Journal of Organometallic Chemistry, 347 (1988) 181–205
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Cluster chemistry

LVI *. Stereochemistry of group 15 ligand-substituted derivatives of $M_3(CO)_{12}$ (M = Ru, Os) B. X-Ray structures of six complexes $M_3(CO)_{10}(L)_2$ (M = Ru, L = PPh_3, $PPh(OMe)_2$, and $P(OCH_2CF_3)_3$; M = Os, L = PPh_3, $PPh(OMe)_2$ and $P(OMe)_3$)

Michael I. Bruce *, Michael J. Liddell,

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001 (Australia)

Caroline A. Hughes, Jennifer M. Patrick, Brian W. Skelton and Allan H. White *

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009 (Australia)

(Received November 2nd, 1987)

Abstract

X-Ray crystal structures of six complexes of the type $M_3(CO)_{10}(L)_2$ (M = Ru, L = PPh_3, $PPh(OMe)_2$, and $P(OCH_2CF_3)_3$; M = Os, L = PPh_3, $PPh(OMe)_2$ and $P(OMe)_3$) have been determined. All contain a triangular M_3 core; the two phosphorus ligands occupy equatorial positions on adjacent metal atoms so that they are approximately *trans* to each other at the ends of the M–M vector. In contrast to complexes $M_3(CO)_{11}(L)$, there is no pronounced lengthening of the M–M bonds *cis* to the group 15 ligand. Other features, including twisting of the ML_4 groups to distort the D_{3h} symmetry towards D_3, are similar to those found for monosubstituted complexes. Thermal reactions between $Os_3(CO)_{12}$ and $P(OMe)_3$, which afford $Os_3(CO)_{12-n}\{P(OMe)_3\}_n$ ($n = 1$–4), are described. Crystal data: $Ru_3(CO)_{10}(PPh_3)_2$: orthorhombic, $P2_12_12_1$, a 34.636(15), b 17.007(10), c 14.806(4) Å, U 8721(7) Å^3, $Z = 8$, N_0 (number of 'observed' data with $I > 3\sigma(I)$) = 4773, $R = 0.071$, $R' = 0.080$; $Os_3(CO)_{10}(PPh_3)_2$: monoclinic, $P2_1/n$, a 17.104(6), b 34.507(11), c 14.832(6) Å, β 92.28(3)°, U 8747(5) Å^3, $Z = 8$, $N_0 = 8011$, $R = 0.048$, $R' = 0.040$; $Ru_3(CO)_{10}\{PPh(OMe)_2\}_2$: monoclinic, Pc, a 9.014(4), b 8.545(4), c

* For Part LV (A), see ref. 1.

0022-328X/88/$03.50

21.728(5) Å, β 100.77(3)°, U 1644(1) Å^3, $Z = 2$, $N_0 = 5269$, $R = 0.024$, $R' = 0.027$; $Os_3(CO)_{10}\{PPh(OMe)_2\}_2$: monoclinic, Pc, a 9.007(5), b 8.565(7), c 21.716(12) Å, β 100.87(5)°, U 1645(1) Å^3, $Z = 2$, $N_0 = 5266$, $R = 0.041$, $R' = 0.043$; $Ru_3(CO)_{10}\{P(OCH_2CF_3)_3\}_2$: orthorhombic, $P2_12_12_1$, a 29.79(2), b 15.827(8), c 8.283(4) Å, U 3906(3) Å^3, $Z = 4$, $N_0 = 2652$, $R = 0.063$, $R' = 0.070$; $Os_3(CO)_{10}\{P(OMe)_3\}_2$: triclinic, $P\bar{1}$, a 24.955(10), b 9.439(4), c 8.944(4) Å, α 84.02(3), β 87.24(3), γ 84.18(3)°, U 2083(1) Å^3, $Z = 3$, $N_0 = 4084$, $R = 0.057$, $R' = 0.068$.

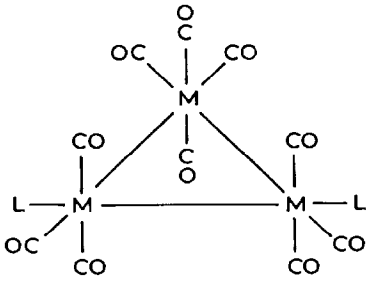
Introduction

The previous paper [1] described our X-ray structural studies of six complexes of the type $M_3(CO)_{11}(L)$, and comparisons of these and several related structures described earlier allowed the stereochemical effects of substituting one CO in $M_3(CO)_{12}$ by a variety of group 15 ligands to be determined. Herein we continue the story with an account of the X-ray structure determinations of the six title complexes **2b-Ru** and **-Os, 2i-Ru** and **-Os, 2l-Ru,** and **2m-Os** (using the convention established in Part A [1]; see Scheme 1 in that paper).

Results and discussion

All complexes described in this paper are disubstituted derivatives $M_3(CO)_{10}(L)_2$. Complexes **2b-Ru** and **2i-Ru** were obtained in high yield from electron transfer-catalysed reactions between $Ru_3(CO)_{12}$ and the group 15 ligand [2]. The other complexes were obtained from mixtures formed by a similar ETC reaction between $Ru_3(CO)_{12}$ and $P(OCH_2CF_3)_3$ [1], or from thermal reactions of $Os_3(CO)_{12}$ with the ligands. In the thermally-induced reaction between $Os_3(CO)_{12}$ and $P(OMe)_3$,

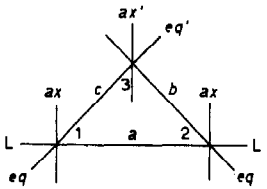
(Continued on p. 187)



L	Ru	Os
CO	**1a-Ru**	**1a-Os**
PPh_3	**2b-Ru**	**2b-Os**
$PPh(OMe)_2$	**2i-Ru**	**2i-Os**
$P(OCH_2CF_3)_3$	**2l-Ru**	
$P(OMe)_3$	**2m-Ru**	**2m-Os**

Table 1

Important bond distances (Å) for $M_3(CO)_{10}(L)_2$ complexes



M	L	No.	Cone angle (°) [a]	M–M			M–P	M–CO				Reference
				a	*b*	*c*		*ax* [c]	*eq* [b]	*ax'* [b]	*eq'* [b]	
Ru	CO	**1a-Ru**	~95	2.852(1)	2.851(1)	2.860(1)	–	1.942(4)	1.921(5)			5
Os	CO	**1a-Os**	~95	2.874(1)	2.875(1)	2.882(1)	–	1.946(6)	1.912(7)			6
Ru	PPh_3 [d]	**2b-Ru**	145	2.846(3)	2.842(4)	2.838(4)	2.357	1.94	1.86	1.84	1.87	[e]
				2.893(3)	2.873(3)	2.881(3)	2.380	1.91	1.87	1.89	1.89	
Os	PPh_3 [d]	**2b-Os**	145	2.887(1)	2.891(1)	2.910(1)	2.362	1.90	1.88	1.86	1.91	[e]
				2.909(1)	2.908(1)	2.899(1)	2.358	1.89	1.88	1.92	1.89	
Ru	$PPh(OMe)_2$	**2i-Ru**	115	2.860(1)	2.865(1)	2.868(1)	2.297	1.929	1.888	1.929	1.907	[e]
Os	$PPh(OMe)_2$	**2i-Os**	115	2.883(1)	2.892(1)	2.895(1)	2.294	1.93	1.86	1.96	1.91	[e]
Ru	$P(OCH_2CF_3)_3$	**2l-Ru**	~110	2.831(2)	2.847(2)	2.861(2)	2.250	1.91	1.87	1.96	1.89	[e]
Ru	$P(OMe)_3$	**2m-Ru**	107	2.845(1)	2.859(1)	2.845(1)	2.298	1.93	1.89	1.94	1.92	4
Os	$P(OMe)_3$ [d]	**2m-Os**	107	2.869(1)	2.890(1)	2.888(2)	2.281	1.91	1.91	1.91	1.91	[e]
				2.881(1)	2.891(1)	2.888(2)	2.291	1.97	1.96	1.81	1.87	

[a] From ref. 8. [b] Average of two. [c] Average of four. [d] Values for two independent molecules. [e] This work.

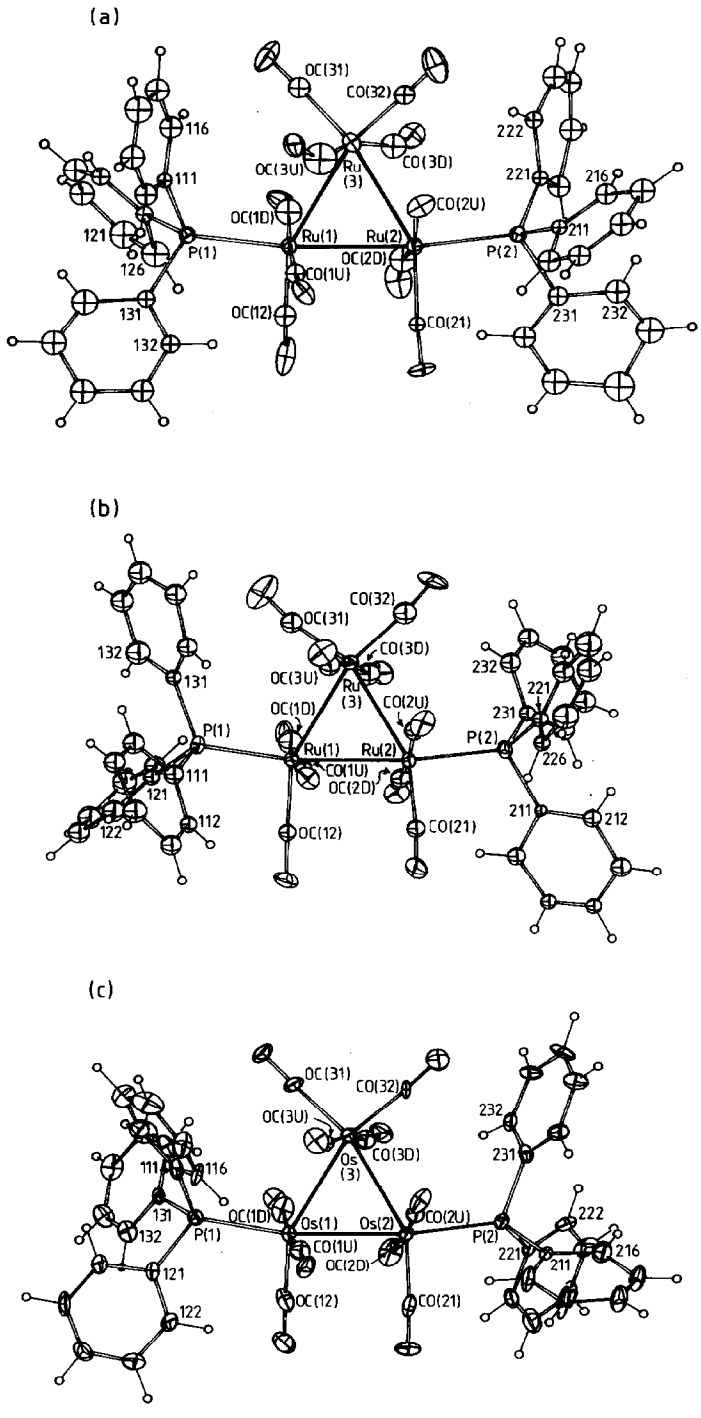


Fig. 1. Molecular projections of the six complexes whose structures are recorded in the present study. 20% probability amplitude thermal ellipsoids are shown for the non-hydrogen atoms, together with labelling. Hydrogen atoms have arbitrary radii of 0.1 Å. (a) $Ru_3(CO)_{10}(PPh_3)_2$ (**2b-Ru**), molecule 1; (b) **2b-Ru**, molecule 2; (c) $Os_3(CO)_{10}(PPh_3)_2$ (**2b-Os**), molecule 1; (d) **2b-Os**, molecule 2; (e) $Ru_3(CO)_{10}\{PPh(OMe)_2\}_2$ (**2i-Ru**); (f) $Os_3(CO)_{10}\{PPh(OMe)_2\}_2$ (**2i-Os**); (g) $Ru_3(CO)_{10}\{P(OCH_2CF_3)_3\}_2$ (**2l-Ru**); (h) $Os_3(CO)_{10}\{P(OMe)_3\}_2$(2m-Os), molecule 1; (i) **2m-Os**, molecule 2.

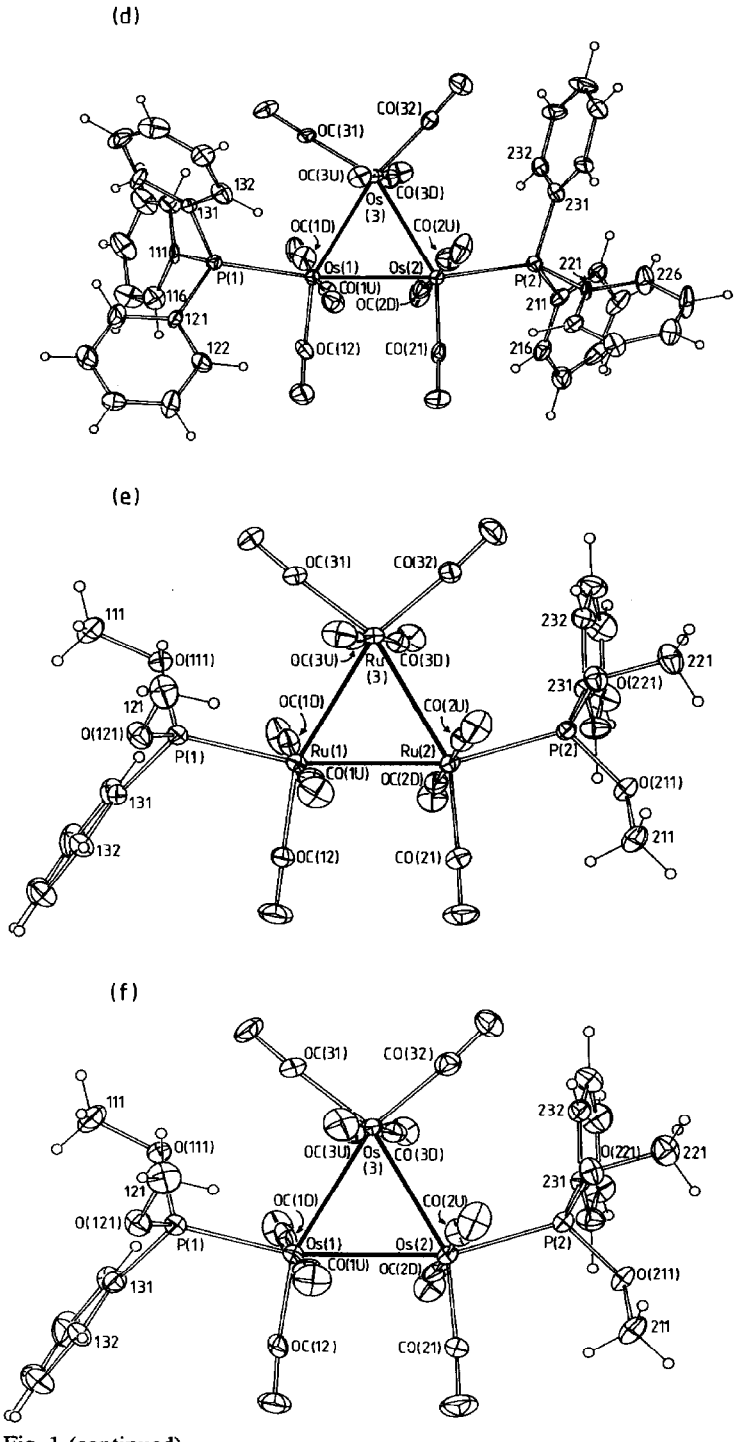


Fig. 1 (continued).

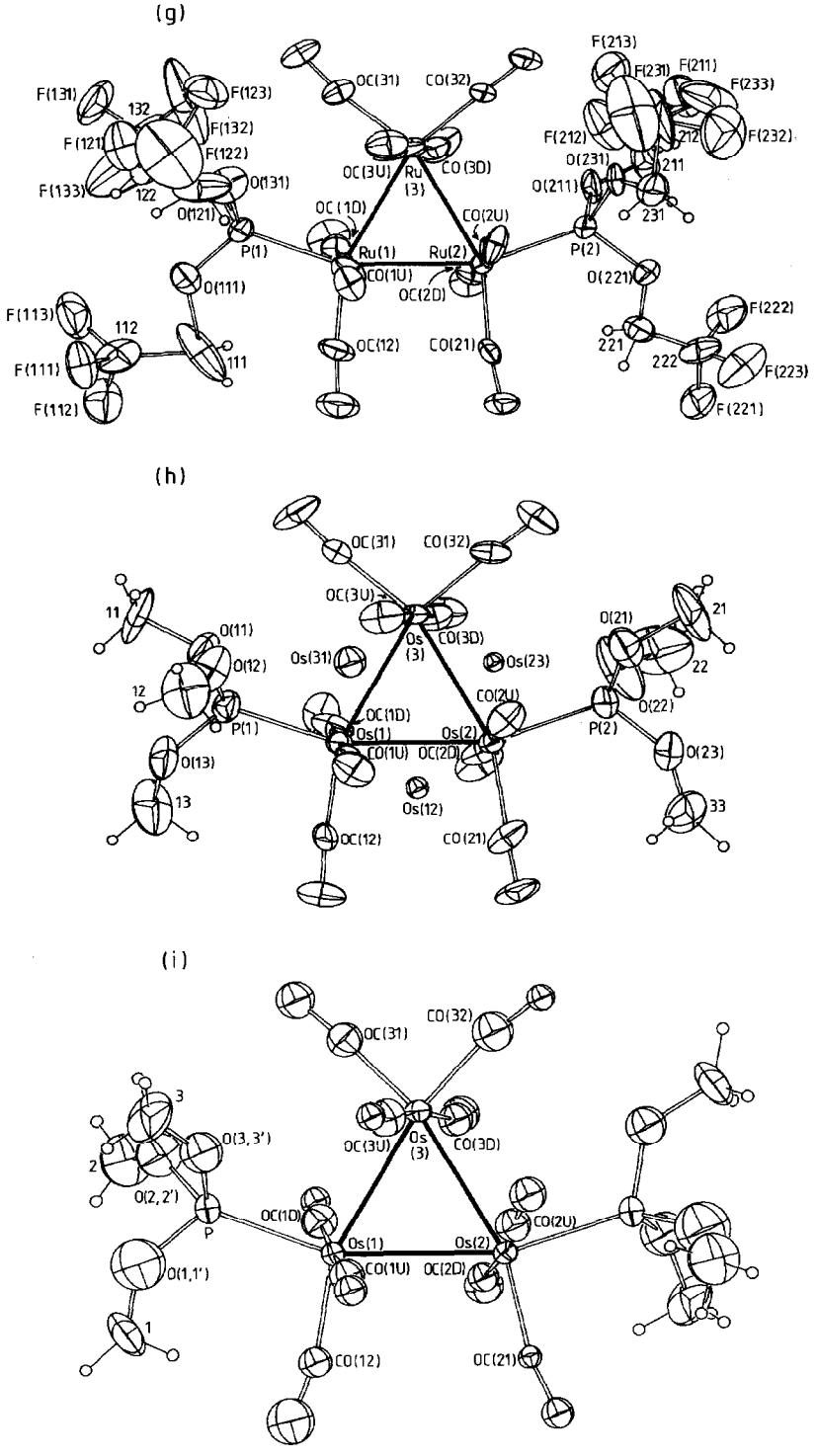


Fig. 1 (continued).

successive introduction of up to four $P(OMe)_3$ ligands was found. This synthesis of the tetrasubstituted product, $Os_3(CO)_8\{P(OMe)_3\}_4$, is similar to that reported recently by others [3]; crystals suitable for an X-ray study were not obtained by us. Complex **2l-Ru** is new, and was characterised by elemental microanalysis and from its IR ν(CO) and FAB-MS spectra [1]. The identities of the osmium complexes were established from their IR ν(CO) spectra and confirmed by the structure determinations.

General structural considerations

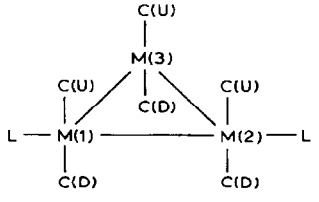
The molecular structures of the six complexes are shown in Fig. 1, while Table 1 summarises important bond lengths found for these compounds and $Ru_3(CO)_{10}\{P(OMe)_3\}_2$ (**2m-Ru**) reported earlier [4]. All contain as common features a triangle of metal atoms with the two group 15 ligands occupying equatorial positions at opposite ends of one of the M–M vectors. The unit cell of **2m-Os** contains two independent molecules, both of which show disorder of the Os_3 core within the ordered $O_{10}P_2$ polyhedron; in molecule 1 the occupancies are 0.95/0.05, whereas in molecule 2, each site has equal occupancy. The disorder was resolved using the model described previously [4].

Metal–metal bond distances

Unlike the monosubstituted complexes, there are no pronounced differences in the M–M separations that can be correlated with the presence of the group 15 ligand. In the examples where two independent molecules make up the asymmetric unit, differences between these exceed the usual criterion of 3σ, although we have some reservations about the significance of the marked differences found for the Ru_3 cores in the two molecules of **2b-Ru**. Differences between Ru–Os pairs (**2b** and

Table 2

Torsion angles (°) in $M_3(CO)_{10}(L)_2$ complexes [a]



L	M	No.	Torsion angles C(n)–M(n)–M($n+1$)–C($n+1$) [b]		
			$n=1$	2	3
PPh_3	Ru [d]	**2b-Ru**	44.8, 34.8	41.0, 37.3	28.7, 41.3
	Os [d]	**2b-Os**	28.6, 28.7	24.5, 24.3	19.8, 30.2
$PPh(OMe)_2$	Ru	**2i-Ru**	24.3, 21.7	21.5, 20.6	20.1, 22.9
	Os	**2i-Os**	22.6, 20.0	22.5, 19.6	18.6, 20.5
$P(OCH_2CF_3)_3$	Ru	**2l-Ru**	11.8, 16.9	13.4, 20.8	10.7, 21.2
$P(OMe)_3$	Ru	**2m-Ru**	32.1, 27.3	31.3, 26.4	35.0, 26.9
	Os	**2m-Os**	(21.7, 14.1)	(20.2, 18.0)	(19.8, 17.0)
			(26.4, 30.0)	(15.2, 31.8)	(24.3, 35.4)

[a] Values in parentheses are for disordered species. [b] Two values for C(nU), C(nD). [c] Ref. 3. [d] Average for two molecules.

Table 3

Non-hydrogen atom coordinates for complex **2b-Ru**

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Ru(1)	0.40281(7)	0.2675(1)	0.8791(1)	0.15944(7)	0.2140(1)	−0.0908(1)
Ru(2)	0.40412(7)	0.2614(1)	1.0712(1)	0.15353(6)	0.2370(1)	0.1023(1)
Ru(3)	0.47429(8)	0.2560(2)	0.9718(2)	0.21435(7)	0.3120(1)	0.0024(2)
Phosphine ligand 1						
P(1)	0.4103(2)	0.2861(4)	0.7232(4)	0.1652(2)	0.2208(4)	−0.2517(5)
C(111)	0.4490(7)	0.351(1)	0.690(2)	0.1286(7)	0.166(1)	−0.310(2)
C(112)	0.4415(9)	0.428(2)	0.666(2)	0.1342(8)	0.129(2)	−0.390(2)
C(113)	0.4687(10)	0.482(2)	0.646(2)	0.1027(9)	0.091(2)	−0.438(2)
C(114)	0.5002(12)	0.459(2)	0.653(3)	0.0662(8)	0.094(1)	−0.399(2)
C(115)	0.5119(10)	0.386(2)	0.678(2)	0.0575(8)	0.130(1)	−0.330(2)
C(116)	0.4846(9)	0.329(2)	0.698(2)	0.0870(8)	0.167(2)	−0.277(2)
C(121)	0.4212(7)	0.198(1)	0.655(2)	0.2078(8)	0.178(2)	−0.297(2)
C(122)	0.4464(8)	0.192(2)	0.586(2)	0.2361(9)	0.219(2)	−0.337(2)
C(123)	0.4488(10)	0.124(2)	0.545(2)	0.2753(12)	0.181(2)	−0.366(3)
C(124)	0.4307(10)	0.060(2)	0.553(2)	0.2797(11)	0.102(2)	−0.354(2)
C(125)	0.4033(12)	0.063(2)	0.618(3)	0.2515(12)	0.064(2)	−0.314(3)
C(126)	0.3923(11)	0.132(2)	0.669(3)	0.2144(8)	0.100(2)	−0.287(2)
C(131)	0.3673(8)	0.326(2)	0.664(2)	0.1628(8)	0.318(1)	−0.304(2)
C(132)	0.3376(8)	0.360(2)	0.704(2)	0.1888(9)	0.375(2)	−0.280(2)
C(133)	0.3070(9)	0.393(2)	0.663(2)	0.1859(10)	0.446(2)	−0.322(2)
C(134)	0.3059(10)	0.393(2)	0.572(2)	0.1617(10)	0.462(2)	−0.385(2)
C(135)	0.3377(10)	0.363(2)	0.526(2)	0.1394(10)	0.410(2)	−0.419(2)
C(136)	0.3646(10)	0.331(2)	0.570(2)	0.1402(9)	0.337(2)	−0.373(2)
Phosphine ligand 2						
P(2)	0.4128(2)	0.2359(4)	1.2272(4)	0.1622(2)	0.2534(4)	0.2597(4)
C(211)	0.4205(7)	0.323(1)	1.294(2)	0.1711(9)	0.158(2)	0.316(2)
C(212)	0.4435(9)	0.322(2)	1.365(2)	0.1486(8)	0.092(2)	0.297(2)
C(213)	0.4481(10)	0.393(2)	1.423(2)	0.1548(9)	0.024(2)	0.338(2)
C(214)	0.4273(10)	0.460(2)	1.394(2)	0.1880(11)	0.019(2)	0.406(2)
C(215)	0.4050(9)	0.455(2)	1.330(2)	0.2094(10)	0.084(2)	0.434(2)
C(216)	0.3990(9)	0.390(2)	1.282(2)	0.2017(9)	0.152(2)	0.389(2)
C(221)	0.4491(7)	0.169(1)	1.257(2)	0.1204(8)	0.291(1)	0.323(2)
C(222)	0.4895(8)	0.192(2)	1.247(2)	0.1042(9)	0.251(2)	0.391(2)
C(223)	0.5180(10)	0.142(2)	1.275(2)	0.0725(9)	0.286(2)	0.438(2)
C(224)	0.5123(10)	0.070(2)	1.296(2)	0.0617(10)	0.353(2)	0.408(2)
C(225)	0.4789(10)	0.042(2)	1.298(2)	0.0774(11)	0.399(2)	0.345(2)
C(226)	0.4414(10)	0.090(2)	1.283(2)	0.1047(10)	0.362(2)	0.304(2)
C(231)	0.3695(8)	0.190(2)	1.288(2)	0.2022(8)	0.316(1)	0.297(1)
C(232)	0.3733(10)	0.189(2)	1.378(2)	0.2002(11)	0.385(2)	0.346(2)
C(233)	0.3460(11)	0.152(2)	1.427(3)	0.2309(10)	0.434(2)	0.371(2)
C(234)	0.3067(12)	0.123(2)	1.380(3)	0.2665(10)	0.406(2)	0.352(2)
C(235)	0.3093(11)	0.123(2)	1.283(2)	0.2714(10)	0.337(2)	0.303(2)
C(236)	0.3403(9)	0.160(2)	1.237(2)	0.2375(9)	0.294(2)	0.284(2)
Carbonyl ligands						
C(1U)	0.3874(9)	0.374(2)	0.894(2)	0.1169(9)	0.287(2)	−0.095(2)
O(1U)	0.3767(6)	0.436(1)	0.909(1)	0.0900(6)	0.323(1)	−0.100(1)
C(1D)	0.4233(12)	0.162(2)	0.873(3)	0.2092(10)	0.151(2)	−0.082(2)
O(1D)	0.4279(7)	0.096(1)	0.861(2)	0.2321(6)	0.106(1)	−0.084(2)
C(12)	0.3546(10)	0.229(2)	0.873(2)	0.1302(9)	0.122(2)	−0.094(2)
O(12)	0.3258(9)	0.198(1)	0.874(1)	0.1140(7)	0.066(1)	−0.089(1)
C(2U)	0.4321(8)	0.367(2)	1.077(2)	0.1351(11)	0.333(2)	0.086(3)

Table 3 (continued)

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
O(2U)	0.4364(6)	0.431(1)	1.087(2)	0.1180(8)	0.397(1)	0.083(1)
C(2D)	0.3915(11)	0.154(2)	1.049(3)	0.1809(8)	0.138(2)	0.102(2)
O(2D)	0.3757(8)	0.091(1)	1.040(2)	0.1946(6)	0.077(1)	0.106(1)
C(21)	0.3520(8)	0.300(1)	1.078(2)	0.1064(9)	0.184(2)	0.109(2)
O(21)	0.3219(5)	0.331(1)	1.088(1)	0.0744(6)	0.151(1)	0.110(2)
C(3U)	0.4655(15)	0.351(3)	0.929(4)	0.1770(11)	0.385(2)	−0.046(3)
O(3U)	0.4767(7)	0.417(1)	0.891(1)	0.1597(7)	0.436(1)	−0.079(1)
C(3D)	0.4694(11)	0.158(2)	1.032(3)	0.2415(10)	0.231(2)	0.055(2)
O(3D)	0.4748(7)	0.096(1)	1.057(2)	0.2695(7)	0.186(1)	0.079(2)
C(31)	0.5101(9)	0.219(2)	0.889(2)	0.2522(11)	0.332(2)	−0.085(3)
O(31)	0.5304(8)	0.190(2)	0.837(2)	0.2747(6)	0.350(2)	−0.131(2)
C(32)	0.5086(9)	0.303(2)	1.054(2)	0.2249(10)	0.389(2)	0.092(2)
O(32)	0.5302(9)	0.333(1)	1.100(2)	0.2342(11)	0.441(1)	0.135(2)

2i) are somewhat larger than those found in the parent carbonyls [5,6]. Within the limited range of examples studied, the average M–M separation increases with increasing ligand cone angle.

Metal–ligand distances

The average M–L distances increase with increasing cone angle of the group 15 ligand. Within each complex, differences in the individual M–L distances do not exceed 5σ; the two molecules of **2b-Ru** have average Ru–P separations differing by 0.05 Å. The Ru–P and Os–P separations are essentially identical in analogous complexes, and are also very close to the values found in the corresponding monosubstituted complexes [1].

Metal–carbonyl distances and angles

As found previously, the M–CO_{ax} distances are longer than M–CO_{eq} on M(1) and M(2), average values over the series being 1.92 and 1.89 Å, respectively. However, this feature is not found with M(3)–CO distances, where in some cases of more dubious precision, M–CO_{eq} is longer than M–CO_{ax}; the average values are both 1.90 Å.

The steric effect of the two group 15 ligands is manifest in the bending away from the ligand of the equatorial CO groups by amounts dependent on the cone angle. Thus, angles M(1)–M(3)–CO(31) and M(2)–M(3)–CO(32) range from 98–107°, while M(1)–M(2)–CO(21) and M(2)–M(1)–CO(12) contract to 92–99°; the M(3)–M(1)–L and M(3)–M(2)–L angles range from 100–113°. In these complexes, the equatorial CO groups may be less inclined to preserve their linearity, M–C–O_{eq} angles being between 165–179°, while M–C–O_{ax} varies between 152–179°. In the one example (**2i-Ru**) where the precision permits some comparison, the CO_{ax} groups on Ru(3) appear to be bent away more from the group 15 ligands (M–C–O 172.2, 171.5(4)°) compared with those on Ru(1)and Ru(2) (173.2–174.6(4)°); similarly the CO_{eq} ligands on Ru(3) have M–C–O angles of 175.8 and 176.2(4)° whereas the averages of the corresponding angles on Ru(1) and Ru(2) are 177.6 and 178.9(3)°.

Table 4

Non-hydrogen atom coordinates for complex **2b-Os**

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Os(1)	0.27852(4)	0.22221(2)	−0.20125(4)	0.77720(4)	0.03399(2)	0.15493(4)
Os(2)	0.23805(4)	0.22327(2)	−0.39208(4)	0.74169(2)	0.02644(2)	0.34434(4)
Os(3)	0.18127(4)	0.16113(2)	−0.28146(5)	0.66860(4)	0.08726(2)	0.23464(5)
Ligand 1						
P(1)	0.2796(3)	0.2175(1)	−0.0421(3)	0.7774(3)	0.0418(1)	−0.0033(3)
C(111)	0.1865(9)	0.2072(5)	0.0124(11)	0.8488(11)	0.0765(5)	−0.0392(10)
C(112)	0.1783(12)	0.1784(5)	0.0767(12)	0.8359(11)	0.1164(5)	−0.0425(13)
C(113)	0.1058(12)	0.1741(7)	0.1200(13)	0.8979(14)	0.1421(5)	−0.0602(15)
C(114)	0.0432(12)	0.1981(7)	0.0950(17)	0.9693(13)	0.1288(6)	−0.0758(15)
C(115)	0.0548(12)	0.2277(7)	0.0344(13)	0.9839(13)	0.0891(6)	−0.0708(16)
C(116)	0.1241(10)	0.2299(6)	−0.0070(10)	0.9241(12)	0.0647(6)	−0.0529(14)
C(121)	0.3112(9)	0.2595(5)	0.0239(10)	0.8023(10)	−0.0018(5)	−0.0681(10)
C(122)	0.3446(12)	0.2920(5)	−0.0122(11)	0.8119(13)	−0.0367(5)	−0.0296(12)
C(123)	0.3737(13)	0.3220(6)	0.0428(14)	0.8320(18)	−0.0681(6)	−0.0807(13)
C(124)	0.3664(14)	0.3205(5)	0.1307(13)	0.8387(16)	−0.0660(6)	−0.1707(15)
C(125)	0.3326(14)	0.2908(6)	0.1701(11)	0.8299(17)	−0.0315(6)	−0.2093(14)
C(126)	0.3048(13)	0.2608(6)	0.1163(12)	0.8112(16)	0.0009(6)	−0.1599(14)
C(131)	0.3485(10)	0.1806(4)	0.0030(10)	0.6877(10)	0.0567(5)	−0.0673(10)
C(132)	0.4215(11)	0.1909(6)	0.0389(12)	0.6162(11)	0.0409(6)	−0.0386(13)
C(133)	0.4732(11)	0.1632(6)	0.0661(13)	0.5481(11)	0.0477(6)	−0.0875(13)
C(134)	0.4571(12)	0.1248(6)	0.0550(14)	0.5483(12)	0.0700(6)	−0.1618(16)
C(135)	0.3837(12)	0.1141(6)	0.0180(15)	0.6163(14)	0.0861(6)	−0.1932(13)
C(136)	0.3327(10)	0.1410(6)	−0.0082(12)	0.6869(13)	0.0786(5)	−0.1445(11)
Ligand 2						
P(2)	0.2104(3)	0.2117(1)	−0.5467(3)	0.7207(3)	0.0362(1)	0.4986(3)
C(211)	0.1613(10)	0.2509(5)	−0.6096(10)	0.8110(10)	0.0434(5)	0.5675(11)
C(212)	0.1342(13)	0.2846(6)	−0.5722(11)	0.8178(11)	0.0709(5)	0.6364(11)
C(213)	0.0998(16)	0.3129(6)	−0.6227(12)	0.8868(14)	0.0729(6)	0.6904(14)
C(214)	0.0877(14)	0.3077(6)	−0.7145(13)	0.9497(12)	0.0502(6)	0.6702(14)
C(215)	0.1172(12)	0.2782(6)	−0.7534(11)	0.9414(11)	0.0226(6)	0.6048(12)
C(216)	0.1520(13)	0.2471(6)	−0.7024(13)	0.8745(11)	0.0192(6)	0.5531(11)
C(221)	0.2984(9)	0.2044(5)	−0.6140(10)	0.6768(10)	−0.0028(4)	0.5617(9)
C(222)	0.3042(11)	0.1768(5)	−0.6793(12)	0.6618(11)	−0.0398(5)	0.5287(11)
C(223)	0.3687(11)	0.1742(6)	−0.7292(14)	0.6315(12)	−0.0691(5)	0.5798(13)
C(224)	0.4295(12)	0.1992(7)	−0.7138(12)	0.6155(12)	−0.0606(6)	0.6680(13)
C(225)	0.4277(13)	0.2263(8)	−0.6503(13)	0.6315(15)	−0.0255(7)	0.7063(13)
C(226)	0.3619(12)	0.2300(6)	−0.5995(11)	0.6608(14)	0.0035(6)	0.6528(13)
C(231)	0.1522(9)	0.1684(5)	−0.5755(10)	0.6598(10)	0.0785(5)	0.5244(10)
C(232)	0.1837(11)	0.1319(5)	−0.5567(10)	0.6947(11)	0.1160(5)	0.5166(11)
C(233)	0.1436(10)	0.0995(5)	−0.5832(12)	0.6495(12)	0.1480(5)	0.5333(13)
C(234)	0.0679(11)	0.1025(6)	−0.6186(14)	0.5740(13)	0.1441(6)	0.5564(14)
C(235)	0.0343(11)	0.1376(5)	−0.6319(14)	0.5396(11)	0.1093(6)	0.5618(12)
C(236)	0.0768(11)	0.1707(5)	−0.6118(12)	0.5828(9)	0.0755(5)	0.5458(12)
Carbonyl groups						
C(1U)	0.2020(11)	0.2603(5)	−0.2010(12)	0.7046(11)	−0.0064(5)	0.1488(12)
O(1U)	0.1603(8)	0.2883(4)	−0.2008(8)	0.6625(8)	−0.0334(4)	0.1403(9)
C(1D)	0.3502(11)	0.1786(6)	−0.2095(12)	0.8435(12)	0.0777(6)	0.1704(12)
O(1D)	0.3987(7)	0.1550(4)	−0.2080(9)	0.8910(9)	0.1029(4)	0.1759(8)
C(12)	0.3639(11)	0.2543(6)	−0.2149(12)	0.8665(10)	0.0029(5)	0.1616(11)
O(12)	0.4168(8)	0.2752(5)	−0.2254(9)	0.9204(8)	−0.0158(5)	0.1694(9)
C(2U)	0.1349(10)	0.2382(5)	−0.3817(11)	0.6418(10)	0.0039(5)	0.3293(12)

Table 4 (continued)

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
O(2U)	0.0679(8)	0.2481(3)	−0.3741(8)	0.5795(8)	−0.0118(4)	0.3272(9)
C(2D)	0.3408(11)	0.2007(5)	−0.3987(11)	0.8376(11)	0.0553(6)	0.3559(13)
O(2D)	0.4020(7)	0.1884(7)	−0.4053(9)	0.8947(7)	0.0733(4)	0.3721(8)
C(21)	0.2787(12)	0.2742(6)	−0.4051(11)	0.7953(12)	−0.0212(5)	0.3534(11)
O(21)	0.3021(9)	0.3054(4)	−0.4079(10)	0.8281(8)	−0.0498(4)	0.3554(9)
C(3U)	0.1074(10)	0.1947(5)	−0.2224(11)	0.5881(10)	0.0529(5)	0.1865(11)
O(3U)	0.0551(7)	0.2099(4)	−0.1945(9)	0.5385(7)	0.0333(4)	0.1607(8)
C(3D)	0.2607(11)	0.1377(5)	−0.3295(12)	0.7495(10)	0.1181(5)	0.2900(12)
O(3D)	0.3080(8)	0.1145(4)	−0.3683(9)	0.7916(8)	0.1414(4)	0.3228(9)
C(31)	0.1787(11)	0.1228(5)	−0.1878(12)	0.6644(10)	0.1185(5)	0.1300(11)
O(31)	0.1755(8)	0.0999(4)	−0.1343(8)	0.6605(8)	0.1381(3)	0.0664(9)
C(32)	0.1012(11)	0.1405(5)	−0.3601(10)	0.5921(11)	0.1105(5)	0.3062(12)
O(32)	0.0502(7)	0.1278(4)	−0.4015(9)	0.5411(8)	0.1245(4)	0.3439(9)

Torsion angles

Inspection of the Figs. 1a–i shows that introduction of the two group 15 ligands has resulted in a considerable degree of twisting of the ML_4 units about the M–M bonds. Table 2 presents the torsion angles of the axial CO groups on adjacent metal atoms. Within Ru–Os pairs (**2b, 2i, 2m**), these angles are larger for Ru than for Os; there is no obvious correlation with the cone angle although the distortion is greatest with the PPh_3 complexes. These distortions lead to the D_3 structure, resulting in relief of steric pressures arising from the interactions between the axial and equatorial CO ligands that can no longer be achieved by M–M bond lengthening, as found in the monosubstituted $M_3(CO)_{11}(L)$ complexes [1]. The various stereochemical and electronic arguments for the adoption of the D_{3h} structure by $M_3(CO)_{12}$ and changes in the substituted complexes leading to the energetically favoured D_3 structure have been summarised by Lauher [7].

Interestingly, in the tris (ligand) arrays described in the subsequent paper, incipient three-fold symmetry is found in all species examined; in the previous paper, although $D_{3h} \rightarrow D_3$ distortions are observed in some degree in all cases, the incipient symmetry of the molecule appears in the disposition of the immediate three substituent atoms of the phosphorus (arsenic). In the present examples, the clash of incipient D_3 and C_{2v} symmetries is particularly evident in the unsymmetrical dispositions of the phosphorus substituents where these are large, e.g. on one ligand two substituents may be directed towards M(3), but on the other they may be directed away (e.g. **2b-Ru**, molecule 2), the overall effect being largely to nullify the systematic U/D torsion angle discrepancies of the mono and tris complexes, and to compound the molecule as an array of "random" distortions.

Conclusions

The conclusions that can be drawn from this study of disubstituted complexes are less clear-cut than those drawn for monosubstituted derivatives:

(*i*) The two group 15 ligands take up positions so that they are as far apart as possible; each occupies an equatorial site, on adjacent metal atoms;

(*ii*) There is no pronounced lengthening of the M–M bonds *cis* to the group 15

(Continued on p. 195)

Table 5

Non-hydrogen atom coordinates for complex **2i–Ru**

Atom	*x*	*y*	*z*
Ru(1)	$\frac{1}{2}$	0.11269(3)	$\frac{1}{4}$
Ru(2)	0.69994(4)	−0.06371(3)	0.34210(2)
Ru(3)	0.46427(3)	0.11940(3)	0.37838(1)
Phosphine ligand 1			
P(1)	0.30143(10)	0.25160(12)	0.19434(4)
O(111)	0.2448(4)	0.3840(4)	0.2360(1)
C(111)	0.1164(7)	0.4830(8)	0.2141(3)
O(121)	0.1524(3)	0.1631(4)	0.1603(2)
C(121)	0.0649(6)	0.0722(8)	0.1946(3)
C(131)	0.3457(5)	0.3530(5)	0.1265(2)
C(132)	0.3045(6)	0.2917(6)	0.0664(2)
C(133)	0.3562(8)	0.3609(9)	0.0173(3)
C(134)	0.4431(7)	0.4929(10)	0.0272(3)
C(135)	0.4804(7)	0.5566(7)	0.0853(3)
C(136)	0.4331(6)	0.4869(7)	0.1359(3)
Phosphine ligand 2			
P(2)	0.84373(10)	−0.13563(11)	0.43665(4)
O(211)	0.9921(3)	−0.2372(3)	0.4359(2)
C(211)	0.9852(6)	−0.3809(5)	0.4006(3)
O(221)	0.7492(3)	−0.2327(4)	0.4787(1)
C(221)	0.8219(7)	−0.3086(7)	0.5361(2)
C(231)	0.9341(4)	0.0198(5)	0.4866(2)
C(232)	0.8647(5)	0.0858(5)	0.5325(2)
C(233)	0.9290(6)	0.2126(7)	0.5673(2)
C(234)	1.0621(6)	0.2755(7)	0.5561(3)
C(235)	1.1322(6)	0.2115(7)	0.5116(3)
C(236)	1.0692(5)	0.0827(6)	0.4769(2)
Carbonyl group			
C(1U)	0.4062(6)	−0.0885(5)	0.2340(2)
O(1U)	0.3489(5)	−0.2052(4)	0.2192(4)
C(1D)	0.6004(5)	0.3101(5)	0.2735(2)
O(1D)	0.6596(5)	0.4281(4)	0.2811(2)
C(12)	0.6036(5)	0.0841(6)	0.1834(2)
O(12)	0.6679(5)	0.0658(6)	0.1438(2)
C(2U)	0.5616(5)	−0.2307(5)	0.3512(2)
O(2U)	0.4898(5)	−0.3360(4)	0.3585(2)
C(2D)	0.8337(5)	0.1097(5)	0.3364(2)
O(2D)	0.9214(4)	0.2027(4)	0.3329(2)
C(21)	0.7888(6)	−0.1772(6)	0.2833(2)
O(21)	0.8378(5)	−0.2429(5)	0.2468(2)
C(3U)	0.3092(5)	−0.0300(6)	0.3476(2)
O(3U)	0.2089(5)	−0.1157(4)	0.3350(2)
C(3D)	0.6341(5)	0.2596(5)	0.4032(2)
O(3D)	0.7232(4)	0.3493(4)	0.4226(2)
C(31)	0.3218(5)	0.2871(5)	0.3720(2)
O(31)	0.2410(4)	0.3885(4)	0.3716(2)
C(32)	0.4739(4)	0.0523(5)	0.4625(2)
O(32)	0.4729(5)	0.0185(6)	0.5134(2)

Table 6

Non-hydrogen atom coordinates for complex **2i-Os**

Atom	*x*	*y*	*z*
Os(1)	$\frac{1}{2}$	0.11257(5)	$\frac{1}{4}$
Os(2)	0.70029(6)	−0.06763(5)	0.34259(3)
Os(3)	0.46279(6)	0.11691(5)	0.37951(2)
Phosphine ligand 1			
P(1)	0.3027(4)	0.2543(4)	0.1955(2)
O(111)	0.2486(13)	0.3874(12)	0.2383(5)
C(111)	0.1194(21)	0.4848(24)	0.2185(11)
O(121)	0.1514(11)	0.1683(14)	0.1622(5)
C(121)	0.0637(22)	0.0803(25)	0.1987(12)
C(131)	0.3438(15)	0.3569(16)	0.1285(7)
C(132)	0.3063(19)	0.2957(22)	0.0675(7)
C(133)	0.3565(29)	0.3696(29)	0.0186(9)
C(134)	0.4427(24)	0.5004(31)	0.0292(10)
C(135)	0.4766(24)	0.5652(25)	0.0857(13)
C(136)	0.4308(20)	0.4909(22)	0.1382(8)
Phosphine ligand 2			
P(2)	0.8422(3)	−0.1405(4)	0.4375(2)
O(211)	0.9894(9)	−0.2425(11)	0.4378(5)
C(211)	0.9875(19)	−0.3839(18)	0.4021(10)
O(221)	0.7441(10)	−0.2365(11)	0.4780(5)
C(221)	0.8143(20)	−0.3110(20)	0.5359(9)
C(231)	0.9327(12)	0.0177(14)	0.4878(6)
C(232)	0.8607(15)	0.0789(16)	0.5337(7)
C(233)	0.9239(21)	0.2002(26)	0.5687(8)
C(234)	1.0568(19)	0.2661(24)	0.5585(9)
C(235)	1.1275(18)	0.2002(18)	0.5136(9)
C(236)	1.0674(17)	0.0793(19)	0.4783(8)
Carbonyl groups			
C(1U)	0.4015(16)	−0.0885(17)	0.2326(8)
O(1U)	0.3413(15)	−0.2039(14)	0.2193(7)
C(1D)	0.6064(14)	0.3083(21)	0.2724(6)
O(1D)	0.6663(16)	0.4265(13)	0.2825(7)
C(12)	0.5997(13)	0.0854(17)	0.1831(6)
O(12)	0.6690(13)	0.0602(18)	0.1451(6)
C(2U)	0.5592(16)	−0.2333(17)	0.3486(8)
O(2U)	0.4890(14)	−0.3440(15)	0.3559(8)
C(2D)	0.8353(15)	0.1034(16)	0.3403(8)
O(2D)	0.9219(11)	0.2001(14)	0.3357(6)
C(21)	0.7957(11)	−0.1709(19)	0.2859(7)
O(21)	0.8433(17)	−0.2431(16)	0.2470(7)
C(3U)	0.3082(14)	−0.0423(17)	0.3488(7)
O(3U)	0.2096(15)	−0.1187(14)	0.3377(8)
C(3D)	0.6296(18)	0.2609(18)	0.4049(7)
O(3D)	0.7225(12)	0.3514(14)	0.4216(6)
C(31)	0.3161(16)	0.2794(19)	0.3723(8)
O(31)	0.2373(14)	0.3849(13)	0.3725(7)
C(32)	0.4724(15)	0.0501(19)	0.4638(8)
O(32)	0.4673(14)	0.0153(15)	0.5134(6)

Table 7

Non-hydrogen atom coordinates for complex **2l-Ru**

Atom	*x*	*y*	*z*
Ru(1)	1.03698(6)	0.76857(10)	0.43940(20)
Ru(2)	0.94220(5)	0.77583(9)	0.46053(19)
Ru(3)	0.98855(6)	0.89483(9)	0.26390(19)
Ligand 1			
P(1)	1.1076(2)	0.8100(4)	0.3934(7)
O(111)	1.1464(6)	0.7682(12)	0.487(2)
C(111)	1.1340(15)	0.657(3)	0.526(7)
C(112)	1.1910(16)	0.651(2)	0.523(7)
F(111)	1.2182(6)	0.681(2)	0.629(3)
F(112)	1.1990(8)	0.571(2)	0.516(3)
F(113)	1.2187(7)	0.664(2)	0.384(4)
O(121)	1.1200(8)	0.9034(12)	0.432(3)
C(121)	1.1398(18)	0.946(2)	0.542(5)
C(122)	1.1605(16)	1.014(2)	0.526(7)
F(121)	1.1935(9)	0.994(2)	0.482(5)
F(122)	1.1663(18)	1.048(3)	0.646(6)
F(123)	1.1385(8)	1.0773(14)	0.462(4)
O(131)	1.1219(5)	0.8080(11)	0.207(2)
C(131)	1.1673(12)	0.829(3)	0.153(4)
C(132)	1.1693(14)	0.911(2)	−0.010(5)
F(131)	1.1994(7)	0.8286(15)	−0.095(3)
F(132)	1.1369(12)	0.824(5)	−0.108(4)
F(133)	1.1719(23)	0.748(3)	−0.044(6)
Ligand 2			
P(2)	0.8708(2)	0.8060(4)	0.3862(7)
O(211)	0.8630(4)	0.7978(11)	0.200(2)
C(211)	0.8249(10)	0.804(3)	0.113(4)
C(212)	0.8222(11)	0.797(6)	−0.024(4)
F(211)	0.7954(7)	0.8246(15)	−0.107(2)
F(212)	0.8476(13)	0.774(2)	−0.112(4)
F(213)	0.8473(11)	0.889(3)	−0.054(5)
O(221)	0.8292(5)	0.7589(10)	0.461(2)
C(221)	0.8320(9)	0.662(2)	0.463(7)
C(222)	0.7900(13)	0.631(2)	0.477(5)
F(221)	0.7900(5)	0.5533(10)	0.501(3)
F(222)	0.7697(7)	0.6404(14)	0.354(3)
F(223)	0.7642(8)	0.6553(14)	0.603(3)
O(231)	0.8521(5)	0.8987(11)	0.415(3)
C(231)	0.8296(12)	0.930(2)	0.532(4)
C(232)	0.8247(18)	1.008(8)	0.433(13)
F(231)	0.8460(12)	1.058(2)	0.524(8)
F(232)	0.7851(10)	1.050(2)	0.587(5)
F(233)	0.7906(13)	1.016(2)	0.364(4)
Carbonyl groups			
C(1U)	1.0383(10)	0.8376(19)	0.638(3)
O(1U)	1.0401(6)	0.8679(10)	0.756(2)
C(1D)	1.0372(9)	0.7124(15)	0.239(3)
O(1D)	1.0394(8)	0.6801(12)	0.116(3)
C(12)	1.0416(10)	0.6723(18)	0.560(3)
O(12)	1.0402(8)	0.6035(14)	0.625(3)
C(2U)	0.9442(6)	0.8614(13)	0.622(3)
O(2U)	0.9403(5)	0.9151(9)	0.719(2)

Table 7 (continued)

Atom	x	y	z
C(2D)	0.9450(8)	0.6908(12)	0.298(3)
O(2D)	0.9442(6)	0.6397(9)	0.206(2)
C(21)	0.9381(7)	0.6951(14)	0.629(3)
O(21)	0.9303(6)	0.6450(11)	0.725(2)
C(3U)	1.0028(15)	0.9690(17)	0.458(4)
O(3U)	1.0141(9)	1.0182(10)	0.546(2)
C(3D)	0.9691(8)	0.8232(14)	0.096(3)
O(3D)	0.9618(7)	0.7812(12)	−0.017(2)
C(31)	1.0386(9)	0.9404(15)	0.141(3)
O(31)	1.0643(6)	0.9770(11)	0.065(2)
C(32)	0.9411(8)	0.9620(13)	0.203(3)
O(32)	0.9125(6)	1.0062(11)	0.170(2)

ligands; indeed, the differences among the three M–M bonds are not large. Differences between Ru–Ru and Os–Os bonds in analogous complexes are similar to the differences found in the parent carbonyls;

(*iii*) Introduction of two group 15 ligands into the $M_3(CO)_{12}$ cluster results in a distortion from D_{3h} symmetry to D_3 by a twisting of the ML_4 moieties about the M–M bonds. In Ru/Os pairs, the degree of twisting is greater for Ru than for Os;

(*iv*) M–P distances are essentially the same as those found in the corresponding monosubstituted complexes, and increase with increasing cone angle;

(*v*) $M–CO_{ax}$ bonds are longer than $M–CO_{eq}$;

(*vi*) $M–CO_{eq}$ bonds on the metal atoms bearing the group 15 ligands are the shortest M–CO separations.

Experimental

General reaction conditions and instrumentation were the same as those described in Part A [1]. Complexes **2b-Ru** [2], **2i-Ru, 2l-Ru, 2b-Os** and **2i-Os** [1] were obtained by the cited methods; $Os_3(CO)_{10}\{P(OMe)_3\}_2$ (**2m-Os**) was isolated as follows.

Reactions between $Os_3(CO)_{12}$ and $P(OMe)_3$

A mixture of $Os_3(CO)_{12}$ (125 mg, 0.14 mmol) and excess $P(OMe)_3$ (0.1 ml, 105 mg, 0.85 mmol) was refluxed in toluene (80 ml) for 16 h. Evaporation of solvent and thin-layer chromatography (TLC) of the residue (silica gel; 1/4 acetone/light petroleum) gave four bands, $R_f = 0.54$, 0.43, 0.35, 0.23, which on separation and crystallization from light petroleum yielded yellow crystals of **1m-Os** (32 mg, 23%), m.p. 88–90 °C, orange crystals of **2m-Os** (71 mg, 47%), m.p. 97 °C, yellow crystals of **3m-Os** (35 mg, 22%), m.p. 152 °C, and **4m-Os** (1 mg) as an orange oil, respectively.

Stirring of a similar reaction mixture in toluene at 90 °C yielded **1m-Os** (45 mg, 41%), **2m-Os** (47 mg, 39%) and **3m-Os** (23 mg, 16%).

IR ν(CO) spectra (C_6H_{12}). $Os_3(CO)_{11}\{P(OMe)_3\}$: 2115w, 2060s, 2044s, 2028vs, 2007w, 2000m, 1992m, 1977w, 1955vw cm^{-1} (lit. [9] 2111m, 2055s, 2039m, 2021s, 2002w, 1992m, 1981w, 1967vw cm^{-1}); $Os_3(CO)_{10}\{P(OMe)_3\}_2$: 2098w, 2040s,

Table 8

Non-hydrogen atom coordinates for complex **2m-Os**

Atom	*x*	*y*	*z*
Molecule 1			
Os(1) [a]	0.87743(4)	0.68653(9)	−0.14474(9)
Os(2) [a]	0.79968(4)	0.53686(8)	0.03914(9)
Os(3) [a]	0.82034(4)	0.82070(8)	0.10011(9)
Os(12) [b]	0.8514(6)	0.5252(15)	−0.0887(15)
Os(23) [b]	0.7882(6)	0.6631(13)	0.1397(13)
Os(31) [b]	0.8607(9)	0.8072(24)	−0.0330(24)
Phosphite ligand 1			
P(1)	0.9204(3)	0.8727(7)	−0.2601(7)
O(11)	0.9522(9)	0.9475(19)	−0.1524(20)
C(11)	0.9776(19)	1.0725(43)	−0.1970(39)
O(12)	0.8821(10)	1.0072(25)	−0.3320(29)
C(12)	0.8633(17)	1.0489(46)	−0.4707(44)
O(13)	0.9600(12)	0.8517(28)	−0.3968(26)
C(13)	1.0019(13)	0.7410(43)	−0.4009(49)
Phosphite ligand 2			
P(2)	0.7440(3)	0.4770(8)	0.2405(7)
O(21)	0.6940(10)	0.5920(24)	0.2552(26)
C(21)	0.6552(15)	0.5842(60)	0.3770(47)
O(22)	0.7689(11)	0.4614(41)	0.3899(22)
C(22)	0.7741(26)	0.4146(57)	0.5231(43)
O(23)	0.7184(13)	0.3344(27)	0.2568(36)
C(23)	0.7121(15)	0.2283(41)	0.1879(41)
Carbonyl groups			
C(1U)	0.8194(10)	0.7326(24)	−0.2834(22)
O(1U)	0.7862(8)	0.7581(22)	−0.3705(18)
C(1D)	0.9316(12)	0.6429(26)	−0.0060(23)
O(1D)	0.9692(8)	0.6259(21)	0.0776(20)
C(12)	0.9073(11)	0.5336(24)	−0.2537(26)
O(12)	0.9205(9)	0.4394(21)	−0.3220(22)
C(2U)	0.7381(9)	0.6339(21)	−0.0564(22)
O(2U)	0.7022(7)	0.6865(18)	−0.1256(20)
C(2D)	0.8614(11)	0.4500(22)	0.1440(26)
O(2D)	0.8970(9)	0.3872(19)	0.2110(22)
C(21)	0.7970(12)	0.3777(23)	−0.0770(24)
O(21)	0.7970(10)	0.2824(17)	−0.1395(19)
C(3U)	0.7762(10)	0.9121(23)	−0.0538(27)
O(3U)	0.7492(8)	0.9765(19)	−0.1528(19)
C(3D)	0.8647(10)	0.7163(24)	0.2528(25)
O(3D)	0.8926(8)	0.6664(18)	0.3457(19)
C(31)	0.8589(10)	0.9880(24)	0.1016(23)
O(31)	0.8795(10)	1.0852(19)	0.1130(25)
C(32)	0.7658(10)	0.8560(24)	0.2492(23)
O(32)	0.7311(8)	0.8759(21)	0.3328(18)
Molecule 2			
Os(1) [c]	0.45767(7)	−0.00076(15)	0.14636(15)
Os(2) [c]	0.51515(7)	0.14569(14)	−0.10032(15)
Os(3) [c]	0.53178(7)	−0.16258(15)	−0.04463(16)

Table 8 (continued)

Atom	x	y	z
Phosphite ligand			
P	0.4170(3)	−0.1894(6)	0.2730(6)
O(1) [c]	0.3627(24)	−0.1600(63)	0.3711(65)
O(1′) [c]	0.3825(15)	−0.0612(38)	0.3292(40)
C(1)	0.3380(14)	−0.0532(40)	0.4263(33)
O(2) [c]	0.4471(18)	−0.3107(46)	0.3826(48)
O(2′) [c]	0.4239(25)	−0.2709(64)	0.4223(67)
C(2)	0.4700(17)	−0.3197(43)	0.5125(36)
O(3) [c]	0.3977(16)	−0.2973(42)	0.1754(43)
O(3′) [c]	0.3681(19)	−0.2678(49)	0.2047(50)
C(3)	0.3681(20)	−0.4061(37)	0.1794(48)
Carbonyl groups [c]			
C(1U)	0.3966(19)	0.0299(50)	0.0044(50)
O(1U)	0.3605(11)	0.0481(29)	−0.0671(29)
C(1D)	0.5203(20)	−0.0499(51)	0.2773(53)
O(1D)	0.5577(10)	−0.0776(26)	0.3460(26)
C(12)	0.4246(18)	0.1665(46)	0.2428(47)
O(12)	0.3999(19)	0.2425(50)	0.3126(52)
C(2U)	0.4723(19)	0.0898(50)	−0.2489(51)
O(2U)	0.4525(13)	0.0416(33)	−0.3623(33)
C(2D)	0.5570(17)	0.1848(42)	0.0714(43)
O(2D)	0.5886(14)	0.2094(36)	0.1519(37)
C(21)	0.4784(13)	0.3372(32)	−0.1098(32)
O(21)	0.4685(11)	0.4528(28)	−0.1243(28)
C(3U)	0.4653(22)	−0.1956(57)	−0.1172(59)
O(3U)	0.4282(10)	−0.2212(25)	−0.1695(26)
C(3D)	0.5897(19)	−0.1022(47)	0.0147(48)
O(3D)	0.6302(14)	−0.0950(36)	0.0904(37)
C(31)	0.5424(20)	−0.3393(50)	0.0538(52)
O(31)	0.5534(14)	−0.4424(36)	0.1389(37)
C(32)	0.5669(24)	−0.2336(62)	−0.2222(63)
O(32)	0.5834(10)	−0.2500(24)	−0.3308(25)

[a] Population: 0.95. [b] Population: 1 − 0.95 = 0.05. [c] Population: 0.5.

2025(sh), 2015vs, 1987s, 1976(sh), 1945w cm^{-1}; $Os_3(CO)_9\{P(OMe)_3\}_3$: 2070vw, 2010ms, 1997s, 1960m(br) cm^{-1}.

^1H NMR spectra. $Os_3(CO)_{11}\{P(OMe)_3\}$: δ ($CDCl_3$) 3.69 (d, J 12 Hz, OMe) ppm; $Os_3(CO)_{10}\{P(OMe)_3\}_2$: δ ($CDCl_3$) 3.58 (d, J 12 Hz, OMe) ppm; $Os_3(CO)_9\{P(OMe)_3\}_3$: δ ($CDCl_3$) 3.57 (d, J 12 Hz, OMe) ppm.

Crystallography. General conditions for measuring data sets, the application of absorption corrections and the refinements were the same as those used in Part A [1]. The molecular plots and atom numbering follow a similar scheme, with the group 15 ligands always occupying the sites of CO(13) and CO(23), so that M(3) is the apex of the M_3 triangle vertical in the page.

Crystal data

2b-Ru: $Ru_3(CO)_{10}(PPh_3)_2 = C_{46}H_{30}O_{10}P_2Ru_3$, M = 1107.9, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a 34.636(15), b 17.007(10), c 14.806(4) Å, U 8721(7) Å^3, D_c (Z = 8) 1.69 g cm^{-3}. $F(000)$ = 3584. μ_{Mo} 10.7 cm^{-1}. Specimen: ca. 0.10 mm^3

Table 9

Ruthenium environments for complex **2b-Ru** (The two values in each entry are for molecules 1, 2, respectively. For C(13,23), read (P1,2) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.846(3), 2.893(3)	2.842(4), 2.873(3)	2.838(4), 2.881(3)
Ru(N)–C(NU)	1.90(3), 1.93(3)	2.04(3), 1.76(4)	1.77(5), 1.94(4)
Ru(N)–C(ND)	1.93(4), 2.03(3)	1.90(4), 1.94(3)	1.90(4), 1.84(3)
Ru(N)–C(NN + 1)	1.80(3), 1.87(3)	*2.370(7), 2.367(7)*	1.86(3), 1.88(4)
Ru(N)–C(NN − 1)	*2.344(7), 2.393(7)*	1.92(3), 1.87(3)	1.88(3), 1.90(4)
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.01(9), 59.67(8)	59.84(8), 59.96(8)	60.15(8), 60.38(8)
Ru(N − 1)–Ru(N)–C(NU)	104.8(9), 98.7(9)	90.9(8), 91.1(13)	90.6(17), 89.3(11)
Ru(N − 1)–Ru(N)–C(ND)	68.7(12), 73.3(9)	81.9(11), 80.9(8)	73.0(12), 79.9(11)
Ru(N − 1)–Ru(N)–C(NN + 1)	144.2(11), 148.9(9)	*169.4(2), 168.6(2)*	157.7(10), 161.8(11)
Ru(N − 1)–Ru(N)–C(NN − 1)	*112.9(2), 113.2(2)*	91.6(7), 92.7(9)	101.2(10), 95.0(11)
Ru(N + 1)–Ru(N)–C(NU)	85.6(9), 83.9(9)	69.1(8), 77.7(12)	67.1(17), 75.8(11)
Ru(N + 1)–Ru(N)–C(ND)	90.3(12), 93.7(9)	94.4(11), 91.5(8)	102.2(12), 96.2(11)
Ru(N + 1)–Ru(N)–C(NN + 1)	92.9(11), 95.7(9)	*113.0(2), 111.2(2)*	106.6(10), 103.6(12)
Ru(N + 1)–Ru(N)–C(NN − 1)	*170.8(2), 169.4(2)*	147.3(7), 151.8(9)	146.6(10), 149.4(11)
C(NU)–Ru(N)–C(ND)	173.5(15), 171.7(13)	163.4(14), 168.8(15)	163.5(21), 168.9(15)
C(NU)–Ru(N)–C(NN + 1)	95.1(14), 97.1(13)	*93.5(8), 94.0(13)*	100.6(10), 95.3(16)
C(NU)–Ru(N)–C(NN − 1)	*90.9(9), 89.9(9)*	98.2(11), 97.8(15)	87.1(19), 86.7(15)
C(ND)–Ru(N)–C(NN + 1)	90.2(16), 91.1(13)	*91.2(11), 92.6(8)*	94.4(15), 94.1(16)
C(ND)–Ru(N)–C(NN − 1)	*92.3(12), 91.3(9)*	97.0(14), 90.5(12)	97.4(15), 97.0(15)
C(NN − 1)–Ru(N)–C(NN + 1)	*95.9(11), 93.5(10)*	*97.3(7), 96.8(9)*	98.5(14), 102.8(16)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.14(3), 1.12(4)	1.11(3), 1.24(3)	1.30(6), 1.15(4)
C(ND)–O(ND)	1.16(5), 1.10(4)	1.22(4), 1.13(3)	1.13(4), 1.29(4)
C(NN − 1)–O(NN − 1)	– –	1.17(3), 1.24(4)	1.14(4), 1.14(4)
C(NN + 1)–O(NN + 1)	1.13(5), 1.10(4)	– –	1.15(4), 1.07(5)
δ(C(NU))	−1.778, −1.899	−1.845, −1.885	−1.578, −1.763
δ(C(ND))	1.747, 1.703	1.852, 1.859	1.636, 1.862
δ(C(NN − 1))	*−0.249, −0.307*	−0.555, −0.644	−0.917, −0.301
δ(C(NN + 1))	0.751, 0.229	*0.332, 0.335*	0.595, 0.625
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	174(3), 174(3)	159(2), 171(3)	152(4), 170(3)
Ru(N)–C(ND)–O(ND)	165(3), 166(3)	166(3), 174(3)	163(3), 162(3)
Ru(N)–C(NN − 1)–O(NN − 1)	– –	173(2), 177(2)	177(3), 169(3)
Ru(N)–C(NN + 1)–O(NN + 1)	173(3), 174(3)	– –	174(3), 173(3)

(no absorption correction). $2\theta_{max}$ 45°. $N = 6340$, $N_0 = 4773$. $R = 0.071$. $R' = 0.080$ (both chiralities) ($n = 5$).

2b-Os: $Os_3(CO)_{10}(PPh_3)_2 = C_{46}H_{30}O_{10}Os_3P_2$, $M = 1375.3$, monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14, variant), a 17.104(6), b 34.507(11), c 14.832(6) Å, β 92.28(3)°, U 8747(5) Å^3, D_c ($Z = 8$) 2.09 g cm^{-3}. $F(000) = 5152$. μ_{Mo} 85 cm^{-1}. Specimen: 0.06 × 0.10 × 0.24 mm. $A^{\star}_{min,max} = 1.64$, 2.36. $2\theta_{max} = 50°$. $N = 14709$, $N_0 = 8011$. $R = 0.048$, $R' = 0.040$ ($n = 5$).

Abnormal features. The cell of this structure is very similar in content to that of its ruthenium counterpart but of monoclinic, rather than orthorhombic symmetry,

and centrosymmetric rather than non-centrosymmetric. As with the ruthenium derivative, the crystal was of less than optimum size, and a few carbon atoms were refined with isotropic thermal parameters.

2i-Ru: $Ru_3(CO)_{10}\{PPh(OMe)_2\}_2 = C_{26}H_{22}O_{14}P_2Ru_3$, $M = 923.6$, monoclinic, space group Pc (C_s^2, No. 7), a 9.014(4), b 8.545(4), c 21.728(5) Å, β 100.77(3)°, U 1644(1) Å^3, D_c ($Z = 2$) 1.87 g cm^{-3}. $F(000) = 904$. μ_{Mo} 14.1 cm^{-1}. Specimen: 0.18 × 0.40 × 0.30 mm. $A^*_{min,max} = 1.29, 1.51$. $2\theta_{max}$ 65°. $N = 5988$, $N_0 = 5269$. $R = 0.024$, $R' = 0.027$ (preferred chirality) ($n = 2$).

2i-Os: $Os_3(CO)_{10}\{PPh(OMe)_2\}_2 = C_{26}H_{22}O_{14}Os_3P_2$, $M = 1119.0$, monoclinic, space group Pc (C_s^2, No. 7), a 9.007(5), b 8.565(7), c 21.716(12) Å, β 100.87(5)°, U

Table 10

Osmium environments for complex **2b-Os** (The two values in each entry are for molecules 1, 2, respectively. For C(13,23) read P(1,2) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Os(N)–Os(N + 1)	2.887(1), 2.909(1)	2.891(1), 2.908(1)	2.910(1), 2.899(1)
Os(N)–C(NU)	1.85(2), 1.87(2)	1.85(2), 1.88(2)	1.95(2), 1.93(2)
Os(N)–C(ND)	1.95(2), 1.89(2)	1.93(2), 1.92(2)	1.76(2), 1.90(2)
Os(N)–C(NN + 1)	1.85(2), 1.87(2)	*2.358(4), 2.354(4)*	1.92(2), 1.89(2)
Os(N)–C(NN − 1)	*2.366(4), 2.362(4)*	1.90(2), 1.88(2)	1.90(2), 1.89(2)
Angles (°)			
Os(N − 1)–Os(N)–Os(N + 1)	59.83(3), 60.08(2)	60.47(3), 59.77(3)	59.69(3), 60.15(3)
Os(N − 1)–Os(N)–C(NU)	97.0(6), 93.3(6)	96.6(5), 98.4(5)	93.0(5), 92.8(5)
Os(N − 1)–Os(N)–C(ND)	76.5(6), 80.5(6)	82.0(5), 80.2(6)	80.1(6), 82.7(5)
Os(N − 1)–Os(N)–C(NN + 1)	146.1(6), 151.6(5)	*169.3(1), 166.3(1)*	159.9(5), 150.8(5)
Os(N − 1)–Os(N)–C(NN − 1)	*109.9(1), 111.0(1)*	92.1(5), 91.6(5)	100.3(5), 106.4(5)
Os(N + 1)–Os(N)–C(NU)	81.4(6), 79.4(5)	79.4(5), 82.2(5)	75.9(5), 85.4(5)
Os(N + 1)–Os(N)–C(ND)	94.3(5), 95.8(5)	93.2(5), 91.3(6)	93.4(6), 93.7(5)
Os(N + 1)–Os(N)–C(NN + 1)	92.6(6), 95.7(5)	*111.6(1), 111.2(1)*	103.4(5), 91.7(5)
Os(N + 1)–Os(N)–C(NN − 1)	*166.2(1), 168.0(1)*	151.0(5), 150.1(5)	155.2(5), 164.6(5)
C(NU)–Os(N)–C(ND)	173.4(8), 173.6(8)	172.2(7), 173.0(8)	169.2(8), 175.2(7)
C(NU)–Os(N)–C(NN + 1)	97.9(9), 96.6(8)	*88.4(5), 90.0(5)*	92.9(7), 92.4(7)
C(NU)–Os(N)–C(NN − 1)	*91.4(6), 93.7(5)*	96.0(8), 94.8(8)	92.0(7), 88.2(7)
C(ND)–Os(N)–C(NN + 1)	87.3(9), 88.1(8)	*91.7(5), 90.1(6)*	91.0(8), 92.3(7)
C(ND)–Os(N)–C(NN − 1)	*91.7(6), 90.3(5)*	91.8(8), 92.0(8)	97.4(8), 91.7(8)
C(NN + 1)–Os(N)–C(NN − 1)	*100.1(6), 94.9(5)*	*96.8(5), 98.5(5)*	98.6(7), 102.4(7)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.20(2), 1.18(2)	1.21(2), 1.19(2)	1.13(2), 1.14(2)
C(ND)–O(ND)	1.16(2), 1.19(2)	1.14(2), 1.18(2)	1.29(2), 1.17(2)
C(NN − 1)–O(NN + 1)	– –	1.15(2), 1.14(2)	1.12(2), 1.16(2)
C(NN + 1)–O(NN + 1)	1.17(2), 1.13(2)	– –	1.13(2), 1.16(2)
δ(C(NU))	−1.784, −1.806	−1.765, −1.806	−1.846, −1.916
δ(C(ND))	1.843, 1.825	1.890, 1.877	1.703, 1.868
δ(C(NN − 1))	*−0.391, −0.344*	−0.302, −0.296	−0.508, −0.254
δ(C(NN + 1))	0.659, 0.504	*0.302, 0.438*	0.379, 0.269
Carbonyl angles (°)			
Os(N)–C(NU)–O(NU)	172(2), 175(2)	179(1), 174(1)	168(1), 177(2)
Os(N)–C(ND)–O(ND)	172(2), 173(2)	177(1), 173(2)	167(2), 170(1)
Os(N)–C(NN − 1)–O(NN − 1)	– –	176(1), 177(1)	175(1), 174(2)
Os(N)–C(NN + 1)–O(NN + 1)	178(2), 177(2)	– –	178(2), 179(2)

1645(1) Å^3, D_c ($Z = 2$) 2.40 g cm^{-3}. $F(000) = 1096$. μ_{Mo} 113 cm^{-3}. Specimen: $0.28 \times 0.27 \times 0.13$ mm. $A^{\star}_{min,max} = 3.3$, 13.8. $2\theta_{max}$ 70°. $N = 7441$, $N_0 = 5266$. $R = 0.041$, $R' = 0.043$ (preferred chirality) ($n = 6$).

Abnormal features. **2i-Ru,Os** are isomorphous and were refined in the same setting.

2i-Ru: $Ru_3(CO)_{10}\{P(OCH_2CF_3)_3\}_2 = C_{22}H_{12}F_{18}O_{16}P_2Ru_3$, $M = 1239.4$, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a 29.79(2), b 15.827(8), c 8.273(4) Å, U 3906(3) Å^3, D_c ($Z = 4$) 2.11 g cm^{-3}. $F(000) = 2384$. μ_{Mo} 13.0 cm^{-1}. Specimen: $0.12 \times 0.25 \times 0.46$ mm. $A^{\star}_{min,max} = 1.17$, 1.38. $2\theta_{max}$ 55°. $N = 4657$, $N_0 = 2652$. $R = 0.063$, $R' = 0.070$ (preferred chirality) ($n = 4$).

Table 11

Ruthenium environments for complex **2i-Ru** (For C(13,23) read P(1,2) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.8595(7)	2.8650(10)	2.8678(7)
Ru(N)–C(NU)	1.919(5)	1.929(4)	1.919(4)
Ru(N)–C(ND)	1.937(4)	1.929(4)	1.939(4)
Ru(N)–C(NN + 1)	1.879(5)	*2.299(1)*	1.912(5)
Ru(N)–C(NN − 1)	*2.295(1)*	1.896(5)	1.902(4)
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.03(2)	60.13(2)	59.84(2)
Ru(N − 1)–Ru(N)–C(NU)	93.9(1)	97.3(1)	94.0(1)
Ru(N − 1)–Ru(N)–C(ND)	81.9(1)	82.5(1)	80.0(1)
Ru(N − 1)–Ru(N)–C(NN + 1)	156.1(1)	*160.54(3)*	155.8(1)
Ru(N − 1)–Ru(N)–C(NN − 1)	*106.50(3)*	95.1(1)	101.4(1)
Ru(N + 1)–Ru(N)–C(NU)	81.6(1)	81.3(1)	81.7(1)
Ru(N + 1)–Ru(N)–C(ND)	94.2(1)	95.9(1)	93.2(1)
Ru(N + 1)–Ru(N)–C(NN + 1)	97.6(1)	*102.91(3)*	98.1(1)
Ru(N + 1)–Ru(N)–C(NN − 1)	*165.69(3)*	153.2(1)	159.3(1)
C(NU)–Ru(N)–C(ND)	175.1(2)	176.9(2)	173.6(2)
C(NU)–Ru(N)–C(NN + 1)	90.5(2)	*88.7(1)*	92.2(2)
C(NU)–Ru(N)–C(NN − 1)	*95.4(1)*	93.1(2)	91.9(2)
C(ND)–Ru(N)–C(NN + 1)	92.3(2)	*90.5(1)*	92.4(2)
C(ND)–Ru(N)–C(NN − 1)	*88.2(1)*	90.1(2)	91.6(2)
C(NN + 1)–Ru(N)–C(NN − 1)	*96.4(1)*	*103.1(1)*	101.8(2)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.142(6)	1.137(6)	1.156(6)
C(ND)–O(ND)	1.138(6)	1.134(6)	1.136(6)
C(NN − 1)–O(NN − 1)	–	1.128(7)	1.131(6)
C(NN + 1)–O(NN + 1)	1.135(6)	–	1.144(6)
δ(C(NU))	−1.872	−1.853	−1.872
δ(C(ND))	1.891	1.876	1.882
δ(C(NN − 1))	*− 0.202*	−0.350	−0.301
δ(C(NN + 1))	0.290	*0.401*	0.350
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	174.2(4)	174.6(4)	172.2(4)
Ru(N)–C(ND)–O(ND)	173.2(4)	174.4(4)	171.5(4)
Ru(N)–C(NN − 1)–O(NN − 1)	–	177.6(4)	175.8(4)
Ru(N)–C(NN + 1)–O(NN + 1)	178.9(4)	–	176.2(4)

Abnormal features. Refinement statistics indicate the asymmetric unit of the non-centrosymmetric crystal studied is the enantiomer of that adopted as conventional for the other structures; Figure 1(g) is thus the inverse of the structure. Ligand thermal motion is very high and possibly a foil for disorder, and in this context and that of the non-centrosymmetric space group, the precision of the molecular geometry is less than desirable. While the prime reason for the thermal motion is probably the high fluorine content, crystal packing in layers normal to a is probably also a substantial contributing factor.

2m-Os: $Os_3(CO)_{10}\{P(OMe)_3\}_2 = C_{16}H_{18}O_{16}Os_3P_2$, $M = 1098.9$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 24.955(10), b 9.439(4), c 8.944(4) Å, α 84.02(3), β 87.24(3),

Table 12

Osmium environments for complex **2i-Os** (For C(13,23) read P(1,2) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Os(N)–Os(N + 1)	2.883(1)	2.892(1)	2.895(2)
Os(N)–C(NU)	1.94(1)	1.93(1)	1.97(1)
Os(N)–C(ND)	1.95(1)	1.91(1)	1.94(2)
Os(N)–C(NN + 1)	1.86(1)	*2.298(3)*	1.91(2)
Os(N)–C(NN − 1)	*2.290(3)*	1.85(2)	1.90(2)
Angles (°)			
Os(N − 1)–Os(N)–Os(N + 1)	60.07(3)	60.16(4)	59.76(2)
Os(N − 1)–Os(N)–C(NU)	93.9(5)	96.2(4)	92.3(4)
Os(N − 1)–Os(N)–C(ND)	83.6(4)	83.6(4)	81.5(5)
Os(N − 1)–Os(N)–C(NN + 1)	157.1(3)	*160.1(1)*	156.1(5)
Os(N − 1)–Os(N)–C(NN − 1)	*106.0(1)*	95.7(5)	101.6(5)
Os(N + 1)–Os(N)–C(NU)	82.2(4)	81.5(5)	82.3(4)
Os(N + 1)–Os(N)–C(ND)	94.2(4)	95.5(4)	93.4(5)
Os(N + 1)–Os(N)–C(NN + 1)	98.5(4)	*102.4(1)*	97.8(5)
Os(N + 1)–Os(N)–C(NN − 1)	*165.3(1)*	154.8(4)	159.6(5)
C(NU)–Os(N)–C(ND)	176.3(6)	176.6(7)	173.7(6)
C(NU)–Os(N)–C(NN + 1)	90.4(7)	*90.1(4)*	92.5(6)
C(NU)–Os(N)–C(NN − 1)	*95.1(4)*	95.0(7)	91.1(6)
C(ND)–Os(N)–C(NN + 1)	90.9(7)	*89.0(5)*	92.7(6)
C(ND)–Os(N)–C(NN − 1)	*88.3(4)*	88.4(7)	91.5(6)
C(NN + 1)–Os(N)–C(NN − 1)	*96.0(4)*	*102.6(4)*	101.8(7)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.14(2)	1.17(2)	1.09(2)
C(ND)–O(ND)	1.15(2)	1.15(2)	1.15(2)
C(NN − 1)–O(NN − 1)	–	1.1992)	1.13(2)
C(NN + 1)–O(NN + 1)	1.15(2)	–	1.15(2)
δ(C(NU))	−1.899	−1.861	−1.940
δ(C(ND))	1.912	1.869	1.897
δ(N(NN − 1))	*−0.191*	−0.251	−0.283
δ(C(NN + 1))	0.268	*0.405*	0.285
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	176(1)	172(1)	169(1)
Ru(N)–C(ND)–O(ND)	176(1)	175(1)	176(1)
Ru(N)–C(NN − 1)–O(NN − 1)	–	174(1)	175(1)
Ru(N)–C(NN + 1)–O(NN + 1)	174(1)	–	173(1)

γ 84.18(3)°, U 2083(1) Å^3, D_c ($Z = 3$) 2.63 g cm^{-3}. $F(000) = 1500$. μ_{Mo} 147 cm^{-1}. Specimen: $0.16 \times 0.09 \times 0.20$ mm. $A^{\star}_{min,max} = 3.2, 7.8$. $2\theta_{max}$ 50°. $N = 6353$, $N_0 = 4084$. $R = 0.057$, $R' = 0.068$ ($n = 4$).

Abnormal features. Two distinct molecular types are found, both with disordered Os_3 cores. In molecule 1, disorder is found only to the extent of 0.05; population of these fragments were constrained at the mean of the three refined values, the smaller components with isotropic thermal parameters. Both ligands were refined as fully ordered species with anisotropic non-hydrogen thermal parameters. Molecule 2 is disposed about a centre of symmetry, each half-weighted component being refined with a full-complement of half-weighted ligands, with the

Table 13

Ruthenium environments for complex **2l-Ru** (For C(13,23) read P(1,2) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Ru(N)–Ru(N + 1)	2.831(2)	2.847(2)	2.861(2)
Ru(N)–C(NU)	1.97(3)	1.90(2)	2.03(3)
Ru(N)–C(ND)	1.88(3)	1.90(2)	1.89(2)
Ru(N)–C(NN + 1)	1.83(3)	*2.265(6)*	1.94(3)
Ru(N)–C(NN − 1)	*2.235(6)*	1.90(2)	1.84(2)
Angles (°)			
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.02(7)	60.52(6)	59.47(7)
Ru(N − 1)–Ru(N)–C(NU)	92.7(8)	92.4(5)	91.8(9)
Ru(N − 1)–Ru(N)–C(ND)	83.4(8)	83.4(7)	82.8(7)
Ru(N − 1)–Ru(N)–C(NN + 1)	153.9(9)	*158.1(2)*	156.5(7)
Ru(N − 1)–Ru(N)–C(NN − 1)	*100.6(2)*	94.7(9)	99.6(7)
Ru(N + 1)–Ru(N)–C(NU)	86.9(8)	85.1(6)	84.1(9)
Ru(N + 1)–Ru(N)–C(ND)	94.4(8)	92.5(6)	96.3(7)
Ru(N + 1)–Ru(N)–C(NN + 1)	94.3(9)	*99.2(2)*	98.0(7)
Ru(N + 1)–Ru(N)–C(NN − 1)	*159.5(2)*	153.9(7)	158.5(7)
C(NU)–Ru(N)–C(ND)	175(1)	175.7(9)	173(1)
C(NU)–Ru(N)–C(NN + 1)	90(1)	*94.0(6)*	92(1)
C(NU)–Ru(N)–C(NN − 1)	*87.8(8)*	88.0(10)	93(1)
C(ND)–Ru(N)–C(NN + 1)	95(1)	*89.9(7)*	94(1)
C(ND)–Ru(N)–C(NN − 1)	*89.2(8)*	92.6(9)	85(1)
C(NN + 1)–Ru(N)–C(NN − 1)	*105.5(9)*	*106.4(7)*	103(1)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.09(3)	1.18(3)	1.12(4)
C(ND)–O(ND)	1.14(3)	1.12(2)	1.17(3)
C(NN − 1)–O(NN − 1)	–	1.15(3)	1.14(3)
C(NN + 1)–O(NN + 1)	1.21(4)	–	1.15(3)
δ(C(NU))	−1.965	−1.888	−2.012
δ(C(ND))	1.844	1.877	1.832
δ(C(NN − 1))	*− 0.264*	−0.286	−0.162
δ(C(NN + 1))	0.155	*0.340*	0.237
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	172(2)	172(2)	168(3)
Ru(N)–C(ND)–O(ND)	177(2)	176(2)	172(2)
Ru(N)–C(NN − 1)–O(NN − 1)	–	172(2)	177(2)
Ru(N)–C(NN + 1)–O(NN + 1)	171(2)	–	170(2)

Table 14

Molecular core geometry for complex **2m-Os** molecule 1 (For C(13,23) read P(1,2) (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Os(N)–Os(N + 1)	2.869(1)	2.890(2)	2.888(2)
Os(N)–C(NU)	1.94(2)	1.90(2)	1.89(2)
Os(N)–C(ND)	1.87(3)	1.91(3)	1.92(2)
Os(N)–C(NN + 1)	1.90(2)	*2.281(7)*	1.93(2)
Os(N)–C(NN − 1)	*2.281(7)*	1.92(2)	1.89(2)
Angles (°)			
Os(N)–Os(N)–Os(N + 1)	60.27(4)	60.19(3)	59.54(3)
Os(N − 1)–Os(N)–C(NU)	94.9(6)	95.9(6)	93.6(7)
Os(N − 1)–Os(N)–C(ND)	83.3(7)	83.8(7)	82.9(7)
Os(N − 1)–Os(N)–C(NN + 1)	156.8(7)	*159.5(2)*	158.5(7)
Os(N − 1)–Os(N)–C(NN − 1)	*100.8(2)*	98.7(8)	100.1(7)
Os(N + 1)–Os(N)–C(NU)	84.5(7)	84.0(6)	83.4(7)
Os(N + 1)–Os(N)–C(ND)	94.0(8)	92.4(7)	94.4(7)
Os(N + 1)–Os(N)–C(NN + 1)	98.3(8)	*100.3(2)*	100.5(6)
Os(N + 1)–Os(N)–C(NN − 1)	*159.4(2)*	157.3(7)	158.5(7)
C(NU)–Os(N)–C(ND)	178.1(10)	176.0(9)	176.4(10)
C(NU)–Os(N)–C(NN + 1)	91.4(10)	*87.6(6)*	91.6(10)
C(NU)–Os(N)–C(NN − 1)	*89.8(7)*	90.7(10)	91.8(10)
C(ND)–Os(N)–C(NN + 1)	90.1(11)	*91.3(7)*	91.6(10)
C(ND)–Os(N)–C(NN − 1)	*91.2(8)*	93.3(11)	89.2(9)
C(NN + 1)–Os(N)–C(NN − 1)	*101.6(8)*	*101.5(8)*	100.6(10)
Disordered fragment:			
Distances (Å)			
Os(NN + 1)–Os(N + 1 N + 2)	2.79(3)	2.86(2)	2.70(3)
Os(N)–Os(NN + 1)	1.73(1)	1.56(1)	1.53(2)
Os(N)–Os(N − 1N)	1.60(2)	1.69(1)	1.76(1)
Angles (°)			
Os(N − 1N)–Os(NN + 1)–Os(N + 1 N + 2)	57.1(6)	60.2(6)	62.7(6)
Carbonyl distances (Å) (δ(C) is the deviation from the Os_3 plane) [a]			
C(NU)–O(NU)	1.15(3)	1.15(3)	1.21(3)
C(ND)–O(ND)	1.22(30	1.17(30	1.14(3)
C(NN − 1)–O(NN − 1)	–	1.11(3)	1.13(3)
C(NN + 1)–O(NN + 1)	1.14(3)	–	1.11(3)
δ(C(NU))	−1.832	−1.886	−1.884
δ(C(ND))	1.906	1.859	1.855
δ(C(NN − 1))	*−0.331*	−0.294	−0.236
δ(C(NN + 1))	0.309	*0.265*	0.280
Carbonyl angles (°)			
Os(N)–C(NU)–O(NU)	179(2)	174(2)	177(2)
Os(N)–C(ND)–O(ND)	174(2)	175(2)	174(2)
Os(N)–C(NN − 1)–O(NN − 1)	–	177(2)	176(2)
Os(N)–C(NN + 1)–O(NN + 1)	174(3)	–	175(2)

[a] Deviations of Os(12,23,31) from the major Os_3 plane are −0.245, −0.036, −0.019 Å.

Table 15

Molecular core geometry for complexes **2m-Os** molecule 2 (For C(13,23) read P as appropriate (italicized))

	N = 1	N = 2	N = 3
Distances (Å)			
Os(N)–Os(N + 1)	2.881(2)	2.891(2)	2.888(2)
Os(N)–C(NU)	2.01(5)	1.89(5)	1.88(6)
Os(N)–C(ND)	1.99(5)	1.98(4)	1.73(5)
Os(N)–C(NN + 1)	1.97(4)	*2.276(6)*	1.80(4)
Os(N)–C(NN − 1)	*2.306(6)*	1.94(3)	1.93(6)
Angles (°)			
Os(N − 1)–Os(N)–Os(N + 1)	60.17(6)	60.04(5)	59.80(5)
Os(N − 1)–Os(N)–C(NU)	96(1)	94(1)	95(2)
Os(N − 1)–Os(N)–C(ND)	79(1)	79(1)	75(1)
Os(N − 1)–Os(N)–C(NN + 1)	158(1)	*158.5(2)*	161(2)
Os(N − 1)–Os(N)–C(NN − 1)	*98.2(2)*	102.1(9)	107(2)
Os(N + 1)–Os(N)–C(NU)	83(1)	79(1)	79(2)
Os(N + 1)–Os(N)–C(ND)	96(1)	96(1)	96(1)
Os(N + 1)–Os(N)–C(NN + 1)	99(1)	*101.0(2)*	106(1)
Os(N + 1)–Os(N)–C(NN − 1)	*155.8(2)*	159(1)	161(2)
C(NU)–Os(N)–C(ND)	174(2)	173(2)	170(2)
C(NU)–Os(N)–C(NN + 1)	88(2)	*91(1)*	94(2)
C(NU)–Os(N)–C(NN − 1)	*89(1)*	93(2)	89(2)
C(ND)–Os(N)–C(NN + 1)	98(2)	*94(1)*	96(2)
C(ND)–Os(N)–C(NN − 1)	*89(1)*	91(1)	94(2)
C(NN + 1)–Os(N)–C(NN − 1)	*104(1)*	*98(1)*	90(2)
Carbonyl distances (Å) (δ(C) is the deviation from the Ru_3 plane)			
C(NU)–O(NU)	1.12(6)	1.29(6)	1.12(6)
C(ND)–O(ND)	1.14(5)	1.15(6)	1.26(6)
C(NN − 1)–O(NN − 1)	–	1.09(4)	1.06(6)
C(NN + 1)–O(NN + 1)	1.12(6)	–	1.19(5)
δ(C(NU))	−1.958	−1.823	−1.795
δ(C(ND))	1.885	1.900	1.607
δ(C(NN − 1))	*− 0.458*	−0.371	−0.495
δ(C(NN + 1))	0.265	*0.458*	0.408
Carbonyl angles (°)			
Ru(N)–C(NU)–O(NU)	176(4)	168(4)	174(5)
Ru(N)–C(ND)–O(ND)	177(4)	168(3)	160(4)
Ru(N)–C(NN − 1)–O(NN − 1)	–	165(3)	167(5)
Ru(N)–C(NN + 1)–O(NN + 1)	166(4)	–	167(4)

exception of the phosphine ligand, where one ligand suffices as a model, albeit with disordered oxygen atoms. Although all ligand fragments were fully refinable in (x, y, z), only the terminal carbon atoms and phosphorus atoms of the phosphite ligand could be refined using anisotropic thermal parameters, all other C,O thermal parameters being refined with the isotropic form.

Non-hydrogen atom coordinates for all these molecules are given in Tables 3–8, and the metal environments are given in Tables 9–15. Deposited data include non-hydrogen atom thermal parameters, hydrogen atom parameters and phosphorus ligand geometries (see Part LV [1]).

Acknowledgements

We thank the Australian Research Grants Committee for support of this work, and Dr Omar bin Shawkataly for crystals of **2i-Ru**.

References

1 M.I. Bruce, M.J. Liddell, C.A. Hughes, B.W. Skelton, and A.H. White, J. Organomet. Chem., 347 (1988) 157.
2 M.I. Bruce, J.G. Matisons and B.K. Nicholson, J. Organomet. Chem., 247 (1983) 321.
3 R.F. Alex and R.K. Pomeroy, J. Organomet. Chem., 284 (1985) 379.
4 M.I. Bruce, J.G. Matisons, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1983) 2375.
5 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2655.
6 M.R. Churchill and B.G. DeBoer, Inorg. Chem., 16 (1977) 878.
7 J.W. Lauher, J. Am. Chem. Soc., 108 (1986) 1521.
8 C.A. Tolman, Chem. Rev., 77 (1977) 313.
9 B.F.G. Johnson, J. Lewis and D.A. Pippard, J. Chem. Soc., Dalton Trans., (1981) 407.