Journal of Organometallic Chemistry, 347 (1988) 157–180
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Cluster chemistry

LV *. Stereochemistry of group 15 ligand-substituted derivatives of $M_3(CO)_{12}$ (M = Ru, Os)
A. X-Ray structures of six complexes $M_3(CO)_{11}(L)$ (M = Ru, L = $PPh(OMe)_2$, $P(OCH_2CF_3)_3$, $P(OCH_2)_3CEt$ and $AsPh_3$; M = Os, L = PPh_3 and $PPh(OMe)_2$)

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(Received November 2nd, 1987)

Abstract

X-Ray crystal structures of six complexes $M_3(CO)_{11}(L)$ (M = Ru, L = $PPh(OMe)_2$, $P(OCH_2CF_3)_3$, $P(OCH_2)_3CEt$ and $AsPh_3$; M = Os, L = PPh_3 and $PPh(OMe)_2$) have been determined. Consideration of these results, together with other published data, allowed several conclusions to be drawn concerning the effect of substituting one CO group in $M_3(CO)_{12}$ (M = Ru, Os) by a *P*- or *As*-donor ligand. The most important are that L occupies an equatorial site, the M–M separation *cis* to L increases with increasing cone angle of L, while the CO_{eq} ligand *cis* to L on the same metal atom is more tightly bound. Distortions of the M_3L_{12} molecule from D_{3h} to D_3 geometry appear to be related to the σ-donor properties of L. The reactions between $Ru_3(CO)_{12}$ and $P(OCH_2CF_3)_3$, and between $Os_3(CO)_{12}$ and PPh_3 or $PPh(OMe)_2$, to give $M_3(CO)_{12-n}(L)_n$ (n = 1–3), are described. Crystal data: $Ru_3(CO)_{11}\{PPh(OMe)_2\}$, monoclinic, $P2_1/c$, a 9.647(3), b 20.529(7), c 14.692(5) Å, β 119.93(2)°, U 2522(1) Å^3, $Z = 4$, N_0 (observed data, with $I > 3\sigma(I)$) = 5829, $R = 0.035$, $R' = 0.037$; $Ru_3(CO)_{11}\{P(OCH_2CF_3)_3\}$, triclinic, $P\bar{1}$, a 12.920(1), b 11.530(2), c 10.189(1) Å, α 85.93(1), β 86.57(1), γ 70.66(1)°, U 1427(1) Å^3, $Z = 2$, $N_0 = 4061$, $R = 0.038$, $R' = 0.054$; $Ru_3(CO)_{11}\{P(OCH_2)_3CEt\}$, mono-

* For Part LIV see Ref. 29.

0022-328X/88/$03.50

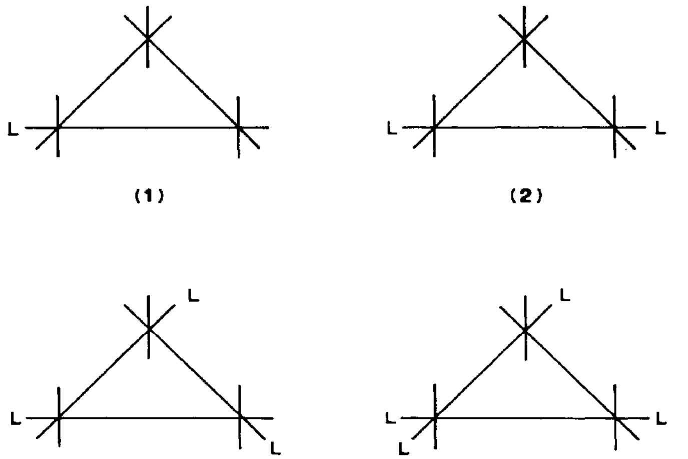
clinic, $P2_1/c$, a 13.57(1), b 14.779(1), c 12.362(3) Å, β 98.34(4)°, U 2453(1) Å^3, $Z = 4$, $N_0 = 5950$, $R = 0.039$, $R' = 0.054$; $Ru_3(CO)_{11}(AsPh_3)$, monoclinic, $C2/c$, a 22.496(6), b 16.348(4), c 17.345(5) Å, β 103.65(2)°, U 6198(3) Å^3, $Z = 8$, $N_0 = 6071$, $R = 0.032$, $R' = 0.028$; $Os_3(CO)_{11}(PPh_3)$, monoclinic, $C2/c$, a 22.196(5), b 16.265(3), c 17.370(5) Å, β 103.86(2)°, U 6088(3) Å^3, $Z = 8$, $N_0 = 4125$, $R = 0.031$, $R' = 0.033$; $Os_3(CO)_{11}\{PPh(OMe)_2\}$, monoclinic, $P2_1/c$, a 10.817(3), b 14.993(4), c 16.174(3) Å, β 101.87(2)°, U 2567(1) Å, $Z = 4$, $N_0 = 5506$, $R = 0.047$, $R' = 0.057$.

Introduction

The recent development of routes to derivatives of $Ru_3(CO)_{12}$ substituted by tertiary phosphines, phosphites, arsines and isocyanides has made many of these simple complexes available for study [1]. We have previously described X-ray studies of the complexes $Ru_3(CO)_{12-n}(L)_n$ (L = PCy_3, $n = 1$; L = $P(OMe)_3$, $n = 2$; L = PMe_3, $n = 3$; L = $PPh(OMe)_2$, $n = 4$) [2,3] noting that the latter is unusual in having the $Fe_3(CO)_{12}$-type structure with two CO ligands bridging one of the Ru–Ru bonds. Other workers have described the structures of $Ru_3(CO)_{11}(PPh_3)$ [4] and of a range of derivatives containing bidentate tertiary phosphine or arsine ligands, $Ru_3(CO)_{12-n}(LL)_n$ (LL = dppm, $n = 1$ or 2; LL = dppe, $n = 1$; LL = ffars, $n = 1$ or 2) [5–7]. Structural studies of related osmium complexes have encompassed the complexes $Os_3(CO)_{11}(L)$ (L = $P(OMe)_3$ [8], $PBu^t_2(NH_2)$ [9]), $\{Os_3(CO)_{11}(As\text{-}Bu^tN{=})\}_2S$ [10] and $Os_3(CO)_9(\mu$-dppm$)(\eta^1$-dppm) [11]. In all cases the group 15 ligand was found to occupy an equatorial site as expected on steric grounds. With the isocyanide complexes $Ru_3(CO)_{12-n}(CNBu^t)_n$ ($n = 1$ or 2) and $Os_3(CO)_{11}(CNBu^t)$ [12,13] and the nitrile derivatives $Os_3(CO)_{12-n}(NCMe)_n$ ($n = 1$ or 2) [14] axial coordination was found for the non-CO ligands, albeit with some distortion of the ligand polyhedron to accommodate the larger ligands. The face-capping tridentate ligand in $Ru_3\{\mu_3\text{-}(PBu_2)_3SiMe\}(CO)_9$ also occupies axial sites [15]. In a previous paper [3], we have made some comments on the variation of the volume of the ligand polyhedron with substitution and a possible correlation with the presence of bridging CO groups, and also about the variation of Ru–Ru bond distances within these clusters. We now present the results of a more detailed investigation of the solid-state molecular structures of group 15 ligand derivatives of the ruthenium and osmium cluster carbonyls. Some 23 complexes have been studied, and for convenience we present the results in four parts, divided according to the degree of substitution. In conjunction with previously available results, this study has enabled us to make more extensive comparisons of changes in molecular geometries resulting from increasing substitution of CO by the same ligand, L, between tertiary phosphines and phosphites, between P and As, and between Ru and Os. In addition, we have extended the synthetic routes to afford a series of tetrasubstituted complexes $Ru_3(CO)_8(L)_4$. This paper describes the structures of six monosubstituted complexes.

Results and discussion

To facilitate reference to the various complexes discussed in this and the following papers, each is denoted by a number-letter-symbol sequence, where the



(1) (2) (3) (4)

	L
a	CO
b	PPh_3
c	$AsPh_3$
d	PCy_3
e	PMe_2Ph
f	$AsMe_2Ph$
g	$PMe_2(CH_2Ph)$
h	PMe_3
i	$PPh(OMe)_2$
j	$P(OPh)_3$
k	$P(OEt)_3$
l	$P(OCH_2CF_3)_3$
m	$P(OMe)_3$
n	$P(OCH_2)_3CEt$

Scheme 1

number (**1**–**4**) denotes the degree of substitution, the letter denotes the group 15 ligand (**a**–**n**; see Scheme 1); the cluster core is indicated by Ru or Os. Thus compound **1a-Ru** is $Ru_3(CO)_{12}$ and compound **4m-Os** is $Os_3(CO)_8\{P(OMe)_3\}_4$. Unfortunately, it has not proved possible to study more than one complete series of complexes $M_3(CO)_{12-n}(L)_n$ (M = Ru, L = $PPh(OMe)_2$, $n = 1$–4), since, although several tetrasubstituted complexes were made, not all could be induced to give X-ray quality crystals.

Synthesis

Compounds **1c-Ru**, **1i-Ru**, and **1n-Ru** were prepared in high yield by electron transfer-catalysed reactions between $Ru_3(CO)_{12}$ and stoichiometric amounts of the appropriate ligands. The osmium derivatives **1b-Os** and **1i-Os** were obtained from thermal reactions between $Os_3(CO)_{12}$ and the group 15 ligand, carried out in refluxing toluene or xylene; they were easily separated from more highly substituted complexes by chromatography. Complexes **1i-Os** and **1l-Ru** are new, and were characterised by elemental microanalyses and from their spectral properties; as shown earlier [1], the degree of substitution can be readily determined from the IR ν(CO) spectrum, monosubstituted complexes being characterised by a high energy absorption around 2100 cm^{-1}. The IR ν(CO) spectra of the osmium complexes are similar in pattern to those of the analogous ruthenium complexes, but individual bands vary slightly in position and relative intensity.

Of some interest is the reaction between $Ru_3(CO)_{12}$ and $P(OCH_2CF_3)_3$, which afforded the first metal cluster complexes containing this fluorinated phosphite. Although the ligand was first reported in 1954 [16], it is only recently that any transition metal derivatives containing the ligand have been prepared, in the form of the complexes $Cr(CO)_2\{P(OCH_2CF_3)_3\}(\eta^6\text{-}C_6H_3Me_3)$, $FeI\{P(OCH_2CF_3)_3\}_2(\eta\text{-}C_5H_5)$ and $Ni(CO)_{4-n}\{P(OCH_2CF_3)_3\}_n$ ($n = 1,2$) [17]. Even using ETC conditions, the reaction between equimolar amounts of $Ru_3(CO)_{12}$ and this ligand afforded

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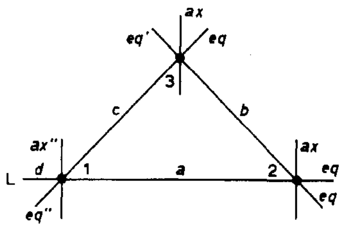
Table 1

Bond distances (Å) in $Ru_3(CO)_{11}(L)$ complexes



M	L	No.	Cone angle (°) [a]	M–M a	M–M b	M–M c	M–L	M–CO ax [b]	M–CO eq [c]	M–CO eq'	M–CO ax'' [d]	M–CO eq''	Reference
Ru	CO	**1a-Ru**	~ 95	2.852(1)	2.851(1)	2.860(1)	–	1.942(4)	1.921(5)				18
Os	CO	**1a-Os**	~ 95	2.874(1)	2.875(1)	2.882(1)	–	1.946(6)	1.912(7)				19
Ru	PCy_3 [e]	**1d-Ru**	170	2.878(2)	2.859(2)	2.902(2)	2.425(3)	1.94	1.92	1.93(1)	1.94	1.90(1)	2
				2.875(2)	2.874(2)	2.920(2)	2.430(3)	1.95	1.91	1.90(1)	1.92	1.87(1)	
Os	$PBu^t_2(NH_2)$ [e]		~160	2.900(1)	2.881(1)	2.953(1)	2.376(4)	1.94	1.87	1.87(3)	1.98	1.85(2)	9
				2.892(1)	2.889(1)	2.925(1)	2.399(4)	1.91	1.87	1.92(2)	1.89	1.82(2)	
Os	$(AsBu^t_2N{=})_2S$		~160	2.884(1)	2.891(1)	2.939(1)	2.488(1)	1.95	1.90	1.86(2)	1.94	1.88(2)	10
Ru	PPh_3	**1b-Ru**	145	2.876(3)	2.875(3)	2.907(3)	2.380(6)	1.94	1.89	1.91(3)	1.92	1.86(3)	4
Os	PPh_3	**1b-Os**	145	2.891(1)	2.886(1)	2.918(1)	2.370(2)	1.94	1.90	1.90(1)	1.94	1.88(1)	[f]
Ru	$AsPh_3$	**1c-Ru**	142	2.850(1)	2.859(1)	2.895(1)	2.464(1)	1.937	1.911	1.895(5)	1.933	1.887(4)	[f]
Ru	$PPh(OMe)_2$	**1i-Ru**	115	2.846(1)	2.858(1)	2.872(1)	2.287(1)	1.943	1.910	1.909(5)	1.933	1.888(4)	[f]
Os	$PPh(OMe)_2$	**1i-Os**	115	2.882(1)	2.882(1)	2.886(1)	2.288(3)	1.95	1.91	1.92(1)	1.96	1.89(1)	[f]
Os	$P(OMe)_3$	**1m-Os**	107	2.890(4)	2.892(4)	2.908(4)	2.285(5)	1.91	1.91	1.91(2)	1.92	1.88(1)	8
Ru	$P(OCH_2CF_3)_3$	**1l-Ru**	~110	2.859(1)	2.846(1)	2.862(1)	2.254(1)	1.943	1.921	1.887(5)	1.931	1.911(5)	[f]
Ru	$P(OCH_2)_3CEt$	**1n-Ru**	101	2.858(1)	2.839(2)	2.829(2)	2.238(1)	1.941	1.900	1.919(7)	1.924	1.879(6)	[f]

[a] From ref. 28. [b] Average of four. [c] Average of three. [d] Average of two. [e] Values for two independent molecules. [f] This work.

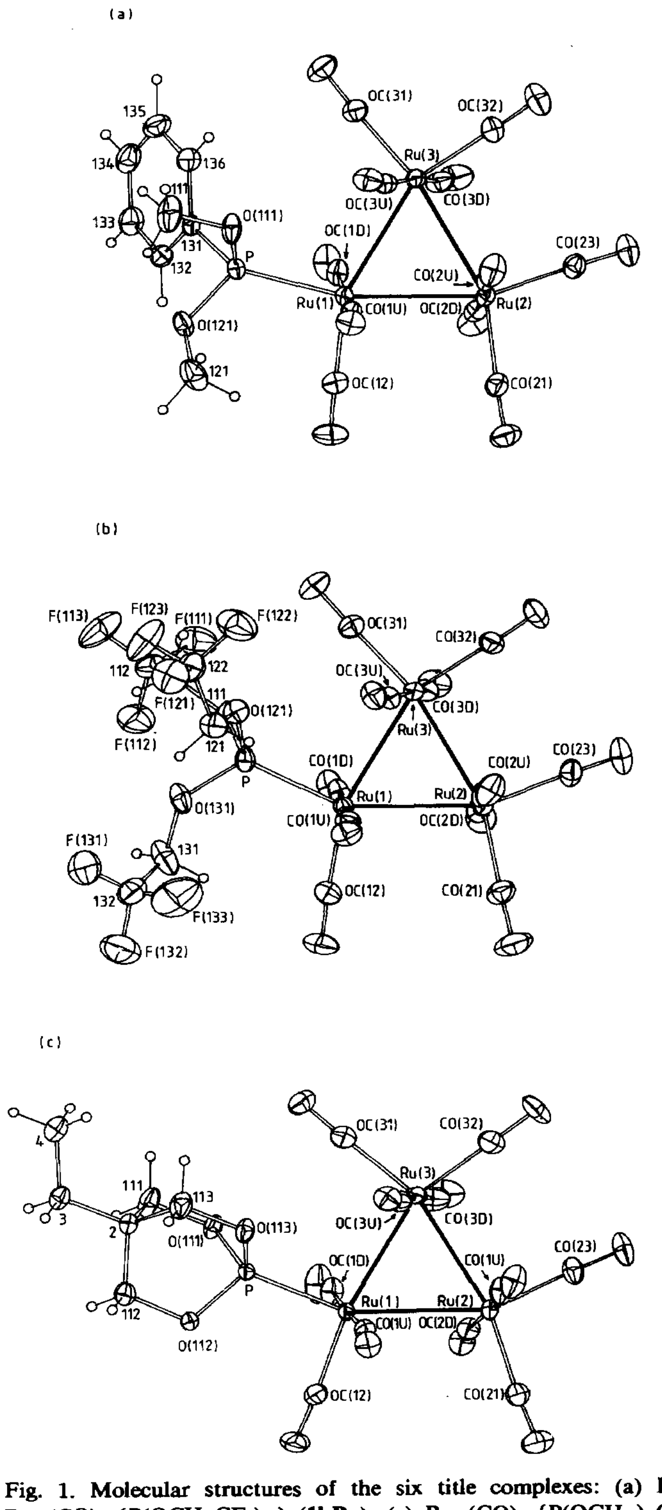


Fig. 1. Molecular structures of the six title complexes: (a) $Ru_3(CO)_{11}\{PPh(OMe)_2\}$ (**1i-Ru**); (b) $Ru_3(CO)_{11}\{P(OCH_2CF_3)_3\}$ (**1l-Ru**); (c) $Ru_3(CO)_{11}\{P(OCH_2)_3CEt\}$ (**1n-Ru**); (d) $Ru_3(CO)_{11}(AsPh_3)$ (**1c-Ru**); (e) $Os_3(CO)_{11}(PPh_3)$ (**1b-Os**); (f) $Os_3(CO)_{11}\{PPh(OMe)_2\}$ (**1i-Os**). 20% probability amplitude thermal ellipsoids are shown for the non-hydrogen atoms, together with labelling. Hydrogen atoms have arbitrary radii of 0.1 Å.

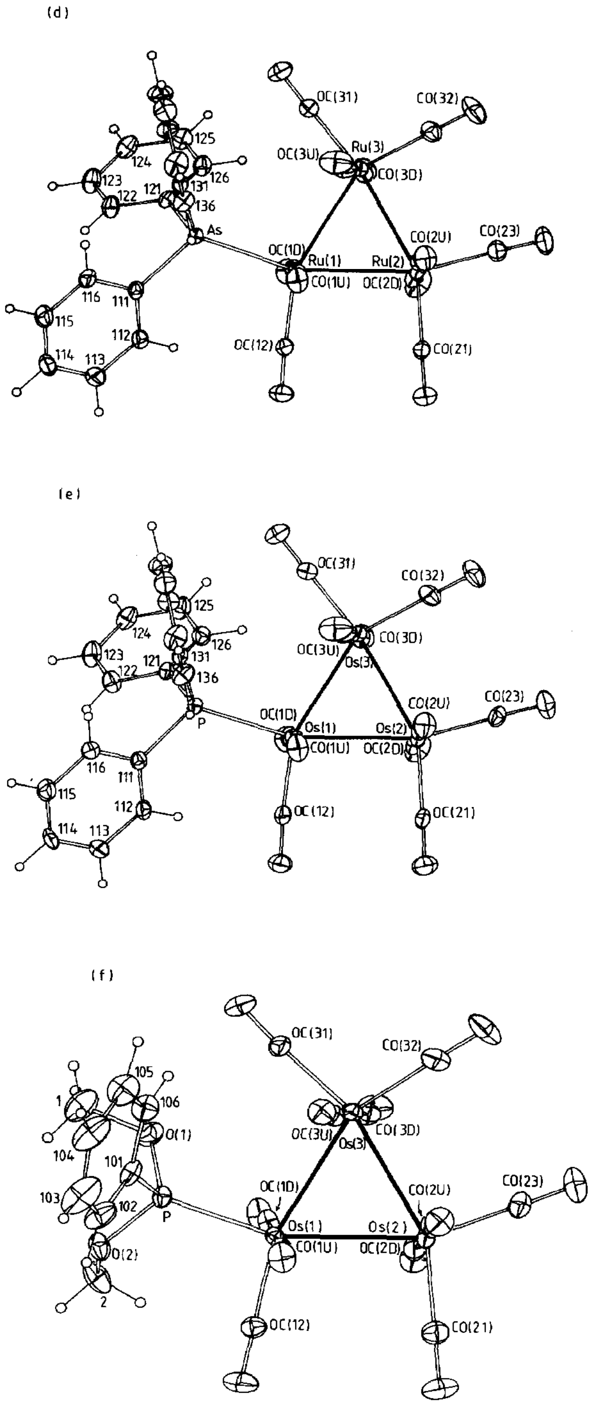


Fig. 1 (continued).

mixtures of the four complexes $Ru_3(CO)_{12-n}\{P(OCH_2CF_3)_3\}_n$ ($n = 0$–3), which were readily separated by preparative TLC. The complexes are relatively low-melting solids, somewhat paler in colour when compared with other tertiary phosphite complexes with a similar degree of substitution.

General structural considerations

The molecular structures of the six complexes **1b-Os**, **1c-Ru**, **1i-Ru** and **-Os**, **1l-Ru** and **1n-Ru** have been determined. Table 1 summarises important bond lengths found for these complexes, together with those reported elsewhere for the parent carbonyls **1a-Ru** and **-Os**, and complexes **1b-Ru**, **1d-Ru** and **1m-Os**, and $Os_3(CO)_{11}\{PBu^t_2(NH_2)\}$ [9] and $\{Os_3(CO)_{11}(AsBu^t_2N{=})\}_2S$ [10]. All compounds contain a triangular arrangement of three metal atoms. The group 15 ligands occupy equatorial sites, as can be seen from Fig. 1, which depicts the molecular structures of the title complexes.

Metal–metal bond distances

In the parent carbonyls, the average M–M separations are 2.854 (Ru) [18] and 2.877 Å (Os) [19], one of the three bonds being slightly longer than the other two. In the monosubstituted derivatives, the M–M separations have ranges 2.839–2.920 (Ru) and 2.881–2.953 Å (Os). With one exception, the M–M bond *cis* to the group 15 ligand is the longest of the three; there is generally little difference between the other two separations (maximum 0.02 Å in three complexes). In **1n-Ru**, it is the Ru–Ru bond *trans* to the group 15 ligand which is the longest, while for **1l-Ru**, the two Ru–Ru bonds from the Ru(1) are identical, the third being 0.014 Å shorter.

Changes in the M(1)–M(3) separation can be related directly to the cone angle of the group 15 ligand. The separations increase by 0.014 to 0.045 Å (Ru; cone angles 115–170°) and 0.03 and 0.063 Å (Os; cone angles 107–160°) from those in the parent $M_3(CO)_{12}$, suggesting that it is the steric bulk of the group 15 ligand which is responsible for the change. The average M–M separation also increases with increasing cone angle, from 2.842 (101°) to 2.890 Å (170°) (Ru), although the changes are not so marked for M = Os: 2.897 (107°) to 2.91 Å (160°). In spite of the generally self-consistent nature of the observed correlations, it should be noted that we have not made any librational corrections, which might be expected to contribute contractions of perhaps up to 0.01 Å in the reported molecular core distances, and greater contractions at the ligand peripheries.

Comparisons of the Ru/Os pairs **1a**, **1b** and **1i** reveal differences in the M–M separations of between 0.012 to 0.025 Å. However, there are no significant differences between corresponding M–P or M–CO distances in these complexes.

Metal–phosphorus and –arsenic distances

The M–P distances fall in the ranges 2.238(1) to 2.430(3) Å (M = Ru) and 2.285(5) to 2.399(4) Å (M = Os), while M–As distances are 2.464(1) Å (M = Ru) and 2.488(1) Å (M = Os) for the two examples studied. Again the shortest M–P distances are found with ligands having the smaller cone angles. The difference in M–P and M–As separations (0.084 Å for the EPh_3 complexes **Ru-1b** and **Ru-1c**) is somewhat smaller than the difference in covalent radii of P and As (0.13 Å) as determined in EPh_3 [20,21]. Similarly, the E–C separations differ by ca. 0.1 Å, but the significance of this observation is limited by the precision of the structure determination of **1b-Ru**.

The group 15 ligand is approximately *trans* to one of the M–M bonds. While in $M_3(CO)_{12}$, the average M–M–CO angles are 98.0 (Ru) and 98.2° (Os), the M–M–P angles range between 93.6 and 112.9°, and the M–M–As angles are 101.2 and 109.4°, for the Ru and Os complexes, respectively. The larger angles result with ligands with the larger cone angles.

Metal–carbonyl distances and angles

As found in the parent carbonyls, the bonds from metal atoms to axial CO ligands are longer than those to the equatorial CO groups. For the $M(CO)_4$ groups, average M–CO_{ax} distances are 1.94 (Ru) and 1.93 Å (Os), with average M–CO_{eq} distances being 1.91 (Ru) and 1.89 Å (Os). The latter figures do not include the equatorial CO group *cis* to the group 15 ligand, which are ca. 0.02 Å shorter (av. 1.89 (Ru), 1.87 Å (Os)). The M–CO_{ax} bonds from M(1) are ca. 1.93 (Ru) and 1.94 Å (Os). In the parent carbonyls, M–CO_{ax} average at 1.942(4) (Ru), 1.946(6) Å (Os), while the average M–CO_{eq} separations are 1.921(5) (Ru) and 1.912(7) Å (Os). These observations are consistent with previously expressed interpretations [4,8,14] of the relative degrees of backbonding experienced by two mutually *trans* CO ligands, i.e. CO_{ax}, compared with a CO *trans* to a metal–metal bond. In addition, the marked shortening of the M–CO_{eq} bond *cis* to the group 15 ligand may be ascribed to increased back-bonding resulting both from the presence of the good σ-donor ligand attached to the same metal atom and the sterically-induced lengthening of the M–M bond *trans* to the CO group.

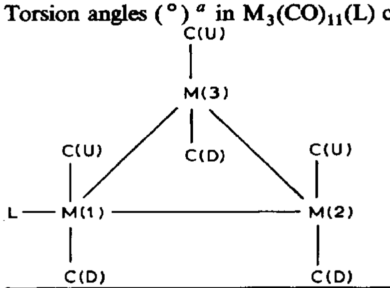
In the parent carbonyls, the M–M–CO angles range from 96.3 to 100.2° (*eq*, Ru), 96.1 to 99.9° (*eq*, Os), 87.7 to 90.6° (*ax*, Ru), 88.2 to 91.6° (*ax*, Os). The CO_{eq}–M–CO_{eq} angles range from 103.3–105.0° (Ru), 102.8–104.2° (Os). The M–CO_{eq} moieties are linear (177.9–179.8° (Ru), 176.9–179.4° (Os), but the M–CO_{ax} are bent by Van der Waals repulsion between the oxygen atoms (172.3–173.3° (Ru), 174.5–175.8° (Os)). In the monosubstituted group 15 ligand complexes the M–CO_{eq} moieties are essentially linear (average value for all complexes studied 177.5°, range 175.7–178.3°), while the M–CO_{ax} groups are bent (average 173.3°, range 172.2–175.2°). These values are similar to those found in the parent carbonyls, suggesting that the relative twisting of the ML_4 units (see below) is a response to the presence of the group 15 ligand.

The disposition of the equatorial ligands also reflects the presence of the bulky group 15 ligand. In the parent carbonyls, angles OC_{eq}–M–CO_{eq} are ca. 104°, while in the substituted complexes, this angle has closed slightly (average 101.2°, range 99.0–103.5°); the angles at the metal atoms in the OC_{eq}–M–M–CO_{eq} units (average 97.2°) do not differ significantly from those in $M_3(CO)_{12}$. However, when examining the (*cis*-) L–M–M–CO_{eq} unit, one finds the average L–M–M angle to be 102.8° (range 93.6–109.4°), and the average M–M–CO_{eq} angle to be 107.2° (range 100.9–110.6°), it is evident that there is a mutual repulsion between the two adjacent equatorial ligands, the general trend reflecting the size (as measured by cone angle) of the group 15 ligand.

It might also be expected that Ru(2)–Ru(1)–C(12) should be smaller; this is true where the phosphorus has immediate hydrocarbon substituents, but where the immediate substituent adjacent to CO(1) is fully substituted with oxygen atoms (as in **1n-Ru**), then instead of diminishing, the angle increases markedly. Note also that where the phosphorus is unsymmetrically substituted, the bulkier substituents lie

Table 2

Torsion angles (°) [a] in $M_3(CO)_{11}(L)$ complexes



M	L	C(1)–M(1)–M(2)–C(2)	C(2)–M(2)–M(3)–C(3)	C(3)–M(3)–M(1)–C(1)
Ru	CO	1.4, 1.9	1.0, 3.2	1.0, 2.9
Os	CO	1.0, 1.9	0.8, 3.8	1.4, 3.6
Ru	PCy_3 [b]	4.8, 3.9	3.5, 4.7	2.4, 4.2
Os	$PBu^t_2(NH_2)$ [b]	9.5, 0.4	3.7, 3.9	9.1, 2.8
Ru	PPh_3	11.5, 5.4	14.4, 5.4	10.6, 5.9
Os	PPh_3	9.4, 4.0	12.3, 4.4	12.1, 5.0
Ru	$AsPh_3$	10.1, 4.7	13.1, 4.3	11.7, 6.1
Ru	$PPh(OMe)_2$	20.6, 24.3	23.9, 21.4	22.8, 24.8
Os	$PPh(OMe)_2$	14.4, 14.7	16.8, 15.4	15.5, 15.0
Os	$P(OMe)_3$	7.4, 1.4	7.2, 0.7	6.2, 0.2
Ru	$P(OCH_2CF_3)_3$	17.6, 13.1	19.1, 11.5	18.1, 13.5
Ru	$P(OCH_2)_3CEt$	23.7, 25.6	22.5, 24.4	22.6, 24.6

[a] Two values for C(NU)–M(N)–M(N+1)–C(N+1U), C(ND)–M(N)–M(N+1)–C(N+1D). [b] Values for molecule 1.

toward M(3) rather than CO(12) (Fig. 1), and in addition one substituent atom tends to be near the equatorial plane toward CO(12), while the other two are directed towards CO(31) and lie astride the plane. M(3)–M(1)–P is very variable, being largest for **1i-Ru** (105.1°) and smallest for **1l-Ru** (93.6°), with no obvious reason.

Ligand polyhedra

Polyhedra constructed from the carbonyl O atoms and the P (or As) atoms of the group 15 ligands are distorted anticuboctahedra. The distortions are manifested as twisting of the ML_4 units about the twofold axis of the M_3 triangle. Table 2 lists the torsion angles of the CO_{ax}–M–M–CO_{ax} moieties, which surprisingly bear no relation to the cone angle of the ligand. The largest twists are found in the $PPh(OMe)_2$ (surprisingly diminished in the Os counterpart) and $P(OCH_2)_3CEt$ complexes, whilst the most bulky ligand studied, PCy_3, induces the least distortion from D_{3h} symmetry found in the parent carbonyls. Lauher has commented [22] that an electronic factor apparently favours the sterically less favoured D_{3h} isomer, which has significant *ax–ax* and *eq–eq* CO interactions. The steric interactions resulting from the introduction of the group 15 ligand are relieved by twisting of the ML_4 groups. Although there is no correlation between the degree of twisting and ligand bulk (as measured by the cone angle), the greater twisting is found in complexes with the shorter M–P distances; the M–M separations indicate a progressive contraction of the M_3 triangle also occurs.

It is of interest to note, however, that one consistent correlation is found in **1b-Os**, **1b-Ru** and **1c-Ru** in that among the U,D pairs, U is always appreciately greater than D *; inspection of the figures suggests that this correlates with an unsymmetrical distribution of the phenyl substituents of the ligand above and below the plane, an asymmetry which becomes even more striking in the symmetrically substituted tris-complexes, to be examined subsequently.

Conclusions

Comparisons of the molecular structures of eleven complexes of the type $M_3(CO)_{11}(L)$ (M = Ru or Os, L = group 15 ligand), six of which have been determined in the present study, suggest the following trends:

(*i*) The group 15 ligand coordinates in an equatorial site;

(*ii*) As a result of steric interactions between the group 15 ligand and the CO group *cis* to it on the adjacent metal atom, the M–M bond *cis* to the *P*- or *As*-ligand is the longest of the three M–M separations;

(*iii*) The lengthening of this bond increases with increasing cone angle of the group 15 ligand;

(*iv*) In compensation, increased back-bonding from the metal to the CO group *trans* to this bond results in a shortening of the M–CO separation;

(*v*) M–P (or As) distances increase with increasing cone-angle;

(*vi*) The separations $M–CO_{ax}$ are greater than $M–CO_{eq}$ as a result of the greater competition between the CO_{ax} ligands, compared with the CO_{eq} ligand and the metal atom, for back-bonding electron density from the same metal orbital [23];

(*vii*) The greater deviations from linearity of the $M–C–O_{ax}$ moieties (5–8°) compared with $M–C–O_{eq}$ (1.7–3°) result from Van der Waals repulsions between the oxygen atoms of the CO_{ax} ligands;

(*viii*) Where comparisons can be made, the atom separations are consistent with differences in atomic radii of ca. 0.2 Å for ruthenium and osmium, and of ca. 0.1 Å for phosphorus and arsenic (smaller atom named first).

Experimental

General conditions. All reactions were run under nitrogen; no special precautions were taken to exclude air during work-up, since all complexes proved to be stable in air as solids, and for short times in solution. Solvents were dried and distilled (dme and thf from sodium diphenylketyl) before use.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^{1}H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 4 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

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* For the definition of U and D, see p. 174.

Starting materials. $Ru_3(CO)_{12}$ [12] and $Os_3(CO)_{12}$ [24] were made by the cited literature methods; the ligands $PPh(OMe)_2$ (Strem) and $P(OCH_2CF_3)_3$ (Aldrich) were commercial products and used as received.

Synthesis

Complexes **1c-Ru**, **1i-Ru**, and **1n-Ru** were available from the earlier study on ETC substitution reactions of $M_3(CO)_{12}$ [1]. The other complexes were obtained from the reactions described below.

(a) Reaction between $Ru_3(CO)_{12}$ and $P(OCH_2CF_3)_3$. Addition of $Na^+[Ph_2CO]^{-\cdot}$ (0.1 ml of a 0.025 *M* solution in thf) to a solution of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and $P(OCH_2CF_3)_3$ (102 mg, 0.31 mmol) in thf (20 ml) resulted in gas evolution. After stirring for 30 min, the solvent was removed from the red-orange solution under reduced pressure. Preparative TLC of the residue (3/1, petroleum spirit/CH_2Cl_2) eluted four major bands. Band 1 (yellow, R_f 0.81) was $[Ru_3(CO)_{12}]$ (40 mg, 20%) (IR, TLC identification); Band 2 (yellow) gave yellow crystalline $Ru_3(CO)_{11}\{P(OCH_2CF_3)_3\}$ (**1l-Ru**) (32 mg, 11%) (from CH_2Cl_2/MeOH), m.p. 54–55°C. Anal. Found: C, 21.75; H, 0.63%; *M* (EI-MS) 941. $C_{17}H_6F_9O_{14}PRu_3$ calc: C, 21.74; H, 0.64%; *M* 941. Band 3 (orange, R_f 0.53) was crystallized (CH_2Cl_2/petroleum spirit) to give pale orange $Ru_3(CO)_{10}\{P(OCH_2CF_3)_3\}_2$ (**2l-Ru**), (81 mg, 21%) m.p. 73–75°C. Anal. Found: C, 21.35; H, 1.04%; *M* (FAB-MS) 1241. $C_{22}H_{12}F_{18}O_{16}P_2Ru_3$ calc: C, 21.31; H, 0.98%; *M* 1241. This product was closely followed by a second orange compound (band 3, R_f 0.48) which was crystallized (Et_2O/pentane) to yield $Ru_3(CO)_9\{P(OCH_2CF_3)_3\}_3$ (**3l-Ru**) (35 mg, 7%), m.p. 71–72°C. Anal. Found: C, 21.08; H, 1.17%; *M* (FAB-MS) 1541. $C_{27}H_{18}F_{27}O_{18}P_3Ru_3$ calc: C, 21.08; H, 1.17%; *M* 1541.

IR ν(CO) spectra: $Ru_3(CO)_{11}\{P(OCH_2CF_3)_3\}$ (C_6H_{12}): 2115w, 2065s, 2049m, 2031s, 2009sh, 2001sh, 1995sh cm^{-1}; $Ru_3(CO)_{10}\{P(OCH_2CF_3)_3\}_2$ (CH_2Cl_2): 2102w, 2051s, 2021vs cm^{-1}; $Ru_3(CO)_9\{P(OCH_2CF_3)_3\}_3$ (CH_2Cl_2): 2079vw, 2014s, 1989sh cm^{-1}.

Thermally-induced reactions between $Os_3(CO)_{12}$ and phosphines

(a) Triphenylphosphine, PPh_3. (*i*) A mixture of $Os_3(CO)_{12}$ (100 mg, 0.11 mmol) and excess triphenylphosphine (100 mg, 0.40 mmol) was refluxed in toluene (50 ml) for 14 h. Evaporation of solvent and TLC of the residue (silica gel; 1/4 acetone/light petroleum) gave four bands, $R_f = 0.73$, 0.58, 0.43, 0.28, which on separation and crystallization from light petroleum yielded recovered $Os_3(CO)_{12}$, yellow crystals of **1b-Os** (13 mg, 10%), m.p. 175–178°C (dec.), orange-red crystals of **2b-Os** (43 mg, 29%) m.p. 205–210°C (dec.), and orange-red crystals of **3b-Os** (92 mg, 52%), m.p. 188–192°C (dec.), respectively.

(*ii*) A mixture of $Os_3(CO)_{12}$ (50 mg, 0.055 mmol) and excess PPh_3 (70 mg, 0.28 mmol) was refluxed in xylene (25 ml) for 14 h. Removal of solvent and TLC of the residue afforded three bands, $R_f = 0.52$, 0.39, 0.23, which on separation and crystallization from light petroleum yielded a yellow minor product [ν(CO) at 2072w, 2057m, 2040w, 2010m, 2000s, 1960m, 1947mw cm^{-1}], orange-red crystals of **2b-Os** (25 mg, 33%) and orange-red crystals of **3b-Os** (48 mg, 55%), respectively.

IR ν(CO) spectra: $Os_3(CO)_{11}(PPh_3)$: 2108w, 2068w, 2055ms, 2035ms, 2020s, 2005m, 1987m, 1965vw, 1950w cm^{-1} (lit. [25]: 2108m, 2055s, 2035ms, 2019s, 2000m, 1989m, 1978m, 1956mw cm^{-1}); $Os_3(CO)_{10}(PPh_3)_2$: 2085w, 2070vw, 2050w, 2032s, 2015m, 2000vs, 1980m(br), 1960sh cm^{-1} (lit. [25]: 2085mw, 2030s, 2012m, 1998s, 1969m, 1951mw cm^{-1}; $Os_3(CO)_9(PPh_3)_3$: 2070vw, 2035vw, 1997m, 1982s, 1955m(br) cm^{-1} (lit. [25]: 2053w, 1999(sh), 1990m, 1976s, 1944m, cm^{-1}).

(b) Dimethoxyphenylphosphine, $PPh(OMe)_2$. (*i*) A mixture of $Os_3(CO)_{12}$ (100 mg, 0.11 mmol) and excess $PPh(OMe)_2$ (214 mg, 1.26 mmol) was refluxed in toluene (80 ml) for 16 h. Removal of solvent and TLC of the residue (silica gel; 1/4 acetone/light petroleum) gave four bands, R_f 0.75, 0.53, 0.42 and 0.33, which on separation and crystallization from petroleum spirit yielded recovered $Os_3(CO)_{12}$, yellow crystals of **1i-Os** (74 mg, 28%), m.p. 90–92°C, orange crystals of **2i-Os** (122 mg, 55%), m.p. 122°C, and **3i-Os** (31 mg 12%) as an orange oil, respectively.

Table 3

Non-hydrogen atom coordinates for **1i-Ru**

Atom	*x*	*y*	*z*
Ru(1)	0.45206(3)	0.08225(1)	0.18847(2)
Ru(2)	0.20301(3)	0.14577(2)	0.00915(2)
Ru(3)	0.44634(3)	0.22188(1)	0.17470(2)
Phosphine ligand			
P	0.69420(11)	0.05766(5)	0.33162(7)
O(111)	0.8314(3)	0.0899(2)	0.3172(2)
C(111)	0.9990(5)	0.0742(3)	0.3830(4)
O(121)	0.7426(4)	−0.0174(3)	0.3574(2)
C(121)	0.7315(8)	−0.0614(3)	0.2780(4)
C(131)	0.7365(4)	0.0799(2)	0.4619(3)
C(132)	0.6877(5)	0.0408(2)	0.5174(3)
C(133)	0.7110(6)	0.0612(3)	0.6137(4)
C(134)	0.7819(7)	0.1174(3)	0.6568(4)
C(135)	0.8332(6)	0.1572(3)	0.6046(4)
C(136)	0.8108(5)	0.1388(2)	0.5056(4)
Carbonyl groups			
C(1U)	0.5504(5)	0.0678(2)	0.1025(3)
O(1U)	0.6123(4)	0.0543(2)	0.0569(2)
C(1D)	0.3665(5)	0.1046(2)	0.2777(3)
O(1D)	0.3235(4)	0.1117(2)	0.3360(3)
C(12)	0.3539(5)	−0.0006(2)	0.1568(3)
O(12)	0.2932(5)	−0.0502(2)	0.1385(3)
C(2U)	0.3431(5)	0.1588(2)	−0.0479(3)
O(2U)	0.4141(4)	0.1665(2)	−0.0892(2)
C(2D)	0.0793(5)	0.1316(2)	0.0803(3)
O(2D)	−0.0011(4)	0.1229(2)	0.1137(3)
C(21)	0.1104(5)	0.0691(2)	−0.0735(4)
O(21)	0.0559(4)	0.0256(2)	−0.1241(3)
C(23)	0.0660(5)	0.2135(2)	−0.0787(3)
O(23)	−0.0166(4)	0.2526(2)	−0.1323(3)
C(3U)	0.6167(5)	0.1999(2)	0.1449(3)
O(3U)	0.7213(4)	0.1939(2)	0.1321(3)
C(3D)	0.2784(5)	0.2334(2)	0.2081(4)
O(3D)	0.1845(4)	0.2467(2)	0.2297(3)
C(31)	0.6000(5)	0.2567(2)	0.3079(4)
O(31)	0.6880(4)	0.2806(2)	0.3848(3)
C(32)	0.3887(5)	0.3002(1)	0.0943(4)
O(32)	0.3577(5)	0.3467(2)	0.0465(3)

(*ii*) A mixture of $Os_3(CO)_{12}$ (50 mg, 0.055 mmol) and excess $PPh(OMe)_2$ (107 mg, 0.63 mmol) was refluxed in xylene (40 ml) for 6.5 h. Removal of solvent and TLC of the residue afforded three bands, $R_f = 0.46$, 0.36, 0.29, which yielded, on

Table 4

Non-hydrogen atom coordinates for **1l-Ru**

Atom	*x*	*y*	*z*
Ru(1)	0.76193(4)	−0.01177(3)	0.87943(3)
Ru(2)	0.91307(4)	−0.24728(3)	0.81711(4)
Ru(3)	0.78910(4)	−0.08808(3)	0.61470(3)
Phosphine ligand			
P	0.6520(1)	0.1803(1)	0.8234(1)
O(111)	0.5396(4)	0.1838(3)	0.7633(4)
C(111)	0.4600(6)	0.2911(5)	0.7056(8)
C(112)	0.3525(5)	0.2777(6)	0.7213(6)
F(111)	0.3525(5)	0.1828(5)	0.6626(5)
F(112)	0.3261(5)	0.2613(5)	0.8442(4)
F(113)	0.2815(4)	0.3742(5)	0.6706(6)
O(121)	0.6934(3)	0.2586(3)	0.7079(3)
C(121)	0.7540(6)	0.3404(5)	0.7228(6)
C(122)	0.7392(7)	0.4214(5)	0.6059(7)
F(121)	0.7940(5)	0.4994(4)	0.6106(5)
F(122)	0.7758(6)	0.3623(5)	0.4983(4)
F(123)	0.6404(5)	0.4850(4)	0.5814(6)
O(131)	0.6152(4)	0.2869(3)	0.9251(4)
C(131)	0.5945(7)	0.2733(6)	1.0612(7)
C(132)	0.6298(7)	0.3509(6)	1.1278(7)
F(131)	0.6045(5)	0.4627(4)	1.0905(5)
F(132)	0.6210(7)	0.3376(5)	1.2565(5)
F(133)	0.7427(6)	0.3120(8)	1.1016(8)
Carbonyl groups			
C(1U)	0.8858(5)	0.0455(4)	0.8743(4)
O(1U)	0.9555(4)	0.0837(4)	0.8806(4)
C(1D)	0.6370(5)	−0.0703(4)	0.8849(5)
O(1D)	0.5595(4)	−0.0953(4)	0.8971(4)
C(12)	0.7682(5)	−0.0274(5)	1.0670(5)
O(12)	0.7741(5)	−0.0386(5)	1.1767(4)
C(2U)	1.0214(6)	−0.1721(5)	0.7583(6)
O(2U)	1.0943(4)	−0.1410(4)	0.7286(5)
C(2D)	0.7932(5)	−0.3133(4)	0.8656(5)
O(2D)	0.7334(4)	−0.3620(4)	0.8961(4)
C(21)	0.9779(6)	−0.3041(5)	0.9823(6)
O(21)	1.0179(5)	−0.3404(5)	1.0802(5)
C(23)	0.9862(6)	−0.3878(5)	0.7133(6)
O(23)	1.0313(4)	−0.4677(4)	0.6570(5)
C(3U)	0.8768(5)	0.0198(4)	0.6057(4)
O(3U)	0.9234(4)	0.0876(3)	0.5888(4)
C(3D)	0.6875(5)	−0.1814(3)	0.6416(5)
O(3D)	0.6265(4)	−0.2346(4)	0.6446(4)
C(31)	0.6832(6)	0.0331(5)	0.5146(5)
O(31)	0.6186(5)	0.1057(4)	0.4512(5)
C(32)	0.8722(5)	−0.1896(5)	0.4769(5)
O(32)	0.9200(4)	−0.2467(3)	0.3948(4)

separation, yellow crystals of **1i-Os** (7 mg, 12%), orange crystals of **2i-Os** (24 mg, 37%) and **3i-Os** (30 mg, 41%) as an orange oil.

IR ν(CO) spectra: $Os_3(CO)_{11}\{PPh(OMe)_2\}$: 2110w, 2067vw, 2052s, 2035s, 2018s, 2000s, 1995s, 1987m, 1955w cm^{-1}; $Os_3(CO)_{10}\{PPh(OMe)_2\}_2$: 2090w, 2070vw, 2030s, 2020(sh), 2005vs, 1975m(br) cm^{-1}; $Os_3(CO)_9\{PPh(OMe)_2\}_3$: 2000s, 1992vs, 1957m(br) cm^{-1}.

^1H NMR ($CDCl_3$): $Os_3(CO)_{11}\{PPh(OMe)_2\}$: δ 3.58 (d, *J* 13 Hz, 6H, OMe), 7.45 (m, 5H, Ph) ppm; $Os_3(CO)_{10}\{PPh(OMe)_2\}$: δ 3.60 (d, *J* 13 Hz, 6H, OMe), 7.42 (m, 5H, Ph) ppm; $Os_3(CO)_9\{PPh(OMe)_2\}_3$: δ 3.47 (d, *J* 13 Hz, 6H, OMe), 7.40 (m, 5H, Ph) ppm.

Table 5

Non-hydrogen atom coordinates for **1n-Ru**

Atom	*x*	*y*	*z*
Ru(1)	0.35391(3)	0.02488(2)	0.18334(3)
Ru(2)	0.33054(3)	−0.16326(2)	0.13247(3)
Ru(3)	0.16199(3)	−0.05410(3)	0.15232(4)
Phosphine ligand			
P(1)	0.30155(9)	0.16863(7)	0.17375(10)
O(111)	0.2437(3)	0.2026(2)	0.2686(3)
C(111)	0.2108(6)	0.2960(4)	0.2604(5)
O(112)	0.3852(3)	0.2433(2)	0.1753(3)
C(112)	0.3492(5)	0.3373(3)	0.1659(5)
O(113)	0.2283(3)	0.1949(2)	0.0651(3)
C(113)	0.1953(5)	0.2880(4)	0.0589(5)
C(2)	0.2382(4)	0.3409(3)	0.1570(4)
C(3)	0.2044(5)	0.4408(3)	0.1498(5)
C(4)	0.0963(6)	0.4558(4)	0.1311(7)
Carbonyl ligands			
C(1U)	0.3667(4)	0.0255(3)	0.0301(3)
O(1U)	0.3810(4)	0.0358(3)	−0.0573(3)
C(1D)	0.3372(5)	0.0197(4)	0.3349(5)
O(1D)	0.3355(6)	0.0220(4)	0.4265(4)
C(12)	0.4895(4)	0.0512(4)	0.2250(5)
O(12)	0.5688(4)	0.0706(4)	0.2546(5)
C(2U)	0.2862(5)	−0.1490(4)	−0.0233(4)
O(2U)	0.2622(5)	−0.1486(3)	−0.1132(4)
C(2D)	0.3769(4)	−0.1647(4)	0.2889(4)
O(2D)	0.4056(4)	−0.1731(3)	0.3772(3)
C(21)	0.4561(5)	−0.2049(4)	0.1020(5)
O(21)	0.5279(4)	−0.2329(4)	0.0797(4)
C(23)	0.2611(5)	−0.2754(4)	0.1336(5)
O(23)	0.2216(5)	−0.3422(3)	0.1337(4)
C(3U)	0.1601(4)	−0.0047(4)	0.0072(5)
O(3U)	0.1497(3)	0.0269(3)	−0.0768(3)
C(3D)	0.1792(5)	−0.1050(5)	0.2985(6)
O(3D)	0.1777(4)	−0.1341(5)	0.3817(4)
C(31)	0.0827(5)	0.0451(4)	0.1908(6)
O(31)	0.0354(4)	0.1028(4)	0.2112(6)
C(32)	0.0667(5)	−0.1447(5)	0.1056(7)
O(32)	0.0092(4)	−0.1977(4)	0.0750(6)

Structure determinations

Unique data sets were measured at ~ 295 K to the specified $2\theta_{max}$ limit using four-circle diffractometers with monochromatic Mo-K_α radiation sources (λ 0.7106$_9$ Å) and operating in conventional $2\theta/\theta$ scan mode. N independent reflections were

Table 6

Non-hydrogen atom coordinates for **1c-Ru**

Atom	x	y	z
Ru(1)	0.77046(1)	0.95129(2)	0.76066(2)
Ru(2)	0.89734(1)	0.98784(2)	0.81478(2)
Ru(3)	0.81309(1)	1.05403(2)	0.89857(2)
Arsine ligand			
As	0.66002(1)	0.94478(2)	0.75454(2)
C(111)	0.6121(1)	0.8693(2)	0.6775(2)
C(112)	0.6238(2)	0.8639(2)	0.6035(2)
C(113)	0.5872(2)	0.8156(2)	0.5465(2)
C(114)	0.5388(2)	0.7733(3)	0.5624(3)
C(115)	0.5274(2)	0.7780(3)	0.6362(3)
C(116)	0.5634(2)	0.8255(2)	0.6947(2)
C(121)	0.6128(2)	1.0443(2)	0.7242(2)
C(122)	0.5543(2)	1.0422(2)	0.6757(2)
C(123)	0.5220(2)	1.1143(3)	0.6549(3)
C(124)	0.5469(2)	1.1882(3)	0.6824(3)
C(125)	0.6045(2)	1.1911(2)	0.7308(3)
C(126)	0.6374(2)	1.1198(2)	0.7512(2)
C(131)	0.6391(2)	0.9120(2)	0.8523(2)
C(132)	0.6123(2)	0.9653(2)	0.8955(2)
C(133)	0.6019(2)	0.9406(3)	0.9670(3)
C(134)	0.6179(2)	0.8638(3)	0.9965(3)
C(135)	0.6437(2)	0.8105(3)	0.9534(3)
C(136)	0.6543(2)	0.8336(2)	0.8810(2)
Carbonyl groups			
C(1U)	0.7847(2)	0.8543(2)	0.8250(2)
O(1U)	0.7916(2)	0.7928(2)	0.8571(2)
C(1D)	0.7571(2)	1.0477(2)	0.6933(2)
O(1D)	0.7459(1)	1.0994(2)	0.6488(2)
C(12)	0.7773(2)	0.8853(3)	0.6740(2)
O(12)	0.7848(1)	0.8453(2)	0.6239(2)
C(2U)	0.9066(2)	0.9018(2)	0.8931(2)
O(2U)	0.9183(1)	0.8508(2)	0.9386(2)
C(2D)	0.8851(2)	1.0782(3)	0.7406(3)
O(2D)	0.8842(2)	1.1300(2)	0.6961(2)
C(21)	0.9210(2)	0.9174(2)	0.7393(2)
O(21)	0.9353(1)	0.8745(2)	0.6961(2)
C(23)	0.9736(2)	1.0338(2)	0.8706(3)
O(23)	1.0198(1)	1.0592(2)	0.9017(2)
C(3U)	0.8085(2)	0.9552(3)	0.9587(3)
O(3U)	0.8038(2)	0.9031(2)	0.9999(2)
C(3D)	0.8079(2)	1.1470(2)	0.8278(2)
O(3D)	0.8015(1)	1.2063(2)	0.7924(2)
C(31)	0.7455(2)	1.0956(3)	0.9340(2)
O(31)	0.7063(1)	1.1239(2)	0.9557(2)
C(32)	0.8797(2)	1.0959(3)	0.9781(2)
O(32)	0.9195(2)	1.1185(2)	1.0264(2)

obtained, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the least-squares refinements (full matrix where possible otherwise 9×9 (or larger) block diagonal) after the application of Gaussian absorption correction.

Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y,

Table 7

Non-hydrogen atom coordinates for **1b-Os**

Atom	x	y	z
Os(1)	0.76720(2)	0.94964(2)	0.76246(2)
Os(2)	0.89816(2)	0.98513(2)	0.81631(2)
Os(3)	0.81281(2)	1.05414(2)	0.90072(2)
Phosphine ligand			
P	0.6592(1)	0.9434(1)	0.7548(1)
C(111)	0.6138(4)	0.8709(5)	0.6815(5)
C(112)	0.6258(4)	0.8675(6)	0.6070(5)
C(113)	0.5886(5)	0.8181(6)	0.5495(6)
C(114)	0.5404(5)	0.7735(6)	0.5660(6)
C(115)	0.5293(5)	0.7778(6)	0.6398(7)
C(116)	0.5662(5)	0.8257(6)	0.6987(6)
C(121)	0.6148(4)	1.0387(5)	0.7259(5)
C(122)	0.5568(5)	1.0373(5)	0.6738(6)
C(123)	0.5245(5)	1.1113(6)	0.6548(7)
C(124)	0.5488(5)	1.1847(5)	0.6844(6)
C(125)	0.6059(5)	1.1853(5)	0.7341(7)
C(126)	0.6388(5)	1.1132(5)	0.7359(6)
C(131)	0.6401(4)	0.9134(5)	0.8482(5)
C(132)	0.6151(5)	0.9668(5)	0.8922(6)
C(133)	0.6044(6)	0.9428(6)	0.9639(6)
C(134)	0.6199(5)	0.8651(7)	0.9922(6)
C(135)	0.6445(6)	0.8100(6)	0.9489(6)
C(136)	0.6547(5)	0.8329(6)	0.8766(6)
Carbonyl groups			
C(1U)	0.7822(4)	0.8515(5)	0.8281(5)
O(1U)	0.7912(3)	0.7907(4)	0.8609(4)
C(1D)	0.7540(4)	1.0444(5)	0.6935(6)
O(1D)	0.7451(4)	1.0978(4)	0.6503(4)
C(12)	0.7740(4)	0.8834(6)	0.6767(6)
O(12)	0.7822(4)	0.8400(5)	0.6270(4)
C(2U)	0.9079(4)	0.8979(6)	0.8945(6)
O(2U)	0.9186(3)	0.8467(4)	0.9401(4)
C(2D)	0.8854(5)	1.0755(6)	0.7409(6)
O(2D)	0.8833(4)	1.1292(4)	0.6979(5)
C(21)	0.9209(4)	0.9138(5)	0.7391(6)
O(21)	0.9340(4)	0.8704(4)	0.6953(4)
C(23)	0.9750(4)	1.0306(6)	0.8709(6)
O(23)	1.0223(4)	1.0566(5)	0.9034(5)
C(3U)	0.8081(6)	0.9557(6)	0.9626(6)
O(3U)	0.8046(5)	0.9013(5)	1.0026(5)
C(3D)	0.8066(5)	1.1476(6)	0.8296(6)
O(3D)	0.8011(4)	1.2050(4)	0.7921(4)
C(31)	0.7455(5)	1.0975(6)	0.9381(6)
O(31)	0.7052(4)	1.1265(5)	0.9592(5)
C(32)	0.8801(5)	1.0970(6)	0.9782(5)
O(32)	0.9222(4)	1.1201(5)	1.0261(4)

Table 8

Non-hydrogen atom coordinates for **1i-Os**

Atom	x	y	z
Os(1)	0.22907(4)	0.30638(3)	0.35850(2)
Os(2)	−0.02222(4)	0.23310(3)	0.31682(3)
Os(3)	0.16156(4)	0.18413(3)	0.21878(2)
Phosphine ligand			
P	0.43954(3)	0.3257(2)	0.3609(2)
O(1)	0.4633(9)	0.3381(6)	0.2679(6)
C(1)	0.5860(18)	0.3615(13)	0.2537(12)
O(2)	0.5079(8)	0.4095(6)	0.4114(6)
C(2)	0.4605(18)	0.4986(10)	0.3903(11)
C(101)	0.5474(10)	0.2417(9)	0.4098(8)
C(102)	0.5992(14)	0.2428(13)	0.4922(10)
C(103)	0.6774(19)	0.1710(2)	0.5293(11)
C(104)	0.7022(18)	0.1035(14)	0.4844(15)
C(105)	0.6481(18)	0.1008(12)	0.4013(13)
C(106)	0.5689(14)	0.1663(9)	0.3640(10)
Carbonyl groups			
C(1U)	0.2652(12)	0.2118(8)	0.4438(7)
O(1U)	0.2911(10)	0.1612(7)	0.4954(6)
C(1D)	0.1928(11)	0.3987(8)	0.2718(7)
O(1D)	0.1797(9)	0.4548(7)	0.2246(6)
C(12)	0.2134(12)	0.3881(8)	0.4443(7)
O(12)	0.2052(11)	0.4363(7)	0.4980(6)
C(2U)	0.0283(12)	0.1224(8)	0.3794(8)
O(2U)	0.0483(10)	0.0596(6)	0.4168(6)
C(2D)	−0.0604(12)	0.3433(9)	0.2564(9)
O(2D)	−0.0968(10)	0.4093(7)	0.2206(6)
C(21)	−0.0790(14)	0.2858(10)	0.4108(8)
O(21)	−0.1134(12)	0.3193(8)	0.4650(7)
C(23)	−0.1658(12)	0.1764(9)	0.2502(9)
O(23)	−0.2525(10)	0.1455(8)	0.2082(8)
C(3U)	0.2443(11)	0.0988(7)	0.3014(7)
O(3U)	0.2954(9)	0.0453(6)	0.3454(6)
C(3D)	0.0814(13)	0.2793(9)	0.1402(7)
O(3D)	0.0425(12)	0.3261(7)	0.0905(6)
C(31)	0.3084(11)	0.1865(10)	0.1691(7)
O(31)	0.3891(10)	0.1861(7)	0.1365(6)
C(32)	0.0576(15)	0.0946(9)	0.1560(8)
O(32)	−0.0027(13)	0.0398(7)	0.1208(7)

z, $U_{iso})_H$ were included constrained at estimated values. Residuals on $|F|$ are quoted at convergence, being conventional R, R' (statistical weights, derived from $\sigma^2(I) = \sigma^2(I)_{diff} + 0.000n\sigma^4(I)_{diff}$). Neutral atom complex scattering factors were employed [26]; computation used the XTAL program system implemented by S.R. Hall on a Perkin–Elmer 3240 computer [27]. Pertinent results are given in Fig. 1(a–f) and Tables 1–14; material deposited comprises structure factor amplitudes, and thermal and hydrogen atom parameters, and non-essential ligand geometries *.

* Copies available on application to the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain).

Table 9

Ruthenium environments for **1i-Ru** (for C(13) read P(1) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.8456(7)	2.8584(7)	2.8723(11)
Ru(N)–C(NU)	1.943(5)	1.932(6)	1.953(5)
Ru(N)–C(ND)	1.922(5)	1.961(6)	1.927(6)
Ru(N)–C(NN + 1)	1.888(4)	1.909(4)	1.909(4)
Ru(N)–C(NN − 1)	*2.2873(9)*	1.915(5)	1.907(5)
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	59.99(2)	60.47(3)	59.54(2)
Ru(N − 1)–Ru(N)–C(NU)	96.1(1)	90.9(1)	96.2(1)
Ru(N − 1)–Ru(N)–C(ND)	79.0(1)	84.0(1)	81.1(1)
Ru(N − 1)–Ru(N)–C(NN + 1)	153.1(1)	160.0(1)	164.8(2)
Ru(N − 1)–Ru(N)–C(NN − 1)	*105.06(3)*	97.0(1)	94.1(1)
Ru(N + 1)–Ru(N)–C(NU)	85.9(1)	80.7(1)	78.3(1)
Ru(N + 1)–Ru(N)–C(ND)	94.0(1)	95.0(1)	95.4(1)
Ru(N + 1)–Ru(N)–C(NN + 1)	95.5(1)	100.1(1)	108.9(1)
Ru(N + 1)–Ru(N)–C(NN − 1)	*162.85(3)*	156.1(1)	151.0(1)
C(NU)–Ru(N)–C(ND)	174.3(2)	174.5(1)	173.5(2)
C(NU)–Ru(N)–C(NN + 1)	92.8(2)	90.3(2)	90.4(2)
C(NU)–Ru(N)–C(NN − 1)	*87.6(1)*	92.6(2)	94.2(2)
C(ND)–Ru(N)–C(NN + 1)	92.9(2)	93.9(2)	90.9(2)
C(ND)–Ru(N)–C(NN − 1)	*90.8(1)*	90.1(2)	91.9(2)
C(NN + 1)–Ru(N)–C(NN − 1)	*100.6(1)*	102.9(2)	99.0(2)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.132(7)	1.130(7)	1.122(7)
C(ND)–O(ND)	1.132(7)	1.120(8)	1.132(8)
C(NN − 1)–O(NN − 1)	–	1.112(6)	1.133(6)
C(NN + 1)–O(NN + 1)	1.137(6)	1.128(5)	1.131(5)
δ(C(NU))	−1.912	−1.894	−1.851
δ(C(ND))	1.850	1.925	1.865
δ(C(NN − 1))	*−0.351*	−0.281	−0.423
δ(C(NN + 1))	0.385	0.161	0.340
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	174.1(3)	174.3(3)	172.3(3)
Ru(N)–C(ND)–O(ND)	172.5(4)	174.8(3)	172.9(4)
Ru(N)–C(NN − 1)–O(NN − 1)	–	177.9(5)	178.4(5)
Ru(N)–C(NN + 1)–O(NN + 1)	178.7(6)	178.5(4)	176.3(4)

Atom numbering. Given the general non-orthogonality of the axial carbonyl groups to the M_3 core plane, the molecules are chiral. The asymmetric units chosen for the structures are given in a common chirality (see Fig. 1a–f), in which the base of the M_3 triangle is horizontal with the unique ligand attached to M(1) directed toward the left of the page, and in consequence of distortions in the coordination polyhedron, lies slightly out of the page toward the reader. (In systems with more than one ligand, ligand 1 always lies in this disposition also.) Axial carbonyl groups directed toward the reader are labelled 'U' (up), while those away are 'D' (down), deviation from the plane of the paper (M_3) being signed −, + respectively. Equatorial carbonyl groups are labelled CO(NM), being attached to M(N) and

Table 10

Ruthenium environments for **1l-Ru** (for C(13) read P(1) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.8591(6)	2.8458(5)	2.8622(5)
Ru(N)–C(NU)	1.920(7)	1.923(7)	1.935(7)
Ru(N)–C(ND)	1.941(7)	1.964(7)	1.951(7)
Ru(N)–C(NN + 1)	1.911(5)	1.936(5)	1.887(5)
Ru(N)–C(NN − 1)	*2.254(1)*	1.900(6)	1.928(5)
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	59.66(2)	60.23(2)	60.12(2)
Ru(N − 1)–Ru(N)–C(NU)	96.8(1)	90.2(1)	93.8(1)
Ru(N − 1)–Ru(N)–C(ND)	83.2(1)	86.8(1)	86.5(1)
Ru(N − 1)–Ru(N)–C(NN + 1)	158.0(2)	158.2(2)	166.2(2)
Ru(N − 1)–Ru(N)–C(NN − 1)	*93.61(4)*	101.0(2)	93.0(1)
Ru(N + 1)–Ru(N)–C(NU)	87.2(1)	83.1(2)	79.1(1)
Ru(N + 1)–Ru(N)–C(ND)	92.6(1)	91.6(1)	94.2(2)
Ru(N + 1)–Ru(N)–C(NN + 1)	99.4(1)	98.2(2)	107.2(2)
Ru(N + 1)–Ru(N)–C(NN − 1)	*152.50(4)*	160.8(2)	151.6(2)
C(NU)–Ru(N)–C(ND)	179.8(2)	174.7(2)	172.0(2)
C(NU)–Ru(N)–C(NN + 1)	88.3(3)	91.3(3)	88.7(3)
C(NU)–Ru(N)–C(NN − 1)	*90.0(1)*	93.5(3)	95.0(3)
C(ND)–Ru(N)–C(NN + 1)	91.6(3)	90.5(3)	89.1(2)
C(ND)–Ru(N)–C(NN − 1)	*90.2(1)*	91.3(3)	93.0(3)
C(NN + 1)–Ru(N)–C(NN − 1)	*107.8(2)*	100.7(2)	100.3(2)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.132(9)	1.132(9)	1.133(8)
C(ND)–O(ND)	1.128(9)	1.115(9)	1.146(10)
C(NN − 1)–O(NN − 1)	–	1.139(8)	1.123(6)
C(NN + 1)–O(NN + 1)	1.120(6)	1.093(7)	1.158(7)
δ(C(NU))	−1.891	−1.866	−1.904
δ(C(ND))	1.914	1.933	1.957
δ(C(NN − 1))	*−0.267*	−0.191	−0.129
δ(C(NN + 1))	0.243	0.324	0.143
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	174.4(4)	171.7(4)	173.1(4)
Ru(N)–C(ND)–O(ND)	172.9(4)	172.7(4)	173.4(5)
Ru(N)–C(NN − 1)–O(NN − 1)	–	178.6(5)	178.5(4)
Ru(N)–C(NN + 1)–O(NN + 1)	178.4(5)	177.2(7)	178.6(5)

nearest, but not coordinated to, M(M). The group 15 ligand always occupies the site of CO(13), so that M(3) is the apex of the M_3 triangle vertical in the page. In consequence of the distortion described above CO(NU) are defined so that the angle M(N + 1)–M(N)–C(NU) is acute, while M(N + 1)–M(N)–C(ND) is obtuse. (Note that in the cyclic permutation, N = 1,2,3, for N = 3, N + 1 is 1). In consequence, the torsion angle defined in Table 2, here (and in subsequent papers) must be obtuse; the modulus is quoted in all cases.

No disorder was observed in the present series of structures. **1c-Ru** and **1b-Os** are isomorphous and have been refined with a common coordinate setting. **1i-Ru** and **1i-Os** are *not* isomorphous and differ in the disposition of the ligand phenyl substituent relative to the rest of the molecule.

Table 11

Ruthenium environments for **1n-Ru** (for C(13) read P(1) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.8582(5)	2.8387(16)	2.8291(20)
Ru(N)–C(NU)	1.927(6)	1.943(5)	1.934(6)
Ru(N)–C(ND)	1.921(6)	1.945(5)	1.940(7)
Ru(N)–C(NN + 1)	1.879(6)	1.908(6)	1.919(7)
Ru(N)–C(NN − 1)	*2.238(1)*	1.900(6)	1.893(7)
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	59.88(2)	59.55(3)	60.57(4)
Ru(N − 1)–Ru(N)–C(NU)	94.6(2)	96.9(2)	92.1(2)
Ru(N − 1)–Ru(N)–C(ND)	83.0(2)	77.4(2)	82.6(2)
Ru(N − 1)–Ru(N)–C(NN + 1)	165.7(2)	152.0(2)	160.6(2)
Ru(N − 1)–Ru(N)–C(NN − 1)	*96.06(5)*	106.5(2)	95.4(2)
Ru(N + 1)–Ru(N)–C(NU)	79.1(1)	83.5(2)	81.8(2)
Ru(N + 1)–Ru(N)–C(ND)	98.7(2)	93.9(2)	92.9(2)
Ru(N + 1)–Ru(N)–C(NN + 1)	109.6(2)	95.1(2)	100.9(2)
Ru(N + 1)–Ru(N)–C(NN − 1)	*152.58(4)*	163.4(2)	155.2(2)
C(NU)–Ru(N)–C(ND)	177.4(2)	174.3(2)	173.9(3)
C(NU)–Ru(N)–C(NN + 1)	92.5(2)	91.1(2)	90.5(3)
C(NU)–Ru(N)–C(NN − 1)	*90.9(1)*	89.8(3)	93.9(3)
C(ND)–Ru(N)–C(NN + 1)	89.5(3)	94.1(2)	93.5(3)
C(ND)–Ru(N)–C(NN − 1)	*90.5(2)*	91.3(2)	89.7(3)
C(NN + 1)–Ru(N)–C(NN − 1)	*96.2(2)*	100.3(3)	103.5(3)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.135(7)	1.113(7)	1.128(7)
C(ND)–O(ND)	1.137(8)	1.112(6)	1.117(9)
C(NN − 1)–O(NN − 1)	–	1.129(8)	1.131(9)
C(NN + 1)–O(NN + 1)	1.123(7)	1.123(7)	1.118(9)
δ(C(NU))	−1.851	−1.888	−1.899
δ(C(ND))	1.848	1.855	1.907
δ(C(NN − 1))	*−0.538*	−0.314	−0.213
δ(C(NN + 1))	0.330	0.413	0.198
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	171.2(5)	173.9(5)	173.2(5)
Ru(N)–C(ND)–O(ND)	173.1(6)	174.0(5)	172.1(6)
Ru(N)–C(NN − 1)–O(NN − 1)	–	176.0(5)	178.1(7)
Ru(N)–C(NN + 1)–O(NN + 1)	175.6(6)	178.8(6)	178.6(6)

Crystal data

1i-Ru $Ru_3(CO)_{11}\{PPh(OMe)_2\}$ = $C_{19}H_{11}O_{13}PRu_3$, M = 781.5, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a 9.647(3), b 20.529(7), c 14.692(5) Å, β 119.93(2)°, U 2522(1) Å^3, D_c ($Z = 4$) 2.06 g cm^{-3}. $F(000) = 1504$. μ_{Mo} 17.6 cm^{-1}. Specimen: 0.26 × 0.25 × 0.50 mm. $A^{\star}_{min,max}$ = 1.41, 1.53. $2\theta_{max}$ 65°. $N = 9185$, N_0 = 5829. $R = 0.035$, $R' = 0.037$ ($n = 5$).

1l-Ru $Ru_3(CO)_{11}\{P(OCH_2CF_3)_3\}$ = $C_{17}H_6F_9O_{14}PRu_3$, M = 939.4, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 12.920(1), b 11.530(2), c 10.189(1) Å, α 85.93(1), β 86.57(1), γ 70.66(1)°, U 1427(1) Å^3. D_c ($Z = 2$) 2.19 g cm^{-3}. $F(000) = 896$. μ_{Mo} 16.4 cm^{-1}. Specimen: 0.21 × 0.15 × 0.45 mm. $A^{\star}_{min,max}$ = 1.25, 1.44. $2\theta_{max}$ 60°. $N = 5161$, $N_0 = 4061$. $R = 0.038$, $R' = 0.054$ ($n = 20$).

Table 12

Ruthenium environments for **1c-Ru** (for C(13) read As(1) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N+1)	2.8498(8)	2.8592(7)	2.8948(7)
Ru(N)–C(NU)	1.922(4)	1.933(4)	1.938(5)
Ru(N)–C(ND)	1.943(4)	1.936(4)	1.940(4)
Ru(N)–C(NN+1)	1.887(4)	1.914(4)	1.895(5)
Ru(N)–C(NN−1)	*2.4639(8)*	1.911(4)	1.909(4)
Angles (°)			
Ru(N−1)–Ru(N)–Ru(N+1)	59.69(1)	60.94(2)	59.37(2)
Ru(N−1)–Ru(N)–C(NU)	91.2(1)	90.7(1)	94.8(1)
Ru(N−1)–Ru(N)–C(ND)	90.0(1)	88.1(1)	85.6(1)
Ru(N−1)–Ru(N)–C(NN+1)	156.5(1)	163.3(1)	168.3(1)
Ru(N−1)–Ru(N)–C(NN−1)	*101.23(2)*	93.8(1)	90.1(1)
Ru(N+1)–Ru(N)–C(NU)	88.0(1)	83.8(1)	84.9(1)
Ru(N+1)–Ru(N)–C(ND)	91.6(1)	92.4(1)	88.5(1)
Ru(N+1)–Ru(N)–C(NN+1)	96.8(1)	102.5(1)	109.9(1)
Ru(N+1)–Ru(N)–C(NN−1)	*160.85(2)*	154.3(1)	148.9(1)
C(NU)–Ru(N)–C(ND)	178.2(2)	176.2(2)	172.0(2)
C(NU)–Ru(N)–C(NN+1)	87.5(2)	89.7(2)	88.6(2)
C(NU)–Ru(N)–C(NN−1)	*91.0(1)*	92.4(2)	92.5(2)
C(ND)–Ru(N)–C(NN+1)	90.8(2)	90.4(2)	89.5(2)
C(ND)–Ru(N)–C(NN−1)	*89.9(1)*	91.3(2)	95.5(2)
C(NN+1)–Ru(N)–C(NN−1)	*102.3(1)*	102.8(2)	101.0(2)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.142(5)	1.135(5)	1.134(6)
C(ND)–O(ND)	1.132(5)	1.143(6)	1.138(5)
C(NN−1)–O(NN−1)	–	1.128(5)	1.134(5)
C(NN+1)–O(NN+1)	1.130(5)	1.131(5)	1.135(6)
δC(NU)	−1.919	−1.916	−1.909
δC(ND)	1.942	1.930	1.934
δC(NN−1)	*−0.075*	−0.166	−0.210
δC(NN+1)	−0.004	0.084	0.165
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	173.9(3)	172.8(4)	172.2(4)
Ru(N)–C(ND)–O(ND)	173.5(3)	172.5(4)	171.8(4)
Ru(N)–C(NN−1)–O(NN−1)	–	178.3(3)	177.8(4)
Ru(N)–C(NN+1)–O(NN+1)	176.2(3)	177.3(4)	176.8(4)

1n-Ru $Ru_3(CO)_{11}\{P(OCH_2)_3CEt\} = C_{17}H_{11}O_{14}PRu_3$, $M = 773.5$, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a 13.57(1), b 14.779(1), c 12.362(3) Å, β 98.34(4)°, U 2453(1) Å^3, D_c ($Z = 4$) 2.10 g cm^{-3}. $F(000) = 1488$. μ_{Mo} 18.2 cm^{-1}. Specimen: 0.45 × 0.25 × 0.17 mm. $A^*_{min,max} = 1.28$, 1.60. $2\theta_{max}$ 60°. $N = 7435$, $N_0 = 5950$. $R = 0.039$, $R' = 0.054$ ($n = 5$).

1c-Ru $Ru_3(CO)_{11}(AsPh_3) = C_{29}H_{15}AsO_{11}Ru_3$, $M = 917.6$, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a 22.496(6), b 16.348(4), c 17.345(5) Å, β 103.65(2)°, U 6198(3) Å^3, D_c ($Z = 8$) 1.97 g cm^{-3}. $F(000) = 3536$. μ_{Mo} 24.3 cm^{-1}. Specimen: 0.20 × 0.28 × 0.32 mm. $A^*_{min,max}$ 1.56, 1.93. $2\theta_{max}$ 60°. $N = 9102$, $N_0 = 6071$. $R = 0.032$, $R' = 0.028$ ($n = 2$).

Table 13

Osmium environments for **1b-Os** (for C(13) read P(1) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Os(N)–Os(N + 1)	2.8905(8)	2.8861(7)	2.9183(7)
Os(N)–C(NU)	1.945(9)	1.939(10)	1.946(10)
Os(N)–C(ND)	1.931(9)	1.944(10)	1.942(10)
Os(N)–C(NN + 1)	1.875(10)	1.892(9)	1.900(12)
Os(N)–C(NN − 1)	*2.370(2)*	1.929(10)	1.889(9)
Angles (°)			
Os(N − 1)–Os(N)–Os(N + 1)	59.58(1)	60.69(2)	59.73(2)
Os(N − 1)–Os(N)–C(NU)	91.1(3)	90.9(3)	95.1(4)
Os(N − 1)–Os(N)–C(ND)	91.0(3)	87.7(3)	86.3(3)
Os(N − 1)–Os(N)–C(NN + 1)	155.6(3)	163.0(3)	169.3(3)
Os(N − 1)–Os(N)–C(NN − 1)	*102.59(6)*	93.7(3)	90.1(3)
Os(N + 1)–Os(N)–C(NU)	87.5(3)	84.6(3)	85.3(3)
Os(N + 1)–Os(N)–C(ND)	91.9(3)	92.4(4)	88.5(3)
Os(N + 1)–Os(N)–C(NN + 1)	96.0(3)	102.5(3)	110.5(3)
Os(N + 1)–Os(N)–C(NN − 1)	*162.10(5)*	154.1(3)	149.4(3)
C(NU)–Os(N)–C(ND)	177.2(5)	176.9(5)	172.1(4)
C(NU)–Os(N)–C(NN + 1)	87.7(4)	89.9(4)	88.0(5)
C(NU)–Os(N)–C(NN − 1)	*91.6(3)*	92.5(4)	92.8(4)
C(ND)–Os(N)–C(NN + 1)	89.7(4)	90.6(4)	89.2(4)
C(ND)–Os(N)–C(NN − 1)	*89.9(3)*	90.3(4)	95.0(4)
C(NN + 1)–Os(N)–C(NN − 1)	*101.8(3)*	103.2(4)	99.9(4)
Carbonyl distances (Å) (δ(C) is the deviation from the Os_3 plane)			
C(NU)–O(NU)	1.13(1)	1.14(1)	1.14(1)
C(ND)–O(ND)	1.13(1)	1.14(1)	1.13(1)
C(NN − 1)–O(NN − 1)	–	1.13(1)	1.15(1)
C(NN + 1)–O(NN + 1)	1.16(1)	1.15(1)	1.15(1)
δC(NU)	−1.940	−1.926	−1.918
δC(ND)	1.930	1.937	1.938
δC(NN − 1)	*−0.069*	−0.140	−0.180
δC(NN + 1)	0.003	0.091	0.150
Carbonyl angles (°)			
Os(N)–C(NU)–O(NU)	174.3(8)	174.4(9)	175.6(9)
Os(N)–C(ND)–O(ND)	177.0(8)	174.1(9)	174.8(10)
Os(N)–C(NN − 1)–O(NN − 1)	–	178.1(8)	177.3(8)
Os(N)–C(NN + 1)–O(NN + 1)	175.0(8)	178.3(9)	177.3(9)

1b-Os $Os_3(CO)_{11}(PPh_3)$ = $C_{29}H_{15}O_{11}Os_3P$, M = 1141.0, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a 22.196(5), b 16.265(3), c 17.370(5) Å, β 103.86(2)°, U = 6088(3) Å^3, D_c (Z = 8) 2.49 g cm^{-3}. $F(000)$ = 4160. μ_{Mo} 124 cm^{-1}. Specimen: 0.05 × 0.37 × 0.32 mm. $A^{\star}_{min,max}$ = 1.8, 15.4. $2\theta_{max}$ 50°. N = 5408, N_0 = 4125. R = 0.031, R' = 0.033 (n = 5).

1i-Os $Os_3(CO)_{11}\{PPh(OMe)_2\}$ = $C_{19}H_{11}O_{13}Os_3P$, M = 1048.9, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a 10.817(3), b 14.993(4), c 16.174(3) Å, β 101.87(2)°, U 2567(1) Å^3, D_c (Z = 4) 2.72 g cm^{-3}. $F(000)$ = 1888. μ_{Mo} = 160 cm^{-1}.

Table 14

Osmium environments for **1i-Os** (for C(13) read P(1) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Os(N)–Os(N + 1)	2.8815(9)	2.8818(9)	2.8863(7)
Os(N)–C(NU)	1.96(1)	1.96(1)	1.93(1)
Os(N)–C(ND)	1.95(1)	1.92(1)	1.99(1)
Os(N)–C(NN + 1)	1.89(1)	1.90(1)	1.92(1)
Os(N)–C(NN − 1)	*2.288(3)*	1.92(1)	1.91(1)
Angles (°)			
Os(N − 1)–Os(N)–Os(N + 1)	59.95(2)	60.11(2)	59.94(2)
Os(N − 1)–Os(N)–C(NU)	94.2(3)	93.0(4)	93.6(4)
Os(N − 1)–Os(N)–C(ND)	84.7(3)	83.4(4)	84.8(4)
Os(N − 1)–Os(N)–C(NN + 1)	160.6(4)	157.8(5)	161.5(4)
Os(N − 1)–Os(N)–C(NN − 1)	*100.64(8)*	95.6(4)	94.3(5)
Os(N + 1)–Os(N)–C(NU)	86.0(4)	85.3(4)	82.7(3)
Os(N + 1)–Os(N)–C(ND)	93.5(3)	92.3(4)	92.9(3)
Os(N + 1)–Os(N)–C(NN + 1)	101.4(4)	98.6(5)	102.6(4)
Os(N + 1)–Os(N)–C(NN − 1)	*160.09(8)*	155.3(4)	153.1(5)
C(NU)–Os(N)–C(ND)	178.9(7)	176.3(6)	175.6(7)
C(NU)–Os(N)–C(NN + 1)	89.3(5)	91.3(5)	89.8(5)
C(NU)–Os(N)–C(NN − 1)	*91.5(4)*	92.3(6)	92.3(5)
C(ND)–Os(N)–C(NN + 1)	91.8(5)	91.8(5)	90.5(6)
C(ND)–Os(N)–C(NN − 1)	*88.6(4)*	88.8(6)	91.9(5)
C(NN + 1)–Os(N)–C(NN − 1)	*98.3(4)*	106.0(6)	103.8(6)
Carbonyl distances (Å) (δ(C) is the deviation from the Os_3 plane)			
C(NU)–O(NU)	1.12(2)	1.12(2)	1.14(1)
C(ND)–O(ND)	1.13(2)	1.17(2)	1.09(2)
C(NN − 1)–O(NN − 1)	–	1.14(2)	1.11(2)
C(NN + 1)–O(NN + 1)	1.15(2)	1.14(2)	1.13(2)
δC(NU)	−1.94	−1.95	−1.90
δC(ND)	1.93	1.90	1.97
δC(NN − 1)	*−0.10*	−0.15	−0.26
δC(NN + 1)	0.18	0.22	0.22
Carbonyl angles (°)			
Os(N)–C(NU)–O(NU)	176 (1)	175 (1)	175 (1)
Os(N)–C(ND)–O(ND)	175 (1)	173 (1)	172 (1)
Os(N)–C(NN − 1)–O(NN − 1)	–	178 (1)	176 (1)
Os(N)–C(NN + 1)–O(NN + 1)	178 (1)	177 (1)	178 (1)

Specimen: 0.15 × 0.20 × 0.35 mm. $A^{\star}_{min,max} = 5.4,\ 12.8$. $2\theta_{max}$ 65°. $N = 8662$, $N_0 = 5506$. $R = 0.047$, $R' = 0.057$ ($n = 5$).

Acknowledgements

Financial support from the Australian Research Grants Scheme is gratefully acknowledged. Some complexes were generously provided by Dr J.G. Matisons and Dr O. bin Shawkataly.

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