

Preliminary communication

THE SYNTHESIS AND DYNAMIC BEHAVIOUR OF COPPER- AND SILVER-RUTHENIUM CLUSTER COMPOUNDS CONTAINING THE ASYMMETRIC BIDENTATE LIGANDS $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$ or 2)

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Summary

The novel mixed-metal cluster compounds $[\text{M}_2\text{Ru}_4(\mu_3\text{-H})_2\{\mu\text{-Ph}_2\text{As}(\text{CH}_2)_n\text{PPh}_2\}(\text{CO})_{12}]$ ($\text{M} = \text{Cu}$ or Ag ; $n = 1$ or 2) have been synthesized in good yield (ca. 65–70%). Variable temperature ^1H and $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectroscopic studies demonstrate that two distinct structural isomers exist in solution at low temperature for both copper-ruthenium clusters and that each of these pairs of isomers undergoes interconversion at ambient temperature by a fluxional process involving an intramolecular metal core rearrangement.

Mixed-metal cluster compounds containing $\text{M}(\text{PR}_3)$ ($\text{M} = \text{Cu}$, Ag or Au ; $\text{R} =$ aryl or alkyl) moieties are currently attracting considerable interest [1–4], but similar species in which bidentate ligands are attached to the coinage metals still remain relatively rare [2–4]. Herein we report the preparation of the novel species $[\text{M}_2\text{Ru}_4(\mu_3\text{-H})_2\{\mu\text{-Ph}_2\text{As}(\text{CH}_2)_n\text{PPh}_2\}(\text{CO})_{12}]$ ($\text{M} = \text{Cu}$ or Ag ; $n = 1$ or 2), the first examples of Group Ib metal heteronuclear clusters containing asymmetric bidentate ligands. Also, we demonstrate that two distinct structural isomers exist in solution at low temperature for both copper-ruthenium clusters and we show that each of these pairs of isomers undergoes interconversion at ambient temperature by a fluxional process involving an intramolecular metal core rearrangement.

Treatment of dichloromethane solutions of the salt $[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_4(\mu\text{-H})_2(\text{CO})_{12}]$ [5] with the complexes $[\text{M}(\text{NCMe})_4]\text{PF}_6$ ($\text{M} = \text{Cu}$ or Ag) at -30°C , followed by the in situ addition of the asymmetric bidentate ligands $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{PPh}_2$ [6], affords the red mixed-metal cluster compounds $[\text{M}_2\text{Ru}_4(\mu_3\text{-H})_2\{\mu\text{-Ph}_2\text{As}(\text{CH}_2)_n\text{PPh}_2\}(\text{CO})_{12}]$ (I, $\text{M} = \text{Cu}$, $n = 1$; II, $\text{M} = \text{Cu}$, $n = 2$; III, $\text{M} = \text{Ag}$, $n = 1$; IV, $\text{M} = \text{Ag}$, $n = 2$) in good yield (ca. 65–70%). Infrared and NMR spectroscopic data for I–IV [7] imply that these species adopt the same

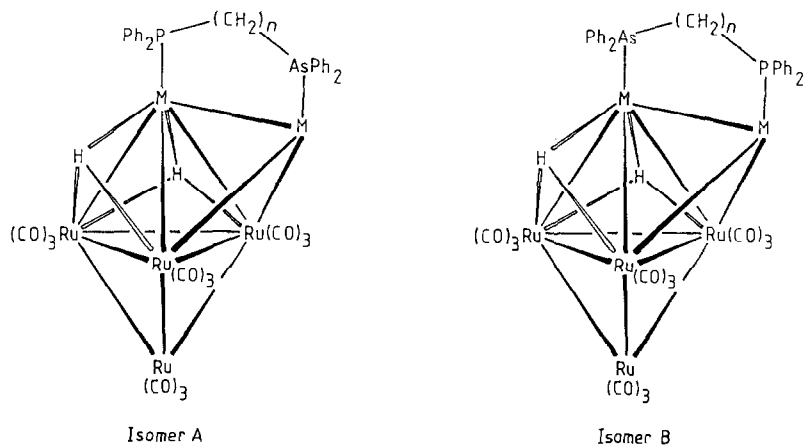


Fig. 1. The two possible structural isomers of $[M_2Ru_4(\mu_3-H)_2\{\mu-Ph_2As(CH_2)_nPPh_2\}(CO)_{12}]$ (I: $M = Cu$, $n = 1$; II: $M = Cu$, $n = 2$; III: $M = Ag$, $n = 1$; IV: $M = Ag$, $n = 2$).

capped trigonal bipyramidal metal core geometry as that previously established for $[Ag_2Ru_4(\mu_3-H)_2(\mu-Ph_2PCH_2PPh_2)(CO)_{12}]$ [4] and $[M_2Ru_4(\mu_3-H)_2(CO)_{12}(PPh_3)_2]$ ($M = Cu$ or Ag) [8]. However, in the case of I–IV, two different structural isomers (labelled A and B in Fig. 1) are possible for each cluster, as either an arsenic atom or a phosphorus atom can be attached to each of the two distinct coinage metal sites in the cluster skeleton.

At $-90^\circ C$, the $^{31}P\{-^1H\}$ NMR spectra of the two copper-ruthenium clusters, I and II, both show two signals with different intensities [7]. Thus, for I and II, both of the two possible structural isomers are present in solution at low temperature. In each case, the two $^{31}P\{-^1H\}$ NMR peaks broaden and eventually coalesce into a singlet as the temperature is raised [7]. The observation of these averaged phosphorus environments demonstrates that some fluxional process is interconverting the two distinct structural isomers of each cluster at ambient temperature. It is reasonable to propose that the dynamic behaviour exhibited by I and II involves an intramolecular metal core rearrangement, as we have previously shown [3, 4, 8] that the structurally very closely related species $[M_2Ru_4(\mu_3-H)_2(CO)_{12}L_2]$ ($M = Cu$ or Ag ; $L = PPh_3$ or $L_2 = \mu-Ph_2P(CH_2)_n PPh_2$, $n = 1-6$) all undergo a fluxional process which exchanges the coinage metals between the two distinct sites in their capped trigonal bipyramidal skeletons.

The conclusions from the $^{31}P\{-^1H\}$ NMR data for I and II are confirmed by variable temperature 1H NMR studies on the high field hydrido ligand signals of these clusters. At $-90^\circ C$, a singlet and a doublet ($J(PH)$ 12 Hz) (relative intensities (r.i.) 0.16/1.00) are observed for I and these two signals broaden and eventually coalesce as the temperature is raised. An averaged signal, consisting of a doublet with a reduced coupling constant ($J(PH)$ 8 Hz), is visible at ambient temperature. Only structural isomer A (Fig. 1), in which the phosphorus is attached to the copper atom bonded to the hydrido ligands, would be expected to show $^{31}P-^1H$ coupling [8]. Thus, isomer A is clearly predominant for I. However, at $-80^\circ C$, the hydrido ligand signals for II consist of a singlet and a doublet ($J(PH)$ 13 Hz) (r.i. 1.00/0.37) (Fig. 2) and, at ambient temperature, one doublet, with the much smaller $^{31}P-^1H$ coupling of 3 Hz, is observed

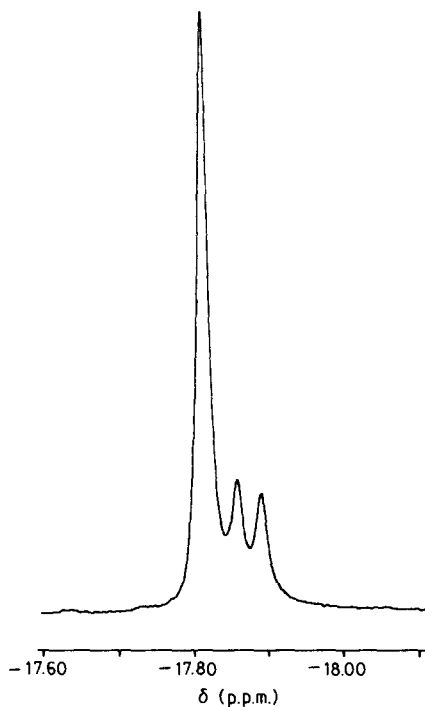


Fig. 2. The high-field hydrido ligand signal in the ^1H NMR spectrum of $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_4(\mu\text{-Ph}_2\text{AsCH}_2\text{-CH}_2\text{PPh}_2)(\text{CO})_{12}]$ (II) at -80°C (CD_2Cl_2). The singlet is due to isomer B and the doublet due to isomer A (relative intensities 1.00/0.37).

[7]. Therefore, in contrast to I, the major isomer of II is B and the addition of just one methylene group to the backbone of asymmetric bidentate ligand $\text{Ph}_2\text{AsCH}_2\text{PPh}_2$ causes a remarkable change in the relative proportions of isomers A and B.

The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of the silver-ruthenium clusters III and IV are very complex, with the hydrido ligand and phosphorus resonances split into a large number of peaks by couplings to ^{107}Ag and ^{109}Ag [3]. In addition, the spectra are also affected by another fluxional process, which probably involves an intermolecular exchange of the $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{PPh}_2$ ligands between clusters [9]. Detailed variable temperature NMR studies are currently in progress to investigate the dynamic behaviour of III and IV.

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References and notes

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- 7 Selected spectroscopic data. For compound I, $\nu_{\max}(\text{CO})$ at 2068s, 2032vs, 2017vs, 2007s, 1982(sh), 1974m and 1927m(br) cm^{-1} (CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ -18.05 (d, 2 H, μ_3 -H, $J(\text{PH})$ 8 Hz), 3.24 (d, 2 H, AsCH_2P , $J(\text{PH})$ 10 Hz) and 7.05-7.55 (m, 20 H, Ph); μ_3 -H at -90°C , δ -18.14 (s, 0.16 H, isomer B) and -17.88 (d, 1.0 H, isomer A, $J(\text{PH})$ 12 Hz); ^{31}P - $\{^1\text{H}\}$ ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$), δ -1.4 ppm (s br, CH_2PCu); at -90°C , δ 3.7 (s, 1.0 P, CH_2PCu in isomer A) and -8.1 ppm (s, 0.16 P, CH_2PCu in isomer B). For compound II, $\nu_{\max}(\text{CO})$ at 2069s, 2032vs, 2018vs, 2005s, 1984(sh), 1975m and 1930m(br) cm^{-1} (CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ -17.76 (d, 2 H, μ_3 -H, $J(\text{PH})$ 3 Hz), 2.48-2.64 (m, 4 H, $\text{AsCH}_2\text{CH}_2\text{P}$) and 7.37-7.59 (m, 20 H, Ph); μ_3 -H at -80°C , δ -17.81 (s, 1.0 H, isomer B) and -17.87 (d, 0.37 H, isomer A, $J(\text{PH})$ 13 Hz); ^{31}P - $\{^1\text{H}\}$ ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$), δ -2.6 ppm (s br, $\text{CH}_2\text{CH}_2\text{PCu}$); at -90°C , δ 3.6 (s, 0.37 P, $\text{CH}_2\text{CH}_2\text{PCu}$ in isomer A) and -5.1 ppm (s, 1.0 P, $\text{CH}_2\text{CH}_2\text{PCu}$ in isomer B). For compound III, $\nu_{\max}(\text{CO})$ at 2067s, 2030vs, 2015vs, 2004s, 1977(sh), 1969m and 1929m(br) cm^{-1} (CH_2Cl_2). For compound IV, $\nu_{\max}(\text{CO})$ at 2067s, 2030vs, 2016vs, 2002s, 1979(sh), 1969m and 1929m(br) cm^{-1} (CH_2Cl_2).
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- 9 Similar dynamic behaviour has been previously observed for a number of other silver heteronuclear cluster compounds. For example, R.A. Brice, K. Henrick, S.C. Pearce and I.D. Salter, *J. Chem. Soc., Dalton Trans.*, (1986) in press, and ref. cited therein.