

Boride Cluster Fusion *via* an M_4 -unit ($M = \text{Cu}$ or Ag): Molecular Structure of $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}_2\text{Cu}_4(\mu\text{-Cl})][\text{Cl}]$ [$\text{ppn} = (\text{PPh}_3)_2\text{N}$]

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The reaction of $[\text{ppn}][\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]$ with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ in the presence of $[\text{ppn}][\text{Cl}]$ yields $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}_2\text{Cu}_4(\mu\text{-Cl})][\text{Cl}]$, which has been structurally characterised; the introduction of silver in place of copper yields $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}_2\text{Ag}][\text{Cl}]$ in addition to $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}_2\text{Ag}_4(\mu\text{-Cl})][\text{Cl}]$.

Fusion of transition metal or borane clusters *via* single $\text{Hg}^{1,2}$, $\text{Tl}^{3,3}$, $\text{Ag}^{1,4}$ or $\text{Au}^{1,5-8}$ atoms has been reported. Fusion *via* multimetal units is less common, for example $[\{\text{M}_9(\text{CO})_{21}\text{C}\}_2\text{Hg}_3]^{2-}$ for $M = \text{Ru}^9$ or Os^2 , $[\text{Au}_2\{\text{AuPEt}_3\}_4\text{-}\{\text{B}_{10}\text{H}_{12}\}_2]^{10}$, $[\{\text{MoC}_2\text{B}_9\text{H}_{10}(\text{CO})_3\}_2\text{Cu}_2(\mu\text{-H})_2]^{2-11}$ and $[\text{Cu}_3\{\text{C}_2\text{B}_9\text{H}_9(4\text{-C}_5\text{H}_4\text{N-CO}_2\text{Me})\}_3(\mu\text{-H})_3]^{12}$. Cu_n -units are central to $[\text{Cu}_3\{\text{Fe}(\text{CO})_4\}_3]^{3-}$,¹³ $[\text{Cu}_5\{\text{Fe}(\text{CO})_4\}_4]^{3-}$,¹³ $[\text{Cu}_6\{\text{Fe}(\text{CO})_4\}_4]^{2-}$,^{13,14} and $[\text{Cu}_3\{\text{Os}(\text{PMe}_2\text{Ph})_3\}_3(\mu\text{-H})_9]^{15}$. We have observed the facile fusion of two ferra- or ruthena-borane butterfly clusters by a gold(I) atom^{7,8} *via* a route that involves Au-P bond cleavage in the phosphine gold(I) chloride precursor. The formation of $[\{\text{M}_4\text{H}(\text{CO})_{12}\text{BH}\}_2\text{Au}]^-$ ($M = \text{Fe}$ or Ru) competes with that of $[\text{M}_4\text{H}(\text{CO})_{12}\text{BHAuL}]$ and $[\text{M}_4\text{H}(\text{CO})_{12}\text{BAu}_2\text{L}_2]$ ($L =$ phosphine) depending upon L .⁸ We now report reactions that introduce copper(I) or silver(I) into the butterfly metallaborane $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]^-$.

Reactions of cluster anions with $[\text{M}(\text{NCMe})_4]^+$ ($M = \text{Cu}$ or Ag) may lead to species incorporating $\{\text{MNCMe}\}$ fragments which, in some cases, have been converted into M^I phosphine fragments.¹⁶ We have investigated the reactivity of $[\text{M}(\text{NCMe})_4][\text{BF}_4]$ towards $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]^-$ with the aim of seeing whether the products obtained were related to those formed in the reactions AuLCl ($L =$ phosphine) with $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]^-$.⁸ An immediate colour change (to deep red for $M = \text{Cu}$ and to brown for $M = \text{Ag}$) is observed upon addition of ≥ 2 mol equiv. of $[\text{M}(\text{NCMe})_4][\text{BF}_4]$ ($M = \text{Cu}^{17}$ or Ag^{18}) to crude $[\text{ppn}][\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]^{19}$ in CH_2Cl_2 , $[\text{ppn}][\text{Cl}]$ being present. AgBF_4 in MeCN may be used in place of the isolated salt $[\text{Ag}(\text{NCMe})_4][\text{BF}_4]$.

For $M = \text{Cu}$, separation of the products by TLC (CH_2Cl_2 :hexane 1:1) gives one major product, red $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}_2\text{Cu}_4(\mu\text{-Cl})][\text{Cl}]$, $[\text{ppn}][\mathbf{1}][\text{Cl}]^\dagger$ in 60% yield. No simple compound of the type $[\text{Ru}_4(\text{CO})_{12}\text{BH-Cu}(\text{NCMe})]$ was observed and, consistent with this fact, the addition of triphenylphosphine to the crude reaction mixture did not yield a compound of the type $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH-CuPPh}_3]$.

[†] $[\text{ppn}][\mathbf{1}][\text{Cl}]$: ^1H NMR [400 MHz; $(\text{CD}_3)_2\text{CO}$] δ 7.8–7.5 (m, Ph), –19.96 (s, Ru–H–Ru); ^{11}B NMR [128 MHz; $(\text{CD}_3)_2\text{CO}$] δ +148.8; IR (CH_2Cl_2) ν/cm^{-1} 2067m, 2046s, 2039vs, 1992m, 1970w. FAB-MS in 3-NBA matrix for $[\mathbf{1}]$, m/z 1797 (P^-) (calc. for $^{12}\text{C}_{24}^{1}\text{H}_2^{11}\text{B}_2^{35}\text{Cl}^{-6}\text{Cu}_4^{16}\text{O}_{24}^{101}\text{Ru}_8$ 1795).

For $M = \text{Ag}$, separation of products by TLC (CH_2Cl_2 :hexane 1:1) yields two major products, yellow $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}\}_2\text{Ag}]$, $[\text{ppn}][\mathbf{2}]^\ddagger$ (30%) and orange $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}_2\text{Ag}_4(\mu\text{-Cl})][\text{Cl}]$, $[\text{ppn}][\mathbf{3}][\text{Cl}]^\S$ (40%). The identity of $[\text{ppn}][\mathbf{3}][\text{Cl}]$ was deduced in part by a comparison of its spectroscopic properties with those of $[\text{ppn}][\mathbf{1}][\text{Cl}]$ crystallographic data for which are presented below. Anion $[\mathbf{2}]^\P$ consists of two $\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}\}$ -subclusters fused in a mutually *trans*-orientation⁸ *via* an Ag^I centre as indicated in Scheme 1. The structure of $\mathbf{2}$ is analogous to that of $[\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}\}_2\text{Au}]^-$.⁸

A suitable crystal of $[\text{ppn}][\mathbf{1}][\text{Cl}]$ was grown from CH_2Cl_2 layered with hexane. The molecular structure of $\mathbf{1}$ is shown in Fig. 1; it cocrystallises with $[\text{ppn}][\text{Cl}]$. $\mathbf{1}$ consists of two $\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}$ -subclusters fused *via* a tetrahedral Cu_4 -unit, one edge of which is bridged by a chloride ligand. Each

[‡] $[\text{ppn}][\mathbf{2}]$: ^1H NMR [400 MHz; $(\text{CD}_3)_2\text{CO}$] δ 7.8–7.5 (m, Ph), –5.1 (br, Ru–H–B), –20.94 (s, Ru–H–Ru); 128 MHz [128 MHz; $(\text{CD}_3)_2\text{CO}$] δ +130.6; IR (CH_2Cl_2) ν/cm^{-1} 2079w, 2049vs, 2021w, 1990m. FAB-MS in 3-NBA matrix for $[\mathbf{2}]$, m/z 1617 (P^-) (calc. for $^{12}\text{C}_{24}^{1}\text{H}_4^{108}\text{Ag}^{11}\text{B}_2^{16}\text{O}_{24}^{101}\text{Ru}_8$ 1614).

[§] $[\text{ppn}][\mathbf{3}][\text{Cl}]$: ^1H NMR [400 MHz; $(\text{CD}_3)_2\text{CO}$] δ 7.8–7.5 (m, Ph), –20.20 (s, Ru–H–Ru); ^{11}B NMR [128 MHz; $(\text{CD}_3)_2\text{CO}$] δ +156.2; IR (CH_2Cl_2) ν/cm^{-1} 2068m, 2048s, 2035vs, 1991m, 1976sh; FAB-MS in 3-NBA matrix for $[\mathbf{3}]$, m/z 1971 (P^-) (calc. for $^{12}\text{C}_{24}^{1}\text{H}_2^{108}\text{Ag}_4^{11}\text{B}_2^{35}\text{Cl}^{16}\text{O}_{24}^{101}\text{Ru}_8$ 1971).

[¶] We have determined crystallographically the structure of anion $[\mathbf{2}]$ (see Scheme 1) and the results will be presented in a full paper.

^{||} *Crystal data* for $[\text{ppn}][\mathbf{1}][\text{Cl}]$: $\text{C}_{60}\text{H}_{32}\text{B}_2\text{Cl}_2\text{Cu}_4\text{NO}_{24}\text{P}_2\text{Ru}_8$, $M = 2366.0$, triclinic, $P\bar{1}$. $a = 10.150(3)$, $b = 17.865(6)$, $c = 20.672(6)$ Å, $\alpha = 83.17(2)$, $\beta = 81.72(2)$, $\gamma = 86.90(2)^\circ$, $U = 3680(2)$ Å³, $Z = 2$, $D_c = 2.135$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 29.09$ cm⁻¹, $T = 298$ K. Intensity data were collected through the 2θ range of 4–50°. Of 13 332 data collected (Siemens P4 diffractometer, SHELXTL PLUS software), 12 941 were independent and 8818 with $F_o \geq 5\sigma(F_o)$ were observed. All non-hydrogen atoms were anisotropically refined except for the cation carbon atoms; hydrogen atom contributions were ignored. Atom Cl(2) is disordered between two sites related by a centre of inversion. $R_F = 5.36\%$, $R_{(wF)} = 6.59\%$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

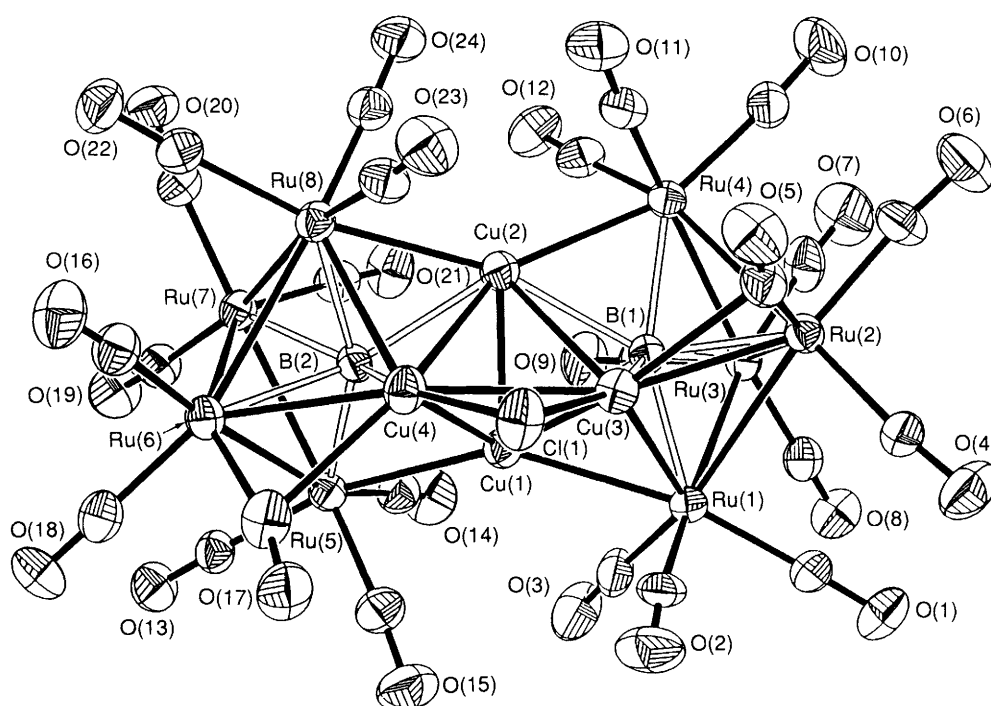
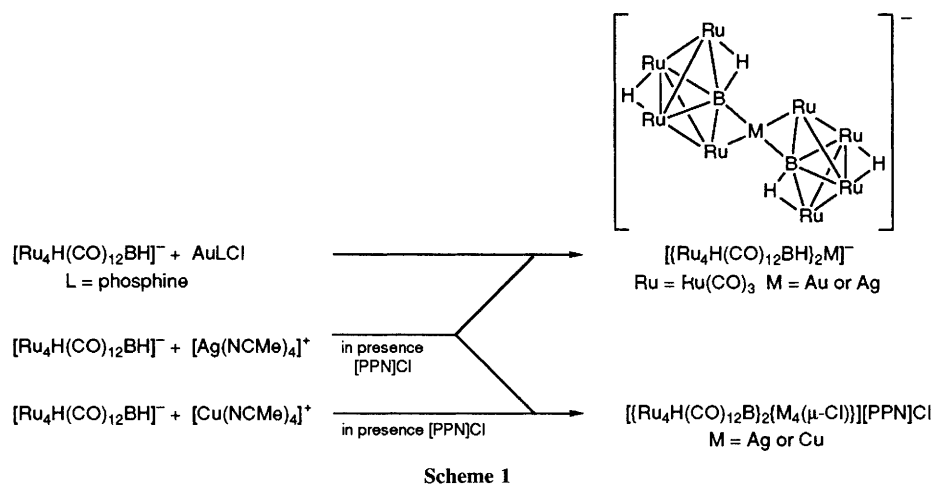


Fig. 1 Molecular structure of **1**: Ru(1)–Ru(2) 2.906(1), Ru(2)–Ru(3) 2.890(1), Ru(1)–Ru(3) 2.835(1), Ru(2)–Ru(4) 2.851(1), Ru(3)–Ru(4) 2.849(1), Ru(5)–Ru(6) 2.855(1), Ru(5)–Ru(7) 2.843(1), Ru(6)–Ru(7) 2.902(1), Ru(6)–Ru(8) 2.913(1), Ru(7)–Ru(8) 2.828(1), Ru(1)–B(1) 2.13(1), Ru(2)–B(1) 2.32(1), Ru(3)–B(1) 2.21(1), Ru(4)–B(1) 2.13(1), Ru(5)–B(2) 2.10(1), Ru(6)–B(2) 2.33(1), Ru(7)–B(2) 2.21(1), Ru(8)–B(2) 2.16(1), Ru(1)–Cu(1) 2.598(2), Ru(5)–Cu(1) 2.559(1), Ru(4)–Cu(2) 2.534(1), Ru(8)–Cu(2) 2.576(2), Ru(2)–Cu(3) 2.703(2), Ru(1)–Cu(3) 2.604(2), Ru(6)–Cu(4) 2.670(2), Ru(8)–Cu(4) 2.618(2), Cu(1)–B(1) 2.33(1), Cu(1)–B(2) 2.28(1), Cu(2)–B(2) 2.29(1), Cu(3)–B(1) 2.09(1), Cu(4)–B(2) 2.10(1), Cu(3)–Cl(1) 2.220(3), Cu(4)–Cl(1) 2.205(3), Cu(1)–Cu(2) 2.442(2), Cu(1)–Cu(3) 2.639(2), Cu(1)–Cu(4) 2.678(2), Cu(2)–Cu(3) 2.679(2), Cu(2)–Cu(4) 2.646(2), Cu(3)–Cu(4) 2.660(2) Å

subcluster retains the Ru_4B -butterfly core of the precursor^{19,20} but in **1** each boron atom is denuded of any B–H interactions and is within bonding contact of four ruthenium and three copper atoms. Each of the two $\text{Ru}_{\text{wingtip}}\text{–B}$ edges of each Ru_4B -core is bridged by a copper atom and the inter-copper distance Cu(1)–Cu(2) is short at 2.442(2) Å. This value compares with 2.55 Å²¹ in copper metal and 2.403(1) Å in $[\{\text{MoC}_2\text{B}_9\text{H}_{10}(\text{CO})_3\}_2\text{Cu}_2(\mu\text{-H})_2]^{2-}$.¹¹ The chloro-bridged edge Cu(3)–Cu(4) is 2.660(2) Å. The Cu(1)–B and Cu(2)–B distances range from 2.28 to 2.33 Å and these values are comparable with those observed for three-centre two-electron bridging B–Cu–B interactions for example in $[\{\mu\text{-Cu}(\text{PPh}_3)_2\}_2\text{B}_3\text{H}_8]$.²² The edges Cu(3)–B(1) and Cu(4)–B(2) are shorter at 2.09(1) and 2.10(1) Å, respectively. From the point of view of each boron atom, the environment in **1** resembles

that found in $[\text{Fe}_4(\text{CO})_{12}\text{BAu}_3(\text{PPh}_3)_3]$ although in **1** ¹H NMR spectroscopic data confirm that each Ru_4B -unit retains one hydride ligand. These hydrogen atoms were not located directly but may be reasonably placed along Ru(2)–Ru(3) and Ru(6)–Ru(7), the hinge-edges of the two butterflies.^{8,19,20,22}

The fusion of two $\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}\}$ -units via Au^I occurs only *via* a single atom.⁸ The present work shows that the introduction of Ag^I leads similarly to fusion *via* a single atom but, as shown in Scheme 1, competing with this is fusion *via* a tetranuclear silver fragment. For copper, fusion *via* a Cu_4 -unit is exclusively observed. In **1** and **3**, the ruthenaboride subclusters are formally $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}]^{2-}$ units and thus the central $[\text{M}_4(\mu\text{-Cl})]$ unit must carry a 4+ charge. Unless another proton, so far unaccounted for, is present in **1** and **3** (and by symmetry this would have to be associated with the

M₄-core) the assignment of the 4+ charge leads to an ambiguity in the assignment of oxidation states to the group 11 metal atoms. This problem is currently being investigated. In addition, the cocrystallisation of **1**, and by analogy, **3**, with [ppn][Cl] begs the question of association in solution. We are studying this aspect of the compounds; it is possible that the solution cluster species carries an extra bridging chloride ligand and in Fig. 1 the exposed nature of the Cu(1)–Cu(2) edge is apparent.

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