The Heteronuclear Cluster Chemistry of the Group 1B Metals. Part 13.[1] Synthesis and Structural Characterization of the Bimetallic Hexanuclear Group 1B Metal Cluster Compounds $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu, Ag, or Au). *X*-Ray Structure Analyses of $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu or Ag)†

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Treatment of the salt $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]$·thf (thf = tetrahydrofuran) with 2 equivalents of the complex $[M(NCMe)_4]PF_6$ (M = Cu or Ag) at −30 °C, followed by the addition of 2 equivalents of PPh_3, affords the mixed-metal cluster compounds $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ [M = Cu (**1**) or Ag (**2**)] in *ca.* 35—40% yield. The analogous gold-containing species, $[Au_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (**3**), was obtained in *ca.* 65% yield by treating a dichloromethane solution of $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]$·thf with a dichloromethane solution containing 2 equivalents of the complex $[AuCl(PPh_3)]$ at −30 °C, in the presence of $TlPF_6$. Single-crystal *X*-ray diffraction studies on (**1**) and (**2**) show that both clusters exhibit similar capped trigonal-bipyramidal metal frameworks, consisting of a tetrahedron of ruthenium atoms with two Ru_3 faces capped by $M(PPh_3)$ (M = Cu or Ag) units [Cu–Ru 2.608(2)—2.848(2), Ru–Ru 2.771(2)—2.981(2) Å for (**1**); Ag–Ru 2.806(1)—2.977(1), Ru–Ru 2.797(1)—3.074(1) Å for (**2**)]. Spectroscopic data suggest that the gold-containing cluster (**3**) also adopts a similar metal core structure. The skeletal geometries of clusters (**1**)—(**3**) are in marked contrast to the capped trigonal-bipyramidal skeletal geometries previously characterized in the solid state for the very closely related dihydrido clusters $[M_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ (M = Cu, Ag, or Au), in which the Group 1B metals are in close contact. Thus, the formal replacement of two hydrido ligands in the latter clusters by the sterically more demanding CO group in (**1**)—(**3**) causes a fundamental change in the positions that the $M(PPh_3)$ (M = Cu, Ag, or Au) units adopt on the ruthenium tetrahedra of these species.

Mixed-metal clusters which contain $M(PR_3)$ (M = Cu, Ag, or Au; R = alkyl or aryl) fragments often exhibit novel properties that are in marked contrast to those displayed by most heteronuclear clusters of other transition metals, because of the bonding capabilities of the Group 1B metal units.[2—4] The differences in energy between various structural types can be very small for coinage metal-containing species[3—6] and clusters with very similar stoicheiometries can exhibit structures with markedly different metal frameworks.[4,5] A significant number of examples of skeletal isomerism are now known to occur not only in solution, but also in the solid state, and the metal skeletons of many Group 1B metal heteronuclear clusters are stereochemically non-rigid in solution.[4—6] We wished to investigate the effect of the formal replacement of two hydrido ligands by the sterically more demanding CO group on the metal framework structures adopted by the previously reported[7] clusters $[M_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ (M = Cu, Ag, or Au). A preliminary account describing some of our results has already been published.[8]

Results and Discussion

Treatment of a dichloromethane solution of the salt $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]$·thf (thf = tetrahydrofuran) with 2 equivalents of the complex $[M(NCMe)_4]PF_6$ (M = Cu or Ag) at −30 °C incorporates two M(NCMe) units into the cluster dianion and the subsequent addition of 2 equivalents of PPh_3 affords the dark brown heteronuclear cluster compounds $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ [M = Cu (**1**) or Ag (**2**)] in *ca.* 35—40% yield. The analogous gold-containing species, $[Au_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (**3**), was obtained in *ca.* 65% yield by treating a dichloromethane solution of the salt $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]$·thf with a dichloromethane solution containing 2 equivalents of the complex $[AuCl(PPh_3)]$ at −30 °C, in the presence of $TlPF_6$. The clusters (**1**)—(**3**) were characterized by microanalysis and by spectroscopic measurements (Tables 1 and 2).

The i.r. spectra of (**1**)—(**3**) are closely similar, suggesting that these clusters all adopt the same metal core geometry. The peak between 1 800 and 1 785 cm^{-1} observed for each cluster is diagnostic of bridging carbonyl groups. At −90 °C, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**1**)—(**3**) are in marked contrast to those previously reported[7] for the closely related dihydrido clusters $[M_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ [M = Cu (**4**), Ag (**5**), or Au (**6**)]. Whereas signals due to two phosphorus environments, consistent with the ground-state structures, were observed for (**4**) and (**5**) and a very broad singlet was reported for (**6**), the low-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**1**)—(**3**) all consist of single phosphorus resonances with narrow linewidths. Thus, the spectroscopic data suggest that (**1**)—(**3**) do not adopt capped

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† 1,2;1,3;2,4-Tri-μ-carbonyl-1,1,2,2,3,3,3,4,4,4-decacarbonyl-1,2,3;1,2,4-bis(μ_3-triphenylphosphinecuprio)-*tetrahedro*-tetraruthenium and 1,2;-1,3;2,4-tri-μ-carbonyl-1,1,2,2,3,3,3,4,4,4-decacarbonyl-1,2,3;1,2,4-bis-(μ_3-triphenylphosphineargentio)-*tetrahedro*-tetraruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

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

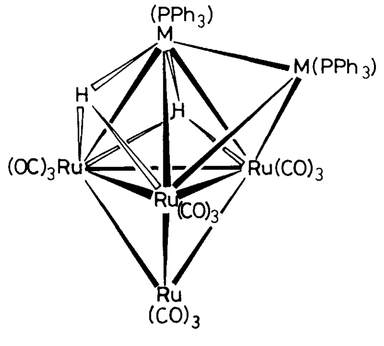
Compound	M.p. (θ_c/°C) (decomp.)	$\nu_{max.}$(CO)[b]/cm^{-1}	Yield (%)[c]	Analysis (%) C	Analysis (%) H
(1) $[Cu_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$	193—196	2 062m, 2 016vs, 2 002s, 1 949m, br, 1 799w, vbr	40	41.3 (41.4)	2.2 (2.1)
(2) $[Ag_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$	159—164	2 060m, 2 014vs, 1 997s, 1 951m, br, 1 787w, vbr	36	39.0 (39.0)	2.0 (2.0)
(3) $[Au_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$	145—149	2 066m, 2 023vs, 2 006s, 1 967m, br, 1 789w, vbr	65	34.7 (34.9)	1.9 (1.8)

[a] Calculated values given in parentheses. [b] Measured in dichloromethane solution. [c] Based on ruthenium reactant.

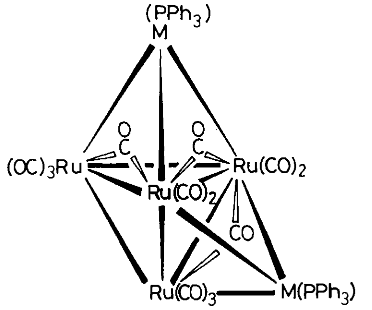
Table 2. N.m.r. data[a] for the new Group 1B metal cluster compounds

Cluster	θ_c/°C	^1H[b]	$^{31}P\text{-}\{^1H\}$[c]
(1)	Ambient	7.27—7.58 (m,Ph)	5.0 (s,br)
	−90		3.6 (s)
(2)	Ambient	7.28—7.54 (m,Ph)	17.3 [2 × d, $J(^{109}AgP)$ 505, $J(^{107}AgP)$ 438]
	−90		16.4 [2 × d, $J(^{109}AgP)$ 514, $J(^{107}AgP)$ 446]
(3)	−20	7.15—7.55 (m,Ph)	63.8 (s)
	−90		62.9 (s)

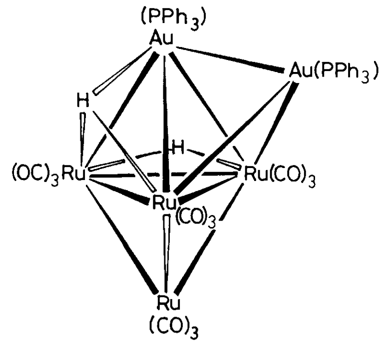
[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in $[^2H_2]$dichloromethane solution. [c] Hydrogen-1 decoupled, measured in $[^2H_2]$dichloromethane–CH_2Cl_2 solution, chemical shifts positive to high frequency of 85% H_3PO_4 (external).



M
(4) Cu
(5) Ag



M
(1) Cu
(2) Ag
(3) Au



(6)

trigonal-bipyramidal metal core structures with the Group 1B metals in close contact, similar to those previously characterized for (4)—(6).[7] In addition, the complex second-order splitting patterns observed in the ambient-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of $[Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (n = 1—6)[9] and $[Ag_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)_2]$,[10] due to $^{107,109}Ag$–$^{107,109}Ag$ couplings and $^{107,109}Ag$-^{31}P couplings through two bonds, do not occur for the silver-containing cluster (2). This observation provides further evidence that the two silver atoms in (2) are not in close contact. To investigate the structures of (1)—(3) in detail, single-crystal *X*-ray diffraction studies were performed on (1) and (2).

The molecular structures of the mixed-metal clusters (1) and (2) are displayed in Figures 1 and 2, respectively, together with the crystallographic numbering. Selected interatomic distances and angles for both compounds are summarized in Table 3 and Figure 3 compares the values of the metal–metal separations in the metal frameworks of (1) and (2).

In the solid state the clusters (1) and (2) adopt similar capped trigonal-bipyramidal metal core structures, in which two Ru_3 faces [Ru(1)Ru(2)Ru(3) and Ru(1)Ru(2)Ru(4)] of a Ru_4 tetrahedron are capped by $M(PPh_3)$ (M = Cu or Ag) fragments so that the Group 1B metals are not in close contact. In the structures of both (1) and (2), two terminal CO groups are bonded to each of Ru(1) and Ru(2) and three terminal CO ligands are attached to each of Ru(3) and Ru(4). The remaining three CO ligands in both clusters, CO(13), CO(21), and CO(24), bridge the Ru(1)–Ru(3), Ru(1)–Ru(2), and Ru(2)–Ru(4) vectors, respectively.

The range of Cu–Ru distances in $[Cu_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (1) [2.608—2.848(2) Å] is slightly larger than that reported for the closely related dihydrido cluster $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (4) [2.669—2.809(2) Å],[7] although the mean values of the Cu–Ru separations in (1) [2.702(2) Å] and (4) [2.706(2) Å] are not significantly different. However, the

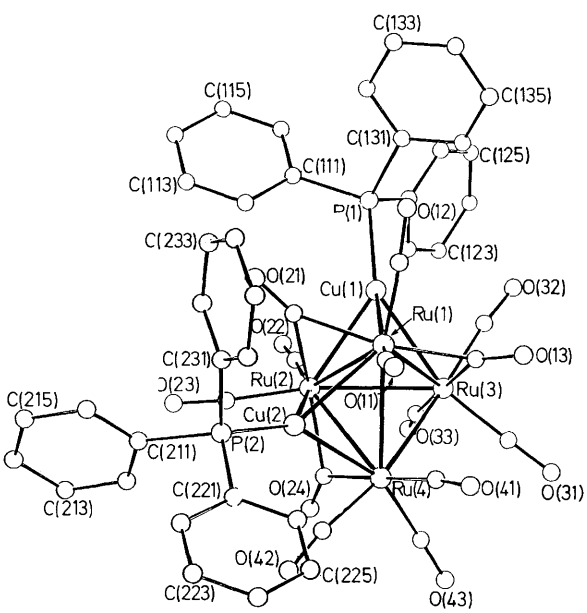


Figure 1. Molecular structure of $[Cu_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (1), showing the crystallographic numbering. The carbon atom of each carbonyl group has the same number as the oxygen atom

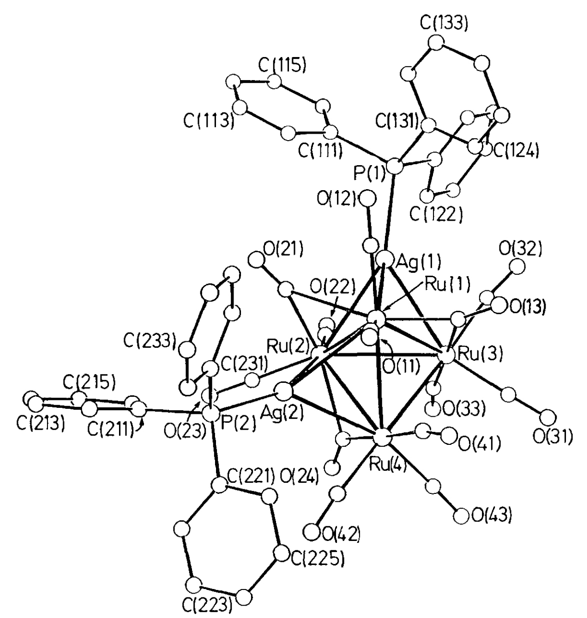


Figure 2. Molecular structure of $[Ag_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (2), showing the crystallographic numbering. The carbon atom of each carbonyl group has the same number as the oxygen atom

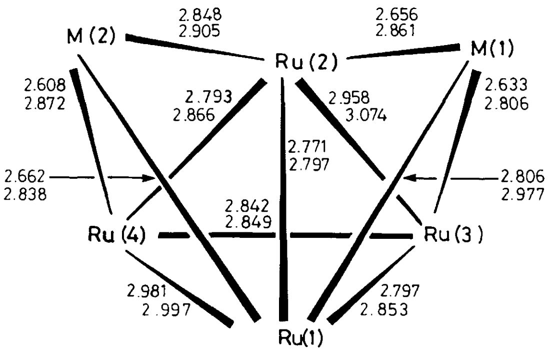


Figure 3. A comparison of the metal–metal separations (Å) in the capped trigonal-bipyramidal metal cores of $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ [M = Cu (1) or Ag (2)]. Distances are given first for (1), then for (2)

mean Cu–Ru separation for the capping $Cu(PMePh_2)$ unit in the pentanuclear cluster $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}(PMePh_2)]$ [2.738(1) Å][11] is significantly longer than the mean Cu–Ru distance in (1), whereas that for the two capping $Cu(C_6H_5Me)$ fragments in the octanuclear species $[Cu_2Ru_6(CO)_{18}(C_6H_5Me)_2]$ [2.650(9) Å][12,13] is considerably shorter. The significant differences observed between the various Cu–Ru distances are not surprising, as the relative 'softness' of the metal–metal bonding in Group 1B metal heteronuclear cluster compounds is well established.[1–6,14] The two $Cu(PPh_3)$ groups in (1) cap the respective Ru_3 faces asymmetrically, with one Cu–Ru distance in each cap [Cu(1)–Ru(1) and Cu(2)–Ru(2)] being significantly longer than the other two (Figure 3). It seems likely that these variations in the Cu–Ru distances are caused by the steric constraints imposed by the CO ligands which bridge two of the three Ru–Ru edges of each of the Ru_3 faces capped by the copper atoms. The Ru–Ru separations in the two Ru_3 faces capped by the $Cu(PPh_3)$ fragments also show marked asymmetry. In each Ru_3 face, the Ru–Ru vector which is not bridged by a CO group [Ru(2)–Ru(3) and Ru(1)–Ru(4)] is very much longer than the other two (Figure 3). However, the mean values of the lengths of the three Ru–Ru vectors capped by the copper atoms are not significantly different for Cu(1) [2.842(2)] and Cu(2) [2.848(2) Å]. The tetrahedral Cu(1)Ru(1)Ru(2)Ru(3) unit is slightly larger than the symmetry-related Cu(2)Ru(1)-Ru(2)Ru(4) fragment, with the mean value of the six metal–metal separations in the former [2.770(2) Å] being *ca.* 0.03 Å larger than that in the latter [2.739(2) Å].

The mean value of the Ag–Ru separations in the silver-containing cluster $[Ag_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (2) [2.876(1) Å] is significantly smaller than that observed in the structure of the closely related dihydrido cluster $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (5) [2.894(1) Å],[7] but it is considerably larger than the mean Ag–Ru distance reported for the capping $Ag(PPh_3)$ fragment in $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ [2.822(1) Å].[15] Again, the significant differences observed between the various Ag–Ru distances are not surprising, as the relative 'softness' of the metal–metal bonding in Group 1B metal heteronuclear cluster compounds is well established.[1–6,14] As observed for the $Cu(PPh_3)$ groups in complex (1), the two $Ag(PPh_3)$ units in (2) adopt asymmetric capping positions, with one Ag–Ru distance in each cap [Ag(1)–Ru(1) and Ag(2)–Ru(2)] being significantly longer than the other two (Figure 3). Again, it seems likely that these variations in the Ag–Ru distances are caused by the bridging CO ligands. However, the difference between the longer and the mean value of the two shorter Ag–Ru distances for Ag(2) (*ca.* 0.05 Å) is not nearly as marked as that for Ag(1) (*ca.* 0.14 Å) or the analogous differences in Cu–Ru separations observed for the capping $Cu(PPh_3)$ groups in (1) [*ca.* 0.16 Å for Cu(1) and *ca.* 0.21 Å for Cu(2)]. The Ru–Ru separations in the two Ru_3 faces capped by the $Ag(PPh_3)$ fragments also show considerable asymmetry. In each Ru_3 face the Ru–Ru vector which is not bridged by a CO group [Ru(2)–Ru(3) and Ru(1)–Ru(4)] is significantly longer than the other two (Figure 3). Interestingly, the mean value of the lengths of the three Ru–Ru vectors capped by Ag(1) [2.908(1) Å] is *ca.* 0.02 Å larger than that for Ag(2) [2.887(1) Å]. This structural feature is in marked contrast to the situation observed for the copper-containing cluster (1). However, the mean values of the six metal–metal separations in the tetrahedral units Ag(1)-Ru(1)Ru(2)Ru(3) and Ag(2)Ru(1)Ru(2)Ru(4) differ by only 0.003 Å, compared to a difference of *ca.* 0.03 Å for the corresponding distances in (1).

Table 3. Selected bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ [M = Cu (**1**) or Ag (**2**)]

	(**1**)	(**2**)		(**1**)	(**2**)
Ru(1)–Ru(2)	2.771(2)	2.797(1)	Ru(3)–M(1)	2.633(2)	2.806(1)
Ru(1)–Ru(3)	2.797(2)	2.853(2)	Ru(4)–M(2)	2.608(2)	2.872(2)
Ru(1)–Ru(4)	2.981(2)	2.997(1)	M(1)–P(1)	2.231(6)	2.419(3)
Ru(1)–M(1)	2.806(2)	2.977(1)	M(2)–P(2)	2.236(6)	2.417(3)
Ru(1)–M(2)	2.662(2)	2.838(1)	P(1)–C(111)	1.823(8)	1.834(7)
Ru(2)–Ru(3)	2.958(2)	3.074(1)	P(1)–C(121)	1.820(9)	1.816(9)
Ru(2)–Ru(4)	2.793(2)	2.866(1)	P(1)–C(131)	1.833(9)	1.807(8)
Ru(2)–M(1)	2.656(2)	2.861(1)	P(2)–C(211)	1.816(8)	1.811(8)
Ru(2)–M(2)	2.848(2)	2.905(1)	P(2)–C(221)	1.808(9)	1.809(4)
Ru(3)–Ru(4)	2.842(2)	2.849(1)	P(2)–C(231)	1.812(9)	1.822(8)
Ru–CO (terminal)	1.798(5)—1.891(3)	1.799(3)—1.922(4)	C–O (terminal)	1.148(6)—1.195(6)	1.149(4)—1.194(4)
Ru–CO (bridging)	2.031(4)—2.230(3)	1.953(3)—2.589(3)	C–O (bridging)	1.150(6)—1.204(3)	1.145(5)—1.197(4)
Ru(3)–Ru(1)–Ru(2)	64.2(1)	65.9(1)	C(13)–Ru(3)–Ru(1)	47.3(6)	43.1(3)
Ru(4)–Ru(1)–Ru(2)	58.0(1)	59.2(1)	C(13)–Ru(3)–Ru(2)	104.5(6)	99.2(3)
Ru(4)–Ru(1)–Ru(3)	58.8(1)	58.2(1)	C(13)–Ru(3)–Ru(4)	83.7(6)	86.8(3)
M(1)–Ru(1)–Ru(2)	56.9(1)	59.3(1)	C(31)–Ru(3)–Ru(1)	122.6(7)	118.0(5)
M(1)–Ru(1)–Ru(3)	56.1(1)	57.5(1)	C(31)–Ru(3)–Ru(2)	140.4(7)	146.0(4)
M(1)–Ru(1)–Ru(4)	101.1(1)	103.1(1)	C(31)–Ru(3)–Ru(4)	86.0(7)	89.0(4)
M(2)–Ru(1)–Ru(2)	63.2(1)	62.1(1)	C(32)–Ru(3)–Ru(1)	108.1(7)	111.7(4)
M(2)–Ru(1)–Ru(3)	109.5(1)	112.1(1)	C(32)–Ru(3)–Ru(2)	122.4(6)	122.5(4)
M(2)–Ru(1)–Ru(4)	54.7(1)	58.9(1)	C(32)–Ru(3)–Ru(4)	171.1(7)	174.5(4)
M(2)–Ru(1)–M(1)	118.1(1)	118.4(1)	C(33)–Ru(3)–Ru(1)	132.9(7)	134.6(5)
C(11)–Ru(1)–Ru(2)	132.9(7)	135.6(4)	C(33)–Ru(3)–Ru(2)	75.6(7)	78.8(5)
C(11)–Ru(1)–Ru(3)	136.7(7)	137.7(4)	C(33)–Ru(3)–Ru(4)	96.2(7)	89.6(5)
C(11)–Ru(1)–Ru(4)	94.4(6)	98.4(4)	Ru(2)–Ru(4)–Ru(1)	57.2(1)	56.9(1)
C(12)–Ru(1)–Ru(2)	125.1(9)	116.9(4)	Ru(3)–Ru(4)–Ru(1)	57.4(1)	58.4(1)
C(12)–Ru(1)–Ru(3)	112.6(9)	120.1(4)	Ru(3)–Ru(4)–Ru(2)	63.3(1)	65.1(1)
C(12)–Ru(1)–Ru(4)	169.9(9)	175.9(4)	M(2)–Ru(4)–Ru(1)	56.4(1)	57.8(1)
C(13)–Ru(1)–Ru(2)	112.4(6)	115.9(4)	M(2)–Ru(4)–Ru(2)	63.5(1)	60.8(1)
C(13)–Ru(1)–Ru(3)	48.5(6)	50.1(4)	M(2)–Ru(4)–Ru(3)	109.8(1)	111.3(1)
C(13)–Ru(1)–Ru(4)	80.8(6)	87.3(4)	C(24)–Ru(4)–Ru(1)	103.2(5)	106.3(4)
C(21)–Ru(1)–Ru(2)	52.2(6)	42.6(4)	C(24)–Ru(4)–Ru(2)	46.3(5)	49.8(4)
C(21)–Ru(1)–Ru(3)	109.3(6)	101.0(4)	C(24)–Ru(4)–Ru(3)	81.8(5)	84.4(4)
C(21)–Ru(1)–Ru(4)	102.9(6)	97.6(4)	C(41)–Ru(4)–Ru(1)	77.4(6)	139.7(4)
Ru(3)–Ru(2)–Ru(1)	58.3(1)	57.9(1)	C(41)–Ru(4)–Ru(2)	134.6(6)	126.1(4)
Ru(4)–Ru(2)–Ru(1)	64.8(1)	63.9(1)	C(41)–Ru(4)–Ru(3)	95.7(6)	85.4(4)
Ru(4)–Ru(2)–Ru(3)	59.1(1)	57.2(1)	C(42)–Ru(4)–Ru(1)	120.0(6)	123.4(4)
M(1)–Ru(2)–Ru(1)	62.2(1)	63.5(1)	C(42)–Ru(4)–Ru(2)	103.6(6)	113.0(4)
M(1)–Ru(2)–Ru(3)	55.6(1)	56.3(1)	C(42)–Ru(4)–Ru(3)	166.5(7)	176.6(4)
M(1)–Ru(2)–Ru(4)	110.2(1)	109.5(1)	C(43)–Ru(4)–Ru(1)	145.5(7)	70.6(4)
M(2)–Ru(2)–Ru(1)	56.6(1)	59.7(1)	C(43)–Ru(4)–Ru(2)	124.1(7)	127.3(4)
M(2)–Ru(2)–Ru(3)	100.4(1)	104.3(1)	C(43)–Ru(4)–Ru(3)	91.1(7)	91.9(4)
M(2)–Ru(2)–Ru(4)	55.1(1)	59.7(1)	Ru(2)–M(1)–Ru(1)	60.9(1)	57.2(1)
M(2)–Ru(2)–M(1)	116.9(1)	120.0(1)	Ru(3)–M(1)–Ru(1)	61.8(1)	59.0(1)
C(21)–Ru(2)–Ru(1)	48.9(6)	63.0(4)	Ru(3)–M(1)–Ru(2)	68.0(1)	65.7(1)
C(21)–Ru(2)–Ru(3)	101.1(6)	111.1(4)	P(1)–M(1)–Ru(1)	140.3(2)	135.7(1)
C(21)–Ru(2)–Ru(4)	106.1(6)	120.2(4)	P(1)–M(1)–Ru(2)	141.3(2)	151.0(1)
C(22)–Ru(2)–Ru(1)	131.8(7)	132.1(4)	P(1)–M(1)–Ru(3)	145.0(2)	142.1(1)
C(22)–Ru(2)–Ru(3)	96.5(7)	89.0(4)	Ru(2)–M(2)–Ru(1)	60.3(1)	58.3(1)
C(22)–Ru(2)–Ru(4)	140.3(7)	128.7(5)	Ru(4)–M(2)–Ru(1)	68.9(1)	63.3(1)
C(23)–Ru(2)–Ru(1)	121.7(8)	135.3(5)	Ru(4)–M(2)–Ru(2)	61.4(1)	59.5(1)
C(23)–Ru(2)–Ru(3)	171.2(7)	158.1(5)	P(2)–M(2)–Ru(1)	135.0(2)	139.5(1)
C(23)–Ru(2)–Ru(4)	112.3(7)	109.1(4)	P(2)–M(2)–Ru(2)	143.0(2)	152.0(1)
C(24)–Ru(2)–Ru(1)	114.1(6)	108.8(3)	P(2)–M(2)–Ru(4)	148.4(2)	141.8(1)
C(24)–Ru(2)–Ru(3)	80.7(6)	76.7(3)	C(111)–P(1)–M(1)	114.6(5)	114.5(3)
C(24)–Ru(2)–Ru(4)	49.8(6)	45.3(3)	C(121)–P(1)–M(1)	112.3(5)	111.6(3)
Ru(2)–Ru(3)–Ru(1)	57.5(1)	56.2(1)	C(131)–P(1)–M(1)	113.5(5)	113.8(3)
Ru(4)–Ru(3)–Ru(1)	63.8(1)	63.4(1)	C(211)–P(2)–M(2)	117.7(5)	111.0(3)
Ru(4)–Ru(3)–Ru(2)	57.5(1)	57.7(1)	C(221)–P(2)–M(2)	116.2(5)	114.3(3)
M(1)–Ru(3)–Ru(1)	62.2(1)	63.5(1)	C(231)–P(2)–M(2)	109.2(5)	115.6(3)
M(1)–Ru(3)–Ru(2)	56.4(1)	58.0(1)	Ru–C–O (terminal)	169(2)—178(2)	170(1)—179(1)
M(1)–Ru(3)–Ru(4)	109.4(1)	111.6(1)	Ru–C–O (bridging)	136(2)—142(2)	116(1)—156(1)

The Ru–C–O angles observed for the ten terminal CO ligands in the structures of (**1**) and (**2**) lie in the expected range [169—178(2) for (**1**) and 170—179(1)° for (**2**)]. However, although the three bridging CO groups in (**1**) and two of the three in (**2**) adopt reasonably symmetrical bonding modes, CO(21) in the structure of (**2**) breaks this pattern by bridging the Ru(1)–Ru(2) vector in a markedly asymmetrical manner [Ru(1)–C(21) 2.589(3) and Ru(2)–C(21) 1.967(4) Å]. Four short contacts between the copper atoms and the carbon atoms of CO ligands occur in compound (**1**) [Cu(1)···C(32) 2.59(3), Cu(1)···C(22) 2.63(3), Cu(2)···C(11) 2.66(3), and Cu(2)···C(42) 2.45(3) Å]. In contrast, however, the CO groups in the silver-containing cluster (**2**) only exhibit one significantly short Ag···C contact [Ag(1)···C(32) 2.69(4) Å]. Short M···C contacts between the coinage metals and essentially linear CO ligands which are bonded to adjacent metals seem to be a structural feature of many Group 1B metal heteronuclear cluster compounds, but the exact nature of the interaction is not well understood.[5]

The metal framework structures adopted by compounds (**1**)—(**3**) are in marked contrast to those exhibited by the analogous dihydrido clusters (**4**)—(**6**), in which one face of a Ru_4 tetrahedron is capped by a $M(PPh_3)$ (M = Cu, Ag, or Au) fragment and a MRu_2 face of the MRu_3 tetrahedron so formed is further capped by the second $M(PPh_3)$ unit, resulting in close contact between the two Group 1B metals. Thus, the change in the overall ligand set which occurs with the formal replacement of two hydrido ligands in (**4**)—(**6**) by the sterically more demanding CO group in (**1**)—(**3**) has been shown to cause a fundamental change in the positioning of the Group 1B metal atoms on the ruthenium tetrahedra of these clusters. This alteration in skeletal geometry adds to previous evidence, both experimental[4—6] and theoretical,[3] that the energy differences between the various structural types are small in many cases for heteronuclear clusters containing $M(PR_3)$ groups.

Interestingly, a similar change in Group 1B metal arrangement to that reported herein has been previously observed from *X*-ray diffraction studies of two Cu_2Ru_6 clusters when an interstitial carbido ligand is formally replaced by two CO groups. In the case of the carbido cluster $[Cu_2Ru_6C(CO)_{16}(NCMe)_2]$, one face of a Ru_6 octahedron is capped by a Cu(NCMe) group and one $CuRu_2$ face of the $CuRu_3$ tetrahedron so formed is capped by the second Cu(NCMe) fragment, resulting in close contact between the two copper atoms.[16] However, in the closely related cluster $[Cu_2Ru_6(CO)_{18}(C_6H_5Me)_2]$, the two $Cu(C_6H_5Me)$ units cap opposite faces of a Ru_6 octahedron so that there is no close contact between the copper atoms.[12,13] Bradley and co-workers[12] have suggested that the spatial constraints imposed by the different numbers of carbonyl ligands cause two distinct skeletal geometries to be adopted by the two closely related cluster compounds. However, the possibility that the steric requirements of the ligands attached to the copper atoms influence the metal framework structures of these octanuclear copper–ruthenium species cannot be ruled out on the evidence available. It has recently been shown that the formal replacement of the two PPh_3 ligands bonded to the copper atoms in cluster (**4**) by sterically more demanding $P(cyclo\text{-}C_6H_{11})_3$ groups causes a change to a metal core structure in which there is no close contact between the copper atoms.[17] In addition, it has been suggested that the steric demands of carbonyl ligands influence the structures of a series of heteronuclear clusters containing three gold atoms.[18] Although theoretical calculations indicate that *closo*-Au_3 units are particularly stable,[2] such a unit is only observed in the metal framework of the first member of the series of similar trigold clusters $[Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3]$,[18] $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$,[19] $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$,[20] and $[Au_3CoRu_3(CO)_{12}(PPh_3)_3]$.[21] It has been suggested that the last three clusters are all forced to adopt an electronically less favoured gold atom arrangement because of the greater steric constraints imposed, having nine carbonyl groups attached to the $CoRu_2$ or Ru_3 faces in these species instead of the eight carbonyl ligands bonded to the Ru_3 face of $[Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3]$.[18]

Osmium analogues of the gold-containing clusters $[Au_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (**3**) and $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (**6**) have also been reported.[22,23] The dihydrido cluster $[Au_2Os_4(\mu\text{-}H)_2(CO)_{12}(PPh_3)_2]$ exists as two skeletal isomers in the solid state. One isomer has a somewhat similar structure to that of (**6**), although one Au–Os separation in the metal framework may be too long for there to be any significant bonding interaction between the two atoms, and the structure of the second isomeric form is not known.[22] The formal replacement of the two hydrido ligands in the above osmium-containing cluster compound by a carbonyl ligand in $[Au_2Os_4(\mu\text{-}CO)(CO)_{12}(PPh_3)_2]$ results in a change in the overall skeletal geometry to capped square-based pyramidal, but the gold atoms still remain in close contact.[23] It is interesting that this variation in skeletal geometry is in marked contrast to that reported herein for the same formal change of ligands in the analogous ruthenium-containing clusters (**3**) and (**6**).

In marked contrast to the ambient-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the silver-containing dihydrido cluster (**5**), which is severely broadened by a dynamic process involving intermolecular exchange of PPh_3 ligands,[7] that of the closely related species (**2**) has narrow linewidths. Thus, there is no evidence that the PPh_3 ligands in (**2**) undergo intermolecular exchange between clusters at ambient temperature in solution. This observation is interesting, since similar dynamic behaviour is well established for PR_3 (R = alkyl or aryl) ligands in mixed-metal clusters containing one or two $Ag(PR_3)$ fragments.[5,7,10,11]

Experimental

The techniques used and the instrumentation employed have been described elsewhere.[24] Light petroleum refers to that fraction of b.p. 40—60 °C. Established methods were used to prepare the salt $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]\cdot thf$[25] and the complexes $[Cu(NCMe)_4]PF_6$[26] and $[AuCl(PPh_3)]$.[27] The compound $[Ag(NCMe)_4]PF_6$ was synthesized by an adaptation of the published route.[26,28] Analytical and other physical data for the new cluster compounds are presented in Table 1, together with their i.r. spectra, and Table 2 summarizes the results of n.m.r. spectroscopic measurements. Product separation by column chromatography was performed on Aldrich Florisil (100—200 mesh).

Synthesis of the Compounds $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu *or* Ag).—A dichloromethane (20 cm³) solution of $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]\cdot thf$ (0.60 g, 0.31 mmol) at −30 °C was treated with a solution of $[M(NCMe)_4]PF_6$ (M = Cu, 0.23 g, 0.62 mmol; M = Ag, 0.26 g, 0.62 mmol) in dichloromethane (20 cm³) and then, after stirring the reaction mixture at −30 °C for 1 min, a dichloromethane (10 cm³) solution containing PPh_3 (0.16 g, 0.62 mmol) was added. The mixture was allowed to warm to −15 °C with stirring and the solvent was then removed under reduced pressure at the same temperature. The residue was extracted with a dichloromethane–diethyl ether mixture (1:4; 25-cm³ portions), which had been previously cooled to −15 °C, until the extracts were no longer coloured brown and the combined extracts were filtered through a Celite pad (1 × 3 cm) at −15 °C. The filtrate was collected at −15 °C and the solvent was removed under reduced pressure at the same temperature. The crude product was dissolved in a dichloromethane–light petroleum mixture (M = Cu, 1:1; M = Ag, 2:3), which had been previously cooled to −15 °C, and then chromatographed on a Florisil column (20 × 3 cm) at −20 °C. Elution with a dichloromethane–light petroleum mixture of the same proportions as above afforded a dark brown fraction in each case. After collection of this fraction at −15 °C and removal of the solvent under reduced pressure at the same

Table 4. Fractional atomic co-ordinates, with estimated standard deviations in parentheses, for $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ [M = Cu (**1**) or Ag (**2**)]

	(**1**)			(**2**)		
Atom	*x*	*y*	*z*	*y*	*y*	*z*
Ru(1)	0.320 19(8)	0.209 05(10)	0.093 51(12)	0.279 49(4)	0.062 67(8)	−0.203 21(11)
Ru(2)	0.297 07(7)	0.078 93(9)	0.198 45(13)	0.207 81(4)	−0.137 37(8)	−0.245 81(11)
Ru(3)	0.236 70(7)	0.228 94(10)	0.229 89(12)	0.288 40(4)	−0.076 38(9)	0.010 10(10)
Ru(4)	0.200 45(7)	0.129 16(10)	0.079 74(12)	0.189 70(4)	0.070 77(9)	−0.024 46(11)
M(1)	0.349 9(1)	0.199 1(1)	0.285 3(2)	0.321 67(4)	−0.207 51(8)	−0.239 48(11)
M(2)	0.295 8(1)	0.078 2(1)	0.000 7(2)	0.169 24(4)	0.111 58(8)	−0.296 88(10)
P(1)	0.425 4(2)	0.228 0(3)	0.389 2(4)	0.398 1(1)	−0.328 7(3)	−0.340 4(3)
P(2)	0.334 4(2)	0.018 2(3)	−0.120 0(4)	0.116 4(1)	0.246 5(3)	−0.431 0(3)
C(11)	0.321 9(9)	0.225 9(12)	−0.033 3(16)	0.274 2(5)	0.227 0(13)	−0.220 1(14)
O(11)	0.323 2(7)	0.244 3(9)	−0.112 0(13)	0.273 5(4)	0.336 4(10)	−0.227 8(10)
C(12)	0.386 2(12)	0.271 5(16)	0.111 5(19)	0.333 1(5)	0.045 9(12)	−0.316 7(14)
O(12)	0.430 6(9)	0.309 2(12)	0.125 8(14)	0.366 8(4)	0.039 8(10)	−0.389 6(11)
C(13)	0.265 4(9)	0.301 6(13)	0.123 6(15)	0.330 3(5)	0.080 2(11)	0.960 6(12)
O(13)	0.253 8(7)	0.362 6(10)	0.090 1(11)	0.368 3(4)	0.140 0(9)	0.017 9(10)
C(21)	0.381 1(10)	0.118 2(13)	0.134 3(16)	0.239 8(6)	−0.107 2(13)	−0.405 4(16)
O(21)	0.430 0(6)	0.097 2(8)	0.127 5(10)	0.246 3(4)	−0.121 9(10)	−0.517 8(11)
C(22)	0.314 4(10)	0.056 4(13)	0.319 0(17)	0.219 0(6)	−0.307 4(14)	−0.243 9(14)
O(22)	0.325 4(7)	0.036 1(9)	0.397 5(12)	0.222 4(4)	−0.417 9(10)	−0.241 4(11)
C(23)	0.324 5(10)	−0.018 4(14)	0.166 7(16)	0.142 4(6)	−0.175 8(12)	−0.348 8(14)
O(23)	0.344 9(7)	−0.078 4(10)	0.154 1(12)	0.102 1(4)	−0.202 0(10)	−0.414 3(11)
C(24)	0.209 3(8)	0.043 4(11)	0.187 5(14)	0.154 7(5)	−0.102 9(13)	−0.080 4(14)
O(24)	0.178 4(6)	−0.001 4(8)	0.227 8(10)	0.120 8(4)	−0.164 5(9)	−0.051 3(10)
C(31)	0.163 7(10)	0.277 2(13)	0.206 4(16)	0.299 5(5)	0.015 7(13)	0.189 0(15)
O(31)	0.117 7(8)	0.311 1(10)	0.187 3(13)	0.308 4(4)	0.075 3(11)	0.297 2(12)
C(32)	0.268 7(9)	0.302 7(13)	0.316 6(15)	0.357 3(5)	−0.162 4(12)	0.026 2(13)
O(32)	0.283 0(6)	0.348 8(8)	0.371 0(10)	0.400 1(4)	−0.206 2(9)	0.053 4(10)
C(33)	0.210 8(9)	0.164 4(12)	0.324 3(16)	0.247 5(6)	−0.207 7(15)	0.051 8(16)
O(33)	0.190 0(7)	0.134 5(9)	0.387 1(12)	0.226 6(5)	−0.282 8(12)	0.093 0(13)
C(41)	0.190 1(9)	0.207 4(12)	−0.008 5(15)	0.180 1(6)	0.057 1(13)	0.154 1(16)
O(41)	0.179 5(7)	0.253 2(9)	−0.066 7(12)	0.173 5(4)	0.043 5(10)	0.262 0(12)
C(42)	0.187 4(9)	0.047 5(13)	−0.001 3(15)	0.122 1(5)	0.159 2(12)	−0.048 8(13)
O(42)	0.172 1(7)	−0.004 9(10)	−0.049 0(12)	0.079 9(4)	0.212 9(9)	−0.054 0(10)
C(43)	0.120 9(11)	0.132 4(13)	0.121 1(16)	0.226 8(6)	0.226 6(14)	0.025 1(15)
O(43)	0.069 4(8)	0.131 6(10)	0.132 6(13)	0.244 0(4)	0.328 1(10)	0.068 6(11)
C(111)	0.478 5(5)	0.148 9(6)	0.415 1(9)	0.382 8(3)	−0.409 5(8)	−0.517 6(7)
C(112)	0.479 6(5)	0.088 8(6)	0.350 4(9)	0.357 9(3)	−0.338 2(8)	−0.609 4(7)
C(113)	0.523 0(5)	0.030 3(6)	0.361 7(9)	0.345 3(3)	−0.396 8(8)	−0.744 8(7)
C(114)	0.565 2(5)	0.031 9(6)	0.437 6(9)	0.357 7(3)	−0.526 7(8)	−0.788 3(7)
C(115)	0.564 0(5)	0.091 9(6)	0.502 3(9)	0.382 7(3)	−0.598 1(8)	−0.696 4(7)
C(116)	0.520 7(5)	0.150 4(6)	0.491 1(9)	0.395 3(3)	−0.539 5(8)	−0.561 0(7)
C(121)	0.398 1(6)	0.258 5(8)	0.500 1(8)	0.454 3(3)	−0.227 4(7)	−0.341 0(9)
C(122)	0.346 5(6)	0.222 1(8)	0.530 4(8)	0.482 0(3)	−0.235 2(7)	−0.455 6(9)
C(123)	0.321 8(6)	0.246 2(8)	0.612 4(8)	0.524 5(3)	−0.154 3(7)	−0.452 0(9)
C(124)	0.348 7(6)	0.306 7(8)	0.664 3(8)	0.539 4(3)	−0.065 6(7)	−0.333 8(9)
C(125)	0.400 3(6)	0.343 1(8)	0.634 0(8)	0.511 8(3)	−0.057 8(7)	−0.219 2(9)
C(126)	0.425 0(6)	0.319 0(8)	0.552 0(8)	0.469 2(3)	−0.138 7(7)	−0.222 8(9)
C(131)	0.472 7(6)	0.308 8(7)	0.353 7(9)	0.425 8(3)	−0.453 2(6)	−0.253 7(8)
C(132)	0.534 5(6)	0.299 7(7)	0.342 0(9)	0.481 6(3)	−0.482 9(6)	−0.239 4(8)
C(133)	0.568 3(6)	0.361 9(7)	0.311 1(9)	0.501 2(3)	−0.584 4(6)	−0.178 4(8)
C(134)	0.540 3(6)	0.433 1(7)	0.291 8(9)	0.464 9(3)	−0.656 2(6)	−0.131 8(8)
C(135)	0.478 5(6)	0.442 1(7)	0.303 5(9)	0.409 0(3)	−0.626 5(6)	−0.146 1(8)
C(136)	0.444 7(6)	0.379 9(7)	0.334 4(9)	0.389 5(3)	−0.525 1(6)	−0.207 1(8)
C(211)	0.357 9(6)	−0.082 1(6)	−0.104 4(10)	0.072 4(3)	0.359 2(8)	−0.328 4(8)
C(212)	0.320 3(6)	−0.131 2(6)	−0.057 0(10)	0.015 7(3)	0.354 3(8)	−0.344 5(8)
C(213)	0.335 3(6)	−0.209 3(6)	−0.045 4(10)	−0.015 5(3)	0.437 8(8)	−0.255 1(8)
C(214)	0.388 0(6)	−0.238 3(6)	−0.081 2(10)	0.009 9(3)	0.526 4(8)	−0.149 4(8)
C(215)	0.425 7(6)	−0.189 1(6)	−0.128 6(10)	0.066 7(3)	0.531 3(8)	−0.133 3(8)
C(216)	0.410 6(6)	−0.111 0(6)	−0.140 2(10)	0.097 9(3)	0.447 7(8)	−0.222 8(8)
C(221)	0.287 5(6)	0.017 7(9)	−0.227 3(10)	0.156 8(3)	0.346 1(8)	−0.502 8(9)
C(222)	0.294 5(6)	−0.038 3(9)	−0.295 6(10)	0.136 3(3)	0.462 3(8)	−0.532 8(9)
C(223)	0.258 7(6)	−0.035 5(9)	−0.378 7(10)	0.168 6(3)	0.534 7(8)	−0.590 6(9)
C(224)	0.215 9(6)	0.023 3(9)	−0.393 3(10)	0.221 3(3)	0.491 0(8)	−0.618 4(9)
C(225)	0.208 9(6)	0.079 3(9)	−0.325 0(10)	0.241 9(3)	0.374 7(8)	−0.588 3(9)
C(226)	0.244 7(6)	0.076 5(9)	−0.241 9(10)	0.209 6(3)	0.302 3(8)	−0.530 5(9)
C(231)	0.402 5(5)	0.068 2(7)	−0.150 3(10)	0.071 7(3)	0.163 5(8)	−0.572 8(8)
C(232)	0.451 9(5)	0.066 6(7)	−0.085 4(10)	0.063 9(3)	0.034 0(8)	−0.581 8(8)
C(233)	0.503 1(5)	0.111 3(7)	−0.099 6(10)	0.031 7(3)	−0.033 9(8)	−0.691 9(8)
C(234)	0.504 9(5)	0.157 6(7)	−0.178 8(10)	0.007 3(3)	0.027 7(8)	−0.792 8(8)
C(235)	0.455 6(5)	0.159 2(7)	−0.243 8(10)	0.015 1(3)	0.157 2(8)	−0.783 8(8)
C(236)	0.404 3(5)	0.114 5(7)	−0.229 6(10)	0.047 2(3)	0.225 2(8)	−0.673 7(8)

temperature, recrystallization of residue from a diethyl ether–light petroleum mixture by layer diffusion at −20 °C afforded dark brown *microcrystals* of $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu, 0.18 g; M = Ag, 0.17 g).

Synthesis of the Compound $[Au_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$.—A dichloromethane (20 cm^3) solution of $[N(PPh_3)_2]_2[Ru_4(CO)_{13}]$·thf (0.60 g, 0.31 mmol) at −30 °C was treated with a solution of $[AuCl(PPh_3)]$ (0.31 g, 0.63 mmol) in dichloromethane (20 cm^3), which had been previously cooled to −30 °C, and solid $TlPF_6$ (0.40 g, 1.14 mmol). The reaction mixture was stirred at −15 °C for 20 min and the solvent was removed under reduced pressure at the same temperature. The residue was extracted with diethyl ether (20-cm^3 portions), which had been previously cooled to −15 °C, until the extracts were no longer coloured brown and the combined extracts were filtered through a Celite pad (1 × 3 cm) at −15 °C. The filtrate was collected at −15 °C and the solvent was removed under reduced pressure at the same temperature. Three successive recrystallizations of the crude product from diethyl ether–light petroleum by layer diffusion at −20 °C afforded dark brown *microcrystals* of $[Au_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (0.34 g).

Crystal Structure Determinations for Complexes (**1**) *and* (**2**).—Suitable crystals of complexes (**1**) and (**2**) were grown from diethyl ether–light petroleum by slow layer diffusion at −20 °C.

Crystal data: for (**1**). $C_{49}H_{30}Cu_2O_{13}P_2Ru_4$, M = 1 419.79, monoclinic, space group $P2_1/n$, a = 22.110(2), b = 17.247(3), c = 14.407(3) Å, β = 93.44(2)°, U = 5 483.94 $Å^3$, $F(000)$ = 2 768, $\mu(\text{Mo-}K_\alpha)$ = 18.12 cm^{-1}, Z = 4, D_c = 1.72 g cm^{-3}.

For (**2**). $C_{49}H_{30}Ag_2O_{13}P_2Ru_4$, M = 1 508.44, triclinic, space group $P\bar{1}$ (no. 2), a = 24.685(3), b = 10.710(2), c = 10.137(3) Å, α = 102.03(2), β = 96.20(2), γ = 86.47(2)°, U = 2 603.69 $Å^3$, $F(000)$ = 1 456, $\mu(\text{Mo-}K_\alpha)$ = 18.07 cm^{-1}, Z = 2, D_c = 1.93 g cm^{-3}.

Data collection. The methods of data collection and data processing used for clusters (**1**) and (**2**) were similar to those described previously.[29] The crystals selected for data collection had dimensions 0.25 × 0.22 × 0.13 mm for (**1**) and 0.29 × 0.22 × 0.10 mm for (**2**). A scan width of 0.8° in θ was used to collect data in the θ range 3—25° by the ω—2θ technique. Equivalent reflections were merged to give 4 467 and 5 065 unique data with $I/\sigma(I) > 3.0$ for (**1**) and (**2**), respectively. No absorption corrections were applied.

Structure solution and refinement. For both clusters (**1**) and (**2**) the positions of the metal atoms were deduced from a Patterson synthesis. The remaining non-hydrogen atoms were found from subsequent Fourier difference syntheses. Anisotropic thermal parameters were assigned to the metal and phosphorus atoms during final cycles of refinement.[30] Full-matrix refinement of the atomic positional and thermal parameters converged at final R and R' values of 0.0659 and 0.0660 for (**1**) and 0.0503 and 0.0513 for (**2**), with weights of $w = 1/\sigma^2(F_o)$ assigned to individual reflections. The phenyl rings were treated as rigid hexagons [d[C=C] = 1.395, d(C–H) = 1.08 Å] with fixed thermal parameters of 0.08 $Å^2$ for the H atoms.

The final atomic co-ordinates for complexes (**1**) and (**2**) are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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