Journal of Organometallic Chemistry, 330 (1987) C5–C11
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

PREPARATION AND CHARACTERISATION OF SOME MIXED CLUSTERS OF BISMUTH WITH OSMIUM AND RUTHENIUM; CRYSTAL AND MOLECULAR STRUCTURES OF $Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$, $Os_4(CO)_{12}(\mu_4\text{-}Bi)_2$, $Ru_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$, AND $Ru_4(CO)_{12}(\mu_4\text{-}Bi)_2$ *

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(Received January 5th, 1987)

Summary

Reaction of $NaBiO_3$ with $Os_3(CO)_{12}$ and a number of higher nuclearity osmium clusters affords a variety of bismuth-containing products, including $Os_3H_3(CO)_9Bi$ (**1**), $Os_3(CO)_9Bi_2$ (**2**), and $Os_4(CO)_{12}Bi_2$ (**3**). Under similar conditions, $Ru_3(CO)_{12}$ affords only low yields of $Ru_3H_3(CO)_9Bi$ (**5**), but better yields of $Ru_3H_3(CO)_9Bi$ (**5**), $Ru_3(CO)_9Bi_2$ (**6**), $Ru_4(CO)_{12}Bi_2$ (**7**), and $Ru_5H(CO)_{18}Bi$ (**8**), are obtained by reaction of $Bi(NO_3)_3 \cdot 5H_2O$ with the $[Ru_3H(CO)_{11}]^-$ anion. The structures of **1**, **3**, **5**, and **7** have been established by X-ray diffraction; **1** and **5** are isostructural with the known iron analogue, while the metal frameworks in **3** and **7** display different isomeric forms of the M_4Bi_2 octahedron.

The chemistry of transition metal clusters containing main group elements is a rapidly developing area [1]. The introduction of the main group metals into the cluster framework enhances the polarity of the bonding within the core, and leads to a reaction chemistry different from that observed for homometal systems. Furthermore, the heavier metals from Groups 13, 14, and 15 may be incorporated into cluster frameworks as ‘bare’ atoms, without ligands coordinated to them, and, therefore, do not exert the same steric constraints as would the incorporation of additional transition metal atoms with their associated ligands.

Transition metal clusters containing bismuth atoms are of particular interest because of the relevance of these systems to be mixed bismuth-transition metal oxide catalysts [2]. Recently, Whitmire has carried out an elegant series of studies on mixed bismuth-iron carbonyl clusters [3–9], using $NaBiO_3$ as the source of bismuth.

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* Dedicated to Professor L. Sacconi in recognition of his outstanding contribution to organometallic chemistry.

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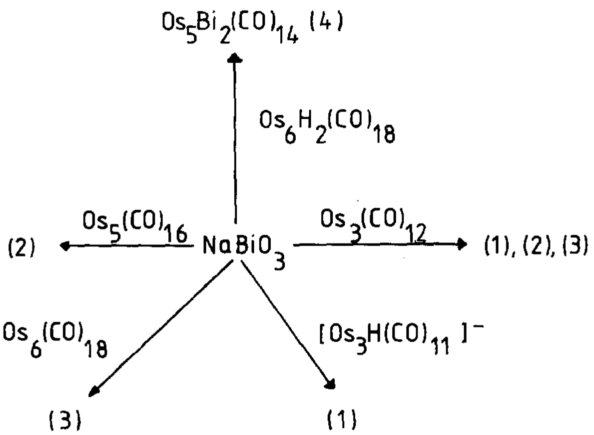
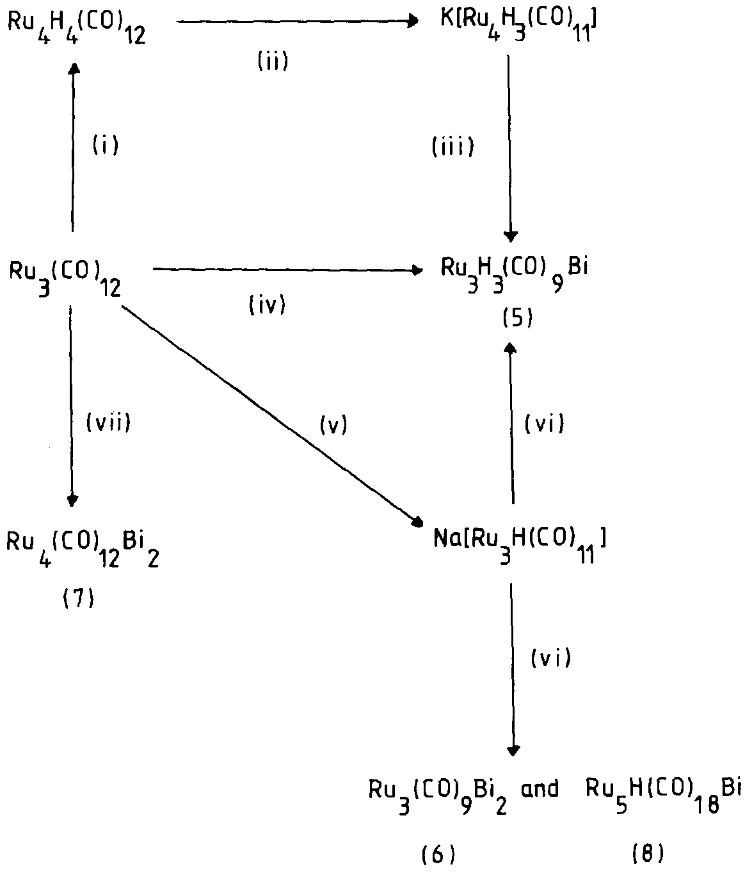


SCHEME 1. Synthesis of the osmium complexes.



SCHEME 2. Synthesis of the ruthenium complexes. (i) octane, 120°C with H_2 bubbling; (ii) 0.1 *M* KOH/MeOH, 55°C for 0.5 h; (iii) $Bi(NO_3)_3 \cdot 5H_2O$ in MeOH, room temp., 0.5 h; (iv) either $NaBiO_3$ or $Bi(NO_3)_3 \cdot 5H_2O$ followed by HCl(g); (v) $NaBH_4$/THF; (vi) 0.6 $Bi(NO_3)_3 \cdot 5H_2O$; (vii) (a) 2 $Bi(NO_3)_3 \cdot 5H_2O$ in KOH/MeOH, room temperature, 2 h, (b) treatment on silica.

TABLE 1

SPECTROSCOPIC DATA FOR THE COMPLEXES

Complex	IR	M^+	^{1}H NMR (ppm)	Analysis (Found (calcd.) (%))	
				C	H
1	2099vw, 2070vs, 2014vs, 2004w,sh	1040	−19.9	9.93 (10.03)	0.21 (0.29)
2	2127w, 2086m, 2067m, 2054m 2033vs, 1978vs	1246		8.96 (8.87)	
3	2053m, 2033vs, 2017vs, 1981m	1522		9.50 (9.47)	
4	2087m, 2048vs, 2034s	1770		9.55 (9.50)	
5	2099vw, 2070vs, 2026s, 2014m 1987vw, 1978vw	769	−17.73	14.00 (14.04)	0.37 (0.39)
6	2036s, 1990m	975		10.95 (11.08)	
7	2045s, 2002m	1160		12.45 (12.40)	
8	2119vw, 2086m, 2081m, 2053s, 2041mw, 2024w 2015vw, 1999mw, 1987mw	1222	−14.84	17.75 (17.69)	– (0.08)

That work revealed the interesting electronic and steric effects caused by the introduction of large main group heteroatom into a transition metal cluster, and prompted us to investigate the chemistry of related mixed bismuth–osmium and bismuth–ruthenium systems. We outline here the synthesis and structures of a variety of mixed cluster systems derived from the interaction of $NaBiO_3$ and related compounds with osmium and ruthenium binary carbonyls and carbonyl anions.

The reaction of $NaBiO_3$ with $Os_3(CO)_{12}$ in methanol affords a mixture of products from which $Os_3H_3(CO)_9Bi$ (**1**), $Os_3(CO)_9Bi_2$ (**2**), and $Os_4(CO)_{12}Bi_2$ (**3**) may be separated in low yields (5–10%) by thin layer chromatography (Scheme 1). Complex **1** may be prepared from a similar reaction starting from the salt $[N(PPh_3)_2][Os_3H(CO)_{11}]$, and complexes **2** and **3** are produced by the reaction of $NaBiO_3$ with $Os_5(CO)_{16}$ and $Os_6(CO)_{18}$, respectively. However, in the case of the hydrido cluster, $Os_6H_2(CO)_{18}$, reaction with $NaBiO_3$ affords a pentaosmium derivative, $Os_5(CO)_{14}Bi_2$ (**4**), in low yield.

Similar reactions of $NaBiO_3$ with $Ru_3(CO)_{12}$ lead only to the isolation of $Ru_3H_3(CO)_9Bi$ (**5**) in 2–10% yield. However, if the complex $Bi(NO_3)_3 \cdot 5H_2O$ is employed instead of $NaBiO_3$ in reactions with the ruthenium anion, $[Ru_3H(CO)_{11}]^-$, higher yields of the mixed bismuth-ruthenium clusters $Ru_3H_3(CO)_9Bi$ (**5**), $Ru_3(CO)_9Bi_2$ (**6**), $Ru_4(CO)_{12}Bi_2$ (**7**), and $Ru_5H(CO)_{18}Bi$ (**8**), are obtained (Scheme 2).

All the complexes **1–8** have been characterised on the basis of mass spectroscopic, IR and micro-analytical data, and, where appropriate, ^{1}H NMR data (Table 1). For complexes **1**, **3**, **5**, and **7** the characterisation has been confirmed and the solid state structure established by single-crystal X-ray diffraction studies.

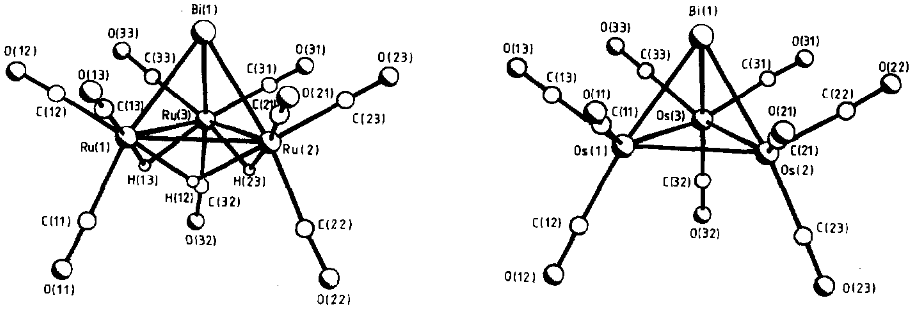


Fig. 1. The molecular structures of $Ru_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$ (**5**) and $Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$ (**1**). Selected bond parameters for **5**: Bi(1)–Ru(1), 2.756(1); Bi(1)–Ru(2), 2.755(1); Bi(1)–Ru(3), 2.763(1); Ru(1)–Ru(2), 2.972(1); Ru(1)–Ru(3), 2.973(1); Ru(2)–Ru(3), 2.962(1); Ru(1)–H(12), 1.72(7); Ru(1)–H(13), 1.77(8); Ru(2)–H(12), 1.80(8); Ru(2)–H(23), 1.79(7); Ru(3)–H(13), 1.88(8); Ru(3)–H(23), 1.77(6) Å; Ru(2)–Bi(1)–Ru(1), 65.3(1); Ru(3)–Bi(1)–Ru(1), 65.2(1); Ru(3)–Bi(1)–Ru(2), 64.9(1); Ru(2)–H(12)–Ru(1), 115(4); Ru(3)–H(13)–Ru(1), 109(5); Ru(3)–H(23)–Ru(2), 113(3)°. Selected bond parameters for **1**: Bi(1)–Os(1), 2.800(2); Bi(1)–Os(2), 2.807(1); Bi(1)–Os(3), 2.799(2); Os(1)–Os(2), 2.971(1); Os(1)–Os(3), 2.983(2); Os(2)–Os(3), 2.984(2) Å; Os(2)–Bi(1)–Os(1), 64.0(1); Os(3)–Bi(1)–Os(1), 64.4(1); Os(3)–Bi(1)–Os(2), 64.3(1)°.

Complexes $Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$ (**1**) and $Ru_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$ (**5**) are isostructural[*] with the known iron analogue [8]. The structures are illustrated in Fig. 1, which includes some important bond parameters. In both clusters the transition metal atoms define a slightly distorted equilateral triangle with the Bi atom sitting above this plane (2.21 Å for **1** and 2.16 Å for **5**), symmetrically coordinated to all three metal atoms, to give a distorted tetrahedral cluster core. In the ruthenium complex **5** the bridging hydrides were directly located, and lie ca. 0.87 Å on the opposite side of the Ru_3 triangle to the capping Bi atom. From the carbonyl ligand

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[*] (1) $C_9H_3BiO_9Os_3$, $M = 1034.69$, triclinic, space group $P\bar{1}$ (No. 2), a 8.230(6), b 9.273(4), c 12.409(8) Å, α 88.36(5), β 71.84(6), γ 69.20(4)°, V 837.6 Å^3, D_c 4.10 g cm^{-3}, $Z = 2$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 331.64 cm^{-1}, $F(000)$ 898.3252. Intensities measured ($5 < 2\theta < 50°$) on a Stoe–Siemens four circle diffractometer. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by full matrix least squares to $R = 0.074$ and $R_w = 0.074$ for 2376 observed reflections [$F > 6\sigma(F)$]. (5) $C_9H_3BiO_9Ru_3$, $M = 767.30$, triclinic, space group $P\bar{1}$ (No. 2), a 8.253(5), b 9.300(4), c 12.568(6) Å, α 88.03(5), β 71.73(5), γ 68.96(4)°, V 851.6 Å^3, D_c 2.99 g cm^{-3}, $Z = 2$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 128.45 cm^{-1}, $F(000)$ 688. 3213 intensities measured ($5 < 2\theta < 50°$) on a Stoe-Siemens four circle diffractometer. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full matrix least squares to $R = 0.033$ and $R_w = 0.031$ for 2791 observed reflections [$F > 4\sigma(F)$]. (3) $C_{12}Bi_2O_{12}Os_4$, $M = 1514.88$, monoclinic, space group $C\,2/c$ (No. 15), a 13.461(3), b 12.648(2), c 12.380(2) Å, β 94.77(1)°, V 2100.5 Å^3, D_c 4.79 g cm^{-3}, $Z = 4$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 408.12 cm^{-1}, $F(000)$ 2600. 4038 Intensities measured ($5 < 2\theta < 50°$) on a Stoe–Siemens four cicle diffractometer. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full matrix least squares to $R = 0.047$ and $R_w = 0.050$ for 1579 observed reflections [$F > 4\sigma(F)$]. (7) $C_{12}Bi_2O_{12}Ru_4$, $M = 1158.36$, monoclinic, space group $P2_1/n$ (alt. setting $P2_1/c$, No. 14), a 11.515(3), b 7.420(3), c 12.602(3) Å, β 91.12(2)°, V 1076.5 Å^3, D_c 3.57 g cm^{-3}, $Z = 2$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 189.59 cm^{-1}, $F(000)$ 1020. 4304 intensities measured ($5 < 2\theta < 50°$) on a Stoe-Siemens four circle diffractometer. Structure solved by a combination of Patterson and Fourier difference techniques, and refined by full matrix least squares to $R = 0.038$ and $R_w = 0.037$ for 1552 observed reflections [$F > 4\sigma(F)$].

distribution in the osmium complex **1** it is assumed that the hydrides occupy similar positions.

In the structure of the iron complex, $Fe_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$ [8], the hydride bridged Fe–Fe distances (average 2.774(2) Å) are significantly longer than the unbridged Fe–Fe distances in $[Fe_3(CO)_{10}Bi]^-$ (average 2.642(7) Å) [3] but comparable with those in $Fe_3(CO)_9(\mu_3\text{-}Bi)_2$ (average 2.745(11) Å) [4]. In complexes **1** and **5**, the average Os–Os and Ru–Ru distances of 2.979(4) and 2.969(4) Å, respectively, are significantly longer than those in the binary carbonyls $Os_3(CO)_{12}$ (average 2.877(3) Å) [10] and $Ru_3(CO)_{12}$ (average 2.854(4) Å) [11], and longer than the corresponding distances in some $Ru_3(\mu\text{-}H)_3$ systems capped by a small bridgehead atom [12]. It is probable, therefore, that the large capping atom exerts a metal–metal edge-lengthening effect within the transition metal cluster triangle in addition to that exerted by the bridging hydrides, but it is difficult to separate the two effects in this case. In this context, it is noteworthy that there is little change in the M–Bi–M angle along the series; the angle averages 63.3° for Fe, 65.1° for Ru, and 64.2° for Os.

The intermolecular Bi...Bi contacts, at 4.715(1) Å in **1** and 4.846(1) Å, in **5** are slightly longer than that, 4.690(1) Å, observed for $Fe_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}Bi)$ [8].

The molecular structures of $Os_4(CO)_{12}(\mu_4\text{-}Bi)_2$ (**3**) and $Ru_4(CO)_{12}(\mu_4\text{-}Bi)_2$ (**7**) are shown in Figs. 2 and 3, respectively, together with selected bond parameters. In

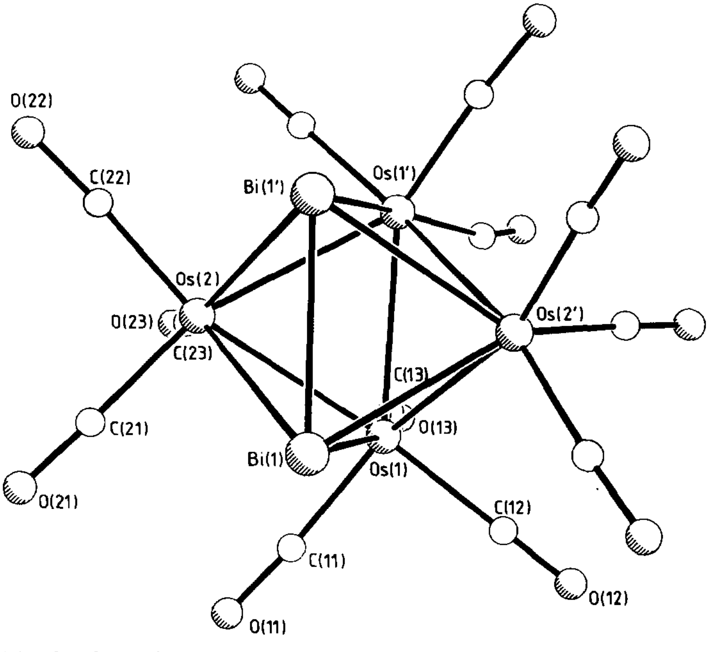

Fig. 2. The molecular structure of $Os_4(CO)_{12}(\mu_4\text{-}Bi)_2$ (3). Selected bond parameters: Bi(1)–Os(1), 2.803(1); Os(2)–Os(1), 2.864(1); Os(1)–Os(1'), 2.878(2); Bi(1)–Os(2), 2.923(1); Os(1')–Os(2), 2.897(1); Os(2')–Bi(1), 2.859(1); Bi(1')–Bi(1), 3.017(2) Å; Bi(1)–Os(1)–Os(2), 62.1(1); Bi(1)–Os(2)–Os(1), 57.9(1); Os(2)–Bi(1)–Os(1), 60.0(1); Bi(1)–Os(1)–Os(1'), 91.4(1); Bi(1)–Os(1)–Os(2'), 60.2(1); Os(2)–Os(1)–Os(1'), 60.6(1); Os(2)–Os(1)–Os(2'), 90.6(1); Os(1)–Os(2)–Os(1'), 59.9(1); Os(1)–Os(2)–Bi(1'), 90.5(1); Bi(1)–Os(2)–Os(1'), 88.6(1); Bi(1)–Os(2)–Bi(1'), 62.9(1); Os(1)–Bi(1)–Os(2'), 61.5(1); Os(1)–Bi(1)–Bi(1'), 88.5(1); Os(2)–Bi(1)–Os(2'), 90.2(1); Os(2)–Bi(1)–Bi(1'), 57.5(1)°.

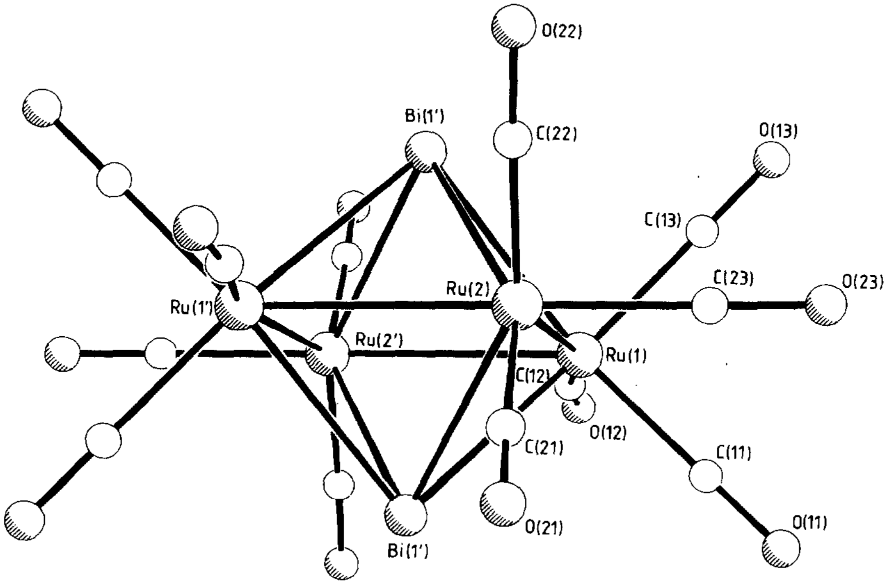

Fig. 3. The molecular structure of $Ru_4(CO)_{12}(\mu_4\text{-Bi})_2$ (7). Selected bond parameters: Bi(1)–Ru(1), 2.834(1); Ru(2)–Ru(1), 2.904(1); Bi(1')–Ru(1), 2.839(1); Ru(2')–Ru(1), 2.910(1); Bi(1)–Ru(2), 2.833(1); Bi(1')–Ru(2), 2.839(1); Ru(1')–Ru(2), 2.910(1) Å; Ru(2)–Bi(1)–Ru(1), 61.6(1); Ru(2)–Ru(1)–Bi(1), 59.2(1); Ru(1)–Bi(1)–Ru(1'), 92.9(1); Ru(1)–Ru(2)–Ru(1'), 90.0(1); Ru(1)–Ru(2)–Bi(1), 59.2(1); Ru(2)–Bi(1)–Ru(2'), 92.9(1); Ru(2)–Ru(1)–Ru(2'), 90.0(1); Ru(1)–Bi(1)–Ru(2'), 61.7(1); Bi(1)–Ru(1)–Bi(1'), 87.1(1); Bi(1)–Ru(1)–Ru(2'), 59.2(1); Ru(2)–Ru(1)–Bi(1'), 59.3(1); Ru(2)–Ru(1)–Ru(2'), 90.0(1); Bi(1)–Ru(2)–Bi(1'), 87.1(1); Bi(1)–Ru(2)–Ru(1'), 59.3(1); Ru(1)–Ru(2)–Bi(1'), 59.2(1)°.

terms of the Wade approach to cluster bonding [13], if each Bi atom donates three electrons to framework bonding, there are a total of seven electron pairs available, consistent with the observed octahedral core geometry. However, in **3** the molecule lies on a crystallographic two-fold axis which bisects the Bi(1)–Bi(1') and Os(1)–Os(1') edges, and the two Bi atoms occupy adjacent octahedral sites. In the structure of **7** the molecule sits on a crystallographic centre of symmetry, and consequently the two Bi atoms occupy opposite octahedral sites. Thus, the two structures display different isomeric forms of the core geometry, and it is interesting to note that there is no spectroscopic evidence for the existence of the alternative isomers in the synthesis of either the osmium or ruthenium clusters, under the conditions used.

The Os atoms in the structure of **3** define a 'butterfly' arrangement with the Os–Os 'hinge' distance intermediate in length between the two unique Os–Os 'hinge'–'wingtip' distances. The Bi–Bi distance is shorter than the shortest Bi–Bi interactions of 3.140(2)–3.168(2) Å in the $[Fe_4(CO)_{13}Bi_4]^{2-}$ anion [7], and is indicative of a direct bonding interaction.

In the structure of **7** the four Ru atoms define a slightly distorted square, with the Ru–Ru distances significantly longer than the average value of 2.854(4) Å found in $Ru_3(CO)_{12}$ [11]. This edge-lengthening is consistent with the presence of the two large μ_4-capping Bi atoms, which lie 1.95 Å above and below the Ru_4 plane. A similar edge-lengthening effect is observed in the case of $Fe_3(CO)_9(\mu_3\text{-}Bi)_2$ [4]. The Ru–Bi distances in **7** are ca. 0.08 Å longer than the related distances in **5**, which is consistent with the Bi atoms' interacting with four Ru atoms rather than three.

The IR spectrum obtained for $Ru_3(CO)_9(\mu_3\text{-}Bi)_2$ (**6**) is similar to that of $Fe_3(CO)_9(\mu_3\text{-}Bi)_2$ [4], and it is reasonable to assume that these complexes are isostructural, and have structures similar to that of $Fe_3(CO)_9(\mu_3\text{-}As)_2$ [14]. However, the IR spectrum of $Os_3(CO)_9Bi_2$ (**2**) exhibits a different band pattern, and indicate a different structure, at least in solution.

The structures of all the complexes described above are based on closed polyhedral core geometries. In terms of electron counting rules, from the formulae of $Os_5(CO)_{14}Bi_2$ (**4**) and $Ru_5H(CO)_{18}Bi$ (**8**) based on spectroscopic data, these clusters are likely to adopt more open structures.

The work presented in this paper illustrates the facinating structural diversity of mixed bismuth–osmium and bismuth–ruthenium clusters, and emphasises some fundamental differences between the osmium and ruthenium systems.

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation.