JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 9
1987

Synthesis and Structural Characterisation of the Hexanuclear, Bimetallic, Ladder-like Cluster $HRu_5Cu(CO)_{18}PPh_3$

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The bimetallic cluster $HRu_5Cu(CO)_{18}PPh_3$ has been prepared by the reaction of CO with $H_3Ru_4(CO)_{12}CuPPh_3$, characterised by *X*-ray crystal structure analysis, and shown to contain a 'ladder-like' arrangement of Ru_5Cu based on triangular units.

Despite the current interest in the synthesis and structural analysis of heterometallic clusters, there is a lack of studies on the reactivity of these compounds. In this communication we report the synthesis and characterisation of the hexanuclear bimetallic cluster $HRu_5Cu(CO)_{18}PPh_3$ which was obtained during a mechanistic study of the reaction of the pentanuclear bimetallic cluster $H_3Ru_4(CO)_{12}CuPPh_3$ with CO. This, to our knowledge, is the first Ru_5Cu cluster to be reported.

$HRu_5Cu(CO)_{18}PPh_3$ (**1**) was obtained in 25% yield after passage of carbon monoxide through an octane solution of $H_3Ru_4(CO)_{12}CuPPh_3$[1] (**2**) at 60 °C for 24 h. Complex (**1**) was separated from other products of the reaction, *i.e.* $H_4Ru_4(CO)_{12}$, 2%; $Ru_3(CO)_{12}$, 33%; $Ru_3(CO)_{11}PPh_3$, 22%; and $Ru(CO)_4PPh_3$, 6%, by column chromatography, and characterised by i.r. and n.m.r. spectroscopy.† The remaining copper in the system seemed to be associated with a partially characterised black powder which is soluble only in polar solvents. This product exhibits no bands in the carbonyl stretching region of the i.r. spectrum. Analysis by energy dispersion by the absorption of *X*-rays (EDAX) indicated a stoicheiometric ratio of Ru : Cu : P of 3 : 2 : 2 and elemental analysis gave %C = 42.0, %H = 3.2. These data suggest a possible empirical formula $Ru_3Cu_2(PPh_3)_2H_x$. The i.r. spectrum of (**1**) exhibits eleven bands in the carbonyl stretching region, reflecting an unsymmetrical arrangement of the carbonyl groups. The ^{31}P chemical shift, by comparison with

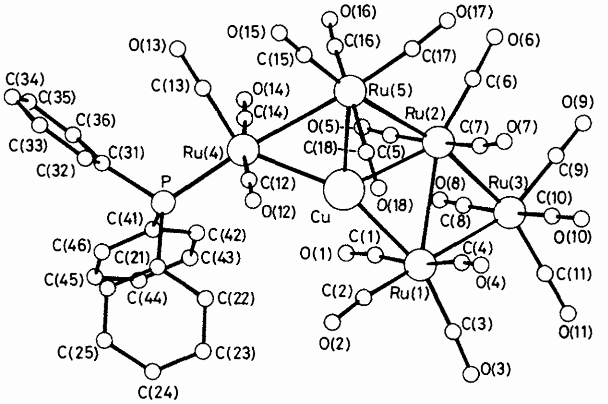

Figure 1. The molecular structure of $HRu_5Cu(CO)_{18}PPh_3$ (**1**) with H-atoms omitted for clarity. Bond lengths: Cu–Ru(1), 2.652(1); Cu–Ru(2), 2.602(1); Cu–Ru(4), 2.675(1); Cu–Ru(5), 2.654(1); Ru(1)–Ru(2), 2.977(1); Ru(1)–Ru(3), 2.893(1); Ru(2)–Ru(3), 2.823(1); Ru(2)–Ru(5), 3.020(1); Ru(4)–Ru(5), 3.051(1); Ru(4)–P, 2.349(1). Dihedral angles; Ru(1)Ru(2)Ru(3) and CuRu(1)Ru(2), 20.9°; CuRu(1)Ru(2) and CuRu(2)Ru(5), 24.8°; CuRu(2)Ru(5) and CuRu(4)Ru(5), 25.2°.

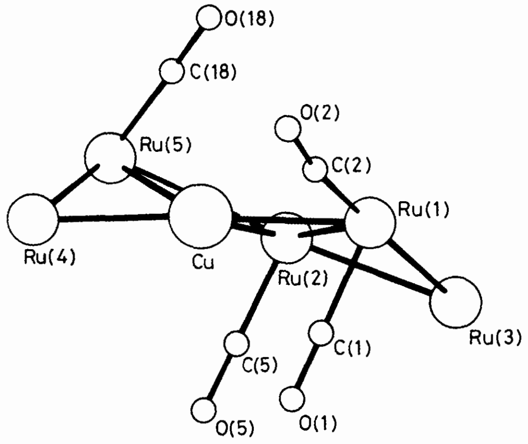

Figure 2. The Ru_5Cu metal skeleton showing the near planarity of the structure and the interaction of the Cu atom with the four semi-bridging carbonyl groups.

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† I.r. ν(CO) (cyclohexane): 2107w, 2080m, 2052s, 2049sh, 2031sh, 2026s, 2014m, 1996w, 1982w, 1971vw, and 1960w cm^{-1}; ^1H n.m.r. δ (CD_2Cl_2) −7.97 (J_{PH} 10.5 Hz); $^{31}P\{^1H\}$ n.m.r. δ (CD_2Cl_2) 39.36 p.p.m. rel. to H_3PO_4. Satisfactory elemental analyses were obtained.

that for $Ru_3(CO)_{11}PPh_3$,[2] suggests that the PPh_3 moiety has been transferred to a ruthenium atom in the carbonylation reaction. Fast atom bombardment mass spectral analysis gave a molecular ion centred at *m/z* 1336 with the expected isotope pattern, and analysis by EDAX indicated a ratio of Ru : Cu : P of 4.7(4) : 1.0(1) : 1.0(1).

Red, air-stable crystals of the complex were obtained from CH_2Cl_2–light petroleum (b.p. 40—60 °C) by vapour diffusion at room temperature.[‡]

The molecular structure of $HRu_5Cu(CO)_{18}PPh_3$ is shown in Figure 1. The metal core geometry is best described as consisting of four triangular units edge-connected in a puckered ladder-like manner, with a Ru–Cu bond forming the central rung (Figure 2). The five Ru–Ru bond lengths fall into two categories; three long, Ru(1)–Ru(2), Ru(2)–Ru(5), and Ru(4)–Ru(5), and two shorter, Ru(1)–Ru(3) and Ru(2)–Ru(3). The former category are those in Ru_2Cu triangular units, whereas the shorter distances in the Ru_3 group are comparable to those reported for $Ru_3(CO)_{12}$[4] and $Ru_3(CO)_{11}PPh_3$.[5] The Ru–Cu distances are consistent with those lengths in $H_2Ru_4(CO)_{12}(CuPPh_3)_2$.[6] The dihedral angles between adjacent triangular units are fairly constant.

The copper atom is relatively exposed. As is evident from Figure 1, there is a void on one side of the Cu atom, with which may be associated the single hydride atom but this was not located in the *X*-ray study. Evidence that the hydride may either bridge the Ru(4)–Cu edge or cap the Ru(4)–Cu–Ru(5) face is apparent from the ^1H n.m.r. spectral analysis. The doublet nature of the hydride resonance indicates phosphorus coupling and thus association of the hydride with Ru(4). In the cluster $H_2Ru_4(CO)_{12}(CuPPh_3)_2$ where the hydrides were proposed to face-bridge RuRuCu faces, the chemical shift of the resonance is δ −16.93.[6] Thus the shift of the resonance in the present molecule (δ −7.97) does suggest a significantly different environment.

This structure represents a very unusual skeletal arrangement for a heterometallic cluster. The molecule may be considered as the combining of the 48 electron fragment $Ru_3(CO)_{10}L^{2-}$ with the 34 electron fragment $Ru_2(CO)_8{}^{2-}$ resulting in the 80 electron cluster $Ru_5(CO)_{18}L^{2-}$ (2 electrons derived by the Ru–Ru bond formation). There have been several *X*-ray structure analyses of homo-pentanuclear ruthenium clusters.[7—9] The five Ru atoms in the clusters $Ru_5C(CO)_{15}$, $Ru_5C(CO)_{14}PPh_3$, and $Ru_5C(CO)_{13}(PPh_3)_2$ adopt a square pyramidal geometry with an exposed carbido-atom lying beneath the basal plane.[7] There have been fewer reports of Ru_5 clusters with hetero-metal atoms, and in each case the hetero-metal moiety is $AuPR_3$.[10—13]

Structural reports of clusters containing exposed metal atoms are very rare. Recent work[14] on the structure of $[Os_{20}M(C)_2(CO)_{48}]^{2-}$ (M = Au, Hg) indicated the central Os_8M unit being reminiscent of the Pt_9 geometry observed in $[Pt_9(CO)_{18}]^{2-}$.[15] Two raft-like structures of $Cu_3Os_3H_9(PMe_2Ph)_9$[16] and $[Os_3(CO)_{11}Hg]_3$[17] have also been reported, in which the Cu and Hg atoms respectively display unusual co-ordination. The present structure is, however, best compared with those of $Cu_3Fe_3(CO)_{12}{}^{3-}$ and $Cu_5Fe_4(CO)_{16}{}^{3-}$ (ref. 18) which consist of planar close-packed arrays of metal atoms. A semi-bridging interaction between the copper atoms and some of the carbonyl groups bound to iron appears to be a common feature in all the Cu–Fe clusters. A similar interaction is apparent between the copper atom and C(1), C(2), C(5), and C(18) illustrated in Figure 2. As with the Cu–Fe clusters the M–C–O angles are nearly linear and the M′–M–C angles are quite small: C(1)–Ru(1)–Cu, 72.0(3); C(2)–Ru(1)–Cu, 70.1(3); C(5)–Ru(2)–Cu, 71.4(3); C(18)–Ru(5)–Cu, 65.0(3)°, leading to short M′–C distances: Cu–C(1), 2.750(9); Cu–C(2), 2.664(9); Cu–C(5), 2.689(9); Cu–C(18), 2.534(9) Å. All remaining Cu–C distances are greater than 3.2 Å.

We thank the S.E.R.C. for financial support (A. C. S.), Dr. M. B. Hursthouse for the *X*-ray data collection by the S.E.R.C.–Q.M.C. Crystallographic Service, Johnson Matthey Ltd. for the loan of ruthenium chloride, and Mrs. J. M. Street for the n.m.r. spectra.

Received, 5th November 1986; Com. 1695

[‡] *Crystal data:* (**1**), $C_{36}H_{16}CuO_{18}PRu_5$, *M* = 1336.3, monoclinic, $P2_1/n$ (No. 14), *a* = 16.043(5), *b* = 14.862(18), *c* = 18.052(4) Å, β = 101.17(2)°, *U* = 4222.6 Å^3, *Z* = 4, D_c = 2.10 g cm^{-3}, *D* (flotation in CCl_4–$BrCH_2CH_2Br$) = 2.06(2) g cm^{-3}, *F*(000) = 2560, μ(Mo-K_α) = 22.85 cm^{-1}, λ(Mo-K_α) 0.7107 Å. Data were collected using an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromator using a crystal at room temperature (0.7 × 0.45 × 0.1 mm) mounted in a thin-wall capillary. 6370 unique reflections (1.5° < θ < 25°) of which 5372 with $F > 4\sigma(F)$ were used in the solution and refinement. Structure solved by direct methods[3] and Fourier techniques and refined by full-matrix least-squares to *R* 0.046 (245 parameters), anisotropic (Ru, Cu, P) and isotropic (O, C, H) atoms, $w = 1/[\sigma^2(F) + 0.0001F^2]$, *R′* = 0.055, empirical absorption correction, rigid C_6 groups [*d*(CC) = 1.395 Å], calculated phenyl H-atom co-ordinates [*d*(CH) = 0.95 Å)]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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