

Synthesis and Characterisation of the Hexanuclear Bimetallic Cluster, $[\{\text{Ru}_2(\text{CO})_8\}(\mu_4\text{-Bi})\{(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}\}]$

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The bimetallic cluster $[\text{Ru}_5\text{H}(\text{CO})_{18}(\mu_4\text{-Bi})]$ has been prepared from the reaction of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$ in methanol, and shown by X-ray analysis to be a spiro-cluster containing a ' $\text{Ru}_2(\text{CO})_8$ ' fragment connected to a ' $\text{Ru}_3\text{H}(\text{CO})_{10}$ ' fragment by a μ_4 -bismuth atom with a pseudo-tetrahedral co-ordination geometry.

There is much current interest in the synthesis and reactions of mixed transition metal-bismuth clusters. The elegant work of Whitmire *et al.*,¹ Schmidbaur *et al.*,^{2a} and Errington,^{2b} with iron precursors, has produced a range of novel clusters with 'bare' bismuth atoms as an integral part of the metal framework. The bismuth atoms in these molecules exhibit a number of bonding modes and can formally donate either three or five of their valence electrons to the metal framework bonding within the cluster. In continuing our investigations into the mixed clusters of bismuth and ruthenium or osmium,^{3,4} we report the synthesis and characterisation of $[\text{Ru}_5\text{H}(\text{CO})_{18}(\mu_4\text{-Bi})]$ (**1**) which is, to our knowledge, the first pentaruthenium cluster with a naked *p*-block element included in the cluster core.

Complex (**1**) was obtained in 10–20% yield from the slow addition of a methanolic suspension of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.5 equiv.) to a stirred methanolic solution of $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]^\ddagger$ at -78°C , followed by warming to room temperature. Complex (**1**) was separated from the other reaction products, $[\text{Ru}_3\text{H}_3(\text{CO})_9(\mu_3\text{-Bi})]$ (5% yield),⁴ $[\text{Ru}_3(\text{CO})_{12}]$, and an uncharacterised anionic product, by t.l.c. on silica. The compound was characterised by i.r., ^1H n.m.r., and mass spectroscopy, and by C, H elemental analysis.‡ The i.r. spectrum exhibits twelve bands in the carbonyl stretching region which suggest an asymmetric arrangement of CO

ligands. The ^1H n.m.r. signal at $\delta -14.84$ is indicative of a hydride ligand bridging a Ru–Ru edge and the elemental analysis is consistent with the proposed formulation. In the mass spectrum a molecular ion envelope centred at about m/z 1221 corresponds to the ion $[\text{Ru}_5(\text{CO})_{18}\text{Bi}]^+$.

Dark red, slightly air sensitive needle shaped crystals of (**1**) were obtained from CH_2Cl_2 /hexane solution at -30°C and an X-ray analysis was undertaken.§ The crystal structure shows that the asymmetric unit contains two independent but structurally similar cluster molecules together with a disordered solvent CH_2Cl_2 molecule. The molecular structure of one molecule is shown in Figure 1 together with selected bond parameters. The metal core geometry can best be described as a ' $\text{Ru}_2(\text{CO})_8$ ' fragment connected to a ' $\text{Ru}_3\text{H}(\text{CO})_{10}$ ' fragment by a pseudo-tetrahedral μ_4 -bismuth atom resulting in a spiro-cluster. The Ru–Ru edge lengths fall into two categories with two long Ru(1)–Ru(2) and Ru(3)–Ru(4) edges which are bridged by the bismuth atom, and which are similar in length to Bi bridged Ru–Ru edges in other clusters,^{3,4} and the shorter non-bridged Ru(3)–Ru(4) and Ru(4)–Ru(5) which are similar

§ *Crystal Data:* (**1**), $\text{C}_{18}\text{HBiO}_{18}\text{Ru}_5$, $M = 1240.75$, triclinic, space group *PT* (No. 2), $a = 11.378(2)$, $b = 16.286(8)$, $c = 17.391(4)$ Å, $\alpha = 73.52(3)$, $\beta = 89.71(3)$, $\gamma = 80.22(3)^\circ$. $U = 3042$ Å³, $Z = 4$, $D_c = 2.71$ g cm⁻³, $F(000) = 2248$, λ (Mo- K_α) = 0.71069 Å, μ (Mo- K_α) = 81.89 cm⁻¹. 8434 Reflections collected on a Stoe-Siemens four-circle diffractometer in the range $5 < 2\theta < 45^\circ$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked full-matrix least squares (Bi, Ru, and O anisotropic) to $R = 0.0615$, $R_w = 0.0575$ $\{w = 2.3818/[\sigma^2(F) + 0.0005F^2]\}$, for 4801 unique observed reflections $[F > 5\sigma(F)]$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See notice to Authors, Issue No. 1.

† The reaction does not proceed along the same pathway if the $(\text{Me}_2\text{P})_2\text{N}^+$ salt of $[\text{HRu}_3(\text{CO})_{11}]^-$ is used in place of the sodium salt (the products from this reaction have not been identified).

‡ I.r. $\nu(\text{CO})$ (hexane): 2119vw, 2085.5ms, 2080.5ms, 2053vs, 2041m, 2037w,sh, 2031vw, 2024w, 2015vw, 2002w,sh, 1999m, 1987w cm⁻¹; ^1H n.m.r. δ (CDCl_3) -14.84 (s); M^+ m/z 1221.

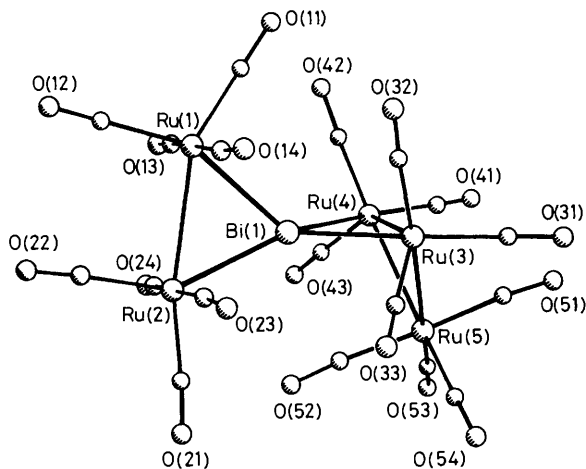


Figure 1. The molecular structure of $[\{\text{Ru}_2(\text{CO})_8\}(\mu_4\text{-Bi})(\text{H-Ru}_3(\text{CO})_{10})]$ (**1**). Molecule 1 [Molecule 2]. Bond distances: Bi(1)–Ru(1) 2.751(2) [2.759(2)], Bi(1)–Ru(2) 2.729(2) [2.729(3)], Bi(1)–Ru(3) 2.698(2) [2.706(3)], Bi(1)–Ru(4) 2.710(2) [2.704(2)], Bi(1)–Ru(5) 2.959(3) [2.963(3)], Ru(3)–Ru(4) 2.959(3) [2.947(3)], Ru(3)–Ru(5) 2.873(4) [2.871(3)], Ru(4)–Ru(5) 2.842(3) [2.856(3)] Å. Bond angles: Ru(1)–Bi(1)–Ru(2) 65.4(1) [65.3(1)], Ru(3)–Bi(1)–Ru(4) 66.3(1) [66.0(1)], Ru(1)–Bi(1)–Ru(3) 126.1(1) [125.5(1)], Ru(1)–Bi(1)–Ru(4) 127.3(1) [125.6(1)], Ru(2)–Bi(1)–Ru(3) 135.9(1) [137.9(1)], Ru(2)–Bi(1)–Ru(4) 146.8(1) [146.8(1)], Ru(1)–Ru(2)–Bi(1) 57.7(1) [57.8(1)], Ru(2)–Ru(1)–Bi(1) 57.0(1) [56.8(1)], Ru(3)–Ru(4)–Bi(1) 56.6(1) [57.0(1)], Ru(4)–Ru(3)–Bi(1) 57.0(1) [56.9(1)], Ru(3)–Ru(4)–Ru(5) 59.3 [59.3(1)], Ru(4)–Ru(3)–Ru(5) 58.3(1) [58.8(1)], Ru(3)–Ru(5)–Ru(4) 62.3(1) [61.9(1)], Bi(1)–Ru(3)–Ru(5) 85.5(1) [87.5(1)], Bi(1)–Ru(4)–Ru(5) 85.9(1) [87.8(1)]°. Dihedral angle between planes Bi(1)–Ru(3)–Ru(4) and Ru(3)–Ru(4)–Ru(5) = 016.8 [019.5]°.

in length to those found in $[\text{Ru}_3(\text{CO})_{12}]$.⁵ The Ru–Bi distances are also of two types. The average distance from the Bi to the Ru_2 fragment [2.740(2) Å] is slightly longer than that to the Ru_3 fragment [2.704(2) Å]. Although the hydride ligand was not located directly from the X-ray study, potential energy calculations⁶ suggest that it is bridging the Ru(3)–Ru(4) edge.

The Ru–Bi–Ru angles in (**1**) are significantly distorted from the idealised tetrahedral value of 109.5°. The angle observed between two bonded Ru atoms is *ca.* 66°, while the angles between non-bonded Ru atoms vary between *ca.* 125 and *ca.* 147°. These distortions suggest that the ‘soft’ nature of the Bi atom, as expected, does not impose strong directional constraints on the bonding in the cluster.

In terms of electron counting rules, the co-ordination geometry of the Bi atom in (**1**) suggests the donation of its five electrons to the cluster core. Therefore, the cluster is an 82 electron species and the ‘effective atomic number’ (EAN) rule (including the Bi as a core element requiring 8 electrons) predicts the presence of eight metal–metal contacts (Ru–Ru or Bi–Ru) as observed.

Although there have been previous reports of clusters in which the five electrons of a Bi atom are involved in bonding to four other metal atoms,^{1a–c} to our knowledge, this is the first case in which the bismuth atom is the link between two closed, and otherwise unconnected Bi–M₂ triangles to give a spiro-type cluster. The Bi atom is in an isoelectronic environment to the antimony atoms in the closely related cluster,

$[\text{Fe}_2(\text{CO})_8(\mu_4\text{-Sb})_2][\text{Fe}_2(\text{CO})_6]^7$ and also to the main group atoms (E) in other spiro-clusters $[\{\text{Fe}_2(\text{CO})_8\}_2\text{Ge}]^8$ and $[\{\text{Co}_2(\text{CO})_7\}_2\text{E}]$ (E = Ge,⁹ Si¹⁰).

Formally, the bismuth atom can be seen to act as a two electron donor to the $\text{Ru}_2(\text{CO})_8$ fragment to give what is, to our knowledge, the first structurally characterised example of an $\text{Ru}_2(\text{CO})_8(\mu\text{-ligand})$ compound which is isoelectronic to the known but not structurally characterised complex, $\text{Ru}_2(\text{CO})_9$.¹¹ It also acts as a three electron donor to the Ru_3 fragment which is similar to the behaviour of OR or NO groups in $[\text{Ru}_3\text{H}(\text{CO})_{10}\text{X}]$ [X = NO,¹² OR (R = Me, Et, n-Prⁿ, Buⁿ)¹³]. Although quantum chemical calculations would be more informative, this formalised interpretation of the bonding in terms of two centre, two electron bonds is consistent with the Bi–Ru bond distance data where the distances to the Ru_3 unit are less than to the Ru_2 unit.

We are grateful to the ‘Cambridge Commonwealth Trust,’ the O.R.S. award scheme, and to Trinity College, Cambridge for financial support for A. J. W.

Received, 19th November 1987; Com. 1688

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