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Use of the monocationic fragment $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ as a capping reagent in the synthesis of mixed-metal clusters: synthesis and structural characterisation of $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ and $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$

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The reaction of the monoanion $[Os_3H(CO)_{11}]^-$ **1** with 1 equivalent of the cation $[Ru(C_5H_5)(MeCN)_3]^+$ **2**, in CH_2Cl_2, formed the mixed-metal, tetranuclear cluster $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **3** in high yield. Subsequent deprotonation of **3** with 1,8-diazabicyclo[5.4.0]undec-7-ene, in CH_2Cl_2, afforded the anion $[Os_3Ru(CO)_{11}(\eta^5\text{-}C_5H_5)]^-$ **4**, and reaction of **4** with a second equivalent of $[Ru(C_5H_5)(MeCN)_3]^+$ provided the new bis(cyclopentadienyl) cluster $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5** in *ca.* 80% yield. Alternatively, reduction of $[Os_3(CO)_{12}]$ with K/Ph_2CO afforded the known cluster dianion $[Os_3(CO)_{11}]^{2-}$ **6** which can be treated with 2 equivalents of $[Ru(C_5H_5)(MeCN)_3]^+$ to produce **5** in 75% yield. The clusters **3** and **5** have been fully characterised by both spectroscopic and crystallographic methods. The structure of **3** contains an Os_3Ru tetrahedron in which the cyclopentadienyl ligand is co-ordinated to the Ru atom in an η^5 terminal mode. The metal framework in **5** is a trigonal bipyramid, but may be viewed as an Os_3Ru tetrahedral unit, as in **3**, to which a second Ru atom capping an Os_2Ru triangular face has been added. Both the cyclopentadienyl ligands remain in η^5 terminal bonding sites co-ordinated to the two Ru atoms.

The chemistry of arene-substituted metal carbonyl clusters has been studied extensively.[1,2] Much of the research within our group has focused on the synthesis and characterisation of high-nuclearity arene-containing ruthenium and osmium clusters.[3] A number of methods have been developed for the incorporation of arene ligands into clusters,[2] but we have found that the arene may be conveniently introduced by coupling the preformed dication $[M(C_6H_6)(MeCN)_3]^{2+}$ (where M = Os or Ru) with a range of dianionic clusters.[4] Recently, we have extended this capping methodology to introduce a cyclopentadienyl ligand as the aromatic substituent on the metal cluster.[5,6] Here, we describe an extension of this work, and employ the cation $[Ru(C_5H_5)(MeCN)_3]^+$ as the capping agent in the synthesis of the new mixed-metal clusters $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ and $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$. Recently, pentamethylcyclopentadienyl ligands have been incorporated into clusters *via* the rhodium dicationic capping agent $[Rh(C_5H_5)(MeCN)_3]^{2+}$.[7] However, the capping reagent $[Ru(C_5H_5)(MeCN)_3]^+$ has several advantages over the rhodium dication and similar osmium and ruthenium arene-substituted complexes. The ionic coupling of dicationic species with anions appears to be limited to certain systems because other reactions such as fragmentation, recombination or electron transfer can occur depending on the relative stability of the parent cluster and the anion.[6] Since $[Ru(C_5H_5)(MeCN)_3]^+$ is monocationic, electron-transfer processes must occur in two separately defined steps, and consequently there is less redox activity to compete with the ionic coupling. Also, the reaction of a dianion with monocationic species allows for the possibility of increasing the nuclearity of the resultant neutral cluster by two metal units, in one reaction, instead of just one.

Results and Discussion

Treatment of a dichloromethane solution of $[(Ph_3P)_2N][Os_3H(CO)_{11}]$ **1** with 1 equivalent of the monocation $[Ru(C_5H_5)(MeCN)_3]^+$ **2**, as its $[PF_6]^-$ salt, affords a dark red solution from which the new mixed-metal cluster $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **3** is isolated as the sole product in *ca.* 90% yield, after separation by TLC. Complex **1** may be deprotonated by reaction with an excess of dbu (dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene) to produce the anionic cluster $[Os_3Ru(CO)_{11}(\eta^5\text{-}C_5H_5)]^-$ **4**. This unstable, oxygen-sensitive anion was treated immediately with a second equivalent of the cation **2** and after 30 min the bicapped pentanuclear cluster $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5** was obtained in high yield after separation by TLC. A second route exists for the preparation of **5** in which both Ru atoms are incorporated into the cluster in one reaction. The reduction of a thf solution of $[Os_3(CO)_{12}]$ with K/Ph_2CO affords the known dianion $[Os_3(CO)_{11}]^{2-}$ **6**,[8] which when treated with 2 equivalents of **2** gives **5** in 75% yield. The analogous reaction was attempted using 1 equivalent of the cation $[Ru(C_6H_6)(MeCN)_3]^{2+}$ instead of 2 equivalents of **2**, but redox reactions predominated and no mixed-metal products were isolated. The syntheses described above are depicted in Scheme 1.

The clusters **3** and **5** have been fully characterised by IR, mass, ^1H and ^{13}C NMR spectroscopy (Table 1) and microanalysis (Experimental section), while **4** has been characterised on the basis of IR spectroscopy only (Table 1) due to its reactive nature. The IR spectrum of **3** confirms the presence of both terminal and bridging carbonyls, while the carbonyl stretching band at 1714 cm^{-1} in the spectrum of **5** indicates the presence of at least one face-capping carbonyl group in addition to the terminal carbonyls. The ^1H NMR spectrum of **3** exhibits singlets at δ 5.56 and −21.81, indicative of the protons on a η^5-cyclopentadiene ring and an edge-bridging hydride ligand, respectively. The chemical shift for the cyclopentadienyl ligand is comparable with that observed for $[Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2]$ (δ 5.19)[5] and the $[MoRu_3(CO)_{12}(\eta^5\text{-}C_5H_5)]^-$ anion (δ 5.32).[9] Similarly, complex **5** shows singlets at δ 5.71 and 5.47 in the ^1H NMR spectrum which are representative of two non-equivalent cyclopentadienyl ligands in the molecule, as expected. The ^{13}C NMR spectrum gives a peak at δ 87.63 for **3** and peaks at δ 90.49 and 95.13 for **5**, which can be assigned to the carbon

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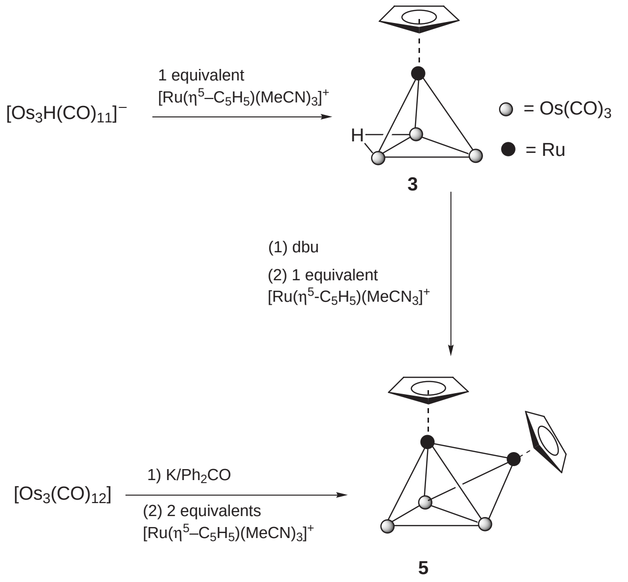
Table 1 Spectroscopic data for the new complexes

Compound	IR, ṽCO/cm^{-1}	Mass (m/z)^c exptl. (calc.)	^{1}H NMR,^{b} δ	^{13}C nmr,^{b} δ
3	2089m, 2063vs, 2034vs, 2007s, 1830m (br)^c	1047 (1045)	5.56 (s, C_5H_5) −21.81 (s, hydride)	87.63 (C_5H_5)
4	1991vs, 1957w^d	—	—	—
5	2064s, 2021vs, 1991m, 1968w, 1714w	1218 (1220)	5.71 (s, C_5H_5) 5.47 (s, C_5H_5)	90.49 (s, C_5H_5) 95.13 (s, C_5H_5)

v = Very; s = strong, m = medium, w = weak and br = broad. ^{a} Positive-ion FAB based on ^{190}Os and ^{101}Ru. ^{b} Spectrum run in $CDCl_3$. ^{c}Spectrum run in dichloromethane. ^{d} Spectrum run in thf.



Scheme 1 Carbonyl ligands have been omitted from the structures of **3** and **5**

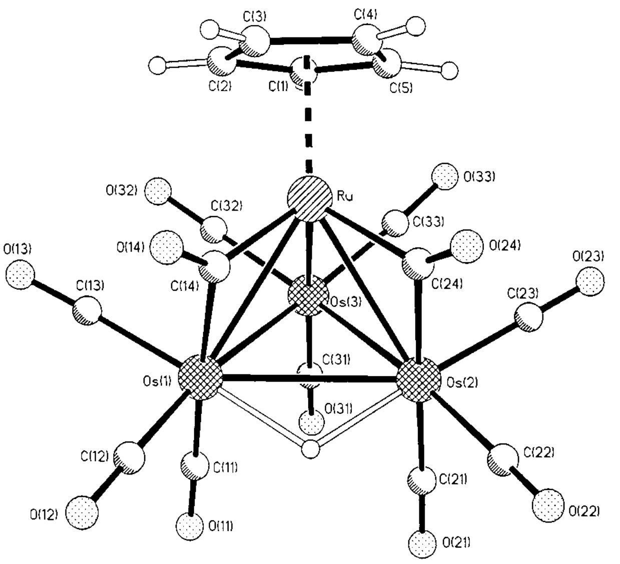


Fig. 1 Molecular structure of one independent molecule of $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **3** showing the atom numbering scheme

atoms of the cyclopentadienyl ligands. The mass spectra give parent ion peaks which correspond to the molecular formula for **3** and **5**, respectively, and sequential loss of carbonyl ligands is also visible.

In order to confirm the spectroscopic assignments for the clusters **3** and **5**, and to determine the relative sites of the Os- and Ru-containing fragments in the metal cores, single-crystal X-ray diffraction studies were undertaken on both compounds. Crystals of both clusters were grown by slow evaporation of their dichloromethane solutions. Molecules of **3** crystallise in the orthorhombic space group $P2_12_12_1$ with two independent but chemically similar molecules in the asymmetric unit. There are no close intermolecular cyclopentadienyl–cyclopentadienyl contacts in the crystal structure which might be attributed to π-stacking interactions. The molecular structure of one of the independent molecules of **3** is illustrated in Fig. 1, and selected bond parameters for both molecules are listed in Table 2 (the second molecule is denoted by superscript ′ associated with the atom numbers).

Table 2 Selected bond lengths (Å) and angles (°) for $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **3**

	Molecule 1		Molecule 2
Os(1)–Os(2)	2.943(2)	Os(1′)–Os(2′)	2.942(2)
Os(1)–Os(3)	2.784(2)	Os(1′)–Os(3′)	2.765(2)
Os(2)–Os(3)	2.775(2)	Os(2′)–Os(3′)	2.781(2)
Os(1)–Ru	2.803(3)	Os(1′)–Ru′	2.828(3)
Os(2)–Ru	2.825(3)	Os(2′)–Ru′	2.795(3)
Os(3)–Ru	2.773(3)	Os(3′)–Ru′	2.774(3)
Os(1)–C(14)	2.18(3)	Os(1′)–C(14′)	2.24(4)
Ru–C(14)	1.95(4)	Ru′–C(14′)	1.92(5)
Os(2)–C(24)	2.22(4)	Os(2′)–C(24′)	2.21(3)
Ru–C(24)	2.02(4)	Ru′–C(24′)	2.02(4)
Ru–Cp(centroid)	1.906	Ru′–Cp(centroid)	1.896
Os(3)–Os(1)–Os(2)	57.89(5)	Os(3′)–Os(1′)–Os(2′)	58.23(5)
Ru–Os(1)–Os(2)	58.82(7)	Ru′–Os(1′)–Os(2′)	57.92(6)
Os(3)–Os(1)–Ru	59.50(7)	Os(3′)–Os(1′)–Ru′	59.46(7)
Os(3)–Os(2)–Os(1)	58.17(5)	Os(3′)–Os(2′)–Os(1′)	58.17(5)
Os(3)–Os(2)–Ru	59.35(7)	Os(3′)–Os(2′)–Ru′	59.66(7)
Ru–Os(2)–Os(1)	58.12(6)	Ru′–Os(2′)–Os(1′)	59.00(6)
Os(2)–Os(3)–Os(1)	63.94(5)	Os(2′)–Os(3′)–Os(1′)	64.06(5)
Ru–Os(3)–Os(1)	60.60(7)	Ru′–Os(3′)–Os(1′)	61.40(7)
Ru–Os(3)–Os(2)	61.21(7)	Ru′–Os(3′)–Os(2′)	60.43(7)
Os(1)–Ru–Os(2)	63.06(6)	Os(1′)–Ru′–Os(2′)	63.08(6)
Os(3)–Ru–Os(1)	59.90(6)	Os(3′)–Ru′–Os(1′)	59.14(7)
Os(3)–Ru–Os(2)	59.44(7)	Os(3′)–Ru′–Os(2′)	59.91(6)
Ru–C(14)–Os(1)	85.3(14)	Ru′–C(14′)–Os(1′)	85.0(20)
O(14)–C(14)–Os(1)	136(3)	O(14′)–C(14′)–Os(1′)	132(4)
O(14)–C(14)–Ru	138(3)	O(14′)–C(14′)–Ru′	143(4)
Ru–C(24)–Os(2)	83.4(14)	Ru′–C(24′)–Os(2′)	82.6(13)
O(24)–C(24)–Os(2)	137(3)	O(24′)–C(24′)–Os(2′)	136(3)
O(24)–C(24)–Ru	140(3)	O(24′)–C(24′)–Ru′	140(3)

The metal skeleton in $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **3** is an Os_3Ru tetrahedron, consistent with the 60-electron count for the molecule. The Ru atom has the cyclopentadienyl group η^5 bound to it, as in the starting material, and two bridging carbonyl ligands, which span the Os(1)–Ru and Os(2)–Ru edges, are also associated with it. The remaining nine carbonyl ligands are terminally bound, three to each Os atom. The hydride was not located directly, but its position, spanning the Os(1)–Os(2) edge, was established from potential-energy calculations.[10] This Os(1)–Os(2) edge is significantly longer, at 2.943(2) Å [2.942(2) Å in the second molecule], than the other two Os–Os distances in the cluster, average 2.780(3) (for molecule 1) and 2.773(3) Å (for molecule 2), as is expected for metal–metal edges bridged by a hydride.[11] The length of the Os(1)–Os(2) edge is comparable to hydride-bridged edges in other mixed-metal tetrahedral clusters: $[FeOs_3(\mu\text{-}H)_2(CO)_{13}]$, 2.934(1)

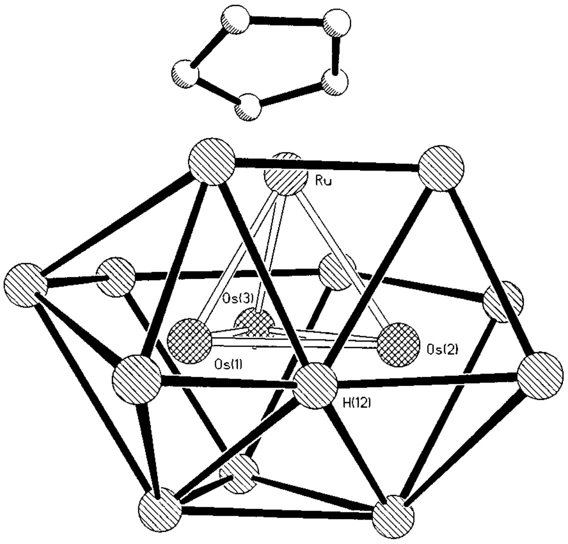


Fig. 2 The ligand polyhedron for $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **3** showing the contacts between the midpoints of the carbonyl ligands and the hydride

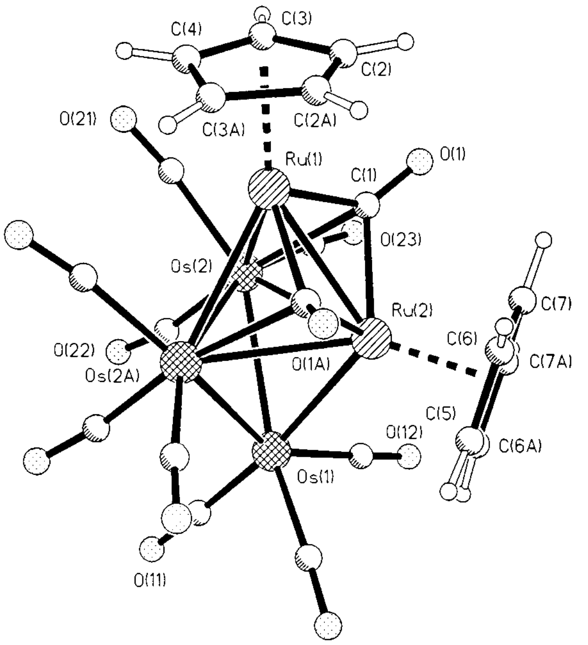


Fig. 3 Molecular structure of $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5** showing the atom numbering scheme

Table 3 Selected bond lengths (Å) and angles (°) for $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5**

Os(1)–Os(2)	2.7768(14)	Os(1)–Ru(2)	2.762(3)
Os(2)–Ru(1)	2.794(2)	Os(2)–Os(2A)	2.787(2)
Os(2)–Ru(2)	2.825(2)	Ru(1)–Ru(2)	2.691(3)
Ru(1)–C(1)	2.03(2)	Ru(2)–C(1)	2.10(2)
Os(2)–C(1)	2.38(3)	Ru(1)–Cp1(centroid)	1.864
Ru(2)–Cp2(centroid)	1.891		
Ru(2)–Os(1)–Os(2)	61.35(5)	Ru(2)–Os(1)–Os(2A)	61.35(5)
Os(2)–Os(1)–Os(2A)	60.25(5)	Os(1)–Os(2)–Os(2A)	59.88(2)
Os(1)–Os(2)–Ru(1)	106.89(5)	Ru(1)–Os(2)–Os(2A)	60.08(3)
Os(1)–Os(2)–Ru(2)	59.06(6)	Ru(2)–Os(2)–Os(2A)	60.45(3)
Ru(1)–Os(2)–Ru(2)	57.21(7)	Ru(2)–Ru(1)–Os(2)	61.98(7)
Os(2)–Ru(1)–Os(2A)	59.83(6)	Ru(1)–Ru(2)–Os(1)	110.32(11)
Ru(1)–Ru(2)–Os(2)	60.81(7)	Os(1)–Ru(2)–Os(2)	59.59(6)
Ru(1)–C(1)–Ru(2)	81.2(8)	O(1)–C(1)–Ru(1)	139(2)
O(1)–C(1)–Ru(2)	132(2)	O(1)–C(1)–Os(2)	126(2)
Ru(1)–C(1)–Os(2)	78.2(8)	Ru(2)–C(1)–Os(2)	77.9(7)

Symmetry transformation to generate the equivalent atoms denoted ‘A’ is x, $0.5 - y$, z.

and 2.937(1) Å,[12] and $[CoOs_3(\mu\text{-}H_3)(CO)_{13}]$, 2.893(1)–2.909(1) Å.[13] The $Ru(\eta^5\text{-}C_5H_5)$ group caps the Os_3 triangle asymmetrically, with the shortest bond involving the Os(3)–Ru edge, at 2.773(3) Å [2.774(3) Å for molecule 2], which does not have a carbonyl group spanning it. The carbonyl-bridged Os–Ru edges have an average length of 2.814(5) (for molecule 1) and 2.812(5) Å (for molecule 2). A similar asymmetry of the capping group is observed in the structure of $[Os_3W(\mu\text{-}H)_3(CO)_{11}(\eta^5\text{-}C_5H_5)]$,[14] but here two Os–W edges are bridged by hydrides rather than carbonyl ligands. In **3** the two bridging carbonyls also show significant asymmetry, with the shorter bonds to the Ru atom [average 1.99(6) for molecule 1 and 1.97(6) Å for molecule 2] and the longer bonds to the Os atoms [2.20(6) for molecule 1 and 2.23(6) Å for 2]. The presence of bridging carbonyl ligands has been previously ascribed to the need to disperse the additional electron density donated by the $Ru(\eta^5\text{-}C_5H_5)$ group into the metal core,[5,6] since bridging carbonyl groups act as better π-acceptor ligands than do terminal carbonyls. An examination of the ligand polyhedron, as defined by the midpoint of the eleven carbonyl groups and the hydride ligand (Fig. 2), shows that the cyclopentadienyl group has a fundamental influence on the ligand arrangement compared to that of related binary carbonyl complexes.[15] The ligand polyhedron resembles a fragment of a cuboctahedral arrangement (Fig. 2), but with one vertex missing from the top of the polyhedron, and an extra vertex, the H(12) site, inserted into the equatorial, six-vertex girdle. This arrangement does not correspond to any of the most energetically favourable geometries for 13-, 14- or 15-vertex polyhedra calculated using a simple model[15] (it may be argued that the cyclopentadienyl ligand may occupy one, two or three co-ordination sites), and the observed geometry may be more dependent on electronic rather than steric influences.

The cluster $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5** crystallises in the monoclinic space group $P2_1/m$ with two molecules in the cell, such that each molecule of **5** has a crystallographic mirror plane which passes through the Os(1), Ru(1), Ru(2), C(11), O(11), C(4) and C(5) atoms (Fig. 3). As with **3** the crystal packing shows no intermolecular contacts between the cyclopentadienyl rings, but only cyclopentadienyl–carbonyl oxygen contacts. Selected bond parameters for **5** are presented in Table 3.

The metal framework in cluster **5** may be viewed as a trigonal bipyramid in which one of the $Ru(\eta^5\text{-}C_5H_5)$ units occupies an equatorial site, while the second takes up an axial position. Alternatively, the metal core can be considered as an Os_3Ru tetrahedron, as in **3**, with the second $Ru(\eta^5\text{-}C_5H_5)$ unit capping one of the Os_2Ru triangular faces. Both approaches are consistent with the 72-electron count for the cluster. There are nine terminal carbonyl ligands, three bound to each Os atom, and two face-capping carbonyls which span the Os(2)Ru(1)Ru(2) and Os(2A)Ru(1)Ru(2) triangular faces. The shortest metal–metal edge in the cluster core is the Ru(1)–Ru(2) edge, at 2.691(3) Å, between the two $Ru(\eta^5\text{-}C_5H_5)$ units, perhaps suggesting the presence of additional bonding electron density between the two ‘electron rich’ centres. The other three edges involving the Ru atom in the equatorial position, Ru(2), are the three longest in the trigonal-bipyramidal core, a trend which is also observed in $[Os_5(CO)_{16}]$,[16] where the Ru(2) site in **5** corresponds to the ‘electron rich’, 20-electron Os atom (in terms of localised electron counting) which is co-ordinated to four carbonyl ligands in $[Os_5(CO)_{16}]$ (Fig. 4). Two of the carbonyls on the 20-electron Os centre, in $[Os_5(CO)_{16}]$, form ‘incipient’ asymmetric μ-carbonyl bridges to the ‘electron poor’ osmium centres, but in the case of **5** there are no ‘incipient’ bridges but the two asymmetrically face-capping carbonyl groups. These face-capping carbonyl groups have significantly shorter Ru–C

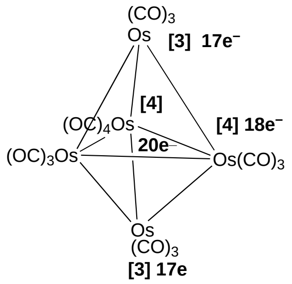


Fig. 4 Structure of $[Os_5(CO)_{16}]$ showing the metal–metal connectivity and electron count (using the 18-electron rule) at each osmium centre

than Os–C contacts, as was observed for **3**. This can again be rationalised in terms of the need to distribute the additional electron density associated with the $Ru(\eta^5\text{-}C_5H_5)$ groups over the cluster framework.

It has been noted previously[17] that in the structures of all the crystallographically characterised trigonal-bipyramidal carbonyl clusters of ruthenium and osmium which contain a metal cyclopentadienyl or metal arene fragment this unit occupies the equatorial site equivalent to the 20-electron centre in $[Os_5(CO)_{16}]$. On electronic grounds, this appears reasonable because the metal–carbocyclic ligand fragment is a better donor than a metal carbonyl fragment, and so if it occupies the centre which is 'electron rich', in terms of a localised bonding scheme, in the binary carbonyl, then it will cause the least additional disruption to the metal framework bonding. In this context it is interesting that in the structure of $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5** the second $Ru(\eta^5\text{-}C_5H_5)$ does not occupy a second equatorial site, but an axial one. Both steric and electronic explanations for this observation are possible. There is less steric repulsion between the two cyclopentadienyl rings if one is axial and one equatorial, and although the second 'electron rich' $Ru(\eta^5\text{-}C_5H_5)$ group occupies a formally 'electron poor' axial site, the two face-capping carbonyl groups accept excess of electron density from the two ruthenium centres.

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, precoated to 0.25 mm thickness with Merck Kieselgel 60 F_{254}, as supplied by Merck, or using laboratory-prepared glass plates coated to 1 mm thickness with Merck Kieselgel 60 F_{254}. The complexes $[(Ph_3P)_2N][Os_3H(CO)_{11}]$,[18] $[Os_3(CO)_{12}]$,[19] $K_2[Os_3(CO)_{11}]$[8] and $[Ru(C_5H_5)(MeCN)_3][PF_6]$[20] were prepared by literature procedures. 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 and ^{13}C NMR spectra on a Bruker WH 250 MHz spectrometer.

Preparations

$[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ 3. To a solution of the salt $[(Ph_3P)_2N][Os_3H(CO)_{11}]$ (150 mg, 10.6×10^{-5} mol), in dichloromethane (25 cm^3), was added 1 molar equivalent of $[Ru(C_5H_5)(MeCN)_3]PF_6$ (48 mg, 10.0×10^{-5} mol) and the solution, which becomes deeper red immediately, was stirred for *ca.* 15 min. After removal of solvent, the solid residue was chromatographed by TLC using CH_2Cl_2–hexane (4:1) as eluent. The red cluster $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **3** was isolated as the sole product and recrystallised from dichloromethane–hexane (yield 90%, 98 mg, 9.5×10^{-5} mol) {Found: C, 18.66; H, 0.71. Calc. for $[Os_3RuH(CO)_{11}(\eta^5\text{-}C_5H_5)]$: C, 18.37; H, 0.57%}.

Table 4 Crystallographic data* for compounds **3** and **5**

	3	**5**
Molecular formula	$C_{16}H_6O_{11}Os_3Ru$	$C_{21}H_{10}O_{11}Os_3Ru_2$
M	1045.88	1211.03
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/m$
a/Å	8.718(2)	9.678(3)
b/Å	14.026(3)	12.117(5)
c/Å	33.224(7)	10.497(3)
β/°		93.59(2)
U/Å^3	4063(2)	1228.6(7)
Z	8	2
D_c/Mg m^3	3.420	3.274
Crystal size/mm	0.48 × 0.46 × 0.32	0.25 × 0.20 × 0.05
Crystal habit	Block	Plate
$F(000)$	3696	1080
μ/mm^{-1}	19.492	16.716
Maximum, minimum relative transmission	0.164, 0.047	0.739, 0.005
Data collection range/°	$5.28 < 2\theta < 45.10$	$5.14 < 2\theta < 45.08$
Index range	$-9 \leqslant h \leqslant 9$, $-15 \leqslant k \leqslant 15$, $-35 \leqslant l \leqslant 35$	$0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 13$, $-11 \leqslant l \leqslant 11$
Reflections measured	6292	1788
Independent reflections (R_{int})	5329 (0.059)	1619 (0.045)
Parameters, restraints	400, 0	178, 0
$wR2$ (all data)	0.149	0.199
x, y	0.0700, 166.471	0.1673, 0
$R1[I > 2\sigma(I)]$	0.054	0.068
Observed reflections	4498	1391
Goodness of fit on F^2 (all data)	1.038	1.071
Maximum shift/σ	0.00	0.002
Absolute structure parameter	0.00(4)	
Peak, hole in final difference map/e Å^{-3}	2.19, −2.17	4.14, −2.75

* Data in common: $T = 293(2)$ K; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$; goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{\frac{1}{2}}$ where n is the number of reflections and p the number of parameters.

$[Os_3Ru(CO)_{11}(\eta^5\text{-}C_5H_5)]^-$ 4. To a solution of compound **3** (98 mg, 9.5×10^{-5} mol) in dichloromethane (25 cm^3) was added an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene and the solution stirred overnight. The resultant solution was used for further reaction without purification.

$[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ 5. *Method* 1. One molar equivalent of $[Ru(C_5H_5)(MeCN)_3]PF_6$ (42 mg, 9.7×10^{-5} mol) was added to a solution of compound **4** (prepared from 98 mg, 9.5×10^{-5} of **3**). The solution was stirred for 30 min and the solid obtained after removing the solvent was chromatographed by TLC, eluting with CH_2Cl_2–hexane (3:2). The cluster $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5** was isolated as the major product in approximately 80% yield (87 mg, 7.4×10^{-5} mol) {Found: C, 22.14; H, 0.82. Calc. for $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$: C, 22.70; H, 0.91%}.

Method 2. Two molar equivalents of $[Ru(C_5H_5)(MeCN)_3]PF_6$ (72 mg, 16.8×10^{-5} mol) were added to a dichloromethane solution (25 cm^3) of $[(Ph_3P)_2N]_2[Os_3(CO)_{11}]$ (150 mg, 7.7×10^{-5} mol) {prepared from 150 mg of $[Os_3(CO)_{12}]$ by reduction with an excess of K/Ph_2CO in thf (10 cm^3)} and the solution, which turns red immediately, was stirred for 15 min. Evaporation of the solvent, followed by purification, as above gave $[Os_3Ru_2(CO)_9(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ **5** as the major product (*ca.* 75% yield, 70 mg, 5.8×10^{-5} mol) together with a small amount of **3**.

Crystallography

Suitable single crystals for compounds **3** and **5** were mounted on glass fibres with epoxy resin, and data were recorded at room temperature on a Siemens R3mV diffractometer, using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å), and an ω-scan procedure for **3** and an ω–2θ scan procedure for **5**. Data were corrected for absorption using a semiempirical method based on ψ scans. Details of crystal data, data collection and structure refinement are summarised in Table 4. The structures were solved by direct methods[21] (Os and Ru atom positions) and by subsequent Fourier-difference syntheses, and refined by full-matrix least squares[22] on F^2, with Os, Ru and O atoms assigned anisotropic displacement parameters in **3** and all non-hydrogen atoms assigned anisotropic displacement parameters in **5**. In both structures the cyclopentadienyl H atoms were placed in idealised positions and allowed to ride on the relevant carbon atom; H atoms were refined with common isotropic displacement parameters. The hydride in the structure of **3** was located using the HYDEX program,[10] and included but not refined in the final cycles of refinement. For each structure, in the final cycles of refinement, a weighting scheme of the form $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ was introduced which gave a relatively flat analyses of variance.

CCDC reference number 186/892.

See http: //www.rsc.org/suppdata/dt/1998/1091/ for crystallographic files in .cif format.

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