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Cluster chemistry

LVII *. Stereochemistry of group 15 ligand-substituted derivatives of $M_3(CO)_{12}$ (M = Ru, Os) C. X-Ray structures of $Ru_3(CO)_9(L)_3$ (L = $PMe_2(CH_2Ph)$, PMe_2Ph, $AsMe_2Ph$, $PPh(OMe)_2$, $P(OEt)_3$, and $P(OCH_2CF_3)_3$) and $Os_3(CO)_9(PPh_3)_3$

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Abstract

The molecular structures of $Ru_3(CO)_9(L)_3$ (L = $PMe_2(CH_2Ph)$, PMe_2Ph, $AsMe_2Ph$, $PPh(OMe)_2$, $P(OEt)_3$ and $P(OCH_2CF_3)_3$) and $Os_3(CO)_9(PPh_3)_3$ have been determined by single-crystal X-ray diffraction methods. The tertiary phosphine, arsine or phosphite ligands occupy equatorial sites, one per metal atom, so arranged that each is as far from the other two as possible. The unit cell of the $PPh(OMe)_2$ complex is unusual in containing four conformationally distinct molecules, two of which contain disordered Ru_3 cores. Metal–metal and metal–ligand separations are similar to those found in $M_3(CO)_{12}$ and mono- or disubstituted complexes, respectively. Considerable distortion towards D_3 symmetry is found, with M–M–CO angles approaching those calculated for semi-bridging CO groups in the case of the $P(OEt)_3$ complex. Crystal data: $Ru_3(CO)_9(PMe_2Ph)_3$, orthorhombic, $P2_12_12_1$, a 21.343(2), b 14.752(4), c 12.170(2) Å, U 3832(1) Å^3, $Z = 4$, N_0 (number of 'observed' data with $I > 3\sigma(I)$) = 3601, $R = 0.040$, $R' = 0.048$; $Ru_3(CO)_9(AsMe_2Ph)_3$, triclinic, $P\bar{1}$, a 19.113(4), b 15.375(4), c 13.756(3) Å, α 89.36(2), β 85.97(2), γ 77.61(2)°, U 3939(2) Å^3, $Z = 4$, $N_0 = 8823$, $R = 0.046$, $R' = 0.047$;

* For Part LVI (B), see ref. 2.

0022-328X/88/$03.50

$Ru_3(CO)_9\{PMe_2(CH_2Ph)\}_3$, trigonal, $P\bar{3}$, a 12.766(10), c 15.583(9) Å, U 2202(2) Å^3, $Z = 2$, $N_0 = 1966$; $R = 0.093$, $R' = 0.117$; $Ru_3(CO)_9\{PPh(OMe)_2\}_3$, triclinic, $P\bar{1}$, a 23.23(1), b 20.87(1), c 20.73(1) Å, α 98.21(4), β 111.07(3), γ 111.95(4)°, U 8237(7) Å^3, $Z = 8$, $N_0 = 16532$, $R = 0.041$, $R' = 0.039$; $Ru_3(CO)_9\{P(OEt)_3\}_3$, triclinic, $P\bar{1}$, a 18.170(6), b 13.016(6), c 10.035(3) Å, α 68.83(3), β 80.42(3), γ 78.10(4)°, U 2154(1) Å^3, $Z = 2$, $N_0 = 4318$, $R = 0.051$, $R' = 0.061$; $Ru_3(CO)_9\{P(OCH_2CF_3)_3\}_3$, triclinic, $P\bar{1}$, a 21.036(2), b 13.146(1), c 9.376(2) Å, α 82.68(1), β 88.40(1), γ 85.59(1)°, U 2564(1) Å^3, $Z = 2$, $N_0 = 3966$, $R = 0.066$, $R' = 0.068$; $Os_3(CO)_9(PPh_3)_3$, triclinic, $P\bar{1}$, a 18.207(5), b 17.911(6), c 12.928(3) Å, α 94.13(2), β 98.98(2), γ 110.56(2)°, U 3862(2) Å^3, $Z = 2$, $N_0 = 3216$, $R = 0.092$, $R' = 0.084$.

Introduction

This is the third of four papers describing X-ray studies of a series of group 15-ligand-substituted derivatives of the trinuclear ruthenium and osmium cluster carbonyls $M_3(CO)_{12}$ (M = Ru or Os), carried out in order to determine the effects of increasing degrees of substitution on the stereochemistry of the system [1,2]. The molecular structures of the seven title complexes are reported below: they are designated according to the ligand/metal convention established in Part A [1] (see Scheme 1 in that paper).

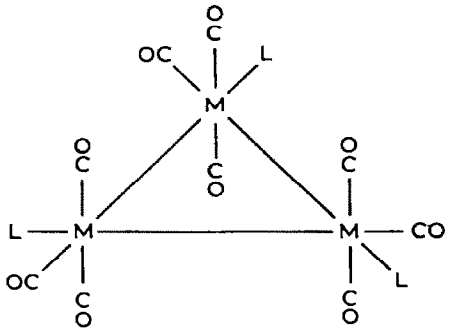
Results and discussion

The trisubstituted complexes $M_3(CO)_9(L)_3$ are obtained in only moderate yields by the electron transfer-catalysed reactions described previously [3]; they are also formed in thermal reactions between $M_3(CO)_{12}$ and the group 15 ligand carried out in refluxing hydrocarbon (cycloalkane, arene) or tetrahydrofuran solvents. Of the compounds studied, **3k-Ru** and **3l-Ru** are new: they were characterised by elemental microanalysis and from their IR ν(CO) and mass spectra, and finally by the X-ray studies. As has been reported before [4,5], the reaction between $Ru_3(CO)_{12}$ and $AsPh_3$ gives only $Ru_3(CO)_{10}(AsPh_3)_2$; however, a derivative containing three tertiary arsine ligands, **3f-Ru**, has been obtained [3] and its structure is reported here. X-Ray quality crystals of $Ru_3(CO)_9(PPh_3)_3$ could not be prepared, but those of the osmium analogue **3b-Os** were satisfactory, so that this complex could also be included in this study.

General structural considerations

Common to all structures are the triangular M_3 cores, and three group 15 ligands bonded one to each metal in equatorial sites, such that each one is as far away from the other two as possible. Plots of the molecular structures are shown in Fig. 1a–k, while Table 1 summarises important bond lengths found for these compounds and $Ru_3(CO)_9(PMe_3)_3$, the only other trisubstituted complex to be described hitherto [6]. Although all have incipient three-fold symmetry, in only one case (**3g-Ru**) does the molecule have perfect three-fold symmetry, crystallographically imposed.

Of note is the disorder found in complexes **3i-Ru** (molecules 1 and 4, see below) and **3k-Ru**, which is of the now familiar type involving occupancy of two metal



L	Ru	Os
CO	**1a-Ru**	**1a-Os**
PPh_3		**3b-Os**
PMe_2Ph	**3e-Ru**	
$AsMe_2Ph$	**3f-Ru**	
$PMe_2(CH_2Ph)$	**3g-Ru**	
PMe_3	**3h-Ru**	
$PPh(OMe)_2$	**3i-Ru**	
$P(OEt)_3$	**3k-Ru**	
$P(OCH_2CF_3)_3$	**3l-Ru**	

atom sites within an invariant peripheral atom polyhedron constructed from the O atoms of the CO groups, and the P atoms of the group 15 ligands. Occupancy factors are 75/25 for **3k-Ru**.

Another point of interest is found in the unusually large unit cell of **3i-Ru**, which contains four molecules in the asymmetric unit; two of these are disordered in the manner described above with occupancy factors 5.4/94.6 (molecule 1) and 17.4/82.6 (molecule 4). With 222 non-hydrogen atoms (including the minor Ru_3 components), the asymmetric unit may be the largest organometallic structure studied to date. The four molecules differ only in the orientations of the substituents on the phosphorus atoms.

Metal–metal separations

Only in the case of **3g-Ru** are all three M–M separations identical. In the other complexes, differences range between 0.01–0.03 Å (3–15σ). With the exception of **3i-Ru**, where they are ca. 0.03 Å longer, the average Ru–Ru separations are essentially identical with those found in $Ru_3(CO)_{12}$ [7]; in the $AsMe_2Ph$ complex **3f-Ru**, they are ca. 0.01 Å *shorter*. The average Os–Os separation in **3b-Os** is 0.033 Å longer than that in $Os_3(CO)_{12}$ [8].

Metal–ligand separations

The M–P and M–As distances are similar to those found in the mono- and di-substituted complexes containing the corresponding ligands, increasing with increasing cone angle, and merit no additional comment.

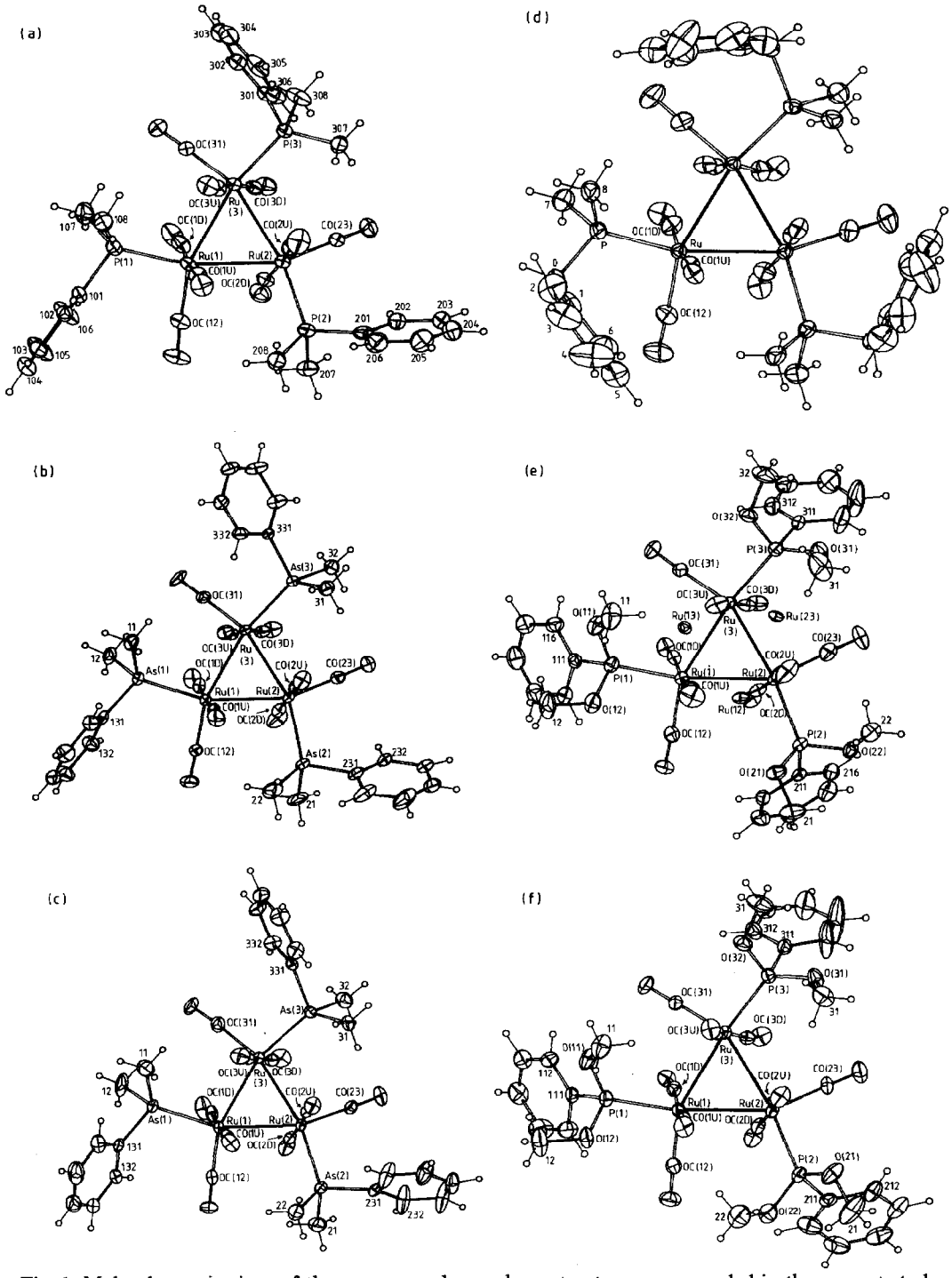


Fig. 1. Molecular projections of the seven complexes whose structures are recorded in the present study. 20% probability amplitude thermal ellipsoids are shown for the non-hydrogen atoms, together with labelling. Hydrogen atoms have arbitrary radii of 0.1 Å. (a) $Ru_3(CO)_9(PMe_2Ph)_3$ (**3e-Ru**); (b) $Ru_3(CO)_9(AsMe_2Ph)$ (**3f-Ru**), molecule 1; (c) **3f-Ru**, molecule 2; (d) $Ru_3(CO)_9\{PMe_2(CH_2Ph)\}_3$ (**3g-Ru**); (e) $Ru_3(CO)_9\{PPh(OMe)_2\}_3$ (**3i-Ru**), molecule 1; (f) **3i-Ru**, molecule 2; (g) **3i-Ru**, molecule 3; (h) **3i-Ru**, molecule 4; (i) $Ru_3(CO)_9\{P(OEt)_3\}_3$ (**3k-Ru**); (j) $Ru_3(CO)_9\{P(OCH_2CF_3)_3\}_3$ (**3l-Ru**); (k) $Os_3(CO)_9(PPh_3)_3$ (**3b-Os**).

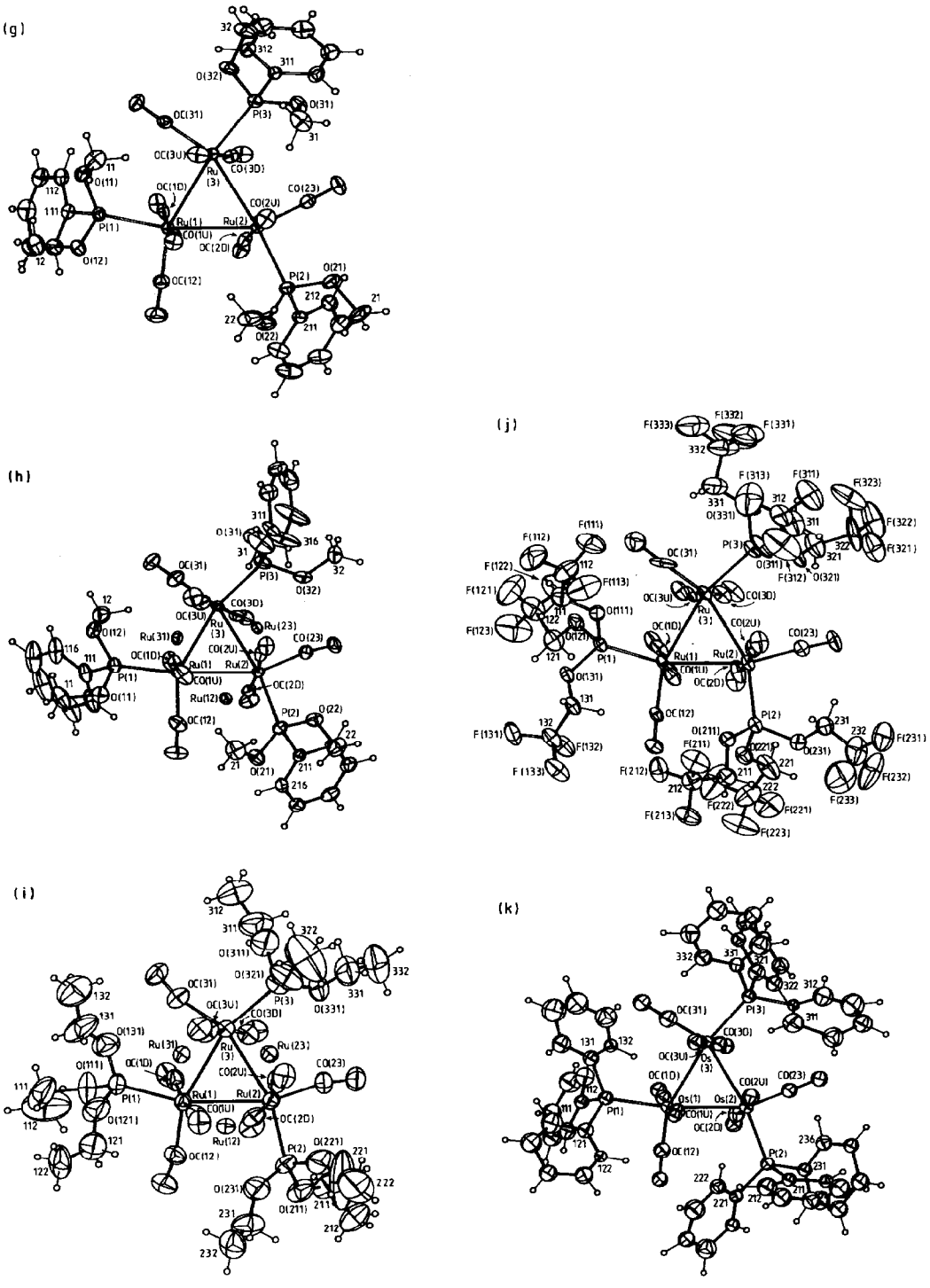


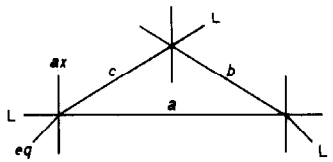
Fig. 1 (continued).

Metal–carbonyl distances

In all cases, the M–CO_{ax} distances are longer than the M–CO_{eq} separations; the values for **3b-Os** appear to be anomalous and imprecise and are not considered further.

Table 1

Important bond distances (Å) in $M_3(CO)_9(L)_3$ complexes



M	L	No.	Cone angle (°) [a]	M–M			M–L (av) [b]	M–CO		Ref.
				a	*b*	*c*		*ax* [c]	*eq* [b]	
Ru	CO	**1a-Ru**	~95	2.852(1)	2.851(1)	2.860(1)	–	1.942(4)	1.921(5)	7
Os	CO	**1a-Os**	~95	2.874(1)	2.875(1)	2.882(1)	–	1.946(6)	1.912(7)	8
Os	PPh_3	**3b-Os**	145	2.904(4)	2.907(4)	2.919(4)	2.35	1.81	1.74	[d]
Ru	PMe_2Ph	**3e-Ru**	122	2.851(1)	2.864(1)	2.860(1)	2.334	1.916	1.871	[d]
Ru	$AsMe_2Ph$ (mol. 1)	**3f-Ru**	~120	2.851(1)	2.846(1)	2.838(1)	2.444	1.919	1.862	[d]
	(mol. 2)			2.846(1)	2.848(1)	2.838(1)	2.446	1.925	1.870	
Ru	$PMe_2(CH_2Ph)$	**3g-Ru**	~120	2.860(2)	2.860(2)	2.860(2)	2.314	1.93	1.88	[d]
Ru	PMe_3	**3h-Ru**	118	2.860(1)	2.862(1)	2.854(1)	2.330	1.920	1.869	6
Ru	$PPh(OMe)_2$ (mol. 1)	**3i-Ru**	115	2.900(1)	2.870(1)	2.887(2)	2.284	1.922	1.909	[d]
	(mol. 2)			2.887(1)	2.894(1)	2.876(2)	2.279	1.927	1.887	
	(mol. 3)			2.884(1)	2.876(1)	2.882(1)	2.278	1.924	1.878	
	(mol. 4)			2.882(4)	2.874(2)	2.885(1)	2.299	1.934	1.915	
Ru	$P(OEt)_3$	**3k-Ru**	109	2.863(1)	2.852(2)	2.851(1)	2.292	1.95	1.90	[d]
Ru	$P(OCH_2CF_3)_3$	**3l-Ru**	~110	2.857(2)	2.866(2)	2.852(2)	2.246	1.93	1.85	[d]

[a] From ref. 11. [b] Average of three. [c] Average of six. [d] This work.

Table 2

Torsion angles (°) in $M_3(CO)_9(L)_3$ complexes [a]

L	M	Torsion angle (°) [b]		
		C(1)–M(1)–M(2)–C(2)	C(2)–M(2)–M(3)–C(3)	C(3)–M(3)–M(1)–C(1)
PPh_3	Os	14.2, 21.0	14.2, 26.6	19.5, 25.4
PMe_2Ph	Ru	25.2, 36.3	27.4, 37.2	24.3, 33.6
$AsMe_2Ph$	Ru [c]	22.8, 28.4	25.8, 29.7	23.1, 29.1
		22.5, 26.8	24.1, 28.7	23.0, 28.1
$PMe_2(CH_2Ph)$	Ru	21.7, 33.2		
PMe_3	Ru [d]	21.0, 28.7	19.5, 31.4	20.8, 30.7
$PPh(OMe)_2$	Ru [e]	(16.4, 32.6)	(15.6, 32.6)	(17.4, 33.1)
		18.5, 36.1	14.5, 34.1	17.1, 35.2
		14.0, 29.6	14.3, 31.8	14.9, 29.4
		(21.5, 33.4)	(25.1, 32.6)	(21.7, 33.3)
$P(OEt)_3$	Ru	(34.4, 40.7)	(32.8, 39.6)	(32.6, 40.4)
$P(OCH_2CF_3)_3$	Ru	23.6, 26.5	26.0, 28.0	23.9, 28.4

[a] Values in parentheses are for disordered species. [b] Two values given, for C(nU)–M(n)–M($n+1$)–C($n+1$U), C(nD)–M(n)–M($n+1$)–C($n+1$D), respectively. [c] Values for two independent molecules given. [d] Ref. 6. [e] Values for four independent molecules given.

Torsion angles

Although the M–M separations are not significantly lengthened, the introduction of the three group 15 ligands results in a considerable distortion of the M_3L_{12} molecule from the D_{3h} symmetry found for the parent carbonyls, towards the energetically more favourable D_3 symmetry. This is achieved by a twisting of the ML_4 moieties about the M–M vectors, as shown by the torsion angles about these bonds (Table 2). In *all* cases, the torsion angle C(nU)–M(n)–M($n+1$)–C($n+1$U) is smaller than C(nD)–M(n)–M($n+1$)–C($n+1$D); for the PMe_2Ph and $PPh(OMe)_2$ complexes, the differences range from 1.4 to 19.6°.

Although the observed twisting results in a relief of steric interaction, there is no obvious correlation between torsion angle and ligand cone angle. However, in the four independent molecules of **3i-Ru**, the consistent differences between the two torsion angles is remarkable, persisting with the disordered molecules. We interpret these results in terms of an unsymmetrical ligand disposition; in these projections, the phenyl group is always below the Ru_3 plane. Similar situations are found with **3g-Ru**, where the molecule has imposed three-fold symmetry, and with **3k-Ru** and **3l-Ru**, in which the ligands are oriented pseudo-symmetrically. In *all* cases, the disposition of the phosphine substituent is such that one lies below the plane, while the other two lie above it (see Fig. 1).

In his description of a surface force-field applied to metal carbonyl cluster structures, Lauher [9] points out that the D_{3h} structure is less stable than the D_3 structure, and that the axial CO groups in the latter are approximately semi-bridging, with M–M–CO angles of 73.5°. In the present study, the corresponding angles found for the axial CO groups range from 73.7 to 84.4° (av.); not surprisingly, the M–C–O angles in the complex **3k-Ru** with the smallest M–M–CO angles are also the smallest, and range between 165.1–169.8(8)°. Similarly, the Ru–C–O_{eq} angles are all ca. 167°. In contrast, the other six complexes have Ru–C–O_{ax} ca. 173° and Ru–C–O_{eq} between 176–178°.

Conclusions

The major conclusions from this study of seven trisubstituted ruthenium and osmium carbonyl complexes, $M_3(CO)_9(L)_3$, are as follows:

(*i*) The three group 15 ligands are each attached to a separate metal atom, occupying an equatorial position as far removed from each other as possible;

(*ii*) The average Ru–Ru separations are similar to those found in $[Ru_3(CO)_{12}]$, with the exceptions of **3f-Ru** (which are shorter) and **3i-Ru** (longer);

(*iii*) The Ru–P(As) distances are similar to those found in analogous mono- and di-substituted complexes, and for P, increase with increasing cone angle;

(*iv*) The $M–CO_{ax}$ bonds are longer than the $M–CO_{eq}$ bonds; $M–C–O_{ax}$ are ca. 173°, $M–C–O_{eq}$ are ca. 177°; the $P(OEt)_3$ complex **3k-Ru** is an exception, one set of $M–M–CO_{ax}$ angles being consistent with the presence of semi-bridging CO groups;

(*v*) Introduction of the group 15 ligands results in a change towards D_3 symmetry, relieving the steric pressures from the larger ligands by twisting of the ML_4 units about the M–M vector.

Experimental

General reaction conditions and instrumentation have been described in Part A [1]. Complexes **3b-Os** [1], **3e-Ru** and **3f-Ru** [3], **3i-Ru** and **3l-Ru** [1] were prepared by the cited methods; **3g-Ru** and **3k-Ru** were obtained as follows.

Reaction between $Ru_3(CO)_{12}$ and $PMe_2(CH_2Ph)$

The reagent $Na[Ph_2CO]$ (0.1 ml of a 0.025 *M* solution in tetrahydrofuran) was added to a mixture of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and $PMe_2(CH_2Ph)$ (112 mg, 0.74 mmol) in the same solvent (20 ml). Gas was evolved, and the mixture became deep orange. After 16 h the solvent was removed under reduced pressure. Column chromatography of the residue gave an orange band (CH_2Cl_2 eluant) which was crystallised ($CHCl_3$/hexane) to give orange crystalline $Ru_3(CO)_9\{PMe_2(CH_2Ph)\}_3$ (**3g-Ru**) (72 mg, 44%). This was characterised by IR (cyclohexane) ν(CO) 2045w, 1975vs, 1941m cm^{-1} (lit. [10] 2043w, 2017w, 1973s, 1937m cm^{-1}); ^1H NMR ($CDCl_3$) δ 7.3–7.7 (m, 5H, Ph), 3.27 (d, *J* 8 Hz, 2H, CH_2), 1.39 (d, *J* 8 Hz, 6H, CH_3); and FAB-MS (Found, *M* 1013; calcd (Ru_3 = 305), 1013).

Reaction between $Ru_3(CO)_{12}$ and $P(OEt)_3$

To a refluxing solution of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and $P(OEt)_3$ (181 mg, 1.09 mmol) in tetrahydrofuran (30 ml) was added $Na[Ph_2CO]$ (1 ml of a 0.025 *M* solution in tetrahydrofuran). After 80 min the solution was cooled and the solvent removed under reduced pressure. The residue was subjected to preparative TLC (petroleum spirit/CH_2Cl_2, 4/1). An orange band (R_f 0.53) was collected and the recovered solid crystallized from MeOH to give orange plates of $Ru_3(CO)_9\{P(OEt)_3\}_3$ (**3k-Ru**) (25 mg, 15%), m.p. 71–72°C. (Found: C, 30.77; H, 4.30%; *M* (FAB-MS) 1055; $C_{27}H_{45}O_{18}P_3Ru_3$ calc: C, 30.79; H, 4.30%; *M*, 1055). IR ν(CO) (cyclohexane) 2053vw, 1985vs, 1959sh, 1930sh, 1917sh cm^{-1}. ^1H NMR: δ ($CDCl_3$) 4.00 (pent, 2H, CH_2); 1.29 (t, 3H, CH_3). The next band (purple, R_f 0.44) was removed quickly and the recovered solid recrystallised (petroleum spirit/CH_2Cl_2) to give deep purple crystalline $Ru_3(CO)_8\{P(OEt)_3\}_4$ (**4k-Ru**) (30 mg, 16%), m.p.

(Continued on p. 217)

Table 3

Non-hydrogen atom coordinates for complex **3e-Ru**

Atom	*x*	*y*	*x*
Ru(1)	0.95823(3)	0.13124(4)	0.10108(5)
Ru(2)	0.87889(3)	0.15591(4)	−0.08504(5)
Ru(3)	0.82522(3)	0.13475(4)	0.12911(5)
Ligand 1			
P(1)	0.9988(1)	0.1390(2)	0.2793(2)
C(101)	1.0836(4)	0.1368(5)	0.2801(6)
C(102)	1.1198(4)	0.2132(6)	0.2946(7)
C(103)	1.1839(4)	0.2086(6)	0.2930(8)
C(104)	1.2122(6)	0.1283(7)	0.2781(9)
C(105)	1.1785(5)	0.0515(8)	0.2640(14)
C(106)	1.1147(5)	0.0560(7)	0.2651(13)
C(107)	0.9796(5)	0.0502(8)	0.3767(9)
C(108)	0.9788(5)	0.2389(7)	0.3585(8)
Ligand 2			
P(2)	0.9433(1)	0.2026(2)	−0.2290(2)
C(201)	0.9009(4)	0.2553(6)	−0.3391(7)
C(202)	0.8589(4)	0.2054(7)	−0.4003(7)
C(203)	0.8221(5)	0.2440(7)	−0.4820(7)
C(204)	0.8278(5)	0.3320(9)	−0.5050(9)
C(205)	0.8657(6)	0.3861(8)	−0.4499(10)
C(206)	0.9039(6)	0.3485(8)	−0.3657(10)
C(207)	0.9853(5)	0.1138(9)	−0.3021(9)
C(208)	1.0056(5)	0.2833(10)	−0.1993((9)
Ligand 3			
P(3)	0.7198(1)	0.1743(2)	0.1118(2)
C(301)	0.6929(4)	0.2486(6)	0.2223(6)
C(302)	0.6767(4)	0.2101(7)	0.3201(7)
C(303)	0.6561(5)	0.2607(8)	0.4073(8)
C(304)	0.6549(5)	0.3502(9)	0.3996(9)
C(305)	0.6694(5)	0.3948(7)	0.3021(11)
C(306)	0.6895(4)	0.3407(7)	0.2110(9)
C(307)	0.6929(5)	0.2297(10)	−0.0106(8)
C(308)	0.6656(5)	0.0788(8)	0.1186(10)
Carbonyl groups			
C(1U)	0.9676(4)	0.2592(5)	0.0849(7)
O(1U)	0.9773(3)	0.3356(4)	0.0767(6)
C(1D)	0.9371(4)	0.0078(5)	0.1257(9)
O(1D)	0.9309(4)	−0.0682(4)	0.1441(7)
C(12)	1.0334(4)	0.1091(6)	0.0281(8)
O(12)	1.0782(3)	0.0947(6)	−0.0207(8)
C(2U)	0.8583(5)	0.2811(6)	−0.0580(7)
O(2U)	0.8461(4)	0.3561(4)	−0.0538(7)
C(2D)	0.9111(4)	0.0345(6)	−0.0945(7)
O(2D)	0.9297(3)	−0.0366(5)	−0.1156(6)
C(23)	0.8072(4)	0.1268(6)	−0.1669(6)
O(23)	0.7658(3)	0.1029(4)	−0.2171(5)
C(3U)	0.8460(4)	0.2558(5)	0.1759(7)
O(3U)	0.8527(3)	0.3264(4)	0.2108(6)
C(3D)	0.8099(4)	0.0190(5)	0.0631(7)
O(3D)	0.7970(3)	−0.0520(4)	0.0303(6)
C(31)	0.8195(4)	0.0891(6)	0.2724(6)
O(31)	0.8169(3)	0.0585(5)	0.3576(5)

Table 4

Non-hydrogen atom coordinates for complex **3f-Ru**

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Ru(1)	0.86097(4)	−0.00255(4)	0.17035(6)	0.13925(4)	0.42075(5)	0.32942(6)
Ru(2)	0.72439(4)	0.09982(4)	0.12486(6)	0.27190(4)	0.45926(4)	0.37733(5)
Ru(3)	0.75534(4)	−0.08893(4)	0.10599(6)	0.24929(4)	0.28245(4)	0.39470(6)
Arsine ligand 1						
As(1)	0.94759(5)	−0.13166(6)	0.22567(7)	0.05518(5)	0.33398(6)	0.27654(7)
C(11)	0.9111(6)	−0.2201(7)	0.3047(9)	0.0937(6)	0.2273(6)	0.1976(8)
C(12)	1.0087(6)	−0.2055(7)	0.1245(8)	−0.0049(6)	0.2892(8)	0.3785(8)
C(131)	1.0185(5)	−0.1035(5)	0.3040(6)	−0.0166(5)	0.4011(6)	0.1965(6)
C(132)	1.0714(6)	−0.0633(7)	0.2617(8)	−0.0694(6)	0.4699(7)	0.2396(8)
C(133)	1.1238(7)	−0.0402(8)	0.3151(9)	−0.1196(6)	0.5210(7)	0.1823(9)
C(134)	1.1212(6)	−0.0547(7)	0.4128(9)	−0.1194(7)	0.5061(8)	0.0859(8)
C(135)	1.0698(7)	−0.0908(8)	0.4560(8)	−0.0679(7)	0.4393(9)	0.0436(8)
C(136)	1.0170(6)	−0.1151(7)	0.4035(7)	−0.0167(7)	0.3868(8)	0.0981(8)
Arsine ligand 2						
As(2)	0.73251(6)	0.24424(6)	0.19054(9)	0.25988(6)	0.60899(6)	0.30943(8)
C(21)	0.7883(6)	0.3143(6)	0.1140(11)	0.2021(8)	0.7084(7)	0.3832(12)
C(22)	0.7714(9)	0.2500(9)	0.3151(11)	0.2211(8)	0.6337(10)	0.1842(11)
C(231)	0.6413(6)	0.3271(6)	0.2069(9)	0.3498(5)	0.6478(6)	0.2913(7)
C(232)	0.6009(7)	0.3417(7)	0.1337(12)	0.3913(6)	0.6431(7)	0.3717(9)
C(233)	0.5336(9)	0.4034(8)	0.1358(18)	0.4575(7)	0.6660(8)	0.3621(13)
C(234)	0.5123(7)	0.4434(9)	0.2230(18)	0.4800(7)	0.6961(8)	0.2765(14)
C(235)	0.5499(9)	0.4321(9)	0.3012(14)	0.4408(8)	0.7012(9)	0.1952(12)
C(236)	0.6169(8)	0.3719(8)	0.2951(11)	0.3751(7)	0.6779(7)	0.2045(9)
Arsine ligand 3						
As(3)	0.63938(5)	−0.12625(6)	0.08728(7)	0.36861(5)	0.18996(6)	0.41338(8)
C(31)	0.5596(6)	−0.0772(7)	0.1811(8)	0.4479(6)	0.2075(8)	0.3257(10)
C(32)	0.5935(6)	−0.0982(7)	−0.0335(7)	0.4094(7)	0.1890(8)	0.5371(9)
C(331)	0.6429(5)	−0.2528(5)	0.1039(6)	0.3693(5)	0.0655(6)	0.3923(7)
C(332)	0.6699(6)	−0.2942(6)	0.1863(8)	0.3657(10)	0.0348(8)	0.3002(9)
C(333)	0.6757(6)	−0.3833(7)	0.2025(9)	0.3595(10)	−0.0495(8)	0.2823(10)
C(334)	0.6539(6)	−0.4333(6)	0.1317(8)	0.3544(8)	−0.1052(7)	0.3558(10)
C(335)	0.6293(8)	−0.3951(7)	0.0479(8)	0.3596(11)	−0.0792(8)	0.4458(10)
C(336)	0.6221(7)	−0.3028(7)	0.0338(8)	0.3660(11)	0.0080(8)	0.4639(9)
Carbonyl groups						
C(1U)	0.8180(5)	0.0184(6)	0.3008(7)	0.1806(5)	0.4204(6)	0.1976(7)
O(1U)	0.7981(4)	0.0308(5)	0.3811(6)	0.2000(4)	0.4233(5)	0.1177(5)
C(1D)	0.8972(5)	−0.0284(6)	0.0375(7)	0.1040(5)	0.4135(6)	0.4624(7)
O(1D)	0.9248(4)	−0.0452(5)	−0.0383(6)	0.0767(4)	0.4096(6)	0.5391(5)
C(12)	0.9131(5)	0.0857(6)	0.1819(9)	0.0837(6)	0.5345(7)	0.3148(8)
O(12)	0.9453(4)	0.1391(5)	0.1909(8)	0.0533(4)	0.6071(5)	0.3066(8)
C(2U)	0.6736(5)	0.0758(6)	0.2434(7)	0.3228(5)	0.4099(6)	0.2572(7)
O(2U)	0.6376(4)	0.0681(5)	0.3119(5)	0.3561(4)	0.3853(5)	0.1884(5)
C(2D)	0.7825(5)	0.1209(6)	0.0094(8)	0.2137(6)	0.5065(6)	0.4927(7)
O(2D)	0.8111(5)	0.1410(5)	−0.0589(6)	0.1839(5)	0.5419(5)	0.5608(6)
C(23)	0.6404(5)	0.1249(6)	0.0613(8)	0.3565(6)	0.4441(6)	0.4429(7)
O(23)	0.5894(4)	0.1385(5)	0.0172(7)	0.4068(4)	0.4329(5)	0.4855(6)
C(3U)	0.7452(5)	−0.1074(5)	0.2432(6)	0.2610(5)	0.2559(6)	0.2580(7)
O(3U)	0.7334(4)	−0.1249(4)	0.3236(5)	0.2716(4)	0.2334(5)	0.1771(5)
C(3D)	0.7631(6)	−0.0552(6)	−0.0278(7)	0.2394(6)	0.3206(6)	0.5293(7)
O(3D)	0.7668(4)	−0.0409(5)	−0.1095(5)	0.2339(5)	0.3349(5)	0.6108(5)
C(31)	0.8113(5)	−0.2034(6)	0.0802(7)	0.1980(5)	0.1928(6)	0.4224(7)
O(31)	0.8462(4)	−0.2722(4)	0.0618(6)	0.1650(4)	0.1416(5)	0.4434(6)

Table 5

Non-hydrogen atom coordinates for complex **3g-Ru**

Atom	*x*	*y*	*z*
Ru	0.42946(9)	0.61567(9)	0.66734(6)
C(U)	0.459(1)	0.660(1)	0.7870(8)
O(U)	0.4785(8)	0.6793(8)	0.8577(5)
C(D)	0.367(1)	0.558(1)	0.5547(9)
O(D)	0.3418(10)	0.5221(10)	0.4865(6)
C(12)	0.591(1)	0.696(1)	0.6342(9)
O(12)	0.6896(9)	0.7457(10)	0.6110(7)
P	0.4135(3)	0.4310(3)	0.6996(2)
C(0)	0.556(1)	0.437(1)	0.7248(8)
C(1)	0.610(2)	0.501(2)	0.804(1)
C(2)	0.580(2)	0.443(2)	0.888(1)
C(3)	0.639(2)	0.508(2)	0.962(1)
C(4)	0.731(2)	0.623(2)	0.953(1)
C(5)	0.767(2)	0.699(2)	0.881(1)
C(6)	0.709(2)	0.635(2)	0.808(1)
C(7)	0.357(1)	0.322(1)	0.615(1)
C(8)	0.320(1)	0.353(1)	0.790(1)

130–132°C. (Found: C, 32.69; H, 5.04%; *M* (FAB-MS), 1193. $C_{32}H_{60}O_{20}P_4Ru_3$ calc: C, 32.35; H, 5.07%; *M*, 1193). IR ν(CO) (cyclohexane): 2036w, 1985sh, 1972vs, 1939sh, 1920sh cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 3.98 (m, 2H, CH_2); 1.27 (td, *J* 7, 1Hz, 3H, CH_3).

Crystallography. Data sets were obtained with four-circle diffractometers, and application of absorption corrections and the refinements were carried out as described in Part A [1]. The molecular plots and atom numbering follow a similar scheme; the group 15 ligands always occupy the sites of CO(13), CO(21) and CO(32), with M(3) being the apex of the M_3 triangle vertical in the page. Metal atom sites of minor occupancy are primed. The non-hydrogen atom coordinates for the seven complexes are listed in Tables 3–9; full details of the core geometries are given in Tables 10–16. Other data, including non-hydrogen atom thermal parameters, hydrogen atom parameters and phosphorus (or arsenic) ligand geometries, are deposited.

Crystal data

3e-Ru: $Ru_3(CO)_9(PMe_2Ph)_3 = C_{33}H_{33}O_9P_3Ru_3$, $M = 969.8$, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), *a* 21.343(2), *b* 14.752(4), *c* 12.170(2) Å, *U* 3832(1) $Å^3$, D_c ($Z = 4$) 1.68 g cm^{-3}. $F(000) = 1920$. μ_{Mo} 12.5 cm^{-1}. Specimen: 0.24 × 0.17 × 0.45 mm. $A^*_{min,max} = 1.29, 1.69$. $2\theta_{max}$ 60°, $N = 5538$, N_0 (number of observed data with $I > 3\sigma(I)$) = 3601, $R = 0.040$, $R' = 0.048$ ($n = 3$) (preferred chirality).

3f-Ru: $Ru_3(CO)_9(AsMe_2Ph)_3 = C_{33}H_{33}As_3O_9Ru_3$, $M = 1101.6$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), *a* 19.113(4), *b* 15.375(4), *c* 13.756(3) Å, α 89.36(2), β 85.97(2), γ 77.61(2)°, *U* 3939(2) $Å^3$, D_m 1.86(1), D_c ($Z = 4$) 1.86 g cm^{-3}. $F(000) = 2136$. μ_{Mo} 35.5 cm^{-1}. Specimen: 0.11 × 0.13 × 0.36 mm. $A^*_{min,max} = 1.41, 1.62$. $2\theta_{max}$ 50°, $N = 13993$, $N_0 = 8823$, $R = 0.046$, $R' = 0.047$ ($n = 7$).

(Continued on p. 222)

Table 6

Non-hydrogen atom coordinates for complex **3i-Ru** (molecules 1–4)

Atom	*x*	*y*	*z*
Molecule 1. Ru populations: 0.944(2) 0.940(2), 0.939(2)			
Ru(1)	0.23576(3)	1.01648(3)	0.36829(3)
Ru(2)	0.17260(3)	0.89386(3)	0.23741(3)
Ru(3)	0.29936(3)	0.92261(3)	0.35800(3)
Ligand 1			
P(1)	0.2878(1)	1.0900(1)	0.4860(1)
O(11)	0.2291(3)	1.1032(3)	0.5013(3)
C(11)	0.2476(6)	1.1525(7)	0.5713(6)
O(12)	0.3256(3)	1.0690(3)	0.5544(3)
C(12)	0.2929(7)	1.0049(6)	0.5658(5)
C(111)	0.3554(4)	1.1807(4)	0.5125(4)
C(112)	0.3384(4)	1.2309(5)	0.4853(4)
C(113)	0.3884(5)	1.3028(5)	0.5058(5)
C(114)	0.4551(5)	1.3243(5)	0.5535(6)
C(115)	0.4725(4)	1.2760(5)	0.5810(5)
C(116)	0.4240(4)	1.2041(5)	0.5609(4)
Ligand 2			
P(2)	0.0694(1)	0.8829(1)	0.1559(1)
O(21)	0.0202(3)	0.8898(3)	0.1913(3)
C(21)	−0.0508(4)	0.8732(6)	0.1456(6)
O(22)	0.0207(3)	0.8086(3)	0.0884(2)
C(22)	−0.0016(5)	0.7384(4)	0.0974(5)
C(211)	0.0736(3)	0.9447(4)	0.1029(4)
C(212)	0.0776(4)	1.0117(4)	0.1302(4)
C(213)	0.0867(5)	1.0620(4)	0.0926(5)
C(214)	0.0961(4)	1.0474(5)	0.0323(5)
C(215)	0.0928(5)	0.9829(5)	0.0056(4)
C(216)	0.0815(4)	0.9307(4)	0.0411(4)
Ligand 3			
P(3)	0.3279(1)	0.8299(1)	0.3409(1)
O(31)	0.2717(3)	0.7478(3)	0.2941(3)
C(31)	0.2175(7)	0.7096(6)	0.3103(8)
O(32)	0.3685(3)	0.8283(3)	0.4205(3)
C(32)	0.4002(7)	0.7798(7)	0.4339(6)
C(311)	0.3851(4)	0.8348(4)	0.2998(4)
C(312)	0.4499(5)	0.8922(5)	0.3303(4)
C(313)	0.4965(5)	0.8996(6)	0.3021(5)
C(314)	0.4775(6)	0.8489(8)	0.2408(6)
C(315)	0.4149(7)	0.7925(10)	0.2099(8)
C(316)	0.3677(5)	0.7844(8)	0.2370(6)
Carbonyl groups			
C(1U)	0.1644(4)	0.9489(4)	0.3868(4)
O(1U)	0.1236(3)	0.9140(4)	0.4030(4)
C(1D)	0.3163(4)	1.0752(4)	0.3579(4)
O(1D)	0.3641(3)	1.1164(3)	0.3554(3)
C(12)	0.1840(4)	1.0663(4)	0.3318(4)
O(12)	0.1550(3)	1.0975(4)	0.3122(3)
C(2U)	0.1241(4)	0.8236(4)	0.2741(4)
O(2U)	0.0908(3)	0.7779(3)	0.2892(3)
C(2D)	0.2191(3)	0.9781(4)	0.2149(4)
O(2D)	0.2422(3)	1.0246(3)	0.1935(3)
C(23)	0.1817(4)	0.8248(4)	0.1754(4)
O(23)	0.1849(4)	0.7838(3)	0.1370(3)

Table 6 (continued)

Atom	x	y	z
Carbonyl groups (continued)			
C(3U)	0.2478(4)	0.8741(4)	0.4066(4)
O(3U)	0.2217(3)	0.8427(3)	0.4374(3)
C(3D)	0.3346(4)	0.9592(4)	0.2936(4)
O(3D)	0.3606(3)	0.9802(3)	0.2574(3)
C(31)	0.3830(4)	0.9848(4)	0.4458(4)
O(31)	0.4334(3)	1.0209(3)	0.4947(3)
Disordered Ru populations: 0.057(2), 0.052(2), 0.053(2)			
Ru(12)	0.1703(6)	0.9445(6)	0.2714(6)
Ru(23)	0.2517(6)	0.8673(6)	0.2833(6)
Ru(31)	0.2949(5)	0.9890(6)	0.4046(6)
Molecule 2			
Ru(1)	0.22698(3)	0.51107(3)	0.84838(3)
Ru(2)	0.16312(3)	0.38831(3)	0.71843(3)
Ru(3)	0.28358(3)	0.41005(3)	0.84541(3)
Ligand 1			
P(1)	0.2792(1)	0.5916(1)	0.9630(1)
O(11)	0.3130(3)	0.5726(3)	1.0346(3)
C(11)	0.2785(6)	0.5100(5)	1.0496(5)
O(12)	0.2234(3)	0.6130(3)	0.9741(3)
C(12)	0.2439(6)	0.6704(6)	1.0396(7)
C(111)	0.3521(4)	0.6779(4)	0.9865(4)
C(112)	0.4188(4)	0.7002(4)	1.0390(4)
C(113)	0.4713(4)	0.7685(5)	1.0558(5)
C(114)	0.4581(5)	0.8137(5)	1.0205(6)
C(115)	0.3937(5)	0.7928(5)	0.9666(6)
C(116)	0.3407(4)	0.7247(4)	0.9499(5)
Ligand 2			
P(2)	0.0598(1)	0.3759(1)	0.6367(1)
O(21)	0.0005(3)	0.2945(3)	0.6147(3)
C(21)	−0.0724(5)	0.2705(7)	0.5688(6)
O(22)	0.0252(3)	0.4249(4)	0.6547(3)
C(22)	0.0079(6)	0.4325(7)	0.7119(6)
C(211)	0.0524(4)	0.3901(4)	0.5512(4)
C(212)	0.0360(4)	0.3304(5)	0.4946(4)
C(213)	0.0297(5)	0.3363(6)	0.4282(5)
C(214)	0.0358(6)	0.3997(6)	0.4159(5)
C(215)	0.0535(6)	0.4594(7)	0.4662(6)
C(216)	0.0618(6)	0.4535(6)	0.5387(6)
Ligand 3			
P(3)	0.3120(1)	0.3168(1)	0.8373(1)
O(31)	0.2564(3)	0.2366(3)	0.7827(3)
C(31)	0.1914(5)	0.1985(5)	0.7807(6)
O(32)	0.3382(3)	0.3070(3)	0.9155(3)
C(32)	0.3606(6)	0.2527(6)	0.9302(6)
C(311)	0.3794(4)	0.3257(4)	0.8104(4)
C(312)	0.4446(4)	0.3816(5)	0.8499(5)
C(313)	0.4971(4)	0.3906(5)	0.8300(5)
C(314)	0.4857(5)	0.3478(7)	0.7711(6)
C(315)	0.4227(7)	0.2903(11)	0.7374(9)
C(316)	0.3694(6)	0.2763(8)	0.7530(7)

continued

Table 6 (continued)

Atom	x	y	z
Carbonyl groups			
C(1U)	0.1529(4)	0.4508(4)	0.8680(4)
O(1U)	0.1105(3)	0.4215(3)	0.8844(3)
C(1D)	0.3098(4)	0.5604(4)	0.8378(4)
O(1D)	0.3604(3)	0.5974(3)	0.8358(3)
C(12)	0.1826(4)	0.5620(4)	0.8010(4)
O(12)	0.1590(3)	0.5948(3)	0.7719(3)
C(2U)	0.1133(4)	0.3226(4)	0.7580(4)
O(2U)	0.0788(3)	0.2802(3)	0.7747(3)
C(2D)	0.2109(4)	0.4688(4)	0.6914(4)
O(2D)	0.2355(3)	0.5132(3)	0.6689(3)
C(23)	0.1671(4)	0.3175(4)	0.6544(3)
O(23)	0.1696(3)	0.2763(3)	0.6154(3)
C(3U)	0.2305(4)	0.3650(4)	0.8946(4)
O(3U)	0.2023(3)	0.3359(3)	0.9252(3)
C(3D)	0.3181(4)	0.4373(4)	0.7768(4)
O(3D)	0.3434(3)	0.4507(3)	0.7391(3)
C(31)	0.3671(4)	0.4750(4)	0.9290(4)
O(31)	0.4187(3)	0.5156(3)	0.9780(3)
Molecule 3			
Ru(1)	0.82905(3)	0.56015(3)	0.73277(3)
Ru(2)	0.70486(3)	0.55801(3)	0.63010(3)
Ru(3)	0.75713(3)	0.62502(3)	0.78398(3)
Ligand 1			
P(1)	0.9303(1)	0.5880(1)	0.8303(1)
O(11)	0.9659(3)	0.6555(3)	0.9034(3)
C(11)	0.9832(5)	0.7289(4)	0.9029(5)
O(12)	0.9902(2)	0.6017(3)	0.8055(3)
C(12)	1.0616(5)	0.6280(6)	0.8567(6)
C(111)	0.9293(4)	0.5192(4)	0.8746(4)
C(112)	0.9144(4)	0.5188(4)	0.9331(4)
C(113)	0.9084(4)	0.4613(5)	0.9614(4)
C(114)	0.9172(5)	0.4070(5)	0.9330(5)
C(115)	0.9325(5)	0.4046(5)	0.8743(5)
C(116)	0.9375(5)	0.4615(5)	0.8443(4)
Ligand 2			
P(2)	0.6795(1)	0.5136(1)	0.5109(1)
O(21)	0.6386(3)	0.5527(3)	0.4669(2)
C(21)	0.6120(6)	0.5361(6)	0.3882(5)
O(22)	0.7375(3)	0.5213(3)	0.4844(3)
C(22)	0.7946(5)	0.5881(6)	0.5036(6)
C(211)	0.6235(4)	0.4169(4)	0.4622(4)
C(212)	0.5555(4)	0.3878(5)	0.4499(4)
C(213)	0.5109(5)	0.3135(5)	0.4129(5)
C(214)	0.5343(5)	0.2701(5)	0.3923(5)
C(215)	0.6009(6)	0.2953(5)	0.4054(6)
C(216)	0.6473(5)	0.3707(5)	0.4412(5)
Ligand 3			
P(3)	0.7007(1)	0.6879(1)	0.8059(1)
O(31)	0.6641(3)	0.7209(3)	0.7481(3)
C(31)	0.7009(6)	0.7692(5)	0.7185(6)
O(32)	0.7561(3)	0.7573(3)	0.8776(3)
C(32)	0.7375(5)	0.8071(5)	0.9082(6)
C(311)	0.6290(4)	0.6442(4)	0.8264(3)

Table 6 (continued)

Atom	x	y	z
Ligand 3 (continued)			
C(312)	0.6423(4)	0.6324(5)	0.8913(4)
C(313)	0.5885(5)	0.6011(5)	0.9094(5)
C(314)	0.5223(5)	0.5801(5)	0.8610(5)
C(315)	0.5076(4)	0.5915(5)	0.7959(5)
C(316)	0.5609(4)	0.6237(4)	0.7780(4)
Carbonyl groups			
C(1U)	0.8767(4)	0.6440(4)	0.7088(4)
O(1U)	0.9106(3)	0.6922(3)	0.6968(3)
C(1D)	0.7796(3)	0.4873(3)	0.7670(4)
O(1D)	0.7552(3)	0.4418(3)	0.7886(3)
C(12)	0.8353(4)	0.4949(4)	0.6668(4)
O(12)	0.8394(3)	0.4530(3)	0.6287(3)
C(2U)	0.7548(4)	0.6542(4)	0.6289(4)
O(2U)	0.7793(3)	0.7099(3)	0.6213(3)
C(2D)	0.6716(4)	0.4608(4)	0.6341(4)
O(2D)	0.6465(3)	0.3997(3)	0.6282(3)
C(23)	0.6201(4)	0.5602(4)	0.6088(4)
O(23)	0.5674(3)	0.5598(4)	0.5969(3)
C(3U)	0.8246(4)	0.7136(4)	0.7840(4)
O(3U)	0.8632(3)	0.7686(3)	0.7886(3)
C(3D)	0.6785(4)	0.5350(4)	0.7652(4)
O(3D)	0.6315(3)	0.4847(3)	0.7587(3)
C(31)	0.8078(4)	0.6583(4)	0.8834(4)
O(31)	0.8369(3)	0.6449(3)	0.9435(3)
Molecule 4. Ru populations: 0.821(2), 0.826(2), 0.830(2)			
Ru(1)	0.16097(4)	−0.08599(4)	0.73485(4)
Ru(2)	0.28462(4)	−0.10158(4)	0.80540(3)
Ru(3)	0.24473(3)	−0.02177(4)	0.89081(4)
Ligand 1			
P(1)	0.0611(1)	−0.0761(1)	0.6954(1)
O(11)	0.0017(3)	−0.1522(3)	0.6314(3)
C(11)	−0.0698(5)	−0.1652(6)	0.5929(6)
O(12)	0.0236(3)	−0.0641(2)	0.7435(3)
C(12)	0.0027(5)	−0.1126(6)	0.7802(5)
C(111)	0.0557(5)	−0.0079(5)	0.6522(5)
C(112)	0.0827(6)	0.0043(6)	0.6046(6)
C(113)	0.0802(6)	0.0555(7)	0.5692(7)
C(114)	0.0516(6)	0.0978(7)	0.5885(9)
C(115)	0.0227(5)	0.0878(6)	0.6332(9)
C(116)	0.0256(5)	0.0348(5)	0.6673(6)
Ligand 2			
P(2)	0.2859(1)	−0.1882(1)	0.7234(1)
O(21)	0.2221(3)	−0.2463(3)	0.6504(3)
C(21)	0.1572(5)	−0.2938(5)	0.6495(6)
O(22)	0.3122(3)	−0.2348(3)	0.7702(3)
C(22)	0.3222(6)	−0.2941(5)	0.7401(6)
C(211)	0.3459(4)	−0.1548(4)	0.6854(4)
C(212)	0.4169(4)	−0.1231(4)	0.7315(4)
C(213)	0.4653(4)	−0.0949(5)	0.7061(5)
C(214)	0.4435(5)	−0.0960(5)	0.6355(5)
C(215)	0.3733(5)	−0.1273(5)	0.5887(5)
C(216)	0.3252(4)	−0.1560(4)	0.6145(4)

continued

Table 6 (continued)

Atom	x	y	z
Ligand 3			
P(3)	0.3139(1)	−0.0090(1)	1.0096(1)
O(31)	0.2712(3)	−0.0411(3)	1.0525(3)
C(31)	0.2432(7)	−0.1129(7)	1.0502(6)
O(32)	0.3618(3)	−0.0461(4)	1.0180(3)
C(32)	0.4109(6)	−0.0412(7)	1.0867(6)
C(311)	0.3709(4)	0.0814(5)	1.0747(4)
C(312)	0.3682(5)	0.1030(6)	1.1389(5)
C(313)	0.4160(6)	0.1713(7)	1.1875(6)
C(314)	0.4655(6)	0.2167(6)	1.1743(6)
C(315)	0.4694(7)	0.1964(8)	1.1139(6)
C(316)	0.4221(7)	0.1274(7)	1.0642(5)
Carbonyl groups			
C(1U)	0.1143(5)	−0.1801(5)	0.7439(4)
O(1U)	0.0829(3)	−0.2372(3)	0.7442(3)
C(1D)	0.2146(4)	0.0169(4)	0.7469(4)
O(1D)	0.2401(3)	0.0718(3)	0.7429(3)
C(12)	0.1560(5)	−0.1221(5)	0.6412(4)
O(12)	0.1522(4)	−0.1389(4)	0.5852(3)
C(2U)	0.2412(4)	−0.1726(4)	0.8468(5)
O(2U)	0.2194(3)	−0.2199(3)	0.8669(3)
C(2D)	0.3157(4)	−0.0328(4)	0.7584(4)
O(2D)	0.3442(3)	0.0087(3)	0.7375(3)
C(23)	0.3766(4)	−0.0682(4)	0.8811(4)
O(23)	0.4329(3)	−0.0486(3)	0.9172(3)
C(3U)	0.1689(5)	−0.1048(5)	0.8881(5)
O(3U)	0.1264(3)	−0.1498(3)	0.8934(4)
C(3D)	0.3217(4)	0.0480(4)	0.8835(4)
O(3D)	0.3653(3)	0.0980(3)	0.8851(3)
C(31)	0.2053(4)	0.0414(5)	0.9033(5)
O(31)	0.1851(4)	0.0814(3)	0.9123(3)
Disordered Ru populations: 0.172(2), 0.171(2), 0.176(2)			
Ru(12)	0.2278(2)	−0.1220(2)	0.7286(2)
Ru(23)	0.2936(2)	−0.0608(2)	0.8844(2)
Ru(31)	0.1752(2)	−0.0444(2)	0.7973(2)

3g-Ru: $Ru_3(CO)_9\{PMe_2(CH_2Ph)\}_3 = C_{36}H_{39}O_9P_3Ru_3$. $M = 1011.8$, trigonal, space group $P\bar{3}$ (C_{3i}^1, No. 147), a 12.803(10), c 15.657(9) Å, U 2202(2) Å^3, D_c ($Z = 2$) 1.53 g cm^{-3}. $F(000) = 1008$. μ_{Mo} 10.9 cm^{-1}. Specimen: 0.45 × 0.35 × 0.22 mm. $A^{\star}_{min,max} = 1.25$, 1.37. $2\theta_{max}$ 60°, $N = 4361$, $N_0 = 2445$; $R = 0.066$, $R' = 0.094$ ($n = 2$) (preferred chirality).

3i-Ru: $Ru_3(CO)_9\{PPh(OMe)_2\}_3 = C_{33}H_{33}O_{15}P_3Ru_3$, $M = 1065.8$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 23.23(1), b 20.87(1), c 20.73(1) Å, α 98.21(4), β 111.07(3), γ 111.95(4)°, U 8237(7) Å^3, D_c ($Z = 8$) 1.72 g cm^{-3}. $F(000) = 4224$. μ_{Mo} 11.8 cm^{-1}. Specimen: 0.24 × 0.25 × 0.22 mm. $A^{\star}_{min,max} = 1.22$, 1.33. $2\theta_{max}$ 50°, $N = 28977$, $N_0 = 16532$, $R = 0.041$, $R' = 0.039$ ($n = 3$).

(Continued on p. 234)

Table 7

Non-hydrogen atom coordinates for complex **3k-Ru**

Atom	*x*	*y*	*z*
Ru(1) [a]	0.80090(5)	0.80253(6)	0.62474(8)
Ru(2) [a]	0.77522(5)	0.59192(6)	0.83441(8)
Ru(3) [a]	0.69016(5)	0.79394(6)	0.86434(9)
Ligand 1			
P(1)	0.7747(2)	0.9834(2)	0.4750(3)
O(111)	0.8370(6)	1.0548(7)	0.4666(9)
C(111)	0.868(2)	1.159(2)	0.367(2)
C(112)	0.924(1)	1.136(3)	0.409(4)
O(121)	0.7739(7)	0.9961(7)	0.3171(9)
C(121)	0.809(1)	0.955(1)	0.215(2)
C(122)	0.819(1)	1.013(1)	0.080(1)
O(131)	0.7013(5)	1.0588(8)	0.4897(3)
C(131)	0.657(1)	1.138(1)	0.420(2)
C(132)	0.596(1)	1.200(2)	0.458(2)
Ligand 2			
P(2)	0.8367(2)	0.4712(2)	0.7182(3)
O(211)	0.9134(5)	0.4049(6)	0.7652(8)
C(211)	0.9373(8)	0.349(1)	0.894(2)
C(212)	0.9864(8)	0.245(1)	0.914(2)
O(221)	0.7863(6)	0.3852(9)	0.7504(13)
C(221)	0.784(2)	0.309(2)	0.735(3)
C(222)	0.748(2)	0.265(2)	0.697(3)
O(231)	0.8513(5)	0.5071(7)	0.5636(8)
C(231)	0.8971(8)	0.4801(13)	0.4628(21)
C(232)	0.8842(9)	0.4877(12)	0.3272(13)
Ligand 3			
P(3)	0.5999(2)	0.7256(2)	1.0473(3)
O(311)	0.5612(6)	0.8123(8)	1.1187(10)
C(311)	0.575(1)	0.861(2)	1.185(2)
C(312)	0.556(1)	0.954(1)	1.220(2)
O(321)	0.5272(5)	0.7085(10)	0.9974(10)
C(321)	0.462(1)	0.694(2)	1.037(2)
C(322)	0.416(1)	0.675(2)	0.965(2)
O(331)	0.6184(7)	0.6243(7)	1.1733(9)
C(331)	0.602(1)	0.579(2)	1.298(2)
C(332)	0.613(1)	0.520(2)	1.418(2)
Carbonyl groups			
C(1U)	0.7421(6)	0.7437(9)	0.5278(10)
O(1U)	0.7072(4)	0.7250(5)	0.4566(7)
C(1D)	0.8425(6)	0.8569(7)	0.7483(9)
O(1D)	0.8784(4)	0.8870(6)	0.8000(7)
C(12)	0.8928(6)	0.7533(8)	0.5300(9)
O(12)	0.9482(4)	0.7430(7)	0.4673(8)
C(2U)	0.6745(7)	0.5970(8)	0.7832(11)
O(2U)	0.6223(4)	0.5831(6)	0.7461(8)
C(2D)	0.8712(6)	0.6181(7)	0.8620(10)
O(2D)	0.9270(4)	0.6157(5)	0.9006(8)
C(23)	0.7527(6)	0.4903(8)	1.0173(10)
O(23)	0.7512(4)	0.4189(6)	1.1171(8)
C(3U)	0.6261(6)	0.8270(7)	0.7084(12)
O(3U)	0.5808(4)	0.8460(6)	0.6356(8)

continued

Table 7 (continued)

Atom	x	y	z
C(3D)	0.7626(6)	0.7396(8)	1.0076(10)
O(3D)	0.7982(4)	0.7300(6)	1.0927(7)
C(31)	0.6777(6)	0.9509(8)	0.8359(10)
O(31)	0.6629(4)	1.0341(5)	0.8459(8)
Fractional rutheniums			
Ru(12) [a]	0.8188(1)	0.6669(2)	0.6748(3)
Ru(23) [a]	0.7091(1)	0.6569(2)	0.9152(3)
Ru(31) [a]	0.7319(1)	0.8673(2)	0.7056(3)

[a] Populations: Ru(1, 2, 3), 0.75_5; Ru(12, 23, 31), $1-0.75_5$.

Table 8

Non-hydrogen atom coordinates for complex **3l-Ru**

Atom	x	y	z
Ru(1)	0.18326(5)	0.06145(10)	0.38228(12)
Ru(2)	0.28250(6)	−0.04996(11)	0.24018(12)
Ru(3)	0.27330(5)	0.17024(10)	0.20080(13)
Ligand 1			
P(1)	0.1315(2)	0.1883(3)	0.4877(4)
O(111)	0.1773(5)	0.2642(8)	0.5409(11)
C(111)	0.1554(9)	0.348(1)	0.609(2)
C(112)	0.209(1)	0.402(2)	0.652(2)
F(111)	0.2444(7)	0.436(1)	0.541(2)
F(112)	0.1911(8)	0.478(1)	0.721(2)
F(113)	0.2465(8)	0.341(1)	0.737(2)
O(121)	0.0844(5)	0.2707(8)	0.399(1)
C(121)	0.0201(8)	0.260(2)	0.377(2)
C(122)	−0.0081(9)	0.362(2)	0.301(3)
F(121)	−0.0053(9)	0.430(1)	0.363(3)
F(122)	0.0170(8)	0.368(2)	0.176(2)
F(123)	−0.0680(7)	0.344(2)	0.284(2)
O(131)	0.0857(5)	0.1625(8)	0.626(1)
C(131)	0.0974(7)	0.081(1)	0.733(2)
C(132)	0.0362(8)	0.035(1)	0.776(2)
F(131)	−0.0078(5)	0.097(1)	0.821(1)
F(132)	0.0115(5)	0.000(1)	0.660(1)
F(133)	0.0450(5)	−0.046(1)	0.871(1)
Ligand 2			
P(2)	0.2664(2)	−0.2041(3)	0.3623(4)
O(211)	0.2593(5)	−0.2027(8)	0.5327(10)
C(211)	0.2457(10)	−0.290(1)	0.631(2)
C(212)	0.2320(9)	−0.255(1)	0.770(2)
F(211)	0.2770(6)	−0.211(1)	0.821(1)
F(212)	0.1841(6)	−0.183(1)	0.764(1)
F(213)	0.2166(6)	−0.331(1)	0.865(1)
O(221)	0.2040(5)	−0.2611(9)	0.3401(10)
C(221)	0.1950(9)	−0.323(2)	0.231(2)
C(222)	0.132(1)	−0.361(2)	0.247(2)
F(221)	0.1223(7)	−0.408(1)	0.134(2)
F(222)	0.0904(7)	−0.285(1)	0.237(2)
F(223)	0.1254(9)	−0.419(1)	0.353(2)
O(231)	0.3157(5)	−0.3003(8)	0.349(1)
C(231)	0.3804(8)	−0.297(2)	0.347(3)

Table 8 (continued)

Atom	x	y	z
C(232)	0.408(1)	−0.397(3)	0.341(4)
F(231)	0.4704(7)	−0.402(1)	0.364(2)
F(232)	0.3914(9)	−0.465(1)	0.296(2)
F(233)	0.3975(10)	−0.437(2)	0.487(2)
Ligand 3			
P(3)	0.3660(2)	0.2071(4)	0.0894(5)
O(311)	0.4220(5)	0.203(1)	0.199(1)
C(311)	0.486(1)	0.214(2)	0.161(2)
C(312)	0.5147(8)	0.250(2)	0.269(2)
F(311)	0.5757(6)	0.256(1)	0.246(2)
F(312)	0.5201(8)	0.181(2)	0.380(2)
F(313)	0.4929(9)	0.330(1)	0.311(2)
O(321)	0.3992(6)	0.133(1)	−0.020(1)
C(321)	0.3961(10)	0.141(2)	−0.169(2)
C(322)	0.446(1)	0.098(3)	−0.234(2)
F(321)	0.4902(6)	0.053(1)	−0.171(2)
F(322)	0.4528(7)	0.114(2)	−0.362(1)
F(323)	0.4858(8)	0.194(2)	−0.231(2)
O(331)	0.3724(6)	0.3105(10)	−0.012(1)
C(331)	0.349(1)	0.402(2)	0.019(2)
C(332)	0.374(1)	0.477(2)	−0.067(4)
F(331)	0.4363(8)	0.481(1)	−0.062(2)
F(332)	0.3636(9)	0.492(2)	−0.202(2)
F(333)	0.3579(9)	0.573(1)	−0.036(2)
Carbonyl groups			
C(1U)	0.2419(6)	0.031(1)	0.542(1)
O(1U)	0.2702(5)	0.0165(9)	0.6415(10)
C(1D)	0.1344(6)	0.101(1)	0.208(1)
O(1D)	0.1021(5)	0.1257(9)	0.1155(10)
C(12)	0.1361(7)	−0.050(1)	0.444(1)
O(12)	0.1060(5)	−0.1199(8)	0.4800(11)
C(2U)	0.3481(7)	−0.022(1)	0.368(2)
O(2U)	0.3903(5)	−0.0181(10)	0.4385(11)
C(2D)	0.2108(7)	−0.061(1)	0.113(2)
O(2D)	0.1748(6)	−0.0744(11)	0.0383(12)
C(23)	0.3435(7)	−0.088(1)	0.095(2)
O(23)	0.3792(5)	−0.1138(10)	0.0126(12)
C(3U)	0.3078(7)	0.187(1)	0.387(1)
O(3U)	0.3293(5)	0.2073(9)	0.4856(10)
C(3D)	0.2412(7)	0.141(1)	0.018(2)
O(3D)	0.2239(5)	0.1358(11)	−0.0915(11)
C(31)	0.2323(9)	0.291(1)	0.193(2)
O(31)	0.2033(7)	0.3774(10)	0.1852(16)

Table 9

Non-hydrogen atom coordinates for complex **3b-Os**

Atom	x	y	z
Os(1)	0.8060(1)	0.7752(1)	0.5710(2)
Os(2)	0.8794(1)	0.6872(1)	0.4513(2)
Os(3)	0.7867(1)	0.6105(1)	0.6043(2)

Table 9 (continued)

Atom	x	y	z
Ligand 1			
P(1)	0.7257(9)	0.8218(8)	0.6614(11)
C(111)	0.780(3)	0.887(3)	0.778(4)
C(112)	0.804(3)	0.854(3)	0.858(4)
C(113)	0.849(4)	0.904(4)	0.934(5)
C(114)	0.890(3)	0.995(3)	0.954(4)
C(115)	0.865(3)	1.020(3)	0.865(4)
C(116)	0.807(3)	0.965(3)	0.775(4)
C(121)	0.677(3)	0.880(3)	0.580(4)
C(122)	0.689(3)	0.901(2)	0.491(3)
C(123)	0.642(3)	0.935(3)	0.434(4)
C(124)	0.597(3)	0.968(3)	0.481(4)
C(125)	0.580(4)	0.940(2)	0.581(5)
C(126)	0.630(4)	0.900(4)	0.630(5)
C(131)	0.637(3)	0.748(3)	0.696(4)
C(132)	0.597(3)	0.682(2)	0.628(3)
C(133)	0.529(4)	0.619(4)	0.631(5)
C(134)	0.510(4)	0.635(4)	0.719(5)
C(135)	0.547(5)	0.969(4)	0.805(6)
C(136)	0.625(3)	0.767(3)	0.792(4)
Ligand 2			
P(2)	0.9309(8)	0.7610(8)	0.3175(11)
C(211)	1.038(3)	0.797(3)	0.345(3)
C(212)	1.077(3)	0.858(3)	0.429(4)
C(213)	1.160(4)	0.886(3)	0.461(5)
C(214)	1.205(4)	0.850(3)	0.406(5)
C(215)	1.164(4)	0.786(4)	0.337(5)
C(216)	1.086(3)	0.763(3)	0.301(3)
C(221)	0.900(3)	0.844(2)	0.284(3)
C(222)	0.816(3)	0.821(3)	0.259(4)
C(223)	0.799(3)	0.884(4)	0.245(5)
C(224)	0.852(3)	0.963(3)	0.253(4)
C(225)	0.931(4)	0.980(4)	0.269(5)
C(226)	0.954(3)	0.914(3)	0.285(4)
C(231)	0.913(3)	0.706(3)	0.186(4)
C(232)	0.928(3)	0.748(3)	0.112(4)
C(233)	0.917(3)	0.714(3)	0.008(4)
C(234)	0.886(3)	0.628(3)	−0.016(4)
C(235)	0.866(3)	0.579(3)	0.073(4)
C(236)	0.881(3)	0.623(3)	0.166(4)
Ligand 3			
P(3)	0.7718(8)	0.4738(8)	0.5909(11)
C(311)	0.795(2)	0.429(2)	0.483(3)
C(312)	0.844(4)	0.392(4)	0.482(5)
C(313)	0.872(4)	0.372(4)	0.417(6)
C(314)	0.841(3)	0.371(3)	0.310(4)
C(315)	0.781(4)	0.411(4)	0.284(5)
C(316)	0.757(4)	0.440(4)	0.394(5)
C(321)	0.829(4)	0.452(3)	0.693(4)

Table 9 (continued)

Atom	x	y	z
Ligand 3 (continued)			
C(322)	0.911(3)	0.475(3)	0.715(4)
C(323)	0.963(3)	0.463(3)	0.802(4)
C(324)	0.932(3)	0.434(3)	0.876(4)
C(325)	0.854(3)	0.406(3)	0.875(4)
C(326)	0.801(3)	0.418(3)	0.788(4)
C(331)	0.675(3)	0.406(3)	0.587(4)
C(332)	0.619(3)	0.422(3)	0.626(4)
C(333)	0.543(3)	0.374(3)	0.632(5)
C(334)	0.526(4)	0.292(3)	0.600(5)
C(335)	0.580(3)	0.267(3)	0.558(4)
C(336)	0.655(4)	0.333(4)	0.552(5)
Carbonyl groups			
C(1U)	0.735(3)	0.738(3)	0.458(4)
O(1U)	0.674(2)	0.721(2)	0.383(2)
C(1D)	0.882(3)	0.799(3)	0.694(4)
O(1D)	0.928(2)	0.814(2)	0.776(2)
C(12)	0.848(3)	0.866(3)	0.530(4)
O(12)	0.899(2)	0.934(2)	0.522(2)
C(2U)	0.784(3)	0.634(2)	0.357(3)
O(2U)	0.724(2)	0.598(2)	0.288(3)
C(2D)	0.965(3)	0.749(3)	0.558(4)
O(2D)	1.024(2)	0.791(2)	0.608(3)
C(23)	0.932(3)	0.619(3)	0.442(4)
O(23)	0.961(2)	0.567(2)	0.426(2)
C(3U)	0.687(3)	0.582(3)	0.510(4)
O(3U)	0.624(2)	0.559(2)	0.449(3)
C(3D)	0.879(3)	0.634(3)	0.674(4)
O(3D)	0.951(2)	0.658(2)	0.733(2)
C(31)	0.744(3)	0.618(3)	0.713(4)
O(31)	0.724(2)	0.625(2)	0.797(3)

Table 10

Ruthenium environments for complex **3e-Ru**; in this and subsequent Tables values pertinent to P or As are italicised

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.851(1)	2.864(1)	2.860(1)
Ru(N)–C(NU)	1.909(8)	1.927(10)	1.925(8)
Ru(N)–C(ND)	1.900(8)	1.922(9)	1.915(8)
Ru(N)–C(NN + 1)	1.863(9)	1.876(8)	1.873(8)
Ru(N)–P(N)	*2.338(2)*	*2.330(3)*	*2.334(2)*
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.19(2)	60.05(3)	59.76(2)
Ru(N − 1)–Ru(N)–C(NU)	95.6(3)	97.0(3)	94.4(3)
Ru(N − 1)–Ru(N)–C(ND)	76.3(3)	73.5(3)	77.5(2)
Ru(N − 1)–Ru(N)–C(NN + 1)	156.2(3)	151.3(2)	155.8(3)
Ru(N − 1)–Ru(N)–P(N)	*104.85(6)*	*106.55(6)*	*106.03(6)*
Ru(N + 1)–Ru(N)–C(NU)	81.6(3)	81.8(2)	79.9(3)
Ru(N + 1)–Ru(N)–C(ND)	96.1(3)	95.5(2)	95.9(2)

Table 10 (continued)

	N = 1	N = 2	N = 3
Ru(N + 1)–Ru(N)–C(NN + 1)	98.9(3)	97.6(2)	99.7(2)
Ru(N + 1)–Ru(N)–P(N)	*161.93(7)*	*162.21(7)*	*161.94(6)*
C(NU)–Ru(N)–C(ND)	171.5(4)	170.1(4)	171.9(4)
C(NU)–Ru(N)–C(NN + 1)	92.0(4)	97.1(4)	94.2(4)
C(NU)–Ru(N)–P(N)	*90.5(3)*	*88.9(3)*	*90.9(3)*
C(ND)–Ru(N)–C(NN + 1)	96.4(4)	92.7(4)	93.4(3)
C(ND)–Ru(N)–P(N)	*89.4(3)*	*91.1(3)*	*91.2(2)*
C(NN + 1)–Ru(N)–P(N)	*97.6(3)*	*98.6(2)*	*96.4(3)*
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.150(10)	1.138(11)	1.135(10)
C(ND)–O(ND)	1.151(10)	1.150(12)	1.154(10)
C(NN + 1)–O(NN + 1)	1.144(12)	1.131(10)	1.133(10)
δ(C(NU))	−1.851	−1.859	−1.858
δ(C(ND))	1.779	1.809	1.765
δ(P(N))	*−0.432*	*−0.494*	*−0.473*
δ(C(NN + 1))	0.387	0.438	0.610
Carbonyl angles (°)			
Ru(N)–C(NU)–C(NU)	175.5(8)	172.7(8)	172.6(8)
Ru(N)–C(ND)–O(ND)	172.6(8)	170.5(8)	174.2(7)
Ru(N)–C(NN + 1)–O(NN + 1)	177.1(9)	174.8(7)	177.4(7)

Table 11

Ruthenium environments for complex **3f-Ru** (The two values in each entry are for molecules 1 and 2)

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.851(1), 2.846(1)	2.846(1), 2.848(1)	2.838(1), 2.838(1)
Ru(N)–C(NU)	1.922(9), 1.926(10)	1.912(9), 1.934(9)	1.909(9), 1.917(10)
Ru(N)–C(ND)	1.923(9), 1.915(10)	1.938(10), 1.927(10)	1.911(10), 1.932(10)
Ru(N)–C(NN + 1)	1.862(11), 1.858(8)	1.847(10), 1.875(11)	1.876(8), 1.877(10)
Ru(N)–As(N)	*2.448(1), 2.449(1)*	*2.446(1), 2.445(1)*	*2.437(1), 2.444(1)*
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.03(3), 60.13(3)	59.75(3), 59.80(3)	60.22(3), 60.08(4)
Ru(N − 1)–Ru(N)–C(NU)	95.2(3), 95.2(3)	96.1(3), 93.9(3)	93.4(2), 96.2(3)
Ru(N − 1)–Ru(N)–C(ND)	79.3(3), 80.4(3)	79.7(3), 81.1(3)	79.5(3), 78.2(3)
Ru(N − 1)–Ru(N)–C(NN + 1)	158.8(3), 159.3(4)	155.7(3), 155.9(3)	157.3(3), 157.0(3)
Ru(N − 1)–Ru(N)–As	*99.90(4), 100.53(4)*	*99.58(5), 100.11(4)*	*104.77(4), 104.67(4)*
Ru(N + 1)–Ru(N)–C(NU)	81.5(3), 83.7(3)	83.0(2), 81.0(3)	79.3(3), 80.9(2)
Ru(N + 1)–Ru(N)–C(ND)	95.8(3), 94.3(3)	95.8(3), 96.7(3)	96.9(3), 96.2(3)
Ru(N + 1)–Ru(N)–C(NN + 1)	101.6(3), 101.4(4)	98.5(3), 98.6(3)	100.3(3), 100.9(3)
Ru(N + 1)–Ru(N)–As	*157.25(4), 158.66(4)*	*156.89(4), 156.84(5)*	*160.78(4), 160.32(5)*
C(NU)–Ru(N)–C(ND)	175.0(4), 175.6(4)	175.7(4), 175.0(5)	173.0(4), 174.4(4)
C(NU)–Ru(N)–C(NN + 1)	92.0(5), 91.6(3)	91.3(4), 92.9(4)	94.2(4), 93.0(4)
C(NU)–Ru(N)–As	*90.5(3), 89.7(3)*	*89.7(3), 89.7(3)*	*90.4(3), 89.1(3)*
C(ND)–Ru(N)–C(NN + 1)	92.8(5), 92.7(4)	93.0(4), 91.9(4)	92.3(4), 92.3(4)
C(ND)–Ru(N)–As	*90.4(3), 90.8(3)*	*89.8(3), 90.7(3)*	*91.5(3), 92.1(3)*
As–Ru(N)–C(NN + 1)	*99.9(3), 99.0(4)*	*103.6(3), 103.0(3)*	*96.5(3), 96.5(3)*

Table 11 (continued)

	N = 1	N = 2	N = 3
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.147(12), 1.139(12)	1.148(12), 1.123(11)	1.153(11), 1.160(11)
C(ND)–O(ND)	1.141(12), 1.150(12)	1.128(13), 1.141(12)	1.143(12), 1.138(12)
C(NN + 1)–O(NN + 1)	1.139(14), 1.150(12)	1.164(14), 1.143(14)	1.144(10), 1.132(13)
δ(C(NU))	−1.845, −1.856	−1.822, −1.832	−1.858, −1.854
δ(C(ND))	1.865, 1.887	1.845, 1.847	1.861, 1.881
δ(As(N))	*−0.480, −0.405*	*−0.463, −0.515*	*−0.531, −0.552*
δ(C(NN + 1))	0.370, 0.347	0.100, 0.106	0.301, 0.350
Carbonyl angles (°)			
Ru(N)–C(NU)–O–NU)	174.1(9), 174.9(8)	173.0(7), 174.7(10)	171.7(9), 174.5(7)
Ru(N)–C(ND)–O(ND)	173.7(9), 173.7(9)	172.9(8), 171.9(10)	175.0(9), 173.6(8)
Ru(N)–C(NN + 1)–O(NN + 1)	178.6(11), 175.4(10)	176.6(9), 177.3(8)	177.9(8), 176.1(8)

Table 12

Ruthenium environments for complex **3g-Ru**

Distances (Å)	
Ru–Ru′	2.861(3)
Ru–C(U)	1.93(1)
Ru–C(D)	1.92(1)
Ru–C(12)	1.86(1)
Ru–P	*2.318(5)*
Angles (°)	
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.00(–)
Ru(N − 1)–Ru(N)–C(U)	95.1(4)
Ru(N − 1)–Ru(N)–C(D)	74.0(5)
Ru(N − 1)–Ru(N)–C(12)	154.6(6)
Ru(N − 1)–Ru(N)–P	*105.1(1)*
Ru(N + 1)–Ru(N)–C(U)	80.5(5)
Ru(N + 1)–Ru(N)–C(D)	96.5(6)
Ru(N + 1)–Ru(N)–C(12)	99.7(6)
Ru(N + 1)–Ru(N)–P	*160.9(1)*
C(U)–Ru(N)–C(D)	168.6(6)
C(U)–Ru(N)–C(12)	96.2(5)
C(U)–Ru(N)–P	*89.7(5)*
C(D)–Ru(N)–C(12)	95.2(6)
C(D)–Ru(N)–P	*89.9(5)*
C(12)–Ru(N)–P	*97.6(6)*
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)	
C(NU)–O(NU)	1.13(1)
C(ND)–O(ND)	1.14(2)
C(NN + 1)–O(NN + 1)	1.15(2)
δ(C(NU))	−1.865
δ(C(ND))	1.755
δ(P)	*−0.502*
δ(C(NN + 1))	0.516
Carbonyl angles (°)	
Ru(N)–C(NU)–C(NU)	175(1)
Ru(N)–C(ND)–O(ND)	172(1)
Ru(N)–C(NN + 1)–O(NN + 1)	178(1)

Table 13

Ruthenium environments for complex **3i-Ru** (molecules 1–4) [a]

	Molecule 1			Molecule 2			Molecule 3			Molecule 4		
N =	1	2	3	1	2	3	1	2	3	1	2	3
Distances (Å)												
Ru(N)–Ru(N+1)	2.900(1)	2.870(1)	2.887(2)	2.887(1)	2.894(1)	2.876(2)	2.884(1)	2.876(2)	2.882(1)	2.882(4)	2.874(2)	2.885(1)
Ru(N)–C(NU)	1.936(10)	1.924(9)	1.930(9)	1.934(9)	1.926(9)	1.937(9)	1.932(8)	1.916(8)	1.925(8)	1.931(10)	1.955(9)	1.931(9)
Ru(N)–C(ND)	1.924(9)	1.910(8)	1.909(10)	1.922(9)	1.921(8)	1.923(9)	1.929(8)	1.909(8)	1.932(7)	1.961(10)	1.914(10)	1.911(8)
Ru(N)–C(NN+1)	1.898(11)	1.913(10)	1.915(6)	1.883(10)	1.893(9)	1.884(5)	1.871(10)	1.876(10)	1.886(7)	1.925(10)	1.917(7)	1.903(12)
Ru(N)–P(N)	*2.279(2)*	*2.285(2)*	*2.289(3)*	*2.280(2)*	*2.277(2)*	*2.279(3)*	*2.276(2)*	*2.281(2)*	*2.278(3)*	*2.267(3)*	*2.315(3)*	*2.316(2)*
Angles (degrees)												
Ru(N−1)–Ru(N)–Ru(N+1)	59.46(4)	60.06(3)	60.48(4)	60.30(4)	59.66(3)	60.04(3)	59.85(4)	60.04(3)	60.11(3)	59.77(3)	60.16(3)	60.07(4)
Ru(N−1)–Ru(N)–C(NU)	94.8(3)	94.8(2)	90.6(2)	95.1(3)	92.5(2)	94.4(2)	93.8(3)	92.8(2)	92.0(2)	91.7(2)	93.0(3)	97.3(3)
Ru(N−1)–Ru(N)–C(ND)	76.1(3)	74.3(2)	79.8(2)	74.5(3)	77.2(2)	75.2(2)	77.5(3)	77.6(2)	78.8(2)	77.1(2)	79.7(3)	72.7(3)
Ru(N−1)–Ru(N)–C(NN+1)	155.2(3)	149.4(2)	152.9(3)	150.6(3)	151.9(2)	148.7(3)	154.4(2)	149.9(2)	153.7(3)	147.7(3)	152.5(3)	151.5(3)
Ru(N−1)–Ru(N)–P(N)	*109.33(7)*	*110.63(7)*	*111.31(5)*	*110.77(7)*	*111.40(7)*	*114.46(5)*	*107.66(8)*	*114.00(8)*	*111.46(6)*	*112.86(7)*	*109.00(6)*	103.50(8)
Ru(N+1)–Ru(N)–C(NU)	81.6(3)	87.5(2)	82.8(3)	84.3(2)	83.2(2)	85.7(3)	84.3(2)	85.9(2)	83.5(3)	84.1(3)	77.6(3)	80.8(3)
Ru(N+1)–Ru(N)–C(ND)	97.5(2)	91.8(2)	96.2(3)	94.4(2)	96.6(2)	95.8(3)	94.0(2)	94.5(2)	96.9(3)	92.6(3)	99.1(3)	93.9(2)
Ru(N+1)–Ru(N)–C(NN+1)	99.1(2)	91.3(2)	93.9(3)	94.4(2)	95.1(2)	92.2(3)	96.8(2)	92.2(2)	95.5(3)	90.0(3)	95.4(3)	95.7(2)
Ru(N+1)–Ru(N)–P(N)	*164.55(6)*	*170.14(7)*	*168.64(5)*	*168.49(7)*	*167.40(7)*	*171.47(5)*	*165.79(7)*	*171.77(7)*	*167.80(7)*	*170.75(8)*	*164.74(7)*	*159.57(6)*
C(NU)–Ru(N)–C(ND)	169.7(4)	167.7(4)	169.3(2)	168.6(4)	168.0(4)	166.7(2)	170.7(4)	168.6(4)	169.0(3)	168.4(4)	172.7(4)	170.0(4)
C(NU)–Ru(N)–C(NN+1)	93.8(4)	94.4(4)	95.2(3)	97.2(4)	96.7(4)	97.9(3)	94.1(4)	96.8(4)	95.1(3)	96.6(4)	93.7(3)	92.9(5)
C(NU)–Ru(N)–P(N)	*89.3(3)*	*90.2(3)*	*89.7(3)*	*89.5(2)*	*88.6(2)*	*88.4(3)*	*90.1(2)*	*88.8(2)*	*88.2(3)*	*90.8(3)*	*93.1(3)*	*90.1(3)*
C(ND)–Ru(N)–C(NN+1)	96.4(4)	97.9(4)	95.5(3)	94.3(4)	95.3(4)	95.2(3)	95.2(4)	94.5(4)	95.8(3)	94.6(4)	93.2(3)	96.0(4)
C(ND)–Ru(N)–P(N)	*89.2(2)*	*88.3(2)*	*89.6(3)*	*89.7(2)*	*89.4(2)*	*88.6(3)*	*89.3(2)*	*89.4(2)*	*89.5(3)*	*90.9(3)*	*88.7(3)*	*92.2(2)*
C(NN+1)–Ru(N)–P(N)	*93.9(2)*	*98.5(2)*	*95.2(3)*	*96.0(2)*	*95.4(2)*	*94.7(3)*	*96.6(3)*	*94.7(2)*	*94.1(3)*	*98.3(3)*	*97.3(3)*	*103.0(3)*

Disordered core

Distances (Å)												
Ru(NN+1)–Ru(N+1 N+2)	2.88(2)	2.87(2)	2.89(1)							2.865(5)	2.874(6)	2.865(7)
Ru(N)–Ru(NN+1)	1.96(1)	2.06(1)	1.63(1)							1.993(5)	1.635(4)	1.872(3)
Ru(N)–Ru(N−1 N)	1.66(1)	1.21(1)	1.50(1)							1.303(4)	1.527(3)	1.655(5)
Angles (°)												
Ru(N−1 N)–Ru(NN+1) –Ru(N+1 N+2)	59.6(4)	60.4(4)	59.9(4)							60.2(1)	59.9(1)	59.9(1)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)												
C(NU)–O(NU)	1.15(1)	1.15(1)	1.14(1)	1.14(1)	1.14(1)	1.15(1)	1.15(1)	1.15(1)	1.13(1)	1.15(1)	1.14(1)	1.13(1)
C(ND)–O(ND)	1.15(1)	1.15(1)	1.16(1)	1.16(1)	1.15(1)	1.14(1)	1.15(1)	1.15(1)	1.14(1)	1.11(1)	1.12(1)	1.14(1)
C(NN+1)–O(NN+1)	1.12(1)	1.13(1)	1.11(1)	1.14(1)	1.13(1)	1.14(1)	1.15(1)	1.15(1)	1.14(1)	1.12(1)	1.12(1)	1.12(1)
δ(C(NU))	−1.881	−1.908	−1.909	−1.900	−1.898	−1.915	−1.905	−1.902	−1.902	−1.912	−1.875	−1.850
δ(C(ND))	1.780	1.802	1.29	1.794	1.804	1.788	1.842	1.819	1.832	1.877	1.802	1.762
δ(P(N))	*−0.438*	*−0.133*	*−0.323*	*−0.298*	*−0.364*	*−0.265*	*−0.281*	*−0.231*	*−0.361*	*−0.228*	*−0.449*	*−0.512*
δ(C(NN+1))	0.432	0.378	0.314	0.516	0.428	0.499	0.360	0.401	0.346	0.400	0.444	0.521
Carbonyl angles (°)												
Ru(N)–C(NU)–O(NU)	173.8(6)	173.5(5)	173.5(9)	173.1(7)	173.4(5)	174.9(9)	173.1(8)	173.1(6)	174.0(9)	174.4(9)	170.1(9)	173.3(8)
Ru(N)–C(ND)–O(ND)	172.8(8)	172.5(5)	174.2(7)	172.2(7)	173.9(5)	172.7(8)	173.3(8)	172.2(6)	174.4(8)	169.7(7)	168.9(8)	168.2(9)
Ru(N)–C(NN+1)–O(NN+1)	177.8(6)	177.6(7)	176.4(9)	176.1(8)	178.6(8)	177.5(8)	176.6(8)	177.6(8)	178.1(6)	174.7(10)	169.9(8)	176.7(6)

[a] Dihedral angles between the principal and disordered Ru_3 planes of molecules 1 and 4 are: 2.2, 4.9°. Deviations of Ru(12, 23, 31) from the Ru(1, 2, 3) plane are: molecule 1: −0.043, 0.005, −0.107; molecule 4: 0.047, −0.141, 0.089 Å.

Table 14

Ruthenium environments for complex **3k-Ru** [a]

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.863(1)	2.852(2)	2.851(1)
Ru(N)–C(NU)	1.97(1)	1.96(1)	1.97(1)
Ru(N)–C(ND)	1.94(1)	1.93(1)	1.95(1)
Ru(N)–C(NN + 1)	1.89(1)	1.872(9)	1.93(1)
Ru(N)–P(N)	*2.291(2)*	*2.290(3)*	*2.296(3)*
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	59.88(4)	59.87(4)	60.25(5)
Ru(N − 1)–Ru(N)–C(NU)	95.0(3)	95.9(2)	96.1(3)
Ru(N − 1)–Ru(N)–C(ND)	74.1(3)	73.0(2)	74.0(3)
Ru(N − 1)–Ru(N)–C(NN + 1)	154.8(2)	156.9(4)	152.5(3)
Ru(N − 1)–Ru(N)–P(N)	*102.96(8)*	*101.40(7)*	*100.88(9)*
Ru(N + 1)–Ru(N)–C(NU)	76.6(2)	75.6(3)	78.5(3)
Ru(N + 1)–Ru(N)–C(ND)	97.2(2)	95.9(3)	95.3(3)
Ru(N + 1)–Ru(N)–C(NN + 1)	98.4(3)	100.6(3)	95.1(3)
Ru(N + 1)–Ru(N)–P(N)	*159.05(9)*	*157.31(7)*	*158.79(9)*
C(NU)–Ru(N)–C(ND)	169.0(4)	168.5(3)	170.0(4)
C(NU)–Ru(N)–C(NN + 1)	91.6(5)	90.4(4)	90.1(4)
C(NU)–Ru(N)–P(N)	*94.4(3)*	*95.3(3)*	*95.3(3)*
C(ND)–Ru(N)–C(NN + 1)	98.3(5)	98.8(4)	98.4(5)
C(ND)–Ru(N)–C(NN − 1)	88.4(2)	89.9(3)	87.7(3)
C(NN + 1)–Ru(N)–P(N)	*100.7(3)*	*100.1(3)*	*105.2(3)*
Disordered core			
Distances (Å)			
Ru(N)–Ru(NN + 1)	1.629(3)	1.602(3)	1.680(2)
Ru(N)–Ru(NN − 1)	1.631(3)	1.707(2)	1.646(3)
Ru(NN + 1)–Ru(N + 1 N + 2)	2.844(3)	2.849(3)	2.849(4)
Ru(N − 1 N)–P(N)	2.367(3)	2.385(4)	2.397(4)
Angles (°)			
Ru(N − 1 N)–Ru(NN + 1)- –Ru(N + 1 N + 2)	60.06(9)	60.05(9)	59.89(9)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.15(1)	1.14(2)	1.12(1)
C(ND)–O(ND)	1.10(1)	1.13(1)	1.11(1)
C(NN + 1)–O(NN + 1)	1.11(1)	1.09(1)	1.10(1)
δ(C(NU))	−1.862	−1.830	−1.878
δ(C(ND))	1.772	1.757	1.805
δ(P)	*−0.502*	*−0.535*	*−0.406*
δ(C(NN + 1))	0.441	0.426	0.432
Carbonyl angles (°)			
Ru(N)–C(NU)–C(NU)	169.8(8)	167.2(9)	169.4(9)
Ru(N)–C(ND)–O(ND)	166.1(8)	166.9(9)	165.1(9)
Ru(N)–C(NN + 1)–O(NN + 1)	168.0(10)	166.7(7)	166.0(8)

[a] The dihedral angle between the Ru(1,2,3) and Ru(12,23,31) planes is 0.9°. Deviations of Ru(12,23,31) from the Ru(1,2,3) plane are −0.088, −0.074, −0.116 Å.

Table 15

Ruthenium environments for complex **3l-Ru**

Atoms	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.855(2)	2.863(2)	2.854(2)
Ru(N)–C(NU)	1.95(1)	1.94(2)	1.95(2)
Ru(N)–C(ND)	1.95(1)	1.97(2)	1.95(1)
Ru(N)–C(NN + 1)	1.86(1)	1.93(2)	1.75(2)
Ru(N)–P(N)	*2.242(4)*	*2.242(4)*	*2.242(5)*
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.21(4)	59.88(5)	59.91(4)
Ru(N − 1)–Ru(N)–C(NU)	93.3(4)	94.0(5)	96.3(5)
Ru(N − 1)–Ru(N)–C(ND)	78.6(5)	80.1(5)	78.8(5)
Ru(N − 1)–Ru(N)–C(NN + 1)	154.6(4)	161.0(5)	154.1(7)
Ru(N − 1)–Ru(N)–P(N)	*101.9(1)*	*95.9(1)*	*102.7(1)*
Ru(N + 1)–Ru(N)–C(NU)	81.8(4)	79.1(5)	81.3(4)
Ru(N + 1)–Ru(N)–C(ND)	93.8(5)	94.4(6)	96.9(5)
Ru(N + 1)–Ru(N)–C(NN + 1)	96.6(4)	104.4(5)	97.0(7)
Ru(N + 1)–Ru(N)–P(N)	*160.0(1)*	*153.7(1)*	*159.8(1)*
C(NU)–Ru(N)–C(ND)	171.9(6)	172.9(8)	175.1(7)
C(NU)–Ru(N)–C(NN + 1)	93.4(6)	93.1(7)	90.9(7)
C(NU)–Ru(N)–P(N)	*91.0(5)*	*93.7(5)*	*91.1(4)*
C(ND)–Ru(N)–C(NN + 1)	93.9(6)	91.3(7)	93.9(8)
C(ND)–Ru(N)–P(N)	*90.8(5)*	*90.8(6)*	*89.0(5)*
C(NN + 1)–Ru(N)–P(N)	*102.5(4)*	*101.3(5)*	*101.9(7)*
Carbonyl distances (δ(C) is the deviation from Ru_3 plane)			
C(NU)–O(NU)	1.11(2)	1.13(2)	1.12(2)
C(ND)–O(ND)	1.12(2)	1.09(2)	1.12(2)
C(NN + 1)–O(NN + 1)	1.16(2)	1.13(2)	1.24(3)
δ(C(NU))	−1.91	−1.87	−1.88
δ(C(ND))	1.87	1.91	1.85
δ(P)	*−0.37*	*−0.42*	*−0.43*
δ(C(NN + 1))	0.38	0.38	0.37
Carbonyl angles (°)			
Ru(N)–C(NU)–C(NU)	173(1)	171(1)	172(1)
Ru(N)–C(ND)–O(ND)	174(1)	173(2)	172(2)
Ru(N)–C(NN + 1)–O(NN + 1)	178(1)	177(2)	180(1)

Table 16

Osmium environments for complex **3b-Os**

	N = 1	N = 2	N = 3
Distances (Å)			
Os(N)–Os(N + 1)	2.904(4)	2.907(4)	2.919(4)
Os(N)–C(NU)	1.71(4)	1.85(4)	1.90(5)
Os(N)–C(ND)	1.85(5)	1.86(4)	1.67(5)
Os(N)–C(NN + 1)	1.69(5)	1.81(6)	1.73(6)
Os(N)–P(N)	*2.33(2)*	*2.36(1)*	*2.36(1)*

Table 16 (continued)

	N = 1	N = 2	N = 3
Angles (°)			
Os(N − 1)–Os(N)–Os(N + 1)	59.91(9)	60.31(9)	59.79(9)
Os(N − 1)–Os(N)–C(NU)	89(2)	91(2)	94(2)
Os(N − 1)–Os(N)–C(ND)	82(2)	79(2)	80(2)
Os(N − 1)–Os(N)–C(NN + 1)	156(2)	151(2)	150(2)
Os(N − 1)–Os(N)–P(N)	*111.2(4)*	*109.4(4)*	*109.3(4)*
Os(N + 1)–Os(N)–C(NU)	79(2)	83(1)	85(2)
Os(N + 1)–Os(N)–C(ND)	95(2)	92(2)	96(2)
Os(N + 1)–Os(N)–C(NN + 1)	97(2)	96(2)	91(2)
Os(N + 1)–Os(N)–P(N)	*168.6(3)*	*166.9(4)*	*167.2(4)*
C(NU)–Os(N)–C(ND)	171(2)	170(2)	173(3)
C(NU)–Os(N)–C(NN + 1)	93(2)	103(2)	92(2)
C(NU)–Os(N)–P(N)	*94(2)*	*89(1)*	*90(2)*
C(ND)–Os(N)–C(NN + 1)	94(2)	86(2)	96(3)
C(ND)–Os(N)–P(N)	*90(2)*	*94(2)*	*89(2)*
C(NN + 1)–Os(N)–P(N)	*92(2)*	*96(2)*	*100(2)*
Carbonyl distances (Å) (δ(C) is the deviation from the Os_3 plane)			
C(NU)–O(NU)	1.29(6)	1.23(5)	1.21(6)
C(ND)–O(ND)	1.20(5)	1.13(5)	1.32(6)
C(NN + 1)–O(NN + 1)	1.27(5)	1.23(7)	1.22(7)
δ(C(NU))	−1.67	−1.83	−1.88
δ(C(ND))	1.80	1.80	1.61
δ(P)	*−0.29*	*−0.35*	*−0.28*
δ(C(NN + 1))	0.21	0.56	0.27
Carbonyl angles (°)			
Os(N)–C(NU)–C(NU)	165(5)	175(4)	176(5)
Os(N)–C(ND)–O(ND)	176(5)	168(4)	175(4)
Os(N)–C(NN + 1)–O(NN + 1)	161(4)	172(4)	171(5)

Abnormal features. The unit cell is unusually large with four molecules in the asymmetric unit. Nevertheless the quality of the data permitted meaningful refinement of anisotropic thermal parameters for all non-hydrogen atoms, and also populations for the disordered Ru_3 cores of molecules 1 and 4; for the latter no ligand disorder could be deconvoluted and it has been modelled as being contained by the thermal motion envelope. The usual *caveat* about associated geometry applies.

3k-Ru: $Ru_3(CO)_9\{P(OEt)_3\}_3 = C_{27}H_{45}O_{18}P_3Ru_3$, $M = 1053.8$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 18.170(6), b 13.016(6), c 10.035(3) Å, α 68.83(3), β 80.42(3), γ 78.10(4)°, U 2154(1) Å^3, D_c ($Z = 2$) 1.62 g cm^{-3}. $F(000) = 1056$. μ_{Mo} 11.3 cm^{-1}. Specimen: 0.37 × 0.10 × 0.40 mm. $A^{\star}_{min,max} = 1.12, 1.50$. $2\theta_{max}$ 50°, $N = 6700$, $N_0 = 4318$, $R = 0.051$, $R' = 0.061$ ($n = 6$).

Abnormal features. The ruthenium triangular core is disordered over two sets of sites; populations were refined independently, and constrained at the mean of the values for the major component, that of the minor component summing to unity. Ligand disorder was not resolvable and was modelled in terms of containment by a single set of thermal envelopes, a fact which should be taken into account in considering the credibility and usefulness of metal–ligand distances.

3l-Ru: $Ru_3(CO)_9\{P(OCH_2CF_3)_3\}_3 = C_{27}H_{18}F_{27}O_{18}P_3Ru_3$, $M = 1539.5$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 21.036(2), b 13.146(1), c 9.376(2) Å, α 82.68(1), β 88.40(1), γ 85.59(1)°, U 2564(1) Å^3, D_c ($Z = 2$) 1.99 g cm^{-3}. $F(000) = 1488$. μ_{Mo} 10.7 cm^{-1}. Specimen: $0.08 \times 0.23 \times 0.17$ mm. $A^*_{min,max} = 1.09$, 1.20. $2\theta_{max}$ 50°, $N = 9169$, $N_0 = 3966$, $R = 0.066$, $R' = 0.068$ ($n = 3$).

3b-Os: $Os_3(CO)_9(PPh_3)_3 = C_{63}H_{45}O_9Os_3P_3$, $M = 1609.6$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 18.207(5), b 17.911(6), c 12.928(3) Å, α 94.13(2), β 98.98(2), γ 110.56(2)°, U 3862(2) Å^3, D_c ($Z = 2$) 1.38 g cm^{-3}. $F(000) = 1536$. μ_{Mo} 48.2 cm^{-1}. Specimen: $0.03 \times 0.08 \times 0.20$ mm. $A^*_{min,max} = 1.14$, 1.51. $2\theta_{max}$ 40°, $N = 7251$, $N_0 = 3216$, $R = 0.092$, $R' = 0.084$ ($n = 2$).

Abnormal features. Weak and limited data would not support refinement of anisotropic thermal parameters other than those of the osmium. U_{iso} were refined for all other non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were calculated for hydrogen atoms and included constrained in the refinement.

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