

Acta Cryst. (1996). **C52**, 2463–2464***cis*-Dichloro(triethylphosphine-*P*)[tris(2,6-difluorophenyl)phosphite-*P*]platinum(II)**JOHN FAWCETT,^{a*} JOHN H. HOLLOWAY,^a ERIC G. HOPE,^a
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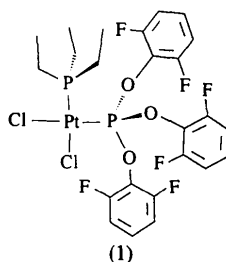
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Abstract

In *cis*-[PtCl₂(C₁₈H₉F₆O₃P)(C₆H₁₅P)], the Pt—P and Pt—Cl distances are comparable to those of the triphenylphosphite analogue, while the P—Pt—P angle is *ca* 5° larger.

Comment

It has been found that the presence of F atoms in the *ortho* positions of triphenylphosphite has a negligible electronic effect but a considerable steric effect on the properties of the phosphite and its transition metal complexes (Holloway *et al.*, 1993; Coleman *et al.*, 1995). A single-crystal X-ray diffraction study of *cis*-dichloro-(triethylphosphine-*P*)[tris(2,6-difluorophenyl)phosphite-*P*]platinum(II), (1), confirms that there is a negligible difference between the electronic properties of the P atoms of triphenylphosphite and tris(2,6-difluorophenyl)-phosphite.



The Pt—P1 distance of 2.1772(14) Å in (1) (Fig. 1) is comparable to that of 2.182(2) Å for the Pt—P(phosphite) distance of *cis*-dichloro(triethylphosphine)(triphenylphosphite)platinum(II) [(2); Cauldwell, Manojlovic-Muir & Muir, 1977]. The Pt—P(phosphine) [2.274(2) *cf.* 2.269(1) Å], Pt—Cl(*trans* to phosphite) [2.3248(14) *cf.* 2.344(1) Å] and Pt—Cl(*trans* to phosphine) [2.3616(14) *cf.* 2.355(2) Å] distances are similar for the fluorine-containing and perptio complexes. It is thus evident that the greater bulk of the tris(2,6-difluorophenyl)phosphite ligand has no

effect on the Pt—P and Pt—Cl distances. The P—Pt—P angle of 103.14(6)° for compound (1) is, however, *ca* 5° greater than that of compound (2), indicative of the greater steric demands of the tris(2,6-difluorophenyl)-phosphite ligand.

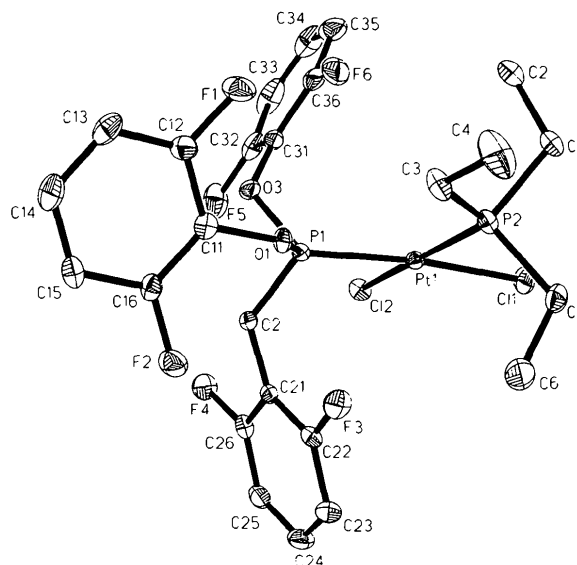


Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme and 30% displacement ellipsoids. H atoms have been omitted for clarity.

The coordination about both P atoms is distorted tetrahedral. The Pt—P—O, O—P—O and P—O—C angles are comparable to those found in *trans*-dichloro-(triethylphosphine)[tris(2,6-difluorophenyl)phosphite]-platinum(II) (Coleman *et al.*, 1995). The Pt—P—O angles are slightly larger than those of the triphenylphosphite analogue, presumably due to the greater bulk of tris(2,6-difluorophenyl)phosphite. The phosphine P—C distances and Pt—P—C angles are comparable to those of the triphenylphosphite analogue, but the P—C distances are *ca* 0.04 Å shorter than for the *trans* isomer.

Experimental

The title complex was prepared by allowing a solution of *trans*-[PtCl₂{P(C₂H₅)₃}{P(O-2,6-C₆H₃F₂)₃}] (Coleman *et al.*, 1995) in acetone to stand at room temperature for several weeks. Evaporation of the solvent afforded colourless crystals of the *cis* isomer and pale yellow crystals of the *trans* isomer, which were separated manually. ¹H NMR (CDCl₃): δ 7.13 (*m*, 3H, *para*-H), 6.95 (*m*, 6H, *meta*-H), 2.29 (*m*, 6H, CH₂), 1.28 (*dt*, ³*J*_{PH} = 17.95, ³*J*_{HH} = 7.6 Hz, 9H, CH₃). ¹⁹F NMR (CDCl₃): δ -124.02 (*d*, ⁴*J*_{PF} = 5.5, ⁵*J*_{PF} = 29.7 Hz). ³¹P{¹H}: δ 69.47 [*dm*, ²*J*_{PP} = 19.0 Hz, ¹*J*_{PP} = 6389 Hz, P(OC₆H₃F₂)₃], 17.32 [*d*, ²*J*_{PP} = 19.0 Hz, ¹*J*_{PP} = 3187 Hz, P(CH₂CH₃)₃]. FAB-MS (*m/z*) 802 (*M*⁺), 767 [(*M*—Cl)⁺].

Crystal data

[PtCl₂(C₁₈H₉F₆O₃P)-
(C₆H₁₅P)]

M_r = 802.36

Monoclinic

*P*2₁/*c*

a = 9.709 (2) Å

b = 15.482 (2) Å

c = 18.267 (3) Å

β = 96.20 (1)°

V = 2729.7 (8) Å³

Z = 4

D_x = 1.952 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 27
reflections

θ = 5.2–12.9°

μ = 5.520 mm⁻¹

T = 293 (2) K

Block

0.53 × 0.26 × 0.16 mm

Colourless

Data collection

Siemens *P4* diffractometer

ω scans

Absorption correction:

semi-empirical from

ψ scans (*XEMP* in

SHELXTL/PC; Sheldrick,
1990)

T_{min} = 0.169, *T_{max}* =
0.307

5259 measured reflections

4036 independent reflections

3349 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0297

θ_{max} = 23.50°

h = −1 → 10

k = −1 → 17

l = −20 → 20

3 standard reflections

monitored every 100

reflections

intensity decay: <2%

Refinement

Refinement on *F*²

R(*F*) = 0.0293

wR(*F*²) = 0.0669

S = 1.043

4035 reflections

352 parameters

H atoms riding with refined

U_{iso}
w = 1/[σ²(*F_o*²) + (0.0238*P*)²
+ 0.0164*P*]
where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.262

Δρ_{max} = 0.602 e Å⁻³

Δρ_{min} = −0.584 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Pt1	0.19555 (2)	0.187793 (13)	0.193358 (11)	0.01968 (8)
P1	0.32510 (14)	0.19229 (9)	0.29829 (7)	0.0192 (3)
P2	0.3516 (2)	0.16848 (10)	0.11047 (8)	0.0260 (4)
Cl1	0.0306 (2)	0.17799 (10)	0.09153 (8)	0.0356 (4)
Cl2	0.01502 (14)	0.21799 (10)	0.26642 (8)	0.0271 (3)
F1	0.6713 (4)	0.2919 (2)	0.3088 (2)	0.0467 (10)
F2	0.5037 (4)	0.0431 (2)	0.4150 (2)	0.0408 (9)
F3	0.3367 (4)	−0.0017 (2)	0.2775 (2)	0.0400 (9)
F4	0.0615 (4)	0.1232 (2)	0.4424 (2)	0.0395 (9)
F5	0.1241 (4)	0.3503 (3)	0.4053 (2)	0.0560 (11)
F6	0.4432 (4)	0.3698 (3)	0.2331 (2)	0.0516 (11)
O1	0.4834 (4)	0.1630 (2)	0.3003 (2)	0.0236 (9)
O2	0.2738 (4)	0.1374 (2)	0.3641 (2)	0.0212 (9)
O3	0.3414 (4)	0.2817 (2)	0.3425 (2)	0.0266 (9)
C1	0.3313 (7)	0.2513 (4)	0.0382 (3)	0.0317 (15)
C2	0.3529 (8)	0.3436 (4)	0.0657 (4)	0.045 (2)
C3	0.5344 (6)	0.1690 (4)	0.1433 (3)	0.036 (2)
C4	0.6332 (8)	0.1555 (6)	0.0849 (4)	0.068 (3)
C5	0.3233 (7)	0.0688 (4)	0.0585 (3)	0.037 (2)

C6	0.3440 (10)	−0.0132 (4)	0.1023 (4)	0.065 (3)
Cl1	0.5806 (6)	0.1706 (4)	0.3625 (3)	0.0261 (14)
Cl2	0.6786 (6)	0.2357 (4)	0.3651 (3)	0.0327 (15)
C13	0.7821 (6)	0.2426 (4)	0.4221 (4)	0.040 (2)
C14	0.7860 (7)	0.1843 (5)	0.4785 (4)	0.044 (2)
C15	0.6939 (6)	0.1175 (4)	0.4773 (3)	0.035 (2)
C16	0.5929 (6)	0.1102 (4)	0.4182 (3)	0.0272 (14)
C21	0.1971 (6)	0.0624 (4)	0.3585 (3)	0.0225 (13)
C22	0.2280 (6)	−0.0080 (4)	0.3164 (3)	0.0286 (14)
C23	0.1500 (7)	−0.0827 (4)	0.3146 (3)	0.039 (2)
C24	0.0390 (7)	−0.0868 (4)	0.3562 (4)	0.042 (2)
C25	0.0074 (7)	−0.0179 (4)	0.3994 (3)	0.035 (2)
C26	0.0863 (6)	0.0554 (4)	0.3998 (3)	0.0289 (14)
C31	0.2823 (6)	0.3592 (4)	0.3185 (3)	0.0263 (14)
C32	0.1766 (7)	0.3951 (4)	0.3521 (4)	0.039 (2)
C33	0.1255 (8)	0.4758 (5)	0.3325 (5)	0.060 (2)
C34	0.1834 (10)	0.5193 (5)	0.2770 (5)	0.070 (3)
C35	0.2897 (9)	0.4854 (5)	0.2420 (5)	0.063 (3)
C36	0.3377 (7)	0.4059 (4)	0.2643 (4)	0.039 (2)

Table 2. Selected geometric parameters (Å, °)

Pt1—P1	2.1772 (14)	P2—C3	1.812 (6)
Pt1—P2	2.274 (2)	P2—C5	1.816 (6)
Pt1—Cl1	2.3248 (14)	P2—C1	1.835 (6)
Pt1—Cl2	2.3616 (14)	O1—C11	1.401 (6)
P1—O2	1.596 (4)	O2—C21	1.376 (6)
P1—O1	1.599 (4)	O3—C31	1.381 (7)
P1—O3	1.602 (4)		
P1—Pt1—P2	103.14 (6)	O2—P1—Pt1	116.65 (15)
P1—Pt1—Cl1	171.52 (5)	O1—P1—Pt1	118.28 (15)
P2—Pt1—Cl1	84.81 (6)	O3—P1—Pt1	119.2 (2)
P1—Pt1—Cl2	83.66 (5)	C3—P2—Pt1	118.6 (2)
P2—Pt1—Cl2	172.16 (5)	C5—P2—Pt1	112.7 (2)
Cl1—Pt1—Cl2	88.61 (5)	C1—P2—Pt1	111.1 (2)
O2—P1—O1	102.0 (2)	C11—O1—P1	123.9 (3)
O2—P1—O3	95.9 (2)	C21—O2—P1	127.1 (3)
O1—P1—O3	101.0 (2)	C31—O3—P1	125.1 (3)

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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