

# Synthesis and characterisation of the novel mixed-metal cluster $[\text{Ru}_5\text{Rh}(\text{CO})_{12}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$

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The reaction of the octahedral dianion  $[\text{Ru}_6(\text{CO})_{18}]^{2-}$  with the dication  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{MeCN})_3]^{2+}$  afforded the novel mixed-metal cluster  $[\text{Ru}_5\text{Rh}(\text{CO})_{12}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$ , which has been shown by an X-ray analysis to contain a bi-edge bridged tetrahedral framework, with the  $\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)$  unit at the apex of the tetrahedron, and two  $\mu_4\text{-}\eta^2\text{-CO}$  capping carbonyl ligands.

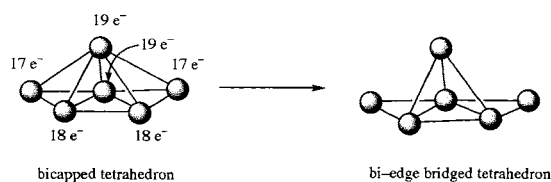
Since its synthesis and characterisation,<sup>1</sup> the chemistry of  $[\text{Os}_6(\text{CO})_{18}]$  has remained a central theme of cluster carbonyl chemistry.<sup>2</sup> The metal framework in  $[\text{Os}_6(\text{CO})_{18}]$  is a bicapped tetrahedron, with each Os atom co-ordinated to three carbonyl ligands. While the overall electron count for the structure of 84 electrons obeys the Effective Atomic Number Rule,<sup>3</sup> individual metal atoms have 17-, 18- or 19- $e^-$  depending on whether they have three, four or five metal connections (Scheme 1). This partial electron imbalance is reflected in the chemistry of the molecule, with the product of substitution by nucleophiles having the nucleophilic reagents at the 'electron poor' 17 $e^-$  capping positions. The recent interest in the preparation of arene-substituted carbonyl clusters<sup>4</sup> *via* coupling reactions between cluster anions and arene-substituted mononuclear cations such as  $[\text{M}(\eta^5\text{-C}_6\text{H}_6\text{-}n\text{Me}_n)(\text{MeCN})_3]^{2+}$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ,  $n = 0$  or  $3$ )<sup>5</sup> has led to a resurgence of interest in the mechanisms by which the bicapped tetrahedral framework is formed, and on the steric and electronic properties of the groups which occupy the different sites in the metal core. For example, the reaction of the trigonal-bipyramidal dianion  $[\text{Os}_5(\text{CO})_{15}]^{2-}$  with  $[\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$  affords  $[\text{Os}_6(\text{CO})_{15}(\eta^6\text{-C}_6\text{H}_6)]$ , in which the benzene molecule is attached to an 18 $e^-$  Os atom in the central tetrahedron, while the reaction of the same anion with  $[\text{Os}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{MeCN})_3]^{2+}$  affords  $[\text{Os}_6(\text{CO})_{15}(\eta^6\text{-C}_6\text{H}_5\text{Me})]$  in which the toluene molecule is attached to a capping 17 $e^-$  Os atom.<sup>5</sup> Clearly, if arene migration can be ruled out, the mechanism for the formation of these bicapped tetrahedral clusters is not the straightforward capping of a face of the anion by the cation, but in some cases a metal framework rearrangement is involved.

By contrast, the ruthenium analogue of  $[\text{Os}_6(\text{CO})_{18}]$  has never been isolated, but a number of derivatives containing ruthenium atoms in a metal core based on the bicapped tetrahedron are known.<sup>6</sup> In order to investigate the ruthenium-based systems and gain further information about the electron distribution in the bicapped tetrahedral geometry using a heterometal marker, we have attempted the reaction of the dianion  $[\text{Ru}_6(\text{CO})_{18}]^{2-}$  with  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{MeCN})_3]^{2+}$ , and now report the synthesis and characterisation of the novel mixed-metal cluster  $[\text{Ru}_5\text{Rh}(\text{CO})_{12}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$  **1**.

The reaction of  $[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_6(\text{CO})_{18}]^{7-}$  (30 mg, 0.0137 mmol) with an excess of  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{MeCN})_3][\text{PF}_6]_2$  (17.8 mg, 0.027 mmol)<sup>8</sup> in dichloromethane (25 cm<sup>3</sup>) under  $\text{N}_2$ , at room temperature, resulted in an immediate colour change of the solution to dark green, and then a further rapid change to orange. The solution was stirred for 1 h at room temperature and separated by TLC using  $\text{CH}_2\text{Cl}_2$ -hexane (1:1) as eluent. The major dark orange product **1** (6 mg) was obtained in ca.

40% yield, and was initially characterised from spectroscopic data (a number of uncharacterised low yield products were also obtained).<sup>†</sup> The FAB mass spectrum gave a molecular ion peak corresponding to  $\text{C}_{25}\text{H}_{15}\text{O}_{15}\text{RhRu}_5$ , while the IR spectrum displayed peaks corresponding to the presence of both terminal and edge-bridging carbonyls, and to carbonyls with a much lower stretching frequency such as the  $\mu_4\text{-}\eta^2\text{-CO}$  ligands found in  $[\text{Ru}_6(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)]$ .<sup>9</sup> The <sup>1</sup>H NMR spectrum displayed a single peak at  $\delta$  1.90 corresponding to the methyl groups in an  $\eta^5\text{-C}_5\text{Me}_5$  ligand, and the <sup>13</sup>C NMR spectrum showed peaks corresponding to the cyclopentadienyl and methyl carbons of the  $\eta^5\text{-C}_5\text{Me}_5$ . Only a broad, ill-defined signal was observed in the carbonyl region of the <sup>13</sup>C NMR spectrum, at room temperature, and on cooling solubility problems prevented a spectrum from being obtained. It is presumed that the carbonyl groups are undergoing a dynamic process at room temperature.

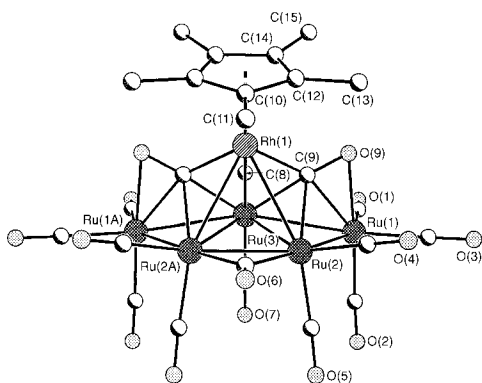
In order to confirm the spectroscopic assignments and determine the full molecular and crystal structure of **1** an X-ray analysis was undertaken.<sup>‡</sup> The crystal structure of **1** corresponds to discrete molecules of  $[\text{Ru}_5\text{Rh}(\text{CO})_{12}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$  separated by normal van der Waals distances. The molecular structure is shown in Fig. 1 which includes some selected bond parameters. In the crystal structure, the asymmetric unit contains two independent but chemically equivalent half molecules lying on mirror planes which bisect  $\text{Rh}(1)$ ,



**Scheme 1** Biccapped tetrahedral and bi-edge bridged tetrahedral metal cores

<sup>†</sup> Spectroscopic data for cluster **1**. IR( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2090m, 2071s, 2026vs, 1996w (sh), 1846w (br), 1415s, 1358w  $\text{cm}^{-1}$ ; positive-ion FAB mass spectrum:  $m/z$  1164 (calc. 1161 based on <sup>101</sup>Ru and <sup>103</sup>Rh) (Found: C, 25.60; H, 1.25. Calc. for  $\text{C}_{25}\text{H}_{15}\text{O}_{15}\text{RhRu}_5$ : C, 25.80; H, 1.30). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  1.90 ( $\text{C}_5\text{Me}_5$ ). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  110.04 [d,  $J(\text{Rh-C})$  4.8 Hz,  $\text{C}_5\text{Me}_5$ ], 9.4 (s,  $\text{C}_5\text{Me}_5$ ).

<sup>‡</sup> Crystal data for  $[\text{Ru}_5\text{Rh}(\text{CO})_{12}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$  **1**:  $M = 1163.63$ , orange block, crystal dimensions  $0.10 \times 0.25 \times 0.30$  mm, monoclinic, space group  $P2_1/m$ ,  $a = 10.743(2)$ ,  $b = 17.276(3)$ ,  $c = 17.523(2)$  Å,  $\beta = 96.191(13)^\circ$ ,  $U = 3233.5(10)$  Å<sup>3</sup>,  $T = 295(2)$  K,  $D_c = 2.39$  Mg  $\text{m}^{-3}$ ,  $Z = 4$ ,  $F(000) = 2200$ , Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu(\text{Mo-K}\alpha) = 2.842$  mm<sup>-1</sup>, Rigaku AFC5R diffractometer, 6222 reflections collected in range  $2.62 \leq \theta \leq 25.01^\circ$ , 5892 unique absorption corrected data ( $R_{\text{int}} = 0.042$ ). Structure solved by direct methods (Ru and Rh atoms) (SHELXTL PLUS<sup>10</sup>) and refined with Ru, Rh, O and ordered C atoms anisotropic by full-matrix least squares based on  $F^2$  (SHELXL 93<sup>11</sup>); methyl H-atoms in idealised positions. The two independent half-molecules in the asymmetric unit lie on mirror planes, the  $\text{C}_5\text{Me}_5$  ring of one of these half molecules is disordered across the mirror plane and has been refined over two sites with partial occupancies summing to unity. Refinement converged at  $R1 = 0.0434$ ,  $wR2 = 0.0873$  for 3677 unique data with  $F > 4\sigma(F)$ , and  $R1 = 0.1170$  and  $wR2 = 0.2099$  (all data), goodness of fit = 1.036, weighting scheme  $w1 = [\sigma^2(F_o^2) + (0.0189P)^2 + 8.08P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Highest and lowest remaining peaks in the difference map were 0.868 and  $-0.923$  e Å<sup>-3</sup>. Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions to Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/339.



**Fig. 1** Molecular structure of one molecule of  $[\text{Ru}_5\text{Rh}(\text{CO})_{12}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$  **1** showing the atom numbering scheme; H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) [data from the second molecule are in square brackets]; Ru(1)–Ru(2) 2.7870(12) [2.7842(12)], Ru(1)–Ru(3) 2.8496(10) [2.8412(10)], Ru(2)–Ru(2A) 2.636(2) [2.639(2)], Ru(2)–Ru(3) 2.7664(12) [2.7637(12)], Ru(2)–Rh(1) 2.8228(13) [2.8032(13)], Ru(3)–Ru(2A) 2.7665(12) [2.7636(12)], Ru(3)–Rh(1) 2.769(2) [2.762(2)], Ru(3)–Ru(1A) 2.8496(10) [2.8411(10)], Rh(1)–Ru(2A) 2.8229(13) [2.8032(13)], Rh(1)–(centroid)( $\text{C}_5\text{Me}_5$ ) 1.891 [1.889], Ru(2)–C(6) 2.142(14) [2.129(14)], Ru(1)–C(9) 2.241(9) [2.255(10)], Ru(1)–O(9) 2.149(6), [2.161(6)], Ru(2)–C(9) 2.158(9) [2.154(9)], Ru(3)–C(9) 2.158(10) [2.167(10)], Rh(1)–C(9) 1.995(9) [2.000(10)], C(9)–O(9) 1.252(11) [1.244(11)]; Ru(2)–C(6)–Ru(2A) 76.0(6) [76.6(6)], Ru(2)–C(6)–O(6) 141.9(3) [141.7(3)], Rh(1)–C(9)–O(9) 131.2(7) [132.7(7)], Ru(2)–C(9)–O(9) 127.7(7) [128.8(7)], Ru(3)–C(9)–O(9) 131.3(7) [129.6(7)], Ru(1)–C(9)–O(9) 69.5(5) [69.5(5)]

Ru(3), C(10), C(11) and the carbonyl groups C(6)O(6), C(7)O(7) and C(8)O(8). The metal framework consists of a central RhRu<sub>3</sub> tetrahedron, with two basal Ru–Ru edges each bridged by a further Ru atom, and the third basal Ru–Ru edge by a carbonyl group, C(6)O(6). The Rh(1) atom with its  $\eta^5\text{-C}_5\text{Me}_5$  ligand then occupies the apical site of the central tetrahedron. Twelve of the remaining carbonyl ligands are linear and terminal, but the other two adopt the uncommon  $\mu_4\text{-}\eta^2$  mode, with each carbon capping a RhRu<sub>2</sub> face of the central tetrahedron, and the C–O bond interacting in a  $\pi$  fashion to the edge-bridging Ru atom.

The metal framework in **1** may be viewed as derived from that of a bicapped tetrahedron [as observed in  $[\text{Os}_6(\text{CO})_{18}]^{11}$ ] by breaking of the two equivalent Rh(1)–Ru(1) edges and the ‘insertion’ of the  $\mu_4\text{-}\eta^2$ -carbonyls. The electron count of 88 for **1** is consistent with this view, the addition of two electron pairs to an ‘electron precise’ 84-electron bicapped tetrahedron being concomitant with the breaking of two edges (Scheme 1). In this context, it is of interest to note that the Rh( $\eta^5\text{-C}_5\text{Me}_5$ ) unit occupies a position in the framework that would be equivalent to a  $19e^-$  site in the bicapped tetrahedron. Since the  $\text{C}_5\text{Me}_5$  group is a much better donor and poorer acceptor than an equivalent number of carbonyl ligands the Rh(1) atom may be considered ‘electron rich’, and it is therefore entirely reasonable that it occupy an electron-rich site. The opening out of the structure from a bicapped tetrahedron to a bi-edge bridged tetrahedron may either be a result of an easing of the steric congestion caused by the presence of the bulky  $\eta^5\text{-C}_5\text{Me}_5$  group, or because of the electron donation from the Rh( $\eta^5\text{-C}_5\text{Me}_5$ ) requiring the  $\mu_4\text{-}\eta^2$ -carbonyls to accept the increased electron density. Similar trends have been observed in the hexaruthenium clusters  $[\text{Ru}_6(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)]$ ,  $[\text{Ru}_6\text{H}(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-CO})(\mu_2\text{-}\eta^7\text{-CH}_2\text{C}_6\text{H}_3\text{Me}_2\text{-3,5})]$ ,<sup>9,12</sup>  $[\text{Ru}_6(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^6\text{-C}_6\text{Me}_6)]$ <sup>13</sup> and  $[\text{Ru}_6\text{H}_3(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ .<sup>14</sup> In all these systems an ‘electron rich’ Ru(arene) unit occupies the position equivalent to the  $19e^-$  site in the bicapped tetrahedron and one or more  $\mu_4\text{-}\eta^2$ -carbonyls are present to accept the electron density. However, **1** represents the first mixed-metal cluster to display this geometry. The only

previously structurally characterised Ru<sub>5</sub>Rh clusters which contain a Rh( $\eta^5\text{-C}_5\text{Me}_5$ ) group are the clusters  $[\text{Ru}_5\text{RhC}(\text{CO})_{14}(\eta^5\text{-C}_5\text{Me}_5)]$  and  $[\text{Ru}_5\text{RhC}(\text{CO})_9(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)_2]$ ,<sup>15</sup> both of which have an octahedral metal core.

Although the presence of  $\mu_4\text{-}\eta^2\text{-CO}$  groups is still rare, their occurrence is not isolated to the Ru and RuRh clusters mentioned above. A number of examples have been observed in a range of metal carbonyl systems across the d block of the periodic table.<sup>16</sup> In all cases the C–O distances show a significant lengthening compared to terminal or edge-bridging carbonyls, and the very low  $\nu(\text{CO})$  stretching frequency, in the range 1450–1350  $\text{cm}^{-1}$ , is consistent with a very high acceptor ability for the ligand and with a significant C–O  $\pi$  interaction to one of the metal atoms.

The formation of **1** is of mechanistic interest. It does not simply involve the ionic coupling reaction between a cluster anion and a metal cation. The expected product from the reaction of the octahedral  $[\text{Ru}_6(\text{CO})_{18}]^{2-}$  anion<sup>7</sup> with the cation  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{MeCN})_3]^{2+}$  would be a heptanuclear Ru<sub>6</sub>Rh cluster species, and this is perhaps observed fleetingly by the green colouration. However, this system is able to undergo redox chemistry, and very rapidly loses a ‘Ru(CO)<sub>3</sub>’ cap, leading to a metal framework rearrangement resulting in the observed bi-edge bridged tetrahedral structure.

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