Crystal and Molecular Structure of Acetatotetrakis(dimethylphenylphosphine)ruthenium(II) Hexafluorophosphate

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The crystal structure of the title complex has been determined by X-ray diffraction methods from counter data. Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 4$, $a = 18.29$, $b = 16.45$, $c = 13.05$ (all ±0.02) Å. The structure was solved by heavy-atom methods and refined by least-squares to R 0.049 for 1 773 observed reflections. The cation is monomeric with a distorted octahedral co-ordination. The mean Ru–P bond length for the two *trans*-PMe_2Ph groups (2.43 Å) is significantly longer than that of the *cis*-PMe_2Ph ligands (2.31 Å), and mean Ru–O is 2.23 Å. The acetate group is bidentate and subtends an angle of 58.7° at ruthenium.

STUDIES[1] on the reactivity of the salt $[(C_8H_{12})RuH(NH_2NMe_2)_3][PF_6]$ have shown that the hydrazine ligands are readily replaced by phosphites and phosphonites to give the cationic complexes $[RuHL_5][PF_6]$ (L = phosphite or phosphonite). Recently, we have synthesised[2] the compound $[RuH(PMe_2Ph)_5][PF_6]$ (I) from the dimethylhydrazine salt and investigations into the reactivity of this complex have produced a large range of new ruthenium(II) cationic species. For example (I) forms the alkyl carbonate complexes $[Ru(O_2COR)(PMe_2Ph)_4][PF_6]$ (R = Me, Et) with carbon dioxide in alcohols,[3] and the series of carboxylate compounds $[Ru(O_2CR)(PMe_2Ph)_4][PF_6]$ (R = Me, Et, $CHMe_2$, or Ph) from oxidation of the corresponding alcohols in air.[2] In fact a series of complexes of general formula $[RuXY(PMe_2Ph)_4][PF_6]$ have been prepared with a characteristic ^1H n.m.r. spectrum of the methyl groups on the phosphine ligands. It was thus decided to determine the crystal structure of the acetate salt $[Ru(OAc)(PMe_2Ph)_4][PF_6]$ to show whether the cation is mono- or di-meric. Also, a confirmation of the characteristic spatial arrangement of the four phosphine ligands would be a further aid in elucidating other similar cationic systems which we have obtained.

EXPERIMENTAL

A yellow crystal of dimensions 0.09 × 0.20 × 0.32 mm was selected for data collection. Unit-cell dimensions were obtained from least-squares refinement of 25 2θ values measured on a Philips diffractometer.

Crystal Data.—$C_{34}H_{47}F_6O_2P_5Ru$, $M = 857.73$, Orthorhombic, $a = 18.29(2)$, $b = 16.45(2)$, $c = 13.05(2)$ Å, $U = 3\,926$ Å^3, D_m (by flotation) = 1.47, $Z = 4$, $D_c = 1.47$, $F(000) = 1\,760$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 6.63 cm^{-1}. Space group $P2_12_12_1$.

Intensity data were collected on a Philips PW 1 100 four-circle automatic diffractometer, equipped with a graphite monochromator, in the ω—2θ scan mode in the θ range 3—20°. Of the 2 081 reflections measured, 1 773 were considered observed with $I > 2\sigma(I)$. Each reflection was scanned for 33 s and the same time was taken for the background count. Standard reflections remeasured every hour [(133), $(\bar{3}17)$, and $(9\bar{2}\bar{5})$] decreased respectively by 0.4, 0.06, and 0.2% during data collection (42 h). Background, Lorentz, and polarization corrections were applied but no corrections were made for extinction or absorption.

Structure Solution and Refinement.—All calculations were done on an IBM 360/65 computer using programs from the 'X-Ray' system.[4] Drawings were made by use of the thermal-ellipsoid plot program ORTEP.[5] The structure was solved by Patterson and Fourier methods. Refinement of the positional parameters and individual isotropic temperature factors of the non-hydrogen atoms by full-matrix least-squares methods gave R 0.074. Further refinement, with anisotropic thermal parameters for all non-hydrogen atoms, was carried out in stages because the 433 parameters could not be refined simultaneously by full-matrix methods. Unit weights were used during refinement. The final R was 0.049 for observed intensities. Observed and calculated structure factors and the thermal parameters from the final least-squares cycle are listed in Supplementary Publication No. SUP 21811 (14 pp., 1 microfiche).* Atomic fractional co-ordinates are listed in Table 1, bond lengths (uncorrected for thermal motion) and angles in Tables 2 and 3, selected non-bonded interatomic distances in Table 4, and some appropriate least-squares planes in Table 5. The Figure gives the atom numbering scheme used in the analysis.

RESULTS AND DISCUSSION

The structure consists of discrete cations and anions; the closest approach of fluorine in the anion to any non-hydrogen atom in the cation is >3.0 Å. The thermal parameters of the fluorine atoms indicate high thermal motion, which is reflected in the large variations in P–F

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

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[3] T. V. Ashworth and E. Singleton, *J.C.S. Chem. Comm.*, 1976, 204.

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TABLE 1

Final atomic co-ordinates ($\times 10^4$), with standard deviations in parentheses

Atom	*x*	*y*	*z*
Ru	2 193(1)	2 353(1)	499(1)
P(1)	2 170(2)	3 121(2)	−1 081(3)
P(2)	2 035(2)	1 359(2)	1 859(3)
P(3)	3 409(2)	2 506(3)	902(3)
P(4)	1 738(2)	3 449(2)	1 395(3)
O(1)	2 172(5)	1 239(5)	−474(7)
O(2)	1 157(5)	1 883(6)	−150(7)
C(1)	1 486(9)	1 300(8)	−611(11)
C(2)	1 058(10)	712(12)	−1 240(15)
C(11)	1 254(8)	3 482(10)	−1 406(11)
C(12)	2 712(9)	4 071(8)	−1 349(10)
C(13)	2 415(7)	2 507(9)	−2 206(9)
C(131)	3 169(8)	2 371(11)	−2 412(11)
C(132)	3 374(10)	1 957(11)	−3 320(16)
C(133)	2 827(12)	1 655(9)	−3 985(12)
C(134)	2 084(10)	1 752(8)	−3 734(11)
C(135)	1 891(8)	2 181(9)	−2 880(11)
C(21)	2 372(11)	1 450(12)	3 174(13)
C(22)	2 435(8)	350(9)	1 541(14)
C(23)	1 069(8)	1 092(9)	2 088(11)
C(231)	747(8)	472(11)	1 546(14)
C(232)	42(13)	231(17)	1 687(18)
C(233)	−376(11)	760(13)	2 373(16)
C(234)	−86(9)	1 345(10)	3 012(14)
C(235)	673(9)	1 543(10)	2 830(12)
C(31)	3 707(9)	2 853(10)	2 203(13)
C(32)	4 021(10)	3 193(11)	139(16)
C(33)	3 853(8)	1 528(10)	720(12)
C(331)	4 283(8)	1 109(11)	1 542(15)
C(332)	4 573(8)	356(10)	1 389(16)
C(333)	4 483(8)	−25(10)	429(20)
C(334)	4 096(9)	341(9)	−360(18)
C(335)	3 802(9)	1 111(10)	−220(15)
C(41)	735(7)	3 376(8)	1 334(12)
C(42)	1 863(10)	3 573(10)	2 806(13)
C(43)	1 950(8)	4 491(8)	1 014(11)
C(431)	2 669(8)	4 771(9)	1 135(12)
C(432)	2 847(11)	5 605(12)	814(11)
C(433)	2 336(10)	6 095(10)	359(13)
C(434)	1 635(11)	5 843(10)	229(12)
C(435)	1 430(9)	4 997(9)	558(14)
P(5)	5 074(3)	1 860(3)	4 557(4)
F(1)	4 738(11)	2 629(13)	4 765(15)
F(2)	4 266(7)	1 556(11)	4 207(13)
F(3)	5 201(7)	2 113(11)	3 406(9)
F(4)	5 359(10)	957(12)	4 338(21)
F(5)	5 860(6)	2 060(9)	4 819(10)
F(6)	4 965(8)	1 650(11)	5 693(12)

TABLE 2

Bond lengths (Å), with standard deviations in parentheses

Ru–P(1)	2.42(1)	Ru–O(1)	2.23(1)
Ru–P(2)	2.43(1)	Ru–O(2)	2.22(1)
Ru–P(3)	2.30(1)	O(1)–C(1)	1.27(2)
Ru–P(4)	2.31(1)	O(2)–C(1)	1.28(2)
C(1)–C(2)	1.49(2)		
P(1)–C(11)	1.83(2)	P(3)–C(31)	1.87(2)
P(1)–C(12)	1.88(2)	P(3)–C(32)	1.88(2)
P(2)–C(21)	1.83(2)	P(4)–C(41)	1.84(2)
P(2)–C(22)	1.86(2)	P(4)–C(42)	1.87(2)
Mean P–C(alkyl)	1.86(2)		
P(1)–C(13)	1.84(2)	P(3)–C(33)	1.82(2)
P(2)–C(23)	1.85(2)	P(4)–C(43)	1.83(2)
Mean P–C(aryl)	1.83(2)		

Mean phenyl C–C for individual rings: C(13) 1.41(2), C(23) 1.40(2), C(33) 1.41(2), C(43) 1.42(2), Overall mean C–C 1.41(2)

P(5)–F(1)	1.43(2)	P(5)–F(4)	1.60(2)
P(5)–F(2)	1.63(2)	P(5)–F(5)	1.51(2)
P(5)–F(3)	1.58(2)	P(5)–F(6)	1.53(2)
Mean P–F	1.55(2)		

TABLE 3

Bond angles (°), with standard deviations in parentheses

P(1)–Ru–P(2)	166.4(2)	O(1)–Ru–O(2)	58.7(4)
P(1)–Ru–P(3)	98.9(1)	P(2)–Ru–P(4)	96.5(2)
P(1)–Ru–P(4)	91.0(2)	P(2)–Ru–P(3)	91.3(1)
P(1)–Ru–O(1)	86.8(3)	P(2)–Ru–O(2)	86.7(3)
P(1)–Ru–O(2)	80.9(3)	P(2)–Ru–O(1)	82.0(3)
P(3)–Ru–O(1)	103.7(3)	P(4)–Ru–O(2)	99.1(3)
Ru–P(1)–C(11)	112.6(6)	Ru–P(2)–C(22)	112.9(6)
Ru–P(1)–C(12)	125.6(6)	Ru–P(2)–C(21)	126.1(6)
Ru–P(1)–C(13)	113.0(6)	Ru–P(2)–C(23)	113.1(6)
Ru–P(3)–C(31)	121.5(6)	Ru–P(4)–C(41)	106.6(6)
Ru–P(3)–C(32)	121.5(6)	Ru–P(4)–C(42)	122.8(6)
Ru–P(3)–C(33)	107.8(6)	Ru–P(4)–C(43)	121.3(6)
Mean Ru–P–C	117.0(6)		
C(11)–P(1)–C(12)	99.8(7)	C(21)–P(2)–C(22)	98.6(7)
C(11)–P(1)–C(13)	102.5(7)	C(21)–P(2)–C(23)	101.0(7)
C(12)–P(1)–C(13)	100.3(7)	C(22)–P(2)–C(23)	101.6(7)
C(31)–P(3)–C(32)	97.1(7)	C(41)–P(4)–C(42)	99.9(7)
C(31)–P(3)–C(33)	104.9(7)	C(41)–P(4)–C(43)	105.2(7)
C(32)–P(3)–C(33)	101.3(7)	C(42)–P(4)–C(43)	98.1(7)
Mean C–P–C	100.9(7)		
O(1)–C(1)–O(2)	117(1)	Ru–O(1)–C(1)	91.9(8)
O(1)–C(1)–C(2)	123(1)	Ru–O(2)–C(1)	92.2(9)
O(2)–C(1)–C(2)	120(1)		

TABLE 4

Selected non-bonded interatomic distances (Å), with standard deviations in parentheses

Ru ··· C(1)	2.60(1)	P(3) ··· O(1)	3.56(1)
P(1) ··· O(2)	3.01(1)	P(4) ··· O(2)	3.44(1)
P(2) ··· O(1)	3.06(1)	P(2) ··· O(2)	3.19(1)
P(1) ··· O(1)	3.19(1)	C(23) ··· O(2)	3.20(2)
C(11) ··· O(2)	3.10(2)	C(335) ··· O(1)	3.00(2)
C(13) ··· O(1)	3.11(2)	C(41) ··· O(2)	3.22(2)
C(22) ··· O(1)	3.05(2)		
Interligand C ··· C contacts			
C(12) ··· C(43)	3.45(2)	C(12) ··· C(32)	3.4(02)
C(12) ··· C(431)	3.44(2)	C(22) ··· C(33)	3.4(02)

TABLE 5

Planarity of groups of atoms in the cation and distances (Å) from least-squares planes. Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space. Deviations (Å) of relevant atoms from plane are given in square brackets

Plane (1): Ru, P(3), P(4), O(1), O(2), C(1)

$$-2.335X - 9.450Y + 10.549Z = -2.203$$

[Ru −0.005, P(3) −0.009, P(4) 0.009, O(1) 0.026, O(2) 0.005, C(1) −0.016, P(1) −2.39, P(2) 2.41, C(2) −0.025]

Plane (2): C(13), C(131)—(135)

$$0.138X + 14.099Y - 6.718Z = 5.031$$

[C(13) 0.019, C(131) −0.025, C(132) 0.005, C(133) 0.019 C(134) −0.025, C(135) 0.005, P(1) −0.13]

Plane (3): C(23), C(231)—(235)

$$-4.637X + 10.712Y - 9.333Z = -1.294$$

[C(23) 0.019, C(231) 0.010, C(232) −0.053, C(233) 0.067, C(234) −0.037, C(235) −0.007, P(2) 0.07]

Plane (4): C(33), C(331)—(335)

$$15.463X + 6.968Y - 4.249Z = 6.732$$

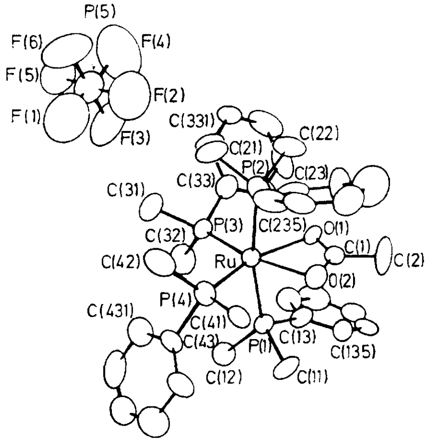
[C(33) −0.015, C(331) 0.009, C(332) −0.002, C(333) 0.001, C(334) −0.008, C(335) 0.015, P(3) −0.10]

Plane (5): C(43), C(431)—(435)

$$-4.495X + 5.789Y + 11.786Z = 2.911$$

[C(43) 0.007, C(431) −0.011, C(432) 0.013, C(433) −0.010, C(434) 0.005, C(435) −0.004, P(4) −0.05] bond lengths (1.43 to 1.63 Å). No attempt was made to correct for the apparent disorder in the anion. The cation is monomeric with a distorted octahedral co-ordination about ruthenium. The four phosphine ligands are arranged as two pairs of *trans*- and *cis*-ligands, with the bidentate acetate group completing the octahedron.

The parameters related to the acetate ligand are: Ru-O 2.23(1) and 2.22(1), O-C 1.27(2) and 1.28(2), C(1)-C(2) 1.49(2) Å, and O-Ru-O 58.7(4)°. These values are similar to those found in the neutral compound [RuH(OAc)$(PPh_3)_3$].[6] The short non-bonded contact distance (2.60 Å) between ruthenium and the acetate carbon atom C(1) prevents closer approach of the acetate group to the metal and may explain the long Ru-O bond lengths found here and in previous studies.[6,7]



FIGURE

Mean Ru-P distances (2.425 Å) of the mutually *trans*-phosphine ligands are significantly longer than those (2.305 Å) for the two *cis*-phosphines. The Ru-P bond lengths of these *cis*-phosphines (*i.e. trans* to the acetate ligand) are similar to those observed for *cis*-phosphines in the cation $[Ru_2Cl_3(PMe_2Ph)_6]^+$ (mean 2.29 Å) [8] although the Ru-P(*trans*) values are slightly longer than those found for the *trans*-phosphines in $[RuCl_3(PEt_2Ph)_3]^-$ [2.39(1) and 2.36(1) Å].[9] The increase in bond length of the *trans*-PMe_2Ph groups is probably a consequence of the high mutual structural *trans*-influence between the strong σ-donor ligands.

The co-ordination geometry of the phosphine ligands shows small deviations from idealized octahedral symmetry of similar magnitude to distortions in other complexes containing facial phosphine ligands. For example, angles P(1)-Ru-P(3) (98.9°), P(2)-Ru-P(4), (96.5°), and P(3)-Ru-P(4), (98.5°) compare well with those [9] between the *cis*-phosphine ligands in $[Ru_2Cl_3(PEt_2Ph)_6]^+$. However, angles P(1)-Ru-P(4) and P(2)-Ru-P(3) (mean 91.1°) are compressed, probably due to close intramolecular contact distances between carbon atoms of different phosphines and between these atoms and the oxygen atoms of the acetate ligand (see Table 4 and Figure 1). To produce these angles, the phosphines represented by P(1) and P(2) have to tilt towards O(2) and O(1) respectively giving acute angles for P(1)-Ru-O(2) and P(2)-Ru-O(1) (mean 81.4°) and a P(1)-Ru-P(2) angle of 166.4°.* Further evidence for steric repulsions between the phosphine ligands is indicated by the large spread (18°) in the tetrahedral angles of the co-ordinated phosphines (Table 3). In the structure of *mer-cis*-$[MoOCl_2(PMe_2Ph)_3]$,[10] in which the long Mo-P bond lengths minimize interligand steric effects, the spread in tetrahedral angles is 6°. Mean P-C(Ph) (1.83 Å), P-C(alkyl) (1.86 Å), and C-C(Ph) (1.41 Å) bond lengths are as expected, and the mean C-P-C bond angle (100.9°) has a value close to that generally found in tertiary phosphine metal complexes. The individual phenyl rings are acceptably planar and the maximum deviation of the non-hydrogen atoms of the acetato-ligand, the ruthenium atom, and phosphorus atoms P(3) and P(4) from their least-squares plane is 0.03 Å (Table 5).

From the ^1H n.m.r. evidence steric strain within the cation is not sufficient to cause a facile ligand dissociation to occur in solution. In the series of complexes $[RuXL_4][PF_6]$ (X = bidentate anionic ligand) ligand dissociation or exchange occurs readily in solution when L is larger than PMe_2Ph or when X has a larger ' bite ' (*e.g.* $CH_3COCHCOCH_3$).[2]

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* An approximate diad symmetry exists in the cation. An 180° rotation about the axis formed by Ru, C(1), and C(2) leaves the cation relatively unchanged [except for the phenyl rings on P(3) and P(4)]. Table 3 lists a number of bond angles together to illustrate this point.

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