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Preliminary communication

SYNTHESIS OF A μ_4-PPh MIXED METAL CLUSTER: THE X-RAY STRUCTURES OF $[Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-PPh})]$ AND $[Ru_3Au(\mu_2\text{-H})(CO)_9(PMe_2Ph)(\mu_3\text{-PPh})]$

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Summary

The synthesis of a (μ_4-PPh) and some related (μ_3-PPh) mixed metal clusters containing ruthenium is described together with the X-ray structures of $[Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-PPh})]$ and $[Ru_3Au(\mu_2\text{-H})(CO)_9(PMe_2Ph)(\mu_3\text{-PPh})]$.

Few transition metal clusters containing μ_4-PR ligands are known [1—3] and a synthetic route leading to the first mixed-metal complexes of this type has only recently been described [4]. We now report an alternative route which also appears to have some generality for the synthesis of μ_4-PR and μ_3-PR mixed-metal clusters, together with the X-ray structures of two such complexes, $[Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-PPh})]$ and $[Ru_3Au(\mu_2\text{-H})(CO)_9(PMePh_2)(\mu_3\text{-PPh}_3)]$. Thus the reaction of $[Ru_3(\mu_2\text{-H})_2(CO)_9(\mu_3\text{-PPh})]$ (1) [5] with excess methanolic KOH followed by addition of $[Rh(CO)_3(PEt_3)_2]BF_4$ gave a major red product (ca. 50% yield) and a minor dark-green product (ca. 5% yield). These were separated by TLC on silica (35% CH_2Cl_2/65% hexane) after evaporation of the reaction mixture to dryness and gave m/e values in their mass spectra of 913 and 1099, respectively. The major product was identified spectroscopically as $[Ru_3Rh(\mu_2\text{-H})(CO)_{10}(PEt_3)(\mu_3\text{-PPh})]$ (2). ν(CO) (CH_2Cl_2) 2085w, 2058m, 2027s, 2020s, 2004m, 1980m, 1867w(sh), 1850w(br); ^1H NMR (CD_2Cl_2, −70°C) δ 8.03 (m, 5H, Ph), 2.0—1.0 (m, 15H, Et), −23.67 (d of d of d ^2J(PH) 14 Hz, ^3J(PH) 5 Hz, ^2J(RhH) 14 Hz, 1H, RuH); ^{31}P NMR (^1H decoupled, $CDCl_2$, −30°C) δ (rel to $P(OMe)_3$ = 0) 78.6 (s, 1P, *P*Ph), −109.0 (d, ^1J(RhP) 128 Hz, 1P, *P*Et_3) and this data suggests the structure shown in Fig. 1.

The minor product may be formulated from its mass spectrum as

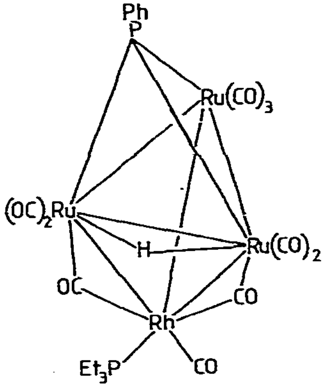

Fig. 1. Probable structure of $[Ru_3Rh(\mu_2\text{-H})(CO)_{10}(PEt_3)(\mu_3\text{-PPh})]$.

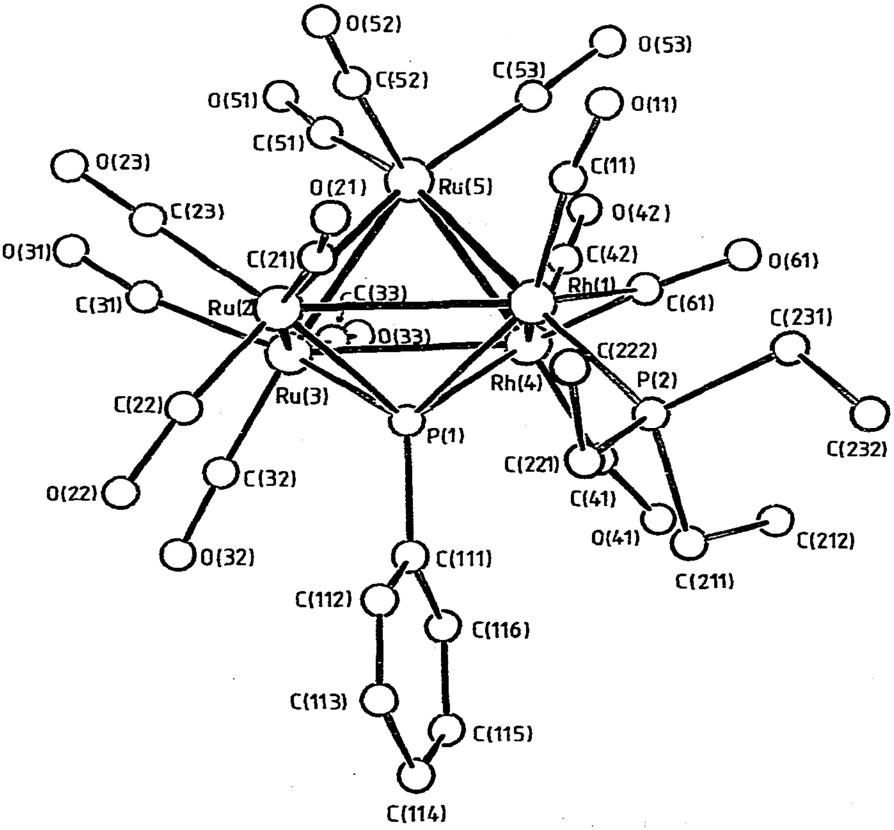

Fig. 2. Molecular structure of $[Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-PPh})]$ (3). Bond lengths: Rh(1)—Ru(2), 2.930(1); Rh(1)—Ru(5), 2.783(1); Ru(2)—Ru(3), 2.837(1); Ru(2)—Ru(5), 2.853(1); Ru(3)—Rh(4), 2.862(1); Ru(3)—Ru(5), 2.874(1); Rh(4)—Ru(5), 2.758(1); Rh(1)—Rh(4), 2.775(1); Rh(1)—P(1), 2.365(2); Rh(4)—P(1), 2.383(2); Ru(2)—P(1), 2.340(2); Ru(3)—P(1), 2.355(2); Rh(1)—P(2), 2.362(2) Å.

$[Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-PPh})]$ (3). ν(CO) (CH_2Cl_2) 2076m, 2045s, 2033s, 2025s, 2006m, 1993m, 1964w, 1838w(br); ^{1}H NMR (CD_2Cl_2, −70°C) δ 7.45 (m, 5H, Ph), 2.0—1.0 (m, 15H, Et). Dark green crystals suitable for an X-ray analysis were obtained by slow crystallisation from hexane at 0°C*.

The molecular structure of 3 is shown in Fig. 2 together with some important bond parameters. The five metal atoms define a square based pyramid with the μ_4-P atom of the PPh ligand lying 1.23 Å below the square base. This geometry has been observed in the structures of $[Os_5(CO)_{15}(\mu_4\text{-POMe})]$ [3] and $[Ru_5(CO)_{15}(\mu_4\text{-PR})]$ [4] (R = Ph, Et). The two Rh atoms occupy adjacent positions in the basal plane and are bridged by a carbonyl group. The phosphine ligand occupies an axial site on Rh(1).

The solution obtained by addition of methanolic KOH to (1) contains the anion $[Ru_3H(CO)_9(\mu_3\text{-PPh})]^-$ (4). ν(CO) (CH_2Cl_2) 2049m, 2017s, 1986s, 1966s, 1947m, 1905m, 1715w(br); ^{1}H NMR (CD_2Cl_2, −70°C) δ 7.90 (m, 5H,

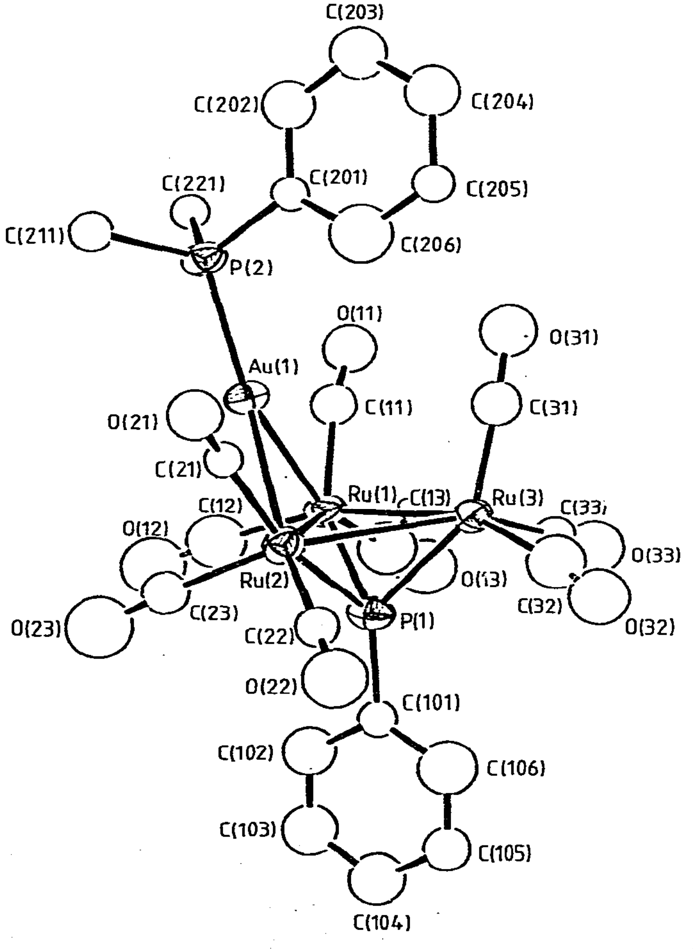

Fig. 3. Molecular structure of $[Ru_3Au(\mu_2\text{-H})(CO)_9(PMe_2Ph)(\mu_3\text{-PPh})]$ (5d). Bond lengths: Ru(1)—Ru(2), 3.002(5); Ru(1)—Ru(3), 2.972(5); Ru(2)—Ru(3), 2.869(5); Au(1)—Ru(1), 2.749(4); Au(1)—Ru(2), 2.763(4); Ru(1)—P(1), 2.347(12); Ru(2)—P(1), 2.258(12); Ru(3)—P(1), 2.279(11); Au(1)—P(2), 2.314(9) Å.

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*Crystal data for (3): $C_{25}H_{20}O_{13}P_2Rh_2Ru_3$, M = 1099.49, monoclinic, $C2/c$, a 20.257(5), b 9.679(3), c 34.726(5) Å, β 90.24(2)°, U 6 808.6 Å^3, Z = 8, D_c 2.145 g cm^{-3}, $F(000)$ = 4216, μ(Mo-K_α) 21.83 cm^{-1}, 4708 diffractometer data were used in structure solution and refinement to R = 0.034.

Ph), –16.69 (d, ^2J(PH) 15 Hz, RuH) and **1** is regenerated essentially quantitatively on reprotonation with dilute acids. This anion may be regarded as a phosphorus-stabilised analogue of $[Ru_3(\mu_2\text{-H})(CO)_{11}]^-$ [6], and its use provides a general route to mixed-metal clusters containing a triangular phosphorus-capped array of ruthenium atoms. Thus treatment with $[M(PEt_3)I]_4$ gives the complexes $[Ru_3MH(CO)_9(PEt_3)(\mu_3\text{-PPh})]$ (**5a**, M = Cu; **5b**, M = Ag), and with $[Au(PR_2R')_2]PF_6$ gives $[Ru_3AuH(CO)_9(PR_2R')(\mu_3\text{-PPh}_3)]$ (**5c**, R = R' = Et; **5d**, R = Me, R' = Ph). Other cationic metal complexes containing e.g. Ir and Pt also give mixed-metal products and these are under investigation. Orange crystals of **5d** suitable for an X-ray analysis were obtained by slow recrystallisation from hexane at 0°C*.

The structure of **5d** is illustrated in Fig. 3 which includes some important bond parameters. One edge of the Ru_3 triangle is bridged by an Au^I atom to give a "butterfly" metal framework with a dihedral angle of 73.8° between the Ru_3 and Ru_2Au planes. The Ru_3 triangle is also capped by the μ_3-P atom which lies 1.54 Å on the opposite side of it to the Au atom. The hydride ligand was not located directly but the distribution of the carbonyls indicates that it bridges the Ru(1)—Ru(3) edge. This is not the case in the related complex $[Os_3Au(\mu_2\text{-H})(CO)_{10}(PPh_3)]$ [7] where the hydride bridges the same edge as the $AuPPh_3$ group. However, in both complexes the $AuPR_3$ group acts as a one electron donor behaving in a similar manner to a hydride. The structures of **5a**, **5b** and **5c** are assumed to be analogous to that of **5d**.

The detailed mechanism of formation of **3** from **1** is not easy to establish. but, since **3** may also be obtained on treatment of **2** with base followed by addition of $[Rh(CO)_3(PEt_3)_2]^+$, it seems likely that successive removal of protons from **1** and addition of cationic Rh fragments is involved. In principle, therefore, it should be possible to prepare (μ_4-PPh) mixed-metal clusters containing three different metal atoms by the same route, and this possibility is being explored.

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*Crystal data for (5d): $C_{23}H_{17}AuO_9P_2Ru_3$, M = 999.51, monoclinic, $P2_1/c$, a 8.805(3), b 20.195(7), c 16.683(6) Å β 100.62(2)°, U 2 915.7 Å^3, Z = 4, D_c 2.276 g cm^{-3}, $F(000)$ = 1872, μ(Mo-K_α) 66.18 cm^{-1}. 1398 diffractometer data were used in structure solution and refinement to R = 0.067.