The heteronuclear cluster chemistry of the Group IB metals

VIII *. Nuclear magnetic resonance investigations of the stereochemical non-rigidity exhibited by the metal frameworks of the cluster compounds [Cu$_2$Ru$_4$(μ_3-H)$_2$(CO)$_{12}$L$_2$] (L = PPh$_3$, PMePh$_2$, PMe$_2$Ph, PEt$_3$, PMe$_3$, P(OEt)$_3$, P(OPh)$_3$, and P(OMe)$_3$) in solution

Paul J. McCarthy, Ian D. Salter, and Vladimir Šik

Department of Chemistry, University of Exeter, Exeter EX4 4QD (Great Britain)

Abstract

The new mixed-metal cluster compounds [Cu$_2$Ru$_4$(μ_3-H)$_2$(CO)$_{12}$L$_2$] (II, L = PMePh$_2$; III, L = PMe$_2$Ph; IV, L = PEt$_3$; V, L = PMe$_3$; VI, L = P(OEt)$_3$; VII, L = P(OPh)$_3$; VIII, L = P(OMe)$_3$) have been synthesized. Infrared and NMR spectroscopic data demonstrate that the metal skeletons of II–VIII adopt the same capped trigonal bipyramidal ground state geometry as that previously established for [Cu$_2$Ru$_4$(μ_3-H)$_2$(CO)$_{12}$(PPh$_3$)$_2$] (I) by single-crystal X-ray diffraction. ^{1}H and ^{31}P{^{1}H} NMR spectroscopic studies between $-90\,^\circ$C and ambient temperature show that, like I, the clusters II–VIII undergo dynamic behaviour involving coinage metal site-exchange in solution. Free energies of activation ($\Delta G^{\neq}$) for the intramolecular metal core rearrangements of I–VIII have been calculated by band-shape analysis of variable temperature ^{31}P{^{1}H} NMR spectra. The values of $\Delta G^{\neq}$ were found to be little altered by changes in the nature of the monodentate phosphine and phosphite ligands attached to the two copper atoms, although increasing the cone angle of the phosphine ligands appears to increase $\Delta G^{\neq}$ for the phosphine-containing clusters I–V.

Introduction

An interesting feature of the chemistry of Group IB metal heteronuclear cluster compounds is the stereochemical non-rigidity exhibited in solution by the metal

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* For Part VII, see ref. 1.

skeletons of some species which contain two or more $M(PR_3)$ (M = Cu, Ag or Au; R = alkyl or aryl) units [1–3]. Dynamic behaviour, which is thought to involve coinage metal site-exchange, is frequently observed when $M(PR_3)$ moieties adopt structurally inequivalent positions in the ground state geometries of such clusters [2–5]. For example, a single-crystal X-ray diffraction study [3] established that, in the solid state, $[Cu_2Ru_4(\mu_3\text{-H})_2(CO)_{12}(PPh_3)_2]$ (I) adopts a capped trigonal bipyramidal metal core structure, with two geometrically distinct $Cu(PPh_3)$ sites. However, only a single resonance was observed in the ambient temperature $^{31}P\text{-}\{^1H\}$ NMR spectrum of the cluster, although a spectrum consistent with the ground state structure was obtained at $-90°C$ [3]. An intramolecular rearrangement of the metal skeleton of the cluster in solution has been proposed [3] to explain these results. Interestingly, we have found that the clusters $[Cu_2Ru_4(\mu_3\text{-H})_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (n = 1–6), which adopt the same skeletal geometry as I, also exhibit dynamic behaviour involving coinage metal site-exchange, even though the copper atoms are linked together by the bidentate diphosphine ligands [5,6]. In fact, the nature of the attached ligand has a considerable effect on the magnitude of the free energy of activation ($\Delta G^{\neq}$) for the fluxional process, with differences of up to ca. 12 kJ mol^{-1} between $\Delta G^{\neq}$ values for the different clusters in the series [5]. In view of these novel results, we have extended this work to the synthesis of a series of compounds analogous to I, in which the copper atoms are ligated by a wide variety of simple phosphine and phosphite groups, in order to investigate the effect of the nature of monodentate ligands on the dynamic behaviour of this type of Group IB metal heteronuclear cluster.

Results and discussion

Treatment of a dichloromethane solution of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ [7] with two equivalents of the complex $[Cu(NCMe)_4]PF_6$ at $-30°C$, followed by the addition of two equivalents of the appropriate phosphine or phosphite ligand, affords the dark red cluster compounds $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ (II, L = $PMePh_2$; III, L = PMe_2Ph; IV, L = PEt_3; V, L = PMe_3; VI, L = $P(OEt)_3$) in ca. 55–70% yield. The phosphite-containing clusters $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ (VII, L = $P(OPh)_3$; VIII, L = $P(OMe)_3$) are readily obtained as dark red crystalline compounds (ca. 40–50% yield) by treating an acetone solution of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with a dichloromethane solution containing
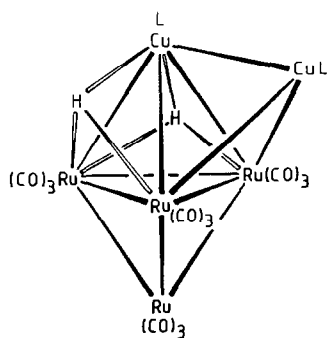
	L
I	PPh_3
II	$PMePh_2$
III	PMe_2Ph
IV	PEt_3
V	PMe_3
VI	$P(OEt)_3$
VII	$P(OPh)_3$
VIII	$P(OMe)_3$

Table 1

Analytical and physical data for the new copper–ruthenium cluster compounds

Cluster	M.p. ($\theta_c/°C$) (decomp.)	$\nu_{max}(CO)$ [a] (cm^{-1})	Yield (%) [b]	Analysis (Found (calc) (%))	
				C	H
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}(PMePh_2)_2]$ (II)	127–129	2071s, 2032vs, 2021vs, 2006s, 1974m(br), 1934w(br)	69	36.0 (35.9)	2.2 (2.2)
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}(PMe_2Ph)_2]$ (III)	109–112	2071s, 2033vs, 2021vs, 2005s, 1974m(br), 1931w(br)	70	29.5 (29.3)	2.1 (2.1)
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}(PEt_3)_2]$ (IV)	128–131	2070s, 2031vs, 2019vs, 2003s, 1972m(br), 1928w(br)	69	25.8 (26.1)	3.0 (2.9)
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}(PMe_3)_2]$ (V)	112–114	2069s, 2030vs, 2018vs, 2003s, 1974m(br), 1928w(br)	71	21.2 (21.2)	2.0 (2.0)
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}\{P(OEt)_3\}_2]$ (VI)	116–119	2074s, 2036vs, 2023vs, 2009s, 1979m(br), 1945w(br)	55	24.2 (24.0)	2.9 (2.7)
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}\{P(OPh)_3\}_2]$ (VII)	106–108	2073s, 2036vs, 2024vs, 2010s, 1982m(br), 1942w(br)	52	38.7 (38.7)	2.2 (2.1)
$[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}\{P(OMe)_3\}_2]$ (VIII)	109–111	2073s, 2035vs, 2023vs, 2008s, 1978m(br), 1943w(br)	41	19.8 (19.3)	1.6 (1.8)

[a] Measured in dichloromethane solution. [b] Based on ruthenium reactant.

two equivalents of the complex [CuClL], in the presence of TlPF$_6$. The clusters II–VIII were characterized by microanalyses and spectroscopic measurements (Tables 1 and 2). The IR spectra of II–VIII closely resemble that reported for I, implying that II–VIII adopt the same capped trigonal bipyramidal metal core structure as that previously established for I [3]. The variable temperature NMR spectra of II–VIII are also very similar to those reported for I. At ambient temperature, the $^{31}P\{^1H\}$ NMR spectrum for each of II–VIII consists of a singlet, broadened by quadrupolar effects from the copper atoms [3,8–10]. However, at low temperatures, two phosphorus resonances are observed, consistent with the proposed ground state structures of the clusters. The high field hydrido ligand signals in the ambient temperature ^1H NMR spectra of II–VIII are triplets ($J(PH)$ 6–9 Hz), showing coupling to two equivalent phosphorus atoms. However, at $-90°C$, the ^1H NMR hydrido ligand peaks are doublets ($J(PH)$ 12–19 Hz) and these signals are consistent with the proposed ground state geometries, in which only one phosphorus atom would be expected to show coupling to the hydrido ligands [3]. In addition, two separate methyl or ethyl signals, corresponding to the two inequivalent phosphine or phosphite sites in the ground state cluster structures, are visible in the ^1H NMR spectra of II, V, VI, and VIII at $-90°C$. Thus, the variable temperature NMR data clearly demonstrate that II–VIII, like I [3], undergo dynamic behaviour which exchanges the phosphorus atoms between the two distinct sites in the ground state structures. The fact that the ^1H NMR hydrido ligand signals of II–VIII retain $^{31}P–^1H$ coupling throughout the temperature range from $-90°C$ to room temperature shows that the fluxional process occurring for these clusters is intramolecular.

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Table 2

^{1}H and ^{31}P NMR data ^{a} for the new copper–ruthenium cluster compounds

Compound	Ambient temperature ^{1}H data ^{b}	Low temperature ^{1}H hydrido ligand signal ^{b,c}	Ambient temperature ^{31}P{^{1}H} data ^{d}	Low temperature ^{31}P{^{1}H} data ^{c,d}
II	−17.21 (t, 2H, μ_3-H, J(PH) 6), 1.69 (d, 6H, Me, J(PH) 6), 7.32–7.45 (m, 20H, Ph)	−17.33 (d, 2H, μ_3-H, J(PH) 12) ^{e}	−12.0 (s,br)	−8.0(s), −15.3(s)
III	−17.31 (t, 2H, μ_3-H, J(PH) 7), 1.52 (d, 12H, Me, J(PH) 7), 7.39–7.56 (m, 10H, Ph)	−17.47 (d, 2H, μ_3-H, J(PH) 13)	−26.6 (s,br)	−21.2(s), −29.6(s)
IV	−17.11 (t, 2H, μ_3-H, J(PH) 6), 1.17 (overlapping d of t, 18H CH_2CH_3, J(PH) 17, J(HH) 8), 1.75 (overlapping d of q, 12H, CH_2CH_3, J(PH) 7, J(HH) 8)	−17.30 (d, 2H, μ_3-H, J(PH) 12)	−3.9 (s,br)	2.5(s), −9.9(s) ^{f}
V	−17.39 (t, 2H, μ_3-H, J(PH) 7), 1.39 (d, 18H, Me, J(PH) 7)	−17.63 (d, 2H, μ_3-H, J(PH) 14) ^{g}	−38.4 (s,br)	−32.6(s), −40.7(s)
VI	−17.83 (t, 2H, μ_3-H, J(PH) 9), 1.24 (t, 18H, CH_2CH, J(HH) 7), 3.98 (overlapping d of q, 12H, CH_2CH_3, J(PH) 8, J(HH) 7)	−18.02 (d, 2H, μ_3-H, J(PH) 18) ^{h}	113.2 (s,br)	121.2(s), 108.1(s) ^{i}
VII	−18.30 (t, 2H, μ_3-H, J(PH) 9), 7.11–7.35 (m, 30H, Ph)	−18.79 (d, 2H, μ_3-H, J(PH) 19)	102.4 (s,br)	109.2(s), 92.6(s)
VIII	−17.88 (t, 2H, μ_3-H, J(PH) 9), 3.71 (d, 18H, Me, J(PH) 12)	−18.08 (d, 2H, μ_3-H, J(PH) 18) ^{j}	119.3 (s,br)	126.1(s), 112.1(a) ^{j}

^{a} Chemical shifts (δ) in ppm, coupling constants in Hz. ^{b} Measured in dichloromethane-d_2 solution. ^{c} Measured at −90 °C, unless otherwise stated. ^{d} ^{1}H decoupled, measured in dichloromethane-d_2-CH$_2$Cl$_2$ solution, chemical shifts positive to high frequency of 85% H$_3$PO$_4$ (external). ^{e} Me signals at −90 °C, δ 1.55 (s,br,3H) and 1.71 (s,br,3H). ^{f} Measured at −80 °C. ^{g} Me signals at −90 °C, δ 1.38 (d, 9H, J(PH) 7 Hz) and 1.46 (d, 9H, J(PH) 7 Hz). ^{h} Et signals at −90 °C, δ 1.31 (t, 9H, CH$_2$CH_3, J(HH) 7 Hz), 1.34 (t, 9H, CH$_2$CH_3, J(HH) 7 Hz), 4.02 (overlapping d of q, 6H, CH_2CH$_3$, J(PH) 8, J(HH) 7 Hz) and 4.05 (overlapping d of q, 6H, CH_2CH$_3$, J(PH) 8, J(HH) 7 Hz). ^{i} Measured at −70 °C. ^{j} Me signals at −90 °C, δ 3.69 (d, 9H, J(PH) 13 Hz) and 3.74 (d, 9H, J(PH) 14 Hz).

Table 3

Energy parameters [a] for the intramolecular metal core rearrangements in the copper–ruthenium clusters $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$

Cluster	L	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1}K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})
I	PPh$_3$ [b]	43.0 ± 0.1	13.8 ± 1.0	47.1 ± 0.2
II	PMePh$_2$	42.0 ± 0.1	0.6 ± 1.7	42.1 ± 0.4
III	PMe$_2$Ph	40.5 ± 0.2	−1.5 ± 2.5	40.1 ± 0.6
IV	PEt$_3$	41.4 ± 0.2	−0.6 ± 2.7	41.2 ± 0.6
V	PMe$_3$	39.7 ± 0.2	−3.4 ± 2.0	38.6 ± 0.4
VI	P(OEt)$_3$	42.7 ± 0.1	−4.7 ± 2.1	41.3 ± 0.5
VII	P(OPh)$_3$	41.8 ± 0.1	−3.4 ± 1.6	40.8 ± 0.4
VIII	P(OMe)$_3$	42.4 ± 0.1	−3.8 ± 5.9	41.3 ± 1.7

[a] Calculated at 298 K by band-shape analysis of variable temperature $^{31}P\{^1H\}$ NMR spectra. [b] We have redetermined the value of $\Delta G^{\neq}$ for I, which we have previously reported as 40.9 ± 0.3 kJ mol^{-1} [5].

As in the case of I [3], a rearrangement of the actual metal skeletons of II–VIII seems to be the only reasonable explanation for the NMR results.

To investigate the effect of the nature of the phosphine or phosphite ligand attached to the copper atoms on the dynamic behaviour of I–VIII, we have calculated the energy parameters for the fluxional process in each cluster by band-shape analysis of their variable temperature $^{31}P\{^1H\}$ NMR spectra (Table 3). It is well-established that energies quoted in terms of $\Delta G^{\neq}$ values are less prone to systematic errors than the other parameters calculated by band-shape analysis and, therefore, $\Delta G^{\neq}$ values are normally used for comparison purposes [11]. It can be seen from Table 3 that the magnitude of $\Delta G^{\neq}$ only varies by ca. 3 kJ mol^{-1} within the series of clusters. Thus, alterations in the nature of the monodentate phosphine and phosphite ligands attached to the copper atoms in I–VIII seem to have a much smaller effect on $\Delta G^{\neq}$ than changes in the bidentate diphosphine ligands bonded to analogous species [5]. The phosphine-containing clusters I–V show an increase in $\Delta G^{\neq}$ values with increasing phosphine cone angle [12]. A restricted Berry pseudo-rotation mechanism, via a capped square-based pyramidal intermediate, has been previously proposed for the dynamic behaviour of I [3,5]. The results for I–V suggest that the more bulky phosphine ligands increase the energy difference between the capped trigonal bipyramidal and capped square-based pyramidal skeletal geometries in these clusters. This observation is not unreasonable, as the Au–Au separations tend to be much longer in gold heteronuclear clusters containing a Au$_2$M$_3$ (M = Ru or Os) unit ligated by monodentate phosphines when the Au$_2$M$_3$ fragment adopts a square-based pyramidal rather than a trigonal bipyramidal structure [3,13,14], suggesting that there is much more steric hindrance between the phosphine ligands in the former geometry. However, no such trend is apparent for the phosphite-containing species VI–VIII. Moreover, there seems to be no correlation between $\Delta G^{\neq}$ values and the electronic properties of the attached ligands [12]. The magnitudes of $\Delta S^{\neq}$ for intramolecular fluxional processes in organometallic compounds are frequently found to be between +20 and −20 J K^{-1} mol^{-1} [15] and the $\Delta S^{\neq}$ values for I–VIII all lie in this range, which is consistent with the proposed intramolecular nature of the dynamic behaviour exhibited by these clusters in solution.

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Experimental

The techniques used and the instrumentation employed have been described elsewhere [1]. Light petroleum refers to the fraction of b.p. 40–60 °C. Established methods were used to prepare $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ [7] and $[Cu(NCMe)_4]PF_6$ [16]. Complexes [CuClL] (L = $P(OPh)_3$ or $P(OMe)_3$) were synthesized by adaptation of a published route [17]. Analytical and other physical data for the new compounds are presented in Table 1, together with their IR spectra, and Table 2 summarizes the results of NMR spectroscopic measurements. Product separation by column chromatography was performed on Aldrich Florisil (100–200 mesh).

Synthesis of the clusters $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ (L = $PMePh_2$, PMe_2Ph, PEt_3, PMe_3 or $P(OEt)_3$)

The clusters were prepared by the procedure previously described for $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ [18], with the two equivalents of the appropriate phosphine or phosphite ligand L used instead of PPh_3. For the $P(OEt)_3$-containing cluster VI, the procedure was modified so that the reaction mixture was refluxed for 1.5 h after the addition of the solution of $P(OEt)_3$, instead of being allowed to warm to ambient temperature with stirring.

Synthesis of the clusters $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ (L = $P(OPh)_3$ or $P(OMe)_3$)

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) was treated with a dichloromethane (30 cm^3) solution of [CuClL] (L = $P(OPh)_3$, 0.27 g, 0.66 mmol or L = $P(OMe)_3$, 0.15 g, 0.67 mmol) and solid TlPF$_6$ (0.30 g, 0.86 mmol) and the mixture was stirred at ambient temperature for 1 h. After filtration of the dark red mixture through a Celite pad (ca. 1 × 3 cm), the solvent was removed under reduced pressure and the crude residue was dissolved in a dichloromethane-light petroleum mixture (L = $P(OPh)_3$, 3/2 proportion or L = $P(OMe)_3$, 2/1 proportion). Chromatography on a Florisil column (20 × 3 cm) at −20 °C, eluting with a dichloromethane-light petroleum mixture (L = $P(OPh)_3$, 3/2 proportion or L = $P(OMe)_3$, 2/1 proportion) afforded a dark red fraction. After removal of the solvent from this fraction under reduced pressure, crystallization of the residue from a dichloromethane-light petroleum mixture yielded dark red microcrystals of $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ (L = $P(OPh)_3$, 0.25 g or L = $P(OMe)_3$, 0.15 g).

NMR studies

Variable temperature $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker AM 250 spectrometer, operating at 101.26 MHz. Samples were prepared under an atmosphere of dry oxygen-free nitrogen in standard 10 mm NMR tubes, using a CD_2Cl_2/CH_2Cl_2 mixture as the solvent. The NMR band-shape analyses were performed with a modified version [19] of the DNMR program of Kleier and Binsch [20].

Acknowledgements

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