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Use of the monocationic fragment $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ as an ionic coupling reagent in the synthesis of mixed-metal phosphine clusters †

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Deprotonation of $[Os_3H_2(CO)_{10}(PPh_3)]$, with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and subsequent treatment with the ionic coupling reagent $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3][PF_6]$ afforded the tetrahedral cluster $[Os_3H(CO)_{10}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$. Reduction of the trinuclear osmium cluster $[Os_3(CO)_{11}(PPh_3)]$ with K/Ph_2CO and subsequent coupling with $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3][PF_6]$ yielded the pentanuclear clusters $[Os_3(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}_2]$, $[Os_3H_2(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ and the butterfly cluster $[Os_3H(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$. In an analogous reaction using $[Os_3(CO)_{11}\{P(OMe)_3\}]$ only one complex $[Os_3(CO)_{11}\{P(OMe)_3\}\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ was isolated. This undergoes an orthometallation when heated under reflux in toluene to yield the novel spiked tetrahedral cluster $[Os_3Ru_2H(CO)_{11}\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)(\mu_3\text{-}\eta^5\text{-}C_5H_4)]$. All the new complexes have been characterised spectroscopically and the molecular and crystal structures of three have been determined by single-crystal X-ray diffraction. The structure of $[Os_3Ru_2H(CO)_{11}\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)(\mu_3\text{-}\eta^5\text{-}C_5H_4)]$ shows an uncommon μ_3-η^5-bonding mode for the deprotonated cyclopentadiene ring.

Introduction

The "rational" synthesis of higher nuclearity transition metal cluster carbonyls has proved to be one of the recent challenges in cluster chemistry. A recent advance in the area has been to develop synthetic strategies that involve systematic cluster build-up by ionic coupling between pre-formed cluster anions and mono- or di-nuclear metal cations.[1] For example, reaction of the pre-formed dications $[M(C_6H_5R)(MeCN)_3]^{2+}$ (M = Ru or Os; R = H or Me) with a range of dianionic clusters leads to an increase in nuclearity of the cluster by one metal and incorporation of the arene ligand.[2–5] Similarly, reaction of the dication $[Rh(\eta^5\text{-}C_5Me_5)(MeCN)_3]^{2+}$ with dianionic species has been used successfully in cluster expansion.[6,7] This methodology has been extended to the incorporation of the "RuCp" moiety into the cluster framework, *via* coupling with the monocation $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$.[8] This reagent has two advantages over the dicationic species: electron transfer to a cluster dianion must occur in two steps, which limits redox activity, and the reaction of a dianion with such a monocationic species provides the opportunity to increase the nuclearity of a neutral product by two metal units.[8,9]

Recently, we have shown that the reaction of the monoanion $[Os_3H(CO)_{11}]^-$ with $[Ru(\eta^5\text{-}C_5H_5)(MeCN)]^+$ generates $[Os_3H(CO)_{11}\{Ru(\eta^5\text{-}C_5H_5)\}]$ **1** in high yield.[10] Subsequent deprotonation and reaction with a further equivalent of capping reagent yields the bis(cyclopentadienyl) cluster $[Os_3(CO)_{11}\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ **2** which may also be synthesized in one step by reaction of the dianion $[Os_3(CO)_{11}]^{2-}$ with two equivalents of the cationic species.[10] In this paper we present the related reactions of the phosphine-substituted triosmium anions $[Os_3H(CO)_{10}(PPh_3)]^-$, $[Os_3(CO)_{11}(PPh_3)]^{2-}$ and $[Os_3(CO)_{11}\{P(OMe)_3\}]^{2-}$ with $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$, and compare differences in their reactivity and in the nature of the products formed.

Results and discussion

Treatment of a solution of $[Os_3H_2(CO)_{10}(PPh_3)]$, in THF, with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) generated the anion $[Os_3H(CO)_{10}(PPh_3)]^-$ *in situ*, as indicated by the solution IR spectrum, to which was added one molar equivalent of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ **3** as its $[PF_6]^-$ salt. The THF was evaporated and dichloromethane added, after which the single product $[Os_3H(CO)_{10}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$ **4** was isolated in *ca.* 50% yield after separation by TLC. This reaction is thus analogous to that of the parent unsubstituted ion $[Os_3H(CO)_{11}]^-$;[10] however attempts to deprotonate **4** with a further equivalent of DBU were unsuccessful, indicating that the presence of the triphenylphosphine ligand reduces the acidity of the bridging proton in **4** as compared to the unsubstituted analogue $[Os_3H(CO)_{11}\{Ru(\eta^5\text{-}C_5H_5)\}]$ **1**. Cluster **4** has been fully characterised by IR, ^1H and ^{31}P NMR spectroscopy, mass spectrometry (Table 1) and microanalysis (Experimental section). The ^1H chemical shifts for the Cp and hydride ligands are very similar to those if **1** (δ 5.56, −21.81) whilst the IR spectrum exhibits more bands (consistent with a lower-symmetry CO ligand polyhedron), those at 1805 and 1766 cm^{-1} indicating the presence of bridging CO ligands. The large J(HP) coupling constant (11.66 Hz) in the ^1H NMR spectrum indicates that the PPh_3 and H ligands share a common osmium vertex. Attempts to synthesize **4** from **1** by substituting PPh_3 for CO *via* thermal or Me_3NO activation methods were not successful.

The molecular structure of compound **4** is shown in Fig. 1 (selected bond lengths and angles are presented in Table 2). It is closely related to that of **1**, having a tetrahedral metal core and the Cp ligand in an η^5-bonding mode. $[Os_4H(\eta^5\text{-}C_5Me_5)(CO)_{11}]$, prepared by pyrolysis of $[Os_4H(\eta^5\text{-}C_5Me_5)(CO)_{12}]$ at 50 °C, also

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† Dedicated in memory of Dr Ron Snaith, a valued colleague and friend.

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Table 1 Spectroscopic data for the new complexes

			NMR (δ, J/Hz)[c]		
	IR,[a] $\tilde{\nu}$(CO)/cm^{-1}	MS (m/z)[b] exptl. (calc.)	^{1}H	^{13}C	^{31}P
4	2070s, 2033vs, 2006s, 1991s,1967m, 1946w, 1805m, 1766vw	1288 (1286)	−21.22 (d, 1H, hydride, J_{HP} = 11.66), 5.46 (s, 5H, C_5H_5), 7.35 (m, 15H, Ph)	—	12.62 (s, 1P, PPh_3)
5	2040w, 2003vs, 1991m (sh), 1972m (sh), 1960m, 1778w (br)	1481 (1480)	5.64 (s, 5H, C_5H_5), 5.38 (s, 5H, C_5H_5), 5.21 (s, 5H, C_5H_5), 4.93 (s, 5H, C_5H_5), 7.42 (m, 15H, Ph), 7.26 (m, 15H, Ph)	—	25.74 (br, 1P, PPh_3), 12.37 (s, 1P, PPh_3)
6	2055vw, 2021m, 1999s (sh), 1991vs, 1968m (br), 1943w (br), 1933w (br), 1799w (br), 1718w (br)	1479 (1480)	major isomer: −21.22 (d, 1H, hydride, J_{HP} = 11.61), 5.23 (s, 10H, C_5H_5) minor isomer: −20.72 (d, 1H, hydride, J_{HP} = 12.5), 5.47 (s, 5H, C_5H_5), 5.21 (s, 5H, C_5H_5)	—	major isomer: 12.16 (s, 1P, PPh_3) minor isomer: 20.34 (s, 1P, PPh_3)
7	2082w, 2038m, 2014s, 2004s, 1970m (br), 1945w (br), 1822w (br), 1778vw (br)	1309 (1314)	−15.23 (d, 1H, hydride, J_{HP} = 10.46), 5.39 (s, 5H, C_5H_5), 7.8 (m, 15H, Ph)	90.07 (s, 5C, C_5H_5)	−5.16 (1P, $OsPPh_3$)
8	2039m, 2000vs, 1991s (sh), 1976m (br), 1933m (br), 1772w (br), 1716w (br), 1652w (br)	1342 (1342)	3.58 (d, 9H, Me, J_{HP} = 8.50), 5.39 (s br, 10H, C_5H_5)	88.80 (s, 5C, C_5H_5), 90.68 (s, 5C, C_5H_5), 53.65 (d, 3C, Me, J_{CP} = 7.95)	103.94 (s, 1P, $P(OMe)_3$)
9	2055s, 2014vs, 2000s, 1981s, 1966m (sh), 1927w (br), 1772vw, 1702w (br)	1343 (1342)	−17.63 (d, 1H, hydride, J_{HP} = 11.46), 3.56 (d, 9H, Me, J_{HP} = 12.12), 5.38 (s, 5H, C_5H_5), 5.75–6.20 (m, 4H, C_5H_4)	—	105.04 (s, 1P, $P(OMe)_3$)

[a] Spectra run in CH_2Cl_2. [b] Positive-ion FAB based on ^{102}Ru and ^{192}Os. [c] Spectra run in $CDCl_3$.

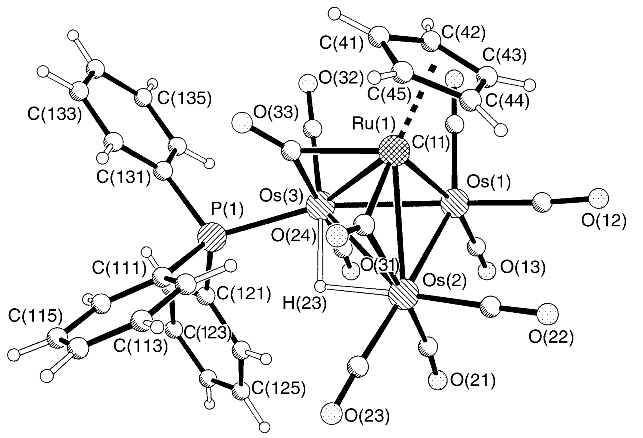


Fig. 1 Molecular structure of compound **4**, showing the atom numbering scheme.

Table 2 Selected bond lengths/Å and angles/° for compound **4**

Os(1)–Os(2)	2.7797(10)	Os(1)–Os(3)	2.7796(12)
Os(1)–Ru(1)	2.755(2)	Os(2)–Os(3)	2.961(2)
Os(3)–Ru(1)	2.7842(14)	Os(3)–P(1)	2.371(3)
Ru(1)–Cp(centroid)	2.232		
Os(2)–C(24)	2.235(11)	Os(3)–C(33)	2.091(12)
Ru(1)–C(24)	1.950(11)	Ru(1)–C(33)	2.045(11)
C(24)–O(24)	1.16(2)	C(33)–O(33)	1.192(14)
P(1)–Os(3)–Os(1)	164.01(6)	P(1)–Os(3)–Ru(1)	131.60(7)
P(1)–Os(3)–Os(2)	115.07(6)		
Os(2)–C(24)–O(24)	133.9(9)	Os(3)–C(33)–O(33)	142.1(8)
Ru(1)–C(24)–O(24)	142.3(9)	Ru(1)–C(33)–O(33)	133.0(9)

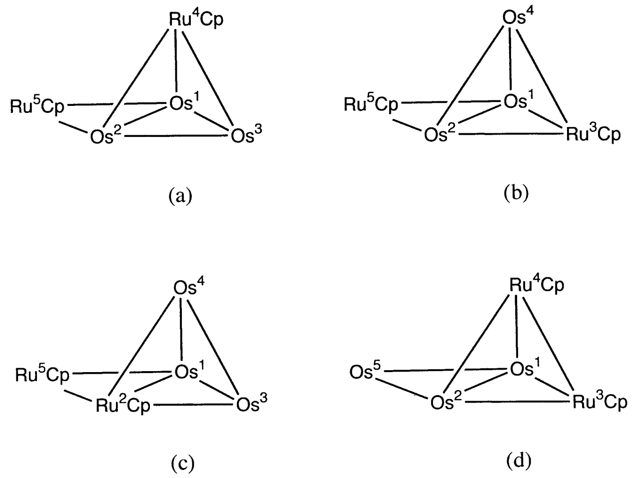


Fig. 2 Possible isomers of an edge-bridged tetrahedral Ru_2Os_3 cluster in which the Os atoms comprise a closed triangle.

has the same geometry and ligand arrangement, but lies on a crystallographic mirror plane.[11] The metal–metal and metal–ligand distances in **4** are generally similar to those in both **1** and [$Os_4H(\eta^5\text{-}C_5Me_5)(CO)_{11}$]. The hydride ligand was not located directly, but its position, spanning Os(2)–Os(3), was inferred from potential energy considerations.[12] The phosphine ligand is *cis* to the hydride, an arrangement which is favoured since it reduces steric interactions between the O atoms of the CO ligands and the aryl groups on the phosphine, on account of the increase in the M–M–L angles when a M–M edge is bridged by a hydride ligand.[13] The H-bridged Os–Os edge is *ca.* 0.02 Å longer than that in **1** [2.943(2), 2.942(2) in the two crystallographically independent molecules]. Two Ru–Os edges are bridged by CO ligands, as in **1**. Whilst that bound to the Os atom without the phosphine is significantly asymmetric [C(24)–Ru(1) 1.950(11), C(24)–Os(2) 2.235(11) Å], as in **1** and [$Os_4H(\eta^5\text{-}C_5Me_5)(CO)_{11}$], that to the Os bound to the phosphine is essentially symmetric [C(33)–Ru(1) 2.045(11), C(33)–Os(3) 2.091(12) Å]. This is a consequence of the greater basicity of the phosphine, the bridging CO orbitals being better placed to accept electron density from the more electron-rich Os(3) centre.

The reduction of a THF solution of $[Os_3(CO)_{11}(PPh_3)]$ with K/Ph_2CO afforded a reactive dianion, that exhibited two bands at 1981 and 1948 cm^{-1} in the IR spectrum, and which was treated immediately with two equivalents of the cation **3**. This afforded 3 products in moderate yield: $[Os_3(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ (green, 35%) **5**, $[Os_3H_2(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ (purple, 25%) **6** and $[Os_3H(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$ (red, 20%) **7**. The ^1H and ^{31}P NMR spectra were consistent with the presence of more than one isomer in solution, however from the NMR data it was clear that in each case one isomer dominated. In both cases the ratio of the peaks was approximately 4 : 1. The principal isomers were denoted **5** and **6**. Unfortunately, attempts to crystallise them failed since the compounds are unstable to prolonged standing in solution, so that the molecular assignments can only be tentative. However, on the basis of electron-counting rules, **5**, with 74 electrons, would be expected to have an edge-bridged tetrahedral or *nido*-octahedral framework and **6**, with 76 electrons, a spiked tetrahedral (*cf.* $[Os_4H(CO)_{13}\{Os(CO)_4Os(CO)_3(\eta^2\text{-}PhNNNPh)\}]$)[14] or raft structure (*cf.* $[Os_5(CO)_{18}]$ and $[Os_5(CO)_{17}(PMe_3)]$).[15] The ^1H chemical shifts indicate that the cyclopentadienyl ligands are bound in an η^5 manner in **5** and **6**, and are equivalent on the NMR timescale in one isomer of **6**. From the spectroscopic data alone, it is not possible to assign structures for these isomers.

Analogy with other capping reactions {*e.g.* those affording $[Os_5H_4(CO)_{12}(\eta^6\text{-}C_6H_6)]$,[4] $[Os_4H_2\{M(CO)_{13}(\eta^6\text{-}C_6H_6)\}]$ (M = Ru or Os)[16,17] and $[Os_4H_2\{Rh(CO)_{13}(\eta^5\text{-}C_5Me_5)\}]$[7]} and thermolyses {*e.g.* of $[Os_3H_2(CO)_{10}]$ with $[RhCp(CO)_2]$ to yield $[Os_4H_2\{Rh(CO)_{13}(\eta^5\text{-}C_5H_5)\}]$}[18] would suggest that an edge-bridged tetrahedral arrangement would be more likely for **5**, as exemplified by $[Os_5H_2(CO)_{16}]$.[19] However, **5** differs in not having any bridging hydride ligands. If the edge-bridged tetrahedral geometry is assumed, there are four isomers which do not require Os–Os bond cleavage (Fig. 2) which have the Cp ligands in inequivalent sites, as suggested by the ^1H NMR data. In the reaction of the dianion $[Os_4H_2(CO)_{12}]^{2-}$ with the cations $[M(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ (M = Ru or Os) the axial isomer of the trigonal bipyramidal cluster $[Os_4MH_2(CO)_{12}(\eta^6\text{-}C_6H_6)]$ is produced initially, from which CO scavenging yields $[Os_4MH_2(CO)_{13}(\eta^6\text{-}C_6H_6)]$ (M = Ru or Os).[16,17] In the case of Os the kinetic trigonal bipyramidal product $[Os_5H_2(CO)_{12}(\eta^6\text{-}C_6H_6)]$ transforms to the more thermodynamically stable equatorial isomer; however, $[Os_4RuH_2(CO)_{12}(\eta^6\text{-}C_6H_6)]$ does not undergo a framework rearrangement and decomposes.[16,17,20] Attempts to decarbonylate **5**, perhaps to generate a trigonal bipyramidal cluster analogous to $[Os_3(CO)_{11}\{Ru(\eta 5\text{-}C_5H_5)\}_2]$, produced only decomposition products.

In contrast, compound **7** exhibits only one isomer and was sufficiently stable for diffraction-quality crystals to be grown. Whilst the ^1H NMR C_5H_5 shift is similar to that of **4**, the hydride resonance is *ca.* 5 ppm upfield. Formally, **7** is related to **4** by the addition of a CO ligand, which is consistent with the observed $62e^-$ butterfly geometry (Fig. 3, Table 3). The Ru atom bound to the cyclopentadienyl ligand in a η^5 bonding mode occupies a wingtip position, as does $Os(\eta^5\text{-}C_5Me_5)$ in the isoelectronic cluster $[Os_4H(CO)_{12}(\eta^5\text{-}C_5Me_5)]$.[21] The dihedral angle between the metal planes in **7** is 111.94(6)°, comparable to that in the Os_4 cluster (115.4°). The hydride ligand in **7** was not located directly, but potential energy calculations[12] suggest that it bridges the Os(2)–Os(3) wingtip edge, *cis* to the phosphine ligand on Os(2) as in **4**. This is the longest M–M edge [3.050(2) Å], whereas the hinge bond Os(1)–Os(3) is considerably shorter than the other four [2.728(2) Å]. In contrast, the hydride bridges the hinge edge in $[Os_4H(CO)_{12}(\eta^5\text{-}C_5Me_5)]$, although this remains the shortest M–M bond [2.793(1) Å].[21] Interestingly, the related $62e^-$ dihydrido cluster $[Os_4H_2(CO)_{13}(PMe_3)]$, which has a similar dihedral angle of 112.7° to **7**, has one hydride ligand bridging the wingtip edge *cis* to the phosphine (as in **7**) [3.115(1) Å] and the other bridging the hinge edge [2.886(1) Å].[22]

Table 3 Selected bond lengths/Å and angles/° for compound **7**

Os(1)–Os(2)	2.895(2)	Os(1)–Os(3)	2.728(2)
Os(1)–Ru(4)	2.940(3)	Os(2)–Os(3)	3.050(2)
Os(3)–Ru(4)	2.861(2)	Os(2)–P(1)	2.366(6)
Ru(4)–Cp(centroid)	2.26		
Os(1)–C(41)	2.54(2)	Ru(4)–C(41)	1.82(3)
Os(2)–Os(1)–Ru(4)	95.33(5)	Os(2)–Os(3)–Ru(4)	93.67(7)
P(1)–Os(2)–Os(1)	164.8(2)	P(1)–Os(2)–Os(3)	110.4(2)
Os(1)–C(41)–O(41)	118(2)	Ru(4)–C(41)–Os(1)	158(2)

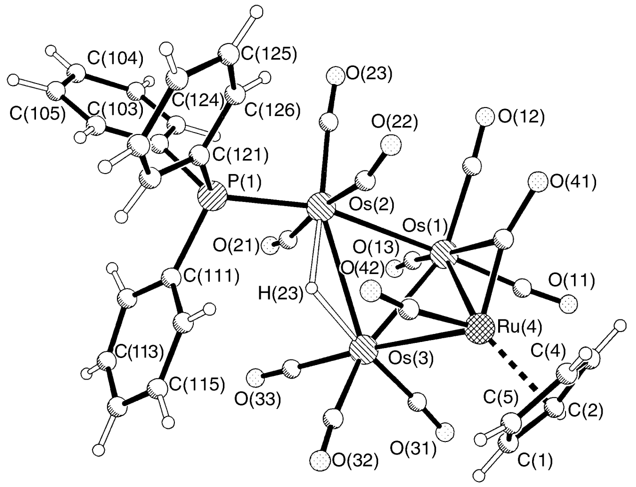


Fig. 3 Molecular structure of compound **7**, showing the atom numbering scheme.

In compound **7** an incipient CO bridge is formed on the Ru(4)–Os(1) edge, diagonally opposite the H-bridged edge {Ru(4)–C(41) 1.82(3), Os(1)–C(41) 2.54(2) Å; Ru(4)–C(41)–Os(1) 158(2)°}. This allows a more even distribution of electron density around the relatively rich $Ru(C_5H_5)$ centre. The pseudo-octahedral disposition of ligands in the hinge position found in $[Os_4H(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ is maintained in **7**, although the three terminal CO ligands on Os(1) and Os(2) are twisted from the mutually eclipsed configuration found in the former. The ligands on Os(2) and Ru(4) are also twisted to avoid a steric clash of O(22) and O(42). The terminal carbonyl groups are pseudo-linearly co-ordinated to the metal atoms except for Os(2)–C(21)–O(21) [167(3)°] and Os(2)–C(22)–O(22) [163(2)°] which deviate significantly from linearity.

The reduction of a THF solution of the phosphite cluster $[Os_3(CO)_{11}\{P(OMe)_3\}]$ with K/Ph_2CO afforded a reduced reactive dianion that exhibited a characteristic broad band at 1972 cm^{-1} in the IR spectrum, to which two equivalents of **3** were added. The resulting green-brown major product $[Os_3(CO)_{11}\{P(OMe)_3\}\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ **8** was isolated as a single isomer after separation by TLC in *ca.* 50% yield, and characterised spectroscopically. This product is analogous to the PPh_3-containing cluster **5**, with an electron count of 74, and the same isomers are possible (Fig. 2). The presence of a weak signal at 1652 cm^{-1} in the IR spectrum suggests the presence of a μ_3-CO ligand. An attempt to decarbonylate **8** by heating in toluene under reflux led to the formation of one yellow-brown complex **9** in *ca.* 80% yield with the same stoichometry as that of **8**, indicated by mass spectrometry. The presence of a hydride signal in the ^1H NMR and a multiplet of integral 4H in place of one Cp signal indicates that one hydrogen is transferred to the metal core to generate a ring metallated species with an electron count of 76. Suitable crystals were grown and the molecular structure confirmed by X-ray analysis.

The molecular structure of compound **9** comprises a $76e^-$ spiked tetrahedral metal core, the spike Ru(5) atom being

Table 4 Selected bond lengths/Å and angles/° for compound **9**

Os(1)–Os(2)	2.9553(11)	Os(1)–Os(3)	2.7479(8)
Os(1)–Ru(4)	2.8766(13)	Os(2)–Os(3)	2.7905(9)
Os(2)–Ru(4)	2.9273(14)	Os(2)–Ru(5)	2.8165(12)
Os(3)–Ru(4)	2.8929(12)	Os(1)–P(1)	2.252(3)
Ru(4)–Cp′(centroid)	2.26	Ru(5)–Cp(centroid)	2.26
Ru(4)–C(1′)	2.256(13)	Ru(4)–C(2′)	2.240(13)
Ru(4)–C(3′)	2.254(13)	Ru(4)–C(4′)	2.250(13)
Ru(4)–C(5′)	2.323(13)	Ru(5)–C(5′)	2.116(13)
Os(2)–C(5′)	2.432(11)	Os(2)–C(52)	2.050(13)
Ru(5)–C(52)	2.03(2)	Ru(4)–C(42)	1.903(15)
Os(1)–Os(2)–Ru(5)	113.80(3)	Os(3)–Os(2)–Ru(5)	157.78(3)
Ru(4)–Os(2)–Ru(5)	97.05(4)	Ru(4)–C(5′)–Ru(5)	151.7(6)
C(1′)–C(5′)–C(4′)	102.7(12)	Os(2)–C(52)–O(52)	137.1(12)
Ru(5)–C(52)–O(52)	135.5(11)	Ru(4)–C(42)–O(42)	160.6(13)

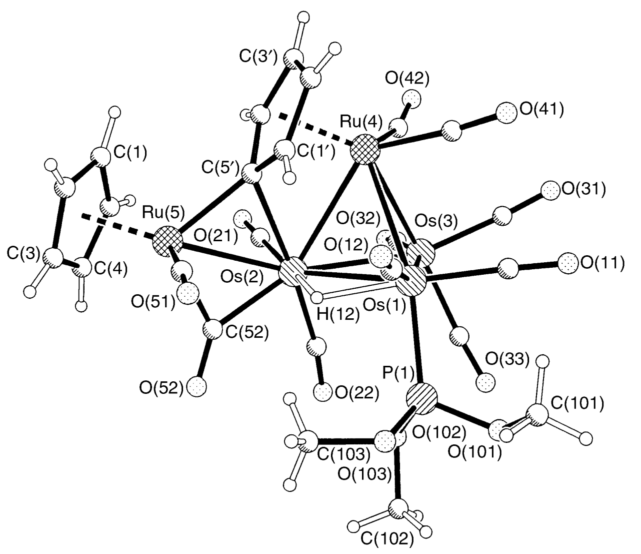
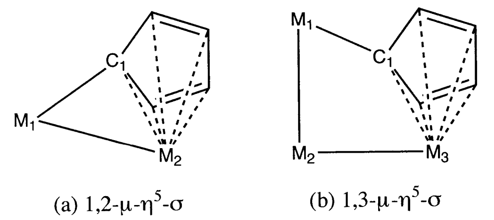


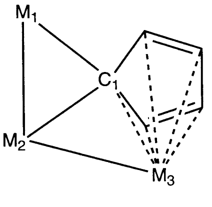
Fig. 4 Molecular structure of compound **9**, showing the atom numbering scheme.

η^5-co-ordinated by one cyclopentadienyl ligand and C(5′) atom of the other cyclopentadienyl ring (Fig. 4, Table 4). The latter is η^5-bound to Ru(4), and asymmetrically bonded to Os(2) [2.432(11) Å] and Ru(5) [2.116(13) Å] across the spike edge, which is also bridged, essentially symmetrically, by a CO ligand {Os(2)–C(52) 2.050(13), Ru(5)–C(52) 2.03(2) Å; Os(2)–C(52)–O(52) 137.1(12), Ru(5)–C(52)–O(52) 135.5(11)°}. With the exception of Ru(4)–C(42)–O(42) [160.6(13)°] the other CO ligands are terminal and pseudo-linearly co-ordinated, the M–C–O angles ranging from 171.8(13) to 179.0(13)°. Potential energy calculations[12] indicate that the proton has transferred from C(5′) to the Os(1)–Os(2) edge, *cis* to the phosphite ligand, also the longest M–M bond in the cluster.

A similar orthometallation occurs in the $P(OMe)_3$- and PPh_2Me-substituted analogues of $[Os_4H_2\{Ru(CO)_{13}(\eta^6\text{-}C_6H_6)\}]$, derived readily from the axial isomer of $[Os_4H_2\{Ru(CO)_{12}(\eta^6\text{-}C_6H_6)\}]$ by nucleophilic addition at the arene-bearing Ru atom.[16,17,20] In this case the edge-bridged tetrahedral addition products transform at room temperature within hours to spiked tetrahedral clusters with the arene ligand η^6-bound to the spike Ru atom and bridging an adjacent Os–Os edge in a 3-centre 2-electron bond, the H atom having transferred to the Ru–Ru edge. In contrast, $P(OMe)_3$ and PPh_2Me substitution on the axial isomer of $[Os_5H_2(CO)_{13}(\eta^6\text{-}C_6H_6)]$ occurs at one of the Os atoms of the bridged Os–Os edge rather than the wing-tip Os bearing the arene, as confirmed by the crystal structure of the PPh_2Me cluster.[16,17] These products do not undergo orthometallation at room temperature, which suggests that phosphine substitution at the bridging metal atom bearing the arene activates the a cluster to orthometallation to a greater extent than substitution at the bridged metal atoms. If the $P(OMe)_3$ ligand remains bound to an Os atom in **8** (as suggested by the crystal structure of **9**) it would also be expected to orthometallate less readily than $[Os_4H_2\{Ru(CO)_{12}(\eta^6\text{-}C_6H_6)\{P(OMe)_3\}\}]$.[20]



(a) 1,2-μ-η^5-σ (b) 1,3-μ-η^5-σ



(c) 1,2,3-μ_3-η^5-σ^2

Fig. 5 Alternative bonding modes of σ,η^5-C_5H_4 ligands (M = Fe, Ru or Os).

A search of the Cambridge Structural Database (CSD)[23] for complexes of iron, ruthenium and osmium revealed three principal bonding modes for 5-membered rings orthometallated at one carbon atom in structurally characterised cluster compounds of the iron triad. The 1,2-μ-η^5-σ mode **A** (Fig. 5a) is only observed for M(1) = Os, M(2) = Fe and the FeCp component is generally derived from a (substituted) ferrocenyl moiety.[24–26] In these 8 structures the Fe–centroid distances range from 1.619 to 1.662 Å, Fe–C(1) π bonds 1.952–2.010 Å and the Os(2)–C(1) σ bonds are only slightly longer at 2.042–2.076 Å. Also related to mode **A** are a series of compounds in which there is no direct metal–metal bond,[27] but these are not directly relevant to the discussion.

The 1,3-μ-η^5-σ **B** and 1,2,3-μ_3-η^5-σ^2 **C** modes (Fig. 5b and c) differ in whether the carbon atom interacts with the central metal M(2). Mode **B** is exemplified by 5 clusters with M(1) = M(2) = M(3) = Ru; in four of these[28,29] the Ru(1)–C(1) σ bonds [2.086–2.130 Å] are rather shorter than the Ru(3)–C(1) π bonds [2.263–2.271 Å] and the Ru(2)–C(1) distances are well outside bonding range [3.197–3.266 Å] (all the M–C distances are longer in the other example, which has the 5-membered aromatic ligand as part of a fused carbon ring system).[30] The M(1)–M(2)–M(3) angles in these examples approach 90°.

The least common 1,2,3-μ_3-η^5-σ^2 mode **C** is found also in 6 of the clusters which exhibit mode **A** (both ligands being η^5-bonded to the same metal) with M(1) = M(2) = Os, M(3) = Fe.[25,26] The Fe–C_5(centroid) distances range from 1.641 to 1.667 Å, Fe–C(1) 2.093–2.123 Å and Os(1)–C(1) 2.148–2.182 Å; all these are slightly longer than for mode **A**. The Os(2)–C(1) distances are considerably longer in all cases, ranging from 2.563 to 2.618 Å, and are at the limit of what might be considered as a bonding interaction. The M(1)–M(2)–M(3) angle is greater than in complexes exhibiting mode **B**, and is reflected in the ligand arrangement, M(2) being bound to two terminal CO and two bridging H ligands, in addition to the Cp groups, in a pseudo-octahedral manner. With two terminal CO and a bridging CO and H ligand bound to M(2), the 3c–2e$^-$ bonds form a symmetric bridge in $[Ru_4H(CO)_{10}(PPh)\{\mu_3\text{-}\eta^5\text{-}C_5H_3(FeCp)\}\{\eta^5\text{-}C_5H_4(FeCp)\}]$ {M(1) = M(2) = Ru, M(3) = Fe; Ru(1)–C(1) 2.248, Ru(2)–C(1) 2.262 Å}.[28] In the case of modes **B** and **C** the degree of symmetry of the bridge is dependent on optimising the bonding in the (planar) M_3C unit, and the smaller size of Fe thus has a significant influence on the resulting geometry. In addition, the geometry around M(2) is influenced by the number and bonding mode of the other ligands. **9** is the first structurally characterised example of mode **C** with a M(1) = M(3) = Ru, M(2) = Os unit, and whilst the bridge is more symmetric than those in the Os_2Fe examples, it is less so than in $[Ru_4H(CO)_{10}PPh\{\mu_3\text{-}\eta^5\text{-}C_5H_3(FeCp)\}\{\eta^5\text{-}C_5H_4(FeCp)\}]$.

In contrast to **9**, the spiked tetrahedral clusters $[Os_4RuH_3(CO)_{12}(PR_3)(\mu_3\text{-}C_6H_5)]$ with a $\mu_3\text{-}C_6H_5$ ligand (note, however, that it is a tetrahedral rather than spike edge which is bridged) have equal M(1)–C(1) and M(2)–C(1) distances within the experimental uncertainty [M(1)–C(1) = 2.24(6), 2.32(3); M(2)–C(1) = 2.24(6), 2.26(3) Å for $PR_3 = P(OMe)_3$, PPh_2Me respectively].[16,17,20] A CSD search for other structures containing orthometallated arene ligands found only homometallic species, and the majority of these adopt the $1,3\text{-}\mu_2\eta^6,\sigma$ mode equivalent to **B**.[31] Whilst the Fe(2)–C(1) distance in $[Fe_3(CO)_9\{\mu_3\text{-}\eta^6,\sigma^2\text{-}C_6H_4CH_2NPh\}]$ [2.427 Å] might be considered within bonding range, the bridge is strongly asymmetric [Fe(1)–C(1) 1.969 Å].[32] Two determinations of the structure $[Ru_6H_2(CO)_{16}\{\mu_4\text{-}\eta^6,\sigma^4\text{-}C_6H_4O\}]$ do display the $\mu_3\text{-}\eta^6,\sigma^2$ mode akin to **C**, with distances of Ru(1)–C(1) 2.214, 2.207; Ru(2)–C(1) 2.347, 2.345 Å respectively.[33]

Related to bonding mode **C** are a number of clusters where there is no direct metal–metal bond between M(2) and M(3) in Fig. 5(c), but again these complexes are sufficiently different not to warrant further comparison.[34]

In conclusion, the introduction of a phosphine or phosphite ligand into the triosmium precursor complex does have a fundamental influence on the subsequent progress of the reaction with the "$[Ru(\eta^5\text{-}C_5H_5)]^+$" capping reagent. In the case of $[Os_3(CO)_{11}(PPh_3)]$ and $[Os_3(CO)_{11}\{P(OMe)_3\}]$ the presence of the phosphorus donor ligand inhibits loss of a carbonyl in the reduction step with K/Ph_2CO and dianions of the form $[Os_3(CO)_{11}(PPh_3)]^{2-}$ and $[Os_3(CO)_{11}\{P(OMe)_3\}]^{2-}$ are presumably produced, whereas reduction of $[Os_3(CO)_{12}]^{2-}$gives $[Os_3(CO)_{11}]^{2-}$ Subsequent reaction with the phosphine- or phosphite-containing dianions having 12 ligands and the $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ cation leads to more open metal core arrangements, and in the case of the phosphite leads to stabilisation of the uncommon bonding mode for the deprotonated cyclopentadiene ring in $[Os_3Ru_2H(CO)_{11}\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)(\mu_3\text{-}\eta^5\text{-}C_5H_4)]$ **9**.

Experimental

All the reactions were performed under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Technical grade solvents were purified by distillation over the appropriate drying agents and under an inert nitrogen atmosphere prior to use. Routine separation of products was performed by thin-layer chromatography (TLC) using commercially prepared glass plates, pre-coated to 0.25 mm thickness with Merck Kieselgel 60 F_{254}, as supplied by Merck, or using laboratory-prepared glass plates coated to 1mm thickness with Merck Kieselgel 60 F_{254}. The complexes $[Os_3H_2(CO)_{10}(PPh_3)]$,[35] $[Os_3(CO)_{11}(PPh_3)]$,[36] $[Os_3(CO)_{11}\{P(OMe)_3\}]$[37] and $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3][PF_6]$[38] were prepared by literature procedures. Other chemicals were used as purchased without further purification.

The FAB mass spectra were recorded using a Kratos model 902 spectrometer, IR spectra on a Perkin-Elmer 1710 FT-IR spectrometer, using 0.5 mm NaCl or CaF_2 cells, and ^1H, ^{31}P and ^{13}C NMR spectra on a Bruker WH 250 MHz or WH 400 MHz spectrometer. The internal reference used for the ^{31}P NMR spectra was H_3PO_4.

Preparations

$[Os_3H(CO)_{10}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$ 4. To a solution of $[Os_3H_2(CO)_{10}(PPh_3)]$ (50 mg, 4.5×10^{-5} mol) in THF was added an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene. IR absorption bands at 2013s, 1982s, 1970s, 1943s and 1647w, (br) cm^{-1} indicated the presence of the deprotonated species $[Os_3H(CO)_{10}(PPh_3)]^-$. This solution was transferred to another Schlenk flask containing 1 molar equivalent of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3][PF_6]$ (20 mg, 4.6×10^{-5} mol), the THF solvent evaporated, CH_2Cl_2 subsequently added and the solution stirred for *ca.* 30 min. After removal of solvent, the solid residue was chromatographed using CH_2Cl_2–hexane (1 : 1) as eluent. A yellow-brown band ($R_f = 0.7$) was obtained in 50% yield (29.5 mg, 2.3×10^{-5} mol) {Found: C, 30.69; H, 1.54; P, 2.42. Calc. for $[Os_3H(CO)_{10}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$: C, 30.59; H, 1.64; P, 2.42%}.

Reduction and ionic coupling of $[Os_3(CO)_{11}(PPh_3)]$. 30 cm^3 of deoxygenated and freshly distilled THF were added to a Schlenk flask containing $[Os_3(CO)_{11}(PPh_3)]$ (100 mg, 8.8×10^{-5} mol). Freshly prepared K/Ph_2CO was added dropwise until a blue colour persisted. The reaction was monitored by IR spectroscopy and a change in absorption peaks to lower frequency indicated the presence of a reduced species. This solution was transferred to another Schlenk flask containing 2 molar equivalents of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3][PF_6]$ (76 mg, 1.8×10^{-4} mol), the THF solvent evaporated, CH_2Cl_2 subsequently added and the solution stirred for *ca.* 30 min. After removal of solvent, the solid residue was chromatographed using CH_2Cl_2–hexane (2 : 3) as eluent. A green band, $[Os_3(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ **5** ($R_f = 0.5$) was obtained in 35% yield (45 mg, 3.1×10^{-5} mol), a red-purple band $[Os_3H_2(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ **6** ($R_f = 0.7$) in 25% yield (32 mg, 2.2×10^{-5} mol) and a red band $[Os_3H(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$ **7** ($R_f = 0.8$) in 20% yield (23 mg, 1.8×10^{-5} mol) {Found for **7**: C, 31.20; H, 1.61. Calc. for $[Os_3H(CO)_{11}(PPh_3)\{Ru(\eta^5\text{-}C_5H_5)\}]$: C, 31.50; H, 1.65%}.

Reduction and ionic coupling of $[Os_3(CO)_{11}\{P(OMe)_3\}]$. 30 cm^3 of deoxygenated and freshly distilled THF were added to a Schlenk flask containing $[Os_3(CO)_{11}\{P(OMe)_3\}]$ (100 mg, 1.0×10^{-4} mol). Freshly prepared K/Ph_2CO was added dropwise until a blue colour persisted. The reaction was monitored by IR spectroscopy and a change in absorption peaks to lower frequency indicated the presence of a reduced species. This solution was transferred to another Schlenk flask containing 2 molar equivalents of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3][PF_6]$ (87 mg, 2.0×10^{-4} mol), the THF solvent evaporated, CH_2Cl_2 subsequently added and the solution stirred for *ca.* 30 min. After removal of solvent, the solid residue was chromatographed using CH_2Cl_2–hexane (1 : 1) as eluent. A green-brown band ($R_f = 0.4$) was obtained as the major product in 50% yield and characterised as $[Os_3(CO)_{11}\{P(OMe)_3\}\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ **8**.

$[Os_3Ru_2H(CO)_{11}\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)(\mu_3\text{-}\eta^5\text{-}C_5H_4)]$ 9. 30 cm^3 of toluene were added to $[Os_3(CO)_{11}\{P(OMe)_3\}\{Ru(\eta^5\text{-}C_5H_5)\}_2]$ **8** (50 mg, 3.7×10^{-5} mol) and the resulting solution heated under reflux for 2 hours, during which it changed from dark green to yellow-brown. After removal of solvent, the solid residue was chromatographed by TLC using CH_2Cl_2–hexane (1 : 1) as eluent. One yellow-brown product $[Os_3Ru_2H(CO)_{11}\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)(\mu_3\text{-}\eta^5\text{-}C_5H_4)]$ **9** ($R_f = 0.5$) was obtained in good yield (80%, 40 mg, 3.0×10^{-5} mol) {Found: C, 22.15; H, 1.68. Calc. for $[Os_3Ru_2H(CO)_{11}\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)(\mu_3\text{-}\eta^5\text{-}C_5H_4)]$: C, 21.58; H, 1.42%}.

Crystallography

Single crystals of compounds **4**, **7**, and **9** were mounted on glass fibres with epoxy resin, cell dimensions were established, and data collection carried out on a Stoe four-circle diffractometer using graphite-monchromated Mo-*Kα* radiation and an $\omega - \theta$ scan mode. Details of crystal data, data collection and structure refinement are summarised in Table 5. Structures were solved

Table 5 Crystal data for compounds **4**, **7** and **9**

	4	**7**	**9**
Molecular formula	$C_{33}H_{21}O_{10}Os_3PRu$	$C_{34}H_{21}O_{11}Os_3PRu$	$C_{24}H_{19}O_{14}Os_3PRu_2$
M	1280.14	1308.15	1335.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1/c$
a/Å	9.213(5)	8.878(4)	17.049(6)
b/Å	15.832(8)	22.669(17)	9.548(2)
c/Å	11.821(6)	9.415(4)	19.163(6)
β/°	106.31(2)	114.06(4)	94.62(3)
U/Å^3	1654.8(14)	1730(2)	3109(2)
Z	2	2	4
μ/mm^{-1}	12.034	11.514	13.281
T/K	153(2)	290(2)	290(2)
Reflections measured	6108	5552	5740
Independent reflections	5651 (R_{int} = 0.056)	2787 (R_{int} = 0.128)	5453 (R_{int} = 0.067)
Observed reflections	5633	2670	4507
$wR2$(all data)	0.089	0.108	0.116
$R1[I > 2\sigma(I)]$	0.033	0.046	0.043
Absolute structure parameter	0.005(8)	0.00(2)	—

via direct methods[39] and refined by full-matrix least squares on F^2.[40] The bridging hydride ligands were located using the program HYDEX[12] and included in the final cycles of refinement in fixed positions. For **9**, disorder in one of the methyl groups of the $P(OMe)_3$ ligand was modelled with two positions with occupancies 0.72 and 0.28, and the η^5-C_5H_5 ring was disordered over two positions with occupancies 0.47 and 0.53.

CCDC reference number 186/2217.

See http://www.rsc.org/suppdata/dt/b0/b006746f/ for crystallographic files in .cif format.

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