Cluster Chemistry. Part 31.[†] An $[Ru_3(CO)_{12}]$ Derivative with an $[Fe_3(CO)_{12}]$-like Structure: Preparation and *X*-Ray Structure of $[Ru_3(\mu\text{-}CO)_2(CO)_6\{PPh(OMe)_2\}_4]$[‡]

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An *X*-ray structural determination of $[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$ shows this complex to be the first example of an $[Ru_3(CO)_{12}]$ derivative with the $[Fe_3(CO)_{12}]$ structure. The three Ru atoms form an isosceles triangle, the shorter edge [2.797(1) Å] of which is asymmetrically bridged by two CO ligands [Ru(1)–C 2.057(8), 2.399(8); Ru(2)–C 2.068(8), 2.389(7) Å; Ru(1)–C–O 150.7(6), 132.5(6); Ru(2)–C–O 131.8(6), 150.4(6)°]; these two Ru atoms are each bonded to an equatorial $PPh(OMe)_2$ ligand [Ru–P 2.277(2) and 2.281(2) Å]. The unique Ru carries two equatorial $PPh(OMe)_2$ ligands [Ru–P 2.265(2) and 2.270(2) Å], and forms two longer Ru–Ru bonds [2.879(1) Å]. The occurrence of $[Fe_3(CO)_{12}]$-type structures is related to the volume of the peripheral-atom polyhedron.

While $[Fe_3(CO)_{12}]$ and several of its derivatives $[Fe_3(CO)_{12-n}L_n]$ (n = 1—3) containing unidentate ligands, L, have long been known to have structure (1), in which two CO groups more or less symmetrically bridge one of the Fe–Fe vectors,[1] $[Ru_3(CO)_{12}]$ and similar complexes $[Ru_3(CO)_{12-n}L_n]$ have been shown to have the non-bridged structure (2).[2] We have been examining the structural consequences of introducing non-CO ligands into the L_{12} polyhedron, particularly with regard to the effects on the peripheral-atom polyhedron (p.a.p.).[3] The p.a.p.s for $[Fe_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ are the icosahedron and the anticuboctahedron, respectively, and the difference can be related to the presence or absence of bridging CO groups in these compounds. In substituted $[Ru_3(CO)_{12}]$ derivatives the p.a.p. is distorted from the ideal polyhedron found for the parent carbonyl, although in the examples so far studied the change is accommodated by a twisting of individual ruthenium environments {*cf.* $[Ru_3(CO)_{11}(CNBu^t)]$[2b]} rather than by any tendency for CO groups to occupy bridging positions.

Only three $[Ru_3(CO)_8L_4]$ complexes have been reported, with L = PH_3,[4] PMe_3,[5] or $PPh(OMe)_2$ (3).[5,6] We have recently made the latter in high yield and purity by the sodium benzophenone ketyl-catalysed reaction between $[Ru_3(CO)_{12}]$ and excess of $PPh(OMe)_2$, and we report below the determination of its structure.

Results and Discussion

The crystal contains discrete molecules of $[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$ (3), four molecules making up the unit cell. The molecular structure of (3) is shown in Figure (*a*), from which it is immediately apparent that it is of the CO-bridged $[Fe_3(CO)_{12}]$ type. One Ru–Ru bond of the isosceles triangular Ru_3 core is asymmetrically bridged by two CO groups [Ru(1)–C(12U) 2.057(8), Ru(1)–C(12D) 2.399(8), Ru(2)–C(12U) 2.389(7), and Ru(2)–C(12D) 2.068(8) Å; Ru(1)C(12U)O(12U) 150.7(6), Ru(1)C(12D)O(12D) 132.5(6), Ru(2)C(12D)O(12U) 131.8(6), and Ru(2)C(12D)O(12D) 150.4(6)°] and the Ru–Ru separation [2.797(1) Å] is 0.06 Å shorter than that found in $[Ru_3(CO)_{12}]$.[2a] In contrast, the other two Ru–Ru bonds are significantly longer [at 2.879(1) Å], as expected when CO is replaced by a better σ donor. The remaining CO groups are attached terminally, two to each Ru atom in axial positions; the Ru–C–O angles are all *ca.* 176.2°. Two of the phosphonite ligands occupy equatorial positions on the CO-bridged Ru atoms, *trans* to the non-bridged Ru–Ru vectors with Ru–P distances of 2.277(2) and 2.281(2) Å; the other two occupy the two equatorial sites of Ru(3) [Ru–P 2.265(2) and 2.270(2) Å]. Both pairs are disposed so that one Ph group of each pair is above the Ru_3 plane, and the second below this plane.

The p.a.p. for complex (3) is shown in Figure (*b*) and approximates to an icosahedron projected down a two-fold symmetry axis. Bonding within the $Ru_3L_8L'_4$ core immediately degrades the symmetry of the molecular core to *mm*, and consideration of the phosphorus substituents brings a further degradation to *2*, vertical, in the plane of the page. Ideally, the four phosphorus atoms should be coplanar with the equatorial plane of the icosahedron; P(1),P(2),P(13),P(23) deviate from their least-squares plane by 0.168, −0.133, −0.239, and 0.188 Å. Atoms Ru(1),Ru(2),Ru(3) deviate from this plane by −0.139, −0.149, and 0.022 Å, suggesting a slight twist of the Ru_3 plane about the molecular *2* axis, relative to the P_4 equator. Deviations of O(1U),O(2U),O(1D),O(2D) from the Ru_3 plane are −1.890, −2.523, 2.531, and 1.889 Å, while the deviations of the upper and lower bridging CO atoms O(12U),O(3U),O(12D),O(3D) are −2.717, −3.010, 2.736, and 3.050 Å. The equatorial co-ordination sites of the phosphonite ligands are probably dictated by both electronic and steric considerations; axial

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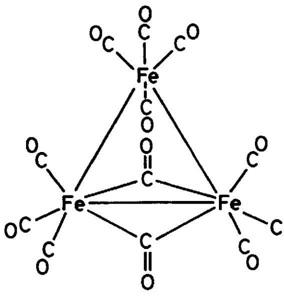
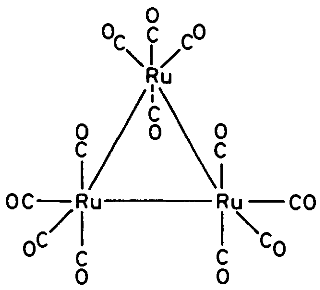
[†] Part 30, M. I. Bruce, B. K. Nicholson, and O. bin Shawkataly, *J. Organomet Chem.*, 1984, **275**, 223.

[‡] 1,2;1,2-Di-μ-carbonyl-1,2,3,3-tetrakis(dimethoxyphenylphosphine)-*cyclo*-tris(dicarbonylruthenium) (3*Ru–Ru*).

Supplementary data available (No. SUP 56184, 9 pp.): thermal parameters, H-atom co-ordinates, ligand planes and geometries. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.



(1)



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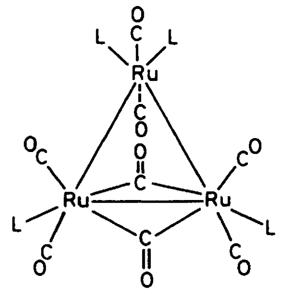


(3) L = PPh(OMe)$_2$

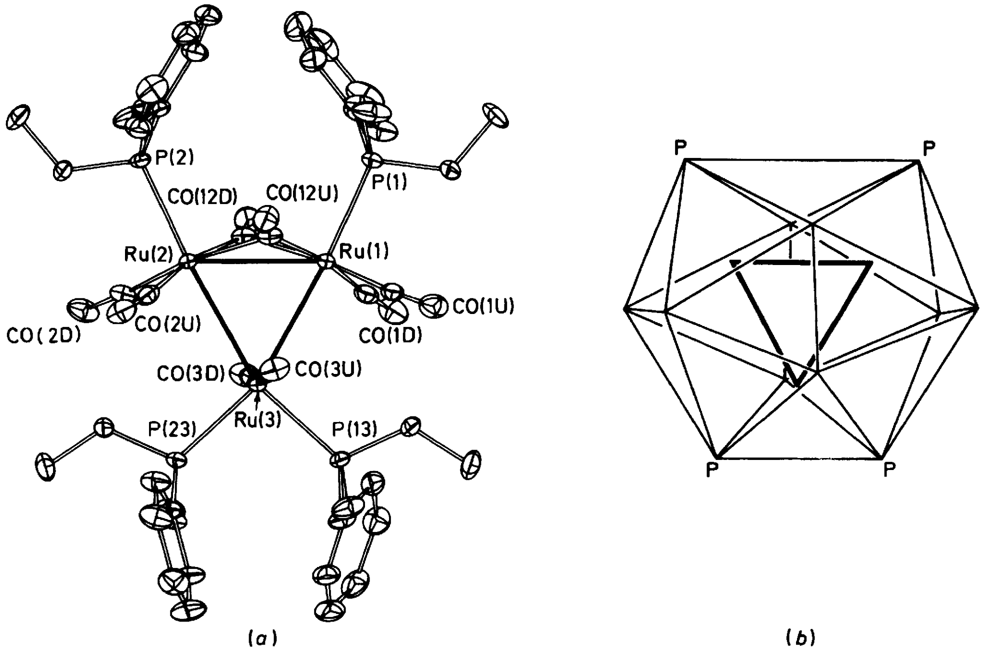


Figure. (*a*) Molecular structure of $[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$ (3), showing atom-numbering scheme for non-hydrogen atoms. The projection is normal to the Ru_3 plane; 20% thermal ellipsoids. (*b*) Peripheral-atom polyhedron for (3), constructed with O and P atoms at the apices

substitution of more than two CO ligands would lead to large steric interactions between the phosphonite ligands, and the minimisation of these interactions in the present case has resulted in the observed CO-bridged structure.

The presence of bridging CO ligands is also consistent with the previously observed trends, increasing numbers of good σ-donor ligands favouring this situation {*cf.* the series $[Ir_4(CO)_{12-n}(PPh_3)_n]$ (n = 0, 2, or 3)[7]}, although others have pointed out that there is little other evidence to support this view.[8] A comparison[9] of the structure of $[Ir_4(CO)_9\{(Ph_2P)_3CH\}]$ (all terminal CO) with that of $[Ir_4(CO)_9\{(Et_2P)_3SiMe\}]$ (CO-bridged)[10] suggested that it is the presence of the bulky Ph groups in the former which is the factor deciding which of the two geometries is adopted.

We have calculated the volumes of the p.a.p. for a series of complexes $[M_3(CO)_{12-n}(PR_3)_n]$ (Table 1). The present calculations employed the experimentally determined $O_{12-n}P_n$ polyhedra; we have shown earlier that a polyhedron constructed from the outer ligand atoms (O of CO, N of CNR, P of PR_3) in complexes $[M_3(CO)_{12-n}L_n]$ remains invariant when disorder of the M_3 core is present.[3] Volumes of the various polyhedra were calculated by a program[11] which identifies triangular elements formed by the peripheral atoms, and sums the volumes of the tetrahedra formed by these elements and the midpoint of the polyhedron.

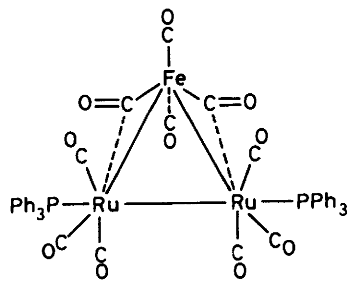
The presence of μ-CO ligands has been rationalised as a result of the p.a.p. being an icosahedron, and it was pointed out several years ago that a close-packed $(CO)_{12}$ icosahedron is too small to incorporate the Ru_3 or Os_3 metal cores.[12] A change in geometry from icosahedral to anticuboctahedral results in generation of a larger internal volume, now sufficient to take the Ru_3 or Os_3 cores. Of necessity, the volume of the p.a.p. will diminish as more PR_3 ligands are incorporated into the polyhedron, since the M–P separations are shorter than the M $\cdots$ O separations.

We note that complexes with p.a.p. volumes between 115 and 125 Å^3 all have the $[Fe_3(CO)_{12}]$-type structure, with two μ-CO ligands, while the ruthenium complexes with p.a.p. volumes between 127 and 140 Å^3 have the $[Ru_3(CO)_{12}]$-type structure, with all CO groups terminal. It is interesting that the complex described herein has a p.a.p. volume of 118.2 Å^3, placing it within the range found for the iron derivatives of similar structure. Of the recently described[13] Fe_2Ru and $FeRu_2$ complexes, $[FeRu_2(CO)_{11}(PPh_3)]$ (p.a.p. volume 133.4 Å^3) has a ligand geometry intermediate between icosahedral and cuboctahedral, with some M–C–O angles $<175°$ 'indicating the

Table 1. Volumes of peripheral atom polyhedra for several complexes

Complex	Volume of p.a.p. (Å^3)[a]	Structure type[b]	Average M–M distance (Å)	Ref.
$[Fe_3(CO)_{12}]$	126.8(43)	A	2.639	1*a*
$[Fe_3(CO)_{11}(PPh_3)]$[c]	117.9(37)	A	2.646	1*c*
$[Fe_3(CO)_{11}(PPh_3)]$[d]	115.5(36)	A	2.657	1*c*
$[Fe_3(CO)_9(PMe_2Ph)_3]$	107.7(19)	A	2.639	1*d*
$[Fe_2Ru(CO)_{11}\{P(OMe)_3\}]$[e]	125.0(10)	A	2.701	12
$[Fe_2Ru(CO)_{11}(PPh_3)]$	125.3(5)	A	2.714	12
$[FeRu_2(CO)_{11}(PPh_3)]$	133.4(7)	B	2.796	12
$[FeRu_2(CO)_{10}(PPh_3)_2]$[f]	123.3(13)	C	2.727	12
$[Ru_3(CO)_{12}]$	140.4(5)	B	2.854	2*a*
$[Ru_3(CO)_{11}(PPh_3)]$	136.9(23)	B	2.886	2*c*
$[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$	136.5(10)	B	2.885[g]	2*d*
$[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$	131.0(46)	B	2.850	2*d*
$[Ru_3(CO)_9(PMe_3)_3]$	127.2(5)	B	2.859	2*d*
$[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$	118.2(6)	A	2.852	This work

[a] Approximate e.s.d.s in last digit in parentheses. [b] A, $[Fe_3(CO)_{12}]$ (with two μ-CO ligands on one M–M bond); B, $[Ru_3(CO)_{12}]$ (all terminal CO ligands); C, $[FeRu_2(CO)_{10}(PPh_3)_2]$ (with two μ-CO ligands on two M–M bonds). [c] Isomer with PPh_3 on Fe with μ-CO groups. [d] Isomer with PPh_3 on Fe not bonded to μ-CO groups. [e] Calculated using unit cell of space group *Pna*2$_1$, with $a = 17.220, b = 8.741, c = 14.573$ Å, *i.e.* *b* and *c* are reversed from those given in the text of ref. 12. [f] Calculated using space group *Pccn* (to give required two-fold axis). [g] Average for two independent molecules.



(4)

tendency to form semibridges.' In $[FeRu_2(CO)_{10}(PPh_3)_2]$ (4) (p.a.p. volume 123.3 Å^3) a third variant of the $[M_3(CO)_{12}]$ structure is found, in which the two Fe–Ru bonds are each bridged asymmetrically by a CO group.

The simple expectation from these results is that, in tertiary phosphine or phosphite derivatives of $[M_3(CO)_{12}]$, bridging carbonyls may be a structural feature when the volume of the p.a.p. is $\leqslant 125$ Å^3. Unfortunately, there are fairly large uncertainties in the light-atom positions, particularly from the earlier structure determinations; these lead to rather large estimated standard deviations (e.s.d.s) in the calculated volumes. Nevertheless, we believe that our results provide an indication of the likely geometry to be adopted by highly substituted $[M_3(CO)_{12-n}L_n]$ complexes. It should also be remembered that μ-CO ligands are present in the transition states for the dynamic interchange of these groups that occurs in solution {and in the solid state for $[Fe_3(CO)_{12}]$ [14]}, and that the activation energies for the CO(terminal) $\rightleftharpoons$ CO(bridge) process are often low [*ca.* 5 kcal mol^{-1} (20.9 kJ mol^{-1})]. As found with $[Fe_3(CO)_{12}]$, the i.r. spectrum of complex (3) in solution contains only weak ν(CO) bands between 1 700 and 1 820 cm^{-1}, which may indicate that a non-bridged isomer predominates in solution. These factors, together with the finding that the p.a.p. can accommodate at least two different orientations of the M_3 core in some cases,[3] suggest that the observed solid-state structure may result from a delicate balance of several influences. Indeed, Benfield and Johnson[8] have concluded that it may be 'the relatively small non-bonded repulsions between carbonyl groups [that] will be important [to determine] which overall structure is adopted.'

An alternative approach has been to analyse the factors influencing the formation of bridging carbonyls using the fragment molecular-orbital method.[15] Bridging carbonyl ligands may furnish two or three σ-donor orbitals, which may interact with ML_n fragments, which for a molecule of the $[Fe_3(CO)_{12}]$ type will be two d^6 $Fe(CO)_3L_3$ fragments and one d^8 $Fe(CO)_4$ fragment. For $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ the clusters are formed from three $M(CO)_4$ fragments. The difference arises from a tendency for the lighter metals to utilise the t_{2g} orbitals in bonding, whereas these orbitals are stabilised by π bonding for Ru and Os; the lighter metal forms a larger number of M–L σ bonds.[16] Following this argument, one can conclude that the presence of several weakly π-accepting PR_3 ligands would tend to destabilise the t_{2g} orbitals, resulting in the adoption of an $[Fe_3(CO)_{12}]$-type structure, as found for complex (3). The contraction in p.a.p. volume is then seen to be a result of the presence of the four Ru–P interactions, which are shorter than the Ru$\cdots$O distances. For M = Ru or Os, volume reductions of the order of *ca.* 15 Å^3 less than that of the parent carbonyls are to be anticipated when more than three tertiary phosphine ligands are present.

Finally, a further comment on the average M–M separations found in the complexes listed in Table 1 is in order. Initial determinations of these parameters were in accord with the suggestion that replacement of CO by better σ-donor ligands resulted in an expansion of the M_3 core. While data for any one series of complexes $[M_3(CO)_{12-n}L_n]$ (n = 0—3) are still lacking, the trends in Table 1 appear to indicate that introduction of one tertiary phosphine or phosphite ligand does have an average M–M bond-lengthening effect, but that complexes with two or more such ligands have average M–M separations comparable with those found in the parent carbonyls. Further results are required, but it is evident that there is not a simple electronic or steric influence on the M–M separations.

Experimental

The complex $[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$ was prepared as described previously;[5] crystals for the *X*-ray study were obtained from light petroleum (b.p. 40—60 °C). When first reported,[5] no ν(CO) bands were noted in the bridging CO region; re-examination of spectra of a CH_2Cl_2 solution and of a Nujol mull revealed weak bands at 1 810, 1 760 cm^{-1} (CH_2Cl_2) or 1 820, 1 772 cm^{-1} (Nujol), with a much weaker absorption at 1 718 cm^{-1} in the latter. These bands may be assigned to the ν(CO) modes of the bridging CO groups.

Crystallography.—Crystal data. $C_{40}H_{44}O_{16}P_4Ru_3$, M = 1 207.9, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 11.829(4), b = 19.902(9), c = 20.546(7) Å, β = 102.66(2)°, U = 4 719(3) Å^3, D_m = 1.69(1), D_c (Z = 4) = 1.70 g cm^{-3}, $F(000)$ = 2 416, monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ = 10.7 cm^{-1}. Specimen: 0.30 × 0.30 × 0.10 mm. T = 295 K.

Structure determination. A unique data set was measured to a $2\theta_{max.}$ limit of 70° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ–θ scan mode; reflections at the higher angles, although weak, were persistent, and a total of N = 16 559 independent reflections were obtained. Of these, N_o = 7 646 with $I > 3\sigma(I)$ were considered 'observed' and used in the (basically) 9 × 9 block-diagonal least-squares refinement after

Table 2. Non-hydrogen atom co-ordinates for the complex $[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$

Atom	*x*	*y*	*z*
Ru(1)	0.195 75(5)	0.320 03(3)	0.322 92(3)
C(1U)	0.226 6(6)	0.363 0(3)	0.246 7(3)
O(1U)	0.252 2(5)	0.390 2(3)	0.203 6(3)
C(1D)	0.089 9(6)	0.386 3(4)	0.341 5(3)
O(1D)	0.032 8(5)	0.428 4(3)	0.353 0(3)
C(12U)	0.286 4(6)	0.237 8(4)	0.301 4(4)
O(12U)	0.357 8(5)	0.215 0(3)	0.279 4(3)
C(12D)	0.129 9(6)	0.270 1(4)	0.414 2(3)
O(12D)	0.106 2(5)	0.292 1(3)	0.460 3(2)
P(1)	0.348 40(16)	0.367 94(10)	0.394 84(9)
O(1a)	0.476 2(4)	0.337 3(3)	0.404 9(2)
C(1a)	0.529 8(7)	0.324 2(6)	0.350 3(4)
O(1b)	0.359 8(5)	0.443 6(2)	0.370 5(3)
C(1b)	0.450 8(10)	0.488 5(5)	0.403 8(5)
C(1c1)	0.347 4(6)	0.376 3(3)	0.482 2(3)
C(1c2)	0.413 4(8)	0.335 9(4)	0.529 9(4)
C(1c3)	0.403 8(10)	0.341 7(5)	0.596 6(4)
C(1c4)	0.333 7(9)	0.386 5(5)	0.614 9(5)
C(1c5)	0.269 4(8)	0.427 6(5)	0.569 0(5)
C(1c6)	0.275 2(7)	0.423 2(4)	0.502 2(4)
Ru(2)	0.147 30(5)	0.188 15(3)	0.355 22(3)
C(2U)	0.155 1(6)	0.122 4(4)	0.288 0(3)
O(2U)	0.162 9(5)	0.081 3(3)	0.252 0(3)
C(2D)	0.024 1(6)	0.146 7(4)	0.384 6(3)
O(2D)	−0.046 2(4)	0.121 0(3)	0.405 3(3)
P(2)	0.289 94(14)	0.137 43(9)	0.432 26(8)
O(2a)	0.324 7(4)	0.164 6(3)	0.507 2(2)
C(2a)	0.240 4(8)	0.172 1(5)	0.546 6(4)
O(2b)	0.253 3(4)	0.060 8(2)	0.438 3(3)
C(2b)	0.324 6(8)	0.014 4(4)	0.482 9(5)
C(2c1)	0.435 8(5)	0.131 2(3)	0.420 0(3)
C(2c2)	0.457 3(7)	0.089 4(4)	0.370 4(4)
C(2c3)	0.568 3(8)	0.082 5(5)	0.359 3(5)
C(2c4)	0.658 0(7)	0.116 6(4)	0.397 0(4)
C(2c5)	0.638 1(7)	0.158 2(4)	0.444 7(4)
C(2c6)	0.529 5(6)	0.165 3(4)	0.456 5(4)
Ru(3)	−0.010 06(4)	0.255 53(2)	0.248 38(2)
C(3U)	0.094 9(6)	0.232 5(3)	0.192 9(3)
O(3U)	0.153 3(4)	0.219 3(3)	0.158 0(2)
C(3D)	−0.087 1(5)	0.281 1(3)	0.317 8(3)
O(3D)	−0.136 2(5)	0.296 1(3)	0.357 9(3)
P(13)	−0.096 83(15)	0.336 91(9)	0.177 73(9)
O(13a)	−0.138 1(4)	0.321 3(3)	0.099 0(2)
C(13a)	−0.055 9(7)	0.302 2(5)	0.060 3(4)
O(13b)	−0.017 6(4)	0.402 2(2)	0.181 3(3)
C(13b)	−0.052 2(8)	0.459 8(4)	0.138 2(5)
C(13c1)	−0.236 2(6)	0.369 8(3)	0.186 7(3)
C(13c2)	−0.238 5(7)	0.414 2(4)	0.237 9(4)
C(13c3)	−0.344 1(8)	0.438 6(4)	0.247 2(4)
C(13c4)	−0.444 7(7)	0.418 4(4)	0.206 4(5)
C(13c5)	−0.443 0(7)	0.375 1(5)	0.156 0(5)
C(13c6)	−0.339 1(7)	0.351 3(4)	0.145 1(4)
P(23)	−0.141 88(15)	0.175 24(8)	0.205 80(8)
O(23a)	−0.277 5(4)	0.190 3(2)	0.195 7(2)
C(23a)	−0.328 3(7)	0.211 7(5)	0.249 7(4)
O(23b)	−0.122 5(4)	0.107 6(2)	0.249 3(2)
C(23b)	−0.196 8(8)	0.050 1(4)	0.230 8(4)
C(23c1)	−0.150 3(6)	0.145 8(3)	0.121 4(3)
C(23c2)	−0.060 7(7)	0.108 9(4)	0.107 3(4)
C(23c3)	−0.059 4(8)	0.089 1(5)	0.042 3(4)
C(23c4)	−0.149 2(8)	0.106 6(4)	−0.008 4(4)
C(23c5)	−0.239 2(9)	0.141 2(5)	0.005 3(4)
C(23c6)	−0.241 4(7)	0.162 4(4)	0.069 3(4)

Table 3. Ruthenium atom environments. In each case the first column in the matrix, *r*, is the ruthenium–ligand distance, Ru–X/Å. Other entries are the angles (°) subtended at the ruthenium by the relevant ligand atoms

Ru(1)	*r*	Ru(3)	C(1U)	C(1D)	C(12U)	C(12D)	P(1)
Ru(2)	2.797(1)	60.95(3)	135.1(2)	115.0(2)	56.5(2)	46.1(2)	114.43(5)
Ru(3)	2.879(1)		93.2(2)	84.2(2)	87.2(2)	81.3(2)	171.9(1)
C(1U)	1.888(7)			96.1(3)	88.7(3)	172.2(3)	94.5(2)
C(1D)	1.915(8)				170.3(3)	77.9(3)	92.4(2)
C(12U)	2.057(8)					96.5(3)	95.5(2)
C(12D)	2.399(8)						90.8(2)
P(1)	2.277(2)						

Ru(2)	*r*	Ru(3)	C(2U)	C(2D)	C(12U)	C(12D)	P(2)
Ru(1)	2.797(1)	60.92(2)	115.1(2)	134.4(2)	45.9(2)	56.7(2)	114.91(5)
Ru(3)	2.879(1)		83.9(2)	91.8(2)	81.4(2)	87.1(2)	172.6(1)
C(2U)	1.920(7)			95.4(3)	78.6(3)	170.3(3)	93.0(2)
C(2D)	1.886(7)				171.3(3)	88.6(3)	95.2(2)
C(12U)	2.389(7)					96.5(3)	91.4(2)
C(12D)	2.068(8)						95.5(2)
P(2)	2.281(2)						

Ru(3)	*r*	Ru(2)	C(3U)	C(3D)	P(13)	P(23)
Ru(1)	2.879(1)	58.13(3)	80.8(2)	88.3(2)	103.51(5)	161.52(6)
Ru(2)	2.879(1)		87.0(2)	83.7(2)	161.44(10)	103.93(5)
C(3U)	1.916(7)			168.3(2)	93.0(2)	94.7(2)
C(3D)	1.922(7)				93.7(2)	94.3(2)
P(13)	2.265(2)					94.58(6)
P(23)	2.270(2)					

Table 4. Ligand geometries

(*a*) Carbonyl geometries: *r* is the C–O distance, θ the Ru–C–O angle [where two entries are given, they are Ru(*l,m*)–C–O, *l* < *m*], and φ is Ru–C–Ru

Carbonyl	r/Å	θ/°	φ/°
1U	1.134(9)	175.3(6)	
1D	1.132(10)	175.6(7)	
12U	1.135(10)	150.7(6), 131.8(6)	77.6(3)
12D	1.134(9)	132.5(6), 150.4(6)	77.1(3)
2U	1.121(9)	175.5(6)	
2D	1.135(9)	176.5(6)	
3U	1.131(9)	177.2(6)	
3D	1.146(9)	177.9(6)	

(*b*) Phosphorus geometries (distances in Å, angles in °)

Ligand	1	2	13	23
P–O(a)	1.601(5)	1.599(5)	1.615(5)	1.600(5)
P–O(b)	1.601(5)	1.598(5)	1.594(5)	1.605(5)
P–C(c)	1.805(7)	1.802(7)	1.820(7)	1.813(7)
O(a)–C(a)	1.43(1)	1.42(1)	1.44(1)	1.44(1)
O(b)–C(b)	1.45(1)	1.44(1)	1.45(1)	1.44(1)
Ru–P–O(a)	121.1(2)	120.9(2)	120.0(2)	120.2(2)
Ru–P–O(b)	107.4(2)	107.7(2)	111.9(2)	111.9(2)
Ru–P–C(c)	120.5(2)	121.3(2)	119.1(2)	119.0(2)
O(a)–P–O(b)	104.9(3)	105.4(3)	104.4(3)	104.3(3)
O(a)–P–C(c)	96.8(3)	96.1(3)	95.1(3)	95.3(3)
O(b)–P–C(c)	104.1(3)	103.3(3)	103.8(3)	103.5(3)
P–O(a)–C(a)	122.4(5)	121.2(5)	120.9(4)	122.1(4)
P–O(b)–C(b)	122.5(5)	122.1(5)	122.1(5)	120.9(4)

Table 5. Atom deviations (Å) from the Ru_3 plane. A least-squares plane, defined by the Ru_3 plane, is $-0.6752X + 0.3456Y + 0.6516Z = 5.838$, relative to the right-hand orthogonal Å frame with X parallel to *a* and Z in the *ac* plane; *n* denotes the ruthenium that the ligand atoms are appended to. The two values in the one entry in column 4 pertain to phosphines 13 and 23 respectively

	$n = 1$	2	3
C(*n*U)	−1.18	−1.60	−1.89
O(*n*U)	−1.89	−2.52	−3.01
C(*n*D)	1.60	1.17	1.91
O(*n*D)	2.53	1.89	3.05
P(*n*)	0.27	−0.25	0.12, −0.19
O(*n*1a)	−0.80	0.87	−0.93, 0.84
C(*n*1a)	−2.20	2.23	−2.34, 2.26
O(*n*1b)	0.31	−0.38	−0.01, −0.10
C(*n*1b)	0.42	−0.56	−0.03
C(*n*c1)	1.74	−1.65	1.60, −1.68

Also: C,O(12U) −1.64, −2.72; C,O(12D): 1.65, 2.74 Å.

analytical absorption correction and solution of the structure by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms. Hydrogen-atom parameters (x,y,z,U) were constrained at estimated values. Residuals at convergence were 0.054, 0.060 (R,R'), reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[17] Computation used the *X*-RAY 76 program system[18] implemented on a Perkin-Elmer 3240 computer.

The ligands are labelled according to the ruthenium atoms they are attached to, and whether they lie up (U) or down (D) relative to the ligand plane (see Figure). Thus carbonyl CO(1U) is attached to Ru(1) and lies up, while carbonyl CO(23) bridges Ru(2) and Ru(3) lying closest to the former; P(13) and P(23) respectively are attached to Ru(3) lying in the equatorial plane towards Ru(1), Ru(2) respectively. 'b'-Type methoxy-substituents lie in the Ru_3 plane, 'a' type project out.

Final atomic co-ordinates for non-hydrogen atoms are given in Table 2, ruthenium atom environments in Table 3, ligand geometries in Table 4, and atom deviations from the Ru_3 plane in Table 5.

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