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Boride cluster fusion through copper and silver. Crystal structure of $[(Ph_3P)_2N][(HRu_4(CO)_{12}BH)_2Ag]$

Catherine E. Housecroft [a,*], Sylvia M. Draper [b], Andrew D. Hattersley [b], Arnold L. Rheingold [c]

[a] *Institute für Anorganische Chemie, Spitalstrasse 51, CH Basel 4056, Switzerland*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*
[c] *Department of Chemistry, University of Delaware, Newark, DE 19716, USA*

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This paper is dedicated to Sheldon Shore on the occasion of his 70th birthday.

Abstract

Reaction of $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ with $[Cu(NCMe)_4][BF_4]$ in the presence of $[(Ph_3P)_2N]Cl$ leads to $[(Ph_3P)_2N][(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)]Cl$, confirmed by a single crystal structure determination. A silver analogue is produced from the reactions of $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ with $[Ag(NCMe)_4][BF_4]$ or $AgBF_4$, but its formation competes with that of $[(Ph_3P)_2N][(HRu_4(CO)_{12}BH)_2Ag]$, the crystal structure of which has been determined. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Silver; Copper; Boron; Cluster fusion

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1. Introduction

The fusion of two cluster anions through a single Group 11 centre has been reported quite widely, see for example [1–12], but fusion through multinuclear groups of Group 11 or 12 metal atoms is less common. Examples include squares of Ag and Au connecting $Fe(CO)_4$ units [13,14], an Ag_5 unit fusing four $Fe(CO)_4$ units [13], an Ag_3 triangle connecting two Ru_5C carbides [15], and Cu_4, Cu_6 or Cu_7 units fusing together two Ru_6C carbides, Ru_{10} or Ru_6 clusters [16–18]. In the copper-containing clusters and in $[(Ru_5(CO)_{14}C)_2Ag_3(\mu\text{-}Cl)]^{2-}$ [15–18], bridging chloro ligands are a feature of the Group 11 metal unit. In a preliminary communication, we reported the formation of $[(HRu_4(CO)_{12}BH)_2Cu_4(\mu\text{-}Cl)][(Ph_3P)_2N]Cl$ from the reaction of $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ and $[Cu(MeCN)_4]^+$ in the presence of $[(Ph_3P)_2N]Cl$ [19]. This was the first example of a multinuclear copper unit acting as a coupling unit between two other clusters. Now we provide a full account of this and the related reaction with $[Ag(MeCN)_4]^+$. The latter leads to the first example of boride cluster fusion through a tetrasilver unit.

2. Experimental

2.1. General data

FT-NMR spectra were recorded on a Bruker WM 250 spectrometer (^1H) or AM 400 spectrometer (^{11}B and ^1H); ^1H shifts are reported with respect to δ 0 for Me_4Si, ^{11}B-NMR with respect to δ 0 for $F_3B{\cdot}OEt_2$. Solution IR spectra were recorded on a Perkin–Elmer FT 1710 spectrophotometer, and fast atom bombardment (FAB) mass spectra using Kratos instruments (3-NBA matrix, 3-nitrobenzyl alcohol).

Reactions were carried out under argon using standard Schlenk techniques; solvents were pre-dried and distilled under N_2. Separation of products was by thin layer plate chromatography (TLC) with Kieselgel 60-PF-254 (Merck). $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ [20] was

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* Corresponding author. Present address: School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK. Tel.: +41-61-267-1004; fax: +41-6-267-1014.

E-mail address: Catherine.Housecroft@unibas.ch (C.E. Housecroft).

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prepared as previously reported. Yields are quoted with respect to starting cluster; yields are often variable and typical values are quoted.

*2.2. Preparation of $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)][(Ph_3P)_2N]Cl$ (**1**)*

$[Cu(MeCN)_4][BF_4]$ (34 mg, 108 μmol) was added to a solution of $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ (92 mg, 71 μmol) in CH_2Cl_2 (10 ml); the latter was made [20] in situ and the reaction was therefore carried out in the presence of $[(Ph_3P)_2N]Cl$. The solution (initially orange) immediately turned deep red. After 20 min stirring at room temperature, solvent was removed in vacuo and the mixture separated by TLC (1:1 CH_2Cl_2:hexane). Two fractions were eluted leaving a brown residue on the baseline. The first fraction (yellow, ≈ 10%) contained both $H_4Ru_4(CO)_{12}$ [21] and $HRu_4(CO)_{12}BH_2$ [20,22] which were not separated from each other. A deep red band (r_f 0.2) constituted the only new product (≈ 60%) and was identified as $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)][(Ph_3P)_2N]Cl$ (**1**). ^{1}H-NMR ($(CD_3)_2O$, 298 K) δ + 7.8–7.5 (m, Ph), − 19.96 (s, Ru–H–Ru); ^{11}B-NMR (CD_2Cl_2, 298 K) δ + 149; IR (CH_2Cl_2, cm^{-1}) $\bar{\nu}$(CO) 2067 m, 2046 s, 2039 vs, 1992 m, 1970 w. FAB-MS: 1797 (P^-, correct isotope distribution); calc. for $^{12}C_{24}{}^1H_2{}^{11}B_2{}^{35}Cl^{64}Cu_4{}^{16}O_{24}{}^{101}Ru_8$ 1795. The crystal structure of **1** was determined and has been reported [19] (see Section 5).

Table 1
Crystallographic data for compound **2**

Formula	$C_{60}H_{31}AgB_2NO_{24}P_2Ru_8$
Formula weight	2149.9
Crystal size (mm)	0.22 × 0.24 × 0.46
Crystal colour and habit	Orange
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a (Å)	9.700(4)
b (Å)	13.921(5)
c (Å)	26.940(15)
α (°)	96.78(4)
β (°)	97.25(4)
γ (°)	91.93(3)
Volume (Å^3)	3579.1(30)
Z	2
D_{calc} (g cm^{-3})	1.995
Radiation	Mo–K$_\alpha$ (γ = 0.71073 Å)
Temperature (K)	299
Diffractometer	Siemens P4
2θ range (°)	4.0–55.0
Reflections (independent, observed 4$\sigma(F_o)$)	14104, 9999
$R(F)$, $R(wF)$ (%)	4.69, 5.80
GOF	1.28
Data: parameter ratio	14.2:1
Maximum peak and hole (e Å^{-3})	1.02, − 1.36

*2.3. Preparations of $[(Ph_3P)_2N][(HRu_4(CO)_{12}BH)_2Ag]$ (**2**) and $[(HRu_4(CO)_{12}B)_2Ag_4(\mu\text{-}Cl)][(Ph_3P)_2N]Cl$ (**3**)*

2.3.1. Method 1

$[Ag(MeCN)_4][BF_4]$ (72 mg, 200 μmol) was added to a solution of $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ (65 mg, 50 μmol) in CH_2Cl_2 (10 ml) in the presence of $[(Ph_3P)_2N]Cl$ (see above). The solution (initially orange) turned brown, and was stirred at room temperature for 20 min. Solvent was removed in vacuo and the mixture separated by TLC (1:1 CH_2Cl_2:hexane). Three fractions were eluted above a brown residue on the baseline. The first fraction (yellow, ≈ 5%) was $H_4Ru_4(CO)_{12}$ [21]. A yellow band (r_f 0.3, ≈ 25%) was identified as $[(Ph_3P)_2N][(HRu_4(CO)_{12}BH)_2Ag]$ (**2**), and the third fraction (r_f 0.1–0.2, ≈ 15%) was orange $[(HRu_4(CO)_{12}B)_2Ag_4(\mu\text{-}Cl)][(Ph_3P)_2N]Cl$ (**3**).

Compound **2**: ^{1}H-NMR ($(CD_3)_2O$, 298 K) δ + 7.8–7.5 (m, Ph), − 5.1 (br, Ru–H–B), − 20.94 (s, Ru–H–Ru); ^{11}B-NMR ($(CD_3)_2O$, 298 K) δ + 131; IR (CD_2Cl_2, cm^{-1}) $\bar{\nu}$(CO) 2079 w, 2049 vs, 2021 w, 1990 m. FAB-MS: 1617 (P^-, correct isotope distribution); calc. for $^{12}C_{24}{}^1H_4{}^{11}B_2{}^{108}Ag^{16}O_{24}{}^{101}Ru_8$ 1614.

Compound **3**: ^{1}H-NMR ($(CD_3)_2O$, 298 K) δ + 7.8–7.5 (m, Ph), − 20.20 (s, Ru–H–Ru); ^{11}B-NMR (CD_2Cl_2, 298 K) δ + 156; IR (CD_2Cl_2, cm^{-1}) $\bar{\nu}$(CO) 2068 m, 2048 s, 2035 vs, 1991 m, 1976 sh. FAB-MS: 1971 (P^-, correct isotope distribution); calc. for $^{12}C_{24}{}^1H_2{}^{11}B_2{}^{35}Cl^{108}Ag_4{}^{16}O_{24}{}^{101}Ru_8$ 1971.

2.3.2. Method 2

$AgBF_4$ (31 mg, 159 μmol) was added to a solution of $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ (88 mg, 68 μmol) in CH_2Cl_2 (6 ml) in the presence of $[(Ph_3P)_2N]Cl$ (see above). The solution (initially orange) turned brown, and was stirred at room temperature for 35 min. Solvent was removed and the mixture separated by TLC (2:1 CH_2Cl_2:hexane). Two major fractions were eluted above a brown, baseline residue: yellow **2** (r_f 0.7, ≈ 30%) and orange **3** (r_f 0.5, ≈ 40%).

*2.4. Crystal structure determination of **2***

A suitable crystal of **2** was grown by hexane diffusion into a CH_2Cl_2 solution kept at − 30°C for several days. Crystallographic data are collected in Table 1. Orange, brick-shaped crystals were found to belong to the triclinic crystal system, and the centrosymmetric space group alternative, $P\bar{1}$, was initially assumed and later verified by the results of refinement. The structure was solved by direct methods and completed from a series of difference Fourier syntheses. Hydrogen atoms were treated as idealized contributions, except for those bonded to Ru, which were located but not refined. Except for the carbon atoms of the $[(Ph_3P)_2N]^+$ cations, all non-hydrogen atoms were anisotropically

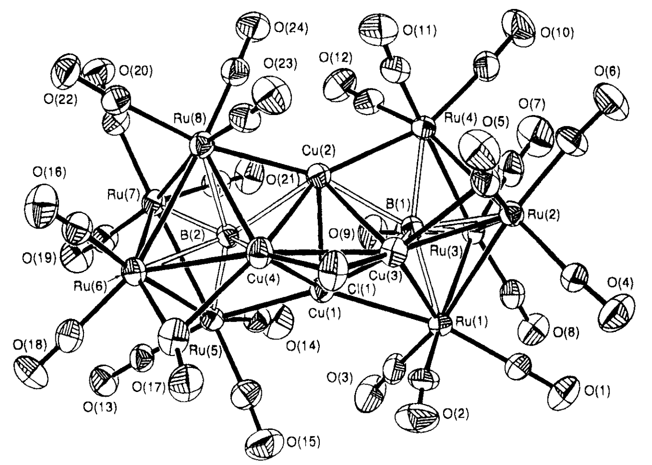


Fig. 1. The molecular structure of the $(HRu_4(CO)_{12}BH)_2Cu_4(\mu\text{-}Cl)$ cluster in compound **1**.

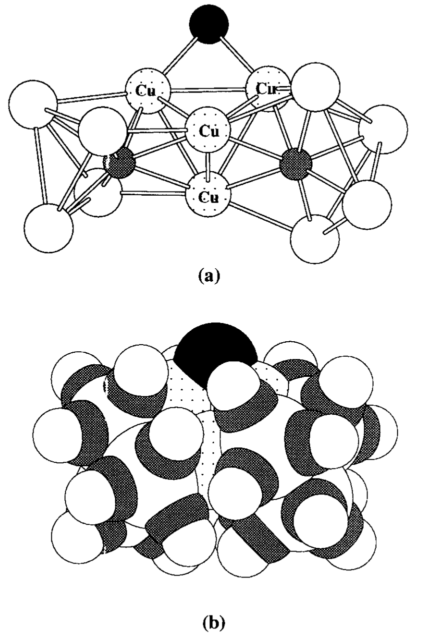
Table 2
Selected bond lengths (Å) in **1**

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(3)–B(1)	2.21(1)
Ru(2)–B(1)	2.32(1)	Ru(7)–B(2)	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(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(3)–Cl(1)	2.220(3)	Cu(4)–Cl	2.205(3)
Cu(1)–B(1)	2.33(1)	Cu(1)–B(2)	2.29(1)
Cu(2)–B(1)	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(1)–Cu(2)	2.442(2)	Cu(3)–Cu(4)	2.660(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)

refined. The asymmetric unit consists of two half anions located on inversion centres and a fully occupied $[(Ph_3P)_2N]^+$ counterion. All software is contained in the SHLXTL 4.2 program library [23].

3. Results and discussion

In previous studies, we have observed that the fusion of two $[HRu_4(CO)_{12}BH]^-$ anions through a single Au(I) centre using R_3PAuCl as the source of Au(I) competes with the formation of $HRu_4(CO)_{12}BAu_2(PR_3)_2$ [10]. Although we have reported a variety of gold-containing derivatives of this type [24,25], we have explored only to a limited extent the reactions of $[HRu_4(CO)_{12}BH]^-$ with Ag(I) and Cu(I). The reaction of $[HRu_4(CO)_{12}BH]^-$ with an excess of $[Cu(MeCN)_4]^+$ yielded one major, deep red product, **1**. The highest mass peak in the FAB mass spectrum of **1** showed an envelope with the most intense peak at *m*/*z* 1797 and an isotopic pattern that was consistent with the cluster $\{(HRu_4(CO)_{12}B)_2Cu_4Cl\}$. The ^{1}H-NMR spectrum however showed resonances due to phenyl protons in addition to a singlet (δ −19.96) assigned to the metal hydride. Working from a formal 2− charge on each $(HRu_4(CO)_{12}B)$ cluster subunit, we initially formulated **1** as the Cu(I) containing species '$[(Ph_3P)_2N][(HRu_4(CO)_{12}B)_2Cu_4Cl]$'. Crystals of the new product were readily grown from CH_2Cl_2 layered with hexane and the structure of the cluster in **1** is shown in Fig. 1. The structural data confirmed that **1** was $[(Ph_3P)_2N][(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)]Cl$ containing discrete $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)]$ molecules, $[(Ph_3P)_2N]^+$ cations and Cl^- anions. Details of the structure analysis have already been communicated [19]. Table 2 lists selected bond distances for $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)]$. The structure is composed of two Ru_4 butterfly units connected by a tetrahedral Cu_4 unit, one edge of which is bridged by a chloro ligand. The two Ru_4 units are twisted with respect to one another through ≈ 38°. Each B atom interacts with seven metal centres: four Ru and three Cu (Fig. 2a). The geometry of the tetracopper core in **1** contrasts with the square arrangement found in $[(Ru_6(CO)_{16}C)_2Cu_4(\mu\text{-}Cl)_2]^{2-}$ [18], and additionally, the chloro-bridged Cu–Cu edges in $[(Ru_6(CO)_{16}C)_2Cu_4(\mu\text{-}Cl)_2]^{2-}$ are significantly longer than in $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)]$. All carbonyl ligands are terminal except for C(5)O(5) and C(17)O(17) which are



(a)

(b)

Fig. 2. The $(Ru_4B)_2Cu_4(\mu\text{-}Cl)$ core of $(HRu_4(CO)_{12}BH)_2Cu_4(\mu\text{-}Cl)$ in compound **1**.

semibridging along edges Ru(2)–Cu(3) and Ru(6)–Cu(4) respectively.

In solution, the cluster in **1** is stereochemically non-rigid, with four ^{13}C-NMR spectroscopic resonances (δ 194.3, 197.3, 199.2, 203.6 with approximately equal relative integrals) observed at 298 K. On cooling, the signal at δ 197.3 broadens first, and has collapsed at 234 K; new signals begin to appear at δ 193.8 and 197.8 This is followed by the collapse of the signal at δ 203.6 which has disappeared at 188 K. The signals at δ 194.3 and 199.2 remain sharp until 209 K and are somewhat broadened at 188 K. The solid state structure contains 12 carbon environments; a contributing factor to this number of environments is the mutually twisted Ru_4 units (see above). We were unable to study the ^{13}C-NMR spectrum at sufficiently low temperature to observe a static situation consistent with the solid state data. The fluxional behaviour is not simple and may involve both localized rotation at the Ru centres (there are four different sites in the solid state) and mutual twisting of the Ru_4 units with respect to the Cu_4 core, the result of which would be to impose a mirror plane on the molecule which is not present in the solid state.

In $[(Ru_6(CO)_{16}C)_2Cu_4(\mu\text{-}Cl)_2]^{2-}$ [18], $[(HRu_4(CO)_{12})_2Cu_7(\mu\text{-}Cl)_3]^{2-}$ [17], $[(HRu_6(CO)_{17})_2Cu_6(\mu\text{-}Cl)_2]^{2-}$ [17] and $[(H_2Ru_{10}(CO)_{24})_2Cu_6(\mu\text{-}Cl)_2]^{4-}$ [16], charges can be formally allocated to the ruthenium cluster subunits and to the chloro-bridged copper subunit such that each copper centre is formally Cu(I), e.g. $[(Ru_6(CO)_{16}C)_2Cu_4(\mu\text{-}Cl_2)]^{2-}$ can be considered to be composed of two $[Ru_6(CO)_{16}C]^{2-}$ units coupled through a $[Cu_4Cl_2]^{2+}$ unit. However, $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)]$ in **1** poses a problem. If each boride unit is taken to $[HRu_4(CO)_{12}B]^{2-}$ (a boride cluster that has been spectroscopically characterized [22]), then the copper unit is formally $[Cu_4Cl]^{4+}$, suggesting a mixed oxidation state $Cu(I)_3Cu(II)$ core. Four Cu(I) centres could be formulated if the Cu_4Cl unit also carried a bridging proton. However, we have been unable to observe and assign an appropriate signal to such a proton in the ^{1}H-NMR spectrum; a CD_2Cl_2 solution of **1** has been studied by ^{1}H-NMR spectroscopy down to 188 K. Early studies of hexanuclear copper hydride clusters reported the absence of ^{1}H-NMR signals [26,27] despite a neutron diffraction study of $H_6Cu_6(P(p\text{-tolyl})_3)_6$ later confirming the presence for six μ_3-H ligands [28]. Work from Caulton and coworkers revealed that the proton signals in $H_6Cu_6(PR_3)_6$ clusters appear in the 'organic' region of the spectrum rather than at highfield, and structural data confirmed μ_3-bridging sites [29,30]. Our own failure to observe a proton resonance for **1** cannot therefore be taken as complete evidence for its absence. However, a spacefilling diagram of $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)]$ (Fig. 2b) reveals that whereas CO ligands bend away from the bridging Cl ligand, no such bending away from the Cu_4 core of any other CO ligands is observed in the solid state structure; the potential site for a proton would be the Cu(1)–Cu(2) edge. Although this suggests that no bridging H atom is associated with the tetracopper core, we cannot rule out that the cluster in **1** may be $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-}Cl)(\mu\text{-}H)]$. There also remains the question as to why we are unable to isolate this cluster without the accompanying presence of $[(Ph_3P)_2N]Cl$. The possibility that the Cl^- ion is associated with the Cu_4 core in solution was investigated by comparing the IR spectra of a CH_2Cl_2 solution of **1** with that of a nujol mull; use of a KBr disc was avoided because of possible halide exchange. The spacefilling diagram in Fig. 2b suggests that addition of another bridging chloro ligand to the Cu_4 core would perturb the arrangement of the CO ligands. The solution and nujol mull IR spectra were similar: in solution $\bar{\nu}$(CO) were observed at 2067 m, 2046 s, 2039 vs, 1992 m, 1970 w cm^{-1} and in a nujol mull, $\bar{\nu}$(CO) 2065 m, 2043 s, 2032 vs, 1995 m, 1978 m, 1969 m and 1944 w cm^{-1}.

The reaction between $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ and an excess of $[Ag(MeCN)_4]^+$ yielded two main products, **2** and **3**. Higher yields of both compounds are obtained by treating $[(Ph_3P)_2N][HRu_4(CO)_{12}BH]$ with $AgBF_4$. The ^{1}H-NMR spectrum of **2** exhibited resonances assigned to Ph protons indicating the retention of the $[(Ph_3P)_2N]^+$ cation, and signals at δ -5.1 and -20.94 were assigned to Ru–H–B and Ru–H–Ru protons respectively. These data, along with the fact that the ^{11}B-NMR spectrum exhibited a signal at δ $+131$, indicated retention of an HRu_4BH-unit. The FAB (negative mode) mass spectrum of **2** showed a parent ion at *m/z* 1614 corresponding to $[(HRu_4(CO)_{12}BH)_2Ag]^-$, suggesting the formation of an analogue of the gold(I) fused cluster $[(HRu_4(CO)_{12}BH)_2Au]^-$ that we reported some time ago [10]. The identity of **2** was confirmed by the results of a single crystal X-ray diffraction study.

The structure of the $[(HRu_4(CO)_{12}BH)_2Ag]^-$ anion in **2** is shown in Fig. 3 and selected bond distances and angles are collected in Table 3. The Ag atom lies on a centre of symmetry and the two $HRu_4(CO)_{12}BH$ units

Table 3
Selected bond distances (Å) and angles (°) for the $[(HRu_4(CO)_{12}BH)_2Ag]^-$ anion in compound **2**

Ru(1)–Ru(2)	2.875(1)	Ru(1)–Ru(3)	2.834(1)
Ru(1)–Ru(4)	2.870(1)	Ru(1)–B(1)	2.204(8)
Ru(2)–Ru(3)	2.827(1)	Ru(2)–Ru(4)	2.861(1)
Ru(2)–B(1)	2.189(9)	Ru(3)–B(1)	2.140(9)
Ru(4)–Ag(1)	2.746(1)	Ru(4)–B(1)	2.036(9)
Ag(1)–B(1)	2.400(9)		
Ru(1)–Ru(4)–Ag(1)	100.3(1)	Ru(2)–Ru(4)–Ag(1)	96.3(1)
Ag(1)–Ru(4)–B(1)	58.0(2)	Ru(4)–Ag(1)–Ru(4a)	180.0(1)
B(1)–Ag(1)–B(1a)	180.0(1)	Ru(3)–B(1)–Ru(4)	162.3(5)
Ru(1)–B(1)–Ru(2)	81.8(3)		

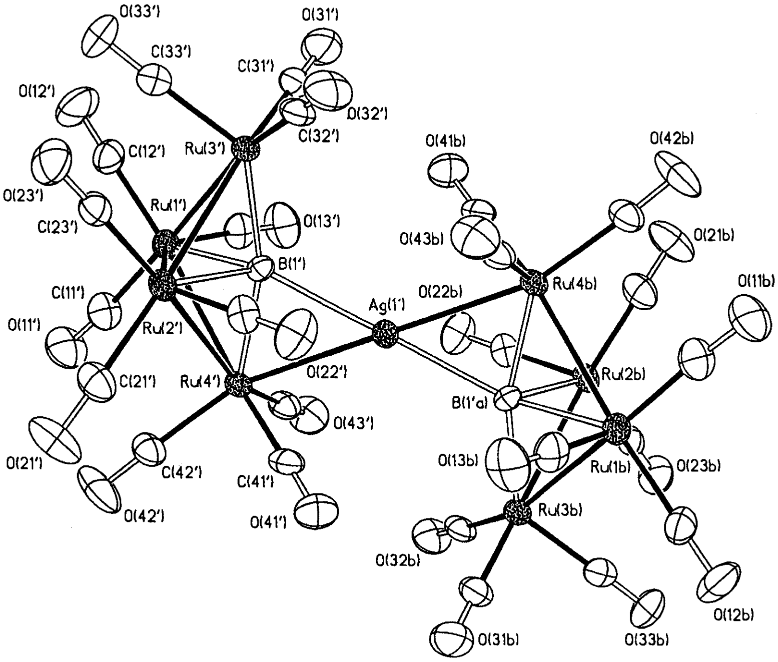


Fig. 3. The molecular structure of the anion in compound **2**.

are in a mutually *trans* orientation. The silver(I)-containing anion is essentially isostructural with $[(HRu_4(CO)_{12}BH)_2Au]^-$ [10], a feature that is expected given the similarity in sizes between the Ag(I) and Au(I) centres.

The ^{11}B-NMR spectrum of compound **3** showed a broad signal at δ +156 indicative of a boride environment. The ^{1}H-NMR spectrum of compound **3** indicated the presence of phenyl protons and an Ru–H–Ru bridging hydride. The combination of these NMR spectroscopic data indicated that the Ru–H–B proton had been removed from the precursor $[HRu_4(CO)_{12}BH]^-$ during reaction in contrast to the formation of compound **2**. Significantly, the IR spectrum in the carbonyl region gave a pattern of absorptions that was almost identical to that in compound **1**, 2068 m, 2048 s, 2035 vs, 1991 m, 1976 sh cm^{-1} (**3**) compared to 2067 m, 2046 s, 2039 vs, 1992 m, 1970 w cm^{-1} (**1**), and unlike that in **2** (2079 w, 2049 vs, 2021 w, 1990 m cm^{-1}). The FAB (negative mode) mass spectrum of **3** gave a parent ion at 1971 which supported the formation of a silver-containing product analogous to the tetracopper compound **1**. The spectroscopic and mass spectrometric data for **3** are therefore in accord with the formation of $[(Ph_3P)_2N][(HRu_4(CO)_{12}B)_2Ag_4(\mu\text{-Cl})]Cl$. We have been unable to grow X-ray quality crystals of **3** but the spectroscopic data are in accord with it being structurally analogous to **1**. Compound **3** therefore represents the first example of the fusion of two boride clusters through a tetrasilver unit.

4. Conclusions

The formation of fused metal clusters, and in particular metal boride clusters, in which the connection unit is a tetrahedral cluster of Group 11 metal atoms is novel. In $[(HRu_4(CO)_{12}B)_2Cu_4(\mu\text{-Cl})]$ and $[(HRu_4(CO)_{12}B)_2Ag_4(\mu\text{-Cl})]$, the Group 11 metal atoms appear to form a mixed oxidation state unit although the presence of an additional proton which would then allow assignment of all Cu(I) or Ag(I) centres cannot be completely ruled out. Fusion through Ag(I) to form $[(HRu_4(CO)_{12}BH)_2Ag]^-$ is analogous to that observed for Au(I), but no analogous cluster product is observed with Cu(I).

5. Supplementary data

Crystallographic data for **1** and **2** have been deposited (as CIF files) with the Cambridge Crystallographic Data Centre, CCDC no. 142906 for **2** and refcode JUDXIP for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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