The Heteronuclear Cluster Chemistry of the Group 1B Metals. Part 15.[1] Effect of the Nature of the Group 1B Metals and the Cone Angles of the Attached Phosphine Ligands on the Metal Framework Structures of Heteronuclear Cluster Compounds. Synthesis, Structures, and Dynamic Behaviour of the Bimetallic Hexanuclear Cluster Compounds $[M_2Ru_4H_2(CO)_{12}(PR_3)_2]$ (M = Cu, R = $CHMe_2$ or C_6H_{11}; M = Ag or Au, R = $CHMe_2$, C_6H_{11}, or CMe_3)

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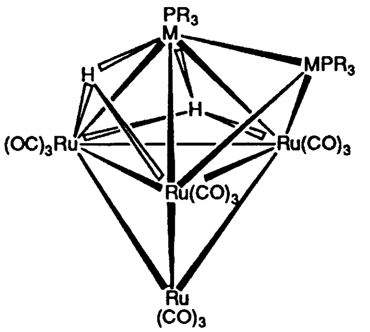
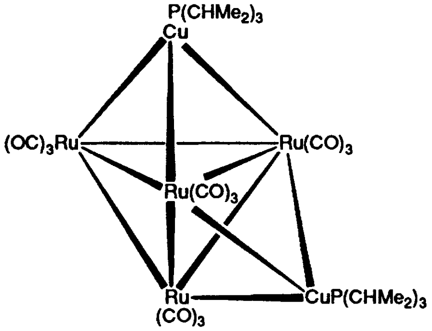
Treatment of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with 2 equivalents of the complex $[M(NCMe)_4]PF_6$ at −30 °C, followed by the addition of 2 equivalents of PR_3, affords the hexanuclear cluster compounds $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PR_3)_2]$ [M = Cu, R = $CHMe_2$, or C_6H_{11} (C_6H_{11} = cyclohexyl); M = Ag, R = $CHMe_2$, C_6H_{11}, or CMe_3] in *ca.* 50—65% yield. The analogous gold-containing species $[Au_2Ru_4H_2(CO)_{12}(PR_3)_2]$ (R = $CHMe_2$, C_6H_{11}, or CMe_3) were prepared in *ca.* 30—50% yield from the reaction of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with 2 equivalents of the compound $[AuCl(PR_3)]$, in the presence of $TlPF_6$. Despite the relatively large size of the $P(C_6H_{11})_3$ ligand, the clusters $[M_2Ru_4H_2(CO)_{12}\{P(C_6H_{11})_3\}_2]$ (M = Ag or Au) still adopt the capped trigonal-bipyramidal skeletal geometry, with the Group 1 B metals in close contact, which previous work has shown is preferred by clusters of general formula $[M_2Ru_4H_2(CO)_{12}L_2]$ (M = Cu, Ag, or Au) when L is a smaller monodentate phosphine or phosphite ligand. However, the smaller size of the copper atom relative to silver and gold means that the $P(C_6H_{11})_3$ ligand is too bulky to allow two adjacent $Cu\{P(C_6H_{11})_3\}$ fragments to be accommodated in the metal framework of $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(C_6H_{11})_3\}_2]$. Thus, the cluster is forced to adopt a sterically less-demanding skeletal geometry, which consists of a Ru_4 tetrahedron with one edge bridged by a $Cu\{P(C_6H_{11})_3\}$ unit and a non-adjacent face capped by the second such group. When the phosphine ligand $P(CMe_3)_3$, which is larger than $P(C_6H_{11})_3$, is attached to the Group 1 B metals in the clusters $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CMe_3)_3\}_2]$ (M = Ag or Au), the silver- and gold-containing species are also forced to adopt a similar sterically less-demanding edge-bridged trigonal-bipyramidal metal core structure. In addition, the $P(CMe_3)_3$ ligand seems to be too bulky to allow a hexanuclear cluster of formula $[Cu_2Ru_4H_2(CO)_{12}\{P(CMe_3)_3\}_2]$ even to adopt an edge-bridged trigonal-bipyramidal metal framework structure and an attempt to prepare this species afforded the pentanuclear cluster $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$ instead. The phosphine ligand $P(CHMe_2)_3$, which is smaller than $P(C_6H_{11})_3$, is not sufficiently bulky to cause the metal cores of $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CHMe_2)_3\}_2]$ (M = Cu, Ag, or Au) to change from the preferred capped trigonal-bipyramidal skeletal geometry in the solid state, but a second isomer of the copper-containing cluster, which probably has two face-capping $Cu\{P(CHMe_2)_3\}$ units with no bonding interaction between them, is also present in solution at low temperatures. Variable-temperature $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopic studies demonstrate that the new Group 1 B metal heteronuclear cluster compounds undergo a variety of interesting dynamic processes in solution.

Theoretical studies[2,3] of the bonding capabilities of $M(PR_3)$ (M = Cu, Ag, or Au; R = alkyl or aryl) units suggest that the differences in energy between the various structural types can be very small for mixed-metal clusters which contain these fragments. This prediction is supported by experimental evidence[4—6] which shows that Group 1B metal heteronuclear clusters with very similar stoicheiometries can exhibit markedly different metal core structures, skeletal isomerism can occur, both in solution and in the solid state, and the metal skeletons of this class of compound are often stereochemically non-rigid in solution.

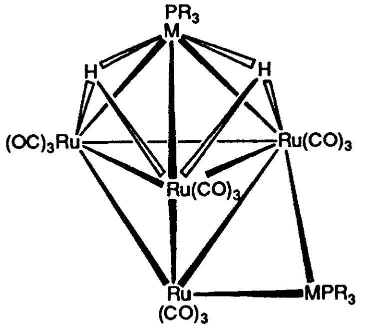
In an earlier paper in this series,[7] one of us demonstrated that the formal replacement of the two hydrido ligands in the clusters $[M_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ [M = Cu, (1); Ag, (2); or Au, (3)] by the sterically more demanding CO group causes a fundamental change in their metal framework structures. The dihydrido species all adopt a capped trigonal-bipyramidal skeletal geometry, with the two coinage metals in close contact,[8] whereas the series of clusters $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu, Ag, or Au) all exhibit a metal core structure which consists of a Ru_4 tetrahedron with two Ru_3 faces capped by the $M(PPh_3)$ fragments.[7] In addition, one of us has recently reported[9—11] that the formal replacement of the two PPh_3 ligands attached to the gold atoms in (3) by the bidentate ligands $Ph_2E(CH_2)_nE'Ph_2$ (n = 1, E = As, E′ = As or P; n = 1 or 2, E = E′ = P) or *cis*-$Ph_2PCH{=}CHPPh_2$ alters the capped trigonal-bipyramidal metal core structure of the former cluster to or towards a capped square-based pyramidal skeletal geometry. In view of these interesting results, we anticipated that we might also be able to alter the skeletal geometries of (1)—(3) by increasing the magnitude of the cone angle[12] of the monodentate phosphine ligands attached to the coinage metals.



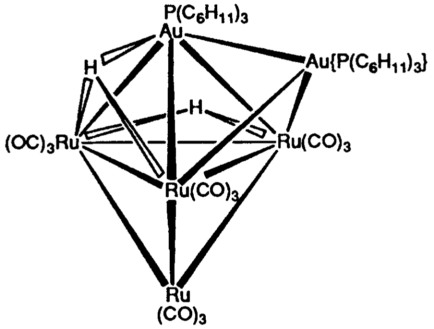
	M	R
(1)	Cu	Ph
(2)	Ag	Ph
(3)	Au	Ph
(4a)	Cu	$CHMe_2$
(6)	Ag	$CHMe_2$
(7)	Ag	C_6H_{11}
(9)	Au	$CHMe_2$



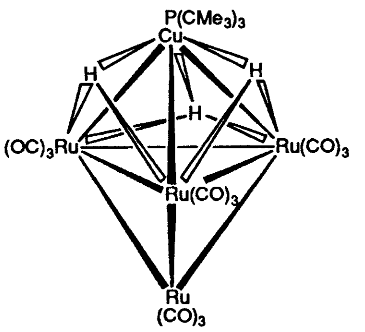
(4b)



	M	R
(5)	Cu	C_6H_{11}
(8)	Ag	CMe_3
(11)	Au	CMe_3
(12)	Cu	CH_2Ph



(10)



(13)

C_6H_{11} = Cyclohexyl. The positions of the hydrido ligands in (**4b**) are not known.

Although a capped trigonal-bipyramidal metal framework structure, with the Group 1B metals in close contact, seems to be the preferred skeletal geometry for clusters of general formula $[M_2Ru_4H_2(CO)_{12}L_2]$ when L is PPh_3[8] or a monodentate phosphine or phosphite ligand with a smaller cone angle than that of PPh_3,[13,14] we thought it possible that more sterically demanding monodentate phosphine ligands might be too bulky to allow two adjacent $M(PR_3)$ (M = Cu, Ag, or Au; R = alkyl or aryl) units to be accommodated in this type of metal core structure. Our interest in studying the problem was also stimulated by previous reports[15,16] stating that small alterations in the nature of the monodentate phosphine ligands

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

	Cluster	M.p. (θ_c/°C) (decomp.)	$\nu_{max.}$(CO)[b]/cm^{-1}	Yield[c] (%)	Analysis (%)	
					C	H
(4)	$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CHMe_2)_3\}_2]$	163—166	2063m, 2027vs, 2000vs (br), 1980 (sh), 1940m (vbr)	59	30.4 (30.3)	3.7 (3.7)
(5)	$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(C_6H_{11})_3\}_2]$	134—137	2063m, 2030s, 2000vs (br), 1975 (sh), 1943m (br), 1928 (sh), 1915 (sh)	64	40.2 (40.3)	4.8 (4.8)
(6)	$[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CHMe_2)_3\}_2]$	177—180	2068s, 2027vs, 2017vs, 2001s, 1980m, 1967m, 1932w (br)	64	28.1 (28.2)	3.5 (3.4)
(7)	$[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(C_6H_{11})_3\}_2]$	153—156	2066s, 2028vs, 2016vs, 2000s, 1975m, 1965m, 1934w (br)	52	37.9 (37.9)	4.5 (4.5)
(8)	$[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CMe_3)_3\}_2]$	166—169	2062m, 2031s, 1999vs (br), 1936w (br)	60	31.7 (31.7)	4.3 (4.1)
(9)	$[Au_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CHMe_2)_3\}_2]$	147—151	2068s, 2028vs, 2020vs, 2003vs, 1982m, 1968m (br)	52	24.8 (24.7)	3.0 (3.0)
(10)	$[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}\text{-}\{P(C_6H_{11})_3\}_2]$	127—129	2066s, 2028 (sh), 2018vs, 2002vs, 1980m, 1965m (br)	46	34.1 (34.0)	4.2 (4.0)
(11)	$[Au_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CMe_3)_3\}_2]$	171—174	2063w, 2035m, 2007vs (br), 1957w (br)	33	28.0 (28.1)	3.6 (3.6)
(13)	$[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$	121—124	2087m, 2060s, 2048vs, 2021vs, 1995s (br)	48[d]	28.6 (28.6)	2.8 (3.0)

[a] Calculated values are given in parentheses. [b] Measured in dichloromethane solution. [c] Based on ruthenium reactant. [d] The yield quoted is that from the preparation using the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ as the starting material. The cluster can also be prepared in 58% yield from $[N(PPh_3)_2][Ru_4(\mu\text{-}H)_3(CO)_{12}]$.

attached to homonuclear gold clusters can have a significant effect on their skeletal geometries.* Therefore, we wished to synthesize clusters analogous to the PPh_3-containing species (1)—(3), in which the Group 1B metals are ligated by a selection of monodentate phosphine ligands with larger cone angles than that of PPh_3 (145°)[12] and to investigate whether the bulky ligands cause alterations in the metal framework structures of these compounds. A part of this investigation, involving the effect of the formal replacement of the two PPh_3 groups in (1) and (2) by one or two $P(CH_2Ph)_3$ ligands (cone angle 165°),[12] has already been published[1] and the remainder of the results from the study are presented herein. A preliminary account[18] describing some aspects of this latter work has previously appeared.

Results and Discussion

Synthesis of the Clusters $[M_2Ru_4H_2(CO)_{12}(PR_3)_2]$ (M = Cu, R = $CHMe_2$ *or* C_6H_{11}; M = Ag *or* Au, R = $CHMe_2$, C_6H_{11}, *or* CMe_3).—Treatment of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with 2 equivalents of the complex $[M(NCMe)_4]PF_6$ (M = Cu or Ag) at −30 °C and the subsequent addition of 2 equivalents of PR_3 (M = Cu, R = $CHMe_2$ or C_6H_{11}; M = Ag, R = $CHMe_2$, C_6H_{11}, or CMe_3) affords the dark red cluster compounds $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PR_3)_2]$ [M = Cu, R = $CHMe_2$, (4), or C_6H_{11}, (5); M = Ag, R = $CHMe_2$, (6), C_6H_{11}, (7) or CMe_3, (8)] in *ca.* 50—65% yield. The analogous gold-containing clusters $[Au_2Ru_4H_2(CO)_{12}(PR_3)_2]$ [R = $CHMe_2$, (9); C_6H_{11}, (10); or CMe_3, (11)] were prepared in *ca.* 30—50% yield from the reaction of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with 2 equivalents of the compound $[AuCl(PR_3)]$, in the presence of $TlPF_6$. The clusters (4)—(11) were characterized by microanalysis and by spectroscopic measurements (Tables 1 and 2).

Spectroscopic Characterization, Skeletal Geometries and Dynamic Behaviour.—$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(C_6H_{11})_3\}_2]$ (5). The i.r. and n.m.r. spectroscopic data (Tables 1 and 2) of compound (5) are significantly different to those reported[8,13] for the analogous copper-containing species (1) and $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ [L = $PMePh_2$, PMe_2Ph, PEt_3, PMe_3, $P(OEt)_3$, $P(OPh)_3$, or $P(OMe)_3$], which all exhibit capped trigonal-bipyramidal skeletal geometries with the two copper atoms in close contact, but they are closely similar to those of $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2]$ (12).[1] Thus, the spectroscopic data suggest that (5) adopts a similar sterically less-demanding metal framework structure, consisting of a Ru_4 tetrahedron with one edge bridged by a $Cu\{P(C_6H_{11})_3\}$ unit and a non-adjacent face capped by the second such group, to that established for the $P(CH_2Ph)_3$-ligated species (12).[1] This hypothesis has been confirmed by a single-crystal *X*-ray diffraction study on (5)[18] and the bond lengths within the edge-bridged trigonal-bipyramidal metal cores of (5) and (12) have been compared elsewhere.[1]

The skeletal geometries of compounds (5) and (12) are very unusual. In almost all previously reported mixed-metal clusters containing two or more $M(PR_3)$ (M = Cu, Ag, or Au; R = alkyl or aryl) units, the Group 1B metal fragments either all adopt face-capping positions or all occupy edge-bridging sites.[5] Also, whenever the possibility of a $Cu(PR_3)$ group being able to adopt either an edge-bridging or a face-capping position arises, the latter bonding mode is preferred in almost every case.[5] However, it is not surprising that (5) and (12) exhibit the same metal framework structure, as we have previously shown[1] that the $P(CH_2Ph)_3$ ligand (cone angle 165°)[12] is too bulky to allow two $Cu\{P(CH_2Ph)_3\}$ units to be adjacent in the metal core structure of (12) and the cone angle of $P(C_6H_{11})_3$ is 5° larger than that of $P(CH_2Ph)_3$.[12] Thus, the $P(C_6H_{11})_3$-ligated species (5), like the analogous $P(CH_2Ph)_3$-containing cluster (12), is forced to adopt a novel edge-bridged trigonal-bipyramidal geometry instead of the capped trigonal-bipyramidal metal framework structure, which is normally preferred.[8,13]

Although the two phosphorus resonances and the two high-field hydrido ligand signals that are observed at −100 °C in the

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* When we began the work described herein, there were no reports of similar studies on heteronuclear Group 1B metal cluster compounds, to the best of our knowledge, but Housecroft *et al*[17] have very recently described how the size of the attached phosphine ligands can influence the skeletal geometries adopted by some gold–iron species.

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

Cluster	Ambient-temp. ^{1}H n.m.r. data[b]	Low-temp. ^{1}H n.m.r. hydrido ligand signal[b,c]	Ambient-temp. ^{31}P-{^{1}H} data[d]	Low-temp. ^{31}P-{^{1}H} data[c,d]
(**4**)	−16.64 [t, 2 H, μ_3-H, *J*(PH) 5], 1.25 [d of d, 36 H, CH*Me*$_2$, *J*(PH) 14, *J*(HH) 7], 2.26 [overlapping d of septets, 6 H, C*H*Me$_2$, *J*(PH) 7, *J*(HH) 7]	−17.09 [d, isomer A, *J*(PH) 10], −16.2 (s,vbr, isomer B)	28.3 (s,br)	[e] 32.0 (s, isomer A, 1 P), 26.0 (s, isomer B, 0.6 P), 18.7 (s, isomer A, 1 P)
(**5**)	−16.44 [t, 2 H, μ_3-H, *J*(PH) 5], 1.25—2.15 (m, 66 H, C_6H_{11})	−17.12 (s,br), −16.18 (s,br)	19.4 (s,br)	17.6 (s,br), 17.2 (s,br)
(**6**)	−16.89 [overlapping t of t, 2 H, μ_3-H, *J*(AgH)$_{av.}$ 11, *J*(PH) 5], 1.32 [d of d, 36 H, CH*Me*$_2$, *J*(PH) 15, *J*(HH) 7], 2.26 [overlapping d of d of septets, 6 H, C*H*Me$_2$, *J*(PH) 7, *J*(HH) 7, *J*(AgH)$_{av.}$ 3]	[e,f] −17.12 [d of d, 2 H, *J*(AgH)$_{av.}$ 23, *J*(PH) 8]	[g] 47.9 (m)	[e] 49.9 [2 × d of d, $^1J(^{109}$AgP) 562, $^1J(^{107}$AgP) 487, ^2J(AgP)$_{av.}$7], 44.3 [2 × d of d, $^1J(^{109}$AgP) 485, $^1J(^{107}$AgP) 420, ^2J(AgP)$_{av.}$11]
(**7**)	−16.80 [overlapping t of t, 2 H, μ_3-H, *J*(AgH)$_{av.}$ 10, *J*(PH) 5], 1.29—2.15 (m, 66 H, C_6H_{11})	[e] −17.12 [d of d, 2 H, *J*(AgH)$_{av.}$ 21, *J*(PH) 7]	[g] 38.1 (m)	[e] 39.3 [2 × d of d, $^1J(^{109}$AgP) 558, $^1J(^{107}$AgP) 483, ^2J(AgP)$_{av.}$6], 37.0 [2 × d of d, $^1J(^{109}$AgP) 483, $^1J(^{107}$AgP) 418, ^2J(AgP)$_{av.}$12]
(**8**)	−14.96 [t, 2 H, μ_3-H, *J*(PH) 11], *1.51* [d, 54 H, CMe$_3$, *J*(PH) 13]	−16.11 (s,br)	9.1 [2 × d, $J(^{109}$AgP) 517, $J(^{107}$AgP) 448]	[e] 14.0 [2 × d br, $J(^{109}$AgP) 512, $J(^{107}$AgP) 443]
(**9**)	−13.90 [t, 2 H, μ_3-H, *J*(PH) 6], 1.31 [d of d, 36 H, CH*Me*$_2$, *J*(PH) 15, *J*(HH) 7], 2.42 [overlapping d of septets, 6 H, C*H*Me$_2$, *J*(PH) 7, *J*(HH) 7]	−13.60 [d, 2 H, *J*(PH) 14]	85.7 (s)	85.0 (s,br), 77.5 (s,br)
(**10**)	−13.98 [t, 2 H, hydrido H, *J*(PH) 6], 0.85—2.12 (m, 66 H, C_6H_{11})	[e] −13.82 (s,br), *ca.* 15 (s,vbr)	76.3 (s)	77.8 (s,br), 66.5 (s,br)
(**11**)	−13.73 [t, 2 H, μ_3-H, *J*(PH) 12], 1.56 [d, 54 H, CMe$_3$, *J*(PH) 14]	[h] −13.7 (s,vbr)	111.9 (s)	*ca.* 109 (s,vbr)
(**13**)	−17.35 (s,br, 3 H, μ_3-H), 1.56 [d, 27 H, CMe$_3$, *J*(PH) 13]	[i] −17.54 [d, 3 H, *J*(PH) 10]		[e] 64.5 (s)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in [$^2H_2$]dichloromethane solution. [c] Measured at −100 °C, unless otherwise stated. [d] Hydrogen-1 decoupled, measured in [$^2H_2$]dichloromethane–CH_2Cl_2 solution, chemical shifts positive to high frequency of 85% H_3PO_4 (external). [e] Measured at −90 °C. [f] CHMe$_2$ signals at −90 °C, δ *ca.* 1.18 and *ca.* 1.23 [2 × d of d (overlapping), 36 H, CH*Me*$_2$, *J*(PH) *ca.* 15, *J*(HH) 7 Hz], 2.11 (m,br, 3 H, C*H*Me$_2$), and 2.22 (m, br, 3 H, C*H*Me$_2$). [g] The multiplets observed for each of compounds (**6**) and (**7**) consist of superimposed subspectra due to the ^{107}Ag^{107}Ag, ^{107}Ag^{109}Ag, and ^{109}Ag^{109}Ag isotopomers of the cluster and they are complicated by second-order effects and by a wide variety of couplings. The pattern of signals in each complex multiplet is very similar to those previously reported[20] in the ambient-temperature ^{31}P-{^{1}H} n.m.r. spectra of $[Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (*n* = 4 or 5). However, the energy barriers for the intramolecular metal core rearrangement and the intermolecular phosphine ligand-exchange processes that both (**6**) and (**7**) undergo in solution are such that it is not possible to obtain a spectrum of either (**6**) or (**7**) which has narrow enough linewidths to allow all of the peaks that are visible for the $Ph_2P(CH_2)_nPPh_2$-containing species to be fully resolved. Therefore, the values of $^1J(^{109}$AgP), $^1J(^{107}$AgP), $^2J(^{109}$AgP), $^2J(^{107}$AgP), $J(^{109}$Ag^{109}Ag), $J(^{109}$Ag^{107}Ag), and $J(^{107}$Ag^{107}Ag) cannot be obtained from the spectra using a similar analysis to that previously described.[20] [h] Measured at −30 °C. At lower temperatures, the hydrido ligand signal is too broad to be observed in the ^{1}H n.m.r. spectrum. [i] Measured at −50 °C.

^{31}P-{^{1}H} and ^{1}H n.m.r. spectra of (**5**) are fully consistent with the solid-state structure of the cluster,[18] the ambient-temperature spectra are very different. Only a single resonance, broadened by quadrupolar effects,[1,8,11,13,19] is observed in the ^{31}P-{^{1}H} n.m.r. spectrum of (**5**) and the hydrido ligand signal in the ^{1}H n.m.r. spectrum is a triplet [*J*(PH) 5 Hz], showing coupling to two equivalent phosphorus atoms. Thus, the two $Cu\{P(C_6H_{11})_3\}$ units in (**5**) must be interchanging between edge-bridging and face-capping bonding modes at ambient temperature in solution and this dynamic behaviour must be accompanied by a concomitant site-exchange process for the two hydrido ligands. Similar dynamic behaviour has been reported[1] for the analogous $P(CH_2Ph)_3$-containing species (**12**) and, as we have previously pointed out,[1] the interchange of the $Cu(PR_3)$ (R = C_6H_{11} or CH_2Ph) fragments between the two different bonding modes is particularly interesting in view of the theoretical work of Wales, Mingos, and Zhenyang,[3] which suggests that such a process should be facile.

$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CHMe_2)_3\}_2]$ (**4**). In contrast to those of (**1**)[8] and (**5**), the ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra of compound (**4**) (Table 2) are consistent with the presence of two distinct skeletal isomers in solution at low temperatures. Three singlets (relative intensities 1:0.6:1) are visible in the ^{31}P-{^{1}H} n.m.r. spectrum at −90 °C and the ^{1}H n.m.r. high-field hydrido ligand signal consists of a sharp doublet [*J*(PH) 10 Hz] and a broadened singlet at −100 °C. The two equal-intensity ^{31}P-{^{1}H} n.m.r. singlets and the ^{1}H n.m.r. high-field doublet closely resemble the low-temperature n.m.r. data reported for (**1**),[8] which suggests that one of the isomers [isomer (**4a**), 77% abundance] adopts a metal core geometry similar to the capped trigonal-bipyramidal structure established for (**1**).[8] The presence in solution of a second isomer [isomer (**4b**), 23% abundance] is deduced from the remaining low-temperature n.m.r. signals, the ^{31}P-{^{1}H} n.m.r. resonance at δ 26.0 p.p.m., and the high-field broadened singlet in the ^{1}H n.m.r. spectrum. The ^{31}P-{^{1}H} n.m.r. signal for (**4b**) is a sharp singlet at −100 °C, which is in marked contrast to the ^{31}P-{^{1}H} n.m.r. spectra of (**5**) and (**12**),[1] which both consist of two broadened singlets. Thus, the n.m.r. evidence suggests that the Cu_2Ru_4 metal framework of (**4b**) is not only different to that of (**4a**) but also different from the edge-bridged trigonal-bipyramidal structures established for the $P(C_6H_{11})_3$-containing cluster (**5**) and the $P(CH_2Ph)_3$-ligated species (**12**).[1] It seems likely that isomer (**4b**) adopts a structure in which the two $Cu\{P(CHMe_2)_3\}$

moieties cap different faces of a Ru_4 tetrahedron.* This group 1B metal arrangement has been previously observed in $[M_2Ru_4(\mu\text{-}CO)_3(CO)_{10}(PPh_3)_2]$ (M = Cu, Ag, or Au).[7]

As the temperature is raised, the three $^{31}P\text{-}\{^1H\}$ n.m.r. singlets attributed to the two different skeletal isomers of $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CHMe_2)_3\}_2]$ [(**4a**) and (**4b**)] all coalesce, as do the two ^1H n.m.r. hydrido ligand signals. At ambient temperature, only a single resonance, broadened by quadrupolar effects,[1,8,11,13,19] is observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**5**) and the high-field hydrido ligand signal in the ^1H n.m.r. spectrum is a triplet [*J*(PH) 5 Hz], showing coupling to two equivalent phosphorus atoms. Clearly, isomers (**4a**) and (**4b**) are interconverting in solution at ambient temperature and isomer (**4a**) additionally undergoes the fluxional process involving coinage metal site-exchange that has been previously observed for (**1**).[8]

Interestingly, although both skeletal isomers of (**4**) are observed at low temperatures in solution, only one type of crystal was obtained from solutions of the cluster. A single-crystal X-ray diffraction study[18] on these crystals showed that (**4**) adopts the structure of isomer (**4a**) in the solid state. Thus, in contrast to the effect of the $P(C_6H_{11})_3$ ligand (cone angle 170°)[12] on (**5**) and the $P(CH_2Ph)_3$ ligand (cone angle 165°)[12] on (**12**), the $P(CHMe_2)_3$ ligand (cone angle 160°)[12] is not bulky enough to force (**4**) to adopt a ground-state skeletal geometry that is less sterically demanding than one in which the two $Cu\{P(CHMe_2)_3\}$ units are adjacent. However, the $P(CHMe_2)_3$ ligand does have sufficient effect to cause a second isomeric form of (**4**), which does not have the copper atoms in close contact, to be present in solution at low temperatures.

Although skeletal isomerism is extremely rare for transition-metal cluster compounds in general, a number of examples have been previously reported for species which contain Group 1B metals.[4–6] Sometimes both skeletal isomers can be isolated in the solid state, although, in other cases, two isomers exist in solution, but only one is observed in the solid state. In addition, examples of the interconversion of skeletal isomers in solution at ambient temperature have also been reported previously.[4–6]

$[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PR_3)_2]$ [R = $CHMe_2$, (**6**) or C_6H_{11}, (**7**)]. In contrast to those of the closely related copper-containing species (**4**) and (**5**), the i.r. and low-temperature n.m.r. spectroscopic data of (**6**) and (**7**) are very similar to those previously reported[8] for their PPh_3-ligated analogue (**2**). At −90 °C, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**6**) and (**7**) both consist of two resonances, each of which is split into two doublets by large $^{107}Ag\text{-}^{31}P$ and $^{109}Ag\text{-}^{31}P$ couplings through one bond. These doublets are all further split by much smaller $^{107,109}Ag\text{-}^{31}P$ couplings through two bonds. The magnitudes of these latter couplings are not sufficient to allow the separate contributions from ^{107}Ag and ^{109}Ag to be resolved. The high-field hydrido ligand signals in the ^1H n.m.r. spectra of (**6**) and (**7**) at −90 °C are each split into a doublet of doublets by couplings to one silver atom and one phosphorus atom. In addition, two sets of resonances due to $CHMe_2$ groups are observed in the ^1H n.m.r. spectrum of (**6**) at −90 °C. The spectroscopic data observed for compounds (**6**) and (**7**) demonstrate that, like that of the analogous PPh_3-containing species (**2**),[8] the metal frameworks of (**6**) and (**7**) exhibit a capped trigonal-bipyramidal skeletal geometry, with the two silver atoms in close contact. Thus, the greater size of the silver atom relative to copper means that (**7**) can adopt a metal core structure in which two adjacent $Ag\{P(C_6H_{11})_3\}$ units are accommodated, whereas the bulky $P(C_6H_{11})_3$ ligand forces the analogous copper-containing species (**5**) to adopt a sterically less-demanding skeletal geometry. In addition, the larger silver atoms mean that the $P(CHMe)_3$ ligand is not bulky enough to cause two skeletal isomers of (**6**) to exist at low temperatures in solution, in contrast to the situation observed for the analogous copper-containing cluster (**4**).

As the temperature is raised from −90 °C, the two phosphorus resonances in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of each of (**6**) and (**7**) coalesce. At ambient temperature, a complex multiplet with reasonably narrow linewidths is observed in both cases and these resonances then begin to broaden again as the temperature is increased further. The two complex multiplets both have a very similar pattern of signals to those previously reported[20] 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* = 4 or 5), although not all of the peaks, which are observed for the latter two clusters, can be fully resolved for compounds (**6**) and (**7**), because the linewidths in the last two cases are not narrow enough at any temperature to allow this. Analysis of the signals observed for the two $Ph_2P(CH_2)_nPPh_2$-containing species has shown that they consist of three superimposed subspectra due to the $^{107}Ag^{107}Ag$, $^{107}Ag^{109}Ag$, and $^{109}Ag^{109}Ag$ isotopomers of each cluster. In each spectrum a single phosphorus resonance is split by $^{107,109}Ag\text{–}^{31}P$ couplings through one and two bonds and by $^{107,109}Ag\text{–}^{107,109}Ag$ couplings and the pattern of signals is further complicated by second-order effects.[20] The high-field hydrido ligand signal in the ambient-temperature ^1H n.m.r. spectrum of each of (**6**) and (**7**) consists of an overlapping triplet of triplets, which is caused by couplings to two equivalent silver atoms and two equivalent phosphorus atoms. Both of these signals also broaden as the temperature is raised further. In addition, the $C\mathit{H}Me_2$ signal in the ambient-temperature ^1H n.m.r. spectrum of (**6**), which is split into an overlapping doublet of doublets of septets by $^{107,109}Ag\text{–}^1H$, $^{31}P\text{–}^1H$, and $^1H\text{–}^1H$ couplings [*J*(AgH)$_{av.}$ 3, *J*(PH) 7, *J*(HH) 7 Hz], broadens and loses the $^{107,109}Ag\text{–}^1H$ coupling as the temperature increases. The variable-temperature n.m.r. data demonstrate that compounds (**6**) and (**7**) both undergo two distinct dynamic processes in solution. The coalescence of the two phosphorus resonances in the low-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra and the observation of equivalent phosphorus atoms in the ambient-temperature $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectra can be explained by a process involving the two silver atoms in each of (**6**) and (**7**) undergoing intramolecular exchange between the distinct Group 1B metal sites in the ground-state metal framework structures of the clusters. Similar dynamic behaviour has been previously observed by $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy for the analogous PPh_3-ligated species (**2**)[8] and the closely related clusters $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ [L = $PMePh_2$[21] or $P(CH_2Ph)_3$[1]] and also detected directly by $^{109}Ag\text{–}\{^1H\}$ INEPT n.m.r. spectroscopy for $[Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (*n* = 1, 2, or 4),[20] which all adopt similar capped trigonal-bipyramidal metal core structures to those established for (**6**) and (**7**). The free energies of activation ($\Delta G^‡$) for the intramolecular metal core rearrangements that compounds (**6**) and (**7**) undergo in solution can be estimated at the coalescence temperature from the coalescence temperatures observed in the variable-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of these clusters. From coalescence temperatures of −30 ± 5 and −40 ± 5 °C for (**6**) and (**7**), respectively, the value of $\Delta G^‡$ for both clusters can be estimated to be 45 ± 1 kJ mol^{-1}. This value is *ca.* 5 kJ mol^{-1} larger than that previously reported[8] for the same dynamic process in the analogous PPh_3-ligated species (**2**). This increase in the magnitude of $\Delta G^‡$ as the cone angle of the

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* It should be noted, however, that the possibility that isomer (**4b**) adopts a similar edge-bridged trigonal-bipyramidal structure to those of (**5**) and (**12**)[1] and that, like those of (**5**) and (**12**),[1] the metal framework of (**4b**) undergoes a dynamic process which exchanges the two $Cu\{P(CHMe_2)_3\}$ moieties between the face-capping and edge-bridging bonding modes cannot be discounted on the available evidence. However, such a fluxional process in (**4b**) would have to have a considerably lower-energy barrier than those observed for (**5**) and (**12**).[1]

attached phosphine ligand becomes larger is consistent with the trend in $\Delta G^{\ddagger}$ previously observed[13] for the metal core rearrangements of some closely related copper-containing species. The loss of ^{107,109}Ag–^{1}H coupling and the other changes in band shape, which occur in the variable-temperature n.m.r. spectra of **(6)** and **(7)**, can be explained by a process involving intermolecular exchange of PR_3 (R = $CHMe_2$ or C_6H_{11}) ligands between clusters. Intermolecular exchange of phosphine ligands in solution is well established for silver-containing heteronuclear clusters[5] and similar dynamic behaviour has been previously observed for **(2)**[8] and the clusters $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ [L = $PMePh_2$[21] or $P(CH_2Ph)_3$[1]].

$[Au_2Ru_4H_2(CO)_{12}(PR_3)_2]$ [R = $CHMe_2$, **(9)**; *or* C_6H_{11}, **(10)**]. The i.r. spectra of compounds **(9)** and **(10)** (Table 1) closely resemble that reported for the analagous PPh_3-ligated species **(3)**, suggesting that **(9)** and **(10)** adopt similar capped trigonal-bipyramidal metal core structures, with the gold atoms in close contact, to that established for **(3)**.[8] This hypothesis is supported by the ^{31}P-{^{1}H} n.m.r. spectra of **(9)** and **(10)** at −90 °C, which both consist of two broad singlets with chemical shift differences of 7.5 and 11.3 p.m., respectively. Thus, the greater size of the gold atom relative to copper means that **(10)** can adopt a metal core structure in which two adjacent $Au\{P(C_6H_{11})_3\}$ units are accommodated, whereas the bulky $P(C_6H_{11})_3$ ligand forces the analogous copper-containing species **(5)** to adopt a sterically less-demanding skeletal geometry. In addition, the larger gold atoms mean that the $P(CHMe_2)_3$ ligand is not bulky enough to cause two skeletal isomers of **(9)** to exist at low temperatures in solution, in contrast to the situation observed for the analogous copper-containing cluster **(4)**.

The high-field hydrido ligand resonances in the ^{1}H n.m.r. spectra of compounds **(9)** and **(10)** at −100 °C strongly suggest that the bonding modes of the hydrido ligands in the two clusters are different. The signal for the $P(CHMe_2)_3$-ligated species **(9)** is a doublet [*J*(PH) 14 Hz], whereas that of the $P(C_6H_{11})_3$-containing cluster consists of two broadened singlets. The similarity between the high-field hydrido ligand signal of **(9)** at low temperatures and that reported[8] for the closely related copper-containing species **(1)** suggests that the two hydrido ligands adopt similar bonding modes in both clusters, which would mean that they cap two adjacent $AuRu_2$ faces in **(9)**.* In marked contrast, the two resonances observed at low temperatures for **(10)** are consistent with the positions of the hydrido ligands being the same as those previously observed for the analogous PPh_3-ligated species **(3)**, in which one hydrido ligand caps a $AuRu_2$ face and the other bridges a Ru–Ru edge.

As the temperature is raised from −90 °C, the two phosphorus signals in the ^{31}P-{^{1}H} n.m.r. spectrum of each of compounds **(9)** and **(10)** coalesce and, at ambient temperature, each spectrum consists of a single resonance. In addition, a triplet [*J*(PH) 6 Hz] is observed for the high-field hydrido ligand signal in the ^{1}H n.m.r. spectrum of each of **(9)** and **(10)** at ambient temperature, which again shows that the two phosphorus atoms in both clusters are equivalent at this temperature. This equivalence can be explained by a dynamic process involving gold atom site exchange, similar to that proposed for the silver atoms in the analogous silver-containing species **(6)** and **(7)**. The free energies of activation ($\Delta G^{\ddagger}$) for the intramolecular metal core rearrangements that **(9)** and **(10)** undergo in solution can be estimated at the coalescence temperature from the coalescence temperatures observed in the variable-temperature ^{31}P-{^{1}H} n.m.r. spectra of these clusters. From the colescence temperatures of -72.5 ± 5 and -70 ± 5 °C for **(9)** and **(10)**, respectively, the value of $\Delta G^{\ddagger}$ for both clusters can be estimated to be 36 ± 1 kJ mol^{-1}.

$[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CMe_3)_3\}_2]$ [M = Ag, **(8)**; *or* Au, **(11)**]. The i.r. and n.m.r. spectroscopic data for compounds **(8)** and **(11)** are fully consistent with the proposed formulations, but they are significantly different to those previously reported[8] for the analogous PPh_3-ligated clusters **(2)** and **(3)**. The ambient-temperature ^{31}P-{^{1}H} n.m.r. spectrum of the silver-containing species **(8)** shows a single resonance, which is split into two doublets by ^{109}Ag–^{31}P and ^{107}Ag–^{31}P couplings. Interestingly, the complex second-order splitting patterns due to ^{107,109}Ag–^{107,109}Ag couplings and ^{107,109}Ag–^{31}P couplings through two bonds, which have been previously observed in the ^{31}P-{^{1}H} n.m.r. spectra of **(6)**, **(7)**, and other silver-containing clusters in which the silver atoms are in close contact,[1,20,22] are not visible for **(8)**. Therefore, **(8)** must adopt a metal core structure in which the silver atoms are not in close contact. Unfortunately, no n.m.r. spectra consistent with the ground-state structure could be obtained at low temperatures for **(8)**, but the broadening observed in the ^{31}P-{^{1}H} n.m.r. spectrum at −90 °C suggests that there are two distinct phosphorus sites in the metal core and that some dynamic process renders them equivalent at ambient temperature. Therefore, it seems reasonable to propose that the cluster adopts a similar skeletal geometry and exhibits similar dynamic behaviour to those established for the copper-containing species **(5)**. Thus, we postulate that the metal framework structure of **(8)** consists of a ruthenium tetrahedron with one edge bridged by a $Ag\{P(CMe_3)_3\}$ unit and a non-adjacent face capped by the second $Ag\{P(CMe)_3\}$ group and that the two $Ag\{P(CMe_3)_3\}$ fragments in **(8)** interchange between edge-bridging and face-capping bonding modes, together with a concomitant hydrido ligand site-exchange process, at ambient temperature in solution. In addition, we propose that the analogous gold-containing cluster **(11)** adopts a similar edge-bridged trigonal-bipyramidal metal core structure and undergoes similar dynamic behaviour at ambient temperature in solution, because of the close resemblance between the i.r. and n.m.r. spectroscopic data for **(8)** and **(11)**. Therefore, the $P(CMe_3)_3$ ligand (cone angle 182°)[12] is clearly too bulky to allow two $M\{P(CMe_3)_3\}$ (M = Ag or Au) units to be adjacent in the metal frameworks of **(8)** and **(11)**, so both of these clusters are forced to adopt a sterically less-demanding edge-bridged trigonal-bipyramidal skeletal geometry. The greater size of the silver and gold atoms relative to copper is reflected by the fact that the much less bulky phosphine $P(CH_2Ph)_3$ (cone angle 165°)[12] is large enough to cause a similar change in metal core structure of $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2]$ **(12)**.[1]

Synthesis, Spectroscopic Characterization, Skeletal Geometry, and Dynamic Behaviour of $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$ **(13)**.—Interestingly, treatment of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with 2 equivalents of the complex $[Cu(NCMe)_4]PF_6$ at −30 °C and the subsequent addition of 2 equivalents of $P(CMe_3)_3$ affords the pentanuclear cluster $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$ **(13)** (48% yield) instead of the expected hexanuclear product $[Cu_2Ru_4H_2(CO)_{12}\{P(CMe_3)_3\}_2]$. The i.r. and n.m.r. spectroscopic data for **(13)** (Tables 1 and 2) are very

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* The possibility that the positions of the hydrido ligands in the ground-state structure of (9) are similar to those in the analogous PPh_3-ligated cluster (3)[8] and that (9) undergoes dynamic behaviour involving hydrido ligand site-exchange in solution, even at −100 °C, cannot be completely ruled out on the evidence available. However, although this type of dynamic behaviour is well established for gold-ruthenium clusters, which are closely similar to (9), the energy barriers for the process are such that the high-field hydrido ligand signals in the ^{1}H n.m.r. spectra of these species are all severely broadened singlets at −90 or −100 °C.[8–10] Since the high-field hydrido ligand resonance in the ^{1}H n.m.r. spectrum of (9) at −100 °C is a doublet with narrow line-widths, it seems very unlikely that the equivalence of the two hydrido ligands is caused by a site-exchange process.

similar to those previously reported for $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}L]$ (L = $PMePh_2$ or PPh_3), which implies that (**13**) adopts a similar trigonal-bipyramidal metal core geometry to that established for the latter two species.[23] The identity of (**13**) was confirmed by preparing the cluster (58% yield) by treating the salt $[N(PPh_3)_2][Ru_4(\mu\text{-}H)_3(CO)_{12}]$ with one equivalent of the complex $[Cu(NCMe)_4]PF_6$ at −30 °C, followed by the addition of one equivalent of $P(CMe_3)_3$. The i.r. and n.m.r. spectra of samples of (**13**) which were prepared by the two different routes are identical.

The fact that only one $Cu\{P(CMe_3)_3\}$ unit is incorporated into the dianion $[Ru_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$ instead of the expected two clearly demonstrates that the $P(CMe_3)$ ligand (cone angle 182°)[12] is too bulky to allow a hexanuclear cluster of formula $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CMe_3)_3\}_2]$ to adopt even the sterically less-demanding edge-bridged trigonal-bipyramidal skeletal geometry which was established for the analogous $P(C_6H_{11})_3$-ligated cluster (**5**). This observation again reflects the smaller size of the copper atom relative to silver and gold, since clusters of formula $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CMe_3)_3\}_2]$ [M = Ag (**8**) or Au (**11**)] have been prepared.

The high-field ^1H n.m.r. hydrido ligand signal of compound (**13**) is a broad singlet at ambient temperature, but a doublet [*J*(PH) 10 Hz] is observed at −50 °C. Dynamic behaviour involving intermolecular exchange of phosphine ligands between clusters has been previously proposed[23] to explain the similar variable-temperature ^1H n.m.r. spectra observed for the analogous cluster $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}(PMePh_2)]$ and (**13**) must also undergo this process at ambient temperature in solution.

Conclusion

The nature of the Group 1B metals and the cone angles of the attached phosphine ligands have a marked effect on the metal core structures adopted by the heteronuclear clusters $[M_2Ru_4H_2(CO)_{12}(PR_3)_2]$ (M = Cu, R = $CHMe_2$ or C_6H_{11}; M = Ag or Au, R = $CHMe_2$, C_6H_{11}, or CMe_3). Previous work has shown that the preferred skeletal geometry for clusters of this general formula, when L is relatively small phosphine or phosphite ligand, is capped trigonal bipyramidal, with the Group 1B metals in close contact. However, the $P(C_6H_{11})_3$ ligand (cone angle 170°)[12] is too bulky to allow two $Cu\{P(C_6H_{11})_3\}$ units to be adjacent in the metal framework of $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(C_6H_{11})_3\}_2]$ and the cluster is forced to adopt a sterically less-demanding edge-bridged trigonal-bipyramidal metal core structure. The greater size of the silver and gold atoms relative to copper means that two adjacent $M\{P(C_6H_{11})_3\}$ (M = Ag or Au) units can be accommodated in the metal frameworks of the analagous silver- and gold-containing species and the even larger phosphine ligand $P(CMe_3)_3$ (cone angle 182°)[12] is required to force a similar change in skeletal geometry for the clusters $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CMe_3)_3\}_2]$ (M = Ag or Au). In addition, the $P(CMe_3)_3$ ligand seems to be too bulky to allow a hexanuclear cluster of formula $[Cu_2Ru_4H_2(CO)_{12}\{P(CMe_3)_3\}_2]$ to adopt even the sterically less-demanding edge-bridged trigonal-bipyramidal metal framework structure and an attempt to prepare this species afforded the pentanuclear cluster $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$ instead. The smaller phosphine ligand $P(CHMe_2)_3$ (cone angle 160°)[12] is not sufficiently bulky to cause the metal frameworks of $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CHMe_2)_3\}_2]$ (M = Cu, Ag, or Au) to change from the preferred capped trigonal-bipyramidal skeletal geometry in the solid state, but a second isomer of the copper-containing cluster, which probably has two face-capping $Cu\{P(CHMe_2)_3\}$ units with no bonding interaction between them, is also present in solution at low temperatures.

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 salts $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$[25] and $[N(PPh_3)_2][Ru_4(\mu\text{-}H)_3(CO)_{12}]$[25] and the complexes $[Cu(NCMe)_4]PF_6$[26] and $[AuCl(SC_4H_8)]$.[27] The compound $[Ag(NCMe)_4]PF_6$ was synthesized by an adaptation of a published route.[26,28] The phosphine ligands $P(CHMe_2)_3$ and $P(CMe_3)_3$ were purchased from Strem Chemicals Inc. and used without further purification. The adduct $P(C_6H_{11})_3{\cdot}CS_2$ was also purchased from Strem Chemicals Inc. Analytical and physical data for the new Group 1B metal heteronuclear cluster 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 $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PR_3)_2]$ (M = Cu, R = $CHMe_2$ *or* C_6H_{11}; M = Ag, R = $CHMe_2$, C_6H_{11} *or* CMe_3) *and* $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$.—A dichloromethane (40 cm^3) solution of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ (0.60 g, 0.33 mmol) at −30 °C was treated with a solution of $[M(NCMe)_4]PF_6$ (M = Cu, 0.25 g, 0.67 mmol; or M = Ag, 0.28 g, 0.67 mmol) in dichloromethane (25 cm^3) and then, after stirring the reaction mixture at −30 °C for 1 min, a dichloromethane (20 cm^3) solution containing the appropriate amount (Table 3) of the desired phosphine ligand was added. The mixture was allowed to warm to ambient temperature with stirring and the solvent was then removed under reduced pressure. The residue was extracted with dichloromethane–diethyl ether (1:4; 50-cm^3 portions) until the extracts were no longer red and the combined extracts were then filtered through a Celite pad (*ca.* 1 × 3 cm). After removal of the solvent under reduced pressure, the crude residue was dissolved and chromatographed, using the appropriate conditions (Table 3). The chromatography afforded one dark red fraction which, after removal of the solvent under reduced pressure and crystallization of the residue from a dichloromethane–light petroleum mixture, yielded dark red *microcrystals* of the product. Table 3 lists the amounts of compounds (**4**)—(**8**) and (**13**) obtained.

Synthesis of the Compounds $[Au_2Ru_4H_2(CO)_{12}(PR_3)_2]$ (R = $CHMe_2$, C_6H_{11} *or* CMe_3).—A dichloromethane (15 cm^3) solution of $[AuCl(SC_4H_8)]$ (0.22 g, 0.69 mmol) was treated with a dichloromethane (20 cm^3) solution of the appropriate amount (Table 3) of the desired phosphine ligand and the mixture was stirred for 15 min. An acetone (40 cm^3) solution of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ (0.60 g, 0.33 mmol), together with solid $TlPF_6$ (0.50 g, 1.43 mmol), was then added to the resultant solution and the mixture was stirred for 1 h. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane–diethyl ether (1:4; 50-cm^3 portions) until the extracts were no longer red. The combined extracts were then filtered through a Celite pad (*ca.* 1 × 3 cm). After removal of the solvent from the filtrate under reduced pressure, the crude residue was dissolved and chromatographed, using the appropriate conditions (Table 3). Chromatography afforded one red fraction which, after removal of the solvent under reduced pressure and crystallization of the residue from a dichloromethane–light petroleum mixture, yielded dark red *microcrystals* of the product. Table 3 lists the amounts of compounds (**9**)—(**11**) obtained.

Alternative Synthesis of the Compound $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$.—A dichloromethane (25 cm^3) solution of $[N(PPh_3)_2][Ru_4(\mu\text{-}H)_3(CO)_{12}]$ (0.35 g, 0.27 mmol) at −30 °C

Table 3. Quantities of phosphine ligand used and product obained and the chromatography conditions employed for the synthesis of the clusters $[M_2Ru_4H_2(CO)_{12}(PR_3)_2]$ (M = Cu, R = $CHMe_2$ or C_6H_{11}; M = Ag or Au, R = $CHMe_2$, C_6H_{11} or CMe_3) and $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$

		Quantity of product obtained (g)			Proportions of dichloromethane–light petroleum mixture used for elution[a]		
R	Quantity of phosphine used (g, mmol)	M = Cu	Ag	Au	M = Cu[b]	Ag[b]	Au[c]
$CHMe_2$	0.11, 0.69	0.23	0.27	0.25	3:1	3:2	1:4
C_6H_{11}	*ca.* 0.19, 0.68[d]	0.30	0.26	0.26	1:1	2:1	1:9
CMe_3	0.14, 0.69	0.16[e]	0.27	0.17	4:1	2:1	1:3

[a] The crude product was initially dissolved in a solvent mixture with the same proportions of dichloromethane and light petroleum as that used for elution. [b] The chromatography was performed on a Florisil column (20 × 3 cm) at −20 °C. [c] The chromatography was performed on an alumina column (20 × 3 cm) at ambient temperature. [d] The phosphine $P(C_6H_{11})_3$ was obtained by refluxing $P(C_6H_{11})_3\cdot CS_2$ (0.24 g, 0.67 mmol) in ethanol (30 cm^3) until the red colour of the adduct had disappeared. The solvent was then removed under reduced pressure and the liberated phosphine ligand was dissolved in CH_2Cl_2 (20 cm^3) prior to use. [e] The pentanuclear cluster $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$ was obtained from this reaction instead of the expected hexanuclear species.

was treated with a dichloromethane (15 cm^3) solution of $[Cu(NCMe)_4]PF_6$ (0.10 g, 0.27 mmol). After stirring at −30 °C for 1 min, a dichloromethane (10 cm^3) solution of $P(CMe_3)_3$ (0.06 g, 0.30 mmol) was added. The mixture was then allowed to warm to ambient temperature with stirring and the solvent was removed under reduced pressure. The crude residue was dissolved in dichloromethane–light petroleum (4:1) and chromatographed at −20 °C on a Florisil column (20 × 3 cm). Elution with dichloromethane–light petroleum (4:1) afforded one orange fraction which, after removal of the solvent under reduced pressure and crystallization of the residue from a dichloromethane–light petroleum mixture, yielded dark orange *microcrystals* of $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}\{P(CMe_3)_3\}]$ (0.16 g, 58%). The i.r. and n.m.r. spectroscopic data for samples of the cluster prepared by this method and by that described previously are identical.

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