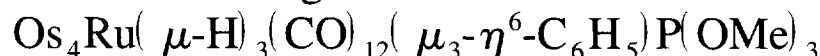


Priority communication

A novel arene bonding mode in the mixed-metal cluster



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Abstract

The ionic coupling of $[\text{Os}_4\text{H}_2(\text{CO})_{12}]^{2-}$ with $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ affords the neutral mixed metal cluster $\text{Os}_4\text{Ru}(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$ **1**. The reaction of **1** with trimethylphosphite leads to the initial formation of the addition product $\text{Os}_4\text{Ru}(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)\text{P}(\text{OMe})_3$ **2**, but this complex rearranges in solution to give $\text{Os}_4\text{Ru}(\mu\text{-H})_3(\text{CO})_{12}(\mu_3\text{-}\eta^6\text{-C}_6\text{H}_5)\text{P}(\text{OMe})_3$ **3**. An X-ray structure of **3** shows that the metal core of the cluster is a ruthenium-spiked Os_4 tetrahedron, with one hydrogen atom from the arene having transferred to the Os_4 core, and one arene carbon bridging an Os–Os edge, while the ring as a whole remains η^6 -bound to the Ru atom.

Keywords: Osmium; Ruthenium; Arene; Phosphite; Crystal structure

1. Introduction

The synthesis of arene-substituted transition metal clusters is now well established [1], and attention is turning to the reactivity [2] and dynamic behaviour [3] of the arene ring once it is coordinated to the cluster. These complexes may then be considered as model systems for surface-catalysed organic reactions [4].

There are three main synthetic routes to arene-substituted metal clusters. The first involves either the dehydrogenation of an unsaturated organic group once it is coordinated to the cluster [5], or the direct exchange of a lightly ligated ligand, such as MeCN, with an arene [6]. The second route involves the ionic coupling of a cluster anion with a mononuclear cationic arene-containing complex [7], and the third involves the direct interaction of a cluster with an arene under thermal conditions [8].

Previously, we have used the ionic coupling route to synthesise a range of penta-, hexa- and heptanuclear

arene-substituted clusters [9,10], and now report an extension of this work, using $[\text{Os}_4\text{H}_2(\text{CO})_{12}]^{2-}$ to generate the mixed-metal cluster $\text{Os}_4\text{Ru}(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$ **1** by the coupling with $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$. We also report the reaction of **1** with $\text{P}(\text{OMe})_3$ which leads to the formation of the novel spiked-tetrahedral cluster $\text{Os}_4\text{Ru}(\mu\text{-H})_3(\text{CO})_{12}(\mu_3\text{-}\eta^6\text{-C}_6\text{H}_5)\text{P}(\text{OMe})_3$ **3** in which the arene adopts an unusual bonding mode.

2. Results and discussion

The reduction of $\text{Os}_4\text{H}_2(\text{CO})_{13}$ [11] with potassium benzophenone ketyl, in tetrahydrofuran, affords the dianion $[\text{Os}_4\text{H}_2(\text{CO})_{12}]^{2-}$, which if reacted in situ, at room temperature, with an excess of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3][\text{BF}_4]$ gives the purple, neutral cluster $\text{Os}_4\text{Ru}(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$ **1**, after purification by TLC using dichloromethane–hexane (60:40) as eluant. This product is not stable in the solid state or solution for more than a few minutes, decomposing to uncharacterised low nuclearity complexes, but has been characterised by IR and ^1H NMR spectroscopies and mass

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spectrometry¹. The mass spectrum corresponds to the formulation for **1**. The room temperature ¹H NMR spectrum exhibits a signal at δ 5.99, which can be assigned to an η^6 -arene, and a broad peak at δ -13.75 which is consistent with two edge-bridging hydrides undergoing exchange. The electron count for **1** (72 electrons) suggests that the metal core should be a trigonal pyramid, and from related work with $\text{Os}_5(\mu\text{-H}_2)(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_5\text{Me})$ [12] it is likely that the ' $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)$ ' unit caps the Os_4 tetrahedron (Scheme 1).

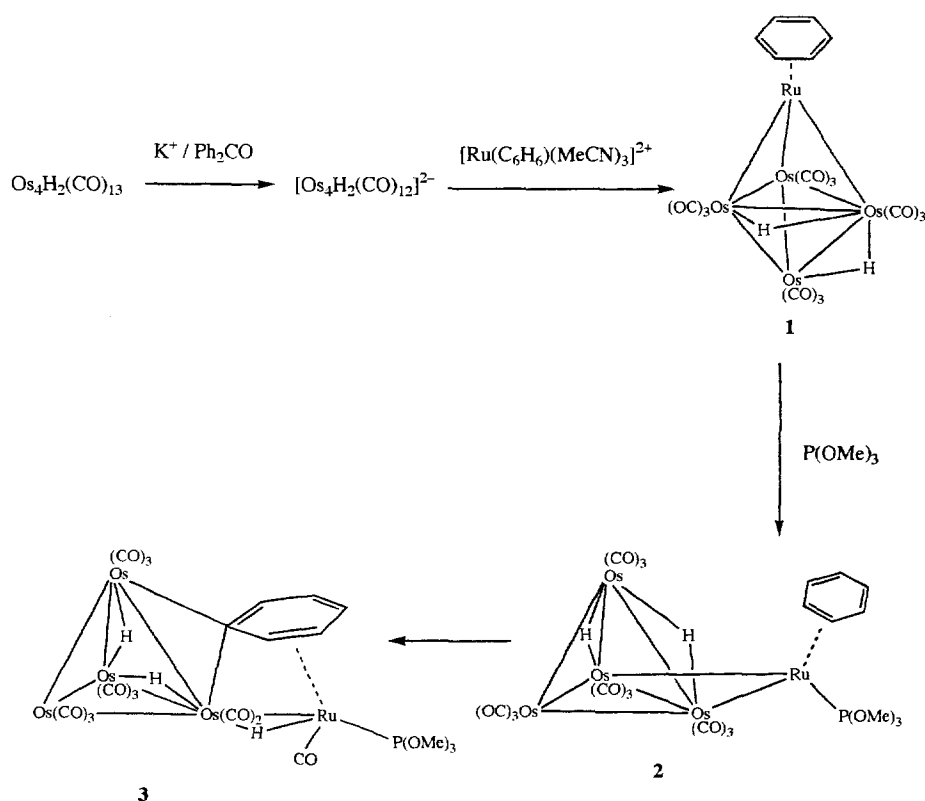
In order to try to improve the stability of **1** towards decomposition, a reaction was carried out with trimethylphosphite. The addition of a drop of $\text{P}(\text{OMe})_3$, at 0 °C, to a stirred dichloromethane solution of freshly prepared $\text{Os}_4\text{Ru}(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$ **1** causes the solution to turn orange-red, and after 15 min concentration and separation of the solution by TLC, using dichloromethane–hexane (30:70) as eluant, affords a major purple band and a minor orange band. If the reaction mixture is left in solution for a longer period of time the proportion of the orange band increases and the purple decreases. If the purple product is isolated as a solid and redissolved in dichloromethane it converts into the orange product over several hours. However, if the orange product is isolated and redissolved it does not convert back to the purple product. This process is consistent with an irreversible isomerisation of the product into the more stable form. The two products were characterised initially by spectroscopy². The purple complex **2** was formulated as $\text{Os}_4\text{Ru}(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)\text{P}(\text{OMe})_3$ from the mass spectrum. The room temperature ¹H NMR spectrum is consistent with the presence of the η^6 -bound arene ring (δ 5.98(s)), a coordinated phosphite (δ 3.59(d), $\text{P}(\text{OMe})_3$), and of two μ_2 -bridging hydrides (δ -17.77(d), -18.61(d)) on the metal core. The phosphite appears to have added to the cluster **1** increasing the count by two electrons to 74 e⁻. This count would be consistent with the breaking of one of the metal–metal edges in the core of **1** to produce either an edge-bridged tetrahedron or a square-based pyramid. By analogy with the structure of

$\text{Os}_5\text{H}_2(\text{CO})_{15}\text{P}(\text{OMe})_3$ [13], the edge-bridged core geometry is more likely with perhaps an ' $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{P}(\text{OMe})_3$ ' unit bridging an edge of the Os_4 tetrahedron (Scheme 1). While the mass spectrum of the orange complex **3** is similar to that of **2**, the ¹H NMR spectrum shows a number of differences. The signal for the phosphite is retained (δ 3.72(d), $\text{P}(\text{OMe})_3$), but there are now five signals in the range δ 6.55–4.07, consistent with the presence of five non-equivalent hydrogen atoms on the arene ring, and there are three signals in the hydride region (δ -9.00(d), -20.92(s) and -21.47(s)) indicating the presence of three non-equivalent, non-fluxional hydrides at room temperature. In order to establish the molecular structure a full X-ray crystal structure analysis was undertaken.

The crystal structure of $\text{Os}_4\text{Ru}(\mu\text{-H})_3(\text{CO})_{12}(\mu_3\text{-}\eta^6\text{-C}_6\text{H}_5)\text{P}(\text{OMe})_3$ **3** consists of discrete molecules separated by normal van der Waals distances. The molecular structure is shown in Fig. 1 which includes some selected bond parameters. The metal core geometry is an Os_4 tetrahedron with an Ru atom spike coordinated to Os(3). The phosphite and one carbonyl are terminally bound to Ru(1). The arene, which has lost one H-atom to the metal framework, is η^6 -bound to Ru(1), and the ring carbon C(1) bridges the Os(2)–Os(3) edge in a novel bonding mode. The remaining 12 carbonyl ligands are terminally bound to the four Os atoms. The hydrides were not located directly but potential energy calculations [14] suggest that one of the hydrides bridges the long Os(3)–Ru(1) edge (2.990(5) Å), and that the other two bridge the two long Os(2)–Os(4) (2.969(3) Å) and Os(3)–Os(4) (2.954(3) Å) edges; these positions are consistent with the ¹H NMR data.

¹ Spectroscopic data for **1**, **2** and **3**. **1**: IR (ν , (CO), cm⁻¹, CH_2Cl_2) 2081(m), 2038(vs), 2028(s), 1997(w), 1981(w). ¹H NMR (δ , CD_2Cl_2) 5.99(s), -13.75(s, br). Mass spectrum, m/z 1280 (obs.) 1280 (calc. based on ¹⁹⁰Os and ¹⁰¹Ru). **2**: IR (ν , (CO), cm⁻¹, CH_2Cl_2) 2073(m), 2037(s), 2020(vs), 1976(w), 1968(w). ¹H NMR (δ , CD_2Cl_2) 5.98(s), 3.59(d, $J_{\text{PH}} = 12.2$ Hz), -17.77(d, $J_{\text{PH}} = 11.9$ Hz), -18.61(d, $J_{\text{PH}} = 13.4$ Hz). Mass spectrum, m/z 1404 (obs.) 1402 (calc. based on ¹⁹⁰Os and ¹⁰¹Ru). **3**: IR (ν , (CO), cm⁻¹, CH_2Cl_2) 2080(w), 2053(m), 2029(vs), 2012(m), 1978(w), 1955(w). ¹H NMR (δ , CD_2Cl_2) 6.55(m), 5.35(m), 5.13(dd), 4.20(d), 4.07(d), 3.72(d, $J_{\text{PH}} = 12.5$ Hz), -9.0(d, $J_{\text{PH}} = 22$ Hz), -20.92(s), -21.47(s). Mass spectrum, m/z 1404 (obs.) 1402 (calc. based on ¹⁹⁰Os and ¹⁰¹Ru).

² Crystal data for $\text{Os}_4\text{Ru}(\mu\text{-H})_3(\text{CO})_{12}(\mu_3\text{-}\eta^6\text{-C}_6\text{H}_5)\text{P}(\text{OMe})_3$ **3**: $\text{C}_{21}\text{H}_{17}\text{O}_{15}\text{Os}_4\text{PRu}$, $M = 1402.19$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.464(4)$, $b = 11.536(6)$, $c = 15.612(6)$ Å, $\alpha = 100.80(3)$, $\beta = 101.38(3)$, $\gamma = 107.76(3)^\circ$, $V = 1534.4(12)$ Å³, $T = 290(2)$ K, $Z = 2$, $D_c = 3.04$ Mg m⁻³, $F(000) = 1252$, Mo K_α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo } K_\alpha) = 17.10$ mm⁻¹, crystal dimensions $0.10 \times 0.12 \times 0.42$ mm³, 3527 independent absorption corrected reflections ($R_{\text{int}} = 0.0175$), $2\theta_{\text{max}} = 43.0^\circ$. The structure was solved by direct methods (SHELXL-PLUS, Program Version 4.0, Siemens Analytical X-Ray Instruments, Madison, WI, 1990) and Fourier difference techniques, refined by full-matrix least squares, based on F^2 , (Os, Ru, P and carbonyl O anisotropic, phosphite C and O atoms disordered over two sites and refined with partial occupancies common displacement parameters, arene H-atoms in idealised positions) (SHELXL-93, G.M. Sheldrick, Program for crystal structure refinement, University of Göttingen, 1993) to $R_1 = 0.089$ for 2348 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.258$ for all data, G.o.f. = 1.068, $w^{-1} = [\sigma^2 F^2 + (0.1375P)^2 + 101.86P]/3$ where $P = [0 \text{ or } F_o^2 + 2F_c^2]/3$. Atomic coordinates, displacement parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. This information may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.



Scheme 1. The synthesis and reaction chemistry of $\text{Os}_4\text{Ru}(\mu\text{-H})_2(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)_1$.

The bonding of the C(1) atom of the arene ring in **3** to the Os(2)–Os(3) edge may be considered as a three-centre two-electron bond, and this carbon donates one electron. Since the arene remains η^6 -coordinated to the

Ru(1) atom, overall this ligand must act as a seven electron donor, and as the additional hydride, lost from the ring, also acts as a one electron donor, the overall count for this cluster is 76 electrons. The observed spiked-tetrahedral core is consistent with this count, and may be viewed as derived from the structure proposed for **2** by the breaking of an Os–Ru edge and the transfer of a carbonyl ligand to the Ru atom.

The coordination mode of the arene ring is unusual, but a related mode of coordination has been observed for the $\text{O}(\text{C}_6\text{H}_3)\text{OMe}$ ligand in the raft cluster $\text{Ru}_6\text{H}_3(\mu\text{-O}:\mu\text{-C}:\eta^6\text{-OC}_6\text{H}_3\text{OMe-4})(\text{CO})_{16}(\text{AuPPh}_3)$ [15] and for the C_6H_4 ring in the mixed metal cluster $\text{Ru}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-AsMe}_2)\text{Cr}(\text{CO})_3(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_3)$ [16]. It is interesting to note that in these systems and in **3** C–H bond cleavage is a favoured process, and presumably stabilises the cluster. There are now a number of examples of C–H activation of arene rings coordinated to ruthenium or osmium clusters which lead to the formation of M_2C three-centre two-electron bonds (for recent examples see Ref. [17]), the novelty of the arene interaction in **3** is that the arene ring also remains η^6 -bound to the single ruthenium centre.

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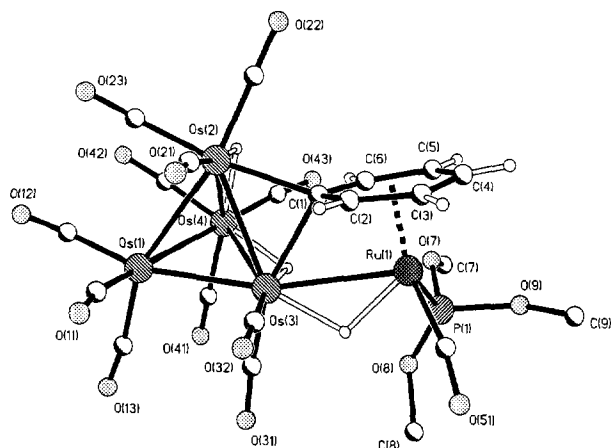


Fig. 1. The molecular structure of $\text{Os}_4\text{Ru}(\mu\text{-H})_3(\text{CO})_{12}(\mu_3\text{-}\eta^6\text{-C}_6\text{H}_5)\text{P}(\text{OMe})_3$ **3** showing the atom numbering scheme; only one component of the disordered phosphite is shown. Selected bond lengths (Å) and angles (deg) include: Os(1)–Os(2), 2.847(3); Os(1)–Os(3), 2.751(3); Os(1)–Os(4), 2.800(3); Os(2)–Os(3), 2.808(3); Os(2)–Os(4), 2.969(3); Os(3)–Os(4), 2.954(3); Os(3)–Ru(1), 2.990(5); Ru(1)–P(1), 2.223(14); Os(2)–C(1), 2.24(6); Os(3)–C(1), 2.24(6); Ru(1)–centroid(C_6H_5), 1.787; C(1)–C(2), 1.49(7); C(1)–C(6), 1.44(7); C(2)–C(3), 1.42(7); C(3)–C(4), 1.47(7); C(4)–C(5), 1.38(6); C(5)–C(6), 1.44(7); Os(2)–C(1)–Os(3), 78(2); P(1)–Ru(1)–Os(3), 100.8(6).

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