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Note

Reaction of the heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ with toluene

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Abstract

The heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**4**) reacts with refluxing toluene to form the clusters $Ru_2Os_3(\mu\text{-}H)_2(CO)_{16}$ (**5**) $RuOs_3(CO)_9(\mu\text{-}CO)_2(\eta^6\text{-}C_6H_5Me)$ (**6**) and $Ru_2Os_3(CO)_{12}(\mu\text{-}CO)(\eta^6\text{-}C_6H_5Me)$ (**7**). Cluster **5** exists as a mixture of five isomers. The interrelationship among the clusters has also been investigated.

Keywords: Heterometallic complexes; Ruthenium; Osmium; Isomers; Toluene

1. Introduction

Heteronuclear clusters in which the two metals are from the same triad provide an opportunity to investigate any subtle synergistic effects that may be present in such juxtaposition of two similar metals. It also allows comparison of the relative reactivity of the two metals which are expected to have very similar chemical behaviour. Towards this end, we had earlier developed a high-yield synthesis of the hetero group 8 tetranuclear cluster $Os_3Ru(\mu\text{-}H)_2(CO)_{13}$ (**4**) via a synthetic route depicted in Scheme 1, and investigated its reactivity with group 15 ligands [1]. Other work on this cluster was on its synthesis and structure [2], and its employment as a catalyst precursor supported on alumina for a number of catalytic reactions including alkene isomerisation and hydrogenation [3], and CO hydrogenation [4]. In the course of our investigations into its reactivity, we have had recourse to the use of aromatic solvents such as toluene. We found that **4** reacted quite readily with toluene to form novel cluster species. Our investigations on this are reported here.

2. Results and discussion

When **4** was refluxed for 12 h in toluene, the colour of the solution changed from orange to brown. Besides unreacted **4**, TLC separation afforded **3** (probably a decomposition product of **4**), and two novel clusters, viz., $RuOs_3(CO)_9(\mu\text{-}CO)_2(\eta^6\text{-}C_6H_5Me)$ (**6**) and $Ru_2Os_3(CO)_{12}(\mu\text{-}CO)(\eta^6\text{-}C_6H_5Me)$ (**7**) in 29% and 35% yields (calculated with respect to consumed **4**), respectively. Shortening the reaction time afforded **6** (20% yield) but no **7**, and another cluster $Ru_2Os_3(\mu\text{-}H)_2(CO)_{16}$ (**5**). All three clusters **5**–**7** have been characterised completely, including by single crystal X-ray structural analyses; the ORTEP plots showing their molecular structure, together with selected bond parameters, are given in Figs. 1–3, respectively.

Cluster **5** was also obtained in trace amounts from the synthesis of cluster **4**. Attempts at a high yield synthesis by reacting **4** with excess **2** under both ambient and elevated temperatures were unsuccessful. Similarly, the reaction of **4** with **1** in refluxing hexane also failed to produce the desired product.

Cluster **5** is formally a 74-valence electron cluster, consistent with the observed edge-bridged tetrahedral metal core [5]. The structural parameters are similar to those of its known homonuclear analogue, $Os_5(\mu\text{-}H)_2(CO)_{16}$ (**5a**) [6]. Other reported dihydrido-ruthenium or osmium carbonyl cluster complexes with an edge-bridged tetrahedral metal framework are $H_2Os_4Rh(CO)_{13}(\eta^5\text{-}C_5R_5)$ (R = H, Me) [7], and $H_2RuOs_4(CO)_{13}(\eta^6\text{-}C_6H_6)$ [8], which contain organic ligands as well as hydride and carbonyl groups. The two hydride ligands in **5** bridge the elongated Os(1)–Ru(5) and Os(2)–Ru(5) edges. The structure possessed

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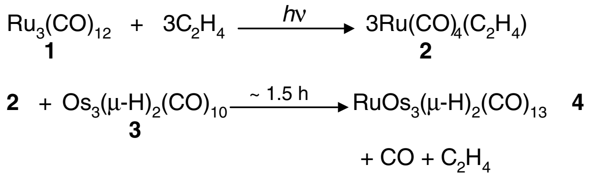

Scheme 1.

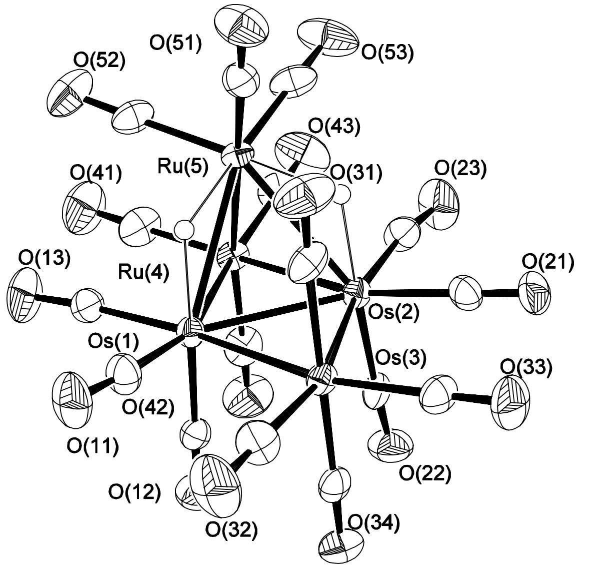

Fig. 1. ORTEP diagram (50% probability thermal ellipsoids) of the main isomer, and selected lengths (Å), for **5**. Os(1)–Os(2) = 2.7909(4); Os(1)–Os(3) = 2.8839(5); Os(1)–Ru(4) = 2.8410(6); Os(1)–Ru(5) = 2.9475(6); Os(2)–Os(3) = 2.8904(5); Os(2)–Ru(4) = 2.8375(6); Os(2)–Ru(5) = 2.9581(6); Ru(4)–Ru(5) = 2.7674(7).

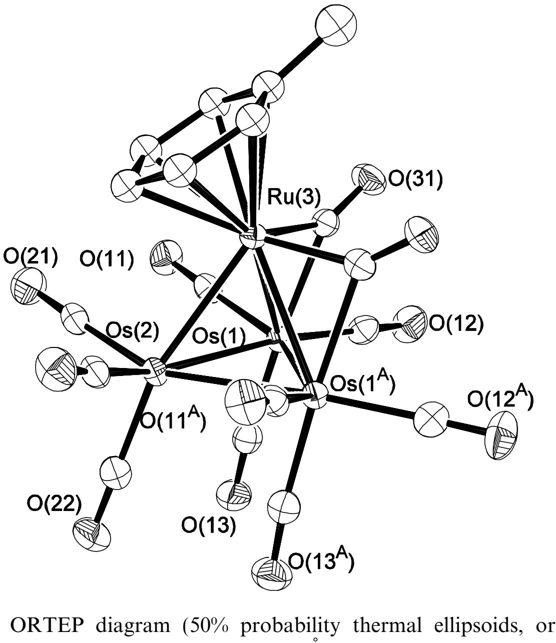

Fig. 2. ORTEP diagram (50% probability thermal ellipsoids, organic hydrogens omitted) and selected lengths (Å) and angles (°) for **6**. Only one orientation of the disordered toluene is shown. Os(1)–Os(2) = 2.7854(4); Os(1)–Ru(3) = 2.8165(7); Os(1)–Os(1A) = 2.9411(5); Os(2)–Ru(3) = 2.7748(8); Os(2)–Os(1A) = 2.7854(4); Os(1)–C(31) = 2.229(7); Ru(3)–C(31) = 1.964(8); Os(1)–C(31)–Ru(3) = 84.1(3).

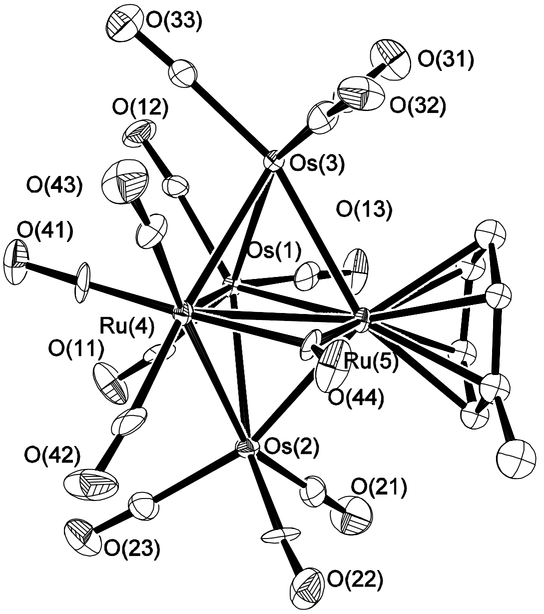

Fig. 3. ORTEP diagram (50% probability thermal ellipsoids, organic hydrogens omitted) of the main isomer, and selected lengths (Å) and angles (°), for **7**. Os(1)–Os(2) = 2.7219(8); Os(1)–Os(3) = 2.7262(8); Os(1)–Ru(4) = 2.7676(11); Os(1)–Ru(5) = 2.7687(13); Os(2)–Ru(5) = 2.7557(13); Os(2)–Ru(4) = 2.8052(11); Os(3)–Ru(5) = 2.7504(13); Os(3)–Ru(4) = 2.7753(11); Ru(4)–Ru(5) = 2.7943(16); Ru(4)–C(44) = 2.179(14); Ru(5)–C(44) = 1.998(15) and Ru(5)–C(44)–Ru(4) = 83.9(5).

approximate mirror symmetry, with the mirror plane passing through Os(3), Ru(4) and Ru(5) and bisecting the Os(1)–Os(2) vector. There was also disorder of the metal framework over three sites, M(3), M(4) and M(5), with osmium occupancies refined to 0.69, 0.14 and 0.17 respectively.

Unlike **5a**, which was reported to exhibit a singlet ^{1}H resonance at −20.55 ppm, assignable to two equivalent edge-bridging hydrides, the ^{1}H NMR spectrum of **5** exhibited five sets of signals having varying intensities. There are three singlet resonances at δ −18.72 (H_C), −19.03 (H_E) and −19.25 (H_F), and two sets of doublet resonances at δ −17.92 (H_A) and −18.99 (H_D), and at −18.16 (H_B) and −19.32 (H_G). These are ascribable to the presence of isomers. We have assumed that these isomers differ only in the positions of the hydride ligands. Based on previous observations that the chemical shift for a metal hydride bridging an Os–Os edge would lie in a higher field than that bridging an Os–Ru edge [9], the tentative structures and ^{1}H NMR assignments are as given in Fig. 4. The coupling giving rise to the doublets assigned to isomers IV and V have been confirmed by selective decoupling, and the relatively large coupling constants suggest that the hydrides share a common metal vertex and are *trans* relative to each other [10]. The isomeric distribution from NMR integration is 0.50:0.15:0.08:0.14:0.14 for I:II:III:IV:V, respectively. This corresponds to a ratio of 0.62:0.28:0.07 for the heavy atom core represented by I/IV, II/V and III, respectively, which quite closely mirrors the solid-state disorder.