Note

Two gold–ruthenium clusters derived from Ru₃(μ-H)₃(μ₃-CBr)(CO)₉

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Abstract

The reaction between AuMe(PPh₃) and Ru₃(μ-H)₃(μ₃-CBr)(CO)₉ (**1**) affords the novel heptanuclear cluster Au₄Ru₃(μ₃-CMe)(Br)(CO)₉(PPh₃)₃ (**2**), containing an Au/Ru₃/Au trigonal pyramidal cluster face-capped by two Au(PPh₃) groups and a CMe ligand, together with Au₂Ru₃(μ-H)(μ₃-CMe)(CO)₉(PPh₃)₂ (**3**), formed by isolobal replacement of two of the three μ-H atoms in **1** by Au(PPh₃) groups. The latter co-crystallises with the analogous μ₃-CH complex, as also shown spectroscopically.
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1. Introduction

The first transition metal–gold clusters were described in 1964 [1], but it was not until the previously acknowledged electronic relationship (isolobality) between an Au(PR₃) fragment and the proton was commented upon in 1981 [2] that significant development occurred in this area [3–6]. Of the main methods used to replace cluster-bound H atoms by Au(PR₃) fragments, deprotonation of the hydrides (with NaOMe, KOBuᵗ or LiBu) followed by addition of AuCl(PR₃) or [Au(PR₃)]⁺ [3], reactions with [{Au(PPh₃)}₃O]⁺ [7], and reactions of AuMe(PPh₃) [8,9] are the most useful. The latter have included the syntheses of AuRu₃(μ-CO-Me)(CO)₁₀(PPh₃) from Ru(μ-H)(μ-COMe)(CO)₁₀, and of AuₙRu₃(μ-H)₃₋ₙ(μ₃-COMe)(CO)₉(PPh₃)ₙ (*n* = 1 to 3) from Ru₃(μ-H)₃(μ₃-COMe)(CO)₉, and the structural characterisation of all but the complex with *n* = 2 [9].

We have used the bromocarbyne cluster Ru₃(μ-H)₃(μ₃-CBr)(CO)₉ (**1**) [10] as a source of complexes containing carbon chains end-capped by the Ru₃(μ-H)₃(CO)₉ cluster, such as {Cp(PPh₃)₂Ru}C≡CC≡C-CC{Ru₃(μ-H)₃(CO)₉} [11]. In the course of developing this chemistry, we sought to replace the cluster-bonded H atoms by different groups, including the isolobal Au(PPh₃) group. While attempted deprotonation with base resulted in low yields of several compounds, presently uncharacterised, and the gold–oxonium cation gave intractable mixtures of products, the reaction between **1** and AuMe(PPh₃) afforded the two products described below.

2. Results and discussion

After stirring a 3/1 mixture of AuMe(PPh₃) and **1** in THF for 19 h, purification by preparative t.l.c. (silica gel, acetone–hexane 3:7) afforded two novel complexes, together with a small amount of recovered **1** (Scheme 1). Orange crystals characterised as Au₄Ru₃(μ₃-CMe)(Br)(CO)₉(PPh₃)₃ (**2**) by a single-crystal X-ray study were obtained from a slow moving band (*R*_f 0.37) in 36% yield, while orange Au₂Ru₃(μ-H)(μ₃-CMe)(CO)₉(PPh₃)₂ (**3**) was found in the fastest band (*R*_f 0.55).

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Fig. 1. Plot of a molecule of $Au_4Ru_3(\mu_3\text{-}CMe)(Br)(CO)_9(PPh_3)_3$ (**2**). Bond distances: Au(1)–Au(2) 2.7992(7), Au(2)–Au(3) 2.8327(5), Au(2)–Au(4) 2.7851(7), Au(1)–Ru(1) 2.848(1), Au(1)–Ru(2) 2.8261(9), Au(2)–Ru(1) 2.9824(7), Au(2)–Ru(2) 2.8900(8), Au(2)–Ru(3) 2.9540(9), Au(3)–Ru(2) 2.8438(8), Au(3)–Ru(3) 2.7957(9), Au(4)–Ru(1) 2.765(1), Au(4)–Ru(3) 2.7846(8), Ru(1)–Ru(2) 2.939(1), Ru(1)–Ru(3) 2.980(1), Ru(2)–Ru(3) 2.937(1), Au(1)–P(1) 2.300(3), Au(2)–P(2) 2.308(2), Au(3)–P(3) 2.296(2), Au(4)–Br 2.457(1), Ru(1)–C(1) 2.075(9), Ru(2)–C(1) 2.089(10), Ru(3)–C(1) 2.097(9), C(1)–C(2) 1.49(1) Å.

Scheme 1.

A molecule of **2** is shown in Fig. 1, while significant bond distances are collected in the caption thereto. The seven-atom Au_4Ru_3 cluster is formed from a central $AuRu_3$ tetrahedron, the four faces of which are capped by two Au(PPh$_3$) groups, an AuBr group and a CMe ligand. There are two equally short Ru–Ru separations [Ru(2)–Ru(1,3) 2.939, 2.937(1) Å] and one longer [Ru(1)–Ru(3) 2.980(1) Å], the latter being opposite the AuBr group [Au(4)–Br 2.457(1) Å]. The nine Au–Ru distances range between 2.765(1) and 2.9824(7) Å, the shortest involving the AuBr group. The longest involve the Au in the central tetrahedron [Au(2)–Ru(1,3) 2.9824(7), 2.9540(9) Å]. This atom is also i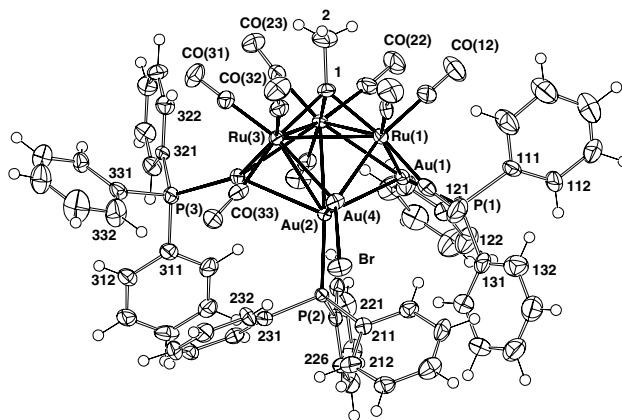nvolved in the only homonuclear Au–Au interactions, of which two are short [Au(2)–Au(4) 2.7851(7), Au(1)–Au(2) 2.7992(7) Å] and one long [Au(2)–Au(3) 2.8327(5) Å]. The M–M connectivities of the core atoms vary between three [Au(1,3,4)], five [Ru(1,2,3)] and six [Au(2)]. Attachment of the CMe group [Ru–C 2.075–2.097(9) Å] is similar to that found in **3** [2.070–2.079(6) Å] and $Ru_3(\mu\text{-}H)(\mu_3\text{-}CMe)(CO)_9$ [2.078(12)–2.086(10) Å] [12]. Atom Au(4) is attached to a bromine [Au(4)–Br 2.457(1) Å] presumably originating from the bromocarbyne ligand in **1**. In turn, this is now attached to a methyl group, i.e., bromine-methyl exchange has occurred.

In accord with the solid-state structure, the IR spectrum contains only terminal v(CO) bands, the simple pattern of five bands reflecting the high symmetry of the molecule. The ES mass spectrum contains $[M + PPh_3]^+$ and $[M - Br]^+$ ions.

Of interest are the changes which have occurred during the formation of **2**. As anticipated, the cluster-bonded H atoms in **1** have indeed been replaced by three Au(PPh$_3$) group which, in common with other Au_3Ru_3 complexes described on previous occasions, have also entered into gold–gold bonding. A fourth gold atom caps the Au(2)–Ru(1)–Ru(3) face, the whole cluster being a tri-capped trigonal pyramid; the four Au atoms take up a T-shaped array. We are unaware of any previous example of an Au_4Ru_3 cluster of this type, although a similar Au_3Ru_4 core is present in $Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3$ [8,13,14]. While unusual, larger clusters containing Au–X (X = Cl, I) bonds have been encountered before, for example, in $Au_{12}Cl_4$-$(PPh_3)_8$ [15] and $Au_9PdI_3(PPh_3)_7$ [16].

Complex **3** was identified as $Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}CMe)$-$(CO)_9(PPh_3)_2$ and results from replacement of two of the cluster-bonded H atoms in **1** by $Au(PPh_3)$ groups accompanied by Br/Me exchange at the carbyne carbon. The structure (Fig. 2) comprises an Ru_3 cluster face-capped by the CMe ligand [Ru–C(1) 2.070–2.079(6) Å] and edge-bridged by the two $Au(PPh_3)$ groups [Ru–Au 2.7174(4)–2.7737(5) Å] and one H atom, which was located during the refinement [Ru(1,3)–H(0) 1.67, 1.68 Å (est.)].

Although the two gold atoms are in conventional bridging positions, the Au···Au distance [3.0419(3) Å] is comparable with many similar distances in systems where "aurophilic" interactions are postulated, although considerably longer than the Au–Au separations found in **2**. Here the evidence for any such interactions is equivocal – the $PAuRu_2$ array about Au(1) is closely planar (angle sum: 359.5°), while that about Au(2) is more clearly pyramidally distorted (angle sum: 355.7°). The Ru_3/Ru_2Au interplanar dihedral angles are 74.14(4)° and 57.89(4)°, respectively, the latter perhaps being the more nearly "normal" of the two. No evidence was found for the formation of either $AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}CMe)(CO)_9(PPh_3)$ or $Au_3Ru_3(\mu_3\text{-}CMe)(CO)_9(PPh_3)_3$ in the reaction.

Refinement of the CMe group gave site occupancy 0.5, suggesting that the $\mu_3\text{-}CMe$ (**3-Me**) complex co-crys-
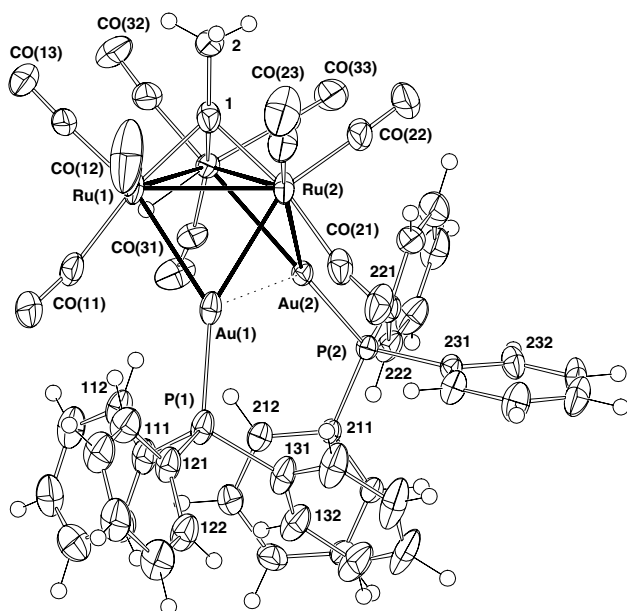

Fig. 2. Plot of a molecule of $Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}CMe)(CO)_9(PPh_3)_2$ (**3**). Bond distances: Au(1)–Au(2) 3.0419(3), Au(1)–Ru(1) 2.7560(5), Au(1)–Ru(2) 2.7174(4), Au(2)–Ru(2) 2.7440(5), Au(2)–Ru(3) 2.7737(5), Ru(1)–Ru(2) 2.8925(6), Ru(1)–Ru(3) 2.8605(6), Ru(2)–Ru(3) 2.8818(7), Au(1)–P(1) 2.301(1), Au(2)–P(2) 2.306(1), Ru(1)–C(1) 2.076(5), Ru(2)–C(1) 2.079(6), Ru(3)–C(1) 2.070(6), C(1)–C(2) 1.45(1), Ru(1)–H(0) 1.67, Ru(3)–H(0) 1.68 Å (both est.). Dihedral angles: Ru(1)–Ru(2)–Ru(3)/Ru(1)–Ru(2)–Au(1) 74.74(4), Ru(1)–Ru(2)–Ru(3)/Au(2)–Ru(2)–Ru(3) 57.89(4)°.

tallised with the analogous $\mu_3\text{-}CH$ complex (**3-H**). This was confirmed by the ^1H NMR spectrum, which contains two Ru–H triplets (ratio 46/54) together with a singlet at δ 11.59 (relative intensity 0.46) assigned to the CH group, and peaks in the ES-MS differing by 14 mass units, with similar ratios. The two complexes proved to be inseparable by chromatography.

In conclusion, we have described an unusual course found for the reaction of $AuMe(PPh_3)$ with $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CBr)(CO)_9$ whereby both a novel Au_4Ru_3 cluster and an Au_2Ru_3 complex are formed by reactions which also result in the exchange of Br and Me groups between C and Au centres.

3. Experimental

3.1. Reaction between $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CBr)(CO)_9$ and $AuMe(PPh_3)$

A mixture of $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CBr)(CO)_9$ (48 mg, 0.074 mmol) and $AuMe(PPh_3)$ (106 mg, 0.223 mmol) was stirred in THF (10 ml) at r.t. for 19 h. After removal of solvent, preparative t.l.c. (silica gel, acetone/hexane 3:7) separated two major bands. Band 1 (orange, R_f 0.37) contained $Au_4Ru_3(\mu_3\text{-}CMe)(Br)(CO)_9(PPh_3)_3$ (**2**) (46.1 mg, 36%). Anal. Found: C, 34.60; H, 2.20. $C_{65}H_{48}Au_4BrO_9P_3Ru_3\cdot0.5CH_2Cl_2$ calc.: C, 34.51; H, 2.17%. M (without solvent), 2238. IR (CH_2Cl_2): $\nu(CO)$ 2054m, 2050 (sh), 2025vs, 1970m (br), 1945 (sh) cm^{-1}. ^1H NMR (CDCl$_3$): δ 3.22, 3.94 ($2\times s$, 3H, Me), 5.30 (s, 1H, CH$_2$Cl$_2$), 6.98–7.66 (m, 45H, Ph). ES-MS (positive ion, MeOH, m/z): 2500, $[M + PPh_3]^+$; 2158, $[M - Br]^+$. Band 2 (yellow, R_f 0.55) contained $Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}CMe)(CO)_9(PPh_3)_2\cdot Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_9(PPh_3)_2$ (**3**) (12.7 mg, 11%), obtained as yellow-orange crystals (CH$_2$Cl$_2$/MeOH). Anal. Found: C, 37.60; H, 2.31. $C_{46.5}H_{33}Au_2O_9P_2Ru_3$ calc.: C, 37.38; H, 2.21%. M, 1503 (CMe), 1489 (CH). IR (CH$_2$Cl$_2$): $\nu(CO)$ 2062m, 2037vs, 2020vs, 1980m, 1973m, 1930w cm^{-1}. ^1H NMR (CDCl$_3$): δ −19.26 [t, $J(HP)$ 0.4 Hz, Ru–H, **3-H**], −18.71 [t, $J(HP)$ 0.4 Hz, **3-Me**] (46/54), 4.45 (s, ca 1.62H, Me), 7.20–7.34 (m, 30H, Ph), 11.59 (s, ca 0.46H, CH). ES-MS (positive ion, MeOH, m/z): 1962, $[\textbf{3-Me} + Au(PPh_3)]^+$; 1948, $[\textbf{3-H} + Au(PPh_3)]^+$; (52/48); 1526, $[\textbf{3-Me} + Na]^+$; 1512, $[\textbf{3-H} + Na]^+$ (53/47); (negative ion, NaOMe + MeOH, m/z): 1534, $[\textbf{3-Me} + OMe]^-$; 1520, $[\textbf{3-H} + OMe]^-$ (53/47). Recovered $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CBr)(CO)_9$ (1 mg, 2%) was in a band with R_f 0.96.

3.2. Crystal structure determinations

Full spheres of diffraction data to the indicated limits were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} quoted) after "empirical"/multiscan

absorption correction (proprietary software), N_0 with $F > 4\,\sigma(F)$ being used in the full-matrix least squares refinement. All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ are given [weights: $(\sigma^2(F) + 0.0006 F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [17]. Pertinent results are given in the figure (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and captions.

3.3. Crystal data and refinement details

(**2**). $Au_4Ru_3(\mu_3\text{-}CMe)(Br)(CO)_9(PPh_3)_3 \cdot 0.5CH_2Cl_2 \equiv C_{65}H_{48}Au_4BrO_9P_3Ru_3 \cdot 0.5CH_2Cl_2$, $M = 2279.5$. Monoclinic, space group $C2/c$, $a = 46.594(6)$, $b = 13.975(2)$, $c = 24.256(3)$ Å, $\beta = 118.736(2)°$, $V = 13,849$ Å^3, $Z = 8$. $D_c = 2.18_6$ g cm^{-3}, μ(Mo Kα) $= 9.8$ mm^{-1}, $T_{min/max} = 0.61$. Crystal size $0.12 \times 0.10 \times 0.06$ mm. $2\theta_{max} = 58°$. $N_{tot} = 65{,}262$, $N = 17{,}276$ ($R_{int} = 0.055$), $N_0 = 12{,}666$. $R = 0.044$, $R_w = 0.048$.

3. $Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}CMe_{0.5}H_{0.5})(CO)_9(PPh_3)_2 \equiv C_{46.5}H_{33}Au_2O_9P_2Ru_3$, $M = 1494.9$. Triclinic, space group $P\bar{1}$, $a = 10.7371(9)$, $b = 10.7644(9)$, $c = 21.783(2)$ Å, $\alpha = 98.014(2)°$, $\beta = 96.108(2)°$, $\gamma = 110.628(2)°$, $V = 2300$ Å^3, $Z = 2$. $D_c = 2.16_8$ g cm^{-3}, μ(Mo Kα) $= 7.4$ mm^{-1}, $T_{min/max} = 0.67$. Crystal size $0.12 \times 0.10 \times 0.07$ mm. $2\theta_{max} = 75°$. $N_{tot} = 46{,}542$, $N = 23{,}807$ ($R_{int} = 0.043$), $N_0 = 14{,}703$. $R = 0.045$, $R_w = 0.048$.

Variata Tentative assignment of the CMe groups in both structures was consistent with the chemistry, as also the hydrido group in **3**. In **2**, the solvent residue occupancy was constrained at 0.5 after trial refinement. However, in **3**, spectroscopic evidence coupled with a high displacement amplitude on the μ_3-CMe methyl group prompted refinement of its site occupancy. This diminished to ca 0.5, at which value it was constrained, superimposed on a μ_3-CH hydrogen.

4. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cam-

bridge Crystallographic Data Centre as CCDC 226009 (**2**), 226010 (**3**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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