

**TRIGOLD(I) PHOSPHINE DERIVATIVES OF CLUSTERS CONTAINING OCTAHEDRAL  $\text{Rh}_2\text{Ru}_4\text{B}$ -BORIDE CORES: THE X-RAY STRUCTURE OF  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{Rh}_2\text{Ru}_4\text{B}\{\text{AuPCy}_3\}_3]$  (Cy = CYCLOHEXYL)**

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*Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday in recognition of his contributions to boron chemistry.*

The reaction of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with  $[\text{HRu}_4(\text{CO})_{12}\text{BH}]^-$  followed by treatment with an excess (at least three-fold) of  $[\text{Cy}_3\text{PAuCl}]$  (Cy = cyclohexyl) leads to the formation of  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}\{\text{AuPCy}_3\}]$  (previously prepared by another route) and  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{B}\{\text{AuPCy}_3\}_3]$ . The new trigold derivative has been characterized by spectroscopic and mass spectrometric methods, and by single crystal X-ray diffraction. It possesses an octahedral  $\text{Rh}_2\text{Ru}_4$  core containing an interstitial boron atom; two of the gold(I) phosphine units cap two adjacent faces and the third bridges an edge of the octahedral cage. There are no close Au...Au contacts. Reactions of  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}]^-$  with  $[(\text{R}_3\text{PAu})_3\text{O}]^+$  (R = Ph, 2-MeC<sub>6</sub>H<sub>4</sub>) resulted in the formation of  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{B}\{\text{AuPR}_3\}_3]$ ; for R = Ph, two isomers in respect of the arrangements of the AuPPh<sub>3</sub> were isolated. Fluxional processes involving the gold(I) phosphine fragments have been observed using solution variable-temperature <sup>31</sup>P NMR spectroscopy.

**Key words:** Borides; Rhodium clusters; Ruthenium clusters; Crystal structure; Gold(I) phosphines.

In a number of studies over the past few years, we have investigated the interactions between octahedral boride cluster anions and gold(I) phosphines<sup>1-7</sup>. With homometallic Ru<sub>6</sub> boron-centred clusters, we have observed the formation of mono-, di- and trigold derivatives, namely  $[\text{Ru}_6(\text{CO})_{17}\text{B}\{\text{AuPR}_3\}]$ ,  $[\text{HRu}_6(\text{CO})_{16}\text{B}\{\text{AuPR}_3\}_2]$  and  $[\text{Ru}_6(\text{CO})_{16}\text{B}\{\text{AuPR}_3\}_3]$  (e.g. R = Ph, 2-tolyl)<sup>6</sup>. The cores of these clusters are shown in Fig. 1; this illustrates the relationships between the positions of the gold(I) units and the

ruthenium framework. Although the trigold system was found to be fluxional in solution (interpreted in terms of a “rocking motion” of the digold unit marked in Fig. 1c)<sup>6</sup>, no structural isomerism in respect of the positions of the gold atoms on the periphery of the Ru<sub>6</sub> cage was observed. In reactions involving heterometallic clusters containing an Rh<sub>2</sub>Ru<sub>4</sub>B core, we have, to date, reported only monogold derivatives<sup>2,5,7</sup>. The precursor is a monoanion, e.g. [Rh<sub>2</sub>Ru<sub>4</sub>(CO)<sub>16</sub>B]<sup>-</sup>, and the addition of one [AuPR<sub>3</sub>]<sup>+</sup> unit is facile. Reactions explored to date have terminated at the formation of the neutral, monogold derivative. In the present paper, we describe the reactions of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> with [HRu<sub>4</sub>(CO)<sub>12</sub>BH]<sup>-</sup> followed by treatment *in situ* with an excess (at least three-fold) of Cy<sub>3</sub>PAuCl (Cy = cyclohexyl) to give [Rh<sub>2</sub>Ru<sub>4</sub>(CO)<sub>16</sub>B{AuPCy<sub>3</sub>}] (ref.<sup>7</sup>) and [Rh<sub>2</sub>Ru<sub>4</sub>(CO)<sub>15</sub>B{AuPCy<sub>3</sub>}<sub>3</sub>] (1). We also discuss the use of [(R<sub>3</sub>PAu)<sub>3</sub>O]<sup>+</sup> (R = Ph, 2-MeC<sub>6</sub>H<sub>4</sub>) to obtain trigold derivatives centred on the Rh<sub>2</sub>Ru<sub>4</sub>B core.

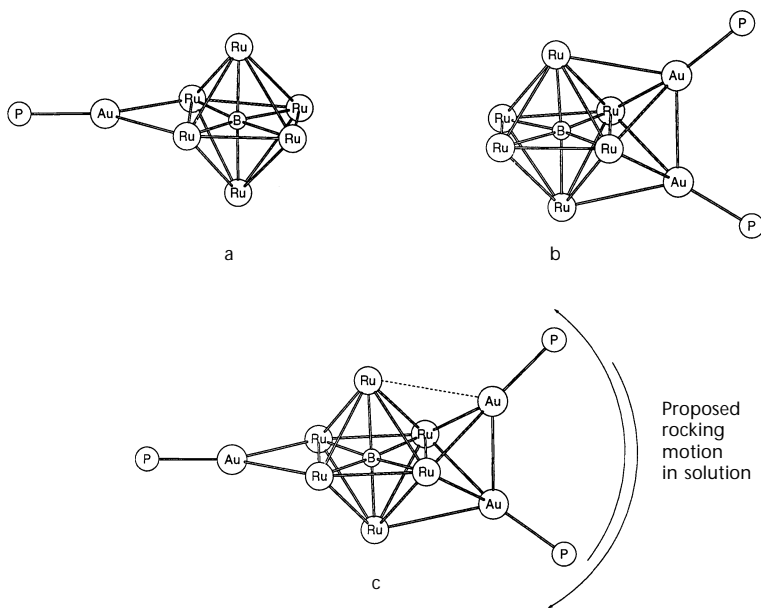


FIG. 1

Core structures of [Ru<sub>6</sub>(CO)<sub>17</sub>B{AuP(2-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>}] (a), [HRu<sub>6</sub>(CO)<sub>16</sub>B{AuPPh<sub>3</sub>}<sub>2</sub>] (b) and [Ru<sub>6</sub>(CO)<sub>16</sub>B{AuPPh<sub>3</sub>}<sub>3</sub>] (c) showing only Ru, B, Au and P atoms<sup>5</sup>

## EXPERIMENTAL

## General Methods

Fourier-transform NMR spectra were recorded on a Bruker WM 250 or AM 400 spectrometer.  $^1\text{H}$  NMR shifts are reported with respect to  $\delta$  0 for  $\text{Me}_4\text{Si}$ ;  $^{11}\text{B}$  NMR with respect to  $\delta$  0 for  $\text{F}_3\text{B}\cdot\text{OEt}_2$ ;  $^{31}\text{P}$  NMR with respect to  $\delta$  0 for 85% aqueous  $\text{H}_3\text{PO}_4$ . All downfield chemical shifts are positive. Infrared spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer. FAB (fast atom bombardment) mass spectra were recorded on Kratos instruments with 3-nitrobenzyl alcohol matrix.

All reactions were carried out under argon using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under  $\text{N}_2$  before use. Separations were carried out by thin layer plate chromatography (TLC) with Kieselgel 60-PF-254 (Merck).  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  was used as received (Aldrich).

$[(\text{Ph}_3\text{P})_2\text{N}][\text{HRu}_4(\text{CO})_{12}\text{BH}]$  (ref.<sup>8</sup>),  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}]$  (ref.<sup>7</sup>),  $[\text{Cy}_3\text{PAuCl}]$  (refs.<sup>9,10</sup>) and  $\{[\text{AuPR}_3\text{O}][\text{BF}_4]\}$  ( $\text{R} = \text{Ph}$ , 2-MeC<sub>6</sub>H<sub>4</sub>)<sup>10</sup> were prepared using literature procedures. For the new products, yields are typical (but may be variable) and are with respect to the particular cluster starting material.

Preparation  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{B}\{\text{AuPCy}_3\}_3]$ 

In a typical reaction,  $[(\text{Ph}_3\text{P})_2\text{N}][\text{HRu}_4(\text{CO})_{12}\text{BH}]$  (65 mg, 0.050 mmol) was dissolved in THF (10 ml) and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (23 mg, 0.060 mmol) was added. After stirring for 35 min, solvent was removed *in vacuo* and the residue redissolved in  $\text{CH}_2\text{Cl}_2$  (15 ml). To this solution,  $\text{TIPF}_6$  ( $\approx 3$  mg) and a minimum of a three-fold excess of solid  $[\text{Cy}_3\text{PAuCl}]$  ( $\text{Cy} = \text{cyclohexyl}$ ) were added. The reaction mixture was stirred for 90 min at room temperature and solvent was then removed *in vacuo*. Products were separated by TLC (hexane- $\text{CH}_2\text{Cl}_2$ , 2 : 1). The first (brown,  $R_F$  0.85) and second (green,  $R_F$  0.75) fractions were identified as the previously reported *cis*- and *trans*-isomers of  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}\{\text{AuPCy}_3\}]$  (ref.<sup>7</sup>). The total yield of these isomers was  $\approx 40\%$ . The third fraction (brown,  $R_F$  0.25, yield  $\approx 10\%$ ) was identified as  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{B}\{\text{AuPCy}_3\}_3]$ . The remaining material was an intractable solid on the baseline of the TLC plate.  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{B}\{\text{AuPCy}_3\}_3]$  (**1**): NMR ( $\text{CDCl}_3$ , 298 K):  $^1\text{H}$  (400 MHz),  $\delta$  +2.2–2.1 (m, Cy);  $^{11}\text{B}$  (128 MHz),  $\delta$  +198.5;  $^{31}\text{P}$  (162 MHz),  $\delta$  +82.9 (s, 1 P), +76.8 (s, 2 P). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2 046 w, 2 016 s, 2 001 vs, 1 822 vw. FAB (negative mode) mass spectrum,  $m/z$ : 2 444 ( $\text{P}^- - \text{CO}$ ); calculated for  $^{12}\text{C}_{69}^{1}\text{H}_{99}^{197}\text{Au}_3^{11}\text{B}^{16}\text{O}_{15}^{31}\text{P}_3^{103}\text{Rh}_2^{101}\text{Ru}_4$  2 472.

Reaction of  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}]$  with  $[(\text{Ph}_3\text{PAu})_3\text{O}][\text{BF}_4]$ 

$[(\text{Ph}_3\text{PAu})_3\text{O}][\text{BF}_4]$  (30 mg, 0.020 mmol) was added to a  $\text{CH}_2\text{Cl}_2$  (5 ml) solution containing  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}]$  (17 mg, 0.011 mmol). The solution was stirred for 35 min, and then solvent was removed *in vacuo*. Products were separated by TLC (hexane- $\text{CH}_2\text{Cl}_2$ , 1.5 : 1). Two fractions were collected: dark brown,  $R_F$  0.5, yield 55% and pale brown,  $R_F$  0.3, yield 20%. These were identified as isomers of  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{B}\{\text{AuPPh}_3\}_3]$  (**2**) (dark brown **2a** and pale brown **2b**).

*Isomer 2a*: NMR ( $\text{CD}_2\text{Cl}_2$ ):  $^1\text{H}$  (400 MHz, 298 K),  $\delta$  +7.8–7.2 (m, Ph);  $^{11}\text{B}$  (128 MHz, 298 K),  $\delta$  +202;  $^{31}\text{P}$  (162 MHz) 298 K,  $\delta$  +63.7 (s, 1 P), +62.2 (s, 2 P); 192 K  $\delta$  +67.3 (s, 1 P), +61.6 (s, 1 P), +53.6 (s, 1 P). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2 049 w, 2 025 s, 2 005 vs, 1 951 w, 1 836 w.

FAB (negative mode) mass spectrum,  $m/z$ : 2 418 ( $P^-$ ); calculated for  $^{12}C_{69}^{1}H_{45}^{197}Au_3^{11}B^{16}O_{15}^{31}P_3^{103}Rh_2^{101}Ru_4$  2 418.

**Isomer 2b:** NMR ( $CD_2Cl_2$ ):  $^1H$  (400 MHz, 298 K),  $\delta$  +7.7–7.2 (m, Ph);  $^{11}B$  (128 MHz, 298 K),  $\delta$  +199;  $^{31}P$  (162 MHz) 298 K,  $\delta$  +58.9 (s); 186 K,  $\delta$  +59.3 (s, 1 P), +56.9 (s, 2 P). IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu(CO)$  2 055 mw, 2 019 vs, 2 001 m, 1 833 vw, 1 843 vw. FAB (negative mode) mass spectrum,  $m/z$ : 2 420 ( $P^-$ ); calculated for  $^{12}C_{69}^{1}H_{45}^{197}Au_3^{11}B^{16}O_{15}^{31}P_3^{103}Rh_2^{101}Ru_4$  2 418.

Reaction of  $[(Ph_3P)_2N][Rh_2Ru_4(CO)_{16}B]$  with  $\{(2-MeC_6H_4)_3PAu\}_3O[BF_4]$

$\{(2-MeC_6H_4)_3PAu\}_3O[BF_4]$  (32 mg, 0.020 mmol) was added to a  $CH_2Cl_2$  (5 ml) solution containing  $[(Ph_3P)_2N][Rh_2Ru_4(CO)_{16}B]$  (17 mg, 0.011 mmol). The solution was stirred for 30 min, and then solvent was removed *in vacuo*. Products were separated by TLC (hexane– $CH_2Cl_2$ , 1 : 1). Two fractions were collected:  $[Rh_2Ru_4(CO)_{16}B\{AuP(2-MeC_6H_4)_3\}]$  (ref.<sup>7</sup>) green,  $R_f$  0.8, yield 40%; **3**, brown,  $R_f$  0.55, yield 7%, leaving intractable material on the baseline as well as several fractions in quantities too small to work up.

$[Rh_2Ru_4(CO)_{15}B\{AuP(2-MeC_6H_4)_3\}_3]$  (**3**): NMR ( $CD_2Cl_2$ ):  $^1H$  (400 MHz, 298 K),  $\delta$  +7.6–7.0 (m, 36 H, Ph), +2.35 (s, 27 H, Me);  $^{11}B$  (128 MHz, 298 K),  $\delta$  +200;  $^{31}P$  (162 MHz, 298 K),  $\delta$  +57.6 (s, 1 P), +58.9 (br, 2 P). IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu(CO)$  2 049 w, 2 024 s, 2 006 vs, 1 958 mw, 1 835 vw. FAB (positive mode) mass spectrum,  $m/z$ : 2 545 ( $P^+$ ); calculated for  $^{12}C_{78}^{1}H_{63}^{197}Au_3^{11}B^{16}O_{15}^{31}P_3^{103}Rh_2^{101}Ru_4$  2 544.

### Crystal Structural Determination

Crystallographic data for **1** are collected in Table I. The sample used for the data collection was cleaved from a larger block and mounted on a glass fibre. Data were collected at room temperature on a Siemens P4 diffractometer. The space group was unambiguously determined from systematic absences in the data. An empirical correction for absorption was applied to the data. Direct methods were used to solve the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were placed in idealized positions. The preferred locations of the Ru and Rh atoms were determined by testing all of the most plausible arrangements; both  $R(F)$  and  $R(wF^2)$  improved by significant extents as determined by a greater than 99% confidence using Hamilton's test<sup>11</sup>. The arrangement shown produced an  $R$  factor of 4.35% whereas all other tested arrangements were in the range of 4.45–4.54%. All software was contained in the SHELXTL library (version 4.05, Siemens XRD, Madison, WI).

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-104526. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

## RESULTS AND DISCUSSION

We have already reported that the reaction of  $[Rh_2Ru_4(CO)_{16}B]^-$  with  $[R_3PAuCl]$  ( $R = Ph, Cy$  or  $2-MeC_6H_4$ ) leads to  $[Rh_2Ru_4(CO)_{16}B\{AuPR_3\}]$  in good yield<sup>7</sup>. No products containing more than one gold unit were isolated from these reactions, despite the fact that about three-fold excess of gold(I) phosphine was used. In this previous study, the precursor,

$[\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}]^-$ , was first isolated from the reaction between  $[\text{HRu}_4(\text{CO})_{12}\text{BH}]^-$  and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (ref.<sup>7</sup>). However, if  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}]^-$  is made *in situ* and treated with an excess of  $[\text{Cy}_3\text{PAuCl}]$  in the presence of  $\text{TIPF}_6$  for 90 min, it is possible to isolate  $\approx 10\%$  of  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{15}\text{B}\{\text{AuPCy}_3\}_3]$  (**1**), in addition to the major product,  $[\text{Rh}_2\text{Ru}_4(\text{CO})_{16}\text{B}(\text{AuPCy}_3)]$ . The formulation of **1** was supported by the observation in the FAB mass spectrum of a peak at  $m/z$  2 444 corresponding to the expected parent ion minus one CO; the observed and calculated isotopic distributions were in agreement. In the  $^{11}\text{B}$  NMR spectrum, a poorly resolved signal at  $\delta$  +198.5 indicated retention of the boron-containing octahedral  $\text{Rh}_2\text{Ru}_4$ -cluster core; the chemi-

TABLE I  
Crystallographic data for compound **1**

Formula	$\text{C}_{69}\text{H}_{99}\text{Au}_3\text{BO}_{15}\text{P}_3\text{Rh}_2\text{Ru}_4$
Formula weight	1 236.60
Crystal size	$0.41 \times 0.14 \times 0.13$
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
$a$ , Å	23.206(5)
$b$ , Å	19.708(4)
$c$ , Å	19.233(4)
$\beta$ , °	114.23(3)
Volume, Å <sup>3</sup>	8 021(3)
$Z$	4
$D_{\text{calc}}$ , Mg m <sup>-3</sup>	2.048
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ Å)
Temperature, K	293(2)
$\theta$ range, °	2.07 to 21.05
Reflections (collected, independent)	8 980, 8 647
$R(F)$ , $R(wF^2)^a$ , %	4.35, 7.66
Goodness-of fit on $F^2$	0.991
Data/restraints/parameters	8 647/0/864
Maximum peak, e Å <sup>-3</sup>	0.905

<sup>a</sup> Refinement method: full matrix least-squares on  $F^2$ .

cal shift is very sensitive to changes in boron-to-metal connectivity and geometry of the metal cage<sup>1,12</sup>. Crystals of **1** suitable for X-ray diffraction were grown by slow diffusion of a layer of EtOH into a CH<sub>2</sub>Cl<sub>2</sub> solution of **1**. Figure 2a shows the molecular structure of **1**, and Fig. 2b shows the Rh<sub>2</sub>Ru<sub>4</sub>BAu<sub>3</sub>P<sub>3</sub> core of the compound. Selected bond distances and angles are listed in Table II. The structural determination confirmed the presence of the octahedral Rh<sub>2</sub>Ru<sub>4</sub> cage containing a boron atom. Although we are not able to distinguish unambiguously between the Rh and Ru atoms, the positions shown in Fig. 2 appear to be the most reasonable (see Experimental). This arrangement is further supported by an inspection of the metal–carbonyl connectivities; it is typical of Rh to bear fewer terminal CO ligands than Ru and to be involved in a greater number of carbonyl bridg-

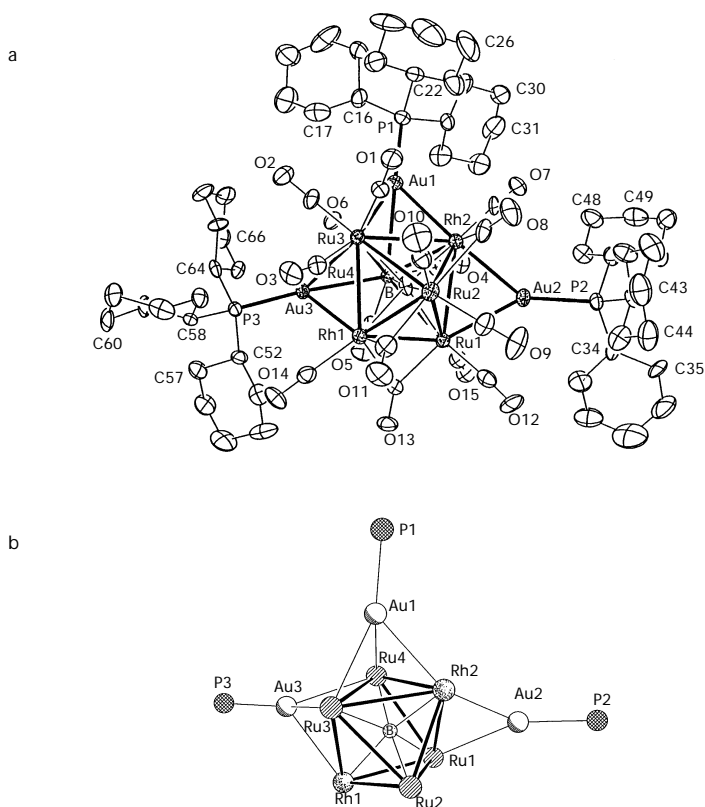


FIG. 2

Molecular structure (a) and the Rh<sub>2</sub>Ru<sub>4</sub>BAu<sub>3</sub>P<sub>3</sub> core (b) of compound **1**

ing interactions. Furthermore, we have noted in a number of related systems that a *trans*-arrangement of Rh atoms in the octahedral cage tends to be preferred over a *cis*-arrangement<sup>7</sup>.

One AuPCy<sub>3</sub> unit is remote from the other two and bridges an edge of the central octahedron (Fig. 2b). The remaining two AuPCy<sub>3</sub> units occupy face-capping sites with respect to the octahedral cage, with an Au(1)⋯Au(3) separation of 4.41 Å, while that of Au(1)⋯Au(2) is 5.32 Å. The long dis-

TABLE II  
Selected bond distances and angles for **1**

Atoms	Bond distances, Å	Atoms	Bond distances, Å
Au1-P1	2.316(4)	Au1-Rh2	2.804(2)
Au1-Ru3	2.817(2)	Au1-Ru4	3.011(1)
Au1-P2	2.292(4)	Au2-Rh2	2.749(2)
Au2-Ru1	2.800(2)	Au3-P3	2.323(4)
Au3-Ru4	2.795(2)	Au3-Rh1	2.827(2)
Au3-Ru3	2.948(2)	Ru1-B	2.10(2)
Ru1-Rh1	2.808(2)	Ru1-Ru4	2.950(2)
Ru1-Ru2	3.008(2)	Ru1-Rh2	3.063(2)
Ru2-B	2.09(2)	Ru2-Rh1	2.798(2)
Ru2-Rh2	2.806(2)	Ru2-Rh3	2.984(2)
Ru3-B	2.15(2)	Ru3-Rh1	2.939(2)
Ru3-Ru4	3.032(2)	Ru3-Rh2	3.101(2)
Ru4-B	2.11(2)	Ru4-Rh2	2.935(2)
Rh1-B	2.12(2)	Rh2-B	2.06(2)
Atoms	Bond angle, °	Atoms	Bond angle, °
Rh2-Au1-Ru3	66.96(4)	Rh2-Au1-Ru4	60.50(4)
Ru3-Au1-Ru4	62.59(4)	Rh2-Au2-Ru1	67.00(4)
Ru4-Au3-Rh1	71.95(4)	Ru4-Au3-Ru3	63.66(4)
Rh1-Au3-Ru3	61.13(4)	Rh2-B-Rh1	167.9(9)
Ru2-B-Ru4	174.3(9)	Ru1-B-Ru3	170.2(9)

tances indicate no gold-gold interaction, and this is in contrast to the case for  $[\text{Ru}_6(\text{CO})_{16}\text{B}\{\text{AuPPh}_3\}_3]$  (Fig. 1c) where two of the  $\text{AuPPh}_3$  units are drawn together such that the Au-Au separation is 2.878(1) Å (ref.<sup>6</sup>). The reason for this difference is not clear. The central octahedra in **1** and  $[\text{Ru}_6(\text{CO})_{16}\text{B}\{\text{AuPPh}_3\}_3]$  are of comparable dimensions; there are fewer CO ligands to accommodate in **1** compared with  $[\text{Ru}_6(\text{CO})_{16}\text{B}\{\text{AuPPh}_3\}_3]$ , although working against this smaller steric requirement is the slightly larger cone angle of the  $\text{AuPCy}_3$  unit ( $110^\circ$ ) compared with that of  $\text{AuPPh}_3$  ( $96^\circ$ ). (We have previously estimated cone angles for  $\text{AuPR}_3$  units<sup>13</sup> based on a method similar to that used by Mingos for gold clusters<sup>14</sup>.) Compared with the large numbers of mono- and digold compounds, trigold derivatives of metal carbonyl clusters are quite limited in number. In those which have been crystallographically characterized<sup>6,15-23</sup>, aggregation of the three gold atoms is the norm; exceptions are **1**,  $[\text{Ru}_6(\text{CO})_{16}\text{B}\{\text{AuPPh}_3\}_3]$  (ref.<sup>6</sup>) and  $[\text{M}_3(\text{CO})_9(\mu\text{-OEt})(\mu_3\text{-OEt})_2\{\text{AuPPh}_3\}_3]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ )<sup>17</sup>. Figures 1c and 3 show examples of the families of fully characterized metal carbonyl clusters reported to date. The compounds in Fig. 3 are arranged in three groups. Figures 3a-3c show trimetal clusters carrying three  $\text{AuL}$  units; Fig. 3d shows

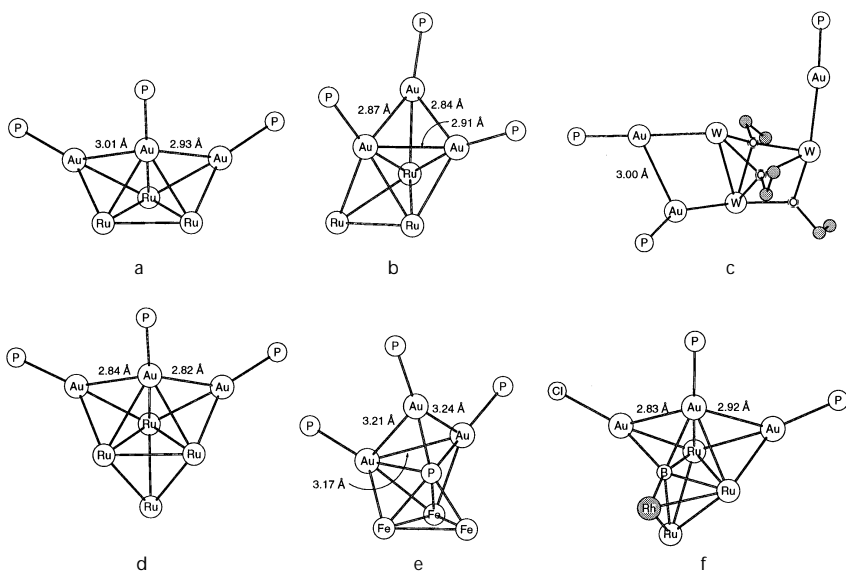


FIG. 3

Core structures of  $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-COMe})\{\text{AuPPh}_3\}_3]$  (ref.<sup>14</sup>) (a),  $[\text{Ru}_3(\text{CO})_8(\text{C}_{12}\text{H}_{15})\{\text{AuPPh}_3\}_3]$  (ref.<sup>15</sup>) (b),  $[\text{W}_3(\text{CO})_9(\mu\text{-OEt})(\mu_3\text{-OEt})_2\{\text{AuPPh}_3\}_3]$  (ref.<sup>16</sup>) (c),  $[\text{HRu}_4(\text{CO})_{12}\{\text{AuPPh}_3\}_3]$  (ref.<sup>17</sup>) (d),  $[\text{Fe}_3(\text{CO})_9\text{P}\{\text{AuPPh}_3\}_3]$  (ref.<sup>18</sup>) (e),  $[\text{HRhRu}_3(\text{CO})_9(\eta^5\text{-C}_5\text{Me}_5)\text{B}\{\text{AuPPh}_3\}_2(\text{AuCl})]$  (ref.<sup>19</sup>) (f)



the arrangement of three AuL units in tetrahedral  $Ru_4$  clusters and, in addition to  $[HRu_4(CO)_{12}\{AuPPh_3\}_3]$  illustrated<sup>18</sup>, the compounds  $[HRu_4(CO)_{12}\{AuPPh_3\}\{Au(Ph_2PCH_2PPh_2)Au\}]$  (ref.<sup>21</sup>) and  $[CoRu_3(CO)_{12}\{AuPPh_3\}_3]$  (ref.<sup>22</sup>) have similar metal and phosphorus atom arrangements; Figs 3e and 3f show metal carbonyl clusters in which the gold atoms interact with a semi-interstitial *p*-block element, and a further member of this group is  $[Fe_4(CO)_{12}B\{AuPPh_3\}_3]$  (ref.<sup>23</sup>). To date and to the best of our knowledge, three "clustered" gold atoms have not been observed supported on an octahedral metal core.

In the solid state structure of **1**, there are three phosphorus environments (irrespective of the arrangement of the Rh and Ru atoms). At room temperature, the solution <sup>31</sup>P NMR spectrum exhibited two signals at  $\delta +82.9$  and  $+76.8$  with relative integrals 1 : 2. Lowering the temperature resulted in collapse of the signal at  $\delta +76.8$  over the range 257 to 232 K while the  $\delta +82.9$  remained sharp. However, well resolved spectra could not be obtained at lower temperatures. These results, while not fully informative, do indicate that **1** is stereochemically non-rigid in solution with respect to the positions of the AuPCy<sub>3</sub> fragments.

In order to extend this chemistry further, we turned our attention to the use of  $\{[R_3PAu]_3O\}[BF_4]$  compounds to encourage the formation of trigold(I) phosphine cluster derivatives containing the  $Rh_2Ru_4B$  core. The reaction of  $[(Ph_3P)_2N][Rh_2Ru_4(CO)_{16}B]$  with  $\{[Ph_3PAu]_3O\}[BF_4]$  gave two products which were separated by TLC. Both products gave essentially the same FAB mass spectrometric results, with parent ions and isotopic distributions consistent with the formulation  $[Rh_2Ru_4(CO)_{15}B\{AuPPh_3\}_3]$  (**2**), and we assigned the products as two isomers **2a** and **2b**. Their <sup>11</sup>B NMR spectroscopic signatures were as expected for the retention of a boron-containing octahedral  $Rh_2Ru_4$  core in each isomer. The solution IR spectrum of isomer **2a** in the carbonyl region was very similar to that of **1**, while that of **2b** was somewhat different. The <sup>31</sup>P NMR spectrum of **2a** at 298 K exhibited two signals ( $\delta +63.7$  and  $+62.2$ ) with relative integrals 1 : 2. Between 298 and 232 K, the signal at  $\delta +62.2$  collapsed leaving the second signal still sharp (Fig. 4). Lowering the temperature to 205 K resulted in the growth of two new signals, the spectrum overall consisting of signals at  $\delta +67.3$ ,  $+61.6$  and  $+53.6$  with relative integrals 1 : 1 : 1. This indicates a fluxional process which renders two of the three AuPPh<sub>3</sub> units equivalent, but a process which does not involve all three units. In contrast, the variable temperature <sup>31</sup>P NMR spectra of isomer **2b** showed one signal at 298 K ( $\delta +58.9$ ) which broadened and finally gave two signals at 196 K at  $\delta +59.3$  (1 P) and  $+56.9$  (2 P). We conclude that **2b** differs from **2a** in the arrangement of the gold(I)

phosphine units on the octahedral core and that the solution fluxional process involves all three AuPPh<sub>3</sub> fragments. Although crystals of **2b** were grown, they were not of X-ray quality, and we are unable to make further comments on the exact structure of this isomer. No interconversion of isomers **2a** and **2b** was observed in solution, and on storing in the solid state under argon, each was stable.

The reaction of [(Ph<sub>3</sub>P)<sub>2</sub>N][Rh<sub>2</sub>Ru<sub>4</sub>(CO)<sub>16</sub>B] with [{(2-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAu}<sub>3</sub>O][BF<sub>4</sub>] gave two isolable products, [Rh<sub>2</sub>Ru<sub>4</sub>(CO)<sub>16</sub>B{AuP(2-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>}] (ref.<sup>7</sup>) as the major product, and a new compound **3** in relatively low yield. The FAB mass spectrum of **3** was consistent with the formulation of [Rh<sub>2</sub>Ru<sub>4</sub>(CO)<sub>15</sub>B{AuP(2-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>}<sub>3</sub>] with a parent ion at *m/z* 2 545 showing the expected isotopic distribution. The <sup>11</sup>B NMR spectrum exhibited a peak at δ +200, and the solution IR spectrum was virtually identical to that of **2a** and similar to that of **1**. In the room-temperature <sup>31</sup>P NMR spectrum, two signals were observed (δ +57.6 and +58.9) with relative integrals in the ratio 1 : 2; the latter signal was broad. These data implied that compound **3** is structurally similar to **1** (Fig. 2) and **2a**. A comparison of the line shapes for the signals in the room-temperature <sup>31</sup>P NMR spectra of **2a** (Fig. 4) and **3** are consistent with a higher activation energy for the fluxional process involving the more bulky AuP(2-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> group in **3** compared with the AuPPh<sub>3</sub> groups in **2a**.

## CONCLUSION

The formation of trigold(I) phosphine derivatives of octahedral borido clusters has now been extended from the homometallic Ru<sub>6</sub>B boride<sup>6</sup> to the heterometallic Rh<sub>2</sub>Ru<sub>4</sub>B boride. The most effective route to these com-

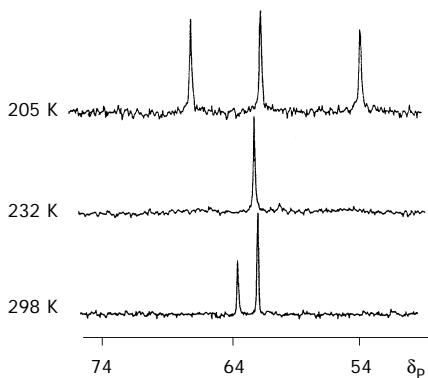


FIG. 4  
Variable-temperature 162 MHz NMR spectra  
of **2a** in CD<sub>2</sub>Cl<sub>2</sub>

pounds is by use of  $\{[R_3PAu]_3O\}^+$ . Aggregation of the gold fragments on the surface of the metal carbonyl cluster core does not occur in **1**, and by inference in **2a** or **3**, and this marks these compounds as being dissimilar from the majority of trigold(I) derivatives of metal carbonyl clusters for which solid-state structures have been determined.

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