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Preliminary communication

STRUCTURAL SIMILARITIES AND DIFFERENCES AMONG MIXED-METAL CLUSTERS CONTAINING A SINGLE M(PPh_3) (M = Cu, Ag or Au) FRAGMENT

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Summary

The heteronuclear metal clusters [$H_3MRu_4(CO)_{12}(PPh_3)$] and [$MFe_3(\mu\text{-COMe})(CO)_{10}(PPh_3)$] (M = Cu, Ag or Au) have been prepared; the gold-tetraruthenium cluster has a different metal core geometry to that adopted by the copper and silver analogues, whereas all three iron-Group IB mixed-metal clusters have the same geometry.

Mixed-metal clusters containing Au(PR_3) (R = alkyl or aryl) groups have attracted much recent interest [1—4]. When these cluster compounds contain only one Au(PR_3) moiety, this unit bonds in either an edge- or a face-bridging mode. Moreover, in almost all of the compounds where structural comparisons are possible, the Au(PR_3) fragment occupies a similar position to that of the isolobal hydrido ligand in the related hydridometal cluster. Theoretical studies on the bonding properties of the Au(PH_3) group indicate that it provides one orbital and one electron for cluster bonding, as does a hydrogen atom. In contrast, the Cu(PH_3) fragment has three frontier orbitals suitable for cluster bonding and is isolobal with the $Mn(CO)_3$ group rather than an H atom [5]. Few heteronuclear metal clusters containing copper or silver have been reported [6—8], and thus, in comparison with compounds containing an Au(PR_3) group, relatively little is known about the bonding capacities of M(PR_3) (M = Cu or Ag) moieties. Herein we report the preparation of two series of analogous mixed-metal clusters containing one M(PR_3) (M = Cu, Ag or Au) unit, and demonstrate an interesting structural difference between the Au species and its Cu and Ag analogues in one group of complexes.

Treatment of dichloromethane solutions of [$N(PPh_3)_2$][$Ru_4(\mu\text{-H})_3(CO)_{12}$] [9] with the complexes [$MX(PPh_3)$] (M = Cu or Au, X = Cl; M = Ag, X = I) in the presence of $TlPF_6$ yields (ca. 60—70%) the orange cluster compounds [$H_3MRu_4(CO)_{12}(PPh_3)$] (I, M = Cu; II, M = Ag; III, M = Au).

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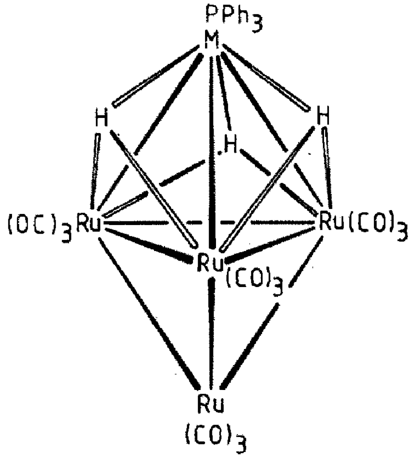
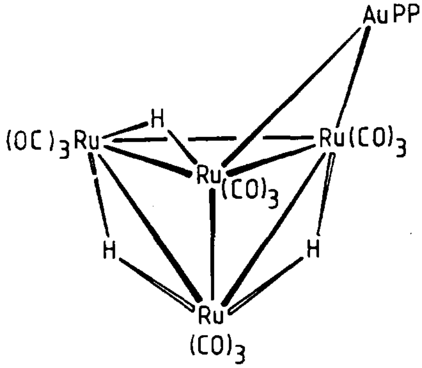
The IR and NMR data for I and II are very similar [10]. At −90°C, the ^1H NMR spectra of both compounds at high-field show a single resonance coupled to a phosphorus nucleus, and in the case of II coupling to the silver atom is also observed. Thus the three hydrido ligands are equivalent and are bonded to the Group IB metal as well as to ruthenium. The $^{31}P\text{-}\{^1H\}$ NMR data for I and II are as expected, showing one PPh_3 environment. Silver (^{109}Ag and ^{107}Ag)—^{31}P coupling is observed in the spectrum of II. The $^{13}C\text{-}\{^1H\}$ NMR resonances for the carbonyl groups of I appear as three sharp singlets (rel. int. 1/2/1) at −90°C. The data for I and II are thus fully consistent with the structure shown with three hydrido ligands triply bridging the MRu_2 faces of a MRu_4 cluster in which the core atoms adopt a trigonal bipyramidal arrangement [11].



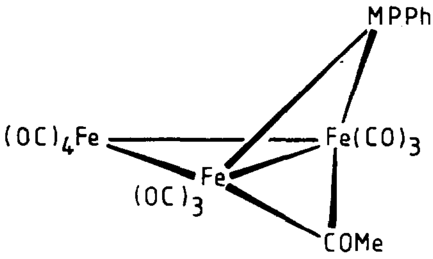
(I , M = Cu ;
II , M = Ag)

There is a close relationship between the proposed structures of I and II and the X-ray crystallographically established structures of the hexanuclear metal clusters $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (M = M′ = Cu or Ag; M = Cu, M′ = Ag or Au; M = Ag, M′ = Au) [8]. A triply bridging hydrido ligand in I or II is replaced by a capping $M(PPh_3)$ (M = Cu, Ag or Au) fragment in the hexanuclear metal compounds.

Lewis and co-workers [2b] have prepared a gold-osmium cluster, $[AuOs_4(\mu\text{-}H)_3(CO)_{12}(PEt_3)]$, analogous to III [12], and established the structure by X-ray crystallography. The $Au(PEt_3)$ fragment bridges an edge of an Os_4 tetrahedron, three other edges being bridged by hydrido ligands. It is reasonable to assume that III has a similar geometry. The proposed structure for III is also reasonable in view of its close similarity to that reported [13] for the isolobally related tetrahydrido cluster $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$. The absence of any ^{31}P—^1H coupling for the hydrido ligand signal in the ^1H NMR spectrum [12] of III implies that these ligands do not cap $AuRu_2$ faces in the cluster. Although the hydrido ligands are not all equivalent in the proposed solid state structure, the broad resonance observed in the −90°C ^1H NMR spectrum is consistent with III



(III)



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

undergoing a dynamic process involving site-exchange of the hydrido groups. Compound III has recently been obtained (10% yield) as one of several products of the reaction of [{Au(PPh$_3$)}$_3$O][BF$_4$] with K[Ru$_4$(μ-H)$_3$(CO)$_{12}$] [4], and the PEt$_3$ analogue has been mentioned briefly [2b].

The Au(PPh$_3$) fragment in compound III takes up an edge-bridging position, similar to that of the isolobal hydrido ligands in [Ru$_4$(μ-H)$_4$(CO)$_{12}$], whereas in I and II the M(PPh$_3$) (M = Cu or Ag) moieties cap an Ru$_3$ face. It is interesting to compare the structure of the anions [MOs$_{10}$C(CO)$_{24}$L]$^-$ (M = Cu, L = NCMe; M = Au, L = PPh$_3$) [6] with those of I—III. Although both MOs$_{10}$C species have the same basic tetracapped octahedral osmium skeleton, the copper complex has the Cu(NCMe) moiety capping an Os$_3$ face, whereas the gold complex has the Au(PPh$_3$) fragment bridging an edge of the same face.

The purple compounds [MFe$_3$(μ-COMe)(CO)$_{10}$(PPh$_3$)] (IV, M = Cu; V, M = Ag; VI, M = Au) have been prepared by treating dichloromethane solutions of [N(PPh$_3$)$_2$][Fe$_3$(μ-COMe)(CO)$_{10}$] [14] with the complexes [MX(PPh$_3$)] (M = Cu or Au, X = Cl; M = Ag, X = I) in the presence of TlPF$_6$. The IR spectra of IV—VI [15,16] are almost identical, strongly suggesting similar structures. Compound IV is unstable at room temperature, in solution and in the solid state, but it could be fully characterised. Complex V is very temperature sensitive and no satisfactory analytical or ^{31}P-{^{1}H} or ^{13}C-{^{1}H} NMR data could be obtained.

The ^{1}H and ^{13}C-{^{1}H} NMR spectra of IV and the ^{1}H NMR spectrum of V [16] show that the bridging μ-COMe ligand of the precursor is present in these products. The singlet resonance in the ^{31}P-{^{1}H} NMR spectrum of IV has a similar chemical shift to those previously reported [8] for Cu(PPh$_3$) groups in mixed-metal clusters. The signal for the CO groups in the ^{13}C-{^{1}H} NMR spectrum of IV at −90°C is a singlet, indicating rapid site-exchange via a low activation energy process.

The complex [AuRu$_3$(μ-COMe)(CO)$_{10}$(PPh$_3$)] has been characterised structurally by X-ray diffraction [1c,e], and it is likely that the iron analogue VI, and its congeners IV and V have a similar 'butterfly' metal atom arrangement, with the Group IB element occupying a wing-tip position. Hence, the M(PPh$_3$) fragments in IV—VI all occupy the position of the hydrido ligand in the analogous hydrido complex [Fe$_3$(μ-H)(μ-COMe)(CO)$_{10}$] [14].

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10 Selected spectroscopic data. For compound I, ν_{max}(CO) at 2087m, 2050vs, 2025vs, 2007m, 1995s, 1987m, 1965w and 1947yw cm^{-1} (cyclohexane). NMR at −90°C: ^{1}H (CD_2Cl_2), δ −17.62 (d, 3 H, μ_3-H, J(PH) 11 Hz); ^{31}P-$\{^1H\}$ (CD_2Cl_2) (rel. to 85% H_3PO_4 (ext)), δ 10.9 ppm; ^{13}C-$\{^1H\}$ (CD_2Cl_2/CH_2Cl_2), δ 197.1 (3 × CO), 196.6 (6 × CO) and 191.4 ppm (3 × CO). For compound II, ν_{max}(CO) at 2086m, 2060s, 2049vs, 2023vs, 2006s, 1996(sh), 1989s, 1980(sh), 1962w and 1945vw cm^{-1} (cyclohexane). NMR (−90°C): ^{1}H (CD_2Cl_2), δ −17.25 (d of d, 3 H, μ_3-H, J(PH) 10, J(AgH) 34 Hz); ^{31}P-$\{^1H\}$ (CD_2Cl_2), δ 22.0 ppm (2 × d, J(^{109}AgP) 693, J(^{107}AgP) 601 Hz); ^{13}C-$\{^1H\}$ (CD_2Cl_2/CH_2Cl_2), δ 196.6—195.1 (br, CO) and 191.3 ppm (br, CO).

11 An alternative C_{3v} arrangement with the hydrido ligands bridging the three MRu edges in I and II cannot definitely be ruled out. However, the close similarity of the J(PH) and J(AgH) values for I and II and those reported [8] for the species [$MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2$] suggest that the hydrido ligands in I and II adopt similar triply bridging positions to those in the hexanuclear metal clusters.

12 Selected spectroscopic data. For compound III, ν_{max}(CO) at 2089m, 2062vs, 2049s, 2035(sh), 2029vs, 2012m, 2003(sh), 1999m, 1978w(br), 1968w and 1956vw cm^{-1} (cyclohexane). NMR: ^{1}H (CD_2Cl_2), δ −17.63 (s, 3 H, μ-H), at −90°C, δ ca. −18 (vbr, 3 H, μ-H); ^{31}P-$\{^1H\}$ (CD_2Cl_2), δ 67.3 ppm.

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15 Compound VI has also been prepared from [$Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}$] and [$AuMe(PPh_3)$] [1c, e].

16 For compound IV, ν_{max}(CO) at 2068m, 2014vs, 1997m, 1991(sh), 1978(sh), 1969m(br) and 1945w cm^{-1} (cyclohexane). NMR: ^{1}H ($CDCl_3$, −30°C), δ 4.31 (s, 3 H, OMe) and 7.49 (m, 15 H, Ph); ^{31}P-$\{^1H\}$ ($CDCl_3$, −30°C), δ 1.0 ppm; ^{13}C-$\{^1H\}$ (CD_2Cl_2/CH_2Cl_2, −90°C), δ 330.1 (μ-*C*OMe), 211.0 (CO 133.7—128.6 (Ph), and 71.2 ppm (μ-CO*Me*). For compound V, ν_{max}(CO) at 2068m, 2013vs, 1996m, 1990(sh), 1979(sh), 1971m(br), and 1946w cm^{-1} (cyclohexane). NMR: ^{1}H ($CDCl_3$, −40°C), δ 4.35 (s 3 H, OMe) and 7.08—7.49 (m, 15 H, Ph).