The Heteronuclear Cluster Chemistry of the Group 1B Metals. Part 3.[1] Synthesis, Structures, and Chemical Properties of the Trimetallic Hexanuclear Group 1B Metal Cluster Compounds $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (M = Cu, M' = Ag or Au; M = Ag, M' = Au). *X*-Ray Crystal Structure of the Complex $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]\cdot CH_2Cl_2$[*]

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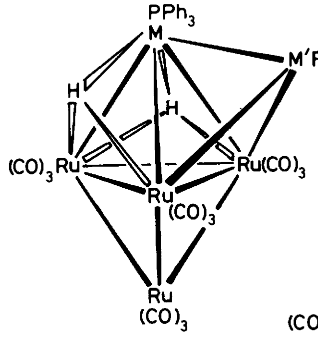
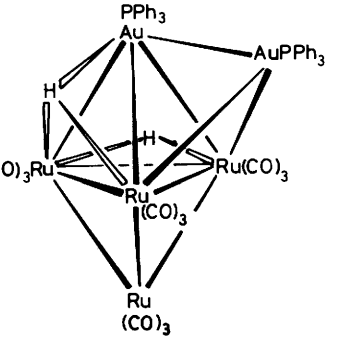
Treatment of dichloromethane solutions of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with dichloromethane solutions containing one equivalent of $[MX(PPh_3)]$ and one equivalent of $[M'X(PPh_3)]$ (M ≠ M'; M,M' = Cu or Au, X = Cl; M,M' = Ag, X = I), in the presence of $TlPF_6$, affords the novel trimetallic clusters $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ [M = Cu, M' = Ag (**1**) or Au (**2**); M = Ag, M' = Au (**3**)] in *ca.* 35—45% yield. A single-crystal *X*-ray diffraction study on (**1**) reveals that the metal skeleton consists of a tetrahedron of ruthenium atoms [Ru–Ru 2.793(1)—2.968(1) Å] capped by a $Cu(PPh_3)$ moiety [Group 1 B metal site M(2)], with one of the $CuRu_2$ faces of the $CuRu_3$ tetrahedron so formed further capped by a $Ag(PPh_3)$ unit [Group 1 B metal site M(1)] to give a capped trigonal bipyramidal metal core geometry [Ag–Cu 2.764(1), Ag–Ru 2.819(1) and 2.825(1), Cu–Ru 2.683(2)—2.796(2) Å]. The other two $CuRu_2$ faces of the cluster are both capped by triply bridging hydrido ligands and each ruthenium atom carries three terminal CO groups. Spectroscopic data demonstrate that (**2**) and (**3**) adopt similar structures to that of (**1**), with the heavier of the pair of Group 1 B metals in each cluster again occupying the position M(1). This coinage metal site preference allows Group 1 B metal exchange reactions to be used as an alternative synthetic route to (**1**)—(**3**) in good yield (*ca.* 70—80%).

Heteronuclear cluster compounds containing one or more $Au(PR_3)$ (R = alkyl or aryl) moieties have attracted a great deal of interest over the last few years, leading to the discovery of novel chemistry.[1–5] More recently, analogous copper and silver species have also received considerable attention.[1,4–7] However, examples of heteronuclear clusters in which more than one type of Group 1B metal are present continue to be extremely rare.[8] Our interest in trying to synthesize such species was stimulated by the prospect of obtaining insight into the site preferences of the various different coinage metals by comparing the metal core geometries adopted by the trimetallic clusters with those of analogous bimetallic compounds. Also, we wished to investigate whether the metal skeletons of the trimetallic species would undergo intramolecular rearrangements in solution. A number of examples of dynamic behaviour involving coinage metal exchange between the distinct sites in the metal frameworks of bimetallic clusters containing two or three $M(PR_3)$ (M = Cu, Ag, or Au) fragments have been reported previously.[1,3–5,7]

Herein we describe the synthesis of a novel series of trimetallic hexanuclear clusters containing two different $M(PPh_3)$ (M = Cu, Ag, or Au) units and compare their structures and chemical properties with those of the previously reported[1] analogous bimetallic species. Preliminary accounts of some of our results have already been published.[9,10]



(**1**) M = Cu, M' = Ag
(**2**) M = Cu, M' = Au
(**3**) M = Ag, M' = Au
(**4**) M = M' = Cu
(**5**) M = M' = Ag



(**6**)

Results and Discussion

Treatment of dichloromethane solutions of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$[11] with dichloromethane solutions containing one equivalent of $[MX(PPh_3)]$ and one equivalent of $[M'X(PPh_3)]$ (M ≠ M'; M,M' = Cu or Au, X = Cl; M,M' = Ag, X = I), in the presence of $TlPF_6$, affords red *microcrystals* of the novel trimetallic clusters $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ [M = Cu, M' = Ag (**1**) or Au (**2**); M = Ag, M' = Au (**3**)] in *ca.* 35—45% yield. These species were characterized by microanalyses and spectroscopic

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[*] 2,2,2,3,3,3,4,4,4,5,5,5-Dodecacarbonyl-1,2,3; 1,2,4-di-μ_3-hydrido-1-triphenylphosphine-1,3,4-μ_3-(triphenylphosphineargentio)-*cyclo*-coppertetraruthenium (*Cu–Ag*)(3*Cu–Ru*)(2*Ag–Ru*)(6*Ru–Ru*)-dichloromethane (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 1. Analytical[a] and physical data for the Group 1B metal heteronuclear cluster compounds

Compound	M.p. (θ_c/°C) (decomp.)	$\nu_{max.}$(CO)[b]/cm^{-1}	Yield[c] (%)	Analysis	
				C	H
(1) [AgCuRu$_4$(μ_3-H)$_2$(CO)$_{12}$(PPh$_3$)$_2$]	177—179	2 070s, 2 031vs, 2 020vs, 2 005s, 1 985 (sh), 1972m, 1 937w br	45	39.8 (40.1)	2.3 (2.2)
(2) [AuCuRu$_4$(μ_3-H)$_2$(CO)$_{12}$(PPh$_3$)$_2$]	192—195	2 071s, 2 033vs, 2 023vs, 2 008s, 1 985 (sh), 1 976m, 1 957w br	36	37.5 (37.7)	2.2 (2.1)
(3) [AgAuRu$_4$(μ_3-H)$_2$(CO)$_{12}$(PPh$_3$)$_2$]	149—152	2 070s, 2 032vs, 2 021vs, 2 005s, 1 984 (sh), 1 973m, 1 952w br	40	36.7 (36.7)	2.4 (2.0)

[a] Calculated values are given in parentheses. Although large crystals of (1), grown slowly over a period of days so that they were suitable for *X*-ray diffraction studies, are dichloromethane solvates, when *microcrystals* of (1)—(3) were grown for analysis, no evidence of dichloromethane of crystallization was found. [b] Measured in dichloromethane solution. [c] The yield quoted is that for the reaction using [N(PPh$_3$)$_2$]$_2$[Ru$_4$(μ-H)$_2$(CO)$_{12}$] as starting material and it is based on the ruthenium reactant.

Table 2. Hydrogen-1, phosphorus-31, and carbon-13 n.m.r. data[a] for the Group 1B metal heteronuclear cluster compounds

Compound	^{1}H[b]	^{31}P-{^{1}H}[c,d]	^{13}C-{^{1}H}[e]	Low temperature ^{13}C-{^{1}H} CO signals[c,e]
(1)	−17.23 [d, 2 H, μ_3-H, *J*(PH) 11], 7.21—7.47 (m, 30 H, Ph)	14.7 [2 × d, PPh$_3$Ag, ^{1}J(^{109}AgP) 481, ^{1}J(^{107}AgP) 417], 6.4 [d, PPh$_3$Cu, ^{2}J(AgP)$_{av}$ 2]	[f] 198.3 (CO), 134.2 and 134.0 [d, C^2(Ph), *J*(PC) 14], 131.5 and 131.0 [C^4(Ph)], 130.4 [d br, C^1(AgPPh$_3$), *J*(PC) 39], 129.6 and 129.4 [d, C^3(Ph), *J*(PC) 9 and 10]	201.5 (2 CO), 200.3 (2 CO), 198.3 (3 CO), 197.8 (2 CO), 196.6 (2 CO), 192.8 (1 CO)
(2)	−16.97 [d, 2 H, μ_3-H, *J*(PH) 11], 7.17—7.48 (m, 30 H, Ph)	66.9 (s, PPh$_3$Au), 4.8 (s, PPh$_3$-Cu)	[g] 199.3 (CO), 134.4 and 134.1 [d, C^2(Ph), *J*(PC) 14 and 12], 131.6 and 131.0 [C^4(Ph)], 129.4 and 129.3 [d, C^3(Ph), *J*(PC) 12 and 11]	204.0 (2 CO), 199.7 (br, 5 CO), 198.7 (2 CO), 197.0 (2 CO), 192.9 (1 CO)
(3)	−16.80 [d of d, 2 H, μ_3-H, *J*(AgH)$_{av}$ 27, *J*(PH) 8], 7.23—7.41 (m, 30 H, Ph)	64.6 [d, PPh$_3$Au, ^{2}J(AgP)$_{av}$ 24], 17.4 [2 × d, PPh$_3$Ag, ^{1}J(^{109}AgP) 596, ^{1}J(^{107}AgP) 515]	[h] 199.4 (CO), 134.3 and 134.1 [d, C^2(Ph), *J*(PC) 14 and 15], 131.9 and 131.3 [C^4(Ph)], 131.4 [d, C^1(AuPPh$_3$), *J*(PC) 48], 129.5 [2 × d, C^3(Ph), *J*(PC) 12 and 9]	204.4(br), 200.0(br), 194.80(vbr)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD$_2$Cl$_2$ solution at ambient temperature. [c] Measured at −90 °C. [d] Hydrogen-1 decoupled, measured in CD$_2$Cl$_2$ solution; chemical shifts positive to high frequency of 85% H$_3$PO$_4$ (external). [e] Hydrogen-1 decoupled; measured in CD$_2$Cl$_2$–CH$_2$Cl$_2$ solution at ambient temperature, unless otherwise stated; chemical shifts positive to high frequency of SiMe$_4$. [f] Only half of the doublet for C^1(CuPPh$_3$) is visible (δ 131.8 p.p.m), the other half is obscured. [g] Only one half of each of the doublets for C^1(AuPPh$_3$) and C^1 (CuPPh$_3$) is visible (δ 132.3 and 131.8 p.p.m.), the other halves are obscured. [h] Only one half of the doublet of doublets for C^1(AgPPh$_3$) is visible [δ 130.6, *J*(AgC) 3 Hz], the other half is obscured.

measurements (Tables 1 and 2). The i.r. spectra of (1)—(3) are almost identical and they are closely similar to those of the previously reported[1] analogous bimetallic clusters [M$_2$Ru$_4$H$_2$(CO)$_{12}$(PPh$_3$)$_2$] [M = Cu (4), Ag (5), or Au (6)], implying that the trimetallic species all adopt the same capped trigonal bipyramidal metal core geometry as that established[1] for (4)—(6). However, to investigate the structure of one of this series of trimetallic clusters in detail, a single-crystal *X*-ray diffraction study was performed on (1). Discussion of the n.m.r. spectroscopic data is best deferred until the *X*-ray diffraction results have been presented.

The molecular structure of (1) is illustrated in Figure 1, which also shows the crystallographic numbering scheme. The interatomic distances and bond angles are summarized in Table 3. The metal skeleton of (1) consists of a tetrahedron of ruthenium atoms with one face [Ru(1)Ru(3)Ru(4)] capped by a Cu(PPh$_3$) moiety [Group 1B metal site M(2)] and one of the faces [Cu(1)Ru(3)Ru(4)] of the CuRu$_3$ tetrahedron so formed further capped by a Ag(PPh$_3$) unit [Group 1B metal site M(1)] to give a capped trigonal bipyramidal metal core geometry. The potential energy minimization program HYDEX[12] and refinement of hydrogen positions against the *X*-ray data suggest that the two hydrido ligands adopt positions capping the Cu(1)Ru(1)Ru(3) and Cu(1)Ru(1)Ru(4) faces of the cluster. Each ruthenium atom carries three terminal CO ligands, which are essentially linear.

Figure 2 compares the interatomic distances within the metal framework of (1) with those in the analogous bimetallic copper and silver species (4) and (5).[1] The two coinage metals are in close contact in each case and the Ag–Cu separation [2.764(1) Å] in (1) is intermediate between the Cu–Cu distance [2.699(2) Å] in (4) and the Ag–Ag separation [2.857(1) Å] in (5), although the variation is not linear. The three M(2)–Ru distances are similar for (1) and (4), with differences of *ca.* 0.013 Å in each case, but the M(2)–Ru separations are significantly longer in (5), as would be expected with the bigger silver atom occupying the M(2) site. In each cluster, it is noticeable that the longest M–Ru separation is M(2)–Ru(1), which is the common edge for the two triply bridging hydrido ligands. The two M(1)–Ru distances in (1) and (5) differ by only 0.017 and 0.036 Å, but the corresponding vectors in (4) are considerably shorter, as would be expected with the smaller copper atom in the M(1) position. Within the Ru$_4$ tetrahedron of each cluster, it is not surprising[1,13] that the unbridged Ru–Ru vectors [Ru(1)–Ru(2), Ru(2)–Ru(3), and Ru(2)–Ru(4)] are considerably shorter than

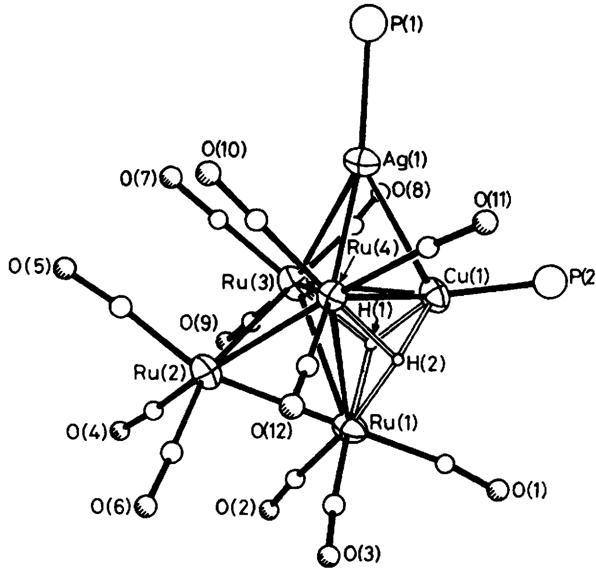


Figure 1. Molecular structure of $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (**1**), showing the crystallographic numbering. Phenyl groups have been omitted for clarity and only the oxygen atom of each carbonyl ligand has been labelled; the carbon atom of each group has the same number as the oxygen atom. The Cu(1)–Ru(1) contact is obscured by the hydrido ligand H(2)

the three Ru–Ru edges which are capped by $M(PPh_3)$ (M = Cu or Ag) fragments or hydrido ligands [Ru(1)–Ru(3), Ru(1)–Ru(4), and Ru(3)–Ru(4)]. The former Ru–Ru separations are also much less sensitive than the latter distances to the changes in the coinage metals between (**1**), (**4**), and (**5**), as would be expected.[1,13] The M–P distances [M = Ag, 2.400(2); M = Cu, 2.203(3) Å] in (**1**) are very similar to those observed[1] in (**4**) and (**5**) and the value for M = Cu is typical for heteronuclear cluster compounds.[1,4,13]

The n.m.r. data (Table 2) for (**1**) are fully consistent with its solid-state structure. Studies on the analogous bimetallic species (**4**) and (**5**)[1] suggest that the two hydrido ligands in (**1**) will show coupling to the phosphorus atom attached to coinage metal M(2), but not to that bonded to M(1). Also, if a silver atom occupies site M(2), additional $^{107,109}Ag\text{-}^{1}H$ coupling would be expected, but this coupling will not be observed when the silver atom is in position M(1).[1] Thus, the high-field ^1H n.m.r. hydrido ligand signal for (**1**) is a doublet [δ −17.23, $J(PH)$ 11 Hz]. The $^{31}P\text{-}\{^1H\}$ n.m.r. chemical shift for the $Cu(PPh_3)$ moiety in (**1**) (δ 6.4 p.p.m.) is also typical for phosphorus bonded to a copper atom occupying the M(2) site in this type of cluster.[1,14] The close similarity between the ^1H chemical shift and the value of $J(PH)$ for the hydrido ligand in (**2**) [δ −16.97, $J(PH)$ 11 Hz] and those for (**1**), and for (**4**) at −90 °C [δ −17.20, $J(PH)$ 12 Hz],[1] suggest that the copper atom occupies site M(2) in (**2**) also. In addition, the $Cu(PPh_3)$ group in (**2**) also exhibits a typical $^{31}P\text{-}\{^1H\}$ n.m.r. chemical shift (δ 4.8 p.p.m.) for phosphorus attached to a copper atom in site M(2).[1,14] In the case of (**3**), the ^1H n.m.r. hydrido ligand signal is a doublet of doublets [δ −16.80, $J(AgH)_{av}$ 27, $J(PH)$ 8 Hz], indicating the presence of the silver atom in site M(2). Thus, for each of the trimetallic clusters (**1**)—(**3**), the lighter of the pair of coinage metals occupies the higher co-ordination number site M(2), whereas the heavier Group 1B metal is in position M(1).

Interestingly, in contrast to the bimetallic species (**4**)—(**6**),[1] no evidence for dynamic behaviour involving coinage metal site exchange in solution is observed for (**1**)—(**3**). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**1**)—(**3**) show no significant change over the temperature range −90 to 30 °C, apart from the reduction of the quadrupolar broadening[13,15] on the peaks due to $Cu(PPh_3)$ moieties as the temperature is decreased. Also, the ^1H n.m.r. hydrido ligand signals all show coupling to one phosphorus atom only and they are not significantly changed over the temperature ranges −90 to 50 °C, −90 to 100 °C, and −90 to 30 °C for (**1**), (**2**), and (**3**), respectively. The clusters all begin to decompose above the upper limits of these temperature ranges.

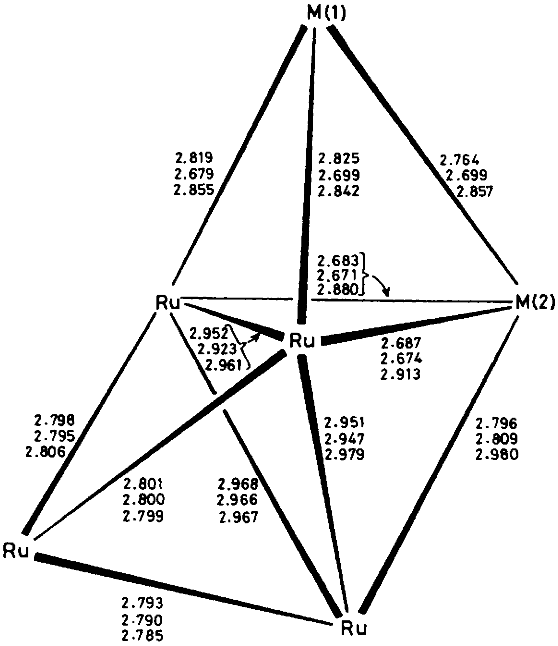


Figure 2. A comparison of the metal–metal separations (Å) within the capped trigonal bipyramidal cores of $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ [M = Cu, M′ = Ag (**1**); M = M′ = Cu (**4**) or Ag (**5**)]. For (**1**), Group 1B metal site M(1) is occupied by the Ag atom and the Cu atom is in position M(2). Distances are given first for (**1**), then for (**4**) and finally for (**5**); the data for (**4**) and (**5**) are taken from ref. 1

In addition, although a number of mixed-metal clusters containing one or two $Ag(PPh_3)$ moieties are known[1,4,13] to exhibit dynamic behaviour involving intermolecular PPh_3 ligand exchange at ambient temperature, there is no evidence that this fluxional process occurs in either (**1**) or (**3**) at room temperature. However, the CO ligands in (**1**)—(**3**) do all undergo complete site exchange at ambient temperature in solution (Table 2), as observed[1] for (**4**)—(**6**). At −90 °C, it is possible to obtain a $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum consistent with the ground-state structure for (**1**), but those of (**2**) and (**3**) are still broadened by the exchange process at this temperature, especially in the case of (**3**). Thus, as in (**4**)—(**6**),[1] the free energy of activation for CO group site exchange in (**1**)—(**3**) is highest for the species containing the lighter coinage metals.

Although an intramolecular pathway for Group 1B metal site exchange exists in the bimetallic species (**4**)—(**6**),[1] there seems to be a thermodynamic site preference for the coinage metals in the analogous trimetallic clusters (**1**)—(**3**). In addition, the fact that the syntheses of (**1**)—(**3**) give only trace amounts of (**4**)—(**6**) [much less than statistical quantities: *e.g.* a 1:2:1 ratio of (**4**), (**1**), and (**5**) in the case of (**1**)], suggests that the product distribution is thermodynamically controlled. To test this hypothesis, equimolar amounts of (**4**) and (**5**) were mixed together in dichloromethane and, after 24 h, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the mixture only showed signals due to (**1**). Similarly, the reaction of (**4**) and (**6**) afforded (**2**) and a mixture of (**5**) and (**6**) yielded (**3**), essentially quantitatively after 24 h, as followed by

Table 3. Selected bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for [$AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2$] (**1**)

H(1)–Ru(1)	1.792(72)	H(1)–Ru(3)	1.774(45)	P(2)–C(221)	1.891(12)	P(2)–C(231)	1.854(9)
H(1)–Cu(1)	1.611(81)	H(2)–Ru(4)	1.797(66)	P(2)–C(241)	1.719(12)	P(2)–C(251)	1.734(14)
H(2)–Ru(1)	1.750(47)	H(2)–Cu(1)	1.685(75)	P(2)–C(261)	1.848(11)	C(11)–O(11)	1.139(12)
Ru(4)–Ag(1)	2.825(1)	Ru(4)–Ru(1)	2.951(1)	C(12)–O(12)	1.140(11)	C(10)–O(10)	1.153(11)
Ru(4)–Ru(2)	2.801(1)	Ru(4)–Ru(3)	2.952(1)	C(3)–O(3)	1.142(12)	C(2)–O(2)	1.121(13)
Ru(4)–Cu(1)	2.687(1)	Ru(4)–C(11)	1.919(10)	C(1)–O(1)	1.134(15)	C(6)–O(6)	1.153(14)
Ru(4)–C(12)	1.892(9)	Ru(4)–C(10)	1.876(9)	C(4)–O(4)	1.127(16)	C(5)–O(5)	1.155(15)
Ag(1)–Ru(3)	2.819(1)	Ag(1)–Cu(1)	2.764(1)	C(8)–O(8)	1.144(12)	C(9)–O(9)	1.134(16)
Ag(1)–P(1)	2.400(2)	Ru(1)–Ru(2)	2.793(1)	C(7)–O(7)	1.150(12)	C(111)–C(112)	1.362(19)
Ru(1)–Ru(3)	2.968(1)	Ru(1)–Cu(1)	2.796(2)	C(111)–C(116)	1.394(13)	C(112)–C(113)	1.375(19)
Ru(1)–C(3)	1.876(10)	Ru(1)–C(2)	1.898(11)	C(113)–C(114)	1.379(20)	C(114)–C(115)	1.372(24)
Ru(1)–C(1)	1.918(12)	Ru(2)–Ru(3)	2.798(1)	C(115)–C(116)	1.391(17)	C(121)–C(122)	1.408(11)
Ru(2)–C(6)	1.877(11)	Ru(2)–C(4)	1.888(12)	C(121)–C(126)	1.354(14)	C(122)–C(123)	1.379(16)
Ru(2)–C(5)	1.891(12)	Ru(3)–Cu(1)	2.683(2)	C(123)–C(124)	1.366(17)	C(124)–C(125)	1.359(14)
Ru(3)–C(8)	1.909(10)	Ru(3)–C(9)	1.874(12)	C(125)–C(126)	1.386(17)	C(131)–C(132)	1.358(20)
Ru(3)–C(7)	1.863(10)	Cu(1)–P(2)	2.203(3)	C(131)–C(136)	1.367(18)	C(132)–C(133)	1.436(24)
P(1)–C(111)	1.798(10)	P(1)–C(121)	1.820(11)	C(133)–C(134)	1.307(39)	C(134)–C(135)	1.295(51)
P(1)–C(131)	1.832(10)	P(2)–C(211)	1.909(12)	C(135)–C(136)	1.385(24)		

Ru(1)–H(1)–Ru(3)	112.6(43)	Ru(1)–H(1)–Cu(1)	110.4(31)	H(2)–Ru(4)–C(10)	168.0(21)	Ag(1)–Ru(4)–C(10)	72.5(3)
Ru(3)–H(1)–Cu(1)	104.8(34)	Ru(4)–H(2)–Ru(1)	112.6(43)	Ru(1)–Ru(4)–C(10)	142.3(3)	Ru(2)–Ru(4)–C(10)	85.3(3)
Ru(4)–H(2)–Cu(1)	100.9(27)	Ru(1)–H(2)–Cu(1)	108.9(32)	Ru(3)–Ru(4)–C(10)	94.6(2)	Cu(1)–Ru(4)–C(10)	132.2(3)
H(2)–Ru(4)–Ag(1)	98.1(23)	H(2)–Ru(4)–Ru(1)	33.2(20)	C(11)–Ru(4)–C(10)	98.2(4)	C(12)–Ru(4)–C(10)	91.3(4)
Ag(1)–Ru(4)–Ru(1)	109.7(1)	H(2)–Ru(4)–Ru(2)	91.2(20)	Ru(4)–Ag(1)–Ru(3)	63.1(1)	Ru(4)–Ag(1)–Cu(1)	57.4(1)
Ag(1)–Ru(4)–Ru(2)	109.5(1)	Ru(1)–Ru(4)–Ru(2)	58.0(1)	Ru(3)–Ag(1)–Cu(1)	57.4(1)	Ru(4)–Ag(1)–P(1)	139.6(1)
H(2)–Ru(4)–Ru(3)	73.9(20)	Ag(1)–Ru(4)–Ru(3)	58.4(1)	Ru(3)–Ag(1)–P(1)	147.3(1)	Cu(1)–Ag(1)–P(1)	148.3(1)
Ru(1)–Ru(4)–Ru(3)	60.4(1)	Ru(2)–Ru(4)–Ru(3)	58.1(1)	H(1)–Ru(1)–H(2)	65.0(32)	H(1)–Ru(1)–Ru(4)	71.8(21)
H(2)–Ru(4)–Cu(1)	38.0(23)	Ag(1)–Ru(4)–Cu(1)	60.1(1)	H(2)–Ru(1)–Ru(4)	34.2(26)	H(1)–Ru(1)–Ru(2)	91.3(19)
Ru(1)–Ru(4)–Cu(1)	59.2(1)	Ru(2)–Ru(4)–Cu(1)	104.4(1)	H(2)–Ru(1)–Ru(2)	92.4(26)	Ru(4)–Ru(1)–Ru(2)	58.3(1)
Ru(3)–Ru(4)–Cu(1)	56.6(1)	H(2)–Ru(4)–C(11)	85.5(20)	H(1)–Ru(1)–Ru(3)	33.5(19)	H(2)–Ru(1)–Ru(3)	74.0(21)
Ag(1)–Ru(4)–C(11)	71.8(2)	Ru(1)–Ru(4)–C(11)	118.6(2)	Ru(4)–Ru(1)–Ru(3)	59.8(1)	Ru(2)–Ru(1)–Ru(3)	58.0(1)
Ru(2)–Ru(4)–C(11)	176.5(2)	Ru(3)–Ru(4)–C(11)	121.4(3)	H(1)–Ru(1)–Cu(1)	32.7(23)	H(2)–Ru(1)–Cu(1)	34.8(24)
Cu(1)–Ru(4)–C(11)	73.4(3)	H(2)–Ru(4)–C(12)	99.6(22)	Ru(4)–Ru(1)–Cu(1)	55.7(1)	Ru(2)–Ru(1)–Cu(1)	101.7(1)
Ag(1)–Ru(4)–C(12)	157.9(3)	Ru(1)–Ru(4)–C(12)	92.4(3)	Ru(3)–Ru(1)–Cu(1)	55.4(1)	H(1)–Ru(1)–C(3)	165.3(23)
Ru(2)–Ru(4)–C(12)	83.3(3)	Ru(3)–Ru(4)–C(12)	140.2(3)	H(2)–Ru(1)–C(3)	98.8(23)	Ru(4)–Ru(1)–C(3)	93.2(3)
Cu(1)–Ru(4)–C(12)	135.8(3)	C(11)–Ru(4)–C(12)	96.6(4)	Ru(2)–Ru(1)–C(3)	86.3(4)	Ru(3)–Ru(1)–C(3)	142.6(3)
Cu(1)–Ru(1)–C(3)	132.3(3)	H(1)–Ru(1)–C(2)	103.2(23)	Ru(2)–Ru(3)–C(9)	91.3(4)	Cu(1)–Ru(3)–C(9)	132.5(4)
H(2)–Ru(1)–C(2)	167.4(21)	Ru(4)–Ru(1)–C(2)	140.4(4)	C(8)–Ru(3)–C(9)	91.8(5)	H(1)–Ru(3)–C(7)	162.9(21)
Ru(2)–Ru(1)–C(2)	83.1(4)	Ru(3)–Ru(1)–C(2)	93.7(3)	Ru(4)–Ru(3)–C(7)	91.0(3)	Ag(1)–Ru(3)–C(7)	74.7(4)
Cu(1)–Ru(1)–C(2)	134.8(3)	C(3)–Ru(1)–C(2)	92.7(5)	Ru(1)–Ru(3)–C(7)	135.8(3)	Ru(2)–Ru(3)–C(7)	78.9(3)
H(1)–Ru(1)–C(1)	88.2(19)	H(2)–Ru(1)–C(1)	87.3(26)	Cu(1)–Ru(3)–C(7)	133.4(4)	C(8)–Ru(3)–C(7)	100.2(4)
Ru(4)–Ru(1)–C(1)	121.4(3)	Ru(2)–Ru(1)–C(1)	179.5(3)	C(9)–Ru(3)–C(7)	93.2(6)	H(1)–Cu(1)–H(2)	70.5(30)
Ru(3)–Ru(1)–C(1)	121.4(3)	Cu(1)–Ru(1)–C(1)	77.8(3)	H(1)–Cu(1)–Ru(4)	82.0(25)	H(2)–Cu(1)–Ru(4)	41.1(21)
C(3)–Ru(1)–C(1)	94.2(5)	C(2)–Ru(1)–C(1)	97.1(5)	H(1)–Cu(1)–Ag(1)	102.0(16)	H(2)–Cu(1)–Ag(1)	103.4(21)
Ru(4)–Ru(2)–Ru(1)	63.7(1)	Ru(4)–Ru(2)–Ru(3)	63.6(1)	Ru(4)–Cu(1)–Ag(1)	62.4(1)	H(1)–Cu(1)–Ru(1)	36.9(22)
Ru(1)–Ru(2)–Ru(3)	64.1(1)	Ru(4)–Ru(2)–C(6)	104.2(4)	H(2)–Cu(1)–Ru(1)	36.3(15)	Ru(4)–Cu(1)–Ru(1)	65.1(1)
Ru(1)–Ru(2)–C(6)	97.6(4)	Ru(3)–Ru(2)–C(6)	160.9(5)	Ag(1)–Cu(1)–Ru(1)	116.3(1)	H(1)–Cu(1)–Ru(3)	39.7(16)
Ru(4)–Ru(2)–C(4)	156.0(4)	Ru(1)–Ru(2)–C(4)	100.3(4)	H(2)–Cu(1)–Ru(3)	83.4(24)	Ru(4)–Cu(1)–Ru(3)	66.7(1)
Ru(3)–Ru(2)–C(4)	93.8(4)	C(6)–Ru(2)–C(4)	95.2(5)	Ag(1)–Cu(1)–Ru(3)	62.3(1)	Ru(1)–Cu(1)–Ru(3)	65.6(1)
Ru(4)–Ru(2)–C(5)	100.9(4)	Ru(1)–Ru(2)–C(5)	163.2(4)	H(1)–Cu(1)–P(2)	127.9(23)	H(2)–Cu(1)–P(2)	129.7(25)
Ru(3)–Ru(2)–C(5)	103.9(3)	C(6)–Ru(2)–C(5)	92.6(5)	Ru(4)–Cu(1)–P(2)	147.7(1)	Ag(1)–Cu(1)–P(2)	114.2(1)
C(4)–Ru(2)–C(5)	92.0(6)	H(1)–Ru(3)–Ru(4)	71.9(21)	Ru(1)–Cu(1)–P(2)	129.5(1)	Ru(3)–Cu(1)–P(2)	143.3(1)
H(1)–Ru(3)–Ag(1)	95.7(25)	Ru(4)–Ru(3)–Ag(1)	58.6(1)	Ag(1)–P(1)–C(111)	113.3(4)	Ag(1)–P(1)–C(121)	119.5(3)
H(1)–Ru(3)–Ru(1)	33.9(27)	Ru(4)–Ru(3)–Ru(1)	59.8(1)	C(111)–P(1)–C(121)	103.7(4)	Ag(1)–P(1)–C(131)	108.5(3)
Ag(1)–Ru(3)–Ru(1)	109.4(1)	H(1)–Ru(3)–Ru(2)	91.5(26)	C(111)–P(1)–C(131)	105.3(5)	C(121)–P(1)–C(131)	105.5(5)
Ru(4)–Ru(3)–Ru(2)	58.2(1)	Ag(1)–Ru(3)–Ru(2)	109.8(1)	Cu(1)–P(2)–C(211)	116.8(4)	Cu(1)–P(2)–C(221)	114.9(4)
Ru(1)–Ru(3)–Ru(2)	57.9(1)	H(1)–Ru(3)–Cu(1)	35.5(26)	Cu(1)–P(2)–C(231)	113.2(4)	Cu(1)–P(2)–C(241)	113.5(5)
Ru(4)–Ru(3)–Cu(1)	56.7(1)	Ag(1)–Ru(3)–Cu(1)	60.3(1)	Cu(1)–P(2)–C(251)	115.1(5)	Cu(1)–P(2)–C(261)	111.8(5)
Ru(1)–Ru(3)–Cu(1)	59.0(1)	Ru(2)–Ru(3)–Cu(1)	104.5(1)	Ru(4)–C(11)–O(11)	170.5(8)	Ru(4)–C(12)–O(12)	176.0(8)
H(1)–Ru(3)–C(8)	88.6(27)	Ru(4)–Ru(3)–C(8)	118.8(3)	Ru(4)–C(10)–O(10)	175.7(7)	Ru(1)–C(3)–O(3)	175.9(12)
Ag(1)–Ru(3)–C(8)	67.1(2)	Ru(1)–Ru(3)–C(8)	122.4(3)	Ru(1)–C(2)–O(2)	173.9(13)	Ru(1)–C(1)–O(1)	172.9(9)
Ru(2)–Ru(3)–C(8)	176.8(3)	Cu(1)–Ru(3)–C(8)	73.8(3)	Ru(2)–C(6)–O(6)	174.9(12)	Ru(2)–C(4)–O(4)	175.7(12)
H(1)–Ru(3)–C(9)	101.3(23)	Ru(4)–Ru(3)–C(9)	147.8(4)	Ru(2)–C(5)–O(5)	177.2(10)	Ru(3)–C(8)–O(8)	171.3(9)
Ag(1)–Ru(3)–C(9)	152.6(3)	Ru(1)–Ru(3)–C(9)	96.6(4)	Ru(3)–C(9)–O(9)	178.4(10)	Ru(3)–C(7)–O(7)	173.9(8)

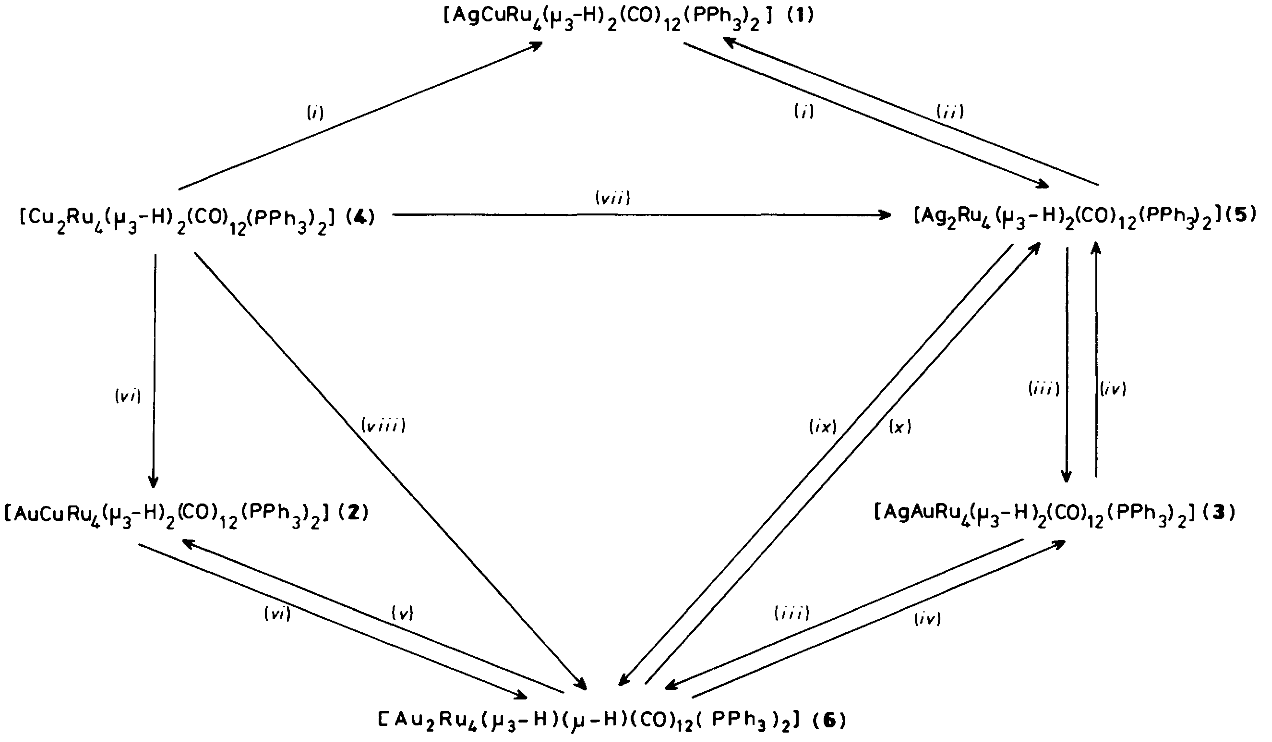
$^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. Thus, intermolecular exchange of $M(PPh_3)$ (M = Cu, Ag, or Au) moieties can occur in solution for (**4**)—(**6**).

The above metathesis reactions suggested that Group 1B metal exchange, with no overall change in cluster nuclearity, might provide a novel alternative route to Group 1B metal heteronuclear clusters. All of the generally applicable procedures for the rational synthesis of Group 1B metal heteronuclear clusters which are currently used involve incorporating one or more $M(PR_3)$ fragments into a preformed

Table 4. Conditions used for the Group 1B metal exchange reactions

Reagents and quantities (g, mmol) used	Product isolated (yield)[a]	Product isolated (yield)[a] when double the stated quantities of mononuclear complex and $TlPF_6$ were used
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.36, 0.26), $[AgI(PPh_3)]$ (0.26, 0.52), $TlPF_6$ (0.28, 0.80)	[b] $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.26 g, 70%)	[c] $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.28 g, 73%)
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.36, 0.26), $[AuCl(PPh_3)]$ (0.16, 0.32), $TlPF_6$ (0.19, 0.54)	$[AuCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.30 g, 76%)	$[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (0.34 g, 79%)
$[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.39, 0.26), $[CuCl(PPh_3)]$ (0.48, 1.33), $TlPF_6$ (0.65, 1.86)	[b] $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.28 g, 74%)	[b] $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.28 g, 74%)
$[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.39, 0.26), $[AuCl(PPh_3)]$ (0.20, 0.40), $TlPF_6$ (0.19, 0.54)	$[AgAuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.33 g, 80%)	$[Au_2Ru_2(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (0.33 g, 76%)
$[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (0.44, 0.27), $[CuCl(PPh_3)]$ (0.14, 0.39), $TlPF_6$ (0.19, 0.54)	$[AuCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.32 g, 79%)	$[AuCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.32 g, 79%)
$[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (0.44, 0.27), $[AgI(PPh_3)]$ (0.47, 0.95), $TlPF_6$ (0.47, 1.35)	$[AgAuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ 0.29 g, 70%)	[c] $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (0.29 g, 74%)

[a] Yields are based on amount of cluster compound taken for reaction. Chromatography was performed on an alumina (10 × 3 cm) column at ambient temperature, unless otherwise stated. [b] Florisil (10 × 3 cm) column at −20 °C. [c] Alumina (10 × 3 cm) column at −20 °C.



Scheme. Group 1B metal exchange reactions for the hexanuclear clusters (**1**)—(**6**). (*i*) $[AgI(PPh_3)]$ (2 equiv.) and $TlPF_6$ (3 equiv.); (*ii*) $[CuCl(PPh_3)]$ (5 equiv.) and $TlPF_6$ (7 equiv.); (*iii*) $[AuCl(PPh_3)]$ (1.5 equiv.) and $TlPF_6$ (2 equiv.); (*iv*) $[AgI(PPh_3)]$ (3.5 equiv.) and $TlPF_6$ (5 equiv.); (*v*) $[CuCl(PPh_3)]$ (1.5 equiv.) and $TlPF_6$ (2 equiv.); (*vi*) $[AuCl(PPh_3)]$ (1.2 equiv.) and $TlPF_6$ (2 equiv.); (*vii*) $[AgI(PPh_3)]$ (4 equiv.) and $TlPF_6$ (6 equiv.); (*viii*) $[AuCl(PPh_3)]$ (2.4 equiv.) and $TlPF_6$ (4 equiv.); (*ix*) $[AuCl(PPh_3)]$ (3 equiv.) and $TlPF_6$ (4 equiv.); (*x*) $[AgI(PPh_3)]$ (7 equiv.) and $TlPF_6$ (10 equiv.)

cluster, dimer, or monomer, thus producing a cluster of higher nuclearity.[1–6,9,13,14,16] We now report that treatment of dichloromethane solutions of the bimetallic clusters (**4**)—(**6**) with the appropriate amounts of the mononuclear complexes $[M'X(PPh_3)]$ (M' = Cu or Au, X = Cl; M' = Ag, X = I), in the presence of $TlPF_6$, results in the replacement of either one or both of the original $M(PPh_3)$ moieties present in the cluster by similar units containing the different Group 1B metal M', as shown in the Scheme. The yields for all of these reactions lie in the range *ca.* 70—80%. Although it is possible to exchange a heavier coinage metal, and in the case of (**6**) both heavier coinage metals, present in the hexanuclear clusters with lighter Group 1B metals using this approach, it can be seen from the Scheme that large excesses of the mononuclear complexes are always

Table 5. Atomic positional parameters (fractional co-ordinates) (× 10^4) for [$AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2$] (**1**) (dichloromethane solvate), with estimated standard deviations in parentheses*

Atom	*x*	*y*	*z*
Ru(4)	3 556(1)	3 073(1)	871(1)
Ag(1)	4 522(1)	1 995(1)	2 360(1)
Ru(1)	1 436(1)	4 051(1)	1 643(1)
Ru(2)	1 829(1)	2 331(1)	967(1)
Ru(3)	2 377(1)	2 129(1)	2 675(1)
Cu(1)	3 113(1)	3 740(1)	2 473(1)
P(1)	6 161(2)	1 002(2)	2 598(2)
P(2)	3 460(2)	4 661(2)	3 261(2)
C(11)	4 683(6)	3 652(6)	825(6)
C(12)	3 427(7)	3 624(7)	−385(6)
C(10)	4 329(7)	1 890(7)	533(5)
C(3)	1 204(7)	4 715(8)	450(7)
C(2)	76(7)	3 806(9)	2 076(8)
C(1)	1 175(7)	5 226(8)	2 115(7)
C(6)	1 471(9)	2 901(10)	−199(7)
C(4)	577(9)	1 900(9)	1 549(8)
C(5)	2 472(10)	1 121(9)	597(6)
C(8)	2 826(7)	1 997(7)	3 801(6)
C(9)	1 133(9)	1 750(10)	3 358(7)
C(7)	2 981(9)	894(7)	2 395(6)
O(11)	5 351(5)	4 043(5)	669(5)
O(12)	3 411(6)	3 944(6)	−1 157(4)
O(10)	4 818(7)	1 195(5)	268(4)
O(3)	1 082(6)	5 164(6)	−268(5)
O(2)	−749(5)	3 734(8)	2 363(6)
O(1)	934(6)	5 951(6)	2 354(6)
O(6)	1 188(8)	3 218(8)	−891(5)
O(4)	−152(7)	1 604(9)	1 860(7)
O(5)	2 842(9)	392(7)	343(6)
O(8)	3 013(6)	1 836(5)	4 527(4)
O(9)	394(7)	1 502(10)	3 783(7)
O(7)	3 336(8)	100(5)	2 308(5)
C(111)	6 268(8)	−271(7)	2 615(6)
C(112)	5 906(11)	−528(8)	1 975(8)
C(113)	5 981(16)	−1 492(10)	1 960(9)
C(114)	6 455(14)	−2 228(9)	2 585(9)
C(115)	6 804(11)	−1 997(9)	3 256(8)
C(116)	6 725(9)	−1 018(8)	3 259(7)
C(121)	6 592(7)	979(7)	3 644(6)
C(122)	5 862(7)	927(7)	4 507(6)
C(123)	6 174(8)	802(7)	5 334(7)
C(124)	7 184(9)	768(8)	5 306(8)
C(125)	7 887(8)	836(8)	4 472(8)
C(126)	7 588(7)	948(8)	3 637(7)
C(131)	7 170(8)	1 404(9)	1 599(7)
C(132)	7 211(10)	2 368(10)	1 398(11)
C(133)	7 970(14)	2 704(19)	594(16)
C(134)	8 623(19)	2 072(27)	120(19)
C(135)	8 593(16)	1 151(23)	307(13)
C(136)	7 854(9)	790(13)	1 054(7)
C(212)	4 005(10)	6 490(9)	3 045(7)
C(213)	4 103	7 450	2 614
C(214)	3 871	7 855	1 731
C(215)	3 542	7 299	1 280
C(216)	3 443	6 339	1 711
C(211)	3 675	5 935	2 593
C(222)	5 102(8)	3 500(8)	4 167(7)
C(223)	6 099	3 280	4 323
C(224)	6 807	3 861	3 789
C(225)	6 517	4 663	3 100
C(226)	5 520	4 883	2 944
C(221)	4 812	4 301	3 478
C(232)	3 031(7)	4 738(8)	5 213(7)
C(233)	2 396	4 688	6 114
C(234)	1 429	4 454	6 292
C(235)	1 096	4 269	5 571
C(236)	1 731	4 318	4 670
C(231)	2 699	4 553	4 492
C(242)	3 124(11)	6 620(9)	3 215(7)
C(243)	3 076	7 591	2 735
C(244)	3 231	7 816	1 756
C(245)	3 433	7 071	1 257
C(246)	3 481	6 101	1 737
C(241)	3 326	5 875	2 716
C(252)	5 506(10)	3 990(10)	3 050(7)
C(253)	6 412	3 544	3 367
C(254)	6 385	3 292	4 330
C(255)	5 451	3 486	4 976
C(256)	4 545	3 932	4 658
C(251)	4 572	4 148	3 695
C(262)	1 850(10)	5 973(8)	4 269(8)
C(263)	1 020	6 161	5 018
C(264)	688	5 386	5 707
C(265)	1 185	4 423	5 648
C(266)	2 015	4 235	4 898
C(261)	2 348	5 010	4 209
C	−321(24)	8 144(21)	3 897(22)
Cl(1)	−246(10)	8 697(12)	2 414(11)
Cl(2)	784(14)	8 819(11)	3 333(16)

* E.s.d.s quoted for phenyl carbons C(212), C(222), C(232), C(242), C(252), and C(262) are those of the rigid groups to which they and the following five carbons belong. Carbons C(212)—C(261) have occupancy 0.5.

required. Moreover, it is not possible to replace both gold atoms in (**6**), both silver atoms in (**5**), the gold atom in (**2**) or the silver atom in (**1**) by copper, however much excess [$CuCl(PPh_3)$] is present. However, the above synthetic approach is more efficient and economical when the lighter of the pair or pairs of coinage metals to be exchanged is initially present in the hexanuclear cluster, as these reactions only require relatively small excesses of the mononuclear complexes (Scheme). Although the bimetallic species (**5**) and (**6**) can be obtained in this manner, the above Group 1B metal exchange reactions are potentially much more useful for the synthesis of trimetallic clusters. These metathesis reactions allow compounds (**1**)—(**3**) to be prepared in high yield with predictable stoicheiometry and controlled regiochemistry and it should be possible to extend this type of synthetic procedure to obtain further examples of cluster compounds containing two different coinage metals, which are at present very rare.

Experimental

The techniques used and the instrumentation employed have been described elsewhere.[1] Light petroleum refers to that fraction of b.p. 40—60 °C. Established methods were used to prepare compounds [$N(PPh_3)_2$]$_2$[$Ru_4(\mu\text{-}H)_2(CO)_{12}$][11] and [$AgI(PPh_3)$].[17] The complexes [$CuCl(PPh_3)$][18] and [$AuCl(PPh_3)$][19] were synthesized by adaptation of published routes. Analytical and other physical data for the new compounds are presented in Table 1, together with their i.r. spectra. Table 2 summarizes the results of n.m.r. spectroscopic measurements. Product separation by column chromatography was performed on Aldrich Florisil (100—200 mesh) or B.D.H. alumina (Brockman activity II).

Synthesis of the Compounds [$MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2$] (M = Cu, M′ = Ag *or* Au; M = Ag, M′ = Au) *from* [$N(PPh_3)_2$]$_2$[$Ru_4(\mu\text{-}H)_2(CO)_{12}$].—A dichloromethane (50 cm^3) solution of of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ (0.76 g, 0.42 mmol) was treated with a dichloromethane (50 cm^3) solution containing $[CuCl(PPh_3)]$ (0.15 g, 0.42 mmol) and $[AgI(PPh_3)]$ (0.21 g, 0.42 mmol). Solid $TlPF_6$ (0.50 g, 1.43 mmol) was added to the mixture, which was then stirred at room temperature for 2 h. After filtration of the dark red mixture through a Celite pad (*ca.* 1 × 3 cm), the solvent was removed under reduced pressure and the crude residue was dissolved in dichloromethane–light petroleum (1:2). Chromatography at −20 °C on a Florisil column (20 × 3 cm), eluting with dichloromethane–light petroleum (1:2), afforded a red fraction containing the product. After removal of the solvent from this fraction under reduced pressure, crystallization of the residue from dichloromethane–light petroleum yielded red *microcrystals* of $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (**1**) (0.27 g).

Red *microcrystals* of $[AuCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (**2**) (0.23 g) and $[AgAuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (**3**) (0.26 g) were prepared similarly using a dichloromethane (50 cm^3) solution of $[CuCl(PPh_3)]$ (0.15 g, 0.42 mmol) and $[AuCl(PPh_3)]$ (0.21 g, 0.42 mmol) or $[AgI(PPh_3)]$ (0.21 g, 0.42 mmol) and $[AuCl(PPh_3)]$ (0.21 g, 0.42 mmol), respectively, in place of the solution containing $[CuCl(PPh_3)]$ and $[AgI(PPh_3)]$. For both clusters, the chromatography was performed at ambient temperature on an alumina column (20 × 3 cm), eluting with dichloromethane–light petroleum (1:2).

Group 1B *Metal Exchange Reactions.*—Using the quantities listed in Table 4, a dichloromethane (50 cm^3) solution of the hexanuclear cluster compound was treated with the mononuclear complex and $TlPF_6$ and the mixture was stirred for 2 h. After filtration of the mixture through a Celite pad (*ca.* 1 × 3 cm), the solvent was removed under reduced pressure and the residue dissolved in dichloromethane–light petroleum (1:2). Chromatography, using the appropriate conditions (Table 4) and eluting with dichloromethane–light petroleum (1:2), afforded one red fraction. After removal of the solvent from this fraction under reduced pressure, crystallization of the residue from dichloromethane–light petroleum yielded red *microcrystals* of the product. Table 4 lists the yields obtained.

Crystal Structure Determination for (**1**)$\cdot CH_2Cl_2$.—Suitable crystals of (**1**)$\cdot CH_2Cl_2$ were grown from dichloromethane–light petroleum by slow layer diffusion at −20 °C.

Crystal data. $C_{48}H_{32}AgCuO_{12}P_2Ru_4\cdot CH_2Cl_2$, $M = 1\,523.3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.739(2)$, $b = 14.429(2)$, $c = 15.074(2)$ Å, $\alpha = 75.11(2)$, $\beta = 74.22(2)$, $\gamma = 75.05(2)°$, $U = 2\,721.3(7)$ Å^3, $Z = 2$, $D_c = 1.86$ g cm^{-3}, $F(000) = 1\,480$, Mo-K_α *X*-radiation, graphite monchromator, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 20.1 cm^{-1}.

The crystal used (a red, multifaceted prism, *ca.* 0.5 × 0.2 × 0.13 mm) was sealed, under N_2, in a thin-walled glass capillary for *X*-ray measurements, which were performed on a Nicolet *P*3*m* diffractometer at room temperature. Intensity data were collected for a unique hemisphere of reciprocal space in the range $4 < 2\theta < 50°$, using θ–2θ scans of width $2.0° + \Delta_{\alpha_1\alpha_2}$ and speeds between 2.0 and 29.3° min^{-1}. The 9 024 intensities measured were corrected for a 4.5% decrease in intensity of three check reflections, remeasured periodically during data collection. An absorption correction was applied, based on 366 azimuthal scan data, giving transmission coefficients in the range 0.363—0.479 for the full data set. Averaging of duplicate and Friedel pair measurements led to 7 205 unique data of which 5 990 with $I > 2.5\sigma(I)$ were used in structure solution and refinement.

The structure was solved by conventional heavy-atom methods (Patterson, Fourier) and refined by blocked-cascade full-matrix least-squares methods, with weights $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ being the variance in F_o due to counting statistics and $g = 0.0007$ being chosen to minimize the variation of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$. All atoms other than hydrogens and the carbon atoms of the disordered phenyl rings [C(212)—C(261)] were refined with anisotropic displacement parameters. Of the isotropic displacement parameters, only those of the carbon atoms and the hydride hydrogens were allowed to refine and the others were fixed at *ca.* 1.2 U_{iso} for their bonded carbon atoms. As observed[1] for the PPh_3 ligand attached to Cu(2) in $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (**4**), the phenyl rings of the PPh_3 group bonded to the copper atom in (**1**) are subject to two-fold disorder. Occupancies of the two orientations were set to 0.50 and the phenyl rings were constrained to D_{6h} symmetry, with C–C 1.395 Å. The phenyl rings attached to P(1) show signs of disorder, but they were modelled by single sites for carbon atoms, with large and highly anisotropic displacement parameters. All phenyl group hydrogens were constrained to idealized (sp^2) geometries, with C–H 0.96 Å. The hydride hydrogens were constrained to have Ru–H distances near 1.80 Å and Cu–H distances near a common value, which refined to 1.65(4) Å. The initial hydrido ligand positions were calculated indirectly.[12] The solvate CH_2Cl_2 molecule is disordered and was modelled by highly anisotropic carbon and chlorine atoms, at unrealistic bond lengths and angles. The crystal structure of (**1**)$\cdot CH_2Cl_2$ is essentially isomorphous with those of the analogous bimetallic species $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]\cdot CH_2Cl_2$ (M = Cu or Ag).[1]

Refinement of the 462 least-squares parameters converged to final residuals $R = 0.0485$, $R' = 0.049$, $S = 1.44$. $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, N_o = number of observations, N_v = number of variables.$\}$ Final difference electron-density syntheses showed no features > 1.22 e Å^{-3}, the largest being near metal atoms. Table 5 lists the positional co-ordinates for the non-hydrogen atoms. All calculations were performed with programs of the SHELXTL[20] package on a Nicolet *R*3*m*/*E* system. Complex neutral-atom scattering factors were taken from ref. 21.

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