Crystal and Molecular Structure of *cis*-Fluoro-(1,1,1,3,3,3-hexafluoroisopropyl)bis(triphenylphosphine)platinum, $PtF[CH(CF_3)_2](PPh_3)_2$: A Square Planar Metal Fluoro-complex

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Crystals of the title compound are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions: a = 18·690(5), b = 18·662(18), c = 9·897(15) Å, β = 94·7(1)°. The structure was solved by conventional heavy-atom methods and refined by least squares to R 0·063 for 1937 independent reflections measured on a diffractometer. The platinum atom is in a square planar configuration. Two adjacent sites are occupied by triphenylphosphine groups, the other two by fluorine and a hexafluoroisopropyl group. The two Pt–P distances are significantly different: that *trans* to fluorine is 2·218(7), while that *trans* to $-CH(CF_3)_2$ is 2·310(7) Å. The geometry of the ligands is as expected.

BIS(TRIFLUOROMETHYL)DIAZOMETHANE reacts with a variety of d^{10} complexes of Ni, Pd, and Pt to afford complexes containing the 1,1,4,4-tetrakis(trifluoromethyl)buta-1,3-azine ligand.[1,2] During the course of the reaction with $Pt(stilbene)(PPh_3)_2$ some minor products were isolated, and of these one has been shown, mainly by X-ray crystallography, to be the title compound. Another, which is isomeric, is presumably the *trans*-analogue. It was suggested that these compounds arose by way of attack of traces of HF on an initially formed adduct $(Ph_3P)_2\overline{Pt{\cdot}N{:}N{\cdot}C}(CF_3)_2$.

EXPERIMENTAL

Crystals of $PtF[CH(CF_3)_2](PPh_3)_2$ are colourless and grow as needles of flattened hexagonal cross-section with the needle axis along a. Lattice parameters were measured from precession photographs by use of a very small crystal. Zirconium-filtered Mo-K_α radiation was used throughout. The dimensions (0·30 × 0·26 × 0·14 mm) of the chosen crystal were carefully measured on a binocular microscope so that an accurate absorption correction could be applied.[3] The crystal was mounted on its b axis. Intensities were measured on a Buerger–Supper-Pace 0·01°-incrementing autodiffractometer with a stationary background–ω-scan–stationary background measuring sequence, as described earlier.[4] Backgrounds were counted for 0·5 min, the scan speed was 1° min^{-1}, and the scan intervals were $(2{\cdot}0 + 0{\cdot}3/L)°$ for layers 0—7, $(2{\cdot}0 + 0{\cdot}5/L)°$ for layers 8—12, and $(2{\cdot}0 + 0{\cdot}6/L)°$ for layers 13—15, where L is the Lorentz correction. Measurements of the layers h0—15l yielded 2021 intensities, of which 1936 were deemed 'observed' according to the criterion $[N_3 - (N_1 + N_2)]/(N_3 + N_1 +$

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[1] J. Clemens, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 1620.

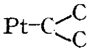
[2] J. Clemens, R. E. Davis, M. Green, J. D. Oliver, and F. G. A. Stone, *Chem. Comm.*, 1971, 1095.

[3] N. W. Alcock, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, 271—278.

[4] C. J. Gilmore and P. Woodward, *J.C.S. Dalton*, 1972, 1387.

$N_2)^{\frac{1}{2}} > 2{\cdot}5$ and were used in the analysis; N_3, N_1, and N_2 are the peak count and the first and second background counts.

Crystal Data.—$C_{39}H_{31}F_7P_2Pt$, $M = 827{\cdot}7$, Monoclinic, $a = 18{\cdot}690(5)$, $b = 18{\cdot}662(18)$, $c = 9{\cdot}897(15)$ Å, $\beta = 94{\cdot}7(1)°$, $U = 3440$ Å^3, D_m (by flotation) $= 1{\cdot}69$, $Z = 4$, $D_c = 1{\cdot}71$, $F(000) = 1624$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 44{\cdot}8$ cm^{-1}. Space group $P2_1/a$.

Structure Solution and Refinement.—The only features of the structure known for certain from chemical and spectroscopic evidence were the presence of one Pt atom, two PPh_3 groups, and one $-C(CF_3)_2$ group. The platinum atom was readily located from a three-dimensional Patterson synthesis, and from successive electron-density syntheses were located first the two phosphorus atoms mutually *cis* (R 0·24), then the phenyl groups, the other carbon atoms and the two (CF_3) groups (R 0·10). It was clear that the  $\mathrm{Pt{-}C}\begin{smallmatrix}\diagup \mathrm{C}\\ \diagdown \mathrm{C}\end{smallmatrix}$ moiety was non-planar (hence not a carbene), and indeed that a fourth tetrahedral position, seemingly unoccupied, probably carried a hydrogen atom. Moreover, the Pt–C bond was coplanar with the two Pt–P bonds, *trans* to one and *cis* to the other. It was not altogether surprising, therefore, when a further electron-density difference map revealed a clear peak, of some 8 or 9 e, *ca.* 2 Å from the Pt atom in the fourth position for a square planar complex. In view of doubts about the chemical nature of this atom, three refinements were carried out in which the extra atom was assumed to be nitrogen, oxygen, or fluorine. For these refinements the Pt and P atoms were ascribed anisotropic thermal parameters (β_{22} constant); all other atoms were given isotropic thermal parameters, and separate scale factors for each reciprocal layer were used. At convergence, N gave R 0·086, B 0·6; O gave R 0·065, B 1·1; and F gave R 0·063, B 3·0. On the basis of lowest R and most realistic B, therefore, our analysis favours fluorine, a conclusion subsequently confirmed by further analytical and spectroscopic studies.[1] The weighting scheme used for the least-squares refinement was: $1/w = \sigma_F^2 + 0{\cdot}01F$ (where σ_F is the standard deviation from counting statistics), devised so as to minimise variation of $w(\Delta F)^2$ with ranges of F and $\sin\theta/\lambda$. No hydrogen atoms were included. Positional and thermal parameters are listed in Table 1, and interatomic distances and angles in Table 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20736 (7 pp., 1 microfiche).* All errors cited are given in parentheses in units of the last significant digit. Interatomic distance errors include cell-parameter errors. All computations were performed on an Atlas computer with the help of the '*X*-Ray System' of programmes.[5] Atomic scattering factors were those of ref. 6.

DISCUSSION

In $PtF[CH(CF_3)_2](PPh_3)_2$ the platinum atom is in a square planar configuration and the two triphenylphosphine ligands are mutually *cis* (Figures 1 and 2). The fluorine atom is directly bonded to the platinum atom, *trans* to P(1), with Pt–F 2·03(1) Å; the $[CH(CF_3)_2]$ moiety is directly bonded to the platinum atom, *trans* to P(2), Pt–C 2·07(2) Å. The Pt–F distance is equal to

TABLE 1

Atomic positional and thermal parameters, with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	*B*/Å^2
Pt	0·12837(6)	0·17636(6)	0·22393(12)	*
P(1)	0·2463(4)	0·1605(3)	0·2374(7)	*
P(2)	0·1260(4)	0·2871(4)	0·1196(7)	*
F(1)	0·0202(6)	0·1895(6)	0·2071(12)	3·0(3)
Hexafluoroisopropyl groups				
C(1)	0·1119(13)	0·0774(12)	0·3118(27)	2·7(5)
C(2)	0·0950(16)	0·0746(16)	0·4480(32)	4·9(7)
C(3)	0·0582(19)	0·0336(18)	0·2253(38)	6·6(8)
F(21)	0·0868(10)	0·0176(10)	0·5166(19)	8·0(5)
F(22)	0·1500(10)	0·1084(9)	0·5275(19)	7·8(5)
F(23)	0·0375(10)	0·1143(9)	0·4761(18)	7·6(5)
F(31)	0·0602(10)	0·0394(9)	0·0977(21)	7·9(5)
F(32)	−0·0104(9)	0·0467(8)	0·2504(17)	6·4(4)
F(33)	0·0625(9)	−0·0400(9)	0·2500(18)	7·2(4)
Phenyl groups				
C(111)	0·293(1)	0·234(1)	0·341(3)	4·0(6)
C(112)	0·258(1)	0·252(1)	0·458(3)	4·6(7)
C(113)	0·292(1)	0·302(1)	0·546(2)	4·0(6)
C(114)	0·355(2)	0·333(2)	0·510(3)	5·1(7)
C(115)	0·386(1)	0·320(2)	0·398(3)	5·2(7)
C(116)	0·358(1)	0·266(1)	0·306(3)	4·1(6)
C(121)	0·282(1)	0·080(1)	0·317(3)	3·3(6)
C(122)	0·276(1)	0·015(1)	0·250(2)	2·4(5)
C(123)	0·299(1)	−0·045(1)	0·317(3)	4·7(7)
C(124)	0·327(2)	−0·047(1)	0·452(3)	5·2(7)
C(125)	0·330(1)	0·016(1)	0·525(3)	3·6(6)
C(126)	0·309(1)	0·081(1)	0·455(3)	3·4(6)
C(131)	0·284(1)	0·154(1)	0·073(2)	3·2(6)
C(132)	0·235(1)	0·149(1)	−0·043(2)	4·2(7)
C(133)	0·264(2)	0·141(1)	−0·166(3)	5·5(7)
C(134)	0·339(2)	0·145(1)	−0·178(3)	3·9(6)
C(135)	0·381(2)	0·145(1)	−0·066(3)	5·6(8)
C(136)	0·358(1)	0·151(1)	0·072(3)	3·7(6)
C(211)	0·073(1)	0·358(1)	0·196(2)	3·0(6)
C(212)	0·036(1)	0·335(1)	0·313(3)	4·9(7)
C(213)	−0·007(1)	0·389(1)	0·377(3)	5·3(7)
C(214)	−0·015(1)	0·453(1)	0·320(3)	4·6(7)
C(215)	0·018(2)	0·473(1)	0·206(3)	5·9(8)
C(216)	0·061(1)	0·422(1)	0·140(3)	3·6(6)
C(221)	0·208(1)	0·339(1)	0·097(3)	4·1(6)
C(222)	0·230(1)	0·392(1)	0·199(3)	4·7(7)
C(223)	0·294(1)	0·430(1)	0·181(3)	4·3(6)
C(224)	0·333(2)	0·419(1)	0·076(3)	6·1(8)
C(225)	0·310(2)	0·363(2)	−0·032(3)	6·6(8)
C(226)	0·248(1)	0·321(1)	−0·010(2)	4·0(5)
C(231)	0·084(1)	0·281(1)	−0·047(3)	3·7(6)
C(232)	0·087(1)	0·336(1)	−0·145(2)	3·9(6)
C(233)	0·051(1)	0·325(2)	−0·278(3)	4·7(6)
C(234)	0·014(2)	0·262(1)	−0·316(3)	5·9(8)
C(235)	0·008(1)	0·208(1)	−0·214(3)	5·1(7)
C(236)	0·043(1)	0·214(1)	−0·081(3)	5·5(7)

* Anisotropic thermal parameters in the form:

$$\exp - [\tfrac{1}{4}B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl].$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	2·62(4)	2·83	3·41(5)	0·003(10)	−0·10(9)	0·46(8)
P(1)	2·5(3)	2·4	3·9(4)	0·03(6)	−0·07(7)	−0·04(8)
P(2)	2·4(3)	3·8	2·2(4)	−0·28(7)	−0·09(7)	0·11(8)

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-sized copies.)

[5] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, 'The *X*-Ray System of Crystallographic Programmes for any Computer,' Computer Science Centre, University of Maryland: available at Atlas Computer Laboratory, Chilton, Didcot, Berkshire.

[6] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

the sum of the covalent radii for dsp^2-Pt (1·31) and for F (0·72), according to the values given, with many reservations, in ref. 7. Likewise the Pt–C distance agrees closely with the sum of the covalent radii for dsp^2-Pt (1·31) and for sp^3-C (0·77).[7] As would be expected, the two Pt–P distances are significantly different: Pt–P(1), *trans* to F, is much the shorter, 2·218(7) Å, while Pt–P(2), *trans* to the $[CH(CF_3)_2]$ group, is 2·310(7) Å. The Pt–P(1) distance is among the shortest that have been recorded[8-14] for square planar complexes of either Pt^0 or Pt^{II}, in accordance with the general observation[12] that Pt^{II}–P bonds are usually shorter than Pt^0–P bonds, and that the Pt–P distance will be at a minimum when no π-acceptor ligands are

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

Pt–P(1)	2·218(7)	C(123)–C(124)	1·39(4)
Pt–P(2)	3·310(7)	C(124)–C(125)	1·38(4)
Pt–F(1)	2·03(1)	C(125)–C(126)	1·44(4)
Pt–C(1)	2·07(2)	C(126)–C(121)	1·42(4)
Hexafluoroisopropyl group		C(131)–C(132)	1·41(4)
C(1)–C(2)	1·41(4)	C(132)–C(133)	1·38(4)
C(1)–C(3)	1·50(4)	C(133)–C(134)	1·41(4)
C(2)–F(21)	1·28(3)	C(134)–C(135)	1·31(4)
C(2)–F(22)	1·39(3)	C(135)–C(136)	1·46(4)
C(2)–F(23)	1·35(4)	C(136)–C(131)	1·40(4)
C(3)–F(31)	1·27(4)		
C(3)–F(32)	1·35(4)	C(211)–C(212)	1·46(4)
C(3)–F(33)	1·39(4)	C(212)–C(213)	1·47(4)
		C(213)–C(214)	1·32(4)
Triphenylphosphine groups		C(214)–C(215)	1·38(4)
P(1)–C(111)	1·88(3)	C(215)–C(216)	1·44(4)
P(1)–C(121)	1·79(2)	C(216)–C(211)	1·33(4)
P(1)–C(131)	1·82(3)		
P(2)–C(211)	1·85(3)	C(221)–C(222)	1·44(4)
P(2)–C(221)	1·85(3)	C(222)–C(223)	1·42(4)
P(2)–C(231)	1·77(3)	C(223)–C(224)	1·34(4)
		C(224)–C(225)	1·53(4)
C(111)–C(112)	1·42(4)	C(225)–C(226)	1·44(4)
C(112)–C(113)	1·40(4)	C(226)–C(221)	1·38(4)
C(113)–C(114)	1·37(4)		
C(114)–C(115)	1·32(4)	C(231)–C(232)	1·40(4)
C(115)–C(116)	1·43(4)	C(232)–C(233)	1·44(4)
C(116)–C(111)	1·41(4)	C(233)–C(234)	1·40(4)
		C(234)–C(235)	1·43(4)
C(121)–C(122)	1·39(3)	C(235)–C(236)	1·43(4)
C(122)–C(123)	1·35(4)	C(236)–C(231)	1·50(4)

(*b*) Angles

P(1)–Pt–P(2)	97·4(2)	P(1)–C(131)–C(136)	118(2)
P(1)–Pt–C(1)	92·1(7)	P(1)–C(131)–C(132)	118(2)
C(1)–Pt–F(1)	87·7(7)	C(131)–C(132)–C(133)	117(2)
F(1)–Pt–P(2)	82·7(4)	C(132)–C(133)–C(134)	122(3)
Pt–C(1)–C(2)	119(2)	C(133)–C(134)–C(135)	118(3)
Pt–C(1)–C(3)	111(2)	C(134)–C(135)–C(136)	126(3)
C(1)–C(2)–F(21)	126(3)	C(135)–C(136)–C(131)	113(2)
C(1)–C(2)–F(22)	108(2)	C(136)–C(131)–C(132)	124(2)
C(1)–C(2)–F(23)	115(2)		
C(1)–C(3)–F(31)	117(3)	P(2)–C(211)–C(216)	123(2)
C(1)–C(3)–F(32)	113(3)	P(2)–C(211)–C(212)	115(2)
C(1)–C(3)–F(3)	114(3)	C(211)–C(212)–C(213)	118(2)
Pt–P(1)–C(111)	110·6(9)	C(212)–C(213)–C(214)	118(3)
Pt–P(1)–C(121)	118·1(9)	C(213)–C(214)–C(215)	124(3)
Pt–P(1)–C(131)	113·9(8)	C(214)–C(215)–C(216)	120(3)
Pt–P(2)–C(211)	116·5(8)	C(215)–C(216)–C(211)	119(2)
Pt–P(2)–C(221)	122·4(8)	C(216)–C(211)–C(212)	121(2)
Pt–P(2)–C(231)	110·6(9)		
P(1)–C(111)–C(116)	123(2)	P(2)–C(221)–C(226)	118(2)
P(1)–C(111)–C(112)	113(2)	P(2)–C(221)–C(222)	117(2)
C(111)–C(112)–C(113)	117(2)	C(221)–C(222)–C(223)	116(2)
C(112)–C(113)–C(114)	118(2)	C(222)–C(223)–C(224)	123(3)
C(113)–C(114)–C(115)	126(3)	C(223)–C(224)–C(225)	120(3)
C(114)–C(115)–C(116)	120(3)	C(224)–C(225)–C(226)	117(3)
C(115)–C(116)–C(111)	115(2)	C(225)–C(226)–C(221)	118(2)
C(116)–C(111)–C(112)	124(2)	C(226)–C(221)–C(222)	125(2)
P(1)–C(121)–C(126)	120(2)	P(2)–C(231)–C(236)	116(2)
P(1)–C(121)–C(122)	121(2)	P(2)–C(231)–C(232)	124(2)
C(121)–C(122)–C(123)	119(2)	C(231)–C(232)–C(233)	119(2)
C(122)–C(123)–C(124)	124(2)	C(232)–C(233)–C(234)	123(3)
C(123)–C(124)–C(125)	119(2)	C(233)–C(234)–C(235)	118(3)
C(124)–C(125)–C(126)	118(2)	C(234)–C(235)–C(236)	123(2)
C(125)–C(126)–C(121)	121(2)	C(235)–C(236)–C(231)	117(2)
C(126)–C(121)–C(122)	118(2)	C(236)–C(231)–C(232)	120(2)

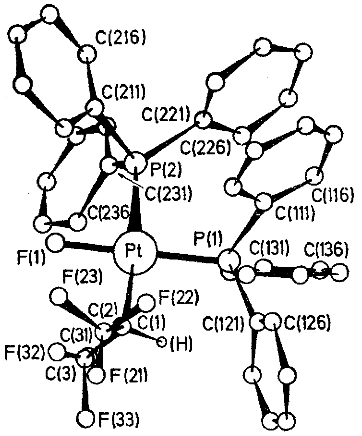

FIGURE 1 The molecule as seen along c^*, showing the atom numbering system. The phenyl carbon atoms are numbered sequentially around the ring, only positions 1 and 6 being indicated

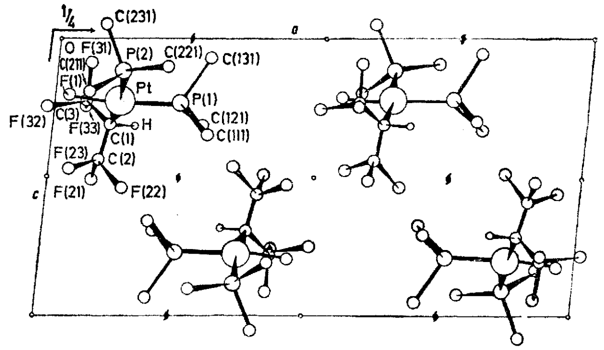

FIGURE 2 The contents of the monoclinic unit cell seen in projection down *b* looking towards the origin. For clarity only one carbon atom of each phenyl group is shown

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[7] A. F. Wells, 'Structural Inorganic Chemistry,' 3rd edn., Clarendon Press, Oxford, 1962.

[8] G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani, and G. Bandoli, *J. Chem. Soc.* (*A*), 1970, 1313.

[9] C. D. Cook, Pei-Tak Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, 1969, **91**, 2123.

[10] J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometallic Chem.*, 1967, **7**, P9.

[11] R. Eisenberg and J. Ibers, *Inorg. Chem.*, 1965, **4**, 773.

[12] V. G. Albano, G. M. Basso Ricci, and P. L. Bellon, *Inorg. Chem.*, 1969, **8**, 2109.

[13] A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc.* (*A*), 1969, 2772.

[14] R. Mason and A. I. M. Rae, *J. Chem. Soc.* (*A*), 1970, 1767.

present. Bonds which are comparably short occur in $(Ph_3P)_2Pt(OCMe_2OO)$[15] (2·24 and 2·27), and in $(Ph_3P)_2Pt(CO_3)$[16] (2·24 Å) where the Pt–P bond is *trans* to an oxygen atom. The longer Pt–P(2) bond in $PtF[CH(CF_3)_2](PPh_3)_2$ is similar to those found in $(Ph_3P)_2Pt[NC(CF_3)]_2N$,[17] (2·28 and 2·31 Å).

The geometry of the triphenylphosphine and hexafluoroisopropyl ligands has not been determined sufficiently accurately for us to be able to detect any minor departures from regularity, but within the standard deviations given nothing calls for comment. The structure determination therefore serves to characterise the material unequivocally and to give a measurement of a Pt–F bond length. As far as we are aware, no other crystal structure determinations have been carried out on molecules of this type.[18,19] The packing of the molecules within the monoclinic unit cell is shown (in projection down *b*) in Figure 2. None of the intermolecular contacts is notably short.

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[3/455 *Received, 1st March,* 1973]

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[15] R. Ugo, F. Conti, S. Cenini, R. Mason, and G. R. Robertson, *Chem. Comm.*, 1968, 1498.

[16] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Comm.*, 1967, 408.

[17] W. J. Bland, R. D. W. Kemmitt, I. W. Nowell, and D. R. Russell, *Chem. Comm.*, 1968, 1065.

[18] R. D. W. Kemmitt, R. D. Peacock, and J. Stocks, *J. Chem. Soc. (A)*, 1971, 846.

[19] K. R. Dixon and J. J. McFarland, *Chem. Comm.*, 1972, 1274.