whereas the TMA compound is green. In the TMA case the structure contains two definitely different Cu sites, one [Cu(2); coordinated to Cl(1), Cl(2), Cl(3), Cl(4) and Cl(5)] being square pyramidal (five coordinated) and the other [Cu(1); coordinated to Cl(1), Cl(2), two Cl(4) ions and two Cl(5) ions] effectively six coordinated although the site symmetry remains approximately C_{4v} as one of the apical Cl ions [Cl(4)] has a much larger bond length [3·2446 (7) Å]. The square-pyramidal environment of Cu is distorted via a pseudo-Jahn–Teller effect in the ground state of the C_{4v} complex as described for other compounds by Bacci (1979).

The Cu–Cl backbone consists of linear arrays of four edge-sharing pyramids coupled together so as to form sheets (Fig. 1) which are held together by the TMA ions.

From a magnetochemists' point of view it might be interesting to see whether this system behaves mag-netically as weakly coupled linear tetramers of four coupled $S = \frac{1}{2}$ ions, since the unpaired electron is most likely confined to the $d_{x^2-y^2}$ orbital which is in the equatorial plane of the pyramid (the d_{z^2} orbital is pointing toward the apical Cl ions).

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Structures of trans- and cis-Dichloro(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-O,O')-bis(triphenylphosphine)ruthenium(II)

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Abstract. (I) trans-[RuCl$_2${CF$_3$C(O)CHC(O)CF$_3$}(PPh$_3$)$_2$], $M_r = 903·61$, monoclinic, $P2_1/n$, $a = 12·151$ (3), $b = 17·613$ (4), $c = 18·542$ (2) Å, $\beta = 103·92$ (1)°, $V = 3852$ (1) Å^3, $Z = 4$, $D_x = 1·56$ g cm^{-3}, λ(Mo Kα) = 0·71069 Å, $\mu = 6·83$ cm^{-1}, $F(000) = 1820$, $T = 295$ K, $R = 0·039$, 4122 unique observed reflections. (II) cis-[RuCl$_2${CF$_3$C(O)CHC(O)CF$_3$}(PPh$_3$)$_2$], $M_r = 903·61$, monoclinic, $P2_1/c$, $a = 9·977$ (1), $b = 16·544$ (2), $c = 23·205$ (3) Å, $\beta = 93·062$ (9)°, $V = 3825$ (1) Å^3, $Z = 4$, $D_x = 1·57$ g cm^{-3}, λ(Mo Kα) = 0·71069 Å, $\mu = 6·88$ cm^{-1}, $F(000) = 1820$, $T = 295$ K, $R = 0·038$, 4516 unique observed reflections. The crystals were prepared from dichlorotris(triphenylphosphine)ruthenium and 1,1,1,-5,5,5-hexafluoro-2,4-pentanedione in cold (I) and warm (II) benzene under aerobic conditions. The Ru atoms in both compounds are in octahedral coordination with two O atoms of the bidentate ligand, the P atoms of two PPh$_3$ groups and two Cl atoms. In (I), the Cl atoms are trans and the PPh$_3$ groups are cis, while in (II) these conformations are reversed.

Introduction. The ruthenium(II) and osmium(II) complexes [MCl$_2$(PPh$_3$)$_3$] undergo 'oxidative substitution' reactions with β-diketones in benzene solution under aerobic conditions to form the corresponding β-diketonates [MCl$_2${RC(O)CHC(O)R'}(PPh$_3$)$_2$] ($R,R' = $ CH$_3$, CF$_3$, C$_2$H$_5$ or C$_6$H$_5$) one of which, [RuCl$_2$-

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Table 1. *Positional and equivalent isotropic thermal parameters for the non-*H *atoms and their e.s.d.'s*

$$B_{eq} = (8\pi^2/3)[U_{22} + (1/\sin^2\beta)(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	y	z	B_{eq}(Å²)		x	y	z	B_{eq}(Å²)
Compound (I)					Compound (II)				
Ru	0·96219 (3)	0·15832 (3)	0·73364 (2)	2·46 (2)	Ru	0·31372 (3)	0·19988 (2)	0·82125 (2)	2·09 (1)
Cl(1)	0·9080 (1)	0·27719 (8)	0·68340 (7)	3·61 (6)	Cl(1)	0·3454 (1)	0·32927 (7)	0·78588 (5)	3·19 (5)
Cl(2)	1·0091 (1)	0·03315 (8)	0·76680 (9)	4·10 (6)	Cl(2)	0·0839 (1)	0·20846 (8)	0·82669 (5)	3·21 (5)
P(1)	0·8681 (1)	0·16619 (8)	0·83257 (7)	2·62 (5)	P(1)	0·2817 (1)	0·14278 (7)	0·72529 (5)	2·36 (5)
P(2)	1·1488 (1)	0·20844 (8)	0·78474 (7)	2·79 (6)	P(2)	0·3528 (1)	0·25315 (7)	0·91840 (5)	2·45 (5)
F(1)	0·9820 (3)	0·0749 (3)	0·4582 (2)	6·8 (2)	F(1)	0·7329 (4)	0·0659 (3)	0·7671 (2)	8·7 (3)
F(2)	1·1329 (3)	0·0839 (3)	0·5433 (2)	6·3 (2)	F(2)	0·8018 (3)	0·0804 (2)	0·8547 (2)	7·3 (2)
F(3)	1·0490 (4)	0·1832 (2)	0·4942 (2)	7·0 (2)	F(3)	0·7674 (3)	0·1828 (2)	0·8009 (2)	6·9 (2)
F(4)	0·6007 (3)	0·1481 (3)	0·5390 (3)	10·9 (3)	F(4)	0·2158 (4)	−0·0469 (2)	0·8964 (2)	7·7 (2)
F(5)	0·6018 (3)	0·0687 (3)	0·6228 (2)	9·0 (3)	F(5)	0·3871 (5)	−0·0335 (2)	0·9540 (2)	8·2 (2)
F(6)	0·6341 (3)	0·0354 (3)	0·5235 (2)	7·5 (2)	F(6)	0·3991 (4)	−0·1040 (2)	0·8786 (2)	7·7 (2)
O(1)	1·0238 (3)	0·1383 (2)	0·6390 (2)	3·4 (2)	O(1)	0·5149 (3)	0·1785 (2)	0·8159 (1)	2·6 (1)
O(2)	0·8022 (3)	0·1227 (2)	0·6721 (2)	3·1 (2)	O(2)	0·2975 (3)	0·0871 (2)	0·8557 (1)	2·7 (1)
C(1)	0·9644 (5)	0·1181 (3)	0·5767 (3)	3·1 (2)	C(1)	0·5757 (4)	0·1137 (3)	0·8295 (2)	3·1 (2)
C(2)	0·8494 (5)	0·1032 (3)	0·5559 (3)	3·5 (2)	C(2)	0·5246 (5)	0·0460 (3)	0·8555 (3)	4·2 (3)
C(3)	0·7791 (4)	0·1070 (3)	0·6042 (3)	2·8 (2)	C(3)	0·3917 (5)	0·0381 (3)	0·8675 (2)	3·4 (2)
C(4)	1·0330 (5)	0·1144 (4)	0·5173 (3)	4·2 (3)	C(4)	0·7220 (5)	0·1116 (4)	0·8126 (3)	4·7 (3)
C(5)	0·6524 (5)	0·0907 (4)	0·5731 (3)	4·1 (3)	C(5)	0·3462 (6)	−0·0366 (3)	0·8991 (3)	4·9 (3)
C(6)	0·7450 (4)	0·1029 (3)	0·8217 (3)	2·9 (2)	C(6)	0·2869 (5)	0·3528 (3)	0·9369 (2)	2·7 (2)
C(7)	0·6562 (5)	0·1236 (4)	0·8527 (3)	4·3 (3)	C(7)	0·3436 (5)	0·3959 (3)	0·9833 (2)	3·5 (2)
C(8)	0·5683 (5)	0·0741 (5)	0·8521 (4)	5·4 (4)	C(8)	0·2876 (6)	0·4669 (3)	1·0009 (2)	4·0 (3)
C(9)	0·5670 (5)	−0·0036 (4)	0·8218 (4)	5·2 (3)	C(9)	0·1726 (6)	0·4964 (3)	0·9727 (2)	4·2 (3)
C(10)	0·6545 (5)	−0·0185 (4)	0·7915 (3)	4·6 (3)	C(10)	0·1160 (5)	0·4550 (3)	0·9265 (3)	4·3 (3)
C(11)	0·7440 (5)	−0·0310 (3)	0·7915 (3)	3·5 (2)	C(11)	0·1723 (5)	0·3835 (3)	0·9082 (2)	3·7 (2)
C(12)	0·8008 (4)	0·2576 (3)	0·8402 (3)	2·9 (2)	C(12)	0·5333 (5)	0·2630 (3)	0·9318 (2)	3·1 (2)
C(13)	0·8264 (5)	0·3017 (3)	0·9041 (3)	3·6 (2)	C(13)	0·6100 (5)	0·2006 (3)	0·9571 (2)	3·8 (2)
C(14)	0·7664 (6)	0·3665 (4)	0·9102 (4)	4·9 (3)	C(14)	0·7486 (6)	0·2052 (4)	0·9596 (3)	5·4 (3)
C(15)	0·6800 (7)	0·3887 (4)	0·8519 (4)	5·7 (4)	C(15)	0·8121 (6)	0·2711 (5)	0·9382 (3)	6·2 (4)
C(16)	0·6528 (5)	0·3462 (4)	0·7874 (4)	5·1 (3)	C(16)	0·7371 (6)	0·3329 (4)	0·9129 (3)	5·1 (3)
C(17)	0·7131 (5)	0·2809 (3)	0·7814 (3)	4·0 (3)	C(17)	0·5990 (5)	0·3291 (3)	0·9094 (2)	3·8 (2)
C(18)	0·9468 (5)	0·1441 (3)	0·9275 (3)	3·2 (2)	C(18)	0·2935 (5)	0·1917 (3)	0·9776 (2)	3·0 (2)
C(19)	1·0463 (5)	0·1816 (3)	0·9584 (3)	3·8 (3)	C(19)	0·3500 (5)	0·1979 (3)	1·0334 (2)	3·9 (2)
C(20)	1·1056 (5)	0·1668 (4)	1·0311 (3)	5·0 (3)	C(20)	0·2993 (7)	0·1531 (4)	1·0780 (2)	4·9 (3)
C(21)	1·0651 (7)	0·1145 (4)	1·0729 (3)	5·5 (4)	C(21)	0·1935 (7)	0·1023 (4)	1·0669 (3)	5·7 (4)
C(22)	0·9656 (7)	0·0768 (4)	1·0431 (4)	5·8 (4)	C(22)	0·1345 (7)	0·0967 (4)	1·0121 (3)	5·9 (4)
C(23)	0·9058 (6)	0·0912 (3)	0·9708 (3)	4·6 (3)	C(23)	0·1852 (6)	0·1412 (3)	0·9672 (2)	4·3 (3)
C(24)	1·1580 (5)	0·3087 (3)	0·8114 (3)	3·2 (2)	C(24)	0·1614 (4)	0·1882 (3)	0·6731 (2)	2·8 (2)
C(25)	1·2531 (5)	0·3519 (4)	0·8073 (3)	4·5 (3)	C(25)	0·0887 (5)	0·2567 (3)	0·6855 (2)	3·4 (2)
C(26)	1·2589 (6)	0·4277 (4)	0·8265 (4)	5·4 (3)	C(26)	−0·0068 (5)	0·2874 (4)	0·6454 (2)	4·5 (3)
C(27)	1·1728 (7)	0·4621 (4)	0·8496 (4)	5·5 (3)	C(27)	−0·0268 (5)	0·2511 (4)	0·5922 (2)	4·6 (3)
C(28)	1·0786 (6)	0·4212 (4)	0·8536 (3)	4·9 (3)	C(28)	0·0486 (6)	0·1846 (4)	0·5781 (2)	4·6 (3)
C(29)	1·0718 (5)	0·3448 (3)	0·8349 (3)	3·5 (2)	C(29)	0·1410 (5)	0·1533 (3)	0·6188 (2)	3·7 (2)
C(30)	1·2422 (4)	0·1612 (4)	0·8647 (3)	3·5 (2)	C(30)	0·2228 (5)	0·0387 (3)	0·7286 (2)	2·8 (2)
C(31)	1·2510 (5)	0·0826 (4)	0·8671 (4)	5·7 (3)	C(31)	0·0864 (5)	0·0221 (3)	0·7250 (2)	3·8 (2)
C(32)	1·3195 (6)	0·0463 (5)	0·9288 (5)	6·8 (4)	C(32)	0·0414 (6)	−0·0575 (4)	0·7269 (3)	4·9 (3)
C(33)	1·3771 (6)	0·0882 (6)	0·9876 (4)	6·9 (5)	C(33)	0·1308 (7)	−0·1195 (3)	0·7318 (3)	5·1 (3)
C(34)	1·3727 (6)	0·1645 (6)	0·9854 (4)	7·1 (4)	C(34)	0·2663 (6)	−0·1048 (3)	0·7376 (2)	4·3 (3)
C(35)	1·3057 (6)	0·2011 (4)	0·9249 (3)	5·4 (3)	C(35)	0·3117 (5)	−0·0257 (3)	0·7372 (2)	3·6 (2)
C(36)	1·2331 (4)	0·2093 (3)	0·7153 (3)	3·4 (2)	C(36)	0·4335 (4)	0·1386 (3)	0·6844 (2)	2·7 (2)
C(37)	1·2003 (5)	0·2576 (4)	0·6547 (3)	4·8 (3)	C(37)	0·4636 (5)	0·0744 (3)	0·6487 (2)	4·1 (3)
C(38)	1·2694 (7)	0·2673 (5)	0·6059 (4)	6·3 (4)	C(38)	0·5774 (6)	0·0756 (4)	0·6174 (3)	5·3 (3)
C(39)	1·3698 (8)	0·2292 (6)	0·6168 (5)	7·4 (5)	C(39)	0·6614 (6)	0·1416 (4)	0·6199 (3)	5·4 (3)
C(40)	1·4022 (6)	0·1808 (5)	0·6762 (5)	6·6 (4)	C(40)	0·6323 (6)	0·2058 (3)	0·6538 (3)	4·5 (3)
C(41)	1·3332 (5)	0·1702 (4)	0·7244 (3)	4·6 (3)	C(41)	0·5181 (5)	0·2044 (3)	0·6858 (2)	3·5 (2)

{CF$_3$C(O)CHC(O)CF$_3$}(PPh$_3$)$_2$], exists in red and yellow isomeric forms. This paper reports the structures of these two isomers.

Experimental. Preparation of (I) was achieved by adding dichlorotris(triphenylphosphine)ruthenium(II) (0·3 g, 0·31 mmol) to a solution of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (0·1 g, 1 mmol) in benzene (10 cm³), stirring the mixture at room temperature under aerobic conditions (open flask) for 1 h and diluting with light petroleum (b.p. 333–353 K). The resultant precipitate crystallized from dichloromethane/ethanol as red platelets (yield 71%). Preparation of (II) was similarly achieved except that the benzene was at 343 K during stirring and was then cooled and diluted with light petroleum. Crystallization produced well-formed shiny black needles which on grinding gave a yellow microcrystalline powder (yield 54%). Crystals used for data collection 0·35 × 0·27 × 0·03 mm, red, platy (I) and 0·31 × 0·28 × 0·07 mm, yellow, orthogonal fragment cut from larger crystal (II). Rigaku AFC5S diffractometer (located in the Crystallographic Laboratory of the Department of Geology, Southern Illinois University), graphite-monochromated Mo Kα radiation, ω–2θ scans for (I), ω scans for (II) (because of peak overlaps with ω–2θ scans), scan speeds 6° min⁻¹ (I) and 9° min⁻¹ (II), maximum of three scan repetitions to obtain $\sigma F/F < 0·10$. Lattice parameters from least-squares fit of 25 (I) and 24 (II) strong reflections in 2θ range 25–33° (I) and 37–46° (II). For (I), 7373 reflections measured (h 0 to 14, k 0 to 20, l −21 to 21), 598 redundant and/or systematically

extinct reflections deleted, data set comprised of 6775 unique reflections. 4122 reflections were considered observed $[I > 3\sigma(I)]$, $R_{int} = 3.7\%$ for 289 pairs of equivalent reflections, $(\sin\theta/\lambda)_{max} = 0.60$ Å^{-1}. Three standard reflections ($\overline{2}00$, $1\overline{1}3$, $02\overline{1}$) changed by -0.2, 0.5 and -1.5%, respectively; no decay correction applied. For (II), 7400 reflections measured (h 0 to 11, k 0 to 19, l -27 to 27), 689 redundant and/or systematically extinct reflections deleted, data set made up of 6711 unique reflections. 4516 reflections were considered observed $[I > 3\sigma(I)]$, $R_{int} = 3.4\%$ for 384 pairs of equivalent reflections, $(\sin\theta/\lambda)_{max} = 0.60$ Å^{-1}. Three standard reflections ($1\overline{1}0$, $0\overline{2}0$, $0\overline{2}\overline{1}$) changed by 0.1, -0.6 and -0.5%, respectively; no decay correction applied. Data for (I) and (II) corrected for Lorentz, polarization and absorption [analytical correction, transmission range 0.83–0.98 for (I); *DIFABS* (Walker & Stuart, 1983) empirical correction, transmission range 0.900–1.164 for (II)]. Direct methods provided the atomic positions of all non-H atoms for both compounds. Full-matrix least-squares refinement was performed to minimize $\sum w(|F_o| - |F_c|)^2$. Both compounds refined uneventfully, F atoms of all CF$_3$ groups exhibited large thermal displacement factors, possibly indicating minor rotational disorder. Final refinements performed with 487 variables including all positional parameters, anisotropic thermal parameters for non-H atoms and one scale factor. H atoms placed in geometrically assumed positions (C—H = 0.95 Å) and fixed, H-atom B's set at $1.2 \times B_{eq}$ of associated C atom. Regeneration of H-atom positions and refinement to convergence repeated until shifts became insignificant. Convergence of (I) yielded $R = 0.039$, $wR = 0.042$, $S = 1.20$ and $(\Delta/\sigma)_{max} = 0.02$ while (II) converged at $R = 0.038$, $wR = 0.041$, $S = 1.23$ and $(\Delta/\sigma)_{max} = 0.03$ [$w = 1/\sigma^2(|F_o|)$]. Final difference syntheses produced $(\Delta\rho)_{max} = 0.72$ e Å^{-3} (I) and 0.75 e Å^{-3} (II), and $(\Delta\rho)_{min} = -0.42$ e Å^{-3} (I) and -0.33 e Å^{-3} (II). Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). All computer programs from the *TEXSAN* crystal structure analysis package (Molecular Structure Corporation, 1985).

Discussion. Atomic coordinates and equivalent isotropic temperature factors for (I) and (II) are listed in Table 1; selected bond distances and angles are presented in Table 2.* Figs. 1 and 2 illustrate the molecular conformations and numbering schemes of (I)

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* Lists of structure factors, calculated H-atom coordinates and temperature factors, anisotropic thermal parameters, distances and angles involving the phenyl rings, intermolecular distances, torsion angles and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51587 (108 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond distances (Å), bond angles (°), and their e.s.d.'s*

Compound (I)

Ru–O(1)	2.097 (3)	F(1)–C(4)	1.320 (7)
Ru–O(2)	2.099 (3)	F(2)–C(4)	1.309 (7)
Ru–Cl(1)	2.322 (1)	F(3)–C(4)	1.315 (7)
Ru–Cl(2)	2.323 (2)	F(4)–C(5)	1.274 (7)
Ru–P(1)	2.387 (1)	F(5)–C(5)	1.285 (6)
Ru–P(2)	2.405 (1)	F(6)–C(5)	1.321 (7)
P(1)–C(12)	1.828 (5)	O(1)–C(1)	1.257 (6)
P(1)–C(18)	1.832 (5)	O(2)–C(3)	1.253 (6)
P(1)–C(6)	1.838 (5)	C(1)–C(2)	1.383 (7)
P(2)–C(36)	1.829 (5)	C(1)–C(4)	1.536 (7)
P(2)–C(24)	1.831 (6)	C(2)–C(3)	1.379 (7)
P(2)–C(30)	1.836 (5)	C(3)–C(5)	1.535 (7)
O(1)–Ru–O(2)	88.0 (1)	C(24)–P(2)–C(30)	103.5 (3)
O(1)–Ru–Cl(1)	86.5 (1)	C(24)–P(2)–Ru	116.8 (2)
O(1)–Ru–Cl(2)	87.0 (1)	C(30)–P(2)–Ru	119.5 (2)
O(1)–Ru–P(1)	170.5 (1)	C(1)–O(1)–Ru	125.0 (3)
O(1)–Ru–P(2)	84.2 (1)	C(3)–O(2)–Ru	124.5 (3)
O(2)–Ru–Cl(1)	85.1 (1)	O(1)–C(1)–C(2)	129.0 (5)
O(2)–Ru–Cl(2)	89.8 (1)	O(1)–C(1)–C(4)	112.3 (5)
O(2)–Ru–P(1)	83.3 (1)	C(2)–C(1)–C(4)	118.6 (5)
O(2)–Ru–P(2)	170.3 (1)	C(3)–C(2)–C(1)	123.5 (5)
Cl(1)–Ru–Cl(2)	171.92 (5)	O(2)–C(3)–C(2)	129.7 (5)
Cl(1)–Ru–P(1)	96.55 (5)	O(2)–C(3)–C(5)	112.4 (5)
Cl(1)–Ru–P(2)	88.65 (5)	C(2)–C(3)–C(5)	117.9 (5)
Cl(2)–Ru–P(1)	89.09 (5)	F(2)–C(4)–F(3)	107.6 (6)
Cl(2)–Ru–P(2)	95.51 (5)	F(2)–C(4)–F(1)	107.3 (6)
P(1)–Ru–P(2)	104.85 (5)	F(2)–C(4)–C(1)	111.6 (5)
C(12)–P(1)–C(18)	104.6 (2)	F(3)–C(4)–F(1)	107.0 (5)
C(12)–P(1)–C(6)	100.1 (2)	F(3)–C(4)–C(1)	110.0 (5)
C(12)–P(1)–Ru	114.6 (2)	F(1)–C(4)–C(1)	113.0 (5)
C(18)–P(1)–C(6)	101.5 (2)	F(4)–C(5)–F(5)	109.3 (6)
C(18)–P(1)–Ru	119.4 (2)	F(4)–C(5)–F(6)	105.0 (5)
C(6)–P(1)–Ru	114.1 (2)	F(4)–C(5)–C(3)	111.6 (5)
C(36)–P(2)–C(24)	100.0 (3)	F(5)–C(5)–F(6)	104.3 (6)
C(36)–P(2)–C(30)	103.3 (2)	F(5)–C(5)–C(3)	113.4 (5)
C(36)–P(2)–Ru	111.1 (2)	F(6)–C(5)–C(3)	112.7 (5)

Compound (II)

Ru–O(2)	2.040 (3)	F(1)–C(4)	1.308 (7)
Ru–O(1)	2.049 (3)	F(2)–C(4)	1.332 (6)
Ru–Cl(2)	2.308 (1)	F(3)–C(4)	1.295 (6)
Ru–Cl(1)	2.320 (1)	F(4)–C(5)	1.311 (7)
Ru–P(1)	2.424 (1)	F(5)–C(5)	1.317 (7)
Ru–P(2)	2.433 (1)	F(6)–C(5)	1.332 (7)
P(1)–C(24)	1.821 (4)	O(1)–C(1)	1.263 (5)
P(1)–C(30)	1.822 (5)	O(2)–C(3)	1.260 (5)
P(1)–C(36)	1.831 (4)	C(1)–C(2)	1.382 (7)
P(2)–C(12)	1.819 (5)	C(1)–C(4)	1.532 (7)
P(2)–C(18)	1.832 (5)	C(2)–C(3)	1.376 (7)
P(2)–C(6)	1.835 (5)	C(3)–C(5)	1.520 (7)
O(2)–Ru–O(1)	88.0 (1)	C(18)–P(2)–C(6)	100.9 (2)
O(2)–Ru–Cl(2)	86.27 (9)	C(18)–P(2)–Ru	116.8 (2)
O(2)–Ru–Cl(1)	176.2 (1)	C(6)–P(2)–Ru	120.1 (1)
O(2)–Ru–P(1)	89.67 (9)	C(1)–O(1)–Ru	126.2 (3)
O(2)–Ru–P(2)	88.88 (9)	C(3)–O(2)–Ru	126.8 (3)
O(1)–Ru–Cl(2)	173.6 (1)	O(1)–C(1)–C(2)	127.8 (4)
O(1)–Ru–Cl(1)	89.17 (9)	O(1)–C(1)–C(4)	113.9 (5)
O(1)–Ru–P(1)	87.60 (8)	C(2)–C(1)–C(4)	118.2 (4)
O(1)–Ru–P(2)	90.57 (8)	C(3)–C(2)–C(1)	123.2 (4)
Cl(2)–Ru–Cl(1)	96.73 (4)	O(2)–C(3)–C(2)	127.7 (5)
Cl(2)–Ru–P(1)	89.53 (4)	O(2)–C(3)–C(5)	112.9 (5)
Cl(2)–Ru–P(2)	92.15 (4)	C(2)–C(3)–C(5)	119.4 (5)
Cl(1)–Ru–P(1)	92.76 (4)	F(3)–C(4)–F(1)	108.1 (6)
Cl(1)–Ru–P(2)	88.59 (4)	F(3)–C(4)–F(2)	107.8 (5)
P(1)–Ru–P(2)	177.70 (5)	F(3)–C(4)–C(1)	112.5 (4)
C(24)–P(1)–C(30)	102.4 (2)	F(1)–C(4)–F(2)	107.3 (5)
C(24)–P(1)–C(36)	101.9 (2)	F(1)–C(4)–C(1)	110.0 (5)
C(24)–P(1)–Ru	120.0 (2)	F(2)–C(4)–C(1)	111.1 (5)
C(30)–P(1)–C(36)	105.3 (2)	F(4)–C(5)–F(5)	107.9 (6)
C(30)–P(1)–Ru	110.9 (1)	F(4)–C(5)–F(6)	106.6 (5)
C(36)–P(1)–Ru	114.8 (1)	F(4)–C(5)–C(3)	113.8 (5)
C(12)–P(2)–C(18)	106.1 (2)	F(5)–C(5)–F(6)	105.7 (5)
C(12)–P(2)–C(6)	104.1 (2)	F(5)–C(5)–C(3)	110.5 (5)
C(12)–P(2)–Ru	107.4 (1)	F(6)–C(5)–C(3)	112.0 (5)

and (II). The Ru atoms in both compounds are in octahedral coordination with two O atoms of the bidentate ligand (1,1,1,5,5,5-hexafluoro-2,4-pentane-

dionate), two P atoms of the triphenylphosphine ligands and two Cl atoms. The major conformational difference between the two compounds is that in (I) the chlorine atoms are *trans* and the triphenylphosphine groups are *cis*, while in (II) these orientations are reversed.

Corresponding bond distances in (I) and (II) exhibit only minor differences, principally in the Ru bonds. In (II), distances involving O—Ru and Cl—Ru are slightly smaller, while P—Ru distances are larger than the equivalent distances in (I). The sum of these bond lengths is 13·633 (11) Å for (I) and 13·574 (10) Å for (II), which indicates shorter average bond distances for (II).

Deviations of Ru bond angles from ideal octahedral geometry are considerable for both compounds with (I) exhibiting the greater overall distortion. For example, in (I) the *trans* Cl(1)—Ru—Cl(2) bond angle is

Fig. 1. Molecular structure and numbering scheme of (I). Thermal ellipsoids at the 50% probability level, ring-H atoms omitted for clarity.

171·92 (5)° and the *cis* P(1)—Ru—P(2) bond angle is 104·85 (5)°. While both (I) and (II) can be expected to exhibit distortions due to steric crowding of the ligands, the *trans* arrangement of the triphenylphosphine ligands in (II) produces less intramolecular crowding. This may be responsible, in part, for the shorter average Ru bond distances and reduced octahedral distortions found in (II).

C—P—C bond angles in the triphenylphosphine ligands of both molecules range from 100·0 (3) to 106·1 (2)° and are similar in distribution. The chelating ligands in (I) and (II), however, are significantly different. In (I) the plane of the pentanedione ligand, defined by O(1)—C(1)—C(2)—C(3)—O(2), is bent along an axis defined by O(1)—O(2) by 4·2° from the plane defined by O(1)—Ru—O(2). In (II) the pentanedione ligand is crowded on both sides by phenyl groups of the *trans* triphenylphosphine ligands, leading to increased distortion of the chelate and causing the trifluoromethyl groups to be rotated 4·9° above and 7·0° below the chelate plane.

While trifluoroacetate complexes of Ru have been studied (Dobson, Moore, Robinson, Hursthouse & New, 1985; Albers, Liles & Singleton, 1987; Albers, Liles, Singleton & Stead, 1986), (I) and (II) are the first reported Ru complexes of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione which have been structurally characterized. The structure of the related complex *mer*-tris[1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionato-*O,O′*]ruthenium(III), (*A*), has been reported (Aynetchi, Hitchcock, Seddon, Seddon, Yousif, Zora & Stuckey, 1986). In this complex the mean O—Ru—O bond angle of the *β*-ketone ligands is 92·0°, whereas the angle in (I) and in (II) is 88·0 (1)° in both molecules. The average Ru—O bond distance in (*A*) is 2·003 Å, while in (I) and (II) it is 2·098 and 2·045 Å, respectively. Although in (*A*) the Ru-atom coordination is nearer octahedral than in (I) and (II), the chelate rings are distorted from planarity in a similar fashion.
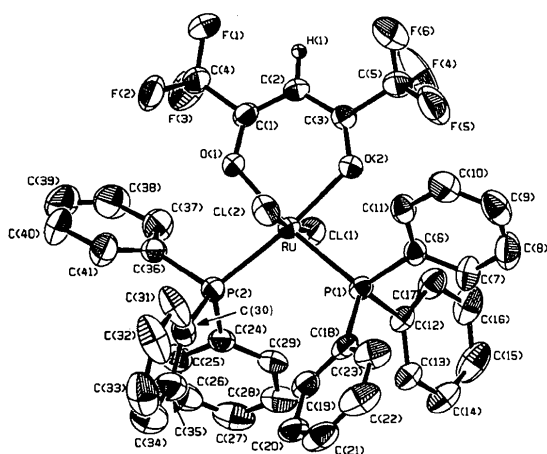
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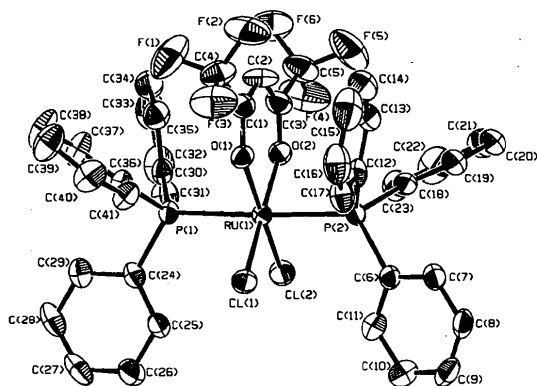
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Fig. 2. Molecular structure and numbering scheme of (II). Thermal ellipsoids at the 50% probability level, H atoms omitted to improve clarity.