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Preliminary communication

The synthesis and structural characterization of the mixed-metal cluster compounds $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu, Ag, Au): X-ray crystal structures of $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu, Ag)

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Abstract

The novel mixed-metal cluster compounds $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu, Ag or Au) have been synthesized from $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]\cdot THF$. Single-crystal X-ray diffraction studies on the copper- and silver-ruthenium clusters reveal that they adopt metal core structures consisting of a Ru_4 tetrahedron with $M(PPh_3)$ (M = Cu or Ag) groups capping two Ru_3 faces, in marked contrast to the capped trigonal bipyramidal skeletal geometries exhibited by the very closely related species $[M_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ (M = Cu, Ag or Au), in which the two coinage metals are in close contact.

A very interesting feature of the chemistry of mixed-metal cluster compounds containing $M(PR_3)$ (M = Cu, Ag or Au; R = alkyl or aryl) fragments is the great variety of bonding modes displayed by the Group IB metal-phosphine groups and the large range of skeletal geometries exhibited by these species [1–5]. Herein we report the synthesis and structural characterization of the novel mixed-metal clusters $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (I, M = Cu; II, M = Ag; III, M = Au) and show that the formal replacement of two hydrido ligands in the closely related species $[M_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ (IV, M = Cu; V, M = Ag; VI, M = Au) [5] by a carbonyl group in I–III has a remarkable effect on the metal framework structures adopted by these clusters.

Treatment of a dichloromethane solution of the salt $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]\cdot$ THF [6] with two equivalents of the complex $[M(NCMe)_4]PF_6$ (M = Cu or Ag) at −30 °C, followed by the addition of two equivalents of PPh_3 affords the mixed-metal

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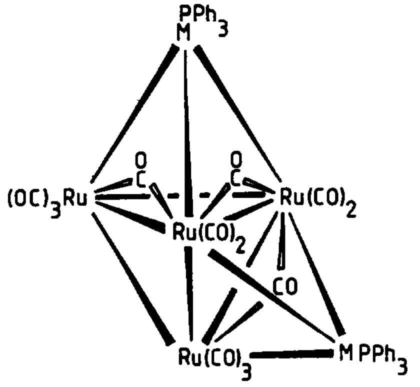
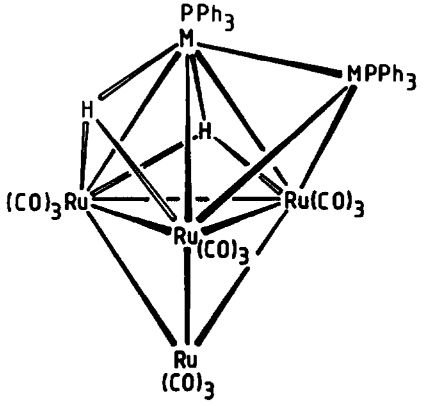
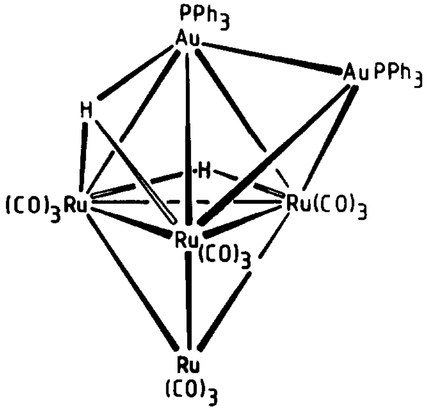


(I , M = Cu ;
II , M = Ag ;
III , M = Au)

cluster compounds I and II in ca. 35–40% yield. The analogous gold species, III, can



(IV , M = Cu ;
V , M = Ag)



(VI)

be obtained in ca. 70% yield by treating a dichloromethane solution of the salt $[N(PPh_3)_2]_2[Ru_4(CO)_{13}] \cdot THF$ with a dichloromethane solution containing two equivalents of the complex $[AuCl(PPh_3)]$ at −30 °C, in the presence of $TlPF_6$. The IR spectra [7 *] of I–III are closely similar, suggesting that these clusters all adopt the same metal core geometry and the band between 1800 and 1785 cm^{-1} observed for each cluster is diagnostic of bridging carbonyl groups in all three. At −90 °C, the $^{31}P\text{-}\{^1H\}$ NMR spectra of I–III [7 *] show marked differences to those of the analogous dihydrido clusters IV–VI [5], suggesting that I–III adopt different metal

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* Reference numbers with asterisks indicate notes in the list of references.

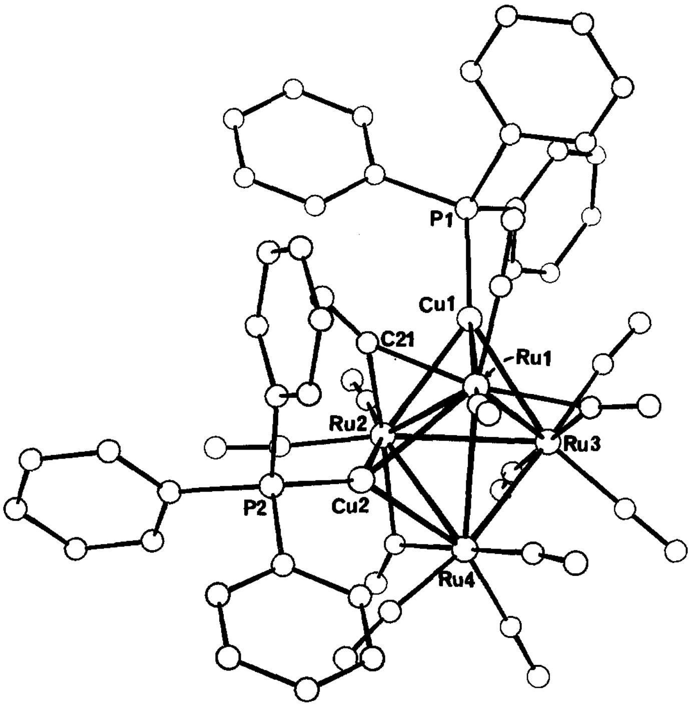

Fig. 1. Molecular structure of [$Cu_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2$] (I), which has virtual C_2 symmetry. Important dimensions: Ru(1)–Ru(2) 2.771(2); Ru(1)–Ru(3) 2.797(2); Ru(1)–Ru(4) 2.981(2); Ru(1)–Cu(1) 2.806(2); Ru(1)–Cu(2) 2.662(2); Ru(2)–Ru(3) 2.958(2); Ru(2)–Ru(4) 2.793(2); Ru(2)–Cu(1) 2.656(2); Ru(2)–Cu(2) 2.848(2); Ru(3)–Ru(4) 2.842; Ru(3)–Cu(1) 2.633(2); Ru(4)–Cu(2) 2.608(2); mean Cu–P 2.234(6); Ru–CO(terminal) 1.798(5)–1.891(3); Ru–CO(bridging) 2.031(4)–2.230(3) Å.

framework structures to those of IV–VI. Significantly, the complex second order splitting patterns reported in the $^{31}P\text{-}\{^1H\}$ NMR spectra of [$Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}$] ($n = 1$, 2 or 4) [8] and [$Ag_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)_2$] [9], due to $^{107,109}Ag\text{–}^{107,109}Ag$ couplings and $^{107,109}Ag\text{–}^{31}P$ couplings through two bonds, are not observed for II, implying that the two silver atoms are not in close contact in the latter cluster.

X-ray structural analyses * of I and II show that both cluster compounds adopt a capped trigonal bipyramidal skeletal geometry (Figs. 1 and 2, respectively) consisting of a tetrahedron of ruthenium atoms with two Ru_3 faces capped by $M(PPh_3)$ ($M = Cu$ or Ag) groups. The metal framework structures adopted by I–III are in marked contrast to those exhibited by the analogous dihydrido clusters IV–VI, in

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* Crystal data for I: $C_{49}H_{30}O_{13}P_2Ru_4Cu_2$, $M = 1419.08$, monoclinic, space group $P2_1/n$, a 22.110(4), b 17.247(3), c 14.407(3) Å, β 93.44(2)°, U 5483.94 $Å^3$, $F(000) = 2768$, $\mu(\text{Mo-}K_\alpha)$ 18.12 cm^{-1}, $Z = 4$, D_c 1.72 g cm^{-3}. Data were collected on a Philips PW1100 diffractometer in the θ-range 3–25°, $I/\sigma(I) > 3.0$; present R-factor 0.0659 for 4467 reflections. Crystal data for II: $C_{49}H_{30}O_{13}P_2Ru_4Ag_2$, $M = 1507.72$, triclinic, space group $P\bar{1}$, a 24.685(5), b 10.710(2), c 10.137(2) Å, α 102.03(2), β 96.20(2), γ 86.47(2)° U 2603.69 $Å^3$, $F(000) = 1456$, $\mu(\text{Mo-}K_\alpha) = 18.07$ cm^{-1}, $Z = 2$, D_c 1.93 g cm^{-3}. Data were collected on a Philips PW1100 diffractometer in the θ-range 3–25°, $I/\sigma(I) > 3.0$; present R-factor 0.0503 for 5065 reflections.

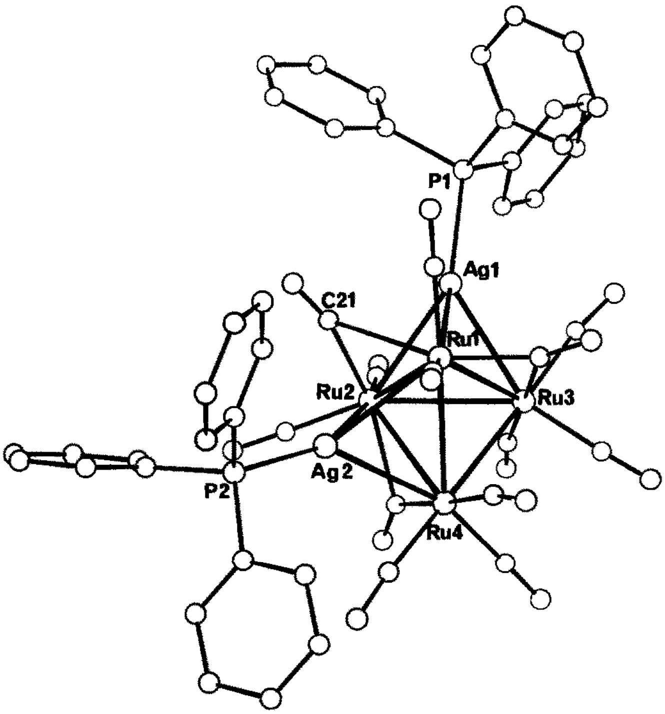

Fig. 2. Molecular structure of $[Ag_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (II). The distances for CO(21) are very asymmetric: Ru(1)–C(21) 2.589(3) and Ru(2)–C(21) 1.967(4) Å. Other important dimensions: Ru(1)–Ru(2) 2.797(1); Ru(1)–Ru(3) 2.853(2); Ru(1)–Ru(4) 2.997(1); Ru(1)–Ag(1) 2.977(1); Ru(1)–Ag(2) 2.838(1); Ru(2)–Ru(3) 3.074(1); Ru(2)–Ru(4) 2.866(1); Ru(2)–Ag(1) 2.861(1); Ru(2)–Ag(2) 2.905(1); Ru(3)–Ru(4) 2.849(1); Ru(3)–Ag(1) 2.806(1); Ru(4)–Ag(2) 2.872(2); mean Ag–P 2.418(3); Ru–CO(terminal) 1.799(3)–1.922(4); Ru–CO(bridging) 1.953(3)–2.589(3) Å.

which one face of a Ru_4 tetrahedron is capped by a $M(PPh_3)$ (M = Cu, Ag or Au) group and a MRu_2 face of the MRu_3 tetrahedron so formed is further capped by the second $M(PPh_3)$ unit, so that the two coinage metals are in close contact [5]. Thus, the formal replacement of a carbonyl group in I–III by two hydrido ligands in IV–VI causes a fundamental change in the positions that the Group IB metals adopt on the ruthenium tetrahedra of these clusters. This alteration in metal framework geometry adds to previous evidence, both experimental [1,2] and theoretical [10], that the energy differences between the various structural types are small in many cases for heteronuclear clusters containing $M(PR_3)$ groups. A similar change in coinage metal arrangement has been previously observed for two Cu_2Ru_6 clusters when two carbonyl groups are formally replaced by a carbido ligand. Whereas in $[Cu_2Ru_6(CO)_{18}(C_6H_5Me)_2]$, the $Cu(C_6H_5Me)$ units cap opposite faces of a Ru_6 octahedron [11], the two copper atoms are in close contact in $[Cu_2Ru_6C(CO)_{16}(NCMe)_2]$ [12].

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References and notes

1 For example, R.A. Brice, S.C. Pearse, I.D. Salter, and K. Henrick, J. Chem. Soc., Dalton Trans., (1986) 2181; and ref. cited therein.

2 For example, I.D. Salter, Adv. Dynamic Stereochem., 2 (1987) in press; K. Henrick, B.F.G. Johnson, J. Lewis, J. Mace, M. McPartlin, and J. Morris, J. Chem. Soc., Chem. Commun., (1985) 1617; S.R. Bunkhall, H.D. Holden, B.F.G. Johnson, J. Lewis, G.N. Pain, P.R. Raithby, and M.J. Taylor, ibid., (1984) 25.

3 For example, M.I. Bruce, M.L. Williams, J.M. Patrick, B.W. Skelton, and A.H. White, J. Chem. Soc., Dalton Trans., (1986) 2557; and ref. cited therein.

4 For example, P. Braunstein, J. Rose, A. Dedieu, Y. Dusausoy, J.-P. Mangeot, A. Tiripicchio, and M. Tiripicchio-Camellini, J. Chem. Soc., Dalton Trans., (1986) 225; and ref. cited therein.

5 M.J. Freeman, A.G. Orpen, and I.D. Salter, J. Chem. Soc., Dalton Trans., (1987) 379.

6 A.A. Bhattacharyya, C.C. Nagel, and S.G. Shore, Organometallics, 2 (1983) 1187.

7 Selected spectroscopic data. For compound I, ν_{max}(CO) at 2062m, 2016vs, 2002s, 1949m(br), and 1799w(br) cm^{-1} (CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ 7.27–7.58 (m, Ph); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2/CH_2Cl_2) at −90 °C, δ 3.6 ppm (s). For compound II, ν_{max}(CO) at 2060m, 2014vs, 1997s, 1951m(br), and 1787w(br) cm^{-1}. NMR: ^1H (CD_2Cl_2), δ 7.28–7.54 (m, Ph); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2/CH_2Cl_2) at −90 °C, δ 16.4 ppm (2×d, $^1J(^{109}AgP)$ 514, $^1J(^{107}AgP)$ 446 Hz). For compound III, ν_{max}(CO) at 2066m, 2023vs, 2006s, 1967m(br), and 1789w(br) cm^{-1}. NMR: ^1H (CD_2Cl_2) at −20 °C, δ 7.15–7.55 (m, Ph); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2/CH_2Cl_2) at −90 °C, δ 62.9 ppm (s).

8 S.S.D. Brown, I.J. Colquhoun, W. McFarlane, M. Murray, I.D. Salter, and V. Šik, J. Chem. Soc., Chem. Commun., (1986) 53.

9 S.S.D. Brown, S. Hudson, I.D. Salter, and M. McPartlin, J. Chem. Soc., Dalton Trans., (1987) in press.

10 D.M.P. Mingos, Polyhedron, 3 (1984) 1289.

11 G.B. Ansell, M.A. Modrick, and J.S. Bradley, Acta Cryst. C, 40 (1984) 365.

12 J.S. Bradley, R.L. Pruett, E. Hill, G.B. Ansell, M.E. Leonowicz, and M.A. Modrick, Organometallics, 1 (1982) 748.