Crystal and Molecular Structures of 2-Bis(methyldiphenylphosphine)- and of 2-Bis(triphenylphosphine)-4,4,6,6-tetrakis(trifluoromethyl)-1,3,5,2-trioxaplatinan: Adducts of Hexafluoroacetone with Peroxobis(methyldiphenylphosphine)platinum(II) and with Peroxobis(triphenylphosphine)platinum(II)

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Crystals of $(MePh_2P)_2{\cdot}Pt{\cdot}[O{\cdot}C(CF_3)_2]_2{\cdot}O$ (I) are orthorhombic, space group $Pca2_1$, with $Z = 4$ in a unit cell of dimensions: $a = 22.040(20)$, $b = 9.683(6)$, $c = 16.235(3)$ Å; the structure was elucidated by heavy-atom methods from 2 611 diffracted intensities measured by diffractometer, and refined to R 0.085. Crystals of $(Ph_3P)_2{\cdot}Pt{\cdot}[O{\cdot}C(CF_3)_2]_2{\cdot}O$ (II) are triclinic, $a = 14.559(9)$, $b = 12.287(6)$, $c = 12.819(3)$ Å, $\alpha = 107.62(3)$, $\beta = 84.57(4)$, $\gamma = 105.74(4)°$, and the structure was similarly elucidated from 5 296 intensities measured by diffractometer; R 0.068. In (I) and (II) the platinum, which is in an approximately square-planar environment, forms part of a six-membered condensed hexafluoroacetone ring which is markedly non-planar. The $O{-}C(CF_3)_2$ bonds from the oxygen atoms adjacent to the metal in this ring are notably short [1.323(14) Å]. The line joining the Pt atom to the furthermost ring oxygen atom is an approximate two-fold axis for the ring.

ZEROVALENT platinum complexes PtL_4 ($L = PPh_3$, $PMePh_2$, or PMe_2Ph) react with organic azides or sulphonyl azides in dry solvents to give azadiene compounds $[Pt{\cdot}N(R)N{:}NN(R)L_2]$ ($R = Ph$, p-MeC_6H_4, or $PhSO_2$, *etc.*).[1] † These products, when treated with hexafluoroacetone containing small amounts of its hydrate $(CF_3)_2C(OH)_2$, afford azobenzene–platinum complexes $[Pt(RN{:}NR)L_2]$ as well as compounds believed, on the basis of ^{19}F n.m.r. and other studies,[1] to contain both six- and seven-membered heterocyclic ring systems:

$$Pt{\cdot}O{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O$$

and

$$Pt{\cdot}O{\cdot}C(CF_3)_2{\cdot}O{\cdot}O{\cdot}C(CF_3)_2{\cdot}O.$$

Earlier it was reported[3] that the dioxygen complex

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† In the presence of moisture or protic solvents complex reactions occur and a variety of products form (ref. 2).

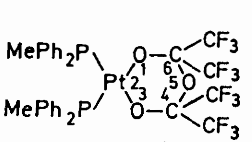
[1] M. I. Bruce, G. Shaw, and F. G. A. Stone, unpublished work.

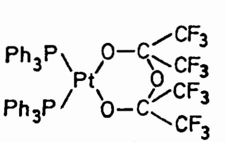
[2] W. Beck, M. Bander, G. La Monnica, S. Cenini, and R. Ugo, *J. Chem. Soc.* (*A*), 1971, 113.

[3] P. J. Hayward and C. J. Nyman, *J. Amer. Chem. Soc.*, **1971, 93**, 617.

$[PtO_2(PPh_3)_2]$ reacts with excess of hexafluoroacetone to give a compound also formulated with a seven-membered ring, *viz.* $[Pt{\cdot}O{\cdot}O{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O(PPh_3)_2]$. Several well authenticated nickel, palladium, and platinum complexes containing the five-membered ring system $M{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O$ are known,[4] and we have already determined the structure of one of these.[5]

The present study was carried out to provide unambiguous structural evidence for the existence of six- and/or seven-membered ring compounds. We have confirmed the presence of the six-membered $Pt{\cdot}O{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O$ ring in (I) (the first example of a structure). Unfortunately, however, the compound believed to contain a peroxy-linkage adjacent to the platinum atom decomposed in the *X*-ray beam, while a crystal of its presumed isomer with a peroxy-linkage between the two $C(CF_3)_3$ groups (II) proved also to contain the same six-membered ring.


(I)


(II)

Showing the systematic numbering system

EXPERIMENTAL

Compound (I), $[(Ph_2MeP)_2{\cdot}Pt{\cdot}O{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O]$, crystallises as large prisms elongated along *c*. Lattice parameters and systematic absences were determined from oscillation, Weissenberg, and precession photographs from a crystal of size 0.05 × 0.19 × 0.51 mm. The crystal, which is orthorhombic, was aligned along *c* on a Buerger–Supper-Pace 0.01°-incrementing two-circle diffractometer, and intensities were measured with a stationary-background–ω-scan–stationary-background sequence, as described earlier.[6] Backgrounds were counted for 0.5 min, the scan rate was 0.750° min^{-1}, and the scan range was $(2.0 + 0.5/L)°$, where L is the Lorentz correction. Measurement of layers $hk0$—18, for $h \leqslant 30$, $k \leqslant 13$, and with $\sin\theta < 0.50$, gave 4 085 reflections of which 2 611 were 'observed' according to the criterion $[N_3 - (N_1 + N_2)]/[N_3 + N_1 + N_2]^{\frac{1}{2}} > 2.5$, and were used in the analysis (where N_3, N_1, and N_2 are the peak count, and the first and second background counts). Standard reflections, one for each layer, were measured between every 20 reflections; the intensities of these check reflections varied only between -0.1 and $+0.7\%$ during data collection. No correction for *X*-ray absorption was made.

Crystal Data for (I).—$C_{32}H_{26}F_{12}O_3Pt$, $M = 920.6$, Orthorhombic, $a = 22.040(20)$, $b = 9.683(6)$, $c = 16.235(3)$ Å, $U = 3\,465$ Å^3, D_m (flotation) $= 1.7(1)$, $Z = 4$, $D_c = 1.76$ g cm^{-3}, $F(000) = 1\,712$. Mo-K_α *X*-radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 45.0$ cm^{-1}. Space group $Pca2_1$ (No. 29).

Structure Solution and Refinement of (I).—The systematic absences of reflections allow space groups *Pcam* (non-standard setting of No. 57: *Pbcm*)[7] or $Pca2_1$ (No. 29). It was clear from the Patterson synthesis that the Pt atom must lie in the mirror plane (at $z = \frac{1}{4}$) if the space group were *Pcam*, and that pseudomirror symmetry $\perp^{\mathrm{r}}$ z would exist if $Pca2_1$ were correct. As the molecule is potentially capable of possessing mirror symmetry, attempts to solve and refine the structure in *Pcam* were made. All failed. The best R (0.226) was given by incorporating the two phosphorus atoms and the three ring oxygen atoms into the mirror plane, but the remaining peaks on the electron-density difference synthesis made no chemical sense. A solution was obtained, however, in $Pca2_1$, largely by trial-and-error occupancy with phosphorus and oxygen atoms of sites related by the pseudo-mirror; after refinement of this structure was complete, attempts were also made to refine a model in which molecules were disordered symmetrically across the plane $z = \frac{1}{4}$ (this would effectively change the pseudomirror into a real one). A much worse R was obtained. Structure solution in $Pca2_1$ proceeded by choosing that arrangement of PtP_2O_3 which gave the lowest R (0.196, R' 0.279) and then locating all other non-hydrogen atoms from electron-density difference syntheses, choosing the more chemically probable of any two mirror-related peaks (R 0.095, R' 0.124). Refinement to convergence made use of two overlapping block-matrices: in the first, the 19 scale factors, positional co-ordinates for all atoms except phenyl-ring carbon atoms (z for Pt fixed), and all thermal parameters were varied; in the second, positional and isotropic thermal parameters for P(1), P(2), O(1), O(2), C(1), C(2), C(10), and C(20) were all kept fixed while all other parameters were allowed to vary. The Pt atom was given anisotropic thermal parameters but with the U_{33} component restrained to the isotropic value, and corrections for the real and imaginary parts of anomalous dispersion by the Pt atom ($\Delta f'$ -2.05, $\Delta f''$ 8.43) were introduced. A weighting scheme of the type: $1/w = (F/85)^2$ for $F > 85$ and $1/w = 1$ for $F \leqslant 85$ gave a satisfactory weight analysis, and refinement converged at R 0.087 (R' 0.111). There were, however, several unsatisfactory features of the structure so derived; in particular, the two Pt–P bond lengths [2.261(9) and 2.183(7) Å] were not identical. In view of the fact that the magnitude of the correction for the imaginary part of anomalous dispersion for Pt is relatively large, however, it is possible that significant changes would occur if the enantiomorphous unit cell were taken as the model for refinement. This was done (by reversing the signs of all co-ordinates), and refinement then resulted in R 0.085 (R' 0.108) with removal of the structural discrepancies. Thus the positional parameters listed in Table 1 refer, we believe, to the absolute configuration of the unit cell of the particular crystal investigated. In the last four cycles of refinement, a partial-shift factor of 0.8 was employed to dampen the oscillation of the variables caused by the high correlations between them. Correlation coefficients >0.2 were present for the following pairs of atoms: O(3), F(53); C(3), C(6); C(3), F(61); F(31), F(62); F(32), C(6); F(32), F(61); F(32), F(63); C(4), F(41); C(4), F(42); C(5), F(52); and C(5), F(53); also between the scale factors and atoms C(3) and Pt. Many of these pairs of atoms are related by pseudosymmetry elements of the Pt array. Since covariances were not taken into account in the calculation of bond length and angle standard deviations, there could be a considerable error in those listed in Table 3 especially for the

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[4] F. G. A. Stone, *Pure Appl. Chem.*, 1972, **30**, 551, and refs. therein.

[5] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

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

[7] 'International Tables for *X*-Ray Crystallography,' vol. 1, Kynoch Press, Birmingham, 1952.

trifluoromethyl groups. The mean shift-to-error in the last two cycles was 0.02 (maximum 0.12) and the highest peaks remaining on a final electron-density difference synthesis were *ca.* 4 e$Å^{-3}$ around the Pt atom and *ca.* 1 e$Å^{-3}$ near CF_3 groups. There was no evidence, however, of disorder among the F positions.

In view of the fact that (II) gave, unexpectedly, an analysis of the same ring system as that of (I) (much more accurately), we did not consider it worthwhile to make absorption corrections, although in principle the correction for anomalous dispersion[8] requires it. The scattering factors used were those of ref. 9 for phosphorus, oxygen, carbon, hydrogen, and platinum, and of ref. 10 for fluorine. Computational work was carried out using the '*X*-Ray System' of programs.[11]

Compound (II), $[(Ph_3P)_2\cdot\overline{Pt\cdot O\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}]$.—This crystallises in three habits: acicular, tabular, and bipyramidal. The crystal chosen for intensity-data collection was tabular and of dimensions 0.08 × 0.25 × 0.37 mm; it was sealed into a Lindemann glass tube with *c* approximately parallel to the tube axis. The crystal faces were the pinacoidal forms {100}, {010}, and $\{1\bar{1}1\}$. A Syntex $P2_1$ four-circle diffractometer[12] was used for data collection according to methods described earlier.[5] Intensities were collected in the range $3.7° \leqslant 2\theta \leqslant 45.0°$ with Mo-K_α *X*-radiation and a graphite monochromator. Scan rates varied from 0.0337 to 0.977° s^{-1} for sample peak counts of 7 and 200. Of 5 530 independent measured intensities, 4 539 were 'observed' [$I \geqslant 2.5\sigma(I)$] and 5 300 had $I > 0$. Analysis of two check reflections remeasured every 30 intensity measurements showed negligible decay (−1.0 and −2.1% over 43.4 h crystal exposure), and the calculated standard deviations were 1.02 and 1.05 times those estimated from counting statistics. Observed intensities were corrected for *X*-ray absorption, employing the Gaussian quadrature method of the programme ABSORB[11] with a grid 4 × 10 × 30. The 991 unobserved reflections were not corrected but were assigned a separate scale factor in the refinement.

Crystal Data for (II).—$C_{42}H_{30}F_{12}O_3Pt$, $M = 1\,067.7$, Triclinic, $a = 14.559(9)$, $b = 12.287(6)$, $c = 12.819$ (3) Å, $\alpha = 107.62(3)$, $\beta = 84.57(4)$, $\gamma = 105.74(4)°$, $U = 2\,103.3$ Å^3, D_m (flotation) $= 1.8(1)$ g cm^{-3}, $Z = 2$, $D_c = 1.69$ g cm^{-3}, $F(000) = 1\,028$. Mo-K_α *X*-radiation, $\lambda = 0.71069$ Å; μ(Mo-K_α) = 36.8 cm^{-1}. Space group $P\bar{1}$ (No. 2).

Structure Solution and Refinement of (II).—The platinum atom was located from a Patterson synthesis and the remaining atoms by successive electron-density difference syntheses, based on observed reflections only. Least-squares refinement of the structures used all 5 300 reflections having $I > 0$, and two block matrices were defined, the first containing all non-phenyl atom parameters, the scale factors, and an overall temperature factor, the second containing only the phenyl-ring carbon parameters. The two scale factors were calculated so that for each group $\Sigma F_o/\Sigma|F_c| = 1$ and then their ratio was held constant at the ratio of these rescale values. This led to *R* 0.072 (*R'* 0.081). Refinement was completed with alternating cycles which included in (i) all thermal and scale factors, in (ii) all atomic co-ordinates and scale factors. Anisotropic thermal motion was allowed for the two phosphorus atoms and for all atoms of the $\overline{Pt\cdot O\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}$ moiety, and hydrogen atoms were introduced at fixed calculated positions [C–H 0.99 Å, *U*(H) 0.08 Å^2], with a weighting scheme of the type $1/w = (F/55)^2$, $F > 55$; $1/w = 1$, $F \leqslant 55$ (which gave a satisfactory weight analysis). Lastly, three reflections which showed strong extinction effects were deleted ($0\bar{3}1$, $1\bar{2}1$, and $2\bar{2}1$) and the reflection ($1\bar{1}0$) was discounted because of a highly asymmetric background

TABLE 1

Atomic positional (fractional co-ordinates) and thermal parameters for (I), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	10^2U/Å^2 *
Pt	0.317 91(4)	0.304 99(10)	0.250 00	†
P(1)	0.3775(4)	0.4848(9)	0.2208(6)	4.2(2)
P(2)	0.3917(3)	0.1627(7)	0.2871(6)	3.9(2)
O(1)	0.246(1)	0.419(2)	0.223(1)	4.5(5)
C(1)	0.193(1)	0.369(3)	0.203(2)	3.3(6)
O(3)	0.166(1)	0.269(2)	0.253(3)	5.9(5)
C(2)	0.201(2)	0.173(4)	0.299(3)	6.2(10)
O(2)	0.256(1)	0.150(2)	0.277(2)	5.7(6)
C(3)	0.191(2)	0.304(3)	0.112(4)	4.1(11)
F(31)	0.145(1)	0.220(3)	0.092(2)	9.5(9)
F(32)	0.238(1)	0.222(3)	0.101(2)	9.6(9)
F(33)	0.195(2)	0.405(4)	0.057(3)	13.1(12)
C(4)	0.145(3)	0.482(6)	0.199(4)	9.2(16)
F(41)	0.146(2)	0.534(4)	0.281(3)	14.2(14)
F(42)	0.092(2)	0.459(4)	0.188(3)	13.4(12)
F(43)	0.158(1)	0.591(4)	0.164(2)	11.0(10)
C(5)	0.160(3)	0.037(6)	0.296(4)	8.4(15)
F(51)	0.195(1)	−0.064(3)	0.332(2)	11.3(10)
F(52)	0.109(2)	0.049(4)	0.323(2)	13.3(12)
F(53)	0.166(2)	−0.001(4)	0.214(3)	12.8(14)
C(6)	0.201(2)	0.225(5)	0.389(4)	8.1(14)
F(61)	0.231(1)	0.339(3)	0.401(2)	9.1(8)
F(62)	0.142(2)	0.280(3)	0.411(2)	11.1(11)
F(63)	0.223(1)	0.132(4)	0.442(3)	12.5(11)
C(10)	0.448(1)	0.451(3)	0.169(2)	4.3(7)
C(11)	0.339(2)	0.615(4)	0.153(3)	4.8(8)
C(111)	0.324(2)	0.560(5)	0.078(3)	7.5(12)
C(112)	0.301(3)	0.658(6)	0.013(4)	10.3(17)
C(113)	0.296(3)	0.781(7)	0.036(5)	12.1(21)
C(114)	0.296(3)	0.843(6)	0.133(4)	10.4(17)
C(115)	0.301(3)	0.658(6)	0.013(4)	7.3(12)
C(12)	0.398(1)	0.581(3)	0.314(2)	4.2(7)
C(121)	0.455(1)	0.632(3)	0.325(2)	5.1(8)
C(122)	0.467(2)	0.693(5)	0.396(3)	7.7(11)
C(123)	0.426(2)	0.727(5)	0.459(4)	8.9(15)
C(124)	0.370(2)	0.678(5)	0.443(4)	9.8(16)
C(125)	0.355(2)	0.590(4)	0.371(3)	5.9(10)
C(20)	0.364(2)	0.022(5)	0.352(4)	9.7(15)
C(21)	0.426(2)	0.076(4)	0.198(3)	6.3(10)
C(211)	0.409(2)	0.114(4)	0.121(3)	5.9(9)
C(212)	0.437(2)	0.046(5)	0.051(3)	7.4(12)
C(213)	0.486(2)	−0.044(5)	0.065(4)	9.7(16)
C(214)	0.505(2)	−0.084(5)	0.149(4)	8.7(14)
C(215)	0.476(2)	−0.023(4)	0.218(3)	6.3(10)
C(22)	0.450(1)	0.237(3)	0.349(2)	3.4(6)
C(221)	0.430(1)	0.306(4)	0.422(3)	5.9(9)
C(222)	0.473(2)	0.365(4)	0.479(3)	6.4(10)
C(223)	0.534(2)	0.351(5)	0.454(4)	9.7(16)
C(224)	0.555(1)	0.285(3)	0.383(2)	4.8(8)
C(225)	0.513(2)	0.230(3)	0.333(3)	5.7(9)

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$, with parameters (Å^2 × 10^2): U_{11} 2.93(3), U_{22} 3.97(4), U_{33} 3.41, U_{12} −0.30(4), U_{13} 0.92(9), and U_{23} 1.60(8).

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

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

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[11] Technical Report TR 192 of the Computer Science Center, University of Maryland, June, 1972.

[12] R. A. Sparkes, SYNTEX P2$_1$ Operations Manual, Syntex Analytical Instruments, Cupertino, U.S.A., 1973.

TABLE 2

Atomic positional (fractional co-ordinates) and thermal parameters for (II), with estimated standard deviations in parentheses

Atom	x	y	z	10^2U/Å^2 *
Pt	0.211 29(3)	0.414 84(4)	0.310 17(3)	†
P(1)	0.1999(2)	0.3456(3)	0.1266(2)	†
P(2)	0.2169(2)	0.2488(3)	0.3444(3)	†
O(1)	0.2115(6)	0.5718(7)	0.2871(6)	†
C(1)	0.2040(10)	0.6680(11)	0.3660(9)	†
O(3)	0.2536(7)	0.6973(8)	0.4663(7)	†
C(2)	0.2702(10)	0.6118(11)	0.5086(10)	†
O(2)	0.2208(6)	0.5018(7)	0.4723(6)	†
C(3)	0.0989(12)	0.6652(16)	0.3990(12)	†
F(31)	0.0502(7)	0.6632(10)	0.3125(8)	†
F(32)	0.0539(6)	0.5706(10)	0.4285(8)	†
F(33)	0.0876(8)	0.7598(11)	0.4786(9)	†
C(4)	0.2493(12)	0.7756(15)	0.3257(13)	†
F(41)	0.2124(9)	0.7685(9)	0.2308(8)	†
F(42)	0.2473(9)	0.8782(8)	0.3932(9)	†
F(43)	0.3419(8)	0.7825(9)	0.3038(9)	†
C(5)	0.3779(12)	0.6222(14)	0.4963(13)	†
F(51)	0.4059(6)	0.5960(10)	0.3921(8)	†
F(52)	0.4063(8)	0.5522(11)	0.5397(11)	†
F(53)	0.4320(7)	0.7335(9)	0.5439(9)	†
C(6)	0.2446(12)	0.6563(13)	0.6336(11)	†
F(61)	0.2840(9)	0.7700(9)	0.6795(7)	†
F(62)	0.2689(9)	0.5984(9)	0.6928(7)	†
F(63)	0.1502(8)	0.6425(10)	0.6454(7)	†
C(10)	0.0863(8)	0.3349(10)	0.0737(9)	3.5(3)
C(101)	0.0203(9)	0.3878(12)	0.1396(11)	4.9(3)
C(102)	−0.0642(10)	0.3866(13)	0.1010(12)	5.8(4)
C(103)	−0.0857(11)	0.3302(14)	−0.0081(13)	6.5(4)
C(104)	−0.0207(11)	0.2766(14)	−0.0759(13)	6.4(4)
C(105)	0.0633(9)	0.2796(11)	−0.0352(11)	4.9(3)
C(11)	0.2864(9)	0.4577(1)	0.0757(10)	4.4(3)
C(111)	0.3744(10)	0.5066(13)	0.1234(12)	6.0(4)
C(112)	0.4416(12)	0.5957(15)	0.0904(14)	7.4(4)
C(113)	0.4192(13)	0.6375(16)	0.0092(16)	8.3(5)
C(114)	0.3323(12)	0.5887(14)	−0.0383(14)	7.0(4)
C(115)	0.2653(10)	0.4982(12)	−0.0058(11)	5.5(3)
C(12)	0.2234(9)	0.2034(11)	0.0471(10)	4.7(3)
C(121)	0.3084(12)	0.2016(15)	−0.0079(14)	7.0(4)
C(122)	0.3226(14)	0.0917(17)	−0.0719(16)	8.7(5)
C(123)	0.2523(14)	−0.0078(17)	−0.0744(16)	8.8(5)
C(124)	0.1683(12)	−0.0075(15)	−0.0198(14)	7.2(4)
C(125)	0.1532(10)	0.0999(12)	0.0428(11)	5.3(3)
C(20)	0.2431(9)	0.2728(11)	0.4872(11)	4.7(3)
C(201)	0.1756(10)	0.3044(12)	0.5660(11)	5.4(3)
C(202)	0.1921(10)	0.3218(13)	0.6762(12)	5.7(3)
C(203)	0.2735(12)	0.3081(15)	0.7072(14)	7.0(4)
C(204)	0.3396(13)	0.2716(16)	0.6283(15)	7.7(5)
C(205)	0.3243(11)	0.2531(13)	0.5169(12)	6.0(4)
C(21)	0.1042(9)	0.1376(11)	0.3274(10)	4.4(3)
C(211)	0.0917(10)	0.0348(13)	0.3593(12)	5.8(4)
C(212)	0.0035(11)	−0.0422(14)	0.3552(13)	6.4(4)
C(213)	−0.0726(12)	−0.0197(15)	0.3190(14)	7.4(4)
C(214)	−0.0643(11)	0.0790(13)	0.2862(14)	6.4(4)
C(215)	0.0261(10)	0.1594(12)	0.2924(11)	5.3(3)
C(22)	0.3111(8)	0.1858(10)	0.2692(10)	4.1(3)
C(221)	0.2990(11)	0.0644(13)	0.2193(13)	6.2(4)
C(222)	0.3777(13)	0.0236(16)	0.1665(15)	7.9(5)
C(223)	0.4623(14)	0.1017(17)	0.1656(16)	8.5(5)
C(224)	0.4782(12)	0.2224(15)	0.2155(14)	7.0(4)
C(225)	0.3984(11)	0.2626(13)	0.2671(13)	6.3(4)

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$, with parameters ($\times 10^2$):

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	4.27(3)	4.31(3)	2.34(3)	1.51(2)	0.07(2)	1.20(2)
P(1)	4.8(2)	5.0(2)	2.5(2)	1.9(1)	0.0(1)	1.3(1)
P(2)	4.7(2)	4.6(2)	3.2(2)	1.7(1)	0.0(1)	1.5(1)
O(1)	6.2(5)	5.1(5)	3.4(5)	2.3(4)	−0.3(4)	1.4(4)
C(1)	6.6(8)	4.6(7)	2.6(6)	2.2(6)	0.1(6)	1.1(6)
O(3)	7.9(7)	4.8(5)	4.3(5)	1.7(5)	−1.4(5)	0.7(4)
C(2)	6.5(8)	4.9(8)	3.3(7)	2.3(7)	−0.6(6)	1.2(6)

TABLE 2 (*Continued*)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{33}
O(2)	6.4(6)	5.1(5)	2.6(4)	1.6(4)	−0.6(4)	1.4(4)
C(3)	8.3(11)	8.7(12)	4.4(8)	3.5(10)	−0.2(8)	0.9(8)
F(31)	8.3(6)	12.3(8)	7.1(6)	5.9(6)	−1.1(5)	2.6(6)
F(32)	5.4(5)	11.8(8)	9.0(7)	2.5(5)	1.9(5)	5.2(6)
F(33)	10.9(8)	12.0(9)	7.4(7)	6.8(7)	0.7(6)	−2.2(6)
C(4)	8.4(12)	7.7(11)	6.0(10)	3.1(9)	−0.9(8)	3.2(9)
F(41)	14.0(9)	7.8(6)	7.8(7)	1.0(6)	−3.3(6)	4.3(5)
F(42)	15.8(10)	4.8(5)	9.0(7)	3.6(6)	−1.6(7)	0.8(5)
F(43)	9.7(8)	8.9(7)	10.0(8)	1.5(6)	0.7(6)	5.5(6)
C(5)	7.3(10)	6.8(10)	6.4(10)	2.2(9)	−1.3(8)	1.1(8)
F(51)	6.0(5)	12.3(8)	6.8(6)	2.3(5)	0.2(5)	0.5(6)
F(52)	9.4(8)	12.5(9)	13.9(10)	5.5(7)	−2.0(7)	5.5(8)
F(53)	7.6(6)	8.8(7)	9.3(7)	1.3(5)	−1.3(5)	0.9(6)
C(6)	8.8(11)	5.4(9)	3.8(8)	2.0(8)	−0.5(7)	−0.2(7)
F(61)	14.4(10)	7.7(7)	4.5(5)	3.1(6)	−1.1(5)	−1.2(5)
F(62)	15.9(10)	8.9(7)	4.0(5)	4.3(7)	−1.4(5)	2.5(5)
F(63)	10.7(8)	12.9(9)	4.1(5)	3.9(7)	2.0(5)	1.2(5)

TABLE 3

Bond lengths (Å) and angles (°) for (I) and (II)

(*a*) Distances

	(I)	(II)
Pt–P(1)	2.232(9)	2.252(3)
Pt–P(2)	2.215(8)	2.236(4)
Pt–O(1)	1.98(2)	2.04(1)
Pt–O(2)	2.07(2)	2.03(1)
O(1)–C(1)	1.31(3)	1.33(1)
O(2)–C(2)	1.29(4)	1.31(1)
C(1)–O(3)	1.40(5)	1.43(2)
C(2)–O(3)	1.41(5)	1.40(2)
C(1)–C(3)	1.60(7)	1.54(2)
C(1)–C(4)	1.52(6)	1.53(2)
C(2)–C(5)	1.60(7)	1.54(2)
C(2)–C(6)	1.55(8)	1.57(2)
C(3)–F(31)	1.34(5)	1.36(2)
C(3)–F(32)	1.31(5)	1.32(2)
C(3)–F(33)	1.34(7)	1.33(2)
C(4)–F(41)	1.43(8)	1.35(2)
C(4)–F(42)	1.20(7)	1.30(2)
C(4)–F(43)	1.23(7)	1.34(2)
C(5)–F(51)	1.38(7)	1.33(2)
C(5)–F(52)	1.20(7)	1.32(3)
C(5)–F(53)	1.39(8)	1.37(2)
C(6)–F(61)	1.31(6)	1.33(2)
C(6)–F(62)	1.46(6)	1.31(2)
C(6)–F(63)	1.34(7)	1.34(2)
P(1)–C(10)	1.79(3)	1.80(1)
P(1)–C(11)	1.87(4)	1.83(1)
P(1)–C(12)	1.83(4)	1.84(1)
P(2)–C(20)	1.83(5)	1.82(1)
P(2)–C(21)	1.84(4)	1.81(1)
P(2)–C(22)	1.78(3)	1.81(1)

(*b*) Angles

P(1)–Pt–P(2)	96.3(3)	98.5(1)
P(1)–Pt–O(1)	89.4(6)	84.4(2)
P(2)–Pt–O(2)	88.6(6)	90.5(3)
P(1)–Pt–O(2)	174.9(6)	171.0(3)
P(2)–Pt–O(1)	174.0(7)	176.5(2)
O(1)–Pt–O(2)	85.6(8)	86.5(4)
Pt–O(1)–C(1)	125(2)	125(1)
Pt–O(2)–C(2)	124(2)	122(1)
O(1)–C(1)–O(3)	119(3)	119(1)
O(2)–C(2)–O(3)	118(4)	119(1)
C(1)–O(3)–C(2)	123(2)	123(1)
C(3)–C(1)–C(4)	103(3)	110(1)
C(5)–C(2)–C(6)	107(4)	109(1)
O(1)–C(1)–C(3)	113(2)	112(1)
O(1)–C(1)–C(4)	112(3)	109(1)
O(2)–C(2)–C(5)	113(3)	111(1)
O(2)–C(2)–C(6)	108(3)	107(1)
O(3)–C(1)–C(3)	104(3)	106(1)
O(3)–C(1)–C(4)	104(3)	102(1)
O(3)–C(2)–C(5)	103(3)	106(1)
O(3)–C(2)–C(6)	107(4)	103(1)

(*c*) Some unweighted mean values, with mean standard deviations in parentheses

TABLE 3 (*Continued*)

(i) Distances

	(I)	(II)
Pt–P	2.223(9)	2.244(4)
Pt–O	2.024(21)	2.032(9)
(Pt)O–C	1.30(3)	1.32(1)
C–O(3)	1.41(5)	1.42(2)
C–CF_3	1.57(7)	1.54(2)
C–F	1.33(7)	1.33(2)
C–C(Ph)	1.41(7)	1.38(2)
P–C	1.82(4)	1.82(1)

(ii) Angles

	(I)	(II)
cis-P–Pt–O	89.0(6)	87.4(3)
trans-P–Pt–O	174.5(7)	173.8(3)
Pt–O–C	124(2)	123(1)
O–C–O	119(3)	119(1)
F_3C–C–CF_3	105(4)	109(1)
(Pt)O–C–CF_3	111(3)	110(1)
F_3C–C–O(3)	104(3)	104(1)
C–C–F	112(4)	113(1)
F–C–F	106(5)	106(1)
C–P–C	106(2)	105(1)
Pt–P–C	114(1)	114(1)
P–C–C	118(3)	120(1)
C–C–C(Ph)	120(5)	120(1)

TABLE 4

(*a*) Equations * of some least-squares planes: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Pt, O(1), C(1), O(3), C(2), O(2)

(I) $-0.882x + 4.504y + 14.257z = 4.662$

[Pt 0.020, O(1) 0.202, C(1) −0.255, O(3) 0.031, C(2) 0.234, O(2) −0.231]

(II) $13.568x - 0.310y - 3.100z = 1.676$

[Pt 0.100, O(1) 0.126, C(1) −0.251, O(3) 0.103, C(2) 0.223, O(2) −0.301]

Plane (2): Pt, P(1), P(2), O(1), O(2)

(I) $-1.372x + 3.090y + 15.353z = 4.366$

[Pt −0.021, P(1) 0.004, P(2) 0.007, O(1) 0.008, O(2) 0.003]

(II) $13.934x + 0.088y - 0.889z = 2.718$

[Pt −0.013, P(1) −0.014, P(2) 0.020, O(1) 0.024, O(2) −0.017]

(*b*) Torsion angles (°) around the oxo-ring

	(I)	(II)
Pt–O(1)–C(1)–O(3)	49.7	40.0
O(1)–C(1)–O(3)–C(2)	−29.6	−31.6
C(1)–O(3)–C(2)–O(2)	−20.5	−16.8
O(3)–C(2)–O(2)–Pt	47.0	52.3
C(2)–O(2)–Pt–O(1)	−25.4	−35.7
O(2)–Pt–O(1)–C(1)	−22.0	−9.4

* *x*, *y*, *z* are fractional crystal co-ordinates.

count. Refinement converged at *R* 0.070 (*R′* 0.089) for 5 296 reflections, with mean and maximum shift-to-error ratios in the last two cycles of 0.015 and 0.11. An electron-density difference map showed a peak of *ca.* 2.4 eÅ^{-3} near the Pt atom, peaks of up to 1.0 eÅ^{-3} close to phenyl groups, and three maxima of *ca.* 1.5 eÅ^{-3} in a region of above-average electron density (*ca.* 2 × 1 × 6 Å) around the centre of symmetry at $\frac{1}{2},0,\frac{1}{2}$. With three half-carbon atoms at the positions of the peaks it was possible to construct a vague hexane molecule C(7)–C(8)–C(9)–C(9)′–C(8)′–C(7)′ and the agreement indices dropped to *R* 0.068 (*R′* 0.086), with no significant changes in any parameters of the metal complex. The bond lengths and angles for this ' molecule ' were unrealistic, however, and a further difference synthesis still showed considerable electron density. A reasonable interpretation of these results is that there is statistical occupation by solvent molecules of the gap in the crystal packing, but that these molecules are present in nonstoicheiometric proportions and are disordered. Attempts at further refinement were considered too costly to be worthwhile, so the results in the Tables refer to refinement with no contribution from clathrated hexane. Atomic parameters for compound (I) are in Table 1, for compound (II) in Table 2; important bond lengths and angles for (I) and (II) are listed in Table 3. Details of the geometry of the trifluoromethyl and phosphine ligands, about least-squares planes and interplanar angles, and about non-bonded interactions are given, with the list of observed and calculated structure factors, in Supplementary Publication No. SUP 21386 (44 pp., 1 microfiche); * only essential planes and torsion angles are given in Table 4.

DISCUSSION

Compounds (I) and (II) both contain the puckered six-membered ring $\overline{\mathrm{Pt\cdot O\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}}$ in which the platinum has approximately square-planar valence orientations; the two other platinum sites are occupied in (I) by methyldiphenyl-, in (II) by triphenyl-phosphines. Although the symmetry of the crystal packing is quite different for (I) and (II), there is only one significant (but small) difference between the two molecules: the P–Pt–P angle is some 2.2(4)° smaller in (I) than in (II). Apart from this feature, the discussion will relate, in general, to compound (II), as this has the more accurately resolved structure.

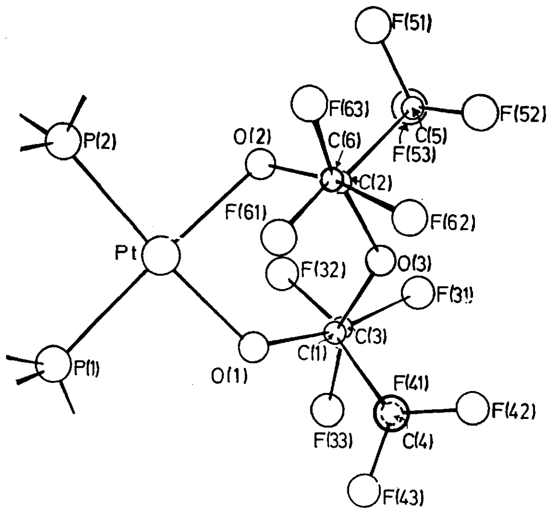

FIGURE 1 The six-membered $\overline{\mathrm{Pt\cdot O\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}}$ ring present in compounds (I) and (II), showing the crystallographic numbering system. For clarity phosphine ligands are omitted

The six-membered oxo-ring is markedly non-planar (Table 4) but has approximate symmetry C_2 [the two-fold axis joining Pt to O(3)]. For compound (I) this symmetry is almost exact and includes the trifluoromethyl groups attached to C(1) and C(2), for all of which the C–C bonds lie in planes closely perpendicular to the local O–C–O ring plane, and with a C–C–C angle not significantly different from the ideal tetrahedral value

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

(Figure 1). There are, however, some fairly short (*ca.* 2.65 Å) contact distances between fluorine atoms of trifluoromethyl groups attached to the same carbon atom (Table 5); these could affect the magnitude of the C–C–C angle which, from ordinary valence-shell electron-pair repulsion theory, might have been expected to be smaller than the ideal tetrahedral value.

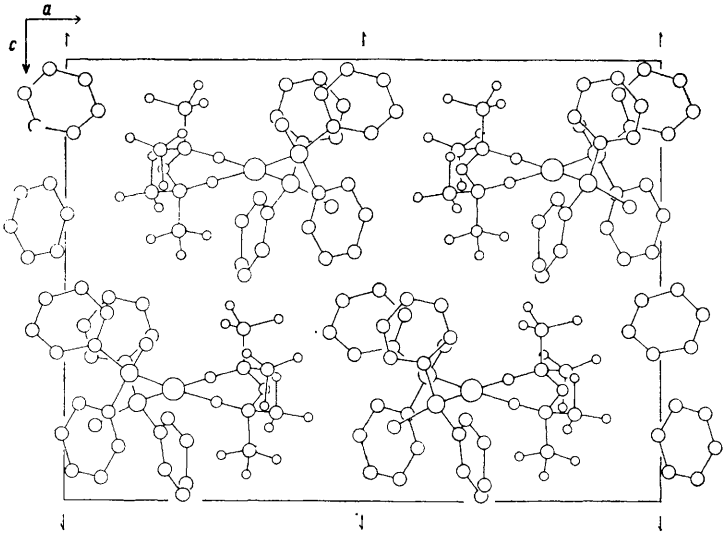

FIGURE 2 The contents of the orthorhombic unit cell of (I) in projection down *b*

Within the six-membered ring, the bond lengths show the same interesting sequence as was found in the five-membered ring of the carbene complex $\overline{Pd\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}(CNBu^t)[C(NEt_2)NHBu^t]$.[5] The metal–oxygen bond (see later) is followed by a C–O bond (*ca.* 1.32 Å) which is decidedly shorter than the succeeding C–O bond (*ca.* 1.42 Å) between the $C(CF_3)_2$ group and the furthest oxygen atom, O(3). As before, we ascribe this to donation by the oxygen lone-pair electrons into antibonding orbitals of the $>C(CF_3)_2$ moiety, the energy levels of the lone-pair orbitals on O(1) and O(2) having been raised as a result of their proximity to the electropositive metal atom. The formal similarity between a $>C(CF_3)_2$ moiety and a $>C=O$ group can here be appreciated.[13] Significantly, the O–C–O angle [119.1(12)°] is near the value expected for sp^2 hybridisation, and the C(2)–O(2) and C(1)–O(1) bond lengths suggest a bond order of *ca.* 1.3.[14] The four CF_3 groups have mean $C-CF_3$ 1.544(21) Å and a mean C–F 1.332(20) Å, both of which can be accepted as normal. The F–C–F angles, however, tend to be less than the ideal tetrahedral value, and the C–C–F angles greater, while the enhanced bond orders of the O(1)–C(1) and O(2)–C(2) bonds are reflected in enlarged angles $O(1)-C-CF_3$ and $O(2)-C-CF_3$ but diminished angles $O(3)-C-CF_3$.

The length of the Pt–O bond [2.032(9) Å] needs to be considered in relation to that of the Pt–P bond [2.244(4) Å] lying *trans* to it. These bond lengths do not correspond to values obtained from tables of covalent radii[15] (1.97 and 2.41 Å), but are nevertheless closely similar to distances in other compounds where Pt–P lies *trans* to Pt–O: *e.g.* $(Ph_3P)_2PtO_2,2CHCl_3$, 2.006(7) and 2.233(3);[16] $(Ph_3P)_2PtO_2,1.5C_6H_6$, 2.01(3) and 2.27(1);[17] $(Ph_3P)_2PtCO_3$, 2.07 and 2.24;[18] and $(Ph_3P)_2\overline{PtO_2CMe_2O}$, 2.01(1) and 2.26(1) Å.[19] Measured $Pt^{II}-P$

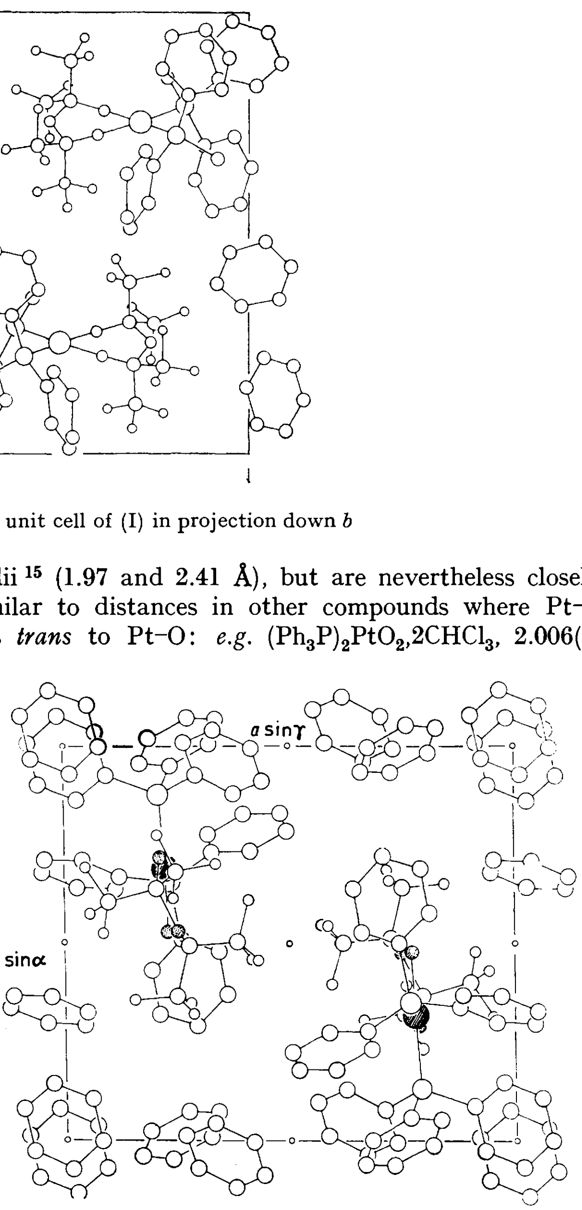

FIGURE 3 The contents of the triclinic unit cell of (II) in projection down *b*

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distances usually lie in the range[20,21] 2.230(9) [for *trans*-$Pt_2Cl_4(PPr_3)_2$][22] to 2.33(1) Å [for Pt(CN)(C:CNC)$(PPh_3)_2$],[23] so that the Pt–P distances recorded in (I) and (II) are among the shortest known. The P–Pt–P angle in (II) [98.5(1)°] is the same as in the compounds of refs. 18 and 19, but slightly larger than the corresponding angle in (I) [96.3(3)°] which in turn is almost identical to that [96.2(4)°] in *cis*-$(Me_3P)_2PtCl_2$.[24] The reason appears to lie in the different packing modes (Figures 2 and 3) of the two crystals: in (I) all intermolecular C···C contacts tend to close the P–Pt–P angle. The phosphines have expected geometry in both compounds except for one minor feature: Pt–P(1)–C(11) in (II) is only 104.7(4)° while Pt–P(1)–C(12) is 123.0(5)°. This can again be understood from non-bonded interactions, but as all this information is of only secondary importance it has been included with the Supplementary Publication.

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