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XXII *. CRYSTAL STRUCTURES OF $[M_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)_2(CO)_7]$, M = Ru AND Os

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Summary

Structure determinations and a comparison of the molecular core geometries of the complexes $[M_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)_2(CO)_7]$ (M = Ru and Os) are reported. The isosceles M_3 triangle (M–M 2.776, 2.759, 2.956(1) Å {2.785, 2.766, 2.975(2) Å}) (values for Ru {Os} given) is edge-bridged by two PPh_2 groups (M–P 2.267, 2.334(2); 2.319, 2.361(2) Å {2.280, 2.361(8); 2.333, 2.387(7) Å}) and a semi-bridging CO ligand (M–C 1.933, 2.625(6) Å {2.04, 2.77(3) Å}; M–C–O 164.4(6)° {166(3)°}). A C_6H_4 moiety is bonded to two metal atoms by σ-bonds (M–C 2.127, 2.135(6) Å {2.14, 2.18(3) Å}) and to the third by a π-bond (M–C 2.303, 2.353(6) Å {2.30, 2.40(3) Å}); C–C bond distances within the six-membered ring indicate some localisation of π-electron density.

Introduction

Several years ago, the formation of the title complexes was severally reported by two groups. The osmium complex was one of nine complexes obtained from the

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* For Part XXI, see ref. 11.

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reaction between $Os_3(CO)_{12}$ and triphenylphosphine in refluxing xylene [1]; a preliminary account of its structure has been given [2]. The ruthenium derivative was obtained by pyrolysis of $[Ru_3(CO)_9(PPh_3)_3]$ in refluxing decalin, and was characterised on the basis of analytical and spectroscopic data [3]. We have recently determined its molecular structure and present below an account of this, together with a comparison with that of the osmium analogue, reported earlier.

The ruthenium complex was prepared by the literature method [3], being isolated by chromatography on alumina, and crystallized as dark red, air-stable prisms from light petroleum/diethyl ether. The osmium complex was obtained as very thin red plates from acetone.

Crystallography

Crystal data. Ru complex. $C_{37}H_{24}P_2O_7Ru_3$, $M = 945.8$, Orthorhombic, space group *Pcab* (variant of *Pbca*, $D_{2h}{}^{15}$, No. 61), *a* 38.264(9), *b* 17.983(5), *c* 10.323(4) Å, *U* 7103(4) Å^3, D_c $(Z = 8)$ 1.77 g cm^{-3}. $F(000) = 3712$. Monochromatic Mo-K_α radiation, λ 0.7106$_9$ Å, μ(Mo) 13.0 cm^{-1}. Specimen size: $0.08 \times 0.19 \times 0.48$ mm. *T* 295(1) K.

Os complex. $C_{37}H_{24}P_2O_7Os_3$, $M = 1213.1$, Orthorhombic, space group *Pcab*, *a* 38.309(7), *b* 18.03(3), *c* 10.354(2) Å, *U* 7152(5) Å^3, D_c $(Z = 8)$ 2.25 g cm^{-3}. $F(000) = 5120$. Zr-filtered Mo radiation, λ 0.7106$_9$ Å, μ(Mo) 115 cm^{-1}. Specimen size: $0.046 \times 0.22 \times 0.45$ mm. *T* 291(1) K.

Unique data sets were measured for the two structures using Syntex $P2_1$ and Hilger-Watts 120Y four-circle diffractometers operating in conventional $2\theta/\theta$ scan mode. Analytical absorption correction was applied to the data. For the ruthenium complex 6170 independent reflections were measured to the limit $2\theta_{max}$ 50°, and 3649 with $I > 3\sigma(I)$ were considered 'observed' and used in the 9×9 block diagonal least-squares refinement after solution of the structure by direct methods; for the osmium analogue 3294 independent reflections with $I > 2\sigma(I)$ were considered 'observed' and used in the refinement. In the refinement of the ruthenium structure, anisotropic thermal parameters were refined for all non-hydrogen atoms; in the osmium structure only osmium and phosphorus atoms were treated in this way, isotropic thermal parameters being refined for the remaining non-hydrogen atoms.

In the ruthenium analogue, hydrogen atoms were included with parameters constrained in (x, y, z, U) at estimated values (see Table 1); in the case of the osmium analogue they were ignored. At convergence, residuals (R, R') were 0.032, 0.040 with reflection weights $(\sigma^2(F_0) + 0.0005(F_0)^2)^{-1}$ for the ruthenium complex; for the osmium complex residuals were 0.062, 0.078 with reflection weights of 1 for reflections with $F_0 > 300$ and $(300/F_0)^2$ with $F_0 \leq 300$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f, f'') [4,5].

Non-hydrogen atom numbering is given in the molecular diagram; hydrogen atom numbering follows that of the parent carbon atom (see Fig. 2).

Results and discussion

The structures of the two complexes $M_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)(CO)_7$ (M = Ru(1) and Os(2)) reported herein offer a rare opportunity to compare similar ruthenium

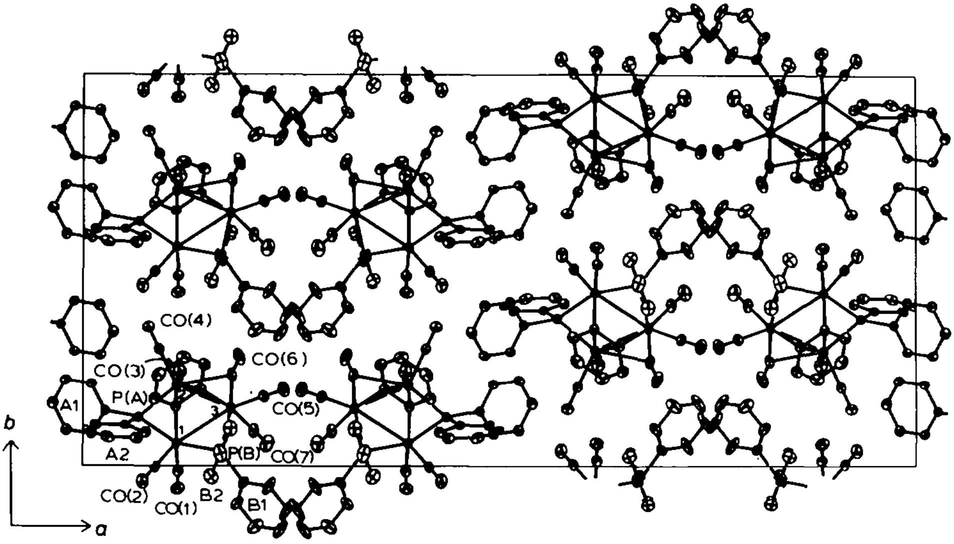


Fig. 1. Unit cell contents projected down *c*, for the ruthenium compound, showing group labelling. 20% probability thermal ellipsoids are shown for the non-hydrogen atoms.

and osmium complexes. The two parent carbonyls, $M_3(CO)_{12}$, are isostructural, but few other examples of closely related trinuclear complexes have been reported.

The two complexes described here share the common features of a triangular M_3 cluster, two edges of which are bridged by PPh_2 groups, and the third by a semi-bridging CO group. All three metal atoms are attached to a cyclic C_6H_4 ligand, which may be considered to be a 'benzyne' ligand, or alternatively a doubly-metallated benzene; two metal atoms are attached by two M–C σ bonds to *ortho* carbons, while the third is also attached to these carbons in an η^2 mode (see Fig. 2).

The most notable feature is the close similarity in lengths of similar bonds involving the two metals. In the parent carbonyls, there are very similar M–M bond distances (Ru, 2.8515(4) (two) and 2.8595(4) Å [6]; Os, 2.8745(5) (two) and 2.8824(5) Å [7]); these have been averaged to give covalent radii of 1.427 (Ru^0) and 1.439 Å (Os^0), a difference of 0.012 Å. In our complexes, the M_3 triangle is nearly isosceles, the two shorter bonds being those bridged by the diphenylphosphido groups; the third is ca. 0.18 Å longer in both cases. The differences in lengths (Os – Ru) are 0.009, 0.008 and 0.019 Å respectively. Larger differences are observed in the bonds to the ligands (i.e. (Os–L) – (Ru–L)), about 0.02 for the metal–phosphorus bonds, 0.02 for metal–carbonyl bonds, and 0.03 Å for metal–carbon σ-bonds.

The C_6H_4 ligand is planar, and forms a dihedral angle with the M_3 plane of 65.2 (Ru) and 65.8°(Os). In the more precise ruthenium structure, there is a systematic variation in bond lengths within this ligand, suggestive of some double bond localization. Metal atom deviations from the good C_6 ligand plane (σ_{Ru} 0.005; σ_{Os} 0.02 Å) are 0.067, -1.980, 0.215 Å (Ru); 0.074, -1.971, 0.249 Å (Os).

(Continued on p. 267)

TABLE 1

ATOMIC COORDINATES

Atom	Ru			Os		
	x	*y*	*z*	*x*	*y*	*z*
M(1)	0.11165(1)	0.05782(3)	0.03851(5)	0.11147(2)	0.05895(6)	0.03716(10)
M(2)	0.11180(1)	0.20515(3)	−0.04183(5)	0.11129(2)	0.20635(6)	−0.04322(10)
M(3)	0.17635(1)	0.14703(3)	0.02103(5)	0.17620(2)	0.14950(7)	0.01907(10)
Phosphine ligand A						
P(A)	0.06660(4)	0.12438(8)	−0.06034(15)	0.0657(2)	0.1258(4)	0.0617(6)
phenyl A1						
C(A1(1))	0.0264(1)	0.1401(3)	0.0302(6)	0.0253(6)	0.1408(12)	0.0360(22)
C(A1(2))	0.0104(2)	0.0812(3)	0.0937(6)	0.0093(7)	0.2115(15)	0.0360(27)
H(A1(2))	0.021(−)	0.032(−)	0.091(−)	−	−	−
C(A1(3))	−0.0202(2)	0.0913(4)	0.1606(7)	−0.0213(7)	0.2198(15)	0.1005(27)
H(A1(3))	−0.031(−)	0.049(−)	0.207(−)	−	−	−
C(A1(4))	−0.0361(2)	0.1595(4)	0.1617(7)	−0.0379(8)	0.1598(17)	0.1664(28)
H(A1(4))	−0.058(−)	0.166(−)	0.209(−)	−	−	−
C(A1(5))	−0.0210(2)	0.2182(3)	0.1010(7)	−0.0208(7)	0.0895(15)	0.1603(26)
H(A1(5))	−0.032(−)	0.267(−)	0.105(−)	−	−	−
C(A1(6))	0.0101(2)	0.2090(3)	0.0324(7)	0.0104(7)	0.0807(15)	0.0926(16)
H(A1(6))	0.020(−)	0.251(−)	−0.013(−)	−	−	−
phenyl A2						
C(A2(1))	0.0505(2)	0.1036(3)	−0.2222(5)	0.0486(6)	0.1047(13)	−0.2223(22)
C(A2(2))	0.0151(2)	0.1045(3)	−0.2529(6)	0.0136(7)	0.1043(15)	−0.2534(27)
H(A2(2))	−0.002(−)	0.115(−)	−0.184(−)	−	−	−
C(A2(3))	0.0045(2)	0.0893(3)	−0.3785(7)	0.0026(8)	0.0884(16)	−0.3763(29)
H(A2(3))	−0.021(−)	0.092(−)	−0.399(−)	−	−	−
C(A2(4))	0.0289(2)	0.0728(4)	−0.4721(6)	0.0270(8)	0.0745(18)	−0.4771(33)
H(A2(4))	0.021(−)	0.062(−)	−0.559(−)	−	−	−
C(A2(5))	0.0638(2)	0.0701(4)	−0.4426(6)	0.0641(7)	0.0712(15)	−0.4409(27)

H(A2(5))	0.081(–)	0.058(–)	−0.510(–)	–	–	–
C(A2(6))	0.0746(2)	0.0857(3)	−0.3184(6)	0.0735(6)	0.0863(14)	−0.3171(6)
H(A2(6))	0.099(–)	0.082(–)	−0.297(–)	–	–	–
Phosphine ligand B						
P(B)	0.16484(4)	0.03772(9)	0.14037(16)	0.1649(2)	0.0392(4)	0.1396(6)
phenyl B1						
C(B1(1))	0.1922(2)	−0.0430(3)	0.1077(6)	0.1919(7)	−0.0401(16)	0.1036(28)
C(B1(2))	0.1844(2)	−0.0950(4)	0.0199(8)	0.1833(8)	−0.0926(17)	0.0215(30)
H(B1(2))	0.162(–)	−0.091(–)	−0.028(–)	–	–	–
C(B1(3))	0.2064(2)	−0.1540(5)	−0.0066(8)	0.2042(10)	−0.1547(22)	−0.0036(37)
H(B1(3))	0.199(–)	−0.190(–)	−0.072(–)	–	–	–
C(B1(4))	0.2359(2)	−0.1618(6)	0.0581(9)	0.2361(12)	−0.1582(26)	0.0590(47)
H(B1(4))	0.252(–)	−0.201(–)	0.035(–)	–	–	–
C(B1(5))	0.2443(3)	−0.1109(7)	0.1489(15)	0.2448(18)	−0.1119(35)	0.1618(70)
H(B1(5))	0.264(–)	−0.120(–)	0.209(–)	–	–	–
C(B1(6))	0.2226(2)	−0.0522(6)	0.1724(12)	0.2239(13)	−0.0450(29)	0.1799(50)
H(B1(6))	0.228(–)	−0.015(–)	0.241(–)	–	–	–
phenyl B2						
C(B2(1))	0.1653(2)	0.0384(4)	0.3173(6)	0.1645(7)	0.0404(15)	0.3167(26)
C(B2(2))	0.1760(2)	0.0980(4)	0.3896(6)	0.1748(9)	0.0998(19)	0.3843(33)
H(B2(2))	0.184(–)	0.143(–)	0.346(–)	–	–	–
C(B2(3))	0.1757(2)	0.0950(5)	0.5251(7)	0.1766(11)	0.994(24)	0.5169(42)
H(B2(3))	0.183(–)	0.139(–)	0.577(–)	–	–	–
C(B2(4))	0.1646(2)	0.0321(5)	0.5858(7)	0.1640(10)	0.0383(23)	0.5842(40)
H(B2(4))	0.164(–)	0.031(–)	0.681(–)	–	–	–
C(B2(5))	0.1534(2)	−0.0279(5)	0.5162(7)	0.1524(10)	−0.0244(21)	0.5137(38)
H(B2(5))	0.147(–)	−0.074(–)	0.562(–)	–	–	–
C(B2(6))	0.1536(2)	−0.0241(4)	0.3815(7)	0.1512(8)	−0.0211(17)	0.3799(30)
H(B2(6))	0.145(–)	−0.066(–)	0.330(–)	–	–	–
Carbonyl ligands						
C(1)	0.1142(2)	−0.0146(3)	−0.0981(6)	0.1144(7)	−0.0146(15)	−0.0984(27)
O(1)	0.1137(1)	−0.0577(3)	−0.1784(5)	0.1153(6)	−0.0534(13)	−0.1833(24)
C(2)	0.0863(2)	−0.0034(4)	0.1509(6)	0.0849(9)	−0.0016(19)	0.1450(34)
O(2)	0.0717(1)	−0.0394(3)	0.2250(5)	0.0705(6)	−0.0403(14)	0.2172(24)

TABLE 1 (continued)

Atom	Ru			Os		
	x	y	z	x	y	z
C(3)	0.1137(2)	0.2254(4)	−0.2185(6)	0.1144(7)	0.2265(14)	−0.2172(25)
O(3)	0.1157(1)	0.2416(3)	−0.3243(4)	0.1173(6)	0.2446(12)	−0.3257(20)
C(4)	0.0909(2)	0.2980(3)	−0.0112(6)	0.0932(8)	0.2955(17)	−0.0243(30)
O(4)	0.0785(1)	0.3544(3)	0.0073(6)	0.0786(6)	0.3560(13)	0.0089(22)
C(5)	0.2156(2)	0.1765(4)	0.1187(7)	0.2147(8)	0.1757(16)	0.1131(29)
O(5)	0.2395(1)	0.1941(3)	0.1776(5)	0.2402(6)	0.1953(14)	0.1733(25)
C(6)	0.1778(2)	0.2319(4)	−0.0938(7)	0.1799(8)	0.2331(18)	−0.1129(32)
O(6)	0.1865(1)	0.2779(4)	−0.1625(6)	0.1871(7)	0.2816(16)	−0.1674(26)
C(7)	0.2036(2)	0.0896(4)	−0.1002(7)	0.2032(9)	0.0934(20)	−0.0996(35)
O(7)	0.2200(1)	0.0563(3)	−0.1700(5)	0.2177(7)	0.0566(15)	−0.1709(28)
Phenylene ligand						
C(P1)	0.1106(1)	0.1513(3)	0.1659(5)	0.1099(5)	0.1530(12)	0.1692(20)
C(P2)	0.1405(2)	0.1957(3)	0.1537(6)	0.1399(7)	0.1978(15)	0.1519(27)
C(P3)	0.1447(2)	0.2589(4)	0.2320(7)	0.1452(7)	0.2651(15)	0.2307(27)
H(P3)	0.166(−)	0.290(−)	0.222(−)	−	−	−
C(P4)	0.1203(2)	0.2764(4)	0.3207(7)	0.1191(10)	0.2790(22)	0.3277(40)
H(P4)	0.124(−)	0.320(−)	0.375(−)	−	−	−
C(P5)	0.0905(2)	0.2328(4)	0.3357(7)	0.0891(8)	0.2314(17)	0.3367(30)
H(P5)	0.073(−)	0.246(−)	0.401(−)	−	−	−
C(P6)	0.0854(2)	0.1718(4)	0.2598(6)	0.0838(6)	0.1711(14)	0.2607(25)
H(P6)	0.064(−)	0.142(−)	0.268(−)	−	−	−

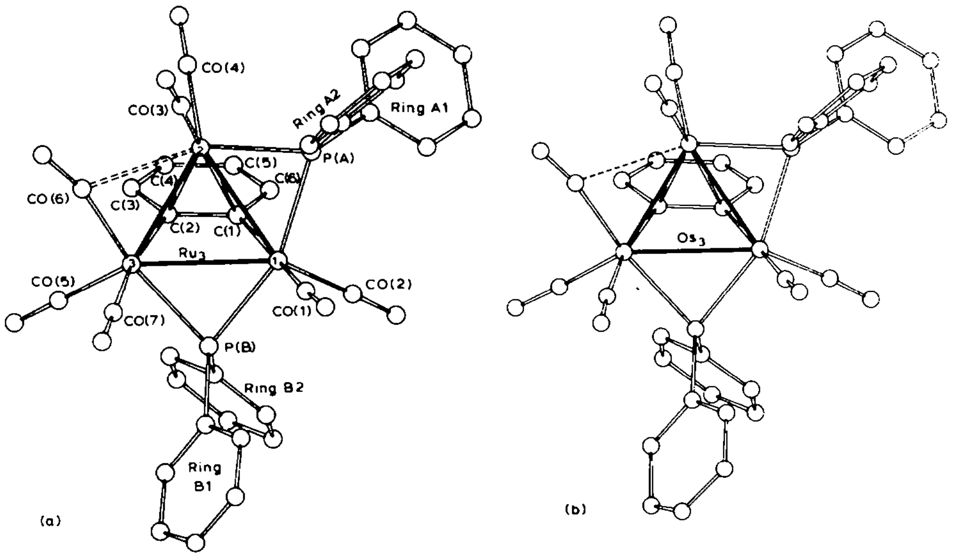
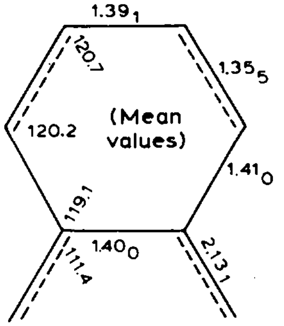


Fig. 2. Molecular projections of the ruthenium (a) and osmium (b) complexes normal to the M_3 plane. Group labelling is shown on the ruthenium complex.



To our knowledge, no ruthenium complexes containing this ligand have been structurally characterised previously; there are several examples containing osmium, including $(\mu\text{-H})Os_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)(CO)_7(PPh_3)$ and $(\mu\text{-H})Os_3(\mu\text{-}PPh_2)(\mu_3\text{-}C_6H_3C_6H_4PPh_2)(CO)_7$, also isolated from the $Os_3(CO)_{12}/PPh_3$ reaction [8], and $H_3Os_3(\mu\text{-}C_6H_4)(\mu\text{-HC=NPh})(CO)_8$ [9]. It is interesting to note that pyrolysis of $Os_3(CO)_{11}(PPh_3)$ affords $Os_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)(CO)_9$, containing an 'open' Os_3 cluster (with only two Os–Os bonds) and an asymmetrically-bonded C_6H_4 ligand [10].

In both complexes the long M–M vector is spanned by the semi-bridging CO group (M(3)–C(6) 1.933(7) {2.04(3)}, M(2)–C(6) 2.625(7) Å {2.77(3) Å}, M(3)–C(6)–O(6) 164.4(6)° {166(3)°}) (Table 3); atom deviations from the M_3 plane are C, 0.676 {0.87}; O, 1.143 {1.17} Å. A simple rationale of this situation is that the long M–M bond is a formal M(3) → M(2) donor bond, as in structure a, the CO group

TABLE 2

MOLECULAR CORE GEOMETRIES (FOR METAL ENVIRONMENTS, SEE TABLE 3)

	Ru	Os
Distances (Å)		
P(A)–C(A1)	1.823(6)	1.87(2)
P(A)–C(A2)	1.820(6)	1.83(2)
P(B)–C(B1)	1.822(6)	1.80(3)
P(B)–C(B2)	1.827(6)	1.83(3)
C(1)–O(1)	1.135(8)	1.12(4)
C(2)–O(2)	1.148(8)	1.16(4)
C(3)–O(3)	1.133(8)	1.18(3)
C(4)–O(4)	1.137(8)	1.27(4)
C(5)–O(5)	1.141(8)	1.21(4)
C(6)–O(6)	1.140(10)	1.08(4)
C(7)–O(7)	1.128(9)	1.14(5)
Angles (°)		
Ru(1)–P(A)–Ru(2)	74.22(5)	73.7(2)
Ru(1)–P(A)–C(A1)	118.6(2)	117.0(7)
Ru(1)–P(A)–C(A2)	123.1(2)	123.7(8)
Ru(2)–P(A)–C(A1)	120.1(2)	119.8(7)
Ru(2)–P(A)–C(A2)	117.9(2)	118.9(8)
C(A1)–P(A)–C(A2)	102.5(3)	103.1(11)
Ru(1)–P(B)–Ru(3)	78.31(5)	78.1(2)
Ru(1)–P(B)–C(B1)	123.0(2)	122.0(10)
Ru(1)–P(B)–C(B2)	117.4(2)	116.5(9)
Ru(3)–P(B)–C(B1)	117.4(2)	116.6(10)
Ru(3)–P(B)–C(B2)	121.0(2)	121.0(9)
C(B1)–P(B)–C(B2)	100.7(3)	102.8(13)
Ru(1)–C(1)–O(1)	176.1(6)	175(2)
Ru(1)–C(2)–O(2)	176.4(6)	175(3)
Ru(2)–C(3)–O(3)	176.0(6)	175(2)
Ru(2)–C(4)–O(4)	179.7(13)	170(3)
Ru(3)–C(5)–O(5)	179.7(16)	178(3)
Ru(2)–C(6)–Ru(3)	72.7(2)	68.3(9)
Ru(2)–C(6)–O(6)	122.8(5)	121(3)
Ru(3)–C(6)–O(6)	164.4(6)	166(3)
Ru(3)–C(7)–O(7)	178.8(5)	176(3)
Ru(1)–C(P1)–Ru(2)	76.3(2)	74.7(6)
Ru(1)–C(P1)–C(P2)	112.2(4)	110(2)
Ru(1)–C(P1)–C(P6)	129.7(4)	128(2)
Ru(2)–C(P1)–C(P2)	70.6(3)	69(1)
Ru(2)–C(P1)–C(P6)	122.0(4)	122(2)
C(P2)–C(P1)–C(P6)	118.0(5)	122(2)
Ru(2)–C(P2)–Ru(3)	76.9(2)	76.9(9)
Ru(2)–C(P2)–C(P1)	74.4(3)	76(1)
Ru(2)–C(P2)–C(P3)	120.0(4)	120(2)
Ru(3)–C(P2)–C(P1)	110.5(4)	112(2)
Ru(3)–C(P2)–C(P3)	129.0(5)	127(2)
C(P1)–C(P2)–C(P3)	120.3(5)	121(2)

facilitating redistribution of electron density, as found in $Fe_2(CO)_6(C_4H_4)$ and related complexes. Although a formal 18*e* configuration can be achieved for each metal atom by a canonical structure such as b, the determined structures are more in

TABLE 3

METAL ENVIRONMENTS (the first column *r*(M–L) is the metal–ligand distance in Å. Other entries in the matrix are the angles subtended by the atoms concerned at the metal (°).)

M(1)

	r(Ru–L)	Ru(3)	P(A)	P(B)	C(1)	C(2)	C(P1)
Ru(2)	2.776(1)	57.47(2)	51.79(4)	106.40(5)	115.3(2)	138.4(2)	55.4(2)
Ru(3)	2.956(1)		108.28(5)	51.47(5)	106.3(2)	142.4(2)	68.0(2)
P(A)	2.334(2)			157.89(7)	93.7(2)	100.9(2)	81.4(2)
P(B)	2.319(2)				100.5(2)	94.8(2)	82.0(2)
C(1)	1.922(6)					94.7(3)	170.6(2)
C(2)	1.871(6)						94.1(3)
C(P1)	2.135(6)						
	r (Os–L)	Os(3)					
Os(2)	2.785(2)	57.28(4)	51.8(2)	106.4(2)	116.0(8)	137.4(11)	56.3(6)
Os(3)	2.975(1)		108.2(2)	51.8(2)	106.4(8)	144.5(11)	68.6(5)
P(A)	2.361(7)			157.9(2)	94.5(8)	98.8(11)	81.6(6)
P(B)	2.333(7)				100.0(8)	96.7(11)	81.8(5)
C(1)	1.93(3)					93.7(13)	172.1(10)
C(2)	1.86(3)						93.7(12)
C(P1)	2.18(2)						

M(2)

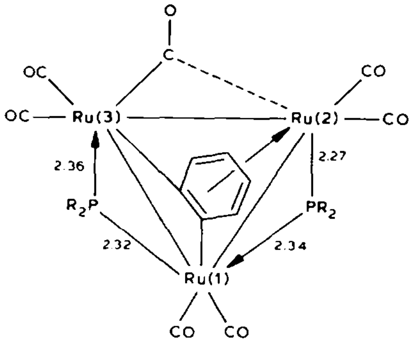
	r(Ru–L)	Ru(3)	P(A)	C(3)	C(4)	C(P1)	C(P2)
Ru(1)	2.776(1)	64.54(2)	53.99(4)	118.7(2)	142.9(2)	48.3(1)	70.6(1)
Ru(3)	2.759(1)		117.39(5)	105.7(2)	132.7(2)	69.4(1)	48.7(1)
P(A)	2.267(2)			94.1(2)	105.1(2)	78.4(1)	112.9(2)
C(3)	1.861(7)				90.4(3)	167.0(3)	148.8(2)
C(4)	1.878(6)					101.8(2)	96.9(2)
(C(6))	(2.625(6))						
C(P1)	2.353(6)						35.0(2)
C(P2)	2.303(6)						
	r(Os–L	Os(3)					
Os(1)	2.785(2)	64.81(3)	54.5(2)	118.7(8)	147.0(10)	49.0(5)	70.9(7)
Os(3)	2.766(1)		118.2(2)	104.1(8)	131.8(10)	70.0(5)	48.9(7)
P(A)	2.280(8)			95.3(8)	106.8(10)	78.7(5)	113.3(7)
C(3)	1.84(3)				87.4(13)	167.6(9)	147.2(11)
C(4)	1.76(3)					104.8(11)	98.7(12)
(C(6))	(2.77(3))						
C(P1)	2.40(2)						35.0(8)
C(P2)	2.30(3)						

M(3)

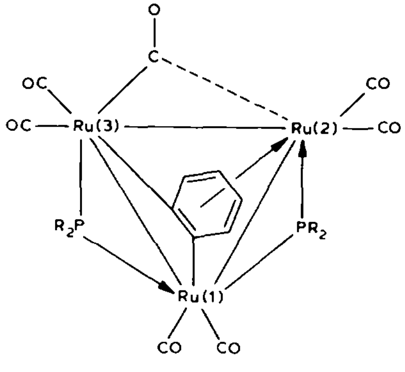
	r(Ru–L)	Ru(2)	P(B)	C(5)	C(6)	C(7)	C(P2)
Ru(1)	2.956(1)	58.01(3)	50.22(4)	141.9(2)	119.3(2)	101.6(2)	69.1(2)
Ru(2)	2.759(1)		105.73(4)	137.1(2)	65.3(2)	122.3(2)	54.4(2)
P(B)	2.361(2)			95.9(2)	169.2(2)	89.6(2)	83.5(2)

TABLE 3 (continued)

M(1)							
	r(Ru–L)	Ru(2)	P(B)	C(5)	C(6)	C(7)	C(P2)
C(5)	1.885(7)				94.8(3)	93.8(3)	93.1(3)
C(6)	1.933(7)					90.6(3)	95.0(3)
C(7)	1.929(7)						170.7(3)
C(P2)	2.127(6)						
	r(Os–L)	Os(2)					
Os(1)	2.975(1)	57.91(3)	50.1(2)	141.3(9)	120.4(9)	101.7(11)	69.0(7)
Os(2)	2.766(1)		105.5(2)	138.9(9)	68.4(9)	122.4(11)	54.2(7)
P(B)	2.387(7)			94.8(9)	168.1(9)	89.6(11)	83.4(7)
C(5)	1.83(3)				96.3(13)	92.5(14)	94.4(12)
C(6)	2.04(3)					85.5(14)	100.1(12)
C(7)	1.90(4)						170.6(13)
C(P2)	2.14(3)						



(a)



(b)

accord with structure a. Another feature of these molecules is the asymmetric μ-PPh_2 groups, consistent with the presence of M–P (donor) and M–P (phosphido) bonds (Table 3).

An alternative explanation is to be found in the nature of the groups *trans* to phosphorus. Whereas on M(3), the CO group is an effective competitor for electron density, the same group is not competitive as far as M(2) is concerned, resulting in a considerable shortening of the M(2)–P bond (to 2.267(2) Å {2.280(8) Å}) compared with the M(3)–P bond (2.361(2) Å {2.387(7) Å}) (see Table 3).

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