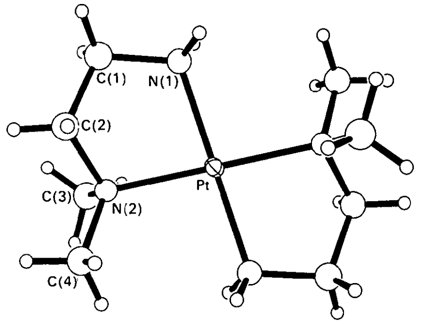

Fig. 1. Structure of [Pt(dmen)$_2$]I$_2$ showing the numbering used.

ligand backbone for [Pt(dmen)$_2$]$^{2+}$ is $-44·1$ (6)° (for the ligand coordinates as given) compared with that calculated for [Pt(dmen)Cl$_2$], $+54·9$ (8)°. However, it should be noted that as the absolute configuration for [Pt(dmen)Cl$_2$] was not determined (it crystallizes in space group $P2_1$) the sign of the torsion angle for this compound has little significance.

The deviations of the C atoms from the ligand plane through Pt, N(1) and N(2) are C(1) $-0·110$ (6), C(2) $-0·660$ (6), C(3) 1·420 (7) and C(4) $-0·756$ (6) Å. They indicate that the ligands in this complex have the asymmetric skew conformation (λ and δ, as required by the centre of symmetry) following the nomenclature of Hawkins (1971), and that C(3) tends to be axial with C(4) tending to be equatorial. The ligand in [Pt(dmen)Cl$_2$] (Melanson *et al.*, 1987) has the symmetric skew conformation, with the deviations of the C atoms from the Pt, N(1) and N(2) plane being C(1) 0·38 (2), C(2) $-0·31$ (2), C(3) 1·35 (2) and C(4) $-1·05$ (2) Å, with C(3) and C(4) approximately equally above and below the Pt-N plane.

The shortest intermolecular distance in [Pt(dmen)$_2$]$^{2+}$, that between N(1) and the I ion [3·594 (5) Å], and the angles subtended at HN(1) and HN(2) by N(1) and the I ion [155·0 (3) and 157·5 (3)° respectively], indicate possible hydrogen bonding.

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[Bis(diphenylphosphino)methane-*P*,*P*′](chloro)(pentafluorophenyl)platinum(II): PtCl(dppm)C$_6$F$_5$

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Abstract. C$_{31}$H$_{22}$ClF$_5$P$_2$Pt, $M_r = 782·0$, triclinic, $P\bar{1}$, $a = 10·119$ (1), $b = 15·676$ (2), $c = 9·934$ (2) Å, $\alpha = 105·64$ (5), $\beta = 112·36$ (1), $\gamma = 84·57$ (1)°, $V = 1403$ (2) Å^3, $Z = 2$, $D_x = 1·851$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 52·67$ cm^{-1}, $F(000) = 756$, $T = 293$ (1) K, $R = 0·022$ for 4107 observed reflections. In the monomeric complex, the approximately square-planar geometry about the Pt atom is defined by a Cl atom [Pt—Cl 2·360 (1) Å], a C atom of the pentafluoroaryl group [Pt—C 2·078 (4) Å] and two P atoms derived from a chelating Ph$_2$PCH$_2$PPh$_2$ ligand [Pt—P 2·224 (1) and 2·295 (1) Å; P—Pt—P 73·9 (1)°]

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such that the P atom forming the shorter Pt—P bond is *trans* to the Cl atom.

Introduction. The PtCl(dppm)C_6F_5 complex was prepared as part of a continuing, systematic study of diene displacement reactions of the previously reported (Deacon, Gatehouse & Nelson-Reed, 1989) PtCl(diene)*R* complexes (*R* = polyfluorophenyl). The structure determination of the title compound was undertaken to resolve the structural ambiguity as to whether the dppm ligand is chelating the Pt centre leading to a monomeric species or bidentate bridging leading to a dimeric (or polymeric) structure.

Experimental. PtCl(dppm)C_6F_5 was prepared by reaction between PtCl(hex)C_6F_5 (hex = hexa-1,5-diene) with dppm in CH_2Cl_2 (Deacon & Nelson, 1990); full details will be given in a later paper. Crystals were obtained by the slow evaporation of a $CDCl_3$ solution of the compound; m.p. 526–529 K. Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/*A* computer, graphite-monochromated Mo $K\alpha$ radiation; ω–2θ scan technique. Cell parameters by least squares on 25 reflections ($10 \leq \theta \leq 14°$) (de Boer & Duisenberg, 1984) on a crystal 0·14 × 0·08 × 0·50 mm. Analytical absorption correction applied; max. and min. transmission factors 0·603 and 0·256 (Sheldrick, 1976). 5045 reflections ($1·5 \leq \theta \leq 25·0°$) measured in the range $-12 \leq h < 12$, $-18 \leq k \leq 18$, $-11 \leq l < 1$. No significant variation in the net intensity of one reference reflection ($\bar{3}\bar{2}5$) measured every 7200 s. 4908 unique reflections ($R_{\text{merge}} = 0·017$) and 4107 satisfied $I \geq 2·5\sigma(I)$. Structure solved by Patterson method, full-matrix least-squares refinement on 362 parameters based on *F* (*SHELX*76; Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms and H atoms included at their calculated positions. At convergence $R = 0·022$, $wR = 0·024$, $w = [\sigma^2(F) + 0·001|F|^2]^{-1}$, $S = 0·77$, $(\Delta/\sigma)_{\max} \leq 0·001$, $\Delta\rho_{\max} = 0·56$, $\Delta\rho_{\min} = -0·89$ e Å^{-3}; no extinction correction applied. Scattering factors for neutral Pt corrected for f' and f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149) and for the remaining atoms as incorporated in *SHELX*76 (Sheldrick, 1976). All calculations on SUN4/280 computer system. Atomic parameters are given in Table 1, selected interatomic parameters in Table 2* and numbering scheme used is shown in Fig. 1 which was drawn with *ORTEP* (Johnson, 1971) at 25% probability levels.

Table 1. *Fractional atomic coordinates and* B_{eq} *values* (Å^2)

$$B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	*y*	*z*	B_{eq}
Pt	0·32665 (1)	0·25611 (1)	0·20985 (2)	2·31
Cl	0·1015 (1)	0·2752 (1)	0·2332 (1)	3·83
P(1)	0·2734 (1)	0·3063 (1)	−0·0015 (1)	2·46
P(2)	0·5323 (1)	0·2600 (1)	0·1791 (1)	2·44
F(2)	0·2360 (3)	0·0783 (2)	0·2525 (3)	3·95
F(3)	0·3123 (3)	0·0071 (2)	0·4877 (3)	4·73
F(4)	0·5243 (3)	0·0821 (2)	0·7511 (3)	5·04
F(5)	0·6516 (3)	0·2342 (2)	0·7803 (3)	4·46
F(6)	0·5675 (3)	0·3122 (2)	0·5527 (3)	4·30
C(1)	0·3987 (4)	0·1993 (3)	0·3913 (3)	2·77
C(2)	0·3388 (5)	0·1204 (3)	0·3823 (5)	2·93
C(3)	0·3767 (5)	0·0818 (3)	0·4999 (5)	3·29
C(4)	0·4836 (5)	0·1195 (3)	0·6350 (5)	3·49
C(5)	0·5474 (5)	0·1969 (3)	0·6494 (4)	3·00
C(6)	0·5030 (4)	0·2346 (3)	0·5281 (5)	3·01
C(11)	0·4568 (4)	0·2903 (3)	−0·0032 (4)	2·97
C(111)	0·1516 (4)	0·2400 (3)	−0·1784 (5)	2·65
C(112)	0·1678 (5)	0·2301 (3)	−0·3158 (5)	3·65
C(113)	0·0710 (6)	0·1790 (4)	−0·4470 (6)	4·52
C(114)	−0·0394 (6)	0·1370 (4)	−0·4429 (6)	4·30
C(115)	−0·0569 (6)	0·1469 (4)	−0·3092 (6)	4·63
C(116)	0·0395 (5)	0·1982 (3)	−0·1766 (5)	3·47
C(121)	0·2276 (4)	0·4212 (3)	0·0014 (4)	2·68
C(122)	0·2197 (5)	0·4564 (3)	−0·1159 (6)	3·95
C(123)	0·1842 (6)	0·5445 (3)	−0·1106 (6)	4·45
C(124)	0·1598 (5)	0·5975 (3)	0·0127 (6)	3·71
C(125)	0·1682 (6)	0·5632 (3)	0·1294 (6)	4·15
C(126)	0·2026 (5)	0·4750 (3)	0·1233 (5)	3·24
C(211)	0·6508 (4)	0·3498 (3)	0·3120 (4)	2·71
C(212)	0·5984 (5)	0·4358 (3)	0·3335 (6)	3·89
C(213)	0·6859 (6)	0·5053 (3)	0·4372 (6)	4·54
C(214)	0·8259 (6)	0·4906 (4)	0·5194 (5)	4·29
C(215)	0·8782 (5)	0·4066 (4)	0·4998 (5)	4·11
C(216)	0·7931 (5)	0·3366 (3)	0·3970 (5)	3·37
C(221)	0·6412 (4)	0·1630 (3)	0·1536 (4)	2·72
C(222)	0·7527 (5)	0·1675 (3)	0·1061 (6)	3·95
C(223)	0·8343 (6)	0·0940 (3)	0·0813 (7)	4·92
C(224)	0·8054 (6)	0·0159 (3)	0·1034 (6)	4·73
C(225)	0·6952 (7)	0·0116 (3)	0·1496 (7)	5·18
C(226)	0·6127 (5)	0·0850 (3)	0·1772 (6)	4·04

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Pt—Cl	2·360 (1)	Pt—P(1)	2·295 (1)
Pt—P(2)	2·224 (1)	Pt—C(1)	2·078 (4)
P(1)—C(11)	1·855 (4)	P(1)—C(111)	1·816 (4)
P(1)—C(121)	1·812 (4)	P(2)—C(11)	1·852 (4)
P(2)—C(211)	1·811 (4)	P(2)—C(221)	1·810 (4)
Cl—Pt—P(1)	99·1 (1)	Cl—Pt—P(2)	170·5 (1)
Cl—Pt—C(1)	88·7 (1)	P(1)—Pt—P(2)	73·9 (1)
P(1)—Pt—C(1)	171·3 (1)	P(2)—Pt—C(1)	98·8 (1)
Pt—P(1)—C(11)	94·4 (1)	Pt—P(1)—C(111)	117·7 (1)
Pt—P(1)—C(121)	120·8 (1)	C(11)—P(1)—C(111)	108·0 (2)
C(11)—P(1)—C(121)	107·3 (2)	C(111)—P(1)—C(121)	106·8 (2)
Pt—P(2)—C(11)	96·9 (1)	Pt—P(2)—C(211)	114·2 (1)
Pt—P(2)—C(221)	123·0 (1)	C(11)—P(2)—C(211)	106·6 (2)
C(11)—P(2)—C(221)	106·8 (2)	C(211)—P(2)—C(221)	107·4 (2)
P(1)—C(11)—P(2)	94·2 (2)		

Discussion. The structure determination confirms the stoichiometry of the compound and proves its monomeric nature. The molecular structure is shown in Fig. 1; there are no significant intermolecular interactions in the lattice. A comprehensive review of the chemistry of Pd and Pt pentahalophenyl complexes has appeared recently (Usón & Forniés, 1988).

The coordination geometry about the Pt atom is approximately square planar and comprises a Cl

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* Lists of structure factors, anisotropic thermal parameters, mean plane data, interatomic parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53788 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

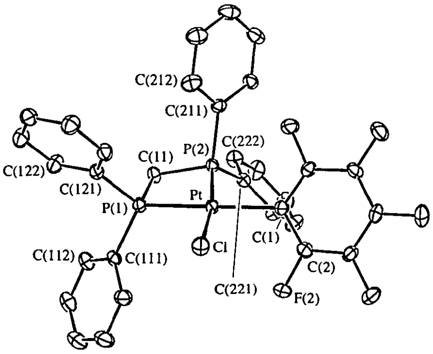

Fig. 1. Molecular structure and crystallographic numbering scheme employed for [$PtCl(dppm)C_6F_5$] (Johnson, 1971).

atom, a C atom from the pentafluoroaryl group and two P atoms from a bidentate dppm ligand. The deviations from the least-squares plane through the four donor atoms are significant: Cl −0·025 (1), P(1) 0·023 (1). P(2) −0·024 (1) and C(1) 0·346 (4) Å; the Pt atom lies 0·1099 (2) Å out of this plane. The distortion from ideal square-planar geometry may be related to the restricted bite distance of the bidentate ligand which imposes a P—Pt—P angle of 73·9 (1)°. As a consequence, the two angles P(1)—Pt—Cl and P(2)—Pt—C(1) are each opened up to approximately 99°. In the related complex, $Pt(C_6H_5)_2(dppm)$, there is also a deviation from square-planar geometry [P—Pt—P 73 (1)°], but the Pt atom and the four donor atoms are coplanar (Braterman, Cross, Manojlovic-Muir, Muir & Young, 1975) by contrast with the present complex.

The Pt—P bond distances, Pt—P(1) 2·295 (1) and Pt—P(2) 2·224 (1) Å, are not equivalent with the shorter bond distance being *trans* to the Cl atom reflecting the greater *trans*-influence of the aryl C atom over that of the Cl atom; this effect has been reported previously for a related complex $PtCl(dcy)C_6F_5$ (dcy = dicyclopentadiene) (Deacon *et al.*, 1989). The longer Pt—P bond distance is comparable to the Pt—P bond distances of 2·30 (1) Å found in $Pt(C_6H_5)_2(dppm)$ (Braterman *et al.*, 1975). In order to relieve possible steric interactions between the phenyl groups bound to the dppm ligand and the C_6F_5 group, the latter is oriented such that the dihedral angle between it and the square plane about the Pt atom is 60·4°; the C_6F_5 group is perpendicular to the coordination plane in $PtCl(dcy)C_6F_5$ (Deacon *et al.*, 1989), where steric interactions are greater.

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Structure of Di-μ-cyanato-bis[cyanato(*N*,*N*-diethylethylenediamine)copper(II)], [$Cu(NCO)_2(diEten)$]$_2$

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Abstract. [$Cu_2(NCO)_4(C_6N_2H_{16})_2$], M_r = 527·56, monoclinic, $P2_1/c$, a = 11·586 (2), b = 7·279 (1), c = 13·742 (2) Å, β = 96·02 (2)°, V = 1152·5 (6) Å^3, Z = 2, D_x = 1·520 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 18·87 cm^{-1}, $F(000)$ = 548, T = 296 K, R = 0·033 for 1393 observed reflections. The compound is in a

0108-2701/91/050957-03$03.00