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Synthesis and the X-Ray Crystal Structure of $[(\mu\text{-H})Os_5Cu(CO)_{18}(PPh_3)]$

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The hexanuclear bimetallic cluster $[(\mu\text{-H})Os_5Cu(CO)_{18}(PPh_3)]$ (**1**), was prepared from the reaction of $[(\mu\text{-H})_2Os_3(CO)_{10}]$ with $CF_3COOCuPPh_3$. **1** was shown by X-ray analysis to consist of a pentaosmium framework with a copper atom bridging four of the osmium atoms to form a puckered "ladder-like" arrangement based on four triangular units.

The considerable interest shown in mixed-clusters in which one or more Cu or Au atoms are incorporated into structures containing a number of osmium atoms ligated by carbonyl groups has led to the isolation of a number of novel species.[1—12] These range from those containing Os_3 or Os_4 moiety such as $[Cu_3Os_3H_9(PMe_2Ph)_9]$,[6] $[(Os_3Au(\mu\text{-CH=CHR})(CO)_{10}(PPh_3)]$[2] and $[M_2M'_4(\mu\text{-H})_2\{\mu\text{-Ph}_2P\text{-}(CH_2)_nPPh_2\}(CO)_{12}]$[3] (M=Cu, Ag; M′=Ru, Os) to those of high nuclearity species including $[(Os_{10}C\text{-}(CO)_{24}Cu(NCMe)]$[5] and $[(Os_{11}C(CO)_{24}Cu(NCMe)]$.[1] However, that containing an Os_5 moiety has not been reported so far. We now report the synthesis and characterization of the mixed-metal hexanuclear osmium cluster, $[(\mu\text{-H})Os_5Cu(CO)_{18}(PPh_3)]$, (**1**) obtained through an entirely different pathway from its ruthenium analogue $[(\mu\text{-H})Ru_5Cu(CO)_{18}(PPh_3)]$,[12] namely by the reaction of $[(\mu\text{-H})_2Os_3(CO)_{10}]$ with $CF_3COOCuPPh_3$.

The triosmium cluster $[(\mu\text{-H})_2Os_3(CO)_{10}]$ was reacted over a period of 24 h, with an equivalent amount of $CF_3COOCu(PPh_3)$[13] in dichloromethane solution at room temperature in vacuo to afford first a dark red solution which subsequently turned orange red. Thin-layered chromatography of the products using 75% cyclohexane/25% ether afforded two major bands. Crystals of cluster $[(\mu\text{-H})Os_5Cu(CO)_{18}(PPh_3)]$ (**1**)[14] were obtained from recrystallisaton of the first major band from CH_2Cl_2/hexane. The infrared spectrum of **1** exhibits carbonyl stretching frequencies at 2114w, 2085m, 2059s, 2031vs, 2026vs, 2017s, 2009m, 1989w, 1966w, 1946w cm^{-1}. In the ^1H NMR (CD_2Cl_2) spectrum, the signal due to the phenyl ^1H is centred at $\delta=7.50$ (m). In the hydride region, a doublet centred at $\delta=-8.04$ ($J_{PH}=$ 13.18 Hz) is present. The $^{31}P\{^1H\}$ NMR (CD_2Cl_2) spectrum consists of a signal centred at $\delta=1.88$.

The molecular structure of **1** has been established by a single crystal X-ray diffraction study[15] and as shown in Fig. 1, is similar to that of the ruthenium analogue, $[(\mu\text{-H})Ru_5Cu(CO)_{18}(PPh_3)]$.[14] The cluster core geometry is further illustrated in Figs. 2 and 3. Selected bond distances and angles are given in Tables 1 and 2. The heteronuclear metal framework forms two "butterfly" arrangements with the wings fused along the Os(3)–Cu(1) bond (Fig. 2). It is interesting to note that the bond distances between Cu(1) and the four Os atoms are almost equal, being 2.589(2), 2.673(2), 2.663(2), and 2.663(2) Å. The three longer Cu-bridged Os–Os bonds are also of similar length, being 3.000(1), 3.041(1), 3.069(1) Å, with the Os(4)–Os(5) bond somewhat longer than the rest. These are significantly longer than the Os–Os bond in the parent $[Os_3(CO)_{12}]$ cluster (2.877(3) Å).[16] The two shorter Os–Os bonds which are not linked to the Cu atom, namely Os(1)–Os(2) and Os(1)–Os(3) are 2.916(1) and 2.839(1) Å respectively. These are quite close to the Os–Os bond lengths in $[Os_3(CO)_{12}]$.[16]

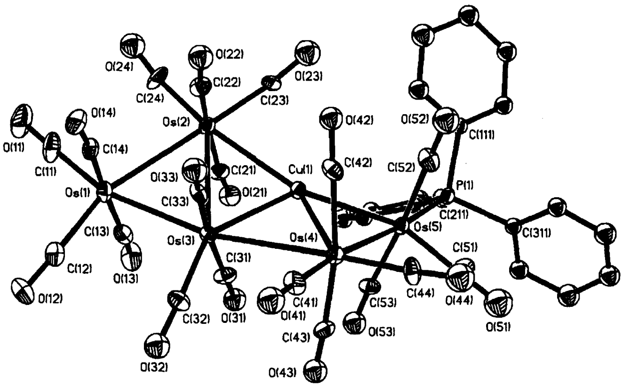

Fig. 1. The molecule structure of (μ-H) $Os_5Cu(CO)_{18}PPh_3$ (**1**) with H-atoms omitted for clarity.

Table 1. Bond Lengths (Å)

Os(1)– Os(2)	2.916(1)	Os(1)– Os(3)	2.839(1)
Os(2)– Os(3)	3.000(1)	Os(2)– Cu(1)	2.673(2)
Os(3)– Os(4)	3.041(1)	Os(3)– Cu(1)	2.589(2)
Os(4)– Os(5)	3.069(1)	Os(4)– Cu(1)	2.663(2)
Os(5)– Cu(1)	2.663(2)	Os(5)– P(1)	2.353(3)
Os(1)– C(11)	1.900(21)	Os(1)– C(12)	1.912(19)
Os(1)– C(13)	1.964(18)	Os(1)– C(14)	1.918(16)
Os(2)– C(21)	1.968(18)	Os(2)– C(22)	1.955(16)
Os(2)– C(23)	1.873(18)	Os(2)– C(24)	1.883(15)
Os(3)– C(31)	1.906(17)	Os(3)– C(32)	1.813(18)
Os(3)– C(33)	1.931(13)	Os(4)– C(41)	1.855(15)
Os(4)– C(42)	1.951(18)	Os(4)– C(43)	1.928(15)
Os(4)– C(44)	1.884(15)	Os(5)– C(51)	1.850(22)
Os(5)– C(52)	1.943(17)	Os(5)– C(53)	1.914(17)

Table 2. Bond Angles (°)

Os(2)- Os(1)- Os(3)	62.8(1)	Os(1)- Os(2)- Os(3)	57.3(1)
Os(1)- Os(2)- Cu(1)	108.6(1)	Os(3)- Os(2)- Cu(1)	53.9(1)
Os(1)- Os(3)- Os(2)	59.8(1)	Os(1)- Os(3)- Os(4)	167.6(1)
Os(2)- Os(3)- Os(4)	107.9(1)	Os(1)- Os(3)- Cu(1)	113.5(1)
Os(2)- Os(3)- Cu(1)	56.6(1)	Os(4)- Os(3)- Cu(1)	55.8(1)
Os(3)- Os(4)- Cu(1)	53.5(1)	Os(3)- Os(4)- Os(5)	104.6(1)
Os(5)- Os(4)- Cu(1)	54.8(1)	Os(4)- Os(5)- Cu(1)	54.8(1)
Os(4)- Os(5)- P(1)	174.3(1)	Cu(1)- Os(5)- P(1)	122.6(1)
Os(2)- Cu(1)- Os(4)	132.5(1)	Os(2)- Cu(1)- Os(3)	69.5(1)
Os(2)- Cu(1)- Os(5)	155.8(1)	Os(3)- Cu(1)- Os(4)	70.7(1)
Os(4)- Cu(1)- Os(5)	70.4(1)	Os(3)- Cu(1)- Os(5)	134.0(1)
Os(5)- P(1)- C(111)	115.2(5)	Os(5)- P(1)- C(211)	119.2(4)
Os(5)- P(1)- C(311)	111.4(4)		

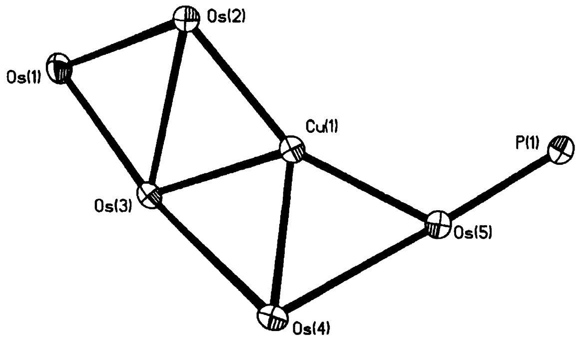

Fig. 2. The Os_5Cu metal skeleton showing the near planarity of the structure.

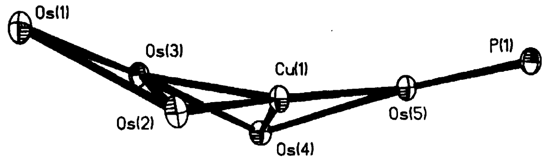

Fig. 3. The Os_5Cu core geometry showing the near equidistance between the three Cu-bridged Os atoms and between the Cu atom and the four bridging Os atoms.

The cluster core geometry can also be described as consisting of four fused metal triangles with varying degrees of puckering. The dihedral angles between Os(1)Os(2)Os(3) and Os(2)Os(3)Cu(1), Os(2)Os(3)Cu(1) and Os(3)Os(4)Cu(1), Os(3)Os(4)Cu(1) and Os(4)Os(5)Cu(1) planes are 20.7°, 26.5° and 25.1° respectively, while the corresponding Os–Cu–Os bond angles are 69.5°, 70.0°, and 70.4° respectively. All the eighteen carbonyl groups are terminally coordinated. The mean axial and equatorial Os–C (carbonyl) distances are 1.938 and 1.871 Å respectively. The bond distances for the two equatorial carbonyls associated with Os(1), which is not bonded to Cu, are longer than those associated with the four Cu-bonded Os atoms, being 1.900(21) and 1.912(19) Å. The bulky PPh_3 group occupies an equatorial position. The bond length of Os(5)–P(1) is 2.353(3) Å and average bond angle of Os–P–C is 115.3(1)°.

^1H NMR spectroscopic study indicates the presence of hydride [$\delta = -8.04$ (d, $J_{PH} = 13.18$ Hz)], although this is not found crystallographically. The cluster is a 90 electron system, containing nine metal-metal bonds, consistent with the EAN rule.[17] The splitting of the ^1H signal is attributed to coupling of phosphorus nucleous bonded to Os(5). As the copper atom is relatively exposed with a void on one side (Fig. 3), this suggests that the hydride may bridge Os(4)–Os(5), Os(5)–Cu(1), or Os(4)–Os(5)–Cu(1). This is similar to the findings of the ruthenium analogue $[(\mu\text{-H})Ru_5Cu(CO)_{18}(PPh_3)]$.[12] The chemical shift of the resonance hydride ($\delta = -8.04$) suggests a significantly different environment from the proposed face-bridged RuRuCu hydride ($\delta = -16.93$)[18] in the $[H_2Ru_4(CO)_{12}(CuPPh_3)_2]$ cluster. As bridging hydride has been shown to result in lengthening of bonds,[2] it is very likely that the bridging hydride may be situated between Os(4) and Os(5). This is also consistent with the somewhat longer bond length between these two Os atoms.

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14) Anal. data for **1**. Found: C, 24.36; H, 0.84%. Calcd for $C_{36}H_{16}O_{16}PCuOs_5$: C, 24.69; H, 0.91%.

15) The crystal data for $[(\mu\text{-H})Os_5Cu(CO)_{18}(PPh_3)]$ are as follows: $C_{36}H_{16}O_{10}PCuOs_5$, MW=1781.69, monoclinic, space group $P2_1/n$, a=16.072(4), b=14.832(2), c=18.032(4) Å, β=100.97(2)°, U=4220.4(15) Å^3, D_c=2.803 g cm^{-3}, T=293 K, Z=4, $F(000)$=3196, $\lambda(\text{Mo}K\alpha)$=0.71073 Å, $\mu(\text{Mo}K\alpha)$=156.0 cm^{-1}. Intensity data were collected on a single crystal of dimensions 0.15×0.25×0.20 mounted on a Siemens R3m/V diffractometer by ω–2θ scan technique ($3.5° \leq 2\theta \leq 50.0°$). A semi-empirical absorption correction was applied to the data ($T_{\min}/T_{\max}$=0.1145/0.2403). The structure was solved by direct methods and refined by Full-Matrix Least-Squares to R=6.40 % and R_w=6.81 % for 7645 observed reflections with $[F>5.0\ F\sigma(F)]$. Goodness-of-Fit=0.48, $\Delta/\sigma_{\text{mean}}$=0.362, $\Delta/\sigma_{\max}$=1.675. Weighting scheme $w^{-1}=\sigma^2(F)+0.0097F^2$. Siemens SHELXTL PLUS software was used for all computations.

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19) The complete F_o-F_c data are deposited as Document No. 66006 at the Office of the Editor of Bull. Chem. Soc. Jpn.