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trans-Bis(diethylphenylphosphine)(difluorophosphonato)chloroplatinum(II)

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Abstract. $(Et_2PPh)_2PtCl(PF_2O)$, $PtClP_3F_2OC_{20}H_{30}$, orthorhombic, $P2_12_12_1$, $a = 22.062$ (3), $b = 14.801$ (2), $c = 7.541$ (1) Å, $M = 647.92$, $Z = 4$, $D_x = 1.75$ g cm^{-3}. The coordination of platinum is square-planar with the diethylphenylphosphine ligands in positions *trans* to one another. The molecular structure confirms that the difluorophosphonato group is bonded to the metal through the phosphorus rather than the oxygen atom.

Introduction. Unit-cell dimensions were determined from measurements of 17 high 2θ angle reflexions with Mo $K\alpha_1$ ($\lambda = 0.70926$ Å) radiation. The intensities, from a prismatic crystal sealed in a Lindemann glass capillary and with approximate dimensions $0.01 \times 0.008 \times 0.01$ cm, were collected on a Stoe 4-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation. Measurements were carried out with standard background counts and θ–2θ scan of fixed range for $2\theta \le 45°$. Three standard reflexions, which were monitored at regular intervals, did not display any significant variations due to crystal deterioration. Of the 1882 reflexions which were recorded, 81 were rejected because the peak count was less than the background count. Lorentz and polarization but no absorption ($\mu_{\text{Mo}K\alpha} = 63.1$ cm^{-1}) corrections were applied.

The space group $P2_12_12_1$ was unambiguously indicated by the observed systematic absences $h00$ (h odd), $0k0$ (k odd) and $00l$ (l odd). A Patterson synthesis was interpreted to yield a self-consistent set of coordinates for the platinum, and the remaining atoms, except for hydrogen, were located from subsequent difference syntheses. In the final cycles of the full-matrix least-squares refinement, adoption of anisotropic tem-

perature factors for the fluorine and oxygen atoms, in addition to those for platinum, chlorine and phosphorus, led to an improvement in the generalized index

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å $\times 10^3$)

	x	y	z	U
Pt	1285 (1)	499 (1)	62 (2)	*
Cl	1183 (3)	−925 (4)	1456 (10)	*
P(1)	2329 (2)	467 (4)	445 (8)	*
P(2)	231 (2)	431 (4)	−236 (9)	*
P(3)	1336 (3)	1826 (4)	−1242 (9)	*
F(1)	941 (6)	2514 (8)	−263 (26)	*
F(2)	1961 (6)	2262 (9)	−1190 (22)	*
O	1102 (8)	1869 (11)	−3066 (22)	*
C(11)	2623 (10)	1368 (14)	1866 (30)	50 (6)
C(12)	3171 (13)	1800 (20)	1503 (41)	83 (9)
C(13)	3433 (13)	2485 (20)	2748 (41)	84 (9)
C(14)	3057 (12)	2666 (18)	4161 (35)	72 (8)
C(15)	2499 (12)	2274 (16)	4471 (35)	75 (8)
C(16)	2265 (10)	1614 (16)	3317 (33)	58 (7)
C(21)	2600 (10)	−568 (17)	1556 (32)	58 (6)
C(22)	3284 (12)	−554 (20)	1921 (38)	85 (9)
C(31)	2764 (11)	534 (18)	−1629 (35)	70 (7)
C(32)	2515 (14)	−216 (20)	−2976 (43)	91 (10)
C(41)	18 (9)	−515 (15)	−1670 (27)	44 (5)
C(42)	342 (10)	−655 (15)	−3113 (31)	54 (6)
C(43)	212 (11)	−1385 (17)	−4296 (32)	65 (7)
C(44)	−319 (12)	−1922 (18)	−3913 (39)	74 (8)
C(45)	−659 (11)	−1769 (17)	−2421 (36)	70 (8)
C(46)	−488 (11)	−1068 (16)	−1247 (34)	60 (7)
C(51)	−185 (11)	1402 (16)	−1192 (33)	58 (7)
C(52)	−862 (12)	1235 (18)	−1420 (38)	77 (8)
C(61)	−133 (11)	262 (16)	1966 (33)	61 (7)
C(62)	74 (14)	1022 (19)	3219 (42)	89 (10)

* Anisotropic temperature factor components are listed in Table 2.

$R_G = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$ which was significant at the 0·005 level (Hamilton, 1965). The possibility of ambiguity in the configuration of the PF_2O^- ligand could be discounted both on grounds of the similarity of the P–F and P–O bond lengths with those in POF_3 (Moritani, Kuchitsu & Morino, 1971) and because exchange of oxygen and fluorine scattering factors between the light atoms attached to P(3) led to unrealistic anisotropic temperature-factor components for the false fluorine. Introduction of anisotropic temperature factors for the carbon atoms was not justified. The final weighted residual $R_w = \sum w^{1/2}\Delta/\sum w^{1/2}F_o$ was 0·050 for the 1801 unique reflexions with a corresponding unweighted R of 0·054. The weights adopted were those obtained from the counting statistics where a standard deviation $\sigma(I) = [N_S + N_B + (0\cdot01N_P)^2]^{1/2}$ was assigned to each net intensity I, N_S being the gross count, N_B the background count corrected to cover the same time span as N_S, and $N_P = N_S - N_B$. Complex neutral-atom scattering factors (Cromer, 1965; Cromer & Waber, 1965) were employed. The final atom coordinates and isotropic temperature factors are listed in Table 1, with the relevant anisotropic temperature factors in Table 2. The full covariance matrix was implemented in the estimation of the bond lengths and angles presented in Tables 3 and 4. Fig. 1 gives the atomic numbering in the molecule and Fig. 2 shows a projection of the structure perpendicular to [001].*

Discussion. Treatment of trans-$(Et_2PPh)_2PtCl_2$ with allyldifluorophosphite, $C_3H_5OPF_2$, in benzene at 20°C, was found to yield the covalent product $(Et_2PPh)_2$–$PtCl(PF_2O)$ and C_3H_5Cl in quantitative yield (Grosse & Schmutzler, 1974). The crystal structure determination confirms spectroscopic evidence that the difluorophosphonato group PF_2O^-, which is isoelectronic with PF_3, is bonded to platinum through the phosphorus rather than the oxygen atom. The profound effect on bond lengths which the structural trans-influence plays in square-planar platinum complexes is by now well documented. In particular, studies on three molecules in which the PMe_3, PEt_3 and PEt_2Ph groups respectively are trans to the Cl^- ligand have displayed Pt–P bond lengths between 2·239 (6) and 2·256 (8) Å, in contrast to values in the range 2·268 (8) to 2·315 (4) Å obtained when alkyl- or mixed alkylarylphosphine ligands are found trans to one another (Muir, 1973).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30355 (11pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
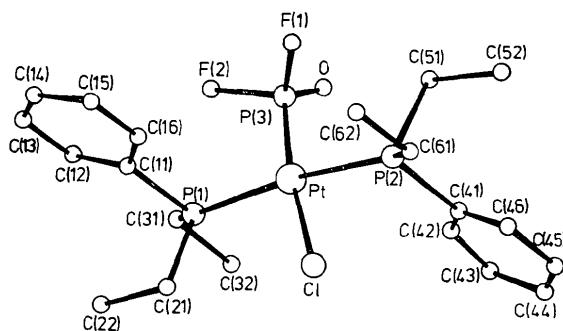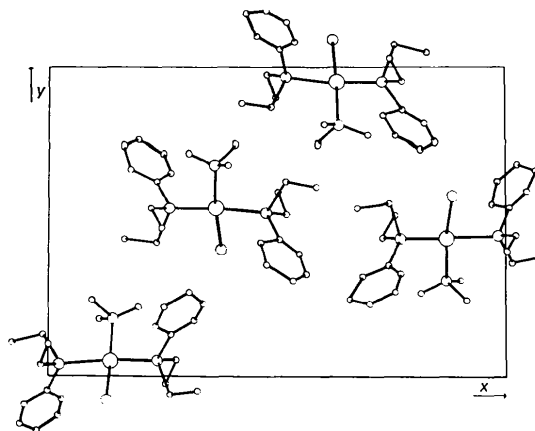
Table 2. *Anisotropic temperature factors* ($\text{Å}^2 \times 10^3$)

The anisotropic temperature factor takes the form:
exp $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	44 (1)	29 (1)	45 (1)	3 (1)	−1 (1)	−2 (1)
Cl	55 (4)	46 (3)	108 (6)	27 (4)	−2 (4)	−3 (3)
P(1)	46 (3)	44 (3)	47 (4)	−8 (4)	−2 (3)	−2 (3)
P(2)	44 (3)	42 (3)	42 (4)	5 (4)	2 (3)	−2 (3)
P(3)	67 (4)	41 (3)	68 (5)	15 (3)	3 (4)	−4 (4)
F(1)	109 (10)	44 (7)	114 (13)	30 (11)	29 (13)	8 (7)
F(2)	79 (10)	59 (9)	113 (13)	31 (9)	−8 (10)	−15 (8)
O	109 (15)	77 (12)	59 (11)	28 (10)	−24 (11)	−9 (11)

Fig. 1. Atom numbering in the molecule.

Table 3. *Bond lengths* (Å)

Pt——Cl	2·366 (6)	Pt——P(1)	2·322 (6)
Pt——P(2)	2·338 (5)	Pt——P(3)	2·199 (6)
P(3)—F(1)	1·530 (15)	P(3)—F(2)	1·523 (15)
P(3)—O	1·471 (17)	P(1)—C(11)	1·83 (2)
P(1)—C(21)	1·85 (2)	P(1)—C(31)	1·84 (3)
P(2)—C(41)	1·83 (2)	P(2)—C(51)	1·85 (2)
P(2)—C(61)	1·86 (2)	C(21)–C(22)	1·54 (3)
C(31)–C(32)	1·60 (4)	C(51)–C(52)	1·52 (3)
C(61)–C(62)	1·54 (4)	C(11)–C(12)	1·40 (3)
C(12)–C(13)	1·50 (4)	C(13)–C(14)	1·38 (4)
C(14)–C(15)	1·38 (3)	C(15)–C(16)	1·41 (3)
C(16)–C(11)	1·40 (3)	C(41)–C(42)	1·32 (3)
C(42)–C(43)	1·43 (3)	C(43)–C(44)	1·44 (3)
C(44)–C(45)	1·37 (4)	C(45)–C(46)	1·41 (3)
C(46)–C(41)	1·42 (3)		

Fig. 2. Projection of the structure perpendicular to [001].

Table 4. *Bond angles* (°)

Cl——Pt——P(1)	91·2 (2)	Cl——Pt——P(2)	84·9 (2)
P(1)—Pt——P(3)	91·3 (3)	P(2)—Pt——P(3)	92·7 (2)
Pt——P(3)—F(1)	110·5 (6)	Pt——P(3)—F(2)	114·4 (6)
Pt——P(3)—O	116·0 (8)	Pt——P(1)—C(11)	114·2 (8)
Pt——P(1)—C(21)	113·2 (7)	Pt——P(1)—C(31)	114·3 (8)
Pt——P(2)—C(41)	110·1 (8)	Pt——P(2)—C(51)	119·8 (8)
Pt——P(2)—C(61)	110·4 (8)	P(1)—C(21)—C(22)	113 (2)
P(1)—C(31)—C(32)	109 (2)	P(2)—C(51)—C(52)	114 (2)
P(2)—C(61)—C(62)	109 (2)	C(11)—C(12)—C(13)	122 (3)
C(12)—C(13)—C(14)	113 (3)	C(13)—C(14)—C(15)	126 (3)
C(14)—C(15)—C(16)	121 (3)	C(15)—C(16)—C(11)	117 (2)
C(16)—C(11)—C(12)	122 (2)	C(41)—C(42)—C(43)	122 (2)
C(42)—C(43)—C(44)	117 (2)	C(43)—C(44)—C(45)	121 (3)
C(44)—C(45)—C(46)	119 (3)	C(45)—C(46)—C(41)	119 (2)
C(46)—C(41)—C(42)	122 (2)		

However, in the case of the title compound, an even more dramatic shortening of the Pt–P(F$_2$O) bond length opposite the Cl$^-$ ligand to 2·199 (6) Å is observed. This suggests the existence of an enhanced degree of π-bonded back-donation of platinum *d*-electrons into the empty phosphorus 3*d* orbitals, the acceptor properties of which are augmented in this case as a result of the lowering of their energy caused by the highly electronegative fluorine atoms. The Pt–Cl bond length of 2·366 (6) and the two Pt–P(Et$_2$Ph) bond lengths of 2·322 (6) and 2·338 (5) Å are, in contrast, very similar to the values for analogous compounds quoted above. It is interesting to note that the values of 1·530 (15) and 1·523 (15) obtained for the P–F bond lengths are very similar to the value of 1·524 (1) Å observed in the electron diffraction study of POF$_3$, a phenomenon identical to that observed in PF$_3$ coordination complexes (Nixon, 1973). The P–O bond length of 1·471 (17) is somewhat longer, albeit not significantly, than the value of 1·436 (2) Å observed in POF$_3$.

There are no particularly interesting short non-bonded distances.

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