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FULL PAPER

Solution decomposition of platinum(II) fluoride cations; single-crystal structure of $[Pt(PPh_3)_2(C_6H_4PPh_2)][SbF_6]\cdot CD_2Cl_2$

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An extended X-ray absorption fine structure (EXAFS) investigation of the metal co-ordination geometry in the cations $[PtF(PR_3)_3]^+$ (R = Et or Ph) indicates that the Pt−F bond lengths are identical and only slightly longer than those typical for low-valent metal fluoride complexes. The solution decomposition of the complexes, $[PtF(PPh_3)_3][X]$ ($X = HF_2$, BF_4 or SbF_6), have been studied in both wet and dry chlorinated solvents and the only reactions observed have been due to the presence of water, producing, initially, $[Pt(OH)(PPh_3)_3]^+$ and subsequently the ortho-metallated products $[Pt(PPh_3)_3(C_6H_4PPh_2)][X]$, which have been characterised by mass spectrometry, multinuclear NMR spectroscopy and, when $X = SbF_6$, by single-crystal X-ray crystallography.

Until fairly recently, in contrast to the extensive chemistry of co-ordination compounds including chloride, bromide or iodide as ligands, the comparable research on species incorporating fluoride as a ligand has been sadly neglected.[1] The increased availability of a range of fluorinating agents, the observation that low-valent metal–fluoride bonds are not necessarily unstable, particularly in the presence of π-acceptor ligands,[2] and the appreciation that novel and potentially interesting synthetic chemistry can be accomplished at the co-ordinated fluoride ligand[3] have revitalised this area. We have a long-standing interest in transition-metal carbonyl fluoride complexes[4,5] and are currently attempting to evaluate the criteria for metal–fluoride bond stability.

Early reports on low-valent platinum fluoride complexes, which describe some poorly characterised derivatives, indicate that, in these systems, the metal–fluoride bond is weak and highly reactive. The best characterised platinum fluoride phosphine complexes are the $[PtFL_3][BF_4]$ ($L = PEt_3$, $PMePh_2$ or PPh_3) species, prepared by halide metathesis or by the reaction of PtL_4 with anhydrous HF, for which ^{19}F NMR and, when $L = PEt_3$, X-ray crystallography has confirmed the presence of a platinum–fluorine bond.[6–9]

The various reports for low-valent platinum fluoride complexes are under investigation and here we describe evidence for reactivity in this class of complex and identify the decomposition products of the $[PtFL_3]^+$ (L = phosphine) cations.

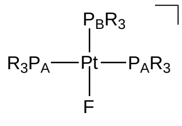
Results and Discussion

The platinum fluoride phosphine complexes $[PtFL_3][X]$ ($L = PPh_3$ or PEt_3; $X = HF_2$, BF_4 or SbF_6) were prepared by the literature routes, or modifications thereof.[6,7] The $[PtF(PEt_3)_3][BF_4]$ complex was also obtained as the only product from an attempted preparation of a platinum(IV) phosphine fluoride complex by the reaction of $[Pt(PEt_3)_4][BF_4]_2$ with XeF_2 in acetonitrile. During the course of this work, a similar fluorination of $[Pt(py)_4][BF_4]_2$ with XeF_2, was reported to give a stable Pt^{IV} fluoride.[10]

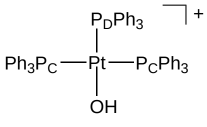
Table 1 NMR spectral data for the cationic complexes **1**–**3**[a]

Complex	$\delta(^{31}P)$[b]	$^1J_{PtP}$[c]	$^2J_{PP}$[c]	$\delta(^{195}Pt)$[b]	$^1J_{PtF}$[c]
1a[d]	26.5(P_A)	2640	19	−4270	67
	3.0(P_B)	3701			
1b[e]	28.0(P_A)	2828	19	−4405	250
	3.0(P_B)	3455			
2	22.8(P_C)	2483	19	—	—
	12.0(P_D)	3644			
3	−68.0(P_E)	2135	366, 18	−4450	—
	21.0(P_F)	2835	366, 18		
	16.8(P_G)	2008	18		

[a] Assignments in parentheses. [b] In ppm. [c] In Hz. [d] $\delta(^{19}F) = -232.0$ ($^2J_{PaF} = 39$, $^2J_{PbF} = 139$ Hz). [e] $\delta(^{19}F) = -251.5$ ($^2J_{PaF} = 32$, $^2J_{PbF} = 140$ Hz).



1a R = Ph
1b R = Et



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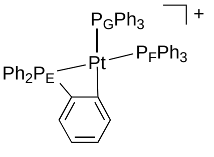

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The ^{19}F and ^{31}P-{^1H} NMR data for $[PtFL_3][BF_4]$ ($L = PEt_3$ **1b**$[BF_4]$ or PPh_3 **1a**$[BF_4]$) are in good agreement with those reported previously[12] whilst the ^{195}Pt-{^1H} NMR spectra, reported for the first time, show the expected single resonances (doublets of triplets of doublets) at *ca.* δ −4350 (Table 1). Surprisingly, these represent the first ^{195}Pt NMR data for a platinum(II) fluoride complex (only the ^{195}Pt NMR chemical shift for $[PtF_2(py)_4][BF_4]_2$[10] and high frequency data for $[PtF_6]^{2-}$ and *fac*-$[PtCl_3F_3]^{2-}$, included in a compilation,[11] have been reported previously) and the data for the 'P_3F' donor sets show the standard shift to high frequency within a series of related halide complexes.[12] It has been noted that the $^1J_{PtF}$ coupling constant for the triphenylphosphine complex is significantly smaller than that for the triethylphosphine complex. This has been used to suggest a weaker and more reactive Pt−F bond in the former. Although the PEt_3 complex is stable in solution over extended periods and has been crystallographically characterised by one of us,[9] all attempts to grow single crystals of the PPh_3 complex resulted in decomposition (see below). It has been shown that EXAFS spectroscopy can be a valuable technique for the determination of the metal–ligand interaction in the absence of crystallographic data[13] and we have investigated the metal environment in these complexes by Pt L_{III}-edge EXAFS.

The reliability of the data collection and treatment was confirmed by the collection and analysis of similar data for $[PtF(PEt_3)_3][BF_4]$ as a model compound (Table 2). The results of the two-shell fit are in satisfactory agreement with the crystallographic data.[9] For $[PtF(PPh_3)_3][SbF_6]$, transmission EXAFS

Table 2 EXAFS and crystal data for $[PtF(PEt_3)_3][BF_4]$ and EXAFS data for $[PtF(PPh_3)_3][SbF_6]$ [a]

	$[PtF(PEt_3)_3][BF_4]$			$[PtF(PPh_3)_3][SbF_6]$	
	X-Ray [b]	EXAFS [c,d]	Debye–Waller factor	EXAFS [c,e]	Debye–Waller factor
d(Pt–F)/Å	2.043(7)	2.028(4)	0.001(1)	2.011(7)	0.014(1)
d(Pt–P)/Å	2.239(3) 2.339(4) 2.335(4)	2.308(3)	0.011(1)	2.294(3)	0.014(1)
EF		−15.3(5)		−11.6(5)	

[a] Standard deviations in parentheses. [b] Taken from ref. 9. [c] AFAC (a factor compensating for the reduction in amplitude due to multi-electron processes) = 0.86 for all refinements. The systematic errors in bond distances arising from the data collection and analysis are *ca.* ±0.02 Å for the first co-ordination shells. [d] Fit index $= \Sigma_i[(\chi^T - \chi^E)k_i^3]^2 = 0.50$ (where T is theoretical and E is experimental). $R = [\int(\chi^T - \chi^E)k^3\ dk/\int\chi^E k^3\ dk] = 0.203$. [e] Fit index = 0.22. $R = 0.196$.

data were collected to $k = 15$ Å^{-1} (k = photoelectron wave vector) beyond the edge but, due to poor signal-to-noise at high k, the data were truncated at $k = 13$ Å^{-1}. Five data sets were collected, averaged and the data multiplied by k^3 to compensate for drop-off in intensity at higher k. No smoothing or Fourier filtering was applied and the fit discussed below is compared with the averaged raw (background-subtracted) EXAFS data. The data were modelled to the same two shells of one fluorine atom at r = *ca.* 2.03 Å and the three phosphorus atoms at r = *ca.* 2.27 Å. Each shell was added stepwise, iterated in the usual way, and the best fits tested for statistical significance.[14]

Examination of the Fourier transforms indicated additional features around 3.5 Å which, for both complexes, could be modelled to backscattering from the carbon backbone. This resulted in significant reductions to the fit index and R factor, but we follow convention in not including these interactions in our models.[15] We note that fitting two shells at similar distance may be dangerous. However, the validity of the fits we obtained can be demonstrated by the level of correlation between the data for the two shells (<0.6) and our attempts to fit the data to chemically unreasonable single-shell or two-shell (2F, 2P) models which give uncharacteristic Debye–Waller factors, unreasonable bond lengths and markedly poorer fits (R > 30%). Although the Pt–F bond length for **1a**$[SbF_4]$ is slightly shorter than that for **1b**$[BF_4]$, the distances are the same within the accuracy of the technique (±0.02 Å), indicating that the variation in the $^1J_{PtF}$ coupling constants results from changes in the s character of the Pt–F bond in line with the differences in basicity of the phosphine ligands. The increased reactivity of the triphenylphosphine complex in solution, therefore, is likely to occur as a result of other interactions in the complex. We note that from the crystal structure, $[PtF(PEt_3)_3]^+$ **1b** shows a marked tetrahedral distortion of the platinum co-ordination resulting from or arising in short intramolecular H···F interactions which could markedly reduce the reactivity of the fluoride ligand in this complex.

The complex $[PtF(PPh_3)_3][X]$ decomposed over a period of days in dichloromethane as evidenced by ^{31}P NMR spectroscopy. After 2 h in CD_2Cl_2, in addition to the resonances observed for the monofluorinated cationic starting material, the formation of two, new, mutually-coupled resonances were observed in the ^{31}P-{^{1}H} NMR spectrum apparently indicative of substitution of fluoride on the metal for an alternative anionic ligand. Despite the fact that these complexes have been reported to undergo facile fluorine/chlorine exchange in chlorinated solvents, we find no evidence for fluoridation of the solvents. This suggests that the new ligand on the platinum metal centre is a hydroxide group, originating from traces of water in the solvent, thus yielding $[Pt(OH)(PPh_3)_3][SbF_6]$ **2**$[SbF_6]$. Evidence for this hypothesis has been provided by confirmatory work in which separate samples of $[PtF(PPh_3)_3][X]$ were dissolved in both rigorously dried and reagent grade CD_2Cl_2 and studied, over a period of days, in a controlled manner by ^{31}P-{^{1}H} NMR spectroscopy. The sample in the dry solvent displayed no evidence of decomposition, even after a period of several weeks at room temperature, whereas the sample in wet solvent was found to decompose rapidly following the same decomposition pathway as previously described. This indicated that (a) the product of this reaction is most probably a hydroxide rather than a chloride derivative, (b) the reaction is independent of the associated anion and (c) since both samples were stored in the absence of light, the reaction is unlikely to have proceeded *via* a radical mechanism.

During a further 2 week period, in addition to increasing production of this new cationic species at the expense of the initial monofluorinated derivative, the formation of a third compound which displayed three mutually-coupled resonances, all showing platinum satellites, could be observed. Resonances attributed to the initial monofluorinated cation completely disappeared over a further 2 week period and the signals due to the monohydroxylated intermediates also decreased as those of the third compound grew in intensity, ultimately resulting in complete conversion to this new compound. The very low-frequency ^{31}P chemical shift for one resonance and the coupling constant data allow assignment to $[Pt(PPh_3)_2(C_6H_4PPh_2)]^+$ **3**, presumably formed by the standard ortho-metallation route at the electron-rich metal centre followed by resulting elimination of H_2O. In particular, $\delta(P_F)$ is comparable to those observed for cyclometallated phosphines *trans* to a second phosphine;[16] $^1J_{PtP_G}$ is characteristic of a phosphine ligand *trans* to an aryl group[17] and the unusually small $^1J_{PtP_E}$ (for phosphorus *trans* to phosphorus) is a consequence of distortion of the angles at platinum and phosphorus. The formation of **3** offers further, indirect evidence that **2** is not a chloro species since there have been no reports of the solution instability of $[PtCl(PPh_3)_3]^+$ in wet or dry solvents.

The ortho-metallated complex was isolated as a colourless solid and crystals suitable for single-crystal X-ray crystallographic study were obtained by slow evaporation from CD_2Cl_2 solution. The unit cell of **3** contains two discrete, crystallographically related, cation–anion pairs with no unusual contacts between the ions and the two molecules of solvent. A perspective view of the complex is shown in Fig. 1 and the relevant bond lengths and angles are given in Table 3. As shown in Fig. 1, the cation can be described as a pseudo-square planar platinum(II) ion containing two normal PPh_3 ligands and an ortho-metallated PPh_3 group. The PPh_3 groups appear normal and the Pt–P(1) and –P(2) bond distances are comparable to those reported for four-co-ordinate platinum(II) cations.[18–20] In the ortho-metallated ring the Pt–P(3) distance is similar to that of the Pt–P(1) and –P(2) bond distances, whilst the Pt–C(12) distance [2.090(4) Å] is unusually long for an ortho-metallated triphenylphosphine ligand.[21,22] As observed in most ortho-metallated phosphine ligands, the geometry around P(3) is significantly distorted from that found in normal PPh_3 ligands. As a result of drawing ring 1 towards the metal, the C(11)–P(3)–Pt angle is only 84.7(2)°, compared to an average of 114.5° for the angles around P(1) and P(2), and the carbon–phosphorus dis-

Table 3 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[Pt(PPh_3)_2(C_6H_4PPh_2)][SbF_6]\cdot CD_2Cl_2$

Pt–C(12)	2.090(4)	Pt–P(1)	2.3079(13)
Pt–P(3)	2.3126(13)	Pt–P(2)	2.3229(12)
P(1)–C(71)	1.820(5)	P(1)–C(81)	1.820(5)
P(1)–C(91)	1.829(5)	P(2)–C(41)	1.813(5)
P(2)–C(51)	1.822(5)	P(2)–C(61)	1.830(5)
P(3)–C(11)	1.800(5)	P(3)–C(21)	1.804(5)
P(3)–C(31)	1.808(5)	C(11)–C(16)	1.381(7)
C(11)–C(12)	1.398(7)	C(12)–C(13)	1.381(7)
C(13)–C(14)	1.395(7)	C(14)–C(15)	1.400(8)
C(15)–C(16)	1.389(8)	Cl(8)–C(1)	1.746(7)
Cl(7)–C(1)	1.751(7)	Sb–F (average)	1.869(3)
C(12)–Pt–P(1)	91.00(14)	C(12)–Pt–P(3)	68.4(2)
P(1)–Pt–P(3)	158.54(4)	C(12)–Pt–P(2)	170.33(14)
P(1)–Pt–P(2)	97.50(4)	P(3)–Pt–P(2)	102.59(4)
C(71)–P(1)–C(91)	101.1(2)	C(71)–P(1)–C(81)	109.9(2)
C(71)–P(1)–Pt	108.7(2)	C(81)–P(1)–C(91)	101.2(2)
C(91)–P(1)–Pt	123.5(2)	C(81)–P(1)–Pt	111.5(2)
C(41)–P(2)–C(61)	99.2(2)	C(41)–P(2)–C(51)	110.3(2)
C(41)–P(2)–Pt	114.8(2)	C(51)–P(2)–C(61)	103.1(2)
C(61)–P(2)–Pt	118.1(2)	C(51)–P(2)–Pt	110.3(2)
C(11)–P(3)–C(31)	104.8(2)	C(11)–P(3)–C(21)	111.6(2)
C(11)–P(3)–Pt	84.7(2)	C(21)–P(3)–C(31)	107.1(2)
C(31)–P(3)–Pt	125.0(2)	C(21)–P(3)–Pt	119.5(2)
C(16)–C(11)–P(3)	133.5(4)	C(16)–C(11)–C(12)	124.9(5)
C(13)–C(12)–C(11)	117.1(4)	C(12)–C(11)–P(3)	101.1(3)
C(11)–C(12)–Pt	104.8(3)	C(13)–C(12)–Pt	138.1(4)
C(13)–C(14)–C(15)	122.0(5)	C(12)–C(13)–C(14)	119.5(5)
C(11)–C(16)–C(15)	117.2(5)	C(16)–C(15)–C(14)	119.3(5)
C(22)–C(21)–P(3)	117.9(4)	C(26)–C(21)–P(3)	121.7(4)
C(32)–C(31)–P(3)	118.5(4)	C(36)–C(31)–P(3)	120.2(4)
Cl(8)–C(1)–Cl(7)	112.0(4)		

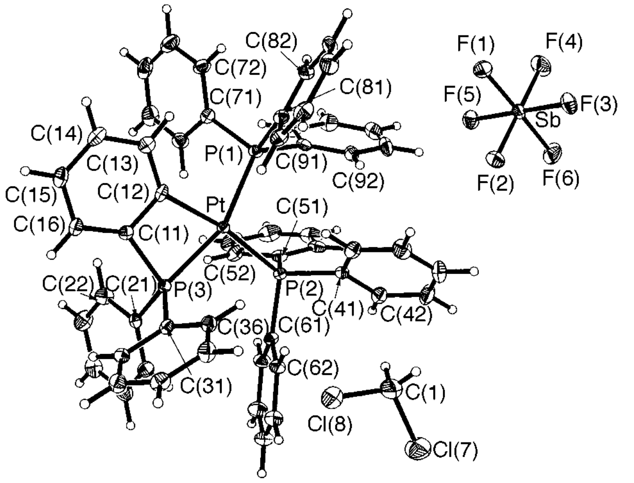

Fig. 1 Molecular structure of $[Pt(PPh_3)_2(C_6H_4PPh_2)][SbF_6]\cdot CD_2Cl_2$. Displacement ellipsoids are shown at 30% probability level

tances around P(3) (average 1.804 Å) are shorter than those around P(1) and P(2) (average 1.822 Å). Similarly, the angles about C(11) deviate considerably from the usual value of 120°; *i.e.* C(12)–C(11)–P(3) is 101.1(3)° and C(16)–C(11)–P(3) is 133.5(4)°. Comparable bond angle variations have been reported for other ortho-metallated platinum(II)–triphenylphosphine complexes.[20] Additionally, the C(31)–P(3)–Pt angle at 125.0(2)° is also outside the 'standard' range, which is a consequence not of ortho-metallation, but steric interactions with the aryl rings bound to P(2) which cause ring 3 to bend away from this ligand. Rings 5,6,7 and 8 stagger themselves with respect to the rings associated with the ortho-metallated phosphine to minimise steric congestion. The anion is unremarkable; the fluorines describe an almost perfect octahedron around the antimony and there are no significant cation–anion interactions.

Experimental

Fluorine-19 and ^{31}P NMR spectroscopic studies were carried out on a Bruker DRX400 spectrometer at 376.50 and 161.98 MHz and referenced to external $CFCl_3$ and 85% H_3PO_4 respectively, whilst the ^{195}Pt NMR studies were recorded on a Bruker AM300 spectrometer at 64.52 MHz, externally referenced to $[Na_2PtCl_6]$–D_2O. All spectra were recorded in CD_2Cl_2 and all chemical shifts are reported using the high-frequency positive convention.

Platinum L_{III}-edge extended X-ray absorption fine structure spectra (EXAFS) were collected at the Daresbury synchrotron radiation source operating at 2 GeV (*ca.* 3.2×10^{-10} J) with an average current of 190 mA on station 7:1 using an order-sorting Si(111) monochromator, offset to 50% of the rocking curve for harmonic rejection. The EXAFS data were collected in transmission mode at room temperature for samples diluted in dry boron nitride and mounted between Sellotape strips in 1 mm aluminium spacers. The EXAFS data treatment utilised the programs EX[23] and EXCURV 92.[24] Several data sets were collected for each compound in *k* space, and averaged to improve the signal-to-noise ratio. The pre-edge background was removed by fitting the spectrum to a quadratic polynomial, and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using polynomials, and the optimum function judged by minimising the intensity of chemically insignificant shells at low *r* in the Fourier transform. Curve fitting used single-scattering curved-wave theory. Ground-state potentials of the atoms were calculated using Von Barth theory and phase shifts using Hedin–Lundqvist potentials. Two-shell (3P, 1F) models were fitted in both cases. Refinements were also carried out using other combinations and better fits were obtained with the spectroscopically correct two-shell model. The distances and Debye–Waller factors were refined for both shells, as well as the Fermi energy difference. Fast atom bombardment mass spectra were recorded on a Kratos Concept 1H mass spectrometer. All preparative manipulations were carried out on a metal vacuum line with facilities to connect Teflon and FEP (perfluoroethylene–propylene co-polymer) reaction vessels. Hydrogen fluoride (ICI) was purified by vacuum transfer, dried by repetitive fluorination at room temperature and stored in Kel-F tubes over dry BiF_5.[25] The complexes $[PtF(PEt_3)_3][BF_4]$,[6] $[Pt(PEt_3)_4][BF_4]_2$[26] and $[PtF(PPh_3)_3][HF_2]$[27] were prepared by literature routes, whilst $[PtF(PPh_3)_3][X]$ ($X = BF_4$ or SbF_6) were prepared by modifications of the literature route.[7] Tetrakis(triphenylphosphine)platinum(0) (Aldrich) (0.3 g, 0.25 mmol) was loaded into a prepassivated 6 mm external diameter FEP tube fitted with a PTFE valve and $NaBF_4$ (Fluorochem) (0.026 g, 0.25 mmol) or $NaSbF_6$ (Fluorochem) (0.028 g, 0.25 mmol) were loaded into a second passivated tube. After evacuation on the metal line, anhydrous HF (*ca.* 1 cm^3) was condensed onto the platinum complex at −196 °C. Upon warming, effervescence was observed, necessitating quenching of the reaction mixture in liquid nitrogen and venting off the hydrogen. When the reaction was complete, the anhydrous HF solution of the metal complex was decanted onto $NaBF_4$ or $NaSbF_6$ and, after 1 h at room temperature, the solvent was removed *in vacuo* to yield brown solids.

The complex $[Pt(PPh_3)_2(C_6H_4PPh_2)][SbF_6]$ was obtained as a colourless solid following removal of the solvent after 3 months from a sample used for the NMR decomposition studies (see above). FAB mass spectrum: *m*/*z* 980 (M^+).

Crystal structure determination of $[Pt(PPh_3)_2(C_6H_4PPh_2)]$-$[SbF_6]\cdot CD_2Cl_2$

Crystal data: $C_{55}H_{44}Cl_2D_2F_6P_3PtSb$, $M = 1303.57$, triclinic, $a = 12.496(1)$, $b = 13.045(2)$, $c = 17.469(2)$ Å, $\alpha = 89.61(1)$, $\beta = 74.43(1)$, $\gamma = 68.16(1)°$, $U = 2532.4(5)$ Å^3, $T = 190$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 3.551 mm^{-1}, 10 035 reflections measured, 8606 unique ($R_{\text{int}} = 0.026$) which were used in all calculations. The final $wR(F^2)$ was 0.0711, $R1 = 0.0325$.

CCDC reference number 186/913.

See http://www.rsc.org/suppdata/dt/1998/1249/ for crystallographic files in .cif format.

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