Crystal Structure of *trans*-Carbonyl(*p*-chlorophenyl)bis(triethylphosphine)platinum(II) Hexafluorophosphate †

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Crystals of the title compound are orthorhombic with $a = 12{\cdot}453(15)$, $b = 15{\cdot}282(17)$, $c = 14{\cdot}360(16)$ Å, $Z = 4$, space group *Pnam*. 1872 Visually estimated intensities were used and the structure determined by Patterson and Fourier methods and refined by full-matrix least-squares to *R* 14·24%. The co-ordination round the platinum is square planar: platinum, the carbonyl group, and the *p*-chlorophenyl group lie in a crystallographic mirror plane. The *trans*-influence of the σ-bonded organic ligand on the Pt–C(CO) bond length (1·97 Å) is discussed.

THE *trans*-influence in square-planar Pt^{II} complexes has been the subject of several experimental and theoretical studies.[1] In particular, use has been made of $^{195}Pt-^{1}H$ and $^{195}Pt-^{13}C$ n.m.r. coupling constants to investigate the *trans*-influences of various ligands.[2-4] Somewhat surprisingly only two structure determinations of platinum(II) carbonyls have been reported: *trans*-Pt(MeO-$C_5H_4NO)(CO)Cl_2$ [5] and *trans*-$[Pt(CO)Cl(PEt_3)_2][SiF_5]$.[6] Additional information concerning the structural details of a Pt^{II} square-planar carbonyl would therefore be of some value in complementing conclusions drawn from n.m.r. and other studies of the *trans*-influence, and we have accordingly determined the crystal structure of $[Pt(CO)(p\text{-}ClC_6H_4)(PEt_3)_2][PF_6]$.

EXPERIMENTAL

Crystal Data.—$C_{19}H_{34}ClF_6OP_3Pt$, $M = 715{\cdot}9$, Orthorhombic, $a = 12{\cdot}453(15)$, $b = 15{\cdot}282(17)$, $c = 14{\cdot}360(16)$ Å, $U = 2733{\cdot}2$ Å^3, $D_m = 1{\cdot}72$ (by flotation CCl_4/EtI), $Z = 4$, $D_c = 1{\cdot}73$ g cm^{-3}, $F(000) = 1400$. Space group $Pna2_1$ or *Pnam* (from absences). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 127·8 cm^{-1}.

White air-stable crystals were prepared [7] and grew as thin plates with the form {010} dominant. Cell dimensions were obtained from oscillation photographs. Weissenberg photographs showed few well-defined and intense reflexions at high values of θ, suggesting disorder and/or high thermal factors. Intensities were collected from equi-inclination Weissenberg photographs of the 0—10*kl* and *hk*0—11 layers with Ni-filtered Cu-K_α radiation and the multiple-film technique. The crystals decompose in the *X*-ray beam, and four crystals were used to collect all the layers. Intensities were estimated visually. Some difficulty was encountered because allowance had to be made for the large variance in spot size, and for deterioration of the crystals, which caused the reflexions to become diffuse. Absorption corrections were made by a method which approximates the crystal to a pseudo-ellipsoid. Lorentz and polarisation corrections were applied, and the data placed on the same scale through common reflexions.[8] 1872 Independent reflexions were assigned non-zero intensities.

Structure Determination and Refinement.—No initial assumption was made about the space group. The *x* and *y* co-ordinates of the Pt atom were determined from a Patterson synthesis; the *z* co-ordinate was assigned a value of $\frac{1}{4}$. Successive Fourier syntheses yielded positions for the phosphorus atoms, the *p*-chlorophenyl group, the carbonyl group, and two fluorine atoms: all but the phosphorus atoms bonded to Pt had *z* co-ordinates of $\frac{1}{4}$. The platinum, chlorine, and phosphorus atoms were assigned anisotropic thermal factors and the remaining atoms individual isotropic thermal factors. Four cycles of refinement in space group *Pnam* reduced *R* to 16·27%. A difference synthesis phased on the refined positions for the above atoms showed prominent peaks in likely positions for the carbon atoms of the ethyl groups. This synthesis would show, in *Pnam* or $Pna2_1$, peaks which reflected across the mirror plane (or pseudo-mirror plane) at $z = \frac{1}{4}$. Thus a careful search was made for alternative positions of the carbon atoms of the ethyl groups: none was located. The region of electron density around P(anion) showed four very diffuse peaks which could be assigned to the remaining four fluorine atoms. The shape of the peaks suggested rotational disorder around the F(1)–P(2)–F(2) axis. The ethyl-group carbon atoms were assigned individual isotropic thermal factors, and a secondary extinction coefficient introduced as a refineable parameter. The six fluorine atoms were assigned an overall temperature factor and subjected to the following constraints: the P–F distances were made equal and the *cis*-F–F distance was set equal to $\sqrt{2}$ times the P–F distance. After four cycles of full-matrix least-squares refinement in *Pnam*, all variable parameters had converged, except *U* for C(31). A re-examination of the earlier difference synthesis confirmed the position of C(31), so *U* was fixed at 0·12 Å^2, and the refinement completed. *R* Converged to 14·24%. Complex neutral scattering factors [9] were used, and the weighting scheme was $w = (a + |F_o| + b|F_o|^2)^{-1}$ with *a* and *b* set to $2F_{\text{min.}}$ and $2/F_{\text{max.}}$ after each cycle. A final difference synthesis showed no features $> \pm 1{\cdot}5$ eÅ^{-3}.

The high temperature factors for ethyl groups 2 and 3 (*U* 0·16 Å^2) suggest that either these atoms are disordered, or that they do not reflect across the mirror plane. In the latter case the correct space group would be $Pna2_1$. However, difference syntheses gave no indication of alternative positions for the ethyl groups, and examination of the temperature factors of the phenyl carbon atoms does not suggest that the phenyl group is twisted out of the mirror plane. Despite this, several attempts were made to break

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† Reprints not available.

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the mirror symmetry and refine the structure in $Pna2_1$, but none was successful. In conclusion, the space group cannot be unambiguously assigned, but any departure from *Pnam* must be slight, and the course of the refinement in *Pnam* indicates that the bonding parameters should be reliable within the standard deviations quoted.

RESULTS AND DISCUSSION

Final co-ordinates and temperature factors are listed in Tables 1 and 2. The abnormally high overall temperature factor for the fluorine atoms (U 0·182 Å^2) confirms the disorder of the anion. No correction has been applied to the lengths and angles for thermal motion. A table of observed and calculated structure factors is available in Supplementary Publication No. SUP 20906 (12 pp., 1 microfiche).*

TABLE 1

Final fractional co-ordinates ($\times 10^4$)

Atom	x/a	y/b	z/c
Pt	2664(2)	836(1)	2500
Cl	6180(20)	−2354(14)	2500
P(1)	2686(11)	741(8)	4095(9)
P(2)	3385(17)	4009(11)	2500
F(1)	3531(39)	3046(33)	2500
F(2)	3239(38)	4972(34)	2500
F(3)	4221(58)	4093(49)	3230(59)
F(4)	2549(61)	393(52)	3230(60)
O(0)	1034(37)	2299(29)	2500
C(0)	1667(46)	1833(39)	2500
C(1)	3756(36)	−176(29)	2500
C(2)	3443(43)	−1058(32)	2500
C(3)	4182(42)	−1715(34)	2500
C(4)	5252(45)	−1526(36)	2500
C(5)	5690(40)	−692(30)	2500
C(6)	4912(41)	−27(35)	2500
C(11)	1732(38)	1623(32)	4644(37)
C(12)	1755(46)	1405(38)	5683(41)
C(21)	4081(67)	961(51)	4866(65)
C(22)	4522(65)	1889(54)	4416(62)
C(31)	2195(51)	−414(49)	4342(53)
C(32)	1029(68)	−507(54)	3706(66)

TABLE 2

(*a*) Anisotropic vibrational amplitudes (Å^2 × 10^3) in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}
Pt	51(1)	59(1)	31(1)	2(1)
Cl	143(18)	96(13)	123(16)	−51(13)
P(2)	126(16)	95(13)	42(8)	10(11)
P(1)	103(9)	83(7)	46(6)	−9(6)

P(1) U_{13} 2(5) U_{23} −3(5)

(*b*) Isotropic vibrational amplitudes

Atom	U	Atom	U	Atom	U
O	86(12)	C(5)	52(11)	C(21)	160(29)
C(1)	47(10)	C(6)	57(12)	C(22)	161(29)
C(3)	60(12)	C(0)	66(13)	C(31)	120
C(4)	64(13)	C(11)	87(13)	C(32)	164(30)
C(5)	52(11)	C(12)	105(16)	F(1)–F(4)	182(11)

The crystal structure of $[Pt(CO)(C_6H_4Cl)(PEt_3)_2][PF_6]$ consists of monomeric ions, with a closest contact between two platinum atoms of 8·04 Å and between a platinum and a fluorine atom of 3·55 Å. The platinum, *p*-chlorophenyl, and carbonyl atoms lie in a crystallographic mirror plane with the *p*-chlorophenyl and carbonyl groups *trans* to each other. The phosphorus atoms bond to platinum above and below the mirror plane with P(1)–Pt–P(1)′ 186°. The P–Pt–C(0) angle is 93° and this increase from the ideal 90° may be attributed to repulsion between the electrons in the Pt–C(0) and Pt–P(1) bonds.[10] Greater electron density is associated with the Pt–C(0) rather than the Pt–C(1) bond because of d_π–p_π bonding between the platinum atom and the carbonyl ligand. Figure 1 gives a view of the cation showing the labelling of the atoms, and Figure 2 shows a projection of the structure down *c*. Bond lengths and angles are listed in Table 3 and significant contacts in Table 4.

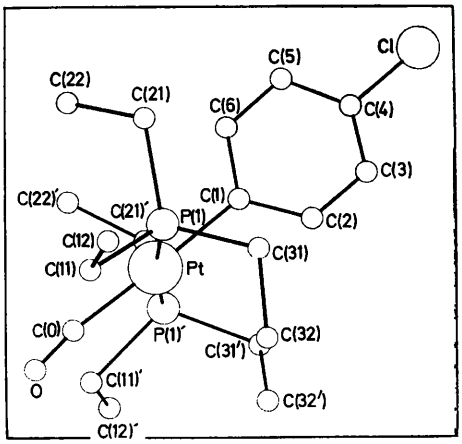

FIGURE 1 A view of the cation, showing the atom labelling system

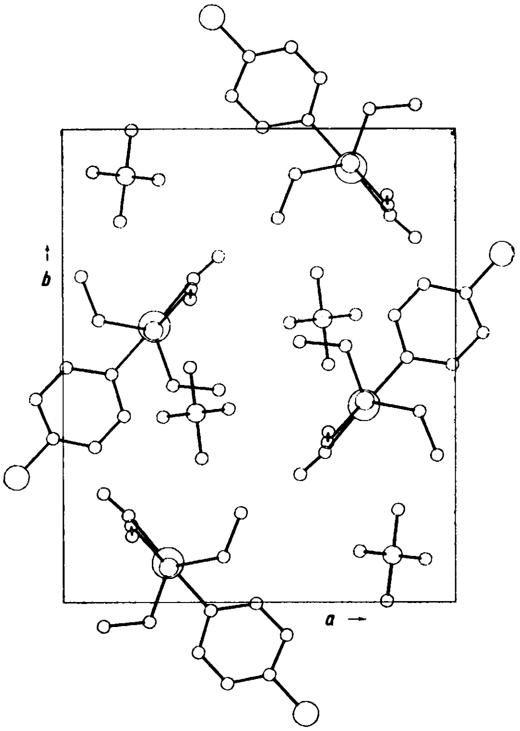

FIGURE 2 A projection of the structure down *c*

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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Average Pt–P distances (Å) in several square-planar Pt^{II} complexes are: 2·247 *cis*-$PtCl_2(PMe_3)_2$,[11] 2·268 *trans*-$Pt(H)Cl(PPh_2Et)_2$,[12] 2·26 *trans*-$Pt(H)Br(PEt_3)_2$,[13] 2·296 (+)-*trans*-[PtCl{SiMe(1-$C_{10}H_7$)Ph}$(PMe_2Ph)_2$],[14] 2·300 *trans*-$PtCl_2(PEt_3)_2$,[15] 2·315 *trans*-$PtBr_2(PEt_3)_2$,[15] and 2·345 in *trans*-$Pt(CO)Cl(PEt_3)_2^+$.[6] Several workers [16-18] have suggested that the Pt–P bond length will depend on the π-acceptor properties of the other ligands; the presence of a ligand with such a property will reduce the amount of d_π–d_π bonding possible between the platinum and phosphorus atoms, and hence the Pt–P distance should be increased. Thus it is not surprising to find the longest Pt–P bonds (2·34 and 2·35 Å) in $Pt(CO)Cl(PEt_3)_2^+$,[6] since CO has strong π-acceptor properties. The Pt–P distance in the present anion (2·30 Å) falls within the range shown, possibly because there is a minimum π-bonding between the platinum atom and the carbonyl group in this species.

TABLE 3

Bond lengths (Å) and angles (°)

(*a*) Distances			
Pt–P(1)	2·30(1)	C(1)–C(2)	1·40(6)
Pt–C(0)	1·97(5)	C(2)–C(3)	1·36(7)
Pt–C(1)	2·06(4)	C(3)–C(4)	1·36(7)
C(0)–O	1·06(6)	C(4)–C(5)	1·39(7)
Cl–C(4)	1·71(7)	C(5)–C(6)	1·40(7)
P(2)–F	1·49(6)	C(6)–C(1)	1·46(7)
P(1)–C(11)	1·96(5)	C(11)–C(12)	1·53(7)
P(1)–C(21)	2·08(9)	C(21)–C(22)	1·65(10)
P(1)–C(31)	1·90(7)	C(31)–C(32)	1·72(10)
(*b*) Angles			
P(1)–Pt–C(0)	93(1)	C(1)–C(2)–C(3)	121(5)
P(1)–Pt–C(1)	87(1)	C(2)–C(3)–C(4)	120(5)
P(1)–Pt–P(1′)	186(1)	C(3)–C(4)–C(5)	125(5)
Pt–C(0)–O	171(5)	C(4)–C(5)–C(6)	113(4)
Pt–C(1)–C(2)	123(6)	C(5)–C(6)–C(1)	125(4)
Pt–C(1)–C(6)	122(7)	C(6)–C(1)–C(2)	115(4)
Pt–P(1)–C(11)	111(2)	P(1)–C(11)–C(12)	103(3)
Pt–P(1)–C(21)	121(2)	P(1)–C(21)–C(22)	102(4)
Pt–P(1)–C(31)	104(2)	P(1)–C(31)–C(32)	105(4)
Cl–C(4)–C(3)	120(5)	C(11)–P(1)–C(21)	100(3)
Cl–C(4)–C(5)	115(5)	C(11)–P(1)–C(31)	112(3)
		C(21)–P(1)–C(31)	109(3)

The *trans*-influence of a ligand is defined as its tendency to weaken the bond *trans* to it, and is generally accepted to operate through a σ-bonding mechanism.[2,19] Strong σ-donor ligands with weak π-acceptor properties are expected to exert strong *trans*-bond-weakening effects.[20] Such a ligand is the *p*-chlorophenyl group. The Pt–C(0) bond length (1·97 Å) is considerably longer than that in $Pt(CO)Cl(PEt_3)_2^+$ (1·78 Å).[6] In the latter complex the Pt–Cl bond has considerable ionic character, and thus the chlorine ligand exerts little or no ***trans***-influence. The C–O distance (1·06 Å) is shorter than that (1·14 Å) in $Pt(CO)Cl(PEt_3)_2^+$ but not significantly so. Indeed, the high standard deviations usually associated with C–O bond lengths limit their use as a guide to the relative *trans*-influences of various ligands. The Pt–C–O bond angle (171°) deviates from linearity, but again the high standard deviation (5°) precludes quantitative discussion.

The Pt–C(1) bond length (2·06 Å) compares favourably with the Pt–C σ-bonds in the square-planar Pt^{II} species $[Pt(C_5H_7O_2)_2Cl]^-$ 2·106,[21] [PtCl(OMe)(dicyclopentadiene)]$_2$ 2·07,[22] and PtCl(OMe)(1,5-C_8H_{12})(pyridine) 2·04 Å.[23]

TABLE 4

Shortest non-bonded distances of various types (Å)

Type	Atoms	Distance
(*a*) Intramolecular		
Pt · · · C	Pt · · · C(31)	3·31
Cl · · · C	Cl · · · C(12)	3·94
P · · · O	P(1) · · · O	3·89
P · · · C	P(1) · · · C(1)	3·00
O · · · C	O · · · C(11)	3·36
C · · · C	C(0) · · · C(11)	3·10
	C(2) · · · C(31)	3·22
(*b*) Intermolecular		
Pt · · · Cl	Pt · · · Cl^{IV}	5·63
Pt · · · P	Pt · · · P(2^{I})	4·93
	Pt · · · P(2^{IV})	5·33
Pt · · · F	Pt · · · F(1^{I})	3·55
	Pt · · · F(3^{IV})	4·42
Pt · · · O	Pt · · · O^{IV}	5·08
Cl · · · F	Cl · · · F(2^{IV})	4·45
Cl · · · C	Cl · · · C(32^{IV})	3·70
	Cl · · · C(2^{IV})	3·72
P · · · F	P(1) · · · F(1^{I})	4·33
P · · · O	P(2) · · · O^{IV}	3·86
P · · · C	P(2) · · · C(32^{IV})	4·37
	P(2) · · · C(0^{IV})	4·29
	P(2) · · · C(5^{IV})	4·23
F · · · O	F(1) · · · O^{IV}	3·16
	F(3) · · · O^{IV}	3·27
F · · · C	F(3) · · · C(32^{IV})	3·20
	F(2) · · · C(5^{IV})	3·36
O · · · C	O · · · C(22^{IV})	3·56
C · · · C	C(5) · · · C(21^{II})	3·82
	C(11) · · · C(22^{IV})	3·59
	C(32) · · · C(32^{III})	3·46

Roman superscripts refer to the following transformations of the co-ordinates of the second atom:

I x, y, z III $x, y, \frac{1}{2} - z$
II $-x, -y, \frac{1}{2} + z$ IV $\frac{1}{2} + x, \frac{1}{2} - y, z$

The bonding parameters in the *p*-chlorophenyl group are as expected.[24] Mean bond lengths and angles for the triethylphosphine ligands are: P–C 1·98, C–C 1·63 Å; Pt–P–C 112, C–P–C 107, and P–C–C 103°. All these parameters have high standard deviations and are not significantly different from corresponding values found in triethylphosphine co-ordinated to platinum.[15] The

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mean P–F bond length (1·49 Å) is not significantly different from values previously reported for the anion.[25]

Intramolecular contacts (Table 4) are all as expected for the nearly ideal square-planar geometry. Apart from the Pt · · · F(1^I) distance (3·55 Å) all other intermolecular contacts are at least 0·3 Å greater than the sum of the van der Waals radii.[26] This rather loose packing is no doubt associated with the high average thermal factor for all the atoms (U_{av} 0·10 $Å^2$) and with the presence of disorder in the crystal.

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