Crystal and Molecular Structure of *cis*-Chloro(3-chloro-1,1,3,3-tetrafluoropropan-2-one)bis(triphenylphosphine)platinum(II)

By **David R. Russell** * and **Paul A. Tucker**, Department of Chemistry, University of Leicester, Leicester LE1 7RH

Crystals of the title compound are monoclinic, space group $P2_1/a$, with a = 20.45 ± 0.02, b = 18.66 ± 0.02, c = 10.43 ± 0.01 Å, β = 114.0 ± 0.4°. The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares analysis of counter intensities to R 0.095 for 3 956 reflections. Important bond lengths are Pt–P(*trans* to C) 2.362(5), Pt–P(*trans* to Cl) 2.247(5), Pt–Cl 2.349(6), and Pt–C 2.06(2) Å.

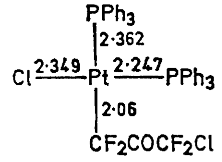
Clarke and Kemmitt[1] have recently found that diphenylacetylenetris(triphenylphosphine)platinum(0) reacts with 1,3-dichloro-1,1,3,3-tetrafluoroacetone to give the previously reported[2] π-bonded ketonic complex $[Pt^0\{OC(CF_2Cl)_2\}(PPh_3)_2]$. In solution this complex rearranges to the oxidative-addition product (1). We

---

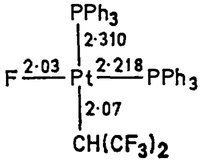
[1] D. Clarke and R. D. W. Kemmitt, unpublished results, 1974.

[2] B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.

undertook the crystal-structure analysis in order to confirm this assignment and to investigate the effect of the $-CF_2\cdot CO\cdot CF_2Cl$ group on the molecular geometry.



(1)



(2)

EXPERIMENTAL

Single crystals of the title compound grow from methylene chloride solutions with the forms $\{100\}$, $\{010\}$, and $\{10\bar{1}\}$ commonly developed. Unit-cell dimensions were measured from precession photographs recorded by use of Mo-K_α radiation.

Crystal Data.—$C_{39}H_{30}Cl_2F_4OP_2Pt$, $M = 918.6$, Monoclinic, $a = 20.45 \pm 0.02$, $b = 18.66 \pm 0.02$, $c = 10.43 \pm 0.01$ Å, $\beta = 114.0 \pm 0.4°$, $U = 3\,635.5$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 450$. Space group $P2_1/a$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ (Mo-K_α) = 43.6 cm^{-1}. Systematic absences: $h0l$ when h is odd and $0k0$ when k is odd.

Intensity data were collected on a Stoe Weissenberg diffractometer in nineteen layers, $h0$—$18l$, from a crystal of dimensions *ca.* 0.072 × 0.024 × 0.012 cm. The intensities were measured by an ω-scan technique and monochromatic Mo-K_α radiation. Significant intensities $[I > 3\sigma(I)]$ with $0.1 < \sin\theta/\lambda < 0.7$ Å^{-1} were corrected for Lorentz and polarisation effects. An absorption correction was applied by the method of deMeulenaer and Tompa.[3,4]

Scattering factors for the atoms were taken from ref. 5. The position of the platinum atom was deduced from a three-dimensional Patterson synthesis and the positions of the remaining atoms were found from successive difference Fourier syntheses. Twelve cycles of block-diagonal least-squares refinement reduced R to 0.095 $[R' = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o| = 0.100]$ for 3 956 reflections. In the later cycles of refinement a weighting scheme, with the weight given by $w = (15.38 - 0.411|F_o| + 0.0121|F_o|^2)^{-1}$, was introduced in order that $w\Delta^2$ be approximately independent of $|F_o|$. Anisotropic temperature factors of the phenyl carbon atoms were not refined in order to reduce computing time. Hydrogen atoms, at positions calculated from the molecular geometry, assuming C–H 1.0 Å, and with a temperature factor of B 5.0 Å,^{2} were included in the structure-factor calculations. Anomalous dispersion corrections [6] for the platinum, chlorine, and phosphorus atoms were applied. The maximum shift in the final cycle was 0.4σ.* A difference-Fourier synthesis calculated from the final atomic co-ordinates showed no maxima or minima with an absolute value >0.3 eÅ^{-3} in general areas of the unit cell and none >1.6 eÅ^{-3} within 1 Å of the platinum atom. Final atomic parameters are listed in Table 1.

TABLE 1

Final atomic parameters with standard deviations, in parentheses, calculated from the least-squares treatment

	x/a	y/b	z/c	B_{11} *	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pt	0.233 50(4)	0.157 31(4)	0.412 81(8)	2.46(3)	3.13(4)	3.65(4)	−0.28(3)	0.68(2)	0.18(3)
P(1)	0.3479(3)	0.1600(3)	0.6001(5)	2.8(2)	3.7(2)	2.8(2)	−0.3(2)	0.9(1)	−0.2(2)
P(2)	0.2082(3)	0.0424(3)	0.4384(6)	2.2(2)	3.2(2)	4.2(2)	−0.1(2)	0.9(2)	−0.4(2)
Cl(1)	0.2549(4)	0.2792(3)	0.3883(7)	5.8(3)	2.8(2)	5.6(3)	0.4(2)	−0.1(2)	−0.8(2)
Cl(2)	0.1105(6)	0.2352(6)	−0.1164(9)	8.7(6)	10.9(7)	5.4(4)	−0.2(4)	0.4(4)	−2.4(5)
F(1)	0.0813(8)	0.1600(9)	0.2429(17)	4.9(7)	7.7(9)	7.6(9)	2.9(7)	2.7(6)	1.2(6)
F(2)	0.1391(9)	0.1190(9)	0.1292(15)	6.2(8)	5.9(8)	5.1(7)	−0.2(6)	−0.3(6)	1.1(6)
F(3)	0.2288(9)	0.2139(11)	0.0849(18)	5.5(8)	11.8(14)	6.8(9)	−1.0(9)	3.0(7)	−0.5(9)
F(4)	0.1900(13)	0.3247(11)	0.0543(22)	12.4(16)	8.0(13)	8.8(11)	−0.6(9)	4.5(11)	−4.5(11)
O(1)	0.0934(11)	0.2882(11)	0.1601(24)	4.9(9)	6.4(11)	10.2(14)	−0.7(10)	2.3(9)	1.4(8)
C(1)	0.1426(12)	0.1692(12)	0.2031(21)	3.7(9)	4.9(12)	3.7(9)	−0.7(8)	1.8(7)	0.6(8)
C(2)	0.1701(15)	0.2534(17)	0.0518(27)	4.7(13)	7.4(18)	4.9(13)	−0.9(11)	0.6(10)	−0.8(12)
C(3)	0.1350(13)	0.2443(13)	0.1528(24)	4.5(12)	4.2(11)	4.8(11)	0.2(8)	1.4(9)	0.7(9)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
C(11)	0.406(1)	0.204(1)	0.534(2)	4.5(4)	C(41)	0.121(1)	0.006(1)	0.330(2)	4.1(4)
C(12)	0.408(2)	0.178(2)	0.408(3)	5.6(6)	C(42)	0.109(1)	−0.039(1)	0.217(3)	5.4(5)
C(13)	0.450(2)	0.211(2)	0.349(3)	7.2(7)	C(43)	0.040(1)	−0.067(2)	0.139(3)	6.0(6)
C(14)	0.493(2)	0.269(2)	0.420(4)	8.2(8)	C(44)	−0.016(2)	−0.047(2)	0.175(3)	6.7(7)
C(15)	0.491(2)	0.296(2)	0.537(4)	7.5(8)	C(45)	−0.004(2)	−0.003(2)	0.283(3)	5.9(6)
C(16)	0.447(1)	0.264(1)	0.597(3)	5.5(5)	C(46)	0.063(2)	0.026(2)	0.362(3)	5.9(6)
C(21)	0.353(1)	0.213(1)	0.748(2)	3.7(4)	C(51)	0.206(1)	0.024(1)	0.609(2)	3.0(3)
C(22)	0.461(1)	0.212(1)	0.875(2)	3.8(4)	C(52)	0.212(2)	0.079(2)	0.699(3)	5.6(6)
C(23)	0.419(1)	0.252(1)	0.989(2)	4.4(4)	C(53)	0.205(2)	0.061(2)	0.826(3)	6.5(7)
C(24)	0.364(1)	0.295(1)	0.980(3)	5.4(5)	C(54)	0.199(2)	−0.006(2)	0.861(3)	6.5(7)
C(25)	0.301(1)	0.297(1)	0.857(3)	5.6(5)	C(55)	0.194(2)	−0.059(2)	0.775(3)	7.1(7)
C(26)	0.298(1)	0.257(1)	0.744(2)	4.2(4)	C(56)	0.197(1)	−0.046(1)	0.646(3)	5.2(5)
C(31)	0.397(1)	0.079(1)	0.683(2)	4.1(4)	C(61)	0.285(1)	0.002(1)	0.288(3)	4.9(5)
C(32)	0.446(1)	0.047(1)	0.638(2)	4.5(4)	C(62)	0.272(1)	−0.015(1)	0.408(2)	3.6(4)
C(33)	0.484(1)	−0.015(1)	0.705(3)	5.4(5)	C(63)	0.305(2)	−0.073(1)	0.490(3)	4.8(5)
C(34)	0.469(2)	−0.047(2)	0.806(3)	5.6(6)	C(64)	0.355(2)	−0.116(2)	0.455(3)	5.8(6)
C(35)	0.419(1)	−0.017(1)	0.849(3)	5.0(5)	C(65)	0.367(2)	−0.096(2)	0.341(3)	6.1(6)
C(36)	0.384(1)	0.044(1)	0.789(2)	4.3(4)	C(66)	0.334(2)	−0.040(2)	0.255(3)	6.1(6)

* Temperature factor in the form: $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2klb^*c^*B_{23} + 2hla^*c^*B_{13})]$.

---

* Observed and calculated structure factors, details of planes, and short intermolecular contacts are listed in Supplementary Publication No. SUP 21400 (23 pp., 1 microfiche). For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[3] J. deMeulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

[4] N. W. Alcock, *Acta Cryst.*, 1969, **A25**, 518.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

DISCUSSION

The molecular geometry and atom numbering for (1) are shown in Figure 1. Bond lengths and angles are listed in Table 2. The co-ordination about the platinum atom is approximately planar, the deviation from planarity being larger than usual for Pt^{II} complexes. Distances from the plane defined by Pt, P(1), P(2), and Cl(1) are Pt 0.03, P(1) −0.02, P(2) 0.00, Cl(1) −0.02, and C(1) 0.30 Å. The angles at platinum follow the expected pattern with the larger angles between the bulkier groups.

It is of interest to compare the Pt–P bond lengths in (1) with those in the formally similar complex (2).[7] In both complexes the Pt–P bond *trans* to a fluoroalkyl group is long and that *trans* to a halogen is short. Indeed in complex (1) the Pt–P bond *trans* to the $^{-}CF_2{\cdot}CO{\cdot}CF_2Cl$ moiety is one of the longest reported. Equally large values have been noted in the complex $[(Et_3P)_2Pt(H){-}B_9H_{10}S]$,[8] where the platinum atom is part of a metallo-borane icosahedron, and in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$,[9] where the long Pt–P bonds are thought to be due to steric interaction between the tricyclohexylphosphine ligands and the iodine atoms. At the opposite extreme the complex (2) has the shortest known Pt–P bond[7] (*trans* to fluorine). The Pt–P bond lengths in the two complexes are consistent with the increasing *trans*-influence of ligands (X), $F^- < Cl^- \leqslant$ fluoroalkyl, which follows the increasing covalent character of the *trans*-Pt–X bond, a correlation first suggested by Syrkin.[10] We also note that the $^{-}CF_2{\cdot}CO{\cdot}CF_3$ group has a larger *trans*-influence than the $^{-}CH(CF_3)_2$ group in (2).

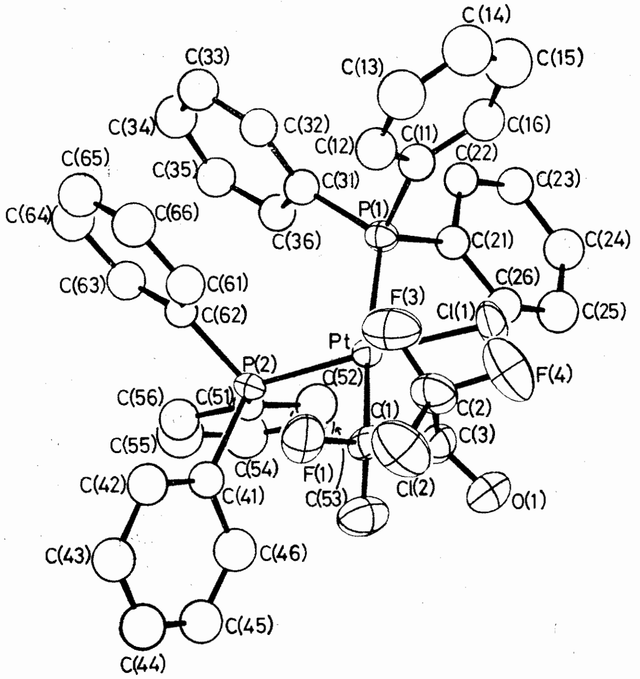


FIGURE 1 Molecular geometry and atom numbering; hydrogen atoms are excluded for the sake of clarity. Thermal ellipsoids are scaled to represent 50% probability

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations, in parentheses. In the phenyl groups mean C–C bond length is 1.386(5) Å and mean C–C–C angle is 120.0(2)°; mean P–C–C angle is 120.8(8)°

Pt–P(1)	2.362(5)	P(1)–Pt–P(2)	96.9(5)
Pt–P(2)	2.247(5)	P(1)–Pt–Cl(1)	84.5(5)
Pt–Cl(1)	2.349(6)	P(2)–Pt–C(1)	92.7(9)
Pt–C(1)	2.06(2)	Cl(1)–Pt–C(1)	86.2(9)
C(1)–F(1)	1.33(3)	Pt–C(1)–F(2)	115(2)
C(1)–F(2)	1.39(3)	Pt–C(1)–F(1)	112(2)
C(2)–F(3)	1.39(4)	Pt–C(1)–C(3)	115(2)
C(2)–F(4)	1.33(4)	F(1)–C(1)–F(2)	103(2)
Mean	1.36	F(1)–C(1)–C(3)	105(2)
C(3)–O(1)	1.21(3)	F(2)–C(1)–C(3)	104(2)
C(2)–Cl(1)	1.72(3)	C(1)–C(3)–O(1)	119(2)
		C(1)–C(3)–C(2)	118(2)
C(1)–C(3)	1.59(3)	C(2)–C(3)–O(1)	121(2)
C(2)–C(3)	1.51(4)		
		Pt–P(1)–C(11)	106(1)
P(1)–C(11)	1.79(2)	Pt–P(1)–C(21)	114(1)
P(1)–C(21)	1.80(2)	Pt–P(1)–C(31)	123(1)
P(1)–C(31)	1.82(2)	Pt–P(2)–C(41)	120(1)
P(2)–C(41)	1.81(2)	Pt–P(2)–C(51)	113(1)
P(2)–C(51)	1.84(2)	Pt–P(2)–C(61)	109(1)
P(2)–C(61)	1.80(2)	Mean	116
Mean	1.81(1)		
		C(1)–Pt–P(1)	168.4(9)
		P(2)–Pt–Cl(1)	177.1(5)

The Pt–Cl(1) bond is slightly shorter than that normally found when *trans* to a phosphine ligand (*e.g.* 2.36—2.39 Å from ref. 11), although the Pt–P(2) bond falls within the range of values normally found *trans* to chloride.[11] The Pt–C(1) bond length is not significantly different from the sum of covalent radii for the atoms (2.07 Å) [12] and is similar to that in (2).[7] There is therefore no direct evidence of any shortening of the Pt–C bond in complex (1) as might be expected if the fluoroalkyl was acting as a π-acceptor.[13] However, for first-row transition elements, where the estimated standard deviation of the M–C bond is smaller, significant shortening (≈ 0.05 Å) of the bond from the metal to a carbon atom to a fluoroalkyl group has been reported.[14,15]

The remaining bond lengths are unexceptional, and equal to accepted values.[16]

The triphenylphosphine groups have the commonly observed propeller conformation. The phenyl rings are planar with the appropriate phosphorus atom no more than 0.06 Å from the mean plane of the ring. Equations

---

[7] J. Howard and P. Woodward, *J.C.S. Dalton*, 1973, 1840.

[8] A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 2571.

[9] N. W. Alcock and P. G. Leviston, *J.C.S. Dalton*, 1974, 1834.

[10] Y. K. Syrkin, *Bull. Acad. Sci. U.S.S.R., Classe Sci. Chim.*, 1948, 69.

[11] 'Molecular Structure by Diffraction Methods,' vol. 1, 1973, Chemical Society, Specialist Periodical Report.

[12] L. Pauling, 'The Nature of the Chemical Bond,' 1960, 3rd edn., Cornell University Press, Ithaca, New York.

[13] F. A. Cotton and R. M. Wing, *J. Organometallic Chem.*, 1967, **9**, 511.

[14] R. Mason and D. R. Russell, *Chem. Comm.*, 1965, 182.

[15] M. R. Churchill, *Inorg. Chem.*, 1967, **6**, 185.

[16] *Chem. Soc. Special Publ.*, No. 18, 1965.

of mean planes and distances of atoms from the planes have been deposited with the structure factor tables. As is usually observed the two triphenylphosphine ligands, *cis*- with respect to the metal, pack with two phenyl rings, (3) and (6), approximately parallel and roughly separated by the van der Waals thickness of an aromatic ring, with C(31) · · · C(62) 3.45, C(33) · · · C(64) 3.43, and C(32) · · · C(63) 3.48 Å.

The molecular packing is illustrated in Figure 2. Those intermolecular contacts shorter than the sum of the van der Waals radii[12] for the atoms are also deposited with the structure factor tables.

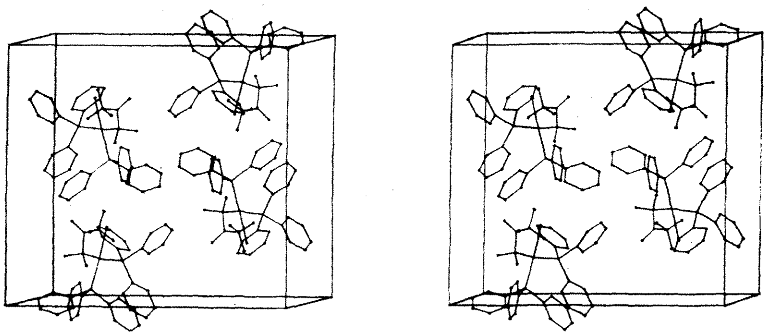


FIGURE 2 Molecular packing. A stereoscopic drawing viewed approximately along the *c* axis

We thank the University of Leicester Computing Centre for facilities, the S.R.C. for financial support, and D. Clarke for the sample of the complex.

[5/222 *Received, 3rd February,* 1975]