



TRIS(2,6-DIFLUOROPHENYL)PHOSPHITE COMPLEXES OF PLATINUM GROUP METALS: STRUCTURE OF *TRANS*-PtCl₂(PEt₃){P(O-2,6-C₆H₃F₂)₃}

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Abstract—The reactions between the fluorine-containing ligand tris(2,6-difluorophenyl)phosphite and the transition metal species [$\{\eta^6\text{-}1,4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2\}\text{RuCl}_2\}_2$, $[\text{Cp}^*\text{RhCl}_2]_2$, $[\text{RhCl}(\text{CO})_2]_2$, $[\text{PtCl}_2(\text{PEt}_3)]_2$ and PtCl_2 yield the complexes $\{\eta^6\text{-}1,4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2\}\text{RuCl}_2\{\text{P}(\text{O-}2,6\text{-C}_6\text{H}_3\text{F}_2)_3\}$, $\text{Cp}^*\text{RhCl}_2\{\text{P}(\text{O-}2,6\text{-C}_6\text{H}_3\text{F}_2)_3\}$, *trans*-RhCl(CO){P(O-2,6-C₆H₃F₂)₃}₂, *trans*-PtCl₂(PEt₃){P(O-2,6-C₆H₃F₂)₃} and *trans*-PtCl₂{P(O-2,6-C₆H₃F₂)₃}₂, respectively. The molecular structure of *trans*-PtCl₂(PEt₃){P(O-2,6-C₆H₃F₂)₃} has been determined by single-crystal X-ray crystallography.

It has been shown that the presence of fluorine in the *ortho* positions of triphenylphosphine can have a dramatic influence on the structural and electronic properties of transition metal complexes of the phosphine. For example, platinum group metal complexes of tris(pentafluorophenyl)phosphine are significantly different from triphenylphosphine complexes of these metals;^{1,2} the greater bulk of P(C₆F₅)₃, which is due to the presence of *ortho*-fluorines, and its weaker σ -donor ability compared to those of PPh₃ can stabilize unusual coordination numbers, geometries and electronic configurations.² We are interested in the effects the presence of fluorine atoms in the *ortho* positions of phenylphosphines and phenylphosphites can bestow on transition metal complexes of these ligands.

We are currently investigating the ligation

properties of fluorine-containing phenylphosphites. Recently, we reported the new fluorine-containing phosphite, tris(2,6-difluorophenyl)phosphite, and the iridium complex $\text{Cp}^*\text{IrCl}_2\{\text{P}(\text{O-}2,6\text{-C}_6\text{H}_3\text{F}_2)_3\}$.³ The structure of the complex indicates that the presence of six fluorine atoms in the *ortho* positions of triphenylphosphite bestows structural properties on the complex that are significantly different from those of triphenylphosphite complexes of iridium. However, the similarity of the values of the chemical shifts of the phosphorous resonances of P(OPh)₃ (δ 128.2)⁴ and P(O-2,6-C₆H₃F₂)₃ (δ 131.79) suggests that their properties are similar. So, the differences between complexes of the two ligands may be ascribed solely to the greater bulk of P(O-2,6-C₆H₃F₂)₃. To investigate the effects of the presence of *ortho*-fluorines in transition metal triphenylphosphite complexes further, we have now synthesized P(O-2,6-C₆H₃F₂)₃ complexes of platinum group metals. Here, we report complexes of ruthenium, rhodium, iridium and platinum and the

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X-ray crystal structure of *trans*-PtCl₂(PEt₃){P(O-2,6-C₆H₃F₂)₃}.

EXPERIMENTAL

[{ η^6 -1,4-CH₃C₆H₄CH(CH₃)₂}RuCl₂]₂ [Cp*RhCl₂]₂, [RhCl(CO)₂]₂ (Aldrich) and PtCl₂ (Johnson Matthey) were used as supplied. P(O-2,6-C₆H₃F₂)₃ was prepared as described previously.³ Petroleum ether (b.p. 40–60°C) was used throughout. NMR spectra were recorded on a Bruker AM300 spectrometer. ¹H NMR spectra were recorded at 300.14 MHz and referenced internally using the residual protio solvent resonance relative to tetramethylsilane (δ = 0 ppm). ¹⁹F NMR spectra were recorded at 282.41 MHz and referenced externally to CFC₃ (δ = 0 ppm). ³¹P NMR spectra were recorded at 121.50 MHz and referenced externally to 85% H₃PO₄ (δ = 0 ppm). All chemical shifts are quoted in δ (ppm) using the high frequency positive convention and coupling constants in Hz. Abbreviations used in multiplicities are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and vt = virtual triplet. IR spectra were recorded as Nujol mulls between KBr plates on a Digilab FTS40 Fourier transform spectrometer. Elemental analyses were performed by Butterworth Laboratories Ltd.

Preparation of { η^6 -1,4-CH₃C₆H₄CH(CH₃)₂}RuCl₂{P(O-2,6-C₆H₃F₂)₃} (1)

A solution of [{ η^6 -1,4-CH₃C₆H₄CH(CH₃)₂}RuCl₂]₂ (0.10 g, 0.165 mmol) and P(O-2,6-C₆H₃F₂)₃ (0.175 g, 0.42 mmol) in benzene (50 cm³) was heated under reflux under nitrogen for 2 h. The resulting pink solid was filtered, washed with petroleum ether and dried *in vacuo*. Yield 0.15 g (63%). Found: C, 45.7; H, 3.2; Cl, 9.6. Calc. for [{ η^6 -1,4-CH₃C₆H₄CH(CH₃)₂}RuCl₂{P(O-2,6-C₆H₃F₂)₃}]₂: C, 46.4; H, 3.2; Cl, 9.8%. ¹H NMR (CDCl₃): δ 7.05 (m, 3H, H_{para}); 6.86 (m, 6H, H_{meta}); 5.86 [d, ³J(HH) = 6.15 Hz, 2H, C₆H₄]; 5.73 [d, ³J(HH) = 6.15 Hz, 2H, C₆H₄]; 3.00 [septet, ³J(HH) = 6.9 Hz, 1H, CH(CH₃)]; 2.24 (s, 3H, C₆H₄CH₃); 1.29 [d, ³J(HH) = 6.9 Hz, 6H, CH(CH₃)₂]. IR (cm⁻¹, Nujol): 1612 (w), 1518 (m), 1509 (s), 1379 (m), 1313 (m), 1298 (s), 1248 (m), 1235 (m), 1208 (m), 1194 (m), 1061 (m), 1013 (s), 1006 (m), 955 (m), 917 (s), 906 (s), 796 (w), 759 (w), 727 (w), 717 (w), 697 (w).

Preparation of Cp*RhCl₂{P(O-2,6-C₆H₃F₂)₃} (2)

A slurry of [Cp*RhCl₂]₂ (0.05 g, 0.08 mmol) and P(O-2,6-C₆H₃F₂)₃ (0.15 g, 0.36 mmol) in benzene

(50 cm³) was heated under reflux under nitrogen for 2 h. The red solution was allowed to cool and was concentrated by rotary evaporation. Petroleum ether was added until the red product, **2**, was precipitated. The solid was filtered and dried *in vacuo*. Yield 0.06 g (56%). Found: C, 46.1; H, 3.5; Cl, 9.1; P, 4.3. Calc. for { η^5 -C₅(CH₃)₅}RhCl₂{P(O-2,6-C₆H₃F₂)₃}₂: C, 46.2; H, 3.3; Cl, 9.75; P, 4.3%. ¹H NMR (CDCl₃): δ 7.03 (m, 3H, H_{para}); 6.67 (m, 6H, H_{meta}); 1.82 [d, ³J(PH) = 6.05 Hz, 15H, CH₃]. IR (cm⁻¹, Nujol): 1607 (m), 1501 (s), 1300 (s), 1247 (w), 1228 (w), 1201 (m), 1154 (w), 1064 (w), 1010 (s), 911 (s), 792 (w), 758 (s), 722 (m), 660 (w).

Preparation of *trans*-RhCl(CO){P(O-2,6-C₆H₃F₂)₃}₂ (3)

A solution of [RhCl(CO)₂]₂ (0.09 g, 0.22 mmol) and P(O-2,6-C₆H₃F₂)₃ (0.38 g, 0.91 mmol) in benzene (50 cm³) was heated under reflux under nitrogen for 2 h. The yellow solution was allowed to cool and concentrated by rotary evaporation. Petroleum ether was added until the yellow product, **3**, was precipitated. The solid was filtered, washed with petroleum ether and dried *in vacuo*. Yield 0.31 g (69%). Found: C, 43.7; H, 1.8; Cl, 3.2. Calc. for RhCl(CO){P(O-2,6-C₆H₃F₂)₃}₂: C, 44.3; H, 1.9; Cl, 3.5%. ¹H NMR (CDCl₃): δ 7.03 (m, 3H, H_{para}); 6.65 (m, 6H, H_{meta}). IR (cm⁻¹, Nujol): 2020 (s) [ν (C≡O)], 1609 (m), 1497 (s), 1480 (s), 1379 (w), 1298 (m), 1251 (w), 1197 (s), 1155 (w), 1060 (m), 1011 (s), 918 (s), 768 (s), 725 (w), 712 (w), 676 (w), 576 (w), 512 (w).

Preparation of *trans*-PtCl₂(PEt₃){P(O-2,6-C₆H₃F₂)₃} (4)

A slurry of [PtCl₂(PEt₃)₂] (0.07 g, 0.09 mmol) and P(O-2,6-C₆H₃F₂)₃ (0.15 g, 0.36 mmol) in acetone (20 cm³) was heated under reflux under nitrogen for 10 min to give a pale yellow solution. The solution was allowed to cool and concentrated by rotary evaporation. Addition of petroleum ether precipitated the product as pale yellow crystals, which were filtered, washed with petroleum ether and dried *in vacuo*. Yield 0.057 g (39%). Found: C, 35.7; H, 3.0; Cl, 8.5; P, 7.5. Calc. for PtCl₂(PEt₃){P(O-2,6-C₆H₃F₂)₃}₂: C, 35.9; H, 3.0; Cl, 8.8; P, 7.7%. ¹H NMR [(CD₃)₂CO]: δ 7.27 (m, 3H, H_{para}); 7.10 (m, 6H, H_{meta}); 1.80 [dq, ²J(PH) = 10.8 Hz, ³J(HH) = 7.6 Hz, 6H, PCH₂]; 1.05 [dt, ³J(PH) = 17.2 Hz, ³J(HH) = 7.6 Hz, 9H, CH₃]. IR (cm⁻¹, Nujol): 1611 (w), 1497 (s), 1467 (s), 1377 (s), 1301 (s), 1247 (m), 1198 (s), 1060 (w), 1014 (s), 941 (m), 912 (m), 786 (w), 769 (s), 721 (m), 682 (w), 576 (w), 519 (w).

Preparation of trans-PtCl₂{P(O-2,6-C₆H₃F₂)₃}₂ (5)

A slurry of PtCl₂ (0.32 g, 1.2 mmol) and P(O-2,6-C₆H₃F₂)₃ (1.20 g, 2.9 mmol) in ethanol (40 cm³) was heated under reflux under nitrogen for 10 min to give a cream-coloured precipitate. The mixture was stirred at room temperature for 10 min, cooled to 0°C and filtered. The solid was recrystallized from acetone to give pure **5**, as a white crystalline solid. Yield *ca* 0.25 g (19%). Found: C, 38.8; H, 1.8; Cl, 7.0; P, 5.8. Calc. for PtCl₂{P(O-2,6-C₆H₃F₂)₃}₂: C, 39.2, H, 1.7; Cl, 6.4; P, 5.6%. ¹H NMR [(CD₃)₂CO]: 7.31 (m, 6H, *H_{para}*); 7.13 (m, 12H, *H_{meta}*). IR (cm⁻¹, Nujol): 1610 (m), 1516 (sh), 1500 (s), 1482 (s), 1378 (w), 1300 (s), 1250 (m), 1200 (s), 1060 (m), 1013 (s), 931 (s), 771 (s), 711 (w), 675 (w), 575 (w), 513 (w).

Crystal structure determination

Crystals suitable for a single-crystal X-ray crystallographic study were obtained by slow evaporation of solvent from a solution of complex **4** in acetone. A crystal with dimensions 0.4 × 0.6 × 0.6 mm was glued to the end of a thin glass fibre using epoxy resin. Unit cell parameters were determined by least squares refinement of omega angles from 38 centred reflections with 10.08 < 2θ < 25.02°. Intensities of 9630 reflections in the range 4 < 2θ < 60° and -1 ≤ *h* ≤ 14, -13 ≤ *k* ≤ 14, -20 ≤ *l* ≤ 20 were measured on a Siemens P4 Diffractometer using a θ-2θ technique and graphite monochromated Mo-*K_α* radiation. No crystal decay was detected from periodically measured check reflections. The data were corrected for Lorentz and polarization effects. The reflections merged to a unique data set of 8335 reflections (*R_{int}* = 5.01%) with 5629 having *I* > 2σ(*I*) regarded as observed. An empirical absorption correction was applied to the data set, maximum and minimum transmission factors 0.9535 and 0.4879, respectively. Crystal data for **4**: [C₂₄H₂₄Cl₂F₆O₃P₂Pt], *M_r* = 802.4, triclinic, *P*₁, *a* = 10.110(2), *b* = 10.213(2), *c* = 14.590(2) Å, α = 85.410(1)°, β = 88.870(1)°, γ = 74.810(1)°, *V* = 1449.2(6) Å³, *Z* = 2, *D* = 1.839 g cm⁻³, λ(Mo-*K_α*) = 0.71073 Å, μ = 5.20 mm⁻¹, *F*(000) = 776, *T* = 293 K. Structure solution by Patterson methods and refinement were carried out using the SHELXTL-pc program package.⁵ All hydrogen atoms were included in calculated positions (C-H = 0.95 Å) with a common fixed isotropic thermal parameter (0.08 Å²). All non-hydrogen atoms were refined as anisotropic. Final *R* = 0.0454 and *R_w* = 0.0662, *w* = [σ²(*F*) + 0.0036*F*²]⁻¹, for the 343 parameters refined with largest Δ/σ 0.625.

Maximum and minimum peak heights in the difference Fourier map were +1.43 and -1.35 e Å⁻³. An analysis of the weighting scheme over |*F_o*| and sin θ/λ was satisfactory.

RESULTS AND DISCUSSION

Tris(2,6-difluorophenyl) phosphite, P(O-2,6-C₆H₃F₂)₃, reacts with the dimeric species [η⁶-1,4-CH₃C₆H₄CH(CH₃)₂]RuCl₂₂, [Cp*RhCl₂]₂ and [PtCl₂(PEt₃)]₂ with cleavage of the dimers to produce the addition products {η⁶-1,4-CH₃C₆H₄CH(CH₃)₂}RuCl₂{P(O-2,6-C₆H₃F₂)₃} (**1**), Cp*RhCl₂{P(O-2,6-C₆H₃F₂)₃} (**2**) and *trans*-PtCl₂(PEt₃){P(O-2,6-C₆H₃F₂)₃} (**4**) in moderate yields. Treatment of [RhCl(CO)₂]₂ with P(O-2,6-C₆H₃F₂)₃ results in cleavage of the dimer and displacement of one of the carbonyl ligands to give *trans*-RhCl(CO){P(O-2,6-C₆H₃F₂)₃}₂ (**3**). The reaction between PtCl₂ and P(O-2,6-C₆H₃F₂)₃ proceeds in refluxing ethanol to give *trans*-PtCl₂{P(O-2,6-C₆H₃F₂)₃}₂ (**5**). Compounds **1–5** were characterized by elemental analysis and ¹H, ¹⁹F and ³¹P NMR and IR spectroscopies. The IR spectra of compounds **1–5** are similar and show bands characteristic of P(O-2,6-C₆H₃F₂)₃ at *ca* 1610, 1300, 1200, 1010 and 760 cm⁻¹. The ¹⁹F{¹H} and ³¹P{¹H} NMR spectral data are presented in Table 1. All the complexes show a phosphorus-fluorine coupling constant, ⁴*J*(PF), of less than 7 Hz, which is significantly smaller than the value of ⁴*J*(PF) for the uncomplexed phosphite.³ These are consistent with the value of ⁴*J*(PF) for Cp*IrCl₂{P(O-2,6-C₆H₃F₂)₃}, and with the fact that values of ³*J*(PF) for uncomplexed *ortho*-fluorine-containing phenyl-

Table 1. ¹⁹F{¹H} and ³¹P{¹H} NMR spectral data for compounds **1–5**

Compound	¹⁹ F{ ¹ H} (ppm)	³¹ P{ ¹ H} (ppm)	⁴ <i>J</i> (PF) (Hz)
1 ^a	-123.32 d	+99.30	2.7
2 ^a	-124.80 d	+111.50 ^c	2.0
3 ^a	-123.97 vt	+117.60 ^d	3.7
4 ^b	-128.81 d ^e	+103.32 ^f	6.8
5 ^b	-124.08 vt	+80.71 ^g	3.4

^a Recorded in CDCl₃.

^b Recorded in (CD₃)₂CO.

^c ¹*J*(RhP) = 239.5 Hz.

^d ¹*J*(RhP) = 228.6 Hz.

^e ⁵*J*(PtF) = 19.7 Hz.

^f ¹*J*(PtP) = 4126 Hz, ²*J*(PP) = 713.4 Hz; δ(PEt₃) = +17.76, ¹*J*(PtP) = 2620.5 Hz.

^g ¹*J*(PtP) = 4762 Hz.

Table 2. Selected bond lengths (Å) and bond angles (°) for *trans*-PtCl₂(PEt₃)₂{P(OC₆H₃F₂)₃} (4)^a

Pt(1)—Cl(1)	2.296(2)	C(12)—F(12)	1.346(10)
Pt(1)—Cl(2)	2.300(3)	C(16)—F(16)	1.362(11)
Pt(1)—P(1)	2.304(3)	C(22)—F(22)	1.318(14)
Pt(1)—P(2)	2.243(2)	C(26)—F(26)	1.331(14)
P(2)—O(1)	1.604(7)	C(32)—F(32)	1.367(16)
P(2)—O(2)	1.580(5)	C(36)—F(36)	1.347(14)
P(2)—O(3)	1.601(5)		
O(1)—C(11)	1.397(9)	F(12)⋯H(13A)	2.564
O(2)—C(21)	1.389(9)	F(16)⋯F(15A)	2.530
O(3)—C(31)	1.388(9)	F(16)⋯H(33A)	2.483
P(1)—C(1)	1.868(13)	F(22)⋯H(23A)	2.599
P(1)—C(3)	1.865(9)	F(26)⋯H(25A)	2.577
P(1)—C(5)	1.864(17)	F(32)⋯H(3A)	2.503
C(1)—C(2)	1.500(17)	F(36)⋯H(35A)	2.567
C(3)—C(4)	1.435(21)		
C(5)—C(6)	1.360(35)		
Cl(1)—Pt(1)—Cl(2)	175.5(1)	O(2)—C(21)—C(22)	120.4(7)
P(1)—Pt(1)—Cl(1)	89.6(1)	O(2)—C(21)—C(26)	120.2(8)
P(1)—Pt(1)—Cl(2)	89.9(1)	C(22)—C(21)—C(26)	119.1(8)
P(2)—Pt(1)—Cl(1)	93.1(1)	C(21)—C(22)—F(22)	118.3(9)
P(2)—Pt(1)—Cl(2)	87.8(1)	C(21)—C(26)—F(26)	118.9(8)
P(1)—Pt(1)—P(2)	175.1(1)	O(3)—C(31)—C(32)	120.8(9)
Pt(1)—P(2)—O(1)	119.2(2)	O(3)—C(31)—C(36)	120.6(8)
P(2)—O(1)—C(11)	123.9(5)	C(32)—C(31)—C(36)	118.6(8)
Pt(1)—P(2)—O(2)	116.7(2)	C(31)—C(32)—F(32)	117.7(9)
P(2)—O(2)—C(21)	125.8(5)	C(31)—C(36)—F(36)	118.0(9)
Pt(1)—P(2)—O(3)	116.9(2)	Pt(1)—P(1)—C(1)	114.5(4)
P(2)—O(3)—C(31)	123.9(5)	Pt(1)—P(1)—C(3)	116.1(5)
O(1)—P(2)—O(2)	103.9(3)	Pt(1)—P(1)—C(5)	112.4(6)
O(2)—P(2)—O(3)	98.7(3)	C(1)—P(1)—C(3)	105.2(7)
O(1)—P(2)—O(3)	98.0(3)	C(1)—P(1)—C(5)	100.8(7)
O(1)—C(11)—C(12)	122.9(8)	C(3)—P(1)—C(5)	106.3(8)
O(1)—C(11)—C(16)	119.5(7)	P(1)—C(1)—C(2)	115.9(11)
C(12)—C(11)—C(16)	117.6(7)	P(1)—C(3)—C(4)	116.3(11)
C(11)—C(12)—F(12)	118.0(7)	P(1)—C(5)—C(6)	121.3(14)
C(11)—C(16)—F(16)	118.3(7)		

^aE.s.d.s are given in parentheses.

phosphines are an order of magnitude larger than those of the complexed phosphines.⁶ The ¹⁹F{¹H} NMR spectra of the monophosphite complexes **1**, **2** and **4** exhibit the ¹⁹F resonance as a doublet, whereas those of the *trans*-diphosphite complexes **3** and **5** appear as triplets. This may be explained by “virtual coupling” between phosphorus and fluorine, similar to that observed between phosphorus and carbon in the ¹³C{¹H} NMR spectra of *trans*-bisphosphite and bisphosphine complexes of palladium and platinum.^{7,8}

Comparison of the relevant ¹H and ³¹P NMR and IR spectral data of complexes **1**–**3** with those of the analogous triphenylphosphite complexes suggests that tris(2,6-difluorophenyl)phosphite

possesses similar σ-donor/π-acceptor properties to those of triphenylphosphite. The ³¹P{¹H} NMR spectrum of complex **1** may be compared to that of {η⁶-1,4-CH₃C₆H₄CH(CH₃)₂}RuCl₂{P(OPh)₃},⁹ which exhibits a singlet at δ 105.06. Thus, the effect of the fluorine atoms in the *ortho* positions of the triphenylphosphite ligand is to shift δ to slightly lower frequency. The ¹H NMR spectrum of {η⁶-1,4-CH₃C₆H₄CH(CH₃)₂}RuCl₂{P(OPh)₃} displays the hydrogen atom resonances at lower frequency to those of **1**. The greatest change is on the C₆H₄ resonances, which are shifted to higher frequency by 0.44 and 0.64 ppm on substituting P(OPh)₃ for P(O-2,6-C₆H₃F₂)₃. These shifts may be ascribed to the greater steric influence of the tris(2,6-difluo-

rophenyl)phosphite ligand, since shifts of less than 0.3 ppm are observed in the ^1H NMR spectrum of $\{\eta^6\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2\}\text{RuCl}_2(\text{PR}_3)_2$ complexes when $\text{P}(\text{OPh})_3$ is substituted for the more electron-donating PPh_3 , PMePh_2 and PMe_2Ph ligands.¹⁰ The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2** may be reasonably compared with that of $\text{Cp}^*\text{RhCl}_2\{\text{P}(\text{OPh})_3\}$,⁹ which exhibits a doublet at δ 104.24 ppm with a coupling constant, $^1J(\text{RhP})$, of 240.0 Hz. Thus, the value of δ is shifted slightly to higher frequency by the presence of fluorine atoms in the *ortho* positions of the triphenylphosphite ligand, but the value of $^1J(\text{RhP})$ is essentially unchanged. Further, the ^1H NMR spectrum of **2** exhibits a doublet assigned to the Cp^* ligand, which is shifted to higher frequency to that of $\text{Cp}^*\text{RhCl}_2\{\text{P}(\text{OPh})_3\}$ by *ca* 0.2 ppm, but the value of $J(\text{PH})$ for **2** is similar to that of 5.8 Hz for $\text{Cp}^*\text{RhCl}_2\{\text{P}(\text{OPh})_3\}$. [This coupling is presumed to be P–H coupling, not Rh–H coupling, on the basis that in the ^1H NMR spectrum of $\text{Cp}^*\text{IrCl}_2\{\text{P}(\text{OC}_6\text{H}_3\text{F}_2)_3\}$ the methyl resonance is a doublet with a coupling constant, $J(\text{PH})$, of 4.0 Hz³.] The value of $\nu(\text{C}=\text{O})$ for **3** of 2020 cm^{-1} is similar to that of 2018 cm^{-1} for *trans*- $\text{RhCl}(\text{CO})\{\text{P}(\text{OPh})_3\}_2$.¹¹ Thus, those spectral properties which are dependent upon the electronic nature of the metal atom, and therefore the phosphorus atom, i.e. $^1J(\text{RhP})$ and $\nu(\text{C}=\text{O})$, are virtually identical for complexes of $\text{P}(\text{OPh})_3$ and $\text{P}(\text{O}-2,6\text{-C}_6\text{H}_3\text{F}_2)_3$, and δ in both the ^{31}P and ^1H NMR spectra, which is dependent on the environment of the nucleus and thus not necessarily an indication of the electronic properties of that nucleus, differs slightly, but significantly, between $\text{P}(\text{OPh})_3$ and $\text{P}(\text{O}-2,6\text{-C}_6\text{H}_3\text{F}_2)_3$ complexes.

The structure of complex **4**, determined by X-ray crystallography (Fig. 1), shows square planar

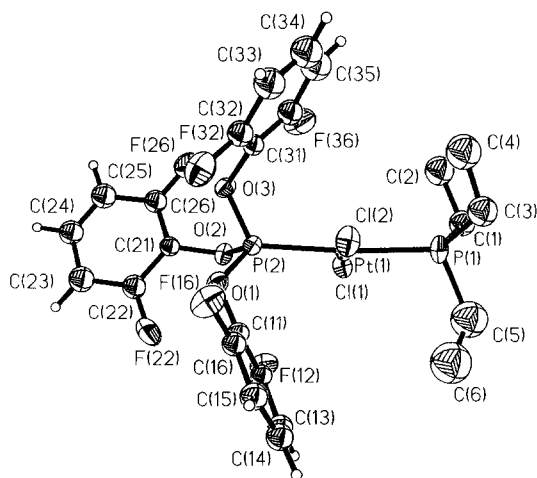


Fig. 1. Molecular structure of *trans*- $\text{PtCl}_2(\text{PET}_3)\{\text{P}(\text{OC}_6\text{H}_3\text{F}_2)_3\}$ (**4**).

geometry about the platinum atom, with a mutually *trans* disposition of the phosphine and phosphite. This contrasts with the *cis* square planar geometry adopted by $\text{PtCl}_2(\text{PET}_3)\{\text{P}(\text{OPh})_3\}$.¹² This difference may be ascribed to the greater bulk of tris(2,6-difluorophenyl)phosphite compared to that of triphenylphosphite. The Pt–Cl bond lengths are 2.296(2) and 2.300(3) Å. The Pt–P(2) bond length is 2.243(2) Å, *ca* 0.06 Å shorter than the Pt–P(1) bond length, consistent with the greater π -bonding capability of phosphites compared to those of phosphines.¹³ The geometry about the phosphite phosphorus atom may be described as pseudo-tetrahedral, with slight distortions from local C_{3v} symmetry about the Pt–P bond. The three Pt–P–O angles are also similar, ranging from 116.7(2) to 119.2(2)°. The P–O–C and O–P–O angles are similar, ranging from 123.9(5) to 125.8(5)° and 98.0(3) to 103.9(3)°, respectively. There are significant differences between the geometries adopted about the phosphite phosphorus atoms of complex **4** and $\text{Cp}^*\text{IrCl}_2\{\text{P}(\text{OC}_6\text{H}_3\text{F}_2)_3\}$.³ These may be ascribed to the greater steric requirements of the Cp^*IrCl_2 moiety compared to that of the $\text{PtCl}_2(\text{PET}_3)$ moiety. The P–O and O–C bond lengths are also slightly longer than those of $\text{Cp}^*\text{IrCl}_2\{\text{P}(\text{O}-2,6\text{-C}_6\text{H}_3\text{F}_2)_3\}$. All other bond lengths and angles of the $\text{P}(\text{O}-2,6\text{-C}_6\text{H}_3\text{F}_2)_3$ ligand of **4** are similar to those of $\text{Cp}^*\text{IrCl}_2\{\text{P}(\text{O}-2,6\text{-C}_6\text{H}_3\text{F}_2)_3\}$.

The structure of complex **4** also exhibits an unusual conformation of the triethylphosphine ligand. The absolute values for the Pt–P–C–C torsional angles (–49, 53 and 72°) are close to 60°. This is in contrast to the much more commonly found values of +60, –60 and +180° for the Pt–P–C–C torsional angles for other triethylphosphine platinum(II) complexes, as judged from a survey of such structures in the Cambridge Crystallographic Database. In addition, the complex possesses short intermolecular H···F distances between the fluorine and hydrogen atoms. In particular, the distance between F(16) and H(33A) is significantly less than the sum of the Van der Waals' radii (2.55 Å).¹⁴

The ^{31}P NMR spectrum of complex **4** is entirely consistent with a *trans* square planar geometry, and this indicates that the geometry adopted in the solid state is maintained in solution. The values of the coupling constants $^1J(\text{PtP})$ and $^2J(\text{PP})$ are typical for *trans*-phosphite and phosphine platinum dichloride complexes.^{15–19} In particular, the values of $^1J[\text{PtP}(\text{phosphite})]$ and $^2J(\text{PP})$ are similar to those of 4116 and 715 Hz respectively for *trans*- $\text{PtCl}_2(\text{P}^i\text{Bu}_3)\{\text{P}(\text{OPh})_3\}$,¹⁷ and the value of $^1J[\text{PtP}(\text{phosphine})]$ is similar to that of 2236 Hz for *trans*- $\text{PtCl}_2(\text{PET}_3)\{\text{P}(\text{OPh})_3\}$.¹⁹ There is no evidence

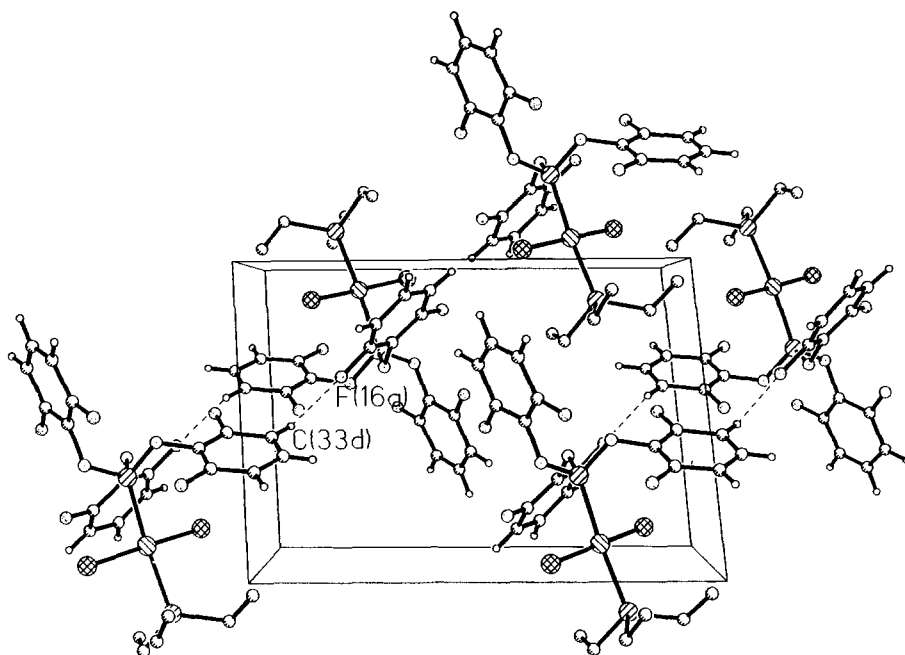


Fig. 2. Unit cell of *trans*-PtCl₂(PEt₃){P(OC₆H₃F₂)₃} (**4**) showing short H...F interactions.

for complex **4** undergoing isomerization to the *cis* isomer in solution.

The *trans* square planar geometry adopted by PtCl₂{P(OC₆H₃F₂)₃}₂ (**5**) is readily discerned from the ³¹P NMR spectral data. The values of δ and ¹*J*(PtP) are similar to those of *trans*-PtCl₂{P(O-*ortho*-tolyl)₃}₂ (74.86 ppm and 4405 Hz, respectively).¹⁵ There is no evidence for the formation of the *cis* isomer. The data suggest that P(OC₆H₃F₂)₃ exhibits similar σ -donor/ π -acceptor properties to P(O-*ortho*-tolyl)₃ in such systems. Furthermore, since PtCl₂{P(OPh)₃}₂ occurs exclusively as the *cis* isomer, and P(O-*ortho*-tolyl)₃ as both *cis* and *trans* isomers,¹⁵ it can be inferred that P(OC₆H₃F₂)₃ is more bulky than both P(OPh)₃, which has a cone angle of 128°, and P(O-*ortho*-tolyl)₃, which has a cone angle of 141°.²⁰

To further investigate the steric effects of substituting hydrogen for fluorine in the *ortho* positions of triphenylphosphite, attempts were made to synthesize the tris{tris(2,6-difluorophenyl)phosphite} complexes MCl{P(O-2,6-C₆H₃F₂)₃}₃ (M = Rh, Ir). The reaction between [(η^2 -C₂H₄)₂ RhCl]₂ and P(O-2,6-C₆H₃F₂)₃ in dichloromethane evolved ethene and yielded a yellow solid. The ³¹P{¹H} NMR spectrum, recorded in CDCl₃, indicated that this was a mixture of P(O-2,6-C₆H₃F₂)₃ and a rhodium phosphite complex. This spectrum exhibited a doublet of triplets of multiplets centred at δ 118.26 ppm, with coupling constants of 305.1 and 51.25 Hz, and a doublet of doublet of multiplets centred at δ 112.19 ppm, with coupling constants of 238.4 and

51.25 Hz. This is similar to the ³¹P{¹H} NMR spectrum of RhCl{P(OPh)₃}₃,²¹ which exhibits a doublet of triplets at δ 118.9 ppm, with coupling constants of 285.0 and 52.7 Hz, and a doublet of doublets at δ 111.9 ppm, with coupling constants of 224.0 and 52.7 Hz. The ¹⁹F{¹H} NMR spectrum showed the presence of a large amount of P(O-2,6-C₆H₃F₂)₃ (δ -126.50 ppm) and two broad signals at δ -122.27 and -123.14 ppm in a 1:2 ratio. These data are entirely consistent with the formulation RhCl{P(O-2,6-C₆H₃F₂)₃}₃ and a square planar geometry. The reaction between [(η^2 -C₈H₁₄)₂ IrCl]₂ and an excess of P(O-2,6-C₆H₃F₂)₃ in benzene yielded an orange solid. The ³¹P{¹H} NMR spectrum showed the presence of P(O-2,6-C₆H₃F₂)₃ and also a doublet of multiplets and a triplet of multiplets centred at δ 100.57 and 81.28 ppm, respectively, with a mutual coupling constant of 51.5 Hz. The ¹⁹F{¹H} NMR spectrum showed P(O-2,6-C₆H₃F₂)₃ and two multiplets at δ -121.95 and -122.84 ppm in a 1:2 ratio. These data are consistent with the formulation IrCl{P(O-2,6-C₆H₃F₂)₃}₃ and a square planar geometry. Attempts to purify these products were unsuccessful. Further, performing the reactions in a 1:6 (dimer: phosphite) stoichiometry gave unreacted metal complex, or decomposition product, and a small amount of MCl{P(O-2,6-C₆H₃F₂)₃}₃ with a large amount of phosphite. Thus, it appears that these complexes may only be stable in the presence of an excess of P(O-2,6-C₆H₃F₂)₃. The similarity of the ³¹P{¹H} NMR spectra of RhCl{P(O-2,6-

$\text{C}_6\text{H}_3\text{F}_2\text{)}_3\}$ and $\text{RhCl}\{\text{P}(\text{OPh})_3\}_3$ strongly suggests that the formulation of the former is correct. However, there is no triphenylphosphite analogue with which to compare $\text{IrCl}\{\text{P}(\text{O}-2,6\text{-C}_6\text{H}_3\text{F}_2)_3\}_3$. $\text{IrCl}\{\text{P}(\text{OPh})_3\}_3$ is postulated as an intermediate in the synthesis of $\text{IrHCl}\{\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\}\{\text{P}(\text{OPh})_3\}_2$,²² but undergoes facile *ortho*-metalation and cannot be isolated. The presence of fluorine atoms in the *ortho* positions of the triphenylphosphite evidently prevents *ortho*-metalation occurring in $\text{IrCl}\{\text{P}(\text{OC}_6\text{H}_3\text{F}_2)_3\}_3$.

In summary, a number of platinum group metal complexes of the *ortho*-fluorine-containing phosphite, tris(2,6-difluorophenyl)phosphite, have been synthesized. NMR and IR spectroscopic data indicate that the donor/acceptor properties of $\text{P}(\text{OC}_6\text{H}_3\text{F}_2)_3$ are similar to those of $\text{P}(\text{OPh})_3$. However, structural studies reveal that $\text{P}(\text{OC}_6\text{H}_3\text{F}_2)_3$ is considerably more bulky than $\text{P}(\text{OPh})_3$, which can be ascribed solely to the presence of the *ortho*-fluorine atoms. These properties can lead to metal complexes adopting unusual geometries. Thus, substitution of fluorine for hydrogen in the *ortho* positions of triphenylphosphite produces a negligible electronic effect, but a significant steric effect on its complexes with transition metals.

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