

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

Sylvia M. Draper,<sup>a</sup> Andrew D. Hattersley,<sup>a</sup> Catherine E. Housecroft<sup>\*a</sup> and Arnold L. Rheingold<sup>\*b</sup>

<sup>a</sup> University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

<sup>b</sup> Department of Chemistry, University of Delaware, Newark, DE 19716, USA

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  $[\text{ppn}][\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}\}_2\text{Ag}]$  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  $\text{Hg}^{\text{I}}$ ,<sup>1,2</sup>  $\text{Tl}^{\text{III}}$ ,<sup>3</sup>  $\text{Ag}^{\text{I}}$ <sup>4</sup> or  $\text{Au}^{\text{I}}$ <sup>5-8</sup> 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  $M = \text{Ru}^{\text{I}}$  or  $\text{Os}^{\text{I}}$ ,<sup>2</sup>  $[\text{Au}_2\{\text{AuPEt}_3\}_4\text{-}\{\text{B}_{10}\text{H}_{12}\}_2]$ ,<sup>10</sup>  $[\{\text{MoC}_2\text{B}_9\text{H}_{10}(\text{CO})_3\}_2\text{Cu}_2(\mu\text{-H})_2]^{2-}$ <sup>11</sup> and  $[\text{Cu}_3\{\text{C}_2\text{B}_9\text{H}_9(4\text{-C}_5\text{H}_4\text{N-CO}_2\text{Me})\}_3(\mu\text{-H})_3]$ .<sup>12</sup>  $\text{Cu}_n$ -units are central to  $[\text{Cu}_3\{\text{Fe}(\text{CO})_4\}_3]^{3-}$ ,<sup>13</sup>  $[\text{Cu}_5\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ ,<sup>13</sup>  $[\text{Cu}_6\{\text{Fe}(\text{CO})_4\}_4]^{2-}$ <sup>13,14</sup> and  $[\text{Cu}_3\{\text{Os}(\text{PMe}_2\text{Ph})_3\}_3(\mu\text{-H})_9]$ .<sup>15</sup> We have observed the facile fusion of two ferra- or ruthena-borane butterfly clusters by a gold(I) atom<sup>7,8</sup> *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  $\text{Ru}$ ) competes with that of  $[\text{M}_4\text{H}(\text{CO})_{12}\text{BH}\text{AuL}]$  and  $[\text{M}_4\text{H}(\text{CO})_{12}\text{BAu}_2\text{L}_2]$  ( $L =$  phosphine) depending upon  $L$ .<sup>8</sup> 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  $\text{Ag}$ ) may lead to species incorporating  $\{\text{MNCMe}\}$  fragments which, in some cases, have been converted into  $M^{\text{I}}$  phosphine fragments.<sup>16</sup> 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  $\text{AuLCl}$  ( $L =$  phosphine) with  $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]^-$ .<sup>8</sup> An immediate colour change (to deep red for  $M = \text{Cu}$  and to brown for  $M = \text{Ag}$ ) is observed upon addition of  $\geq 2$  mol equiv. of  $[\text{M}(\text{NCMe})_4][\text{BF}_4]$  ( $M = \text{Cu}$ <sup>17</sup> or  $\text{Ag}$ <sup>18</sup>) to crude  $[\text{ppn}][\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]^{19}$  in  $\text{CH}_2\text{Cl}_2$ ,  $[\text{ppn}][\text{Cl}]$  being present.  $\text{AgBF}_4$  in  $\text{MeCN}$  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 ( $\text{CH}_2\text{Cl}_2$ :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  $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH-CuPPh}_3]$ .

<sup>†</sup>  $[\text{ppn}][\mathbf{1}][\text{Cl}]$ : <sup>1</sup>H NMR [400 MHz;  $(\text{CD}_3)_2\text{CO}$ ]  $\delta$  7.8–7.5 (m, Ph), –19.96 (s, Ru–H–Ru); <sup>11</sup>B NMR [128 MHz;  $(\text{CD}_3)_2\text{CO}$ ]  $\delta$  +148.8; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu/\text{cm}^{-1}$  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 ( $\text{CH}_2\text{Cl}_2$ :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*-orientation<sup>8</sup> *via* an  $\text{Ag}^{\text{I}}$  centre as indicated in Scheme 1. The structure of  $\mathbf{2}$  is analogous to that of  $[\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}\}_2\text{Au}]^-$ .<sup>8</sup>

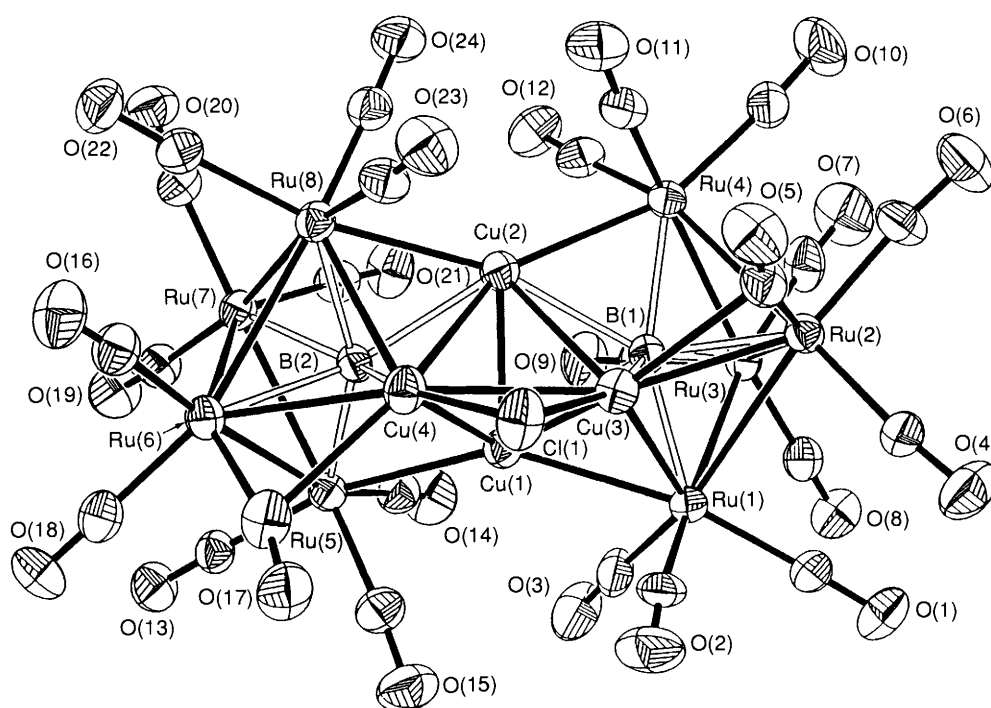
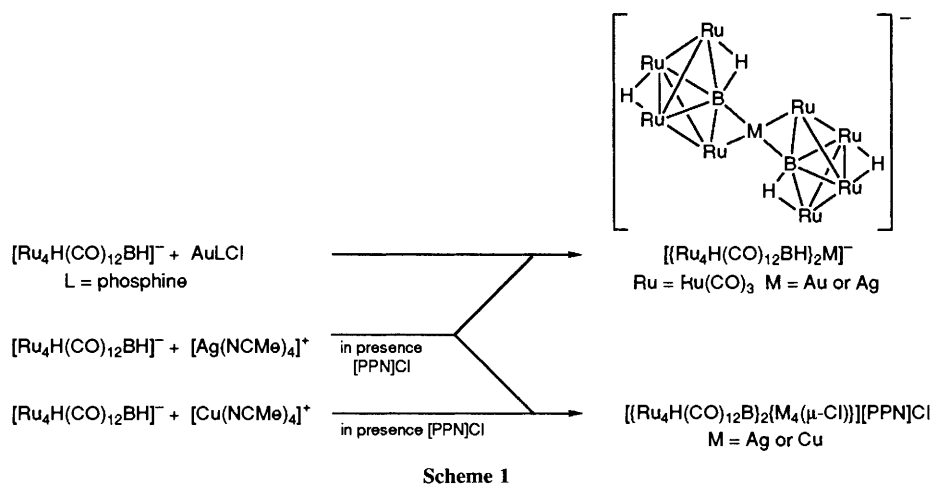
A suitable crystal of  $[\text{ppn}][\mathbf{1}][\text{Cl}]$  was grown from  $\text{CH}_2\text{Cl}_2$  layered with hexane.  $\parallel$  The molecular structure of  $\mathbf{1}$  is shown in Fig. 1; it cocrystallises with  $[\text{ppn}][\text{Cl}]$ .  $\mathbf{1}$  consists of two  $\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{B}\}$ -subclusters fused *via* a tetrahedral  $\text{Cu}_4$ -unit, one edge of which is bridged by a chloride ligand. Each

<sup>‡</sup>  $[\text{ppn}][\mathbf{2}]$ : <sup>1</sup>H NMR [400 MHz;  $(\text{CD}_3)_2\text{CO}$ ]  $\delta$  7.8–7.5 (m, Ph), –5.1 (br, Ru–H–B), –20.94 (s, Ru–H–Ru); 128 MHz [128 MHz;  $(\text{CD}_3)_2\text{CO}$ ]  $\delta$  +130.6; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu/\text{cm}^{-1}$  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).

<sup>§</sup>  $[\text{ppn}][\mathbf{3}][\text{Cl}]$ : <sup>1</sup>H NMR [400 MHz;  $(\text{CD}_3)_2\text{CO}$ ]  $\delta$  7.8–7.5 (m, Ph), –20.20 (s, Ru–H–Ru); <sup>11</sup>B NMR [128 MHz;  $(\text{CD}_3)_2\text{CO}$ ]  $\delta$  +156.2; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu/\text{cm}^{-1}$  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).

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

$\parallel$  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,  $\alpha = 83.17(2)$ ,  $\beta = 81.72(2)$ ,  $\gamma = 86.90(2)^\circ$ ,  $U = 3680(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.135$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 29.09$  cm<sup>-1</sup>,  $T = 298$  K. Intensity data were collected through the  $2\theta$  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  $\text{Ru}_4\text{B}$ -butterfly core of the precursor<sup>19,20</sup> 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  $\text{Ru}_4\text{B}$ -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 Å<sup>21</sup> in copper metal and 2.403(1) Å in  $[\{\text{MoC}_2\text{B}_9\text{H}_{10}(\text{CO})_3\}_2\text{Cu}_2(\mu\text{-H})_2]^{2-}$ .<sup>11</sup> 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  $[\{\mu\text{-Cu}(\text{PPh}_3)_2\}_2\text{B}_3\text{H}_8]$ .<sup>22</sup> 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** <sup>1</sup>H NMR spectroscopic data confirm that each  $\text{Ru}_4\text{B}$ -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.<sup>8,19,20,22</sup>

The fusion of two  $\{\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}\}$ -units *via* Au<sup>I</sup> occurs only *via* a single atom.<sup>8</sup> The present work shows that the introduction of Ag<sup>I</sup> 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  $\text{Cu}_4$ -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

M<sub>4</sub>-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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