Cluster Chemistry. Part 91.[1] Clusters derived from 1,4-Bis(diphenylphosphino)buta-1,3-diyne and Their Pyrolysis Products: A Route to Complexes containing the Tetracarbon Ligand *

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Reactions of $[M_n(CO)_{11}(NCMe)]$ [M_n = Ru_3, Os_3, $Re_3(\mu\text{-}H)_3$, or $Ru_4(\mu\text{-}H_4)_4$] with the linear bis(phosphine) $PPh_2C_2C_2PPh_2$(bdpp) afford the 'barbell' complexes $[\{M_n(CO)_{11}\}_2(\mu\text{-bdpp})]$ [M_n = Ru_3 **1** (38), Os_3 **2** (68), $Re_3(\mu\text{-}H)_3$ **4** (44), or $Ru_4(\mu\text{-}H)_4$ **6** (39%)]. The monosubstituted complexes $[M_n(CO)_{11}(bdpp)]$ [M_n = Os_3 **3** or $Re_3(\mu\text{-}H)_3$ **5**] were isolated when an excess of bdpp was used. Reactions of **3** with $[M_3(CO)_{11}(NCMe)]$ [M_3 = Ru_3 or $Re_3(\mu\text{-}H)_3$] afforded the mixed-metal complexes $[\{Os_3(CO)_{11}\}(\mu\text{-bdpp})\{M_3(CO)_{11}\}]$ [M_3 = Ru **7** (40) or $Re_3(\mu\text{-}H)_3$ **8** (63%)]. In a similar fashion $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}(\mu\text{-bdpp})\{Ru_3(CO)_{11}\}]$ **9** was prepared (38%) from **5** and $[Ru_3(CO)_{11}(NCMe)]$. When a solution of **1** in CH_2Cl_2 was gently heated under a nitrogen purge the C_4 complex $[\{Ru_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3{:}\mu_3\text{-}C_4)]$ **10** was produced in 73% yield. Without purging, the yield is much reduced; a minor product from the reaction is $[\{Ru_4(\mu\text{-}H)(CO)_{12}\}\{\mu_4\text{-}PPh(C_6H_4)C_2C_2PPh_2\}\{Ru_3(CO)_{11}\}]$ **11**. Complex **11** contains an $Ru_3(CO)_{11}$ moiety linked *via* a $PPh_2C_2C_2PPh(C_6H_4)$ ligand to an Ru-spiked Ru_3 cluster. One of the C_2 units is attached in a $\mu\text{-}\sigma,\sigma,\eta^2$-vinylic mode to the spike Ru and to two of the three Ru atoms in the closed triangular core. When **11** was recrystallised from CH_2Cl_2–MeOH the complex $[\{Ru_4(\mu_3\text{-}OMe)(\mu\text{-}PPh_2)(CO)_{10}\}(\mu_4\text{-}CCH\text{-}\mu\text{-}\eta^2\text{-}C_2)\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]$ **12** was formed. This complex contains an Ru_4 rhombus, opposite faces of which carry μ_3-OMe and a μ_4-vinylidene ligand; the latter is attached *via* a C–C single bond to the binuclear fragment. The complex $[\{Os_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3{:}\mu_3\text{-}C_4)]$ **13** was obtained (78%) by pyrolysis of **2** in refluxing toluene. The structures of complexes **6** and **10–13** were determined by single-crystal X-ray studies.

We have described the pyrolysis of complexes containing metal carbonyl cluster fragments attached to each phosphorus atom of 1,2-bis(diphenylphosphino)acetylene ($PPh_2C_2PPh_2$, dppa), such as $[\{Ru_3(CO)_{12}\}_2(\mu\text{-dppa})]$, which give unusual cluster condensation products formed by cleavage of a C(sp)–P bond (to give a μ-PPh_2 group) and incorporation of the C≡C bond into a medium-sized cluster.[2] In several subsequent reactions we have shown that clusters containing dicarbon (C_2) ligands can be obtained.[3]

We have also reported recently some complexes derived from the related ligand 1,3-bis(diphenylphosphino)buta-1,3-diyne-($PPh_2C_2C_2PPh_2$, bdpp) in which one transition metal–ligand moiety is attached to each end of the linear diacetylenic tertiary phosphine.[4] Some of these were shown to react with $[Co_2(CO)_8]$ or $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ to afford the expected products containing $Co_2(CO)_6$ or $Pt(PPh_3)_2$ groups bonded to one of the C≡C triple bonds. This feature is only rarely available in the chemistry of dppa because of the steric hindrance posed by the bulky phenyl groups about the C≡C triple bond.[5]

In seeking to extend this synthetic approach to complexes containing other all-carbon ligands, we have studied the syntheses and pyrolytic reactions of complexes of bdpp with ruthenium, osmium and rhenium cluster carbonyls, their transformations to complexes containing the C_4 ligand, and their reactions with $[Co_2(CO)_8]$ to give a range of heteronuclear clusters with novel core geometries. This is the first of two papers describing this chemistry, some of which has been described in preliminary fashion.[6]

Results

A complex containing two $Ru_3(CO)_{11}$ groups bridged by a bdpp ligand was readily obtained in about 40% yield from reactions of the ligand with $[Ru_3(CO)_{11}(NCMe)]$ or directly from $[Ru_3(CO)_{12}]$ in tetrahydrofuran (thf) in the presence of Me_3NO. The product, formulated as $[\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ **1** (Scheme 1), formed red crystals which were readily identified from its IR ν(CO) spectrum, which was very similar to that of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$,[2] both of which resemble that of $[Ru_3(CO)_{11}(PPh_3)]$,[7] and its FAB mass spectrum, which contained a molecular ion at *m/z* 1642 which fragmented by loss of up to 22 CO groups, producing envelopes of ion clusters between *m/z* 1614 and 1026. The ^1H NMR spectrum was not very informative, containing only resonances assigned to the aromatic protons.

The osmium analogue **2** was prepared as orange crystals from bdpp and 2 equivalents of the $[Os_3(CO)_{11}(NCMe)]$ precursor in 68% yield. This complex had similar spectral properties to those of **1**, most useful being the observation of a molecular ion in the FAB mass spectrum at *m/z* 2176. When 2 equivalents of bdpp were employed the monocluster complex $[Os_3(CO)_{11}(bdpp)]$ **3** was obtained in 67% yield, distinguished from **2** by its molecular ion at *m/z* 1297; the IR ν(CO) spectra of the two complexes were virtually identical.

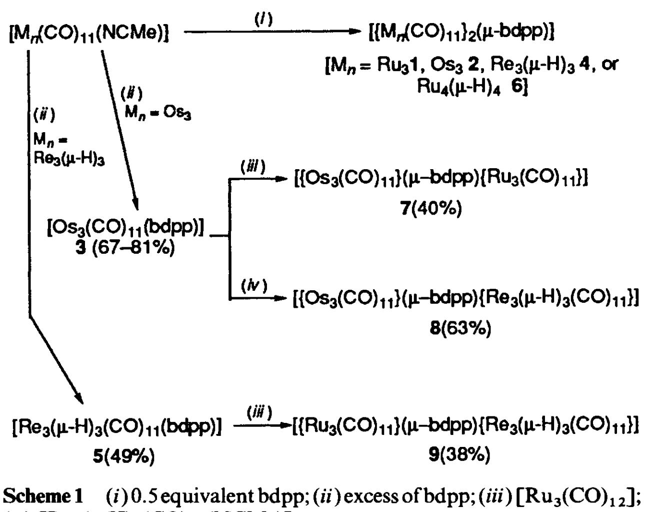
A 44% yield of $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ **4** was ob-

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

tained as a pale yellow solid from the ligand and 2 equivalents of $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$. This complex could be characterised by the molecular ion at *m/z* 2158 in the FAB mass spectrum; the IR ν(CO) spectrum was similar to that of $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}_2(\mu\text{-dppa})]$.[2c] The mono-$Re_3$ derivative **5** was similarly obtained in 49% yield from a reaction using 2 equivalents of the ligand. As found for **2** and **3**, the IR ν(CO) spectra of the two complexes were similar; the molecular ion of **5** was found at *m/z* 1288.

A complex containing two tetranuclear clusters was formed by reaction of bdpp with $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NCMe)]$. Yellow crystals of $[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-bdpp})]$ **6** were formed in 39% yield from a reaction carried out at room temperature. The ^1H NMR spectrum contained the expected high-field doublet resonance at δ −17.26, and a molecular ion at *m/z* 1853 which fragmented by stepwise loss of the 22 CO groups was also consistent with the proposed formulation. As the first representative of its type, **6** was also characterised by a single-crystal X-ray study, which is described below.

The availability of complexes **3** and **5**, with their unco-ordinated *P*-donor centres, allowed the synthesis of complexes containing two different cluster moieties. Thus the reaction between **3** and $[Ru_3(CO)_{11}(NCMe)]$ afforded a 44% yield of the mixed-cluster complex $[\{Os_3(CO)_{11}\}(\mu\text{-bdpp})\{Ru_3(CO)_{11}\}]$ **7** as red needles. The IR ν(CO) spectrum was similar to those of **1** and **2**, while the mass spectrum contained M^+ at *m/z* 1910 together with ions formed by loss of up to 22 CO groups between *m/z* 1882 and 1294. A similar reaction with $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ afforded yellow $[\{Os_3(CO)_{11}\}(\mu\text{-bdpp})\{Re_3(\mu\text{-}H)_3(CO)_{11}\}]$ **8** in 63% yield, while the red Re_3/Ru_3 analogue **9** was obtained from $[Re_3(\mu\text{-}H)_3(CO)_{11}(bdpp)]$ and $[Ru_3(CO)_{11}(NCMe)]$ in 38% yield. Both **8** and **9** were identified from their FAB mass spectra which contained highest ions at *m/z* 2144 (M^+) and 1816 ($[M-3CO]^+$), respectively; the IR ν(CO) spectra approximated to an overlap of those of the constituent clusters, suggesting that there was little interaction between them when separated by a ligand as large as bdpp.



Scheme 1 (*i*) 0.5 equivalent bdpp; (*ii*) excess of bdpp; (*iii*) $[Ru_3(CO)_{12}]$; (*iv*) $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$

Molecular Structure of $[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-bdpp})]$ **6**.—The molecular structure of complex **6** is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The molecule is centrosymmetric, the two Ru_4 clusters adopting a transoid disposition about the PC_2C_2P part of the ligand to minimise steric interactions. The two $Ru_4(\mu\text{-}H)_4(CO)_{11}$ clusters have the same idealised D_{2d} geometry found for $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$[8] and some mono- and di-substituted derivatives, such as $[Ru_4(\mu\text{-}H)_4(CO)_{11}\{P(OMe)_3\}]$[9] and $[Ru_4(\mu\text{-}H)_4(CO)_{10}(PPh_3)_2]$.[8] The intracluster bonds comprise two short [2.787(1), 2.791(2) Å] and four long Ru–Ru separations [2.953(2)–2.978(1) Å] {*cf.* respective average values of 2.786(1) and 2.950(1) Å in $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$, 2.772(2) and 2.966(2) Å in $[Ru_4(\mu\text{-}H)_4(CO)_{10}(PPh_3)_2]$}. The long vectors indicate the position of the four μ-H ligands, which were not located in the X-ray study. The phosphorus atom of the bdpp ligand co-ordinates to Ru(1) [Ru(1)–P(1) 2.325(5) Å] which is also bonded to two H ligands. Within the bdpp ligand, the C≡C distance is 1.19(2) Å, which may be compared to the values of 1.192(7) and 1.201(6) Å found in the two independent molecules of $[\{Fe(CO)_4\}_2(\mu\text{-bdpp})]$.[4] Similarly, the PC_2C_2P unit is nearly linear [angles at the carbon atoms are 171(2) and 176(2)°, respectively].

Pyrolysis Studies.—(*a*) $[\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})]$. Smooth conversion of complex **1** into $[\{Ru_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3\text{:}\mu_3\text{-}C_4)]$ **10** was achieved by heating in refluxing CH_2Cl_2 for 7 h while purging with a nitrogen stream (Scheme 2). This pale yellow complex, obtained in 73% yield, has M^+ at *m/z* 1530 and ions formed by loss of up to 18 CO groups therefrom. It was conclusively identified by the X-ray study which has been briefly reported elsewhere;[6] further discussion is deferred to the description of the analogous osmium complex below.

When the solution of complex **1** was heated for 24 h without a nitrogen purge only 26% of **10** was obtained. It was accompanied by a small amount of $[\{Ru_3(CO)_{11}\}\{\mu\text{-}PPh_2\text{-}$

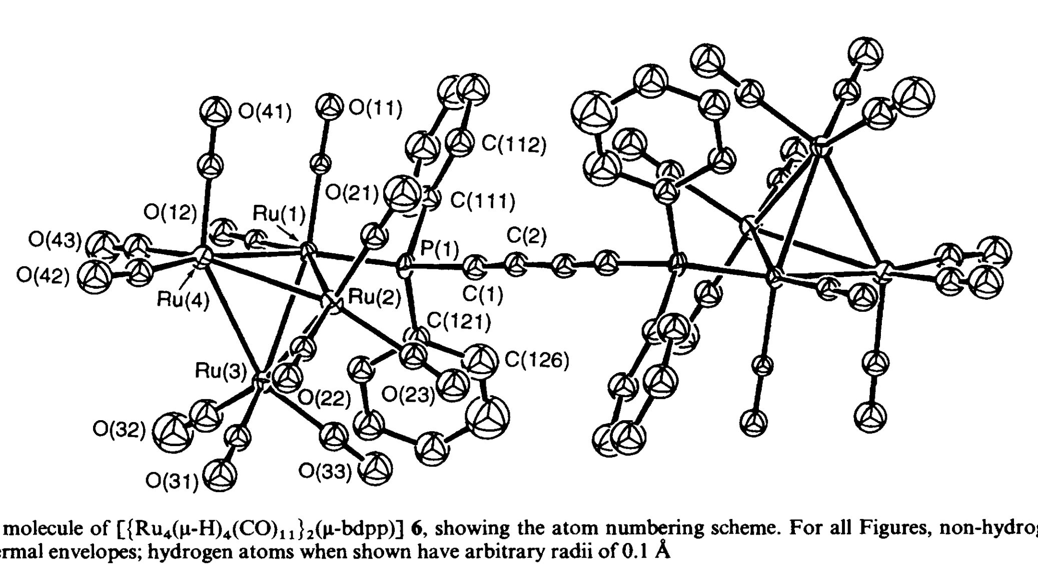
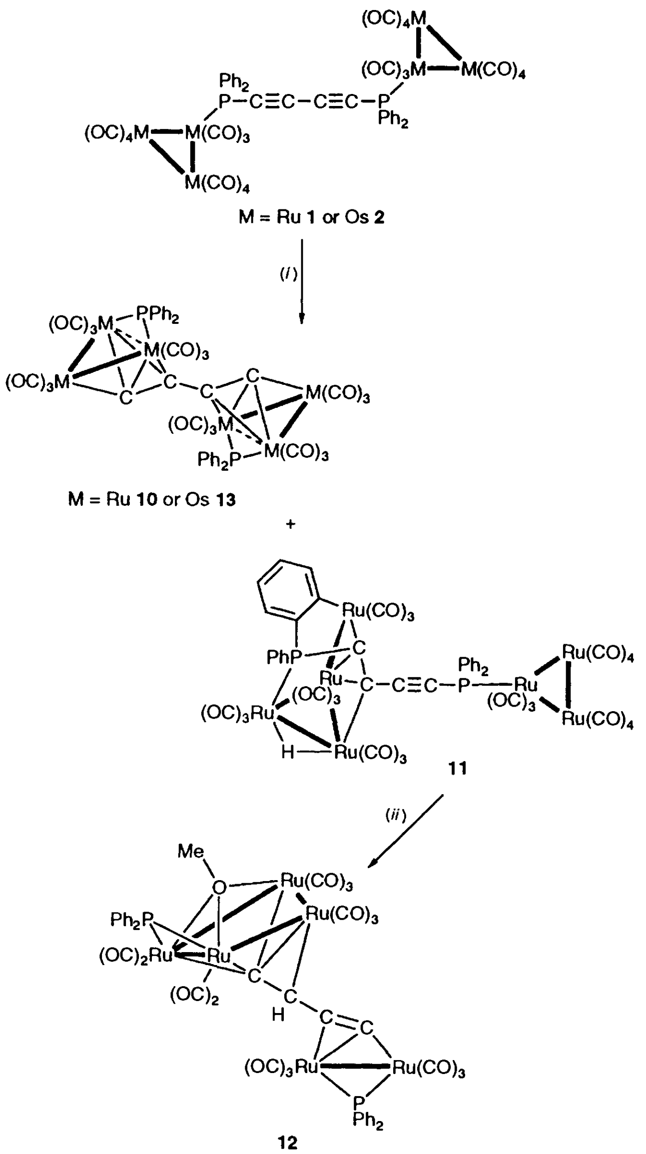


Fig. 1 Plot of a molecule of $[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-bdpp})]$ **6**, showing the atom numbering scheme. For all Figures, non-hydrogen atoms are shown as 20% thermal envelopes; hydrogen atoms when shown have arbitrary radii of 0.1 Å

Table 1 Selected bond parameters (distances in Å, angles in °) for $[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-bdpp})]$ **6**

Ru(1)–Ru(2)	2.974(2)	Ru(3)–Ru(4)	2.953(2)
Ru(1)–Ru(3)	2.978(1)	Ru(1)–P(1)	2.325(5)
Ru(1)–Ru(4)	2.791(2)	P(1)–C(1)	1.78(2)
Ru(2)–Ru(3)	2.787(1)	C(1)–C(2)	1.19(2)
Ru(2)–Ru(4)	2.956(3)	C(2)–C(2′)	1.38(3)
Ru–CO	range 1.83(1)–1.99(3), average 1.89		
C–O	range 1.02(3)–1.22(2), average 1.14		
P–C(Ph)	1.81(1) and 1.842(8), average 1.83		
Ru(1)–P(1)–C(1)	111.4(5)	C(1)–C(2)–C(2′)	176(2)
P(1)–C(1)–C(2)	171(2)		



Scheme 2 (*i*) Heat; (*ii*) MeOH

$C_2C_2PPh(C_6H_4)\}\{Ru_4(\mu\text{-}H)(CO)_{12}\}]$ **11** which was identified crystallographically. Recrystallisation of **11** from solvents containing MeOH resulted in its conversion into red $[\{Ru_4(\mu_3\text{-}OMe)(\mu\text{-}PPh_2)(CO)_{10}\}(\mu_4\text{-}CCH\text{-}\mu\text{-}\eta^2\text{-}C_2)\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]$ **12**, also characterised by X-ray crystallography. Both complexes have all-terminal ν(CO) spectra and their mass spectra contained M^+ ions at *m/z* 1771 and 1506, respectively.

Molecular structure of $[\{Ru_3(CO)_{11}\}\{\mu\text{-}PPh_2C_2C_2PPh(C_6H_4)\}\{Ru_4(\mu\text{-}H)(CO)_{12}\}]$ **11**. Fig. 2 depicts one of two independent molecules of **11** and selected bond parameters are listed in Table 2. In this molecule an intramolecular reaction involving one half of complex **1** has occurred, the $Ru_3(CO)_{11}(PPh_2C_2)$ fragment remaining essentially unchanged from that found in **1** and being comparable to the many complexes of the type $[Ru_3(CO)_{11}(PR_3)]$ that have been structurally characterised [Ru–Ru 2.828–2.846(3); Ru(6)–P(2) 2.331(4) Å].[10] The C_2 unit attached to P(2) does not interact with any metal atom and retains the structural characteristics of an alkyne [C(3)–C(4) 1.20(2), 1.19(2); C(4)–P(2) 1.74(1), 1.75(1) Å; P(2)–C(4)–C(3) 173(2), 178(1); C(4)–C(3)–C(2) 172(2)° (×2) (values for two independent molecules given)].

The other half of the molecule consists of an Ru_3 triangle, to which a fourth Ru atom is joined. The other Ru–Ru bonds have a range of values [Ru(1)–Ru(3) 2.765, 2.787(3); Ru(2)–Ru(3) 2.888, 2.905(3); Ru(1)–Ru(2) 2.987(3), 2.966(4) Å], the length of the last suggesting it to be bridged by the H atom shown to be present by the high-field doublet at δ −19.1 in the ^1H NMR spectrum but not located definitely in the X-ray study. Atom C(2) bridges Ru(1)–Ru(3), and with C(1) is also attached to Ru(3); C(1) is σ bonded to Ru(4) [Ru(4)–C(1) 2.07(1) Å] and to P(1). The latter is bonded to Ru(2) by a normal 2e donor bond [Ru(2)–P(1) 2.322(5), 2.327(4) Å] and carries one Ph group and a C_6H_4 ring which is also σ bonded to Ru(4) [Ru(4)–C(112) 2.16(1) (×2) Å]. Individual electron counts at the four ruthenium atoms indicate that there is a donor bond from Ru(3) to Ru(4); the separation [2.938(3), 2.952(3) Å] is consistent with this feature. The $C_2PPh(C_6H_4)$ part of the bridging ligand acts as an 8e donor, which with the H atom and the 12 CO groups gives a total of 64e for the Ru_4 cluster, which has only four Ru–Ru bonds as predicted by the normal electron-counting rules. The two independent molecules of the asymmetric unit have similar but significantly different conformations, as measured by, *e.g.*, the dihedral angles between the two Ru_3 planes [98.72(6), 95.64(6)° for molecules 1, 2, respectively].

Molecular structure of $[\{Ru_4(\mu_3\text{-}OMe)(\mu\text{-}PPh_2)(CO)_{10}\}(\mu_4\text{-}CCH\text{-}\mu\text{-}\eta^2\text{-}C_2)\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]$ **12**. This molecule is illustrated in Fig. 3 with some bond lengths and angles summarised in Table 3. The molecule consists of two parts, a conventional $Ru_2(\mu\text{-}PPh_2)(\mu\text{-}C_2R)(CO)_6$ complex, formed by addition of one C_2PPh_2 fragment from the bdpp ligand in **2** (or **11**) to the Ru_3 cluster, with concomitant loss of a $Ru(CO)_3$ fragment, and a Ru_4 cluster also containing a (differently) modified C_2PPh_2 fragment. The R group in the binuclear part is the tetranuclear cluster, linked *via* the C(2)–C(3) bond [1.45(2) Å].

In the latter the four Ru atoms form a rhombus bent about the Ru(2)···Ru(4) diagonal [dihedral angle 37.86(5)°]; the Ru–Ru distances range between 2.681 and 2.805(2) Å. A C_2 fragment bridges all four metal atoms *via* C(1) [Ru(1,2,3,4)–C(1) 2.17(1), 2.20(1), 2.10(1), 2.11(2); Ru(3)–C(2) 2.28(1) Å] and a PPh_2 ligand asymmetrically bridges the Ru(1)–Ru(2) vector [Ru(1,2)–P(1) 2.299, 2.335(4) Å]. Three of the Ru atoms are also bridged, on the opposite side of the rhombus, by a μ_3-OMe group [Ru(1,2,4)–O(01) 2.10(1), 2.21(1), 2.127(8) Å]; the OMe protons resonate at δ 1.62. This high-field shift, compared to normal organic OMe groups, probably results from co-ordination to the three metal atoms.

The geometry about atom C(2), *e.g.* C(1)–C(2)–C(3) 120°, suggests that this atom also bears a hydrogen atom, so that the ligand linking the Ru_2 and the Ru_4 units could be described as an alkynylvinylidene. We have not been able to refine this H atom, but a doublet resonance in the ^1H NMR spectrum at δ 4.15, in the region normally associated with vinylidene protons,[11] supports this assignment.

(*b*) $[\{Os_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ **2**. After heating complex **2** in refluxing toluene for 5 d under a nitrogen purge only one pale yellow complex was isolated in 78% yield after the usual work-up. The IR ν(CO) spectrum was very similar to that of **10**, and

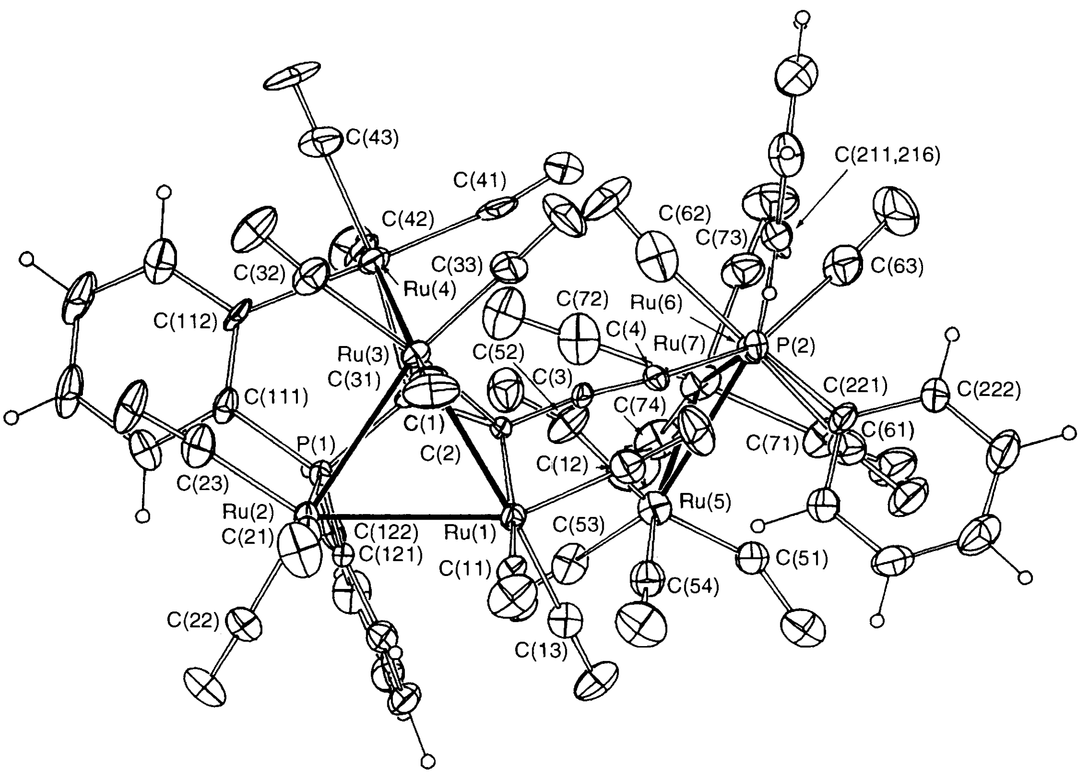


Fig. 2 Plot of one of the two independent molecules of $[\{Ru_4(\mu\text{-}H)(CO)_{12}\}\{\mu_4\text{-}PPh(C_6H_4)C_2C_2PPh_2\}\{Ru_3(CO)_{11}\}]$ **11**, normal to the Ru(1,2,3) plane, showing the atom numbering scheme

Table 2 Selected bond parameters (distances in Å, angles in °) for $[\{Ru_4(\mu\text{-}H)(CO)_{12}\}\{\mu_4\text{-}PPh(C_6H_4)C_2C_2PPh_2\}\{Ru_3(CO)_{11}\}]$ **11** (molecules 1,2)

Ru(1)–Ru(2)	2.987(3), 2.966(4)	Ru(1)–C(2)	2.09(2), 2.10(1)
Ru(1)–Ru(3)	2.765(3), 2.787(3)	Ru(3)–C(1)	2.29(1), 2.24(1)
Ru(2)–Ru(3)	2.888(3), 2.905(3)	Ru(3)–C(2)	2.30(1), 2.23(1)
Ru(3)–Ru(4)	2.938(3), 2.952(3)	Ru(4)–C(1)	2.07(1), 2.05(2)
Ru(5)–Ru(6)	2.848(3), 2.846(3)	Ru(4)–C(112)	2.16(1), 2.16(1)
Ru(5)–Ru(7)	2.829(4), 2.844(3)	P(1)–C(1)	1.75(1), 1.83(1)
Ru(6)–Ru(7)	2.850(3), 2.828(3)	P(2)–C(4)	1.74(1), 1.75(1)
Ru(2)–P(1)	2.322(5), 2.327(4)	C(1)–C(2)	1.50(2), 1.39(2)
Ru(6)–P(2)	2.323(5), 2.331(4)	C(2)–C(3)	1.42(2), 1.45(2)
		C(3)–C(4)	1.20(2), 1.19(2)
Ru–CO	range 1.68–1.99(2), average 1.89		
C–O	range 1.09–1.37(2), average 1.15		
P–C(Ph)	range 1.75–1.81(2), average 1.80		
Ru(1)–Ru(3)–Ru(4)	120.32(7), 119.45(9)	Ru(4)–C(1)–C(2)	125.1(9), 128(1)
Ru(2)–Ru(3)–Ru(4)	106.01(7), 107.76(9)	P(1)–C(1)–C(2)	117(1), 115(1)
Ru(2)–P(1)–C(1)	103.7(5), 104.1(4)	P(2)–C(4)–C(3)	173(2), 178(1)
Ru(2)–P(1)–C(111)	113.7(5), 114.0(4)	C(1)–C(2)–C(3)	118(1), 117(1)
Ru(6)–P(2)–C(4)	116.1(5), 112.9(4)	C(2)–C(3)–C(4)	172(2), 172(2)
Dihedral angles	Ru(1,2,3)/Ru(3,4)	30,55(3), 30.00(3)	
	Ru(1,2,3)/Ru(1,3)C(2)	72.46(5), 72.23(5)	
	Ru(1,2,3)/Ru(5,6,7)	98.72(6), 95.64(6)	

its identity as the osmium analogue **13** was confirmed by a single-crystal X-ray study.

Molecular structures of $[\{M_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3{:}\mu_3\text{-}C_4)]$ (M = Ru **10** *or* Os **13**). As expected, the molecular geometry and dimensions of complex **13** are similar to those of **10**: Fig. 4 depicts a molecule each of **10** and **13** and bond parameters for both complexes are collected in Table 4. In each case, one half of the molecule comprises the asymmetric unit; however, the second half is generated by an inversion centre in **10** and a two-fold axis in **13**. Although the overall aspect of the molecule is slightly changed in consequence, the effect of the cluster geometry is minimal; this is the result of closely similar sizes of the ruthenium and osmium atoms, as has been remarked before.[12]

The molecules consist of two triangular M_3 clusters, one edge of each of which is bridged by a μ-PPh_2 group, formed by cleavage of both C(sp)–P bonds in the bdpp ligand of the precursor (**1** or **2**). The resulting C_4 fragment bridges both M_3 cores in a conventional μ_3-σ,$2\pi(\perp)$ fashion, as a buta-1,3-diyne-1,4-diyl ligand. Thus the complex appears as two $M_3(\mu_3\text{-}C_2)(\mu\text{-}PPh_2)(CO)_9$ fragments linked by a C–C single bond [1.417(8) (**10**); 1.42(2) Å (**13**)] with a symmetry element at its centre.

It is worth noting that M(1) $\cdots$ M(3) vectors in both cores are long, at 3.452(1) and 3.488(3) Å, respectively, and are

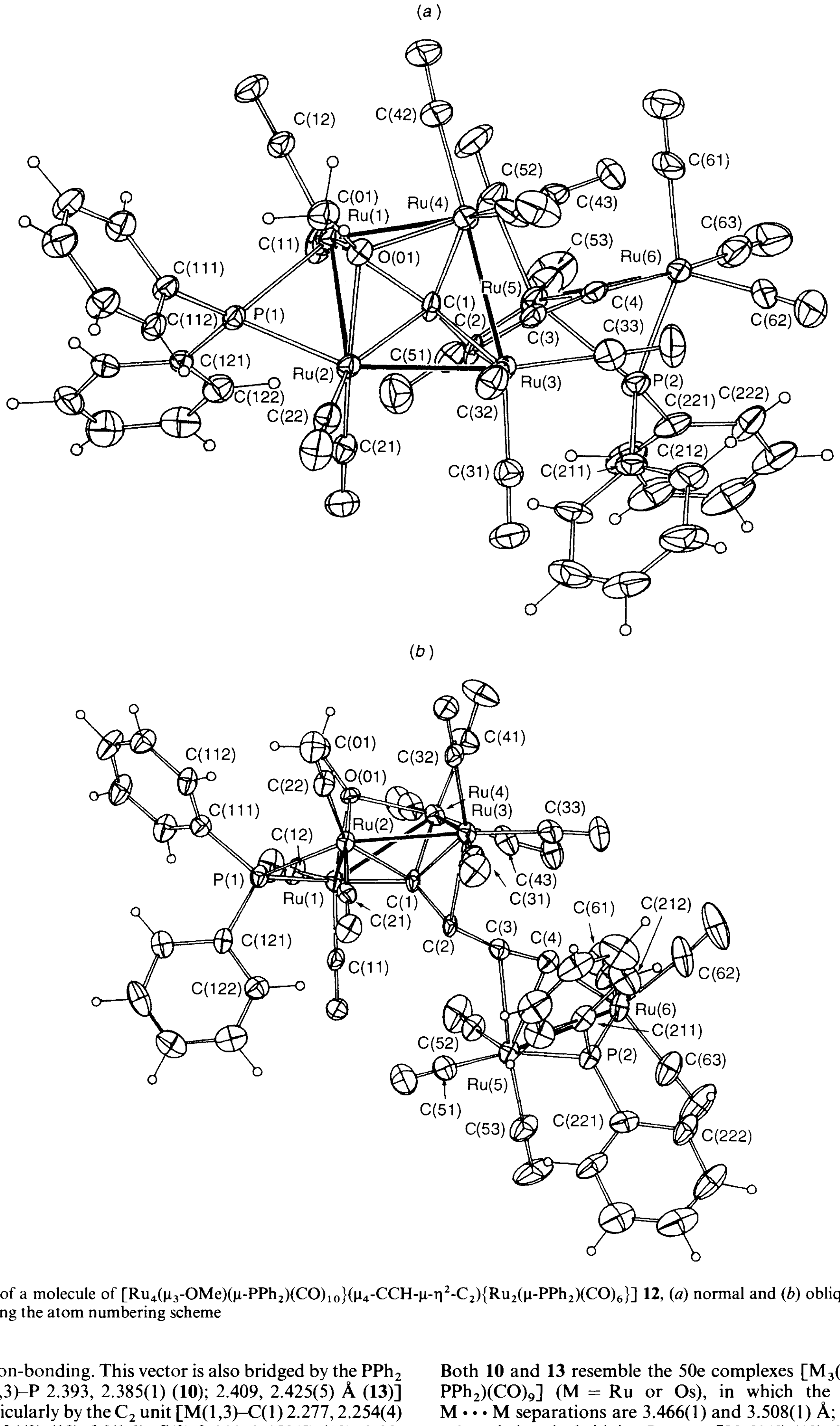


Fig. 3 Plots of a molecule of $[Ru_4(\mu_3\text{-OMe})(\mu\text{-PPh}_2)(CO)_{10}\}(\mu_4\text{-CCH-}\mu\text{-}\eta^2\text{-}C_2)\{Ru_2(\mu\text{-PPh}_2)(CO)_6\}]$ **12**, (*a*) normal and (*b*) oblique to the Ru_4 'plane', showing the atom numbering scheme

essentially non-bonding. This vector is also bridged by the PPh_2 group [M(1,3)–P 2.393, 2.385(1) (**10**); 2.409, 2.425(5) Å (**13**)] and perpendicularly by the C_2 unit [M(1,3)–C(1) 2.277, 2.254(4) (**10**); 2.33, 2.24(2) (**13**); M(1,3)–C(2) 2.444, 2.450(5) (**10**); 2.39, 2.37(2) Å (**13**)]. The long distances to C(2) in **10** are notable. Both **10** and **13** resemble the 50e complexes $[M_3(\mu_3\text{-}C_2Pr^i)(\mu\text{-}PPh_2)(CO)_9]$ (M = Ru or Os), in which the non-bonded M ··· M separations are 3.466(1) and 3.508(1) Å;[13] the angles subtended at the bridging P atoms [92.51(5) (**10**), 92.4(2)° (**13**)] are also similar to those found in Carty's complexes [92.8 (Ru),

Table 3 Selected bond parameters (distances in Å, angles in °) for $[\{Ru_4(\mu_3\text{-}OMe)(\mu\text{-}PPh_2)(CO)_{10}\}(\mu_4\text{-}CCH\text{-}\mu\text{-}\eta^2\text{-}C_2)\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]$ **12**

Ru(1)–Ru(2)	2.681(2)	Ru(4)–O(01)	2.127(8)
Ru(1)–Ru(4)	2.768(2)	Ru(1)–C(1)	2.17(1)
Ru(2)–Ru(3)	2.774(2)	Ru(2)–C(1)	2.20(1)
Ru(2) ··· Ru(4)	3.427(2)	Ru(3)–C(1)	2.10(1)
Ru(3)–Ru(4)	2.805(2)	Ru(4)–C(1)	2.11(2)
Ru(5)–Ru(6)	2.755(2)	Ru(3)–C(2)	2.28(1)
Ru(1)–P(1)	2.299(4)	Ru(5)–C(3)	2.48(2)
Ru(2)–P(1)	2.335(4)	Ru(5)–C(4)	2.27(2)
Ru(5)–P(2)	2.340(4)	Ru(6)–C(4)	2.02(1)
Ru(6)–P(2)	2.328(5)	C(1)–C(2)	1.45(2)
Ru(1)–O(01)	2.10(1)	C(2)–C(3)	1.45(2)
Ru(2)–O(01)	2.21(1)	C(3)–C(4)	1.25(2)
Ru–CO	range 1.76–2.01(2), average 1.89		
C–O	range 1.10–1.18(2), average 1.14		
P–C(Ph)	range 1.77–1.88(2), average 1.81		
Ru(2)–Ru(1)–Ru(4)	77.93(6)	C(1)–C(2)–C(3)	120(1)
Ru(1)–Ru(2)–Ru(3)	96.97(6)	C(2)–C(3)–C(4)	168(1)
Ru(2)–Ru(3)–Ru(4)	75.81(6)	C(3)–C(4)–Ru(6)	162(1)
Ru(1)–Ru(4)–Ru(3)	94.29(7)		

Table 4 Selected bond parameters (distances in Å, angles in °) for $[\{M_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3\text{:}\mu_3\text{-}C_4)]$ (M = Ru **10** or Os **13**)

	10	**13**
M(1)–M(2)	2.841(1)	2.905(2)
M(2)–M(3)	2.846(1)	2.883(2)
M(1) ··· M(3)	3.452(1)	3.488(3)
M(1)–P	2.393(1)	2.409(5)
M(3)–P	2.385(1)	2.425(5)
M(1)–C(1)	2.277(4)	2.33(2)
M(1)–C(2)	2.444(4)	2.39(1)
M(2)–C(1)	1.936(6)	1.93(2)
M(3)–C(1)	2.254(4)	2.24(2)
M(3)–C(2)	2.450(5)	2.37(2)
C(1)–C(2)	1.302(9)	1.34(2)
C(2)–C(2′)	1.417(8)	1.42(2)
P–C(101)	1.835(5)	1.82(1)
P–C(201)	1.836(6)	1.83(2)
M–CO		
range	1.881–1.963(6)	1.83–1.96(2)
average	1.913	1.90
C–O		
range	1.126–1.144(9)	1.11(2)–1.22(3)
average	1.134	1.14
M(1)–M(2)–M(3)	74.74(3)	74.11(7)
M(2)–C(1)–C(2)	159.2(3)	154(1)
C(1)–C(2)–C(2′)	149.6(4)	138(2)

93.2° (Os)]. Most structural dimensions are consistent with a difference of *ca.* 0.04–0.06 Å in the radii of the Ru and larger Os atoms.

Discussion

Reactions between 1 equivalent of the diacetylenic bis(tertiary phosphine) bdpp and 2 equivalents of cluster carbonyls containing labile ligands have provided ready access to complexes containing one cluster moiety attached to each of the two phosphorus atoms in bdpp (Scheme 1). Using this methodology, we have prepared and characterised complexes containing two $M_n(CO)_{11}$ [M_n = Ru_3, Os_3, $Re_3(\mu\text{-}H)_3$ or $Ru_4(\mu\text{-}H)_4$] clusters. Increasing the ratio of ligand:cluster carbonyl to 2:1 allowed the preparation of complexes containing only one cluster unit attached to the bridging ligand, namely $[M_n(CO)_{11}(bdpp)]$ [M_n = Os_3 or $Re_3(\mu\text{-}H)_3$]. In turn, these complexes reacted with suitable precursors to give the Ru_3/Os_3 and $M_3/Re_3(\mu\text{-}H)_3$ (M = Os or Ru) species. The properties of these complexes were in no way exceptional, and indicated that there was little, if any, interaction between the two cluster moieties.

Our motivation for these studies was the use of these complexes as possible precursors of (*a*) C_4 complexes, formed by cleavage of both C(sp)–P bonds in the bridging bdpp ligand, and (*b*) heterometallic clusters, possibly with novel core geometries, formed by condensation of two different clusters around a single bdpp ligand or its alteration products. The preliminary studies reported above and summarised in Scheme 2 show that pyrolysis of the $\{Ru_3\}_2$ and $\{Os_3\}_2$ complexes does indeed afford novel clusters containing the C_4 ligand, and that in the former case, other polynuclear derivatives can also be formed. The following paper describes the partial realisation of (*b*).[14]

In contrast with derivatives of the acetylenic diphosphine dppa, which on heating readily cleave one of the two C(sp)–P bonds,[2] but require treatment with other chemical reagents to produce complexes containing the C_2 ligand,[3] similar complexes containing bdpp undergo ready cleavage of both C(sp)–P bonds. Thus we have obtained complexes **10** and **13**, in which a C_4 ligand spans two M_3 clusters, the two units being joined by a C–C single bond. The conclusion is that the bdpp derivatives are the more reactive, not surprisingly when the stabilities of the two ligands are compared. The interactions of the C_4 ligand with the clusters seem to be limited at present to those of the two C_2 units, which appear to behave independently while remaining joined by the C–C bond. Further studies of the chemistry of these species are necessary to clarify this point. However, the nature of the other two complexes, **11** and **12**, obtained by pyrolysis of the ruthenium cluster **2**, further emphasise this feature.

The formation of these two complexes proceeds by addition of a C(sp)–P bond across an M–M bond of the triangular cluster, probably by initial co-ordination of the C≡C triple bond to the metal atom adjacent to the *P*-co-ordinated metal atom. Cleavage of C(sp)–P bonds is known to be a facile process: addition of the C_2 and PPh_2 ligands (donating a total of 6e) results in opening of the M_3 cluster, as shown by the long M(1) ··· M(3) distances. This type of reaction has been extensively investigated by Carty and his co-workers [*cf.* Scheme 1 in ref. 15(*a*)]; our conclusion in the present instance is that these reactions are further examples of those of $[M_3(CO)_{11}\{PPh_2(C_2R)\}]$ (R = Pr^i or Bu^t) reported many years ago,[13] with **1** and **2** having R = $C_2[M_3(CO)_{11}]$.

These reactions show that bdpp, in combination with suitable substrates, can act as a source of the C_4 ligand. Although there is now a plethora of complexes of various types which contain the C_2 ligand,[16] there are few examples containing the next even-numbered all-carbon ligand. First to be described was $[\{Co_3(CO)_9\}_2(\mu_3\text{:}\mu_3\text{-}C_4)]$ and its PPh_3 and $P(C_6H_{11})_3$ derivatives: the parent complex was obtained by heating solutions of $[Co_3(\mu_3\text{-}CX)(CO)_9]$ (X = Cl or Br) in high-boiling arenes, such as xylene or mesitylene.[17] The four-carbon chain has also been used to link two ML_n units, such as $MCl(PBu_3)_2$ (M = Pd or Pt) in complexes obtained from *trans*-$[MCl_2(PBu_3)_2]$ and HC_2C_2H.[18] Coupling of $[M(C_2C_2H)_2(PBu_3)_2]$ with (CuI/$NHMe_2$) or reactions with $[MCl_2(PR_3)_2]$ have given polymers containing $\{M(PR_3)_2C_2C_2\}$ units (M = Ni, Pd or Pt).[18,19]

More recently, complexes of the type $[\{ML_n\}_2(\mu\text{-}C_4)]$ [ML_n = $(Mo/W)(CO)_2L'(\eta\text{-}C_5H_5)$ or $Fe(CO)L'(\eta\text{-}C_5H_5)$, L′ = CO or PPh_3] have been obtained from Li_2C_4 and the corresponding halides; some examples with two different ML_n groups were also prepared.[20] The complex $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4)]$ exists as two rotamers, both of which have been structurally characterised.[21]

Loss of CO is facilitated by carrying out the reaction under a nitrogen purge, although further loss to give the electron-precise complexes $[\{M_3(\mu\text{-}PPh_2)(CO)_{10}\}_2(\mu\text{-}C_4)]$ {as found for the analogous $[M_3(\mu\text{-}PPh_2)(\mu_3\text{-}C_2R)(CO)_9]$ complexes

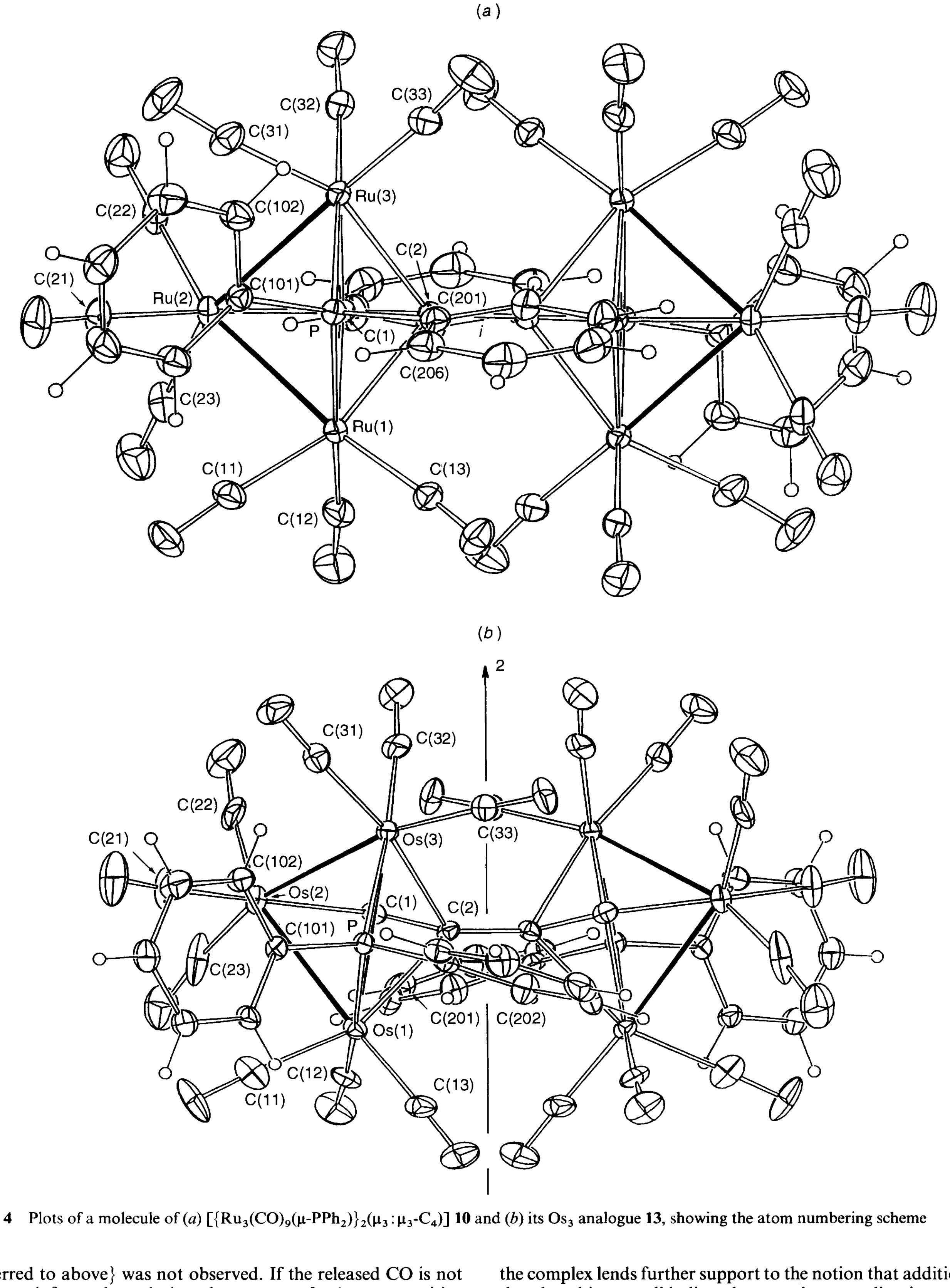


Fig. 4 Plots of a molecule of (*a*) [$\{Ru_3(CO)_9(\mu\text{-}PPh_2)\}_2(\mu_3:\mu_3\text{-}C_4)$] **10** and (*b*) its Os_3 analogue **13**, showing the atom numbering scheme

referred to above} was not observed. If the released CO is not removed from the solution, however, a further competitive reaction resulted in the formation of **11**. This complex retains one half of **2** intact while an intramolecular reaction occurs within the second half. This generates a novel phosphine ligand bearing both a metallated C_6H_4 group and an unusual C_2 linkage with the cluster; in the course of the reaction a fourth ruthenium atom has been acquired. Formation of this part of the complex lends further support to the notion that addition of the phosphinoacetylide ligand occurs by co-ordination of the C≡C triple bond to the cluster. In part also, the complex may be derived from a second reaction, in which the $C_2PPh_2\{Ru_3(CO)_{11}\}$ fragment undergoes an internal oxidative addition of the C(sp)–P bond across the cluster with concomitant elimination of an $Ru(CO)_3$ group.

This type of reaction also occurs readily on treatment of complex **11** with methanol, when **12** is formed. There are several complexes containing μ_3-OR groups attached to ruthenium clusters, most notably $[Ru_4(\mu_4\text{-}CCHPr^i)(\mu_3\text{-}OEt)(\mu\text{-}PPh_2)(CO)_{10}]$ obtained from $[Ru_3(CO)_{11}\{PPh_2(C_2Pr^i)\}]$ and an EtOH–thf mixture, described by Carty *et al.*[22] many years ago. The geometry of this complex is closely similar to that of **12**, as illustrated in Fig. 3(*b*). Facile addition of alcohols, probably to a μ_3-C_2R cluster, results in formation of the CCHR and OR ligands. The binuclear $Ru_2(\mu\text{-}PPh_2)(\mu\text{-}C_2R)(CO)_6$ fragment also present is probably formed by fragmentation of the $Ru_3(PPh_2C_2R)(\mu\text{-}PPh_2)(CO)_{11}$ part of **11**: this reaction has direct precedents in the conversion of $[M_3(CO)_{11}\{PPh_2(C_2R)\}]$ (M = Fe, Ru or Os; R = Pr^i, Bu^t or Ph) into $[M_2(\mu\text{-}PPh_2)(\mu\text{-}C_2R)(CO)_6]$.[15] Recent studies of complexes containing dppa bridging different ML_n groups also support this view of the course of the reaction: when $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}(\mu\text{-}dppa)\{Ru_3(CO)_{11}\}]$ was heated in refluxing toluene it was smoothly transformed to $[Re_3(\mu\text{-}H)_3(CO)_{11}\{PPh_2\text{-}\mu\text{-}\sigma,\eta^2\text{-}C_2\text{-}[Ru_2(\mu\text{-}PPh_2)(CO)_6]\}]$.[2c] Similar reactions are probably the source of the extra ruthenium carbonyl unit required for the formation of **11**.

In this work we have demonstrated that the two halves of complexes of type **1** act independently, what happens in one half having little or no effect on the second half. Under our reaction conditions there was no evidence for the formation of complexes of the type $[\{M_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu\text{:}\mu\text{-}C_4)]$ (M = Ru or Os) from **1** or **2**, although we have recently described the reactions of $[\{Fe(CO)_4\}_2(\mu\text{-}bdpp)]$ with $[Fe_2(CO)_9]$ to give the iron analogue, a reaction which probably proceeds by co-ordination of additional $Fe(CO)_3$ units to the C≡C triple bonds, followed by addition of PPh_2 and C_2R units to the Fe–Fe bonds.[6]

Conclusion

The main conclusions that can be drawn from this stage of the work are: (*a*) that it is possible to co-ordinate metal carbonyl clusters in stepwise fashion to the diacetylenic bis(tertiary phosphine) bdpp; (*b*) that the two cluster units do not seem to interact with each other through the bridging ligand; (*c*) that co-ordinated bdpp, as in the free state, is considerably more reactive than the monoacetylenic analogue dppa, in the present case with respect to C(sp)–P bond breaking to give C_4 ligands; and (*d*) that the two C_2 moieties behave independently, undergoing separate co-ordination and subsequent reactions, but with preservation of the C–C single bond.

The present work, together with that affording the complex $[\{Fe_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu\text{:}\mu\text{-}C_4)]$, previously reported,[6] expands the range of known C_4 complexes at a time when the chemistry of all-carbon ligands is receiving increasing attention. Their reactions will be described further elsewhere.

Experimental

General Conditions.—All reactions were carried out under dry, high-purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumentation.—Infrared: Perkin Elmer 1700X FT-IR or 683 double beam, NaCl optics. NMR: Bruker CXP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz). FAB mass spectroscopy: VG ZAB 2HF (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Reagents.—The compounds $[Ru_3(CO)_{12}]$,[23] $[Ru_3(CO)_{11}(NCMe)]$,[24] $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$,[25] $[Re_3(\mu\text{-}H)_3(CO)_{12}]$,[26] $[Os_3(CO)_{12}]$,[27] $[Os_3(CO)_{11}(NCMe)]$[28] and bdpp[4] were prepared by the cited methods. Trimethylamine oxide $[Me_3NO\cdot 2H_2O$ (Aldrich)] was dehydrated by sublimation [100 °C, 0.1 mmHg (13.3 Pa)].

Preparations.—$[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$. The complex $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (215 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (40 cm^3)–MeCN (3 cm^3). Trimethylamine oxide (20 mg, 0.26 mmol) in CH_2Cl_2 (30 cm^3) was added dropwise until no $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ remained. After filtration through silica the solvents were removed and the residue recrystallised from CH_2Cl_2–MeCN–MeOH to yield white crystals of $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ (149 mg, 68%), m.p. 200–202 °C (decomp.) [Found: C, 17.15; H, 0.75; N, 1.55%; *M* 911 (mass spectrometry). $C_{13}H_6NO_{11}Re_3$ requires C, 17.15; H, 0.65; N, 1.55%; *M* 911]. IR: ν(CO) (CH_2Cl_2) 2114w, 2090m, 2038s, 2017s, 2003s, 1968m, 1942w and 1930w cm^{-1}. FAB mass spectrum: *m/z* 911, M^+; 883–659, $[M - nCO]^+$ (*n* = 1–9); 870–674, $[M - nCO - NCMe]^+$ (*n* = 0–7).

$[\{Ru_3(CO)_{11}\}_2(\mu\text{-}bdpp)]$ **1**. (*a*) From $[Ru_3(CO)_{11}(NCMe)]$. A solution of bdpp (139 mg, 0.33 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise (*ca.* 20 min) to a cooled (−78 °C) solution of $[Ru_3(CO)_{11}(NCMe)]$ [prepared from $[Ru_3(CO)_{12}]$ (500 mg, 0.78 mmol) and used directly from a chromatotron as a light petroleum–CH_2Cl_2–MeCN (20:4:1) solution]. After warming to room temperature (r.t.) the solvent was removed and the residue chromatographed on an alumina column. Light petroleum eluted $[Ru_3(CO)_{12}]$ (39 mg, 8%). Light petroleum–CH_2Cl_2 (4:1) eluted an orange-red band which was crystallised from CH_2Cl_2–MeOH, yielding red crystals of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-}bdpp)]$ **1** (244 mg, 38%), m.p. 141–144 °C (decomp.) [Found: C, 36.45; H, 1.35%; *M* 1642 (mass spectrometry). $C_{50}H_{20}O_{22}P_2Ru_6$ requires C, 36.60; H, 1.25%; *M* 1642]. IR: ν(CO) (cyclohexane) 2099m, 2048s, 2032s, 2017s, 2000(sh), 1991m, 1980m and 1968w cm^{-1}. FAB mass spectrum: *m/z* 1642, M^+; 1614–1026, $[M - nCO]^+$ (*n* = 1–22). Further elution with light petroleum (b.p. 40–60 °C)–CH_2Cl_2 (7:3) yielded a red band comprising two compounds which were further separated by preparative TLC (light petroleum–acetone, 4:1). These compounds (R_f 0.3; 71.2 mg; R_f 0.2, 17.9 mg) have not been identified.

(*b*) *From* $[Ru_3(CO)_{12}]$ *and* Me_3NO. A solution of Me_3NO (14 mg, 0.19 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise to a solution of $[Ru_3(CO)_{12}]$ (116 mg, 0.182 mmol) and bdpp (38 mg, 0.091 mmol) in CH_2Cl_2 (50 cm^3). The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 10:3) to yield four bands. The major product (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield red crystals of complex **1** (71 mg, 39%). Some $[Ru_3(CO)_{12}]$ (R_f 0.8, 4 mg, 3%) was recovered. Two minor red bands (R_f 0.35, 0.30) have not been identified.

$[\{Os_3(CO)_{11}\}_2(\mu\text{-}bdpp)]$ **2**. To a solution of $[Os_3(CO)_{11}(NCMe)]$ (120 mg, 0.13 mmol) in CH_2Cl_2 (25 cm^3) was added bdpp (27 mg, 0.652 mmol) in CH_2Cl_2 (15 cm^3) dropwise (*ca.* 20 min.). After 90 min the solvent was removed and the residue purified by preparative TLC (light petroleum–CH_2Cl_2, 3:1) to yield four bands. The major product (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield orange crystals of $[\{Os_3(CO)_{11}\}_2(\mu\text{-}bdpp)]$ **2** (96 mg, 68%), m.p. > 260 °C (decomp.) [Found: C, 27.45; H, 1.10%; *M* 2176 (mass spectrometry). $C_{50}H_{20}O_{22}Os_6P_2$ requires C, 27.60; H, 0.95%; *M*, 2176]. IR: ν(CO) (CH_2Cl_2) 2109w, 2057s, 2037m, 2021vs, 1992m, 1980m and 1968(sh) cm^{-1}. FAB mass spectrum: *m/z* 2176, M^+; 2120–1560, $[M - nCO]^+$ (*n* = 2, 4–22); 1483, $[M - 22CO - Ph]^+$; 924, $[Os_3(CO)_6(PPh_2)]^+$; 896–755, $[Os_3(CO)_6(PPh_2) - nCO]^+$ (*n* = 1–6); 879, $[Os_3(CO)_{11}]^+$; 851–683, $[Os_3(CO)_{11} - nCO]^+$ (*n* = 1–7); 577, $[Os_2(CO)_7]^+$; 739–683, $[Os_2(CO)_7 - nCO]^+$ (*n* = 1–3). The other major product (R_f 0.4) was recrystallised from CH_2Cl_2–MeOH to yield a yellow powder which has not been identified. IR: ν(CO)(cyclohexane) 2109m, 2057m, 2038m, 2022vs, 2005m, 1993m, 1978m and 1969(sh) cm^{-1}.

$[Os_3(CO)_{11}(bdpp)]$ **3**. A solution of $[Os_3(CO)_{11}(NCMe)]$

(100 mg, 0.109 mmol) in CH_2Cl_2 (100 cm^3) was added dropwise to a solution of bdpp (84 mg, 0.20 mmol) in CH_2Cl_2 (100 cm^3) over *ca.* 1 h and the solution was stirred overnight. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 5:1) to yield three major bands. The major band yielded [$Os_3(CO)_{11}$(bdpp)] **3** (R_f 0.4, 95 mg, 67%) [Found: C, 36.05; H, 1.60%; *M* 1297 (mass spectrometry). $C_{39}H_{20}O_{11}Os_3P_2$ requires C, 36.10; H, 1.55%; *M* 1297]. IR: ν(CO)(cyclohexane) 2108m, 2056m, 2036m, 2020vs, 2002m, 1991m, 1980m, 1973w and 1966w cm^{-1}. FAB mass spectrum: *m/z* 1297, *M*; 1269–989 (*M* − *n*CO) (*n* = 1–11). Some bdpp (R_f 0.5) and complex **2** (R_f 0.25, 38 mg, 32%) were also recovered.

[{$Re_3(\mu\text{-}H)_3(CO)_{11}$}$_2$(μ-bdpp)] **4**. [$Re_3(\mu\text{-}H)_3(CO)_{11}$(NCMe)] (150 mg, 0.165 mmol) and bdpp (33 mg, 0.080 mmol) were stirred for 6 d at room temperature in CH_2Cl_2 (20 cm^3). After the solvent was removed the residue was purified by preparative TLC (light petroleum–CH_2Cl_2, 5:1). The major band was recrystallised from CH_2Cl_2–MeOH yielding [{$Re_3(\mu\text{-}H)_3(CO)_{11}$}$_2$(μ-bdpp)] **4** (79 mg, 44%) as a pale yellow powder, m.p. 153–154 °C (decomp.) [Found: C, 27.80; H, 1.35%; *M* 2158 (mass spectrometry). $C_{50}H_{26}O_{22}P_2Re_6$ requires C, 27.85; H, 1.20%; *M* 2158]. IR: ν(CO) (cyclohexane) 2114w, 2091m, 2055w, 2037s, 2018vs, 2007(sh), 2002s, 1985(sh), 1972vs, 1953m and 1945m cm^{-1}. FAB mass spectrum: *m/z* 2158, M^+.

[$Re_3(\mu\text{-}H)_3(CO)_{11}$(bdpp)] **5**. A solution of [$Re_3(\mu\text{-}H)_3(CO)_{11}$(NCMe)] (98 mg, 0.108 mmol) in benzene (40 cm^3) was added dropwise to a solution of bdpp (84 mg, 0.20 mmol) in benzene (40 cm^3) over *ca.* 18 h at 50 °C. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 5:1) to yield four major bands. The major band yielded [$Re_3(\mu\text{-}H)_3(CO)_{11}$(bdpp)] **5** ($R_f$ 0.5, 68 mg, 49%) [Found: C, 36.50; H, 1.90%; *M* 1288 (mass spectrometry).

Table 5 Crystal data and refinement details for complexes **6** and **10**–**13**

Complex	**6**	**10**	**11**	**12**	**13**
Formula	$C_{52}H_{36}O_{24}P_2Ru_8$	$C_{46}H_{20}O_{18}P_2Ru_6$	$C_{51}H_{20}O_{23}P_2Ru_7$	$C_{45}H_{24}O_{17}P_2Ru_6$	$C_{46}H_{20}O_{18}Os_6P_2$
M	1915.4	1529.0	1770.2	1505.1	2063.8
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a/Å	10.109(2)	15.177(2)	21.38(1)	18.69(2)	25.27(2)
b/Å	12.833(2)	9.752(4)	19.71(2)	16.16(2)	9.785(9)
c/Å	13.923(6)	19.622(7)	15.79(2)	9.736(9)	20.20(2)
α/°	99.98(2)		70.27(10)	74.71(9)	
β/°	98.23(2)	121.55(2)	87.14(8)	87.06(8)	96.94(5)
γ/°	102.24(1)		71.82(7)	74.28(8)	
U/Å^3	1707.8	2474.8	5938	2731	4958
Z	1	2	4	2	4
D_c/g cm^{-3}	1.86	2.05	1.98	1.83	2.76
F(000)	922	1468	3392	1448	3704
Crystal size/mm	0.09 × 0.20 × 0.21	0.18 × 0.27 × 0.32	0.13 × 0.50 × 0.06	0.35 × 0.08 × 0.31	0.16 × 0.42 × 0.33
*A** (minimum, maximum)	1.35, 1.95 (analytical)	1.34, 1.53 (gaussian)	1.37, 1.84 (gaussian)	1.12, 1.75 (gaussian)	9.5, 55.4 (analytical)
μ/cm^{-1}	17.7	19.2	16.9	15.6	171.1
$2\theta_{max}$/°	45	50	45	50	55
N	2758	4343	15 507	9064	5733
N_o	2187	3525	9524	4959	3457
R	0.058	0.028	0.053	0.057	0.052
R'	0.068	0.033	0.054	0.057	0.050

Table 6 Non-hydrogen atomic coordinates for [{$Ru_4(\mu\text{-}H)_4(CO)_{11}$}$_2$(μ-bdpp)] **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	−0.1411(1)	0.5994(1)	0.1860(1)	C(31)	−0.1858(14)	0.9479(11)	0.3182(16)
Ru(2)	0.0342(1)	0.7846(1)	0.3425(1)	C(32)	−0.3966(20)	0.7922(16)	0.1731(22)
Ru(3)	−0.2267(1)	0.8019(1)	0.2612(1)	C(33)	−0.3049(18)	0.7700(13)	0.3680(21)
Ru(4)	−0.0230(1)	0.7913(1)	0.1297(1)	C(41)	0.1100(14)	0.7240(11)	0.0829(16)
P(1)	−0.0234(1)	0.0464(1)	0.0265(1)	C(42)	0.0545(15)	0.9318(12)	0.1148(17)
O(11)	0.0574(9)	0.4729(7)	0.1135(10)	C(43)	−0.1491(18)	0.7482(13)	0.0005(20)
O(12)	−0.3439(11)	0.5037(8)	−0.0097(11)	C(111)	−0.2419(10)	0.3229(7)	0.2036(11)
O(21)	0.3092(16)	0.7281(12)	0.3972(15)	C(112)	−0.1256(10)	0.2810(7)	0.2170(11)
O(22)	0.1352(11)	1.0260(9)	0.4291(12)	C(113)	−0.1291(10)	0.1766(7)	0.1657(11)
O(23)	−0.0672(14)	0.7389(11)	0.5274(15)	C(114)	−0.2488(10)	0.1142(7)	0.1009(11)
O(31)	−0.1683(13)	1.0410(11)	0.3528(13)	C(115)	−0.3651(10)	0.1561(7)	0.0875(11)
O(32)	−0.4967(20)	0.7810(14)	0.1185(17)	C(116)	−0.3616(10)	0.2604(7)	0.1388(11)
O(33)	−0.3619(15)	0.7448(11)	0.4271(14)	C(121)	−0.4040(8)	0.4557(8)	0.2950(12)
O(41)	0.1901(12)	0.6843(9)	0.0556(12)	C(122)	−0.4993(8)	0.4938(8)	0.2364(12)
O(42)	0.1078(13)	1.0184(10)	0.0959(13)	C(123)	−0.6317(8)	0.4863(8)	0.2569(12)
O(43)	−0.2201(15)	0.7302(10)	−0.0651(14)	C(124)	−0.6687(8)	0.4407(8)	0.3361(12)
C(1)	−0.1292(13)	0.4740(10)	0.3822(16)	C(125)	−0.5734(8)	0.4026(8)	0.3947(12)
C(2)	−0.0459(12)	0.4890(10)	0.4556(15)	C(126)	−0.4411(8)	0.4101(8)	0.3741(12)
C(11)	−0.0168(11)	0.5258(9)	0.1430(13)	O(me1)*	0.4169(24)	−0.0174(20)	0.2373(25)
C(12)	−0.2657(12)	0.5419(9)	0.0668(16)	O(me2)*	0.5050(28)	0.0129(22)	0.3965(29)
C(21)	0.2040(15)	0.7520(12)	0.3765(17)	C(me1)*	0.3818(45)	0.1067(36)	0.2803(45)
C(22)	0.0983(13)	0.9356(11)	0.3953(16)	C(me2)*	0.4957(40)	0.1036(33)	0.3716(42)
C(23)	−0.0281(18)	0.7541(13)	0.4664(22)				

* Atom has a 0.5 occupancy factor.

$C_{39}H_{23}O_{11}P_2Re_3$ requires C, 36.35; H, 1.80%; *M* 1288]. IR: ν(CO) (cyclohexane) 2113m, 2091m, 2053w, 2036vs, 2019(sh), 2015vs, 2008m, 2001s, 1987m, 1972vs, 1967(sh), 1951m and 1943m cm^{-1}. FAB mass spectrum: *m/z* 1288, *M*; 1260–980 (*M* − *n*CO) (*n* = 1–11). Some bdpp (R_f 0.6, 42 mg, 50%), complex **4** (R_f 0.35, 21 mg, 18%) and 15.7 mg of an unidentified compound were also isolated.

[{Ru_4(μ-H)$_4$(CO)$_{11}$}$_2$(μ-bdpp)] **6**. To a solution of [Ru_4(μ-H)$_4$(CO)$_{11}$(NCMe)] in light petroleum–CH_2Cl_2–MeCN {from [Ru_4(μ-H)$_4$(CO)$_{12}$] (210 mg, 0.282 mmol}, cooled to −64 °C, was added bdpp (47 mg, 0.11 mmol) in CH_2Cl_2 (20 cm^3) dropwise over *ca.* 25 min. After warming to room temperature the solvents were removed and the residue purified by preparative TLC (light petroleum–CH_2Cl_2, 4:1). The major product (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield yellow crystals of [{Ru_4(μ-H)$_4$(CO)$_{11}$}$_2$(μ-bdpp)] **6** (102 mg, 39%), m.p. 136–138 °C (decomp.) [Found: C, 32.30; H, 1.45%; *M*, 1853 (mass spectrometry). $C_{50}H_{28}O_{22}P_2Ru_8$ requires C, 32.45; H, 1.50%; *M* 1853]. IR: ν(CO) (cyclohexane) 2096m, 2069vs, 2059s, 2030s, 2011s, 1999(sh), 1994(sh) and 1970w cm^{-1}. ^1H NMR ($CDCl_3$): δ −17.26 (8 H, d, J_{HP} = 6.3 Hz, RuH) and 7.49–7.74 (20 H, m, Ph). FAB mass spectrum: *m/z* 1853, M^+; 1236, $[M - 22CO]^+$.

[{Ru_3(CO)$_{11}$}(μ-bdpp){Os_3(CO)$_{11}$}] **7**. A solution of [Ru_3(CO)$_{11}$(NCMe)] {*ca.* 0.13 mmol; from [Ru_3(CO)$_{12}$] (100 mg, 0.16 mmol)} in CH_2Cl_2 (20 cm^3) and MeCN (5 cm^3) was added to a solution of complex **3** (95 mg, 0.073 mmol). The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 4:1) to yield at least four bands. The first band was [Ru_3(CO)$_{12}$] (R_f 0.8, 19 mg, 19%). The major band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield red needles of [{Ru_3(CO)$_{11}$}(μ-bdpp){Os_3(CO)$_{11}$}] **7** (56 mg, 40%), m.p. 146–149 °C (decomp.) [Found: C, 31.35; H, 1.30%; *M* 1910 (mass spectrometry). $C_{50}H_{20}O_{22}Os_3P_2Ru_3$ requires C, 31.45; H, 1.05%; *M* 1910]. IR: ν(CO) (cyclohexane) 2109w, 2099w, 2084vw, 2057m, 2049m, 2033m, 2021vs, 2005(sh), 1993m, 1979m and 1969(sh) cm^{-1}. FAB mass spectrum: *m/z* 1910, M^+; 1882–1294, $[M - nCO]^+$ (*n* = 1–22). A third red band (R_f 0.3, 14 mg) has not been identified.

[{Re_3(μ-H)$_3$(CO)$_{11}$}(μ-bdpp){Os_3(CO)$_{11}$}] **8**. A solution of [Re_3(μ-H)$_3$(CO)$_{11}$(NCMe)] (127 mg, 0.14 mmol) and complex **3** (171 mg, 0.13 mmol) in benzene (40 cm^3) were heated (oil-bath at 65 °C) for 2 h. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 10:3) to yield three major bands. The major band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield [{Re_3(μ-H)$_3$(CO)$_{11}$}(μ-bdpp){Os_3(CO)$_{11}$}] **8** (177 mg, 63%) as a yellow powder, m.p. 98–102 °C [Found: C, 27.00; H, 1.15%; *M* 2144 (mass spectrometry). $C_{50}H_{23}O_{22}Os_3P_2Re_3$ requires C, 27.70; H, 1.05%; *M* 2144]. IR: ν(CO) (cyclohexane) 2110w, 2091m, 2057m, 2038m, 2021vs, 2001m, 1973s, 1948m and 1944(sh) cm^{-1}. FAB mass spectrum: *m/z* 2144, M^+; 2116–1528, $[M - nCO]^+$ (*n* = 1–22). The two other bands, colourless (R_f 0.6, 27 mg) and yellow (R_f 0.2, 18 mg), have not been identified.

[{Re_3(μ-H)$_3$(CO)$_{11}$}(μ-bdpp){Ru_3(CO)$_{11}$}] **9**. A solution of [Ru_3(CO)$_{11}$(NCMe)] {*ca.* 0.064 mmol; from [Ru_3(CO)$_{12}$] (51 mg, 0.080 mmol)} in CH_2Cl_2 (20 cm^3) and MeCN (5 cm^3) was added to a solution of complex **5** (68 mg, 0.053 mmol) in CH_2Cl_2 (40 cm^3) at −64 °C. After warming to room temperature the solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 10:3) to yield three major bands. The first band was [Ru_3(CO)$_{12}$] (R_f 0.8, 29 mg, 57%). The second band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield [{Re_3(μ-H)$_3$(CO)$_{11}$}(μ-bdpp){Ru_3(CO)$_{11}$}] **9** (38 mg, 38%) as a red powder [Found: C, 31.40; H, 1.30%; $[M - 3CO]^+$ 1816 (mass spectrometry). $C_{50}H_{23}O_{22}P_2Re_3Ru_3$ requires C, 31.60; H, 1.20%; *M* − 3CO 1816. IR: ν(CO) (cyclohexane) 2113m, 2099w, 2090m, 2077m, 2049m, 2036s, 2032(sh), 2016vs, 2007s, 2000s, 1987(sh), 1971s, 1951m, 1944m, 1740w and 1719vw cm^{-1}. FAB mass spectrum: *m/z* 1816–1284, $[M - nCO]^+$ (*n* = 3–22). The third red band (R_f 0.3, 23 mg) has not been identified.

Pyrolyses.—Complex **1**. (*i*) *With nitrogen purge and* 6 h *reaction time*. Nitrogen was bubbled through a refluxing solution of complex **1** (100 mg, 0.061 mmol) in CH_2Cl_2 (40 cm^3) for 7 h. The solvent volume was reduced to 15 cm^3 and MeOH (15 cm^3) added. After 24 h at −10 °C the pale yellow crystals of [{Ru_3(μ-PPh_2)(CO)$_9$}$_2$($μ_3$:$μ_3$-C_4)] **10** (45 mg) were filtered off. The solvent was removed from the eluent purified by preparative TLC (light petroleum–acetone, 3:1) to yield further **2** (R_f 0.5, 23 mg) [total yield 68 mg (73%)], m.p. 250–256 °C (decomp.) [Found: C, 35.90; H, 1.45%; *M* 1530 (mass spectrometry). $C_{46}H_{20}O_{18}P_2Ru_6$ requires C, 36.15; H, 1.30%; *M* 1530]. IR: ν(CO) (CH_2Cl_2) 2078(sh), 2071vs, 2046m, 2024m, 2004m and 1985m cm^{-1}. FAB mass spectrum: *m/z* 1530, M^+; 1502–1026, $[M - nCO]^+$ (*n* = 1–18); 949, $[M - 18CO - Ph]^+$.

(*ii*) *With no nitrogen purge and* 24 h *reaction time*. A solution of complex **1** (160 mg, 0.097 mmol) was heated in refluxing CH_2Cl_2 (40 cm^3) for 24 h. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 5:2) to yield two major bands. A yellow band (R_f 0.7) was recrystallised from CH_2Cl_2–MeOH to yield [{Ru_3(μ-PPh_2)(CO)$_9$}$_2$($μ_3$:$μ_3$-C_4)] **10** (39 mg, 26%). An orange band (R_f 0.6) was recrystallised from toluene–hexane to yield red crystals of [{Ru_4(μ-H)(CO)$_{12}$}{PPh(C_6H_4)$C_2C_2PPh_2$}{Ru_3(CO)$_{11}$}]

Table 7 Non-hydrogen atomic coordinates for [{Ru_3(μ-PPh_2)(CO)$_9$}$_2$($μ_3$:$μ_3$-C_4)] **10**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.660 63(3)	0.708 85(4)	0.042 48(2)	O(32)	0.551 3(3)	0.180 0(4)	−0.137 2(2)
Ru(2)	0.670 81(3)	0.592 41(4)	−0.085 96(2)	C(33)	0.698 1(4)	0.223 8(5)	0.082 3(3)
Ru(3)	0.681 03(3)	0.365 85(4)	0.009 39(2)	O(33)	0.714 5(3)	0.136 1(4)	0.125 5(3)
C(11)	0.757 6(4)	0.837 3(5)	0.049 6(3)	C(1)	0.574 9(3)	0.545 2(5)	−0.052 7(3)
O(11)	0.811 3(3)	0.921 2(4)	0.051 8(3)	C(2)	0.541 7(3)	0.514 1(5)	−0.005 4(3)
C(12)	0.554 4(4)	0.837 5(6)	−0.028 2(3)	P	0.777 26(9)	0.525 4(1)	0.115 18(7)
O(12)	0.499 1(3)	0.919 7(5)	−0.068 4(3)	C(101)	0.915 4(3)	0.529 8(5)	0.149 9(3)
C(13)	0.661 1(4)	0.762 9(5)	0.136 9(3)	C(102)	0.969 6(4)	0.406 9(6)	0.176 1(3)
O(13)	0.669 0(3)	0.797 4(4)	0.194 7(2)	C(103)	1.073 7(4)	0.401 9(6)	0.203 5(4)
C(21)	0.811 5(4)	0.631 6(7)	−0.056 0(3)	C(104)	1.125 3(4)	0.517 2(7)	0.206 3(3)
O(21)	0.893 7(3)	0.657 2(6)	−0.037 2(3)	C(105)	1.073 4(4)	0.638 7(6)	0.181 8(4)
C(22)	0.646 3(4)	0.480 7(6)	−0.173 5(3)	C(106)	0.969 0(4)	0.644 8(6)	0.154 6(3)
O(22)	0.633 8(3)	0.413 2(5)	−0.225 0(2)	C(201)	0.784 5(4)	0.490 6(5)	0.210 0(3)
C(23)	0.617 4(4)	0.750 6(6)	−0.149 9(3)	C(202)	0.696 9(4)	0.439 5(6)	0.208 7(3)
O(23)	0.582 6(3)	0.844 6(5)	−0.190 1(3)	C(203)	0.699 4(5)	0.425 1(7)	0.279 9(4)
C(31)	0.796 4(4)	0.324 3(6)	0.001 2(3)	C(204)	0.784 0(6)	0.458 4(7)	0.350 8(4)
O(31)	0.864 4(3)	0.289 3(5)	−0.004 2(3)	C(205)	0.869 9(5)	0.509 4(7)	0.352 8(3)
C(32)	0.593 1(4)	0.252 0(5)	−0.085 0(3)	C(206)	0.872 0(4)	0.523 2(6)	0.283 9(3)

Table 8 Non-hydrogen atomic coordinates for [{$Ru_4(\mu\text{-}H)(CO)_{12}$}{$\mu\text{-}PPh(C_6H_4)C_2C_2PPh_2$}{$Ru_3(CO)_{11}$}] **11**

	Molecule 1			Molecule 2 *		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ru(11)	0.144 44(6)	0.225 96(7)	0.575 28(8)	0.344 80(6)	0.569 35(7)	0.889 79(8)
Ru(12)	0.217 20(6)	0.277 20(7)	0.411 78(8)	0.266 23(6)	0.565 12(7)	1.050 68(8)
Ru(13)	0.141 70(6)	0.375 86(6)	0.505 78(8)	0.341 13(6)	0.670 27(7)	0.979 54(8)
Ru(14)	0.236 86(7)	0.426 72(7)	0.576 28(8)	0.246 42(6)	0.825 20(7)	0.913 51(8)
C(111)	0.086 2(7)	0.207 0(7)	0.503(1)	0.398 3(8)	0.463 4(9)	0.953(1)
O(111)	0.049 8(6)	0.198 6(7)	0.460 6(8)	0.428 5(6)	0.401 9(6)	0.985 7(8)
C(112)	0.078 1(7)	0.241 1(9)	0.656(1)	0.415 4(8)	0.586 5(8)	0.820(1)
O(112)	0.034 9(5)	0.254 8(8)	0.701 2(8)	0.459 4(5)	0.597 7(7)	0.778 2(8)
C(113)	0.182 5(7)	0.120 9(9)	0.645(1)	0.308 4(8)	0.545 8(8)	0.803 3(9)
O(113)	0.204 6(6)	0.059 2(6)	0.686 4(8)	0.285 0(6)	0.532 1(6)	0.750 5(8)
C(121)	0.146 4(8)	0.285(1)	0.337(1)	0.338 8(7)	0.476 4(8)	1.124(1)
O(121)	0.105 9(6)	0.290 2(8)	0.285 9(8)	0.380 3(5)	0.425 7(6)	1.163 2(8)
C(122)	0.278 9(7)	0.203 3(9)	0.371 7(9)	0.204 5(7)	0.508 6(9)	1.069(1)
O(122)	0.316 2(6)	0.160 6(7)	0.346 8(8)	0.168 9(6)	0.476 0(7)	1.080 8(8)
C(123)	0.233 7(8)	0.361(1)	0.322(1)	0.245 7(8)	0.594 7(9)	1.153(1)
O(123)	0.244 5(7)	0.409 3(7)	0.266 4(7)	0.232 0(6)	0.611 5(7)	1.216 5(7)
C(131)	0.071 4(8)	0.373 5(8)	0.444(1)	0.411 2(7)	0.580 4(8)	1.041(1)
O(131)	0.025 9(6)	0.380 0(6)	0.400 0(8)	0.455 8(6)	0.533 5(6)	1.081 3(9)
C(132)	0.148 7(8)	0.465 6(9)	0.414(1)	0.325 9(8)	0.704 7(9)	1.079(1)
O(132)	0.145 5(7)	0.520 1(6)	0.357 8(8)	0.321 1(7)	0.720 6(9)	1.144 1(8)
C(133)	0.080 3(7)	0.422 6(8)	0.574(1)	0.403 3(7)	0.724 9(8)	0.924 7(9)
O(133)	0.038 7(6)	0.452 1(7)	0.610 5(8)	0.443 2(5)	0.748 5(7)	0.900 5(8)
C(141)	0.184 0(8)	0.436 0(8)	0.677(1)	0.299 4(7)	0.860 7(8)	0.816(1)
O(141)	0.157 2(6)	0.449 4(6)	0.738 1(8)	0.325 0(6)	0.894 0(6)	0.758 6(8)
C(142)	0.313 5(8)	0.413 6(8)	0.639(1)	0.170 7(8)	0.899 2(9)	0.852(1)
O(142)	0.361 3(6)	0.404 6(7)	0.674 9(8)	0.122 9(6)	0.942 2(7)	0.817 4(8)
C(143)	0.212 6(9)	0.537 3(9)	0.524(1)	0.262 9(9)	0.888(1)	0.973(1)
O(143)	0.198 3(8)	0.598 9(6)	0.493(1)	0.276 1(8)	0.922 4(9)	1.012 0(9)
C(11)	0.241 4(7)	0.317 7(7)	0.586 1(9)	0.248 6(6)	0.728 6(7)	0.889 2(8)
C(12)	0.193 7(6)	0.277 7(7)	0.633 4(8)	0.296 0(6)	0.686 8(7)	0.846 8(9)
C(13)	0.181 0(6)	0.275 1(7)	0.723 1(9)	0.314 1(6)	0.728 9(7)	0.760 2(8)
C(14)	0.169 2(6)	0.264 3(7)	0.800 6(9)	0.328 0(6)	0.757 2(7)	0.685 4(9)
P(11)	0.291 7(2)	0.279 3(2)	0.512 3(2)	0.194 3(2)	0.678 8(2)	0.957 0(3)
C(1111)	0.334 5(7)	0.348 1(8)	0.463 0(9)	0.153 5(7)	0.742 5(8)	1.013 3(9)
C(1112)	0.308 0(7)	0.415 8(8)	0.475 5(9)	0.173 5(6)	0.803 6(8)	1.009 4(8)
C(1113)	0.334 0(8)	0.473(1)	0.426(1)	0.150 7(8)	0.844(1)	1.063(1)
C(1114)	0.386(1)	0.460(1)	0.376(1)	0.100 0(9)	0.829(1)	1.120(1)
C(1115)	0.413 2(9)	0.389(1)	0.367(1)	0.078 2(9)	0.770(1)	1.125(1)
C(1116)	0.386 9(7)	0.329 8(9)	0.410(1)	0.101 8(8)	0.727 5(9)	1.071(1)
C(1121)	0.354 7(6)	0.193 5(7)	0.578 2(9)	0.135 2(6)	0.680 2(7)	0.879 1(9)
C(1122)	0.406 0(7)	0.198 8(9)	0.621 8(9)	0.086 2(8)	0.747 0(9)	0.837(1)
C(1123)	0.453 9(7)	0.133(1)	0.675(1)	0.044 3(8)	0.749(1)	0.770(1)
C(1124)	0.447 0(8)	0.063 8(9)	0.688(1)	0.048 9(8)	0.692(1)	0.745(1)
C(1125)	0.395 2(7)	0.055 9(8)	0.649(1)	0.095 9(8)	0.622(1)	0.786(1)
C(1126)	0.348 4(7)	0.123 1(8)	0.595(1)	0.139 2(7)	0.617 6(9)	0.855(1)
P(12)	0.158 5(2)	0.255 0(2)	0.913 8(2)	0.345 2(2)	0.800 7(2)	0.574 4(2)
C(1211)	0.096 1(7)	0.340 0(9)	0.905(1)	0.414 2(6)	0.832 3(8)	0.590 9(9)
C(1212)	0.099 2(7)	0.394 2(9)	0.939(1)	0.428 1(8)	0.890 4(9)	0.515(1)
C(1213)	0.049 8(8)	0.464 9(9)	0.922(1)	0.482 4(8)	0.910(1)	0.526(1)
C(1214)	−0.004 4(8)	0.481(1)	0.871(1)	0.519 6(8)	0.882(1)	0.603(1)
C(1215)	−0.009 8(8)	0.431(1)	0.834(1)	0.503 8(8)	0.829(1)	0.675(1)
C(1216)	0.039 7(7)	0.361 4(9)	0.850(1)	0.451 5(7)	0.802 6(9)	0.667(1)
C(1221)	0.114 7(7)	0.186 0(8)	0.950 5(9)	0.348 3(7)	0.722 4(8)	0.534 7(9)
C(1222)	0.078 8(8)	0.180 0(9)	1.028(1)	0.427 8(8)	0.728 5(9)	0.469(1)
C(1223)	0.050 5(9)	0.125(1)	1.063(1)	0.455(1)	0.670(1)	0.435(1)
C(1224)	0.059 8(9)	0.071(1)	1.022(1)	0.440(1)	0.605(1)	0.468(1)
C(1225)	0.092 9(9)	0.073 7(9)	0.948(1)	0.399(1)	0.598(1)	0.537(1)
C(1226)	0.123 0(8)	0.129 7(9)	0.913(1)	0.368 3(8)	0.656(1)	0.567(1)
Ru(15)	0.351 37(7)	0.116 96(8)	0.942 78(9)	0.162 75(7)	0.819 84(8)	0.467 4(1)
Ru(16)	0.253 57(7)	0.224 34(7)	1.002 15(9)	0.252 94(6)	0.893 90(7)	0.488 28(8)
Ru(17)	0.388 24(7)	0.176 92(8)	1.064 9(1)	0.140 12(8)	0.976 31(8)	0.367 9(1)
C(151)	0.349 7(7)	0.046 8(9)	1.039(1)	0.230(1)	0.786(1)	0.400(1)
O(151)	0.367 0(5)	−0.027 2(7)	1.096 3(8)	0.272 7(6)	0.755 6(7)	0.359 8(8)
C(152)	0.332 1(8)	0.213 4(9)	0.847(1)	0.093 9(8)	0.864 3(9)	0.531(1)
O(152)	0.329 1(5)	0.260 3(6)	0.781 2(7)	0.050 5(6)	0.886 1(8)	0.571(1)
C(153)	0.439 8(7)	0.079 9(9)	0.917(1)	0.103 9(9)	0.797(1)	0.406(1)
O(153)	0.491 6(6)	0.060 4(7)	0.896 1(9)	0.066 8(8)	0.783(1)	0.369(1)
C(154)	0.308 2(8)	0.082 1(9)	0.873(1)	0.191 3(9)	0.731 8(9)	0.571(1)
O(154)	0.284 3(6)	0.059 0(8)	0.830 9(9)	0.205 1(7)	0.680 8(7)	0.633 2(9)
C(161)	0.241 7(8)	0.124 6(9)	1.072(1)	0.296 0(7)	0.896 4(8)	0.378 0(9)
O(161)	0.227 7(6)	0.072 3(6)	1.115 4(8)	0.326 9(6)	0.895 8(7)	0.317 6(7)

Table 8 (*continued*)

	Molecule 1			Molecule 2 *		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(162)	0.268 7(8)	0.319(1)	0.931(1)	0.205 5(7)	0.885 6(8)	0.595(1)
O(162)	0.272 7(7)	0.376 6(7)	0.892(1)	0.182 7(5)	0.879 8(7)	0.664 3(7)
C(163)	0.220 6(9)	0.261(1)	1.095(1)	0.269 4(9)	0.980 8(9)	0.491(1)
O(163)	0.201 6(8)	0.285 9(8)	1.151 7(8)	0.277 1(8)	1.033 4(7)	0.497(1)
C(171)	0.365 2(9)	0.101 9(9)	1.168(1)	0.176 7(9)	0.935(1)	0.275(1)
O(171)	0.355 8(7)	0.059 7(7)	1.231 1(8)	0.195 3(7)	0.915 5(7)	0.215 5(8)
C(172)	0.410 1(8)	0.245(1)	0.958(1)	0.113 9(9)	1.004(1)	0.467(1)
O(172)	0.429 2(6)	0.283 7(8)	0.897 8(9)	0.092 6(6)	1.029 5(7)	0.524 1(9)
C(173)	0.369 7(9)	0.246 6(9)	1.124(1)	0.160(1)	1.070(1)	0.311(1)
O(173)	0.357 4(7)	0.288 4(7)	1.162 3(9)	0.169 8(9)	1.123 7(8)	0.277(1)
C(174)	0.480 6(8)	0.125(1)	1.090(1)	0.053(1)	1.001(1)	0.318(1)
O(174)	0.534 2(6)	0.096 7(7)	1.108(1)	0.001 7(7)	1.015(1)	0.289(1)

* For molecule 2 read the first digit of the atom number as 2.

Table 9 Non-hydrogen atomic coordinates for $[\{Ru_4(\mu_3\text{-OMe})(\mu\text{-PPh}_2)(CO)_{10}\}(\mu_4\text{-CCH-}\mu\text{-}\eta^2\text{-}C_2)\{Ru_2(\mu\text{-PPh}_2)(CO)_6\}]$ **12**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.260 43(7)	0.745 35(8)	0.487 9(1)	O(61)	0.548 9(7)	0.363 6(9)	0.727(2)
Ru(2)	0.158 53(7)	0.773 11(8)	0.686 1(1)	C(62)	0.440(1)	0.274(2)	1.057(2)
Ru(3)	0.237 69(7)	0.644 45(8)	0.914 1(1)	O(62)	0.450 8(9)	0.267(1)	1.171(1)
Ru(4)	0.347 41(7)	0.697 71(9)	0.732 3(1)	C(63)	0.462(1)	0.177(1)	0.842(2)
Ru(5)	0.314 82(8)	0.375 19(8)	0.633 4(1)	O(63)	0.490 9(9)	0.106 9(9)	0.834(2)
Ru(6)	0.415 80(7)	0.295 40(9)	0.856 6(1)	C(1)	0.253 7(8)	0.656 4(9)	0.696(1)
O(01)	0.262 4(5)	0.814 6(6)	0.642 0(9)	C(2)	0.238 9(8)	0.569 8(9)	0.745(1)
C(01)	0.274 5(9)	0.900(1)	0.612(2)	C(3)	0.299 5(8)	0.490(1)	0.767(1)
C(11)	0.254 7(8)	0.665(1)	0.391(2)	C(4)	0.351 6(8)	0.422(1)	0.812(1)
O(11)	0.251 8(7)	0.613 7(7)	0.329(1)	P(1)	0.141 9(2)	0.835 9(2)	0.440 9(4)
C(12)	0.314 9(9)	0.799(1)	0.339(2)	C(111)	0.131 1(8)	0.953 2(9)	0.375(1)
O(12)	0.346 7(6)	0.832 5(8)	0.250(1)	C(112)	0.091 1(8)	1.014(1)	0.450(1)
C(21)	0.086(1)	0.721(1)	0.704(2)	C(113)	0.084(1)	1.104(1)	0.402(2)
O(21)	0.038 9(6)	0.683 7(8)	0.714(1)	C(114)	0.116(1)	1.138(1)	0.277(2)
C(22)	0.101 9(9)	0.858(1)	0.778(2)	C(115)	0.153(1)	1.080(1)	0.200(2)
O(22)	0.068 9(7)	0.907 7(8)	0.837(1)	C(116)	0.161 1(9)	0.990(1)	0.248(2)
C(31)	0.150 8(9)	0.614(1)	0.997(2)	C(121)	0.077 8(8)	0.813(1)	0.337(1)
O(31)	0.097 4(7)	0.598 6(9)	1.045(1)	C(122)	0.074(1)	0.727(1)	0.360(2)
C(32)	0.227 3(9)	0.738(1)	1.003(2)	C(123)	0.026(1)	0.706(1)	0.283(3)
O(32)	0.218 2(7)	0.793 9(8)	1.057(1)	C(124)	−0.019(1)	0.767(2)	0.178(2)
C(33)	0.305(1)	0.551(1)	1.048(2)	C(125)	−0.014(1)	0.849(2)	0.153(2)
O(33)	0.345 2(8)	0.492 8(9)	1.123(1)	C(126)	0.033 9(9)	0.877(1)	0.231(2)
C(41)	0.375 2(9)	0.738(1)	0.878(2)	P(2)	0.296 1(2)	0.279 5(3)	0.850 5(4)
O(41)	0.391 2(7)	0.768(1)	0.965(1)	C(211)	0.224 0(9)	0.326(1)	0.970(2)
C(42)	0.421(1)	0.733(1)	0.598(2)	C(212)	0.243(1)	0.320(2)	1.109(2)
O(42)	0.465 6(7)	0.748 5(9)	0.524(1)	C(213)	0.187(1)	0.353(2)	1.194(2)
C(43)	0.413 8(9)	0.591(1)	0.801(2)	C(214)	0.117(1)	0.388(1)	1.144(3)
O(43)	0.461 3(6)	0.525 9(8)	0.844(1)	C(215)	0.098(1)	0.394(2)	1.009(3)
C(51)	0.223(1)	0.432(1)	0.555(2)	C(216)	0.153 4(9)	0.361(1)	0.920(2)
O(51)	0.163 0(8)	0.468(1)	0.503(1)	C(221)	0.281(1)	0.174(1)	0.867(2)
C(52)	0.380(1)	0.439(1)	0.502(2)	C(222)	0.322(1)	0.097(1)	0.961(2)
O(52)	0.419 4(8)	0.471 1(9)	0.435(1)	C(223)	0.307(1)	0.015(2)	0.970(3)
O(53)	0.349(1)	0.225 1(9)	0.489(2)	C(224)	0.250(2)	0.012(2)	0.896(3)
C(53)	0.335(1)	0.281(1)	0.542(2)	C(225)	0.212(1)	0.085(2)	0.793(3)
C(61)	0.500(1)	0.340(1)	0.775(2)	C(226)	0.229(1)	0.166(1)	0.783(2)

11 (14 mg, 9%) [Found: C, 35.35; H, 1.35%; *M* 1771 (mass spectrometry). $C_{51}H_{20}O_{23}P_2Ru_7$ requires C, 34.60; H, 1.15%; *M* 1771]. IR: ν(CO) (cyclohexane) 2096m, 2077vs, 2074vs, 2046s, 2032vs, 2026vs, 2012s, 1997m, 1987m, 1975m and 1916vw cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −19.07 (1 H, d, J_{HP} 17.1 Hz, RuH) and 7.10–7.82 (19 H, m, Ph). FAB mass spectrum: *m/z* 1771, M^+; 1743–1127, $[M - n\text{CO}]^+$ (n = 1, 6–23); 1050, $[M - 23\text{CO} - \text{Ph}]^+$. When recrystallised from CH_2Cl_2–MeOH red crystals of $[\{Ru_4(\mu_3\text{-OMe})(\mu\text{-PPh}_2)(CO)_{10}\}(\mu_4\text{-CCH-}\mu\text{-}\eta^2\text{-}C_2)\{Ru_2(\mu\text{-PPh}_2)(CO)_6\}]$ **12** were obtained, m.p. > 300 °C (decomp.) [Found: C, 35.95; H, 1.70%; *M* 1506 (mass spectrometry). $C_{45}H_{24}O_{17}P_2Ru_6$ requires C, 35.90; H, 1.60%; *M* 1506]. IR: ν(CO) (cyclohexane) 2118vw, 2083s, 2072s, 2050s, 2043vs, 2027s, 2011s, 2007s, 1997s, 1988m, 1979m and 1967m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.62 (3 H, s, CH_3), 4.15 (1 H, d, J_{HP} 2.0 Hz, CCHCC) and 7.00–8.09 (20 H, m, Ph). FAB mass spectrum: *m/z* 1506, M^+; 1420–1028, $[M - n\text{CO} - \text{OMe}]^+$ (n = 3–16).

Complex **2**. Nitrogen was bubbled through a solution of complex **2** (205 mg, 0.094 mmol) in toluene (20 cm^3) and heated at 105–110 °C for 5 d. The solvent was removed and the residue purified by preparative TLC (light petroleum-acetone, 10:3). The major band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield pale yellow crystals of $[\{Os_3(\mu\text{-PPh}_2)(CO)_9\}_2(\mu_3\text{:}\mu_3\text{-}C_4)]$ **13** (151 mg, 78%), m.p. 258–261 °C (decomp.) [Found: C, 26.65; H, 1.15%; *M* 2064 (mass spectrometry). $C_{46}H_{20}O_{18}Os_6P_2$ requires C, 26.75; H, 1.00%; *M* 2064]. IR: ν(CO) (CH_2Cl_2) 2081m, 2073vs, 2062w, 2046m,

Table 10 Non-hydrogen atomic coordinates for $[\{Os_3(\mu-PPh_2)(CO)_9\}_2(\mu_3:\mu_3-C_4)]$ **13**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.416 62(3)	0.637 55(8)	0.676 84(3)	O(32)	0.481 3(5)	1.222(2)	0.672 3(7)
Os(2)	0.412 55(3)	0.863 40(9)	0.583 02(3)	C(33)	0.416 6(7)	1.026(6)	0.807 4(8)
Os(3)	0.412 42(3)	0.985 71(7)	0.712 83(3)	O(33)	0.422 8(5)	1.045(2)	0.862 0(6)
C(11)	0.359 8(8)	0.558(2)	0.616(1)	C(1)	0.462 6(6)	0.839(2)	0.662 5(8)
O(11)	0.329 5(6)	0.509(2)	0.580 2(8)	C(2)	0.476 6(6)	0.808(2)	0.726 7(8)
C(12)	0.468 8(8)	0.549(2)	0.629 7(9)	P	0.357 9(2)	0.787 0(5)	0.728 5(2)
O(12)	0.497 7(6)	0.494(2)	0.598 7(7)	C(101)	0.288 3(6)	0.779(2)	0.692 9(8)
C(13)	0.416 9(7)	0.497(2)	0.742(1)	C(102)	0.258 3(7)	0.900(2)	0.679 5(9)
O(13)	0.418 0(6)	0.409(1)	0.780 0(7)	C(103)	0.205 1(7)	0.891(2)	0.654(1)
C(21)	0.339 0(8)	0.884(3)	0.546 0(9)	C(104)	0.180 2(8)	0.767(2)	0.642 1(9)
O(21)	0.295 2(6)	0.903(2)	0.526 7(8)	C(105)	0.209 1(7)	0.649(2)	0.658 6(9)
C(22)	0.436 3(8)	1.017(2)	0.544(1)	C(106)	0.262 3(7)	0.658(2)	0.683 7(9)
O(22)	0.455 7(7)	1.112(2)	0.522 5(8)	C(201)	0.350 3(7)	0.753(2)	0.815 8(8)
C(23)	0.428 7(8)	0.760(3)	0.512 3(9)	C(202)	0.396 9(8)	0.707(2)	0.859 9(9)
O(23)	0.437 3(7)	0.676(2)	0.470 3(7)	C(203)	0.392 9(9)	0.687(2)	0.926 8(9)
C(31)	0.358 3(7)	1.112(2)	0.683 1(9)	C(204)	0.345(1)	0.710(2)	0.951 4(9)
O(31)	0.328 3(5)	1.196(1)	0.664 3(8)	C(205)	0.299 7(9)	0.756(2)	0.908 4(9)
C(32)	0.459 3(7)	1.132(2)	0.688(1)	C(206)	0.303 0(7)	0.774(2)	0.842 8(9)

2017m, 2000m, 1981m and 1974(sh) cm^{-1}. FAB mass spectrum: *m/z* 2064, M^+; 2036–1560, $[M - nCO]^+$ (n = 1–18); 148, $[M - 18CO - Ph]^+$.

Crystallography.—Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limits using an Enraf-Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ 0.7107_3 Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R,R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^2(I_{diff})$ being used. Computation used the XTAL 2.6 program system implemented by S. R. Hall;[29] neutral atom complex scattering factors were employed. Crystal data are summarised in Table 5, final atomic coordinates in Tables 6–10.

Abnormal features/variations in procedure. Data for complex **6**, as a MeOH solvate, were collected at 195 K; nevertheless the data set was halted at $l = 7$ owing to severe decomposition. Data with $I \geqslant 2.5\sigma(I)$ were considered observed and structure solution and refinement {anisotropic Ru and P; weighting scheme $w = [\sigma^2(F) + gF^2]$} were performed with SHELX 76.[30] Hydrogen atoms were not located. Four residual electron-density peaks were modelled as a disordered molecule of methanol (solvent) such that each component has 0.5 occupancy.

Data for complexes **11** and **12** were less than optimal, being limited in extent, with profiles being broad and unsymmetrical. The existence and location of the core hydrogens in **11** could not be established with any confidence; in **12** the μ_3 species was modelled as methoxide following an NMR assignment. In **11** the behaviour of CO(51) was anomalous, meaningful thermal parameter refinement of C(151) occurring only with the isotropic form. This may be a consequence of deficiencies in the data; however, that CO group has some suggestion of disorder and may be incipiently bridging.

In complex **13** an ill behaved ellipsoid for C(33) was refined using the isotropic form.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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