Cluster Complex Metathesis: Synthesis, Structures, and Dynamic Behaviour of Bi- and Tri-metallic Hexanuclear Cluster Complexes $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (M = M' = Cu, Ag, or Au; M = Cu, M' = Ag or Au; M = Ag, M' = Au)

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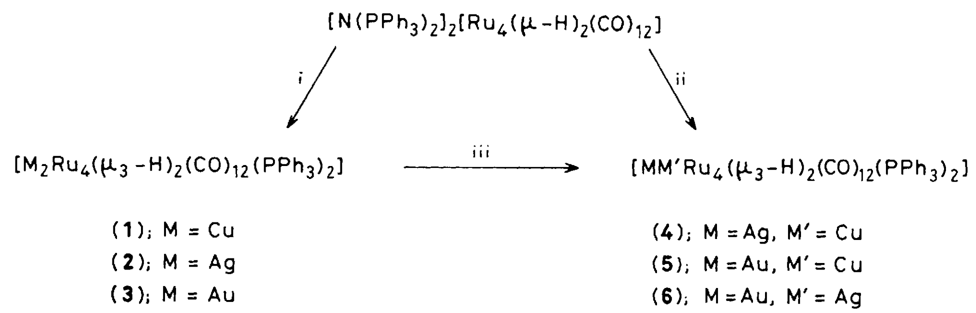
The hexanuclear metal clusters $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (M = M' = Cu, Ag, or Au; M = Cu, M' = Ag or Au; M = Ag, M' = Au) have been prepared by treating the dianion $[Ru_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$ with the complexes $[MX(PPh_3)]$ (M = Au or Cu, X = Cl; M = Ag, X = I) in the presence of $TlPF_6$; the trimetallic clusters may alternatively be synthesised by metathesis of the two appropriate bimetallic species, and the crystal structure of the compounds with the metal cores Cu_2Ru_4, Ag_2Ru_4, and $CuAgRu_4$ have been established by *X*-ray diffraction.

Mixed-metal clusters containing gold atoms are becoming increasingly common, especially species in which $AuPR_3$ fragments are incorporated into structures with ruthenium or osmium atoms ligated by carbonyl groups.[1–6] In contrast,



Scheme 1. i, $[MX(PPh_3)]$ (M = Au or Cu, X = Cl; M = Ag, X = I) (2 equiv.) and $TlPF_6$; ii, $[MX(PPh_3)]$ (1 equiv.) and $[M'X(PPh_3)]$ (1 equiv.), with $TlPF_6$; iii, $[M'_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (1 equiv.) in CH_2Cl_2.

there have been few reports of heteronuclear metal clusters of ruthenium or osmium with copper or silver.[5,6] Moreover, only one class of compound $[M_2Ru_6C(CO)_{16}(NCR)_2]$ (M = Cu or Ag, R = alkyl or aryl), of which $[Cu_2Ru_6C(CO)_{16}(NCMe)_2]$ with a Cu–Cu bond is a well characterised example, has been described[7] with two copper or two silver atoms. Herein we show that the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$[8] can be used as a precursor to the mixed-metal complexes (**1**)—(**6**) shown in Scheme 1, which include the novel trimetal species (**4**)—(**6**).

The method used to synthesise (**1**)—(**3**) involved treating a CH_2Cl_2 solution of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with 2 equiv. of the appropriate complex $[MX(PPh_3)]$, followed by $TlPF_6$.[9] The products were obtained in *ca.* 50% yield as red crystalline materials. The red trimetal compounds (**4**)—(**6**) were prepared (*ca.* 40%) by treating the tetraruthenium salt in CH_2Cl_2 with a solution containing 1 equiv. each of the respective complex halides $[MX(PPh_3)]$ and $[M'X(PPh_3)]$ in the same solvent, followed by addition of solid $TlPF_6$. Only trace amounts of the bimetallic clusters (**1**)—(**3**) were formed using this procedure. The i.r. and n.m.r. data for (**1**)—(**6**)† indicated that they had broadly similar structures, and in order to establish their geometries *X*-ray diffraction studies were carried out on (**1**), (**2**), and (**4**).

Crystals grown from dichloromethane–light petroleum (b.p. 40—60 °C) are essentially isomorphous CH_2Cl_2-solvates differing only in detail (bond lengths and angles, solvent disorder, phenyl group orientation).‡ The molecular structures are illustrated in Figure 1, with a listing of internuclear distances within the M_2Ru_4 core given in Figure 2. The metal atom geometry within the three compounds is bicapped tetrahedral, as observed for other 84 electron hexanuclear clusters, and similar to those observed in $[Au_2Co_2Ru_2(CO)_{12}(PPh_3)_2]$[10] and in $[Au_2Os_4(\mu\text{-}H)_2(CO)_{12}(PPh_3)_2]$,[11] although in the latter, one of the Au–Os edges [3.159(4) Å] of the cluster polyhedron may be considered non-bonding. In (**1**), (**2**), and (**4**) the Group 1B metals are in close contact. There are two distinct sites for the coinage metals; one [M(2)] which is in contact with four other metal atoms, and a second [M(1)] which is in contact with three. In (**4**) the copper atom occupies the site of higher co-ordination number, and the larger silver atom the other site. In each of (**1**), (**2**), and (**4**) the hydrido ligands bridge the $M(2)Ru_2$ faces‡ involving the higher co-ordination number site; it is noticeable that in each structure the doubly bridged M(2)–Ru(1) vector is the longest M–Ru separation. No triply-bridging hydrido ligands bonded to Group 1B metals have been previously reported.

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† Selected spectroscopic data (i.r. measured in CH_2Cl_2, n.m.r. in $CDCl_3$ or CD_2Cl_2, coupling constants in Hz). Compound (**1**), ν_{CO} (max) at 2 071s, 2 032vs, 2 021vs, 2 005s, 1 998w, 1 974m, and 1 938w (br.) cm^{-1}; n.m.r.: ^{1}H δ −16.93 [t, 2 H, μ_3-H, J(PH) 5]; at −90 °C, δ —17.20 [d, 2 H, μ_3-H, J(PH) 12]; ^{31}P{^{1}H}, δ 4.3 (br., s) p.p.m.; at −90 °C, δ 6.8 (s) and −0.4 (s) p.p.m. Compound (**2**), n.m.r.: ^{1}H (at −50 °C), δ −17.16 [tt, 2 H, μ_3-H, J(PH) 5, J(AgH) 14]; at −90 °C, δ −17.17 [dd, 2 H, μ_3-H, J(PH) 9, J(AgH) 27]; ^{31}P{^{1}H} (at −50 °C), δ 16.1 p.p.m. [2 × d, J(^{109}AgP) 522, J(^{107}AgP) 444]; at −90 °C, δ 18.4 [2 × dd, ^1J(^{109}AgP) 565, ^1J(^{107}AgP) 490, ^2J(AgP) 8] and 13.4 p.p.m. [2 × dd, ^1J(^{109}AgP) 473, ^1J(^{107}AgP) 410, ^2J(AgP) 12]; ^{13}C{^{1}H}, δ 198.5 p.p.m. (CO); at −90 °C, δ 201.7 (2 × CO), 200.3 (2 × CO), 199.0 and 198.8 (s and sh., 3 × CO), 198.4 (2 × CO), 196.2 (2 × CO), and 191.3 p.p.m. (1 × CO). Compound (**3**), n.m.r.: ^{1}H, δ −14.67 [t, 2 H, μ_3-H, J(PH) 5]; ^{31}P{^{1}H}, δ 58.7 p.p.m. Compound (**4**), ν_{CO} (max) at 2 070s, 2 031vs, 2 020vs, 2 005s, 1 985 (sh.), 1 972m, and 1 937w (br.) cm^{-1}; n.m.r.: ^{1}H, δ −17.23 [d, 2 H, μ_3-H, J(PH) 11]; ^{31}P{^{1}H} (at −90 °C), δ 14.7 [2 × d, Ag*P*Ph$_3$, J(^{109}AgP) 481, J(^{107}AgP) 417] and 6.4 p.p.m. (s, Ph$_3$*P*Cu). Compound (**5**), ^{1}H, δ −16.97 [d, 2 H, μ_3-H, J(PH) 11]; ^{31}P{^{1}H} (at −90 °C), δ 66.9 (s, Ph$_3$*P*Au) and 4.8 p.p.m. (s, Ph$_3$*P*Cu). Compound (**6**) n.m.r.: ^{1}H, δ −16.80 [dd, 2 H, μ_3-H, J(PH) 8, J(AgH) 27]; ^{31}P{^{1}H} (at −90 °C), δ 64.6 [d, Ph$_3$*P*Au, ^2J(AgP) 24] and 17.4 p.p.m. [2 × d, Ph$_3$*P*Ag, ^1J(^{109}AgP) 596, ^1J(^{107}AgP) 515]. The ^{31}P{^{1}H} n.m.r. spectra of compounds containing AgPPh$_3$ fragments are broadened at room temperature by a further fluxional process involving dissociation of PPh$_3$ groups.

‡ *Crystal data for* (**1**)·CH_2Cl_2: $C_{48}H_{32}Cu_2O_{12}P_2Ru_4 \cdot CH_2Cl_2$, M = 1 479.0, triclinic, space group $P\bar{1}$ (no. 2), a = 13.634(4), b = 14.485(5), c = 15.084(7) Å, α = 74.78(2), β = 74.59(2), γ = 74.37(2)°, U = 2 706(1) Å^3, Z = 2, D_c = 1.81 g cm^{-3}, $F(000)$ = 1 444, Mo-K_α *X*-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 20.6 cm^{-1}; for (**2**)·CH_2Cl_2: $C_{48}H_{32}Ag_2O_{12}P_2Ru_4 \cdot CH_2Cl_2$, M = 1 567.6, triclinic, space group $P\bar{1}$ (no. 2), a = 13.954(4), b = 14.928(3), c = 15.103(3) Å, α = 72.21(1), β = 72.64(2), γ = 73.36(2)°, U = 2 792(1) Å^3, Z = 2, D_c = 1.86 g cm^{-3}, $F(000)$ = 1 516, μ(Mo-K_α) = 19.2 cm^{-1}; for (**4**)·CH_2Cl_2: $C_{48}H_{32}AgCuO_{12}P_2Ru_4 \cdot CH_2Cl_2$, M = 1 523.3, triclinic, space group $P\bar{1}$ (no. 2), a = 13.739(2), b = 14.429(2), c = 15.074(2) Å, α = 75.11(2), β = 74.22(2), γ = 75.05(2)°, U = 2 721.3(7) Å^3, Z = 2, D_c = 1.86 g cm^{-3}, $F(000)$ = 1 480, μ(Mo-K_α) = 20.1 cm^{-1}.

The structures were solved by heavy atom (Patterson and Fourier) methods, and refined using a blocked-cascade full matrix least-squares procedure. Intensity data were collected at 295 K on a Nicolet *P*3*m* diffractometer for a unique hemisphere of reciprocal space, and corrected for absorption. Final residuals (R) were 0.042, 0.047, and 0.048 for 6 300, 5 813, and 5 990 unique observed [$I \geqslant 2.5\sigma(I)$] data for (**1**)·CH_2Cl_2, (**2**)·CH_2Cl_2 and (**4**)·CH_2Cl_2, respectively. In (**2**) the solvent molecule was subjected to a two-fold disorder, in (**1**) and (**4**) one triphenylphosphine ligand showed two-fold disorder of its phenyl rings. All phenyl group hydrogen atoms were incorporated in calculated positions (C–H 0.96 Å). Hydride hydrogen atoms were placed in calculated positions and refined under the constraint that the Ru–H distance = 1.80 Å and the two independent Group 1B metal–H bond lengths be equal [giving Cu–H = 1.62(5) Å in (**1**), Ag–H = 1.72(5) Å in (**2**), and Cu–H = 1.70(5) Å in (**4**)].

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

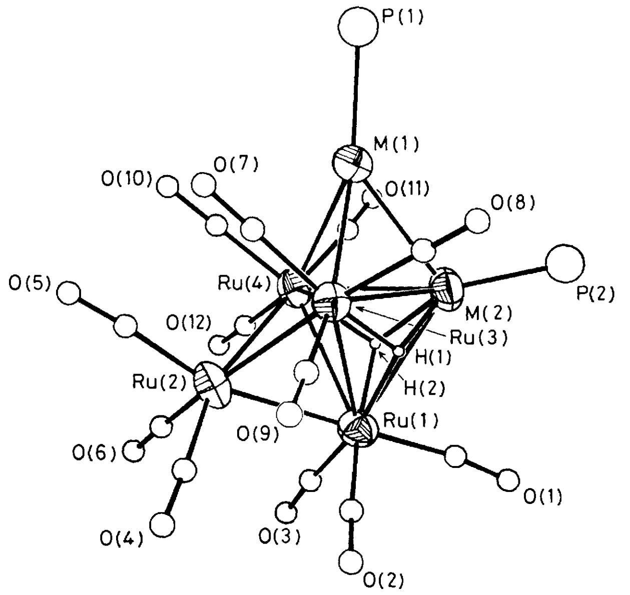

Figure 1. Molecular geometry of $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (**1**, **2**, **4**) showing labelling scheme [(**1**) M(1) = Cu, M(2) = Cu; (**2**) M(1) = Ag, M(2) = Ag; (**4**) M(1) = Ag, M(2) = Cu]. Phenyl groups have been omitted for clarity, only oxygen atoms of the carbonyl ligands have been labelled.

The structures found for (**1**), (**2**), and (**4**) in the solid state are consistent with the limiting low temperature n.m.r. data measured in solution.[†] Thus, at −90 °C (**1**) shows two resonances in the $^{31}P\{^1H\}$ spectrum, and in the ^1H spectrum the chemically equivalent hydrido ligands show coupling to one phosphorus nucleus. In (**4**) these ligands couple with only the copper bound phosphorus nucleus [J(PH) 11 Hz], since no ^{107}Ag and ^{109}Ag coupling is observed. The n.m.r. spectra of (**5**) and (**6**) confirm that in these trimetal species it is the lighter Group 1B element that occupies the higher co-ordination number hydridobridged site [M(2)]. The variable temperature n.m.r. spectra show that an intramolecular polytopal rearrangement of the metal skeleton evidently takes place in solution, resulting in exchange of the Cu atoms between sites in (**1**); and likewise for Ag atoms in (**2**) and Au atoms in (**3**). The estimated $\Delta G^{\ddagger}(T_C)$ for this process [from coalescence temperatures: T_C, (**1**) −45, (**2**) −65, (**3**) < -90 °C] falls in descending order of Group 1B congeners (**1**) 43, (**2**) 40, (**3**) <35 kJ mol^{-1}. In contrast, (**4**), (**5**), and (**6**) show no evidence of dynamic behaviour involving metal-site exchange, but exist as single isomers in solution. Thus, although an intramolecular pathway for Group 1B metal exchange may exist in (**4**)—(**6**), there is a thermodynamic preference for the lighter metal atom to occupy the M(2) site. Since the synthesis of (**4**)—(**6**) gives only trace amounts of (**1**)—(**3**) [much less than statistical quantities, *i.e.* a 1:2:1 ratio of (**1**), (**4**), and (**2**) in the case of (**4**)] this indicates that the product distribution is thermodynamically controlled. To test this hypothesis (**2**) and (**3**) were mixed in CH_2Cl_2 and, as followed by n.m.r. spectroscopy, metathesis occurred to give (**6**), essentially quantitatively after 24 h, thus establishing intermolecular exchange of $M(PPh_3)$ units between clusters. Similarly, (**1**) and (**2**) gave (**4**), and (**1**) and (**3**) yielded (**5**) (Scheme 1).

Thus two types of Group 1B metal-exchange have been established for these clusters, firstly an intramolecular mode observable on the n.m.r. time-scale, and secondly an intermolecular mode which is active on the chemical time-scale. The presence of the latter allows cluster formation with predictable stoicheiometry and controlled regiochemistry.

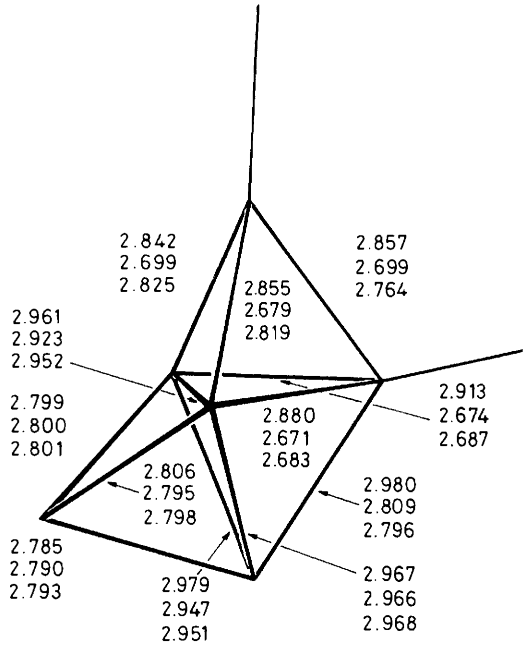

Figure 2. The $M_2Ru_4P_2$ core geometry in (**1**), (**2**), and (**4**). Distances (in Å) are given for the metal–metal contacts within the cluster with that for (**2**) at the top, (**1**) in the middle, and (**4**) at the bottom.

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