra were recorded at 56.4 MHz on a Varian HA60 spectrometer using $CFCl_3$ as external reference and with signal to noise enhancement using a Northern Scientific NS560 time-averaging computer. ^{31}P N.m.r. spectra were recorded at 40.486 MHz on a JEOL PFT-100 Fourier-transform spectrometer using $P(OMe)_3$ as external reference and C_6D_6 as external lock. 8 192 Data points were used in a 10 kHz sweep, giving a resolution of 2.44 Hz, and the coupling constants measured only from ^{31}P n.m.r spectra are thus subject to uncertainties of this magnitude. For both ^{19}F and ^{31}P n.m.r. spectra, protons were decoupled by broad-band ('noise') irradiation at the appropriate frequencies. M.p.s were determined on a Reichert hot-stage apparatus and are uncorrected. Conductance measurements were made on *ca.* 10^{-3}M solutions in nitromethane using a dip-type cell connected to a Radiometer model CDM3 conductivity bridge.

Solvents were of Spectrograde quality and were dried and stored over type 4A molecular sieves. All reactions involving silver (I) fluoride were carried out in subdued lighting conditions under an atmosphere of dry nitrogen using standard 'Schlenk' tube apparatus.[34] Products were isolated as solid materials before exposure to air. Silver(I) fluoride was prepared by mixing concentrated aqueous HF with excess of silver(I) carbonate. The mixture was filtered, the filtrate added to an equal volume of absolute methanol, and the resulting solution slowly added to a large volume of stirred anhydrous diethyl ether to yield AgF as a yellow precipitate which was collected and dried *in vacuo.* It is important to use dry solvents to minimise the total quantity of water present. The complex $[Pt(PPh_3)_4]$ [12] and the hydroxo- [11] and chloro-complexes,[19,35] used below as starting materials, were prepared by standard literature procedures or by minor modifications thereof.

The fluoro-complexes were all prepared by reaction of the corresponding chloro-complexes with AgF. The following is a typical preparation and any necessary variations for other complexes are noted below.

Preparation of Fluorotris(triethylphosphine)platinum(II) *Tetrafluoroborate.*—Silver(I) fluoride (0.132 g, 1.04 mmol) was suspended in a solution of $[PtCl(PEt_3)_3][BF_4]$ (0.600 g, 0.893 mmol) in acetone (15 cm^3) and the reaction mixture was protected from intense light. After stirring for 20 h at 25 °C, the blackish solid residue was removed by filtration and the colourless filtrate was concentrated to *ca.* 2 cm^3 by evaporation *in vacuo.* Dropwise addition of diethyl ether gave the complex (0.471 g, 0.719 mmol) as a colourless crystalline ***precipitate*** which was recrystallised from acetone solution on dropwise addition of diethyl ether (Found: C, 32.6; H, 6.6. $C_{18}H_{45}BF_5P_3Pt$ requires C, 33.0; H, 6.9%), Λ 82 s cm^2 mol^{-1}, ν(Pt–F) at 473 cm^{-1}.

Preparations of the following white (Pt) or yellow (Ir and Rh) crystalline complexes were similar, except for the modifications shown in parentheses: *trans*-$[PtF(PEt_3)_2(PPh_3)][ClO_4]$ (Found: C, 44.7; H, 5.9. $C_{30}H_{45}ClFO_4P_3Pt$ requires C, 44.4; H, 5.6%), Λ 78 s cm^2 mol^{-1}, ν(Pt–F) at 481 cm^{-1}; $[PtF(PPh_3)_3][BF_4]$ [reaction in nitromethane for 3 h in the presence of PPh_3 (3 mmol), recrystallisation from nitromethane–diethyl ether in presence of PPh_3 (3 mmol)] (Found: C, 59.1; H, 4.2. $C_{54}H_{45}BF_5P_3Pt$ requires C, 59.6; H, 4.2%), Λ 92 s cm^2 mol^{-1}, ν(Pt–F) obscured by PPh_3 absorptions; $[RhF(CO)(PPh_3)_2]$ (reaction in 1 : 1 benzene–acetone for 4 h) (Found: C, 66.1; H, 4.4. $C_{37}H_{30}FOP_2Rh$ requires C, 65.9; H, 4.5%), non-electrolyte in nitromethane, ν(Rh–F) obscured by PPh_3 absorption; and $[IrF(CO)(PPh_3)_2]$ (Found: C, 57.3; H, 4.2. $C_{37}H_{30}FIrOP_2$ requires C, 58.2; H, 4.0%), non-electrolyte in nitromethane, ν(Ir–F) at 448 cm^{-1}. The following complexes were prepared by similar procedures, but were too difficult to crystallise for analytical characterisation and their formulations are established by the n.m.r. data given in the Table: *trans*-$[PtF(PEt_3)_2\{P(OPh)_3\}][ClO_4]$; $[PtF(PMe_2Ph)_3][BF_4]$; and $[PdF(PEt_3)_3][BF_4]$.

Reactions of the following complexes with AgF were also attempted, but no isolable fluoro-complexes were obtained: *cis*-$[PtCl_2(PEt_3)_2]$; *cis*-$[PtCl_2(PPh_3)_2]$; *trans*-$[PtH(Cl)(PEt_3)_2]$; $[PdCl(PPh_3)_3][BF_4]$; $[RhCl(PPh_3)_3]$; *cis*-$[PtCl(py)(PEt_3)_2][BF_4]$; *cis*-$[PtCl(Me)(PEt_3)_2]$; *trans*-$[PtCl(CO)(PEt_3)_2][BF_4]$; and $[PtCl(AsPh_3)_3][BF_4]$.

Reactions of $[Pt(PPh_3)_4]$ *with* HF.—Triply distilled anhydrous HF (*ca.* 10 cm^3) was condensed onto $[Pt(PPh_3)_4]$ (0.93 g, 0.75 mmol) at −60 °C in a Teflon bottle connected to a stainless-steel vacuum system. The reaction mixture was warmed to 25 °C for 1 h and the excess of HF removed by vacuum distillation. Recrystallisation by dropwise addition of a solution in nitromethane to a large volume of stirred diethyl ether in an atmosphere of dry nitrogen gave $[PtF(PPh_3)_3][H_nF_{n+1}]$ (*n ca.* 2—3) (0.64 g, *ca.* 0.60 mmol). This product was characterised mainly by n.m.r. spectroscopy (see Discussion section).

Similar products were obtained from the following reactions: (*a*) anhydrous HF with $[Pt(PPh_3)_4]$ in an open polyethylene bottle, the reactants being protected from the atmosphere only by a stream of nitrogen and with product work-up in the open laboratory. (This is the method employed by previous workers.[3,4]); (*b*) a slurry of $[Pt(PPh_3)_4]$ in excess of 33% w/v aqueous HF was stirred for 2 h at 25 °C in a polyethylene beaker and evaporated to dryness at 65 °C.

Reaction of $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$ *with* PPh_3.—A solution of $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$ (0.34 g, 0.21 mmol) with PPh_3 (0.22 g, 0.83 mmol) in acetone (2 cm^3) in a sealed Carius tube was heated for 48 h at 120 °C. Removal of the

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acetone under reduced pressure followed by extraction of the residue with diethyl ether yielded ether-soluble $POPh_3$ (0.09 g, 0.32 mmol) and ether-insoluble $[PtH(PPh_3)_3]$-$[BF_4]$ (0.35 g, 0.33 mmol). The former was characterised by i.r. spectroscopy and the latter by its high-field ^1H n.m.r. spectrum.[31] A similar reaction using $[Pt_2(OH)_2(PEt_3)_4]$-$[BF_4]_2$ gave *trans*-$[PtH(PEt_3)_2(PPh_3)][BF_4]$.

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