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Preliminary communication

Synthesis and X-ray structure analysis of the mixed-metal cluster compound $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2]$

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Abstract

Treatment of $[Ru_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$ with two equivalents of $[CuCl\{P(CH_2Ph)_3\}]$, in the presence of $TlPF_6$, gives a mixture of the known cluster $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{\mu\text{-}P(CH_2Ph)_2(\eta^2\text{-}CH_2Ph)\}]$, as the major product, and the new compound $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2]$, which was shown by an X-ray diffraction study to have an unusual metal framework, consisting of a Ru_4 tetrahedron with one edge bridged by a $Cu\{P(CH_2Ph)_3\}$ unit and a non-adjacent face capped by the second $Cu\{P(CH_2Ph)_3\}$ group.

A wide range of cluster compounds of general formula $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ (I), in which both Cu atoms are bonded to phosphines or phosphites, have been obtained from the reaction of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with two equivalents of $[Cu(NCMe)_4]PF_6$ at −30 °C, followed by addition of two equivalents of the appropriate phosphorus donor ligand L [1,2]. Recently, however, we reported that when two equivalents of $P(CH_2Ph)_3$ are used in this reaction, the novel cluster $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{\mu\text{-}P(CH_2Ph)_2(\eta^2\text{-}CH_2Ph)\}]$ (II) is obtained [3]. In the formation of II, the steric problems, which would arise if bulky $P(CH_2Ph)_3$ groups (cone angle 165° [4]) were attached to two adjacent Cu atoms are avoided by one $P(CH_2Ph)_3$ ligand adopting a novel bidentate bonding mode, in which it bridges the two copper atoms of the capped trigonal bipyramidal metal framework via bonds from the phosphorus atom and an $\eta^2\text{-}(CH_2Ph)$ ring. We now report that if two preformed $Cu\{P(CH_2Ph)_3\}$ units are used in the reaction, the cluster is able to accommodate both of the sterically demanding ligands by a change of metal core geometry.

Treatment of an acetone solution of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ [5] with a dichloromethane solution containing two equivalents of the complex $[CuCl\{P(CH_2Ph)_3\}]$, in the presence of $TlPF_6$, affords a mixture of the previously reported [3] cluster $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{\mu\text{-}P(CH_2Ph)_2(\eta^2\text{-}CH_2Ph)\}]$ (II) (43% yield) and the novel compound $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2]$ (III) (11%

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yield). The clusters II and III are readily separated and purified by column chromatography on Florisil (100–200 mesh) at −20 °C. The identity of II was confirmed by comparison of its spectroscopic data with those of a known sample [3] and the ^{1}H and ^{31}P-{^{1}H} NMR spectra of III * are fully consistent with the proposed formulation.

X-ray structure analysis of the new cluster compound III shows that it adopts an unusual skeletal geometry, consisting of a Ru_4 tetrahedron with one edge bridged by a $Cu\{P(CH_2Ph)_3\}$ unit and a non-adjacent face capped by the second $Cu\{P(CH_2Ph)_3\}$ group (Fig. 1). The only previously reported cluster [2] with a similar metal framework structure to that exhibited by III is the $P(cyclo\text{-}C_6H_{11})_3$-

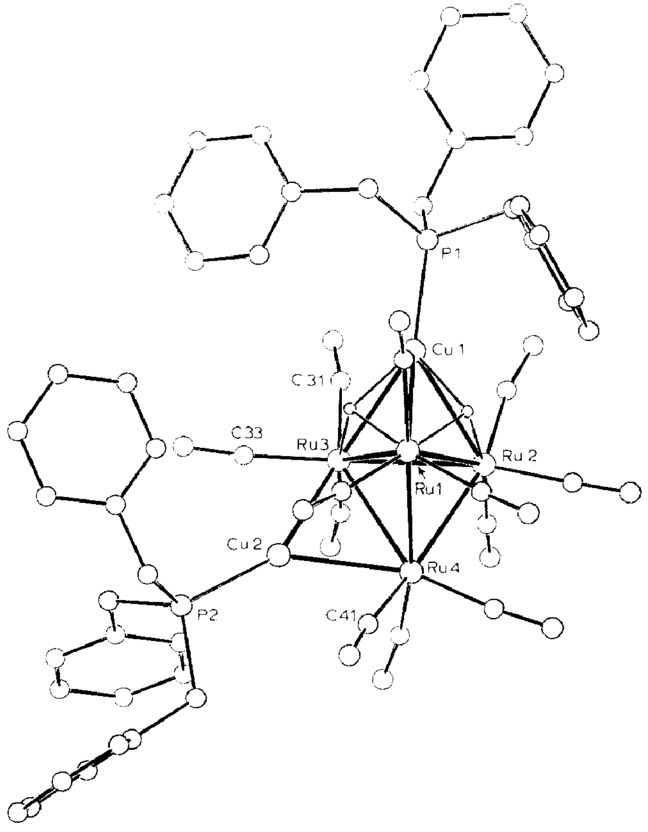

Fig. 1. Molecular structure of $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2]$ (III). Principal bond distances (Å): Ru(1)–Ru(2) 2.969(3), Ru(1)–Ru(3) 2.984(4), Ru(1)–Ru(4) 2.799(4), Ru(2)–Ru(3) 2.826(3), Ru(2)–Ru(4) 2.760(3), Ru(3)–Ru(4) 2.862(3), Ru(1)–Cu(1) 2.724(4), Ru(2)–Cu(1) 2.696(4), Ru(3)–Cu(1) 2.703(5), Ru(3)–Cu(2) 2.589(4), Ru(4)–Cu(2) 2.604(4), Cu(1)–P(1) 2.209(9), Cu(2)–P(2) 2.243(8); non-bonded contacts (Å): Cu(2)...Ru(1) 3.49, Cu(2)...Ru(2) 4.55, Cu(1)...C(31) 2.40, Cu(2)...C(33) 2.41, Cu(2)...C(41) 2.48.

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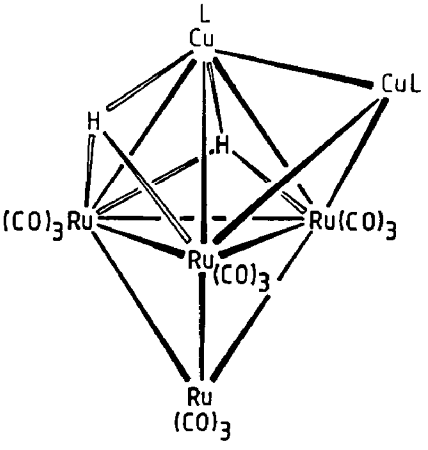
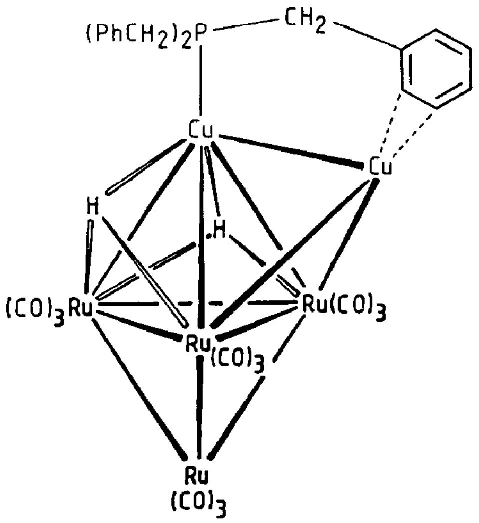
* Selected spectroscopic data for compound (III): ν_{max}(CO) at 2065m, 2034vs, 2003vs(br), 1947m(br), and 1908w(br) cm^{-1} (CH_2Cl_2). NMR: ^{1}H (CD_2Cl_2), δ −16.67 (t br, 2 H, μ_3-H, J(PH) 5 Hz), 3.09 (d, 12H, CH_2Ph, J(PH) 7 Hz), and 7.22–7.33 (m, 30 H, Ph); μ_3-H at −90 °C, δ −17.40 (s br, 1H), and −15.74 (s br, 1 H); ^{31}P-{^{1}H} (CD_2Cl_2/CH_2Cl_2) (rel. to 85% H_3PO_4 (ext.)), δ −5.0 ppm (s br); at −100 °C, δ −5.7 (s br, 1P) and −2.9 ppm (s br, 1P).

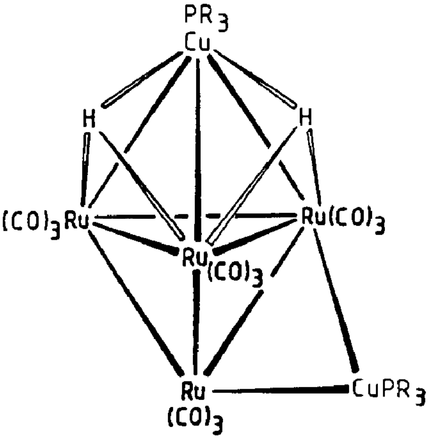


(I)

L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3,
PMe_3, $P(CHMe_2)_3$, or $P(OEt)_3$



(II)



(III, R = CH_2Ph;
IV, R = cyclo-C_6H_{11})

containing species IV. There are some very short contact distances between carbonyl carbon atoms and the copper atoms in III * (Cu(1)–C(31) 2.40, Cu(2)–C(33) 2.41,

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* Crystal data for III: $C_{54}H_{44}O_{12}P_2Cu_2Ru_4$, $M = 1477.70$, triclinic, space group $P\bar{1}$, a 14.748(3), b 19.583(4), c 11.636(2) Å, α 79.99(1), β 110.33(3), γ 107.48(3)°, U 2996.76 Å^3, $F(000) = 1456$, μ(Mo-K_α) 16.58 cm^{-1}, $Z = 2$, D_c 1.64 g cm^{-3}. Data were collected in the θ-range 3–25° with a scan width of 0.90°; $R = 0.0702$ for 3132 reflections with $I/\sigma(I) > 3.0$.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

Cu(2)–C(41) 2.48 Å). Similar structural features have been previously observed for a considerable number of copper-containing heteronuclear clusters [6].

Interestingly, at ambient temperature, the ^{31}P-{^{1}H} NMR spectrum of III is a singlet, broadened by quadrupolar effects [7], whereas at −100 °C, two broad singlets are observed, which is consistent with the ground state structure of the cluster. Thus, the two Cu{$P(CH_2Ph)_3$} units in III must be interchanging between edge-bridging and face-capping bonding modes in solution at ambient temperature. Similar dynamic behaviour has been noted [2] for the P(cyclo-C_6H_{11})$_3$-containing species IV.

The formation of both II and III in the same reaction is very interesting. A capped trigonal bipyramidal metal core structure, with the Cu atoms in close contact, seems to be the preferred skeletal geometry for clusters of general formula $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ when L is a relatively small phosphine or phosphite ligand [1,2]. However, the $P(CH_2Ph)_3$ ligand is too bulky to allow two Cu{$P(CH_2Ph)_3$} units to be adjacent in the metal framework of III. This problem is solved either by a single $P(CH_2Ph)_3$ ligand bridging both Cu atoms in a novel bidentate bonding mode, as occurs for II [3], or by the cluster adopting an apparently less favourable skeletal geometry, in which only one Cu{$P(CH_2Ph)_3$} group is in a face-capping position and the other occupies a sterically less demanding edge-bridging site, as observed for III.

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