

**Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 100.<sup>1</sup> Synthesis of Mixed-metal Compounds *via* the Salts [NEt<sub>4</sub>]-[Rh(CO)L(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R<sub>2</sub>)] (L = PPh<sub>3</sub>, R = H; L = CO, R = Me); Crystal Structures of the Complexes [WRhAu(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>3</sub>(PPh<sub>3</sub>)(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] and [WRh<sub>2</sub>Au<sub>2</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>6</sub>(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)<sub>2</sub>].0.5CH<sub>2</sub>Cl<sub>2</sub>\***

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The rhodacarbaborane salts [NEt<sub>4</sub>][Rh(CO)L(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R<sub>2</sub>)] have been used to prepare the mixed-metal complexes [RhAu(CO)(PPh<sub>3</sub>)L(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R<sub>2</sub>)] (L = PPh<sub>3</sub>, R = H; L = CO, R = Me), [WRhAu(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>3</sub>L(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R<sub>2</sub>)] (L = PPh<sub>3</sub>, R = H; L = CO, R = Me), and [WRh<sub>2</sub>Au<sub>2</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>6</sub>(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)<sub>2</sub>]. In related studies treatment of the salt [WAuCl(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] with Na[Mn(CO)<sub>5</sub>] or [N(PPh<sub>3</sub>)<sub>2</sub>][Co(CO)<sub>4</sub>] yields, respectively, the trimetal compounds [WMAu(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>n</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (M = Mn, n = 7; M = Co, n = 6). The molecular structures of [WRhAu(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>3</sub>(PPh<sub>3</sub>)(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] and [WRh<sub>2</sub>Au<sub>2</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>6</sub>(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)<sub>2</sub>] have been determined by single-crystal X-ray diffraction studies. In the trimetal species there is a bent [156.9(1)°] W–Au–Rh array of metal atoms [W–Au 2.732(1) and Rh–Au 2.640(1) Å] with the W–Au bond asymmetrically bridged by the *p*-tolylmethylidyne group [μ-C–W 1.90(1) and μ-C–Au 2.13(1) Å]. The W atom carries the C<sub>5</sub>H<sub>5</sub> ring and two CO groups, while the Rh atom is ligated by the η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> cage, a CO group, and the PPh<sub>3</sub> ligand [Rh–P 2.340(3) Å]. The pentanuclear metal cluster has a WAu<sub>2</sub> triangular core [W–Au (average) 2.750(2) and Au···Au 2.969(2) Å] capped by the CC<sub>6</sub>H<sub>4</sub>Me-4 group [μ<sub>3</sub>-C–W 2.02(2) and μ<sub>3</sub>-C–Au (average) 2.05(2) Å]. The tungsten atom is co-ordinated by two CO groups and the C<sub>5</sub>H<sub>5</sub> ring. Each gold atom is linked to a Rh(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>) fragment *via* both a Rh–Au bond [average 2.217(2) Å] and a B–H→Au three-centre two-electron bond. This linkage involves for each cage the unique boron atom in the face of the icosahedral C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub> fragment which is β to the CMe groups. The spectroscopic properties (i.r., <sup>1</sup>H, <sup>13</sup>C-{<sup>1</sup>H}, <sup>31</sup>P-{<sup>1</sup>H}, and <sup>11</sup>B n.m.r.) of the new compounds are reported, and where appropriate the data are discussed in relation to their structures.

The salt [NEt<sub>4</sub>][Rh(CO)(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (**1a**) was first reported by Hawthorne and co-workers<sup>2a</sup> as part of an extensive study of hydrogenation reactions homogeneously catalysed by rhodacarbaborane complexes.<sup>2b–e</sup> So far little attention has been given to using (**1a**), or related species, as reagents for preparing organometallic compounds. However, we have recently reported<sup>3</sup> that treatment of (**1a**) with [Co(CO)<sub>2</sub>(NCMe)(η<sup>4</sup>-C<sub>4</sub>Me<sub>4</sub>)] [PF<sub>6</sub>], [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>], and [IrCl(CO)<sub>2</sub>(NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)] affords, respectively, the dimetal compounds [CoRh(CO)<sub>2</sub>(PPh<sub>3</sub>)(η<sup>4</sup>-C<sub>4</sub>Me<sub>4</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (**2**), [Rh<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (**3**), and [RhIrH(μ-σ:η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**). Interestingly, in all three syntheses the carbaborane cage adopts a non-spectator role, forming exopolyhedral B–H→M (M = Co or Rh) or B–Ir bonds.

The syntheses of compounds (**3**) and (**4**) proceed in a non-stoichiometric manner, since two PPh<sub>3</sub> ligands are present in these products rather than one. The acquisition of the second PPh<sub>3</sub> group must be due to a dissociation of this ligand from (**1a**). Even allowing for this side effect, compounds (**3**) and (**4**) are formed in *ca.* 40% yield, while for complex (**2**), the formation of which involves no PPh<sub>3</sub> migration, the yield is *ca.* 70%. It is thus apparent from these preliminary studies that (**1a**) could be a viable precursor to many new species containing metal–metal bonds. In this paper we develop this approach, employing as

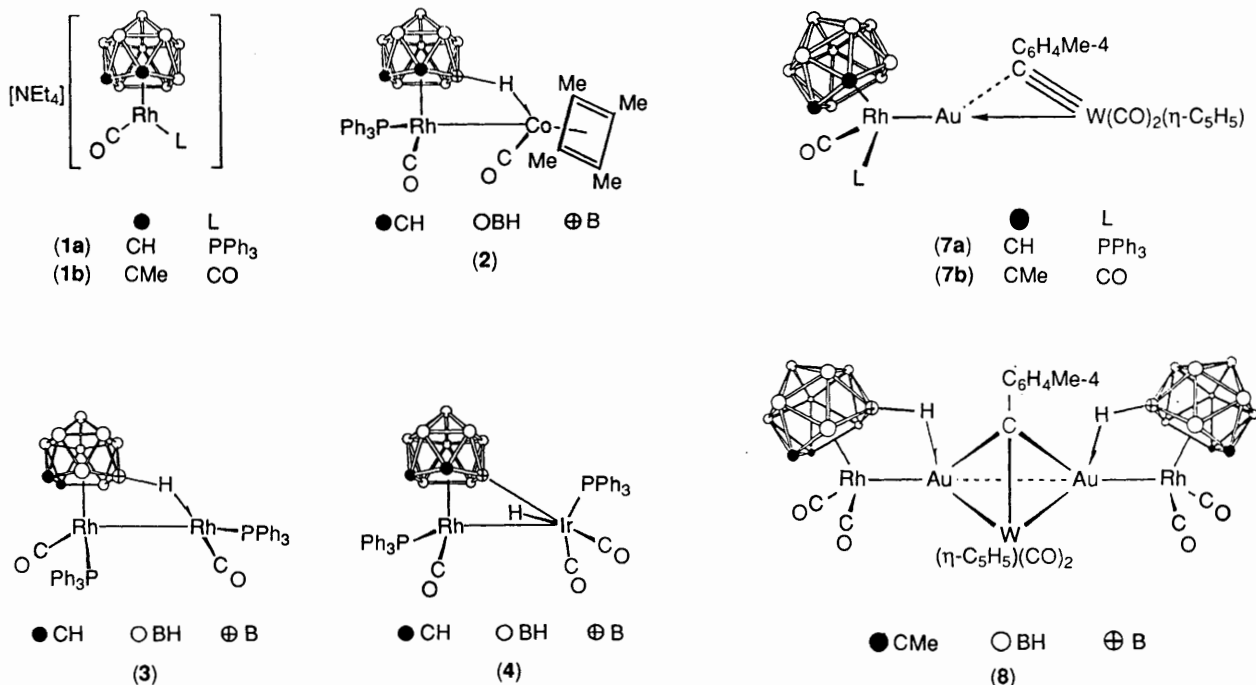
reagents both (**1a**) and the hitherto unreported salt [NEt<sub>4</sub>][Rh(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (**1b**).

### Results and Discussion

The dimetal compound [RhAu(CO)(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (**5a**) is formed in essentially quantitative yield upon treating the salt (**1a**) with [AuCl(PPh<sub>3</sub>)], in thf (tetrahydrofuran), in the presence of TIBF<sub>4</sub>. The latter is added to facilitate removal of chloride as insoluble TlCl. Data for (**5a**) are given in Tables 1 and 2, and are in agreement with the formulation shown.

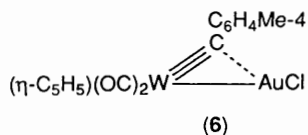
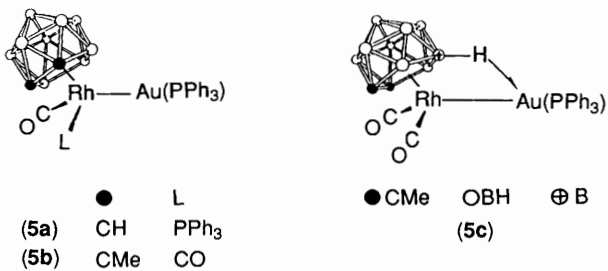
The salt [NEt<sub>4</sub>][Rh(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (**1b**) was prepared by treating thf solutions of [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>] with the thallium reagent Tl<sub>2</sub>[7,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>],<sup>4</sup> followed by addition of NEt<sub>4</sub>Cl. The reaction between compound (**1b**) and [AuCl(PPh<sub>3</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> afforded the species [RhAu(CO)<sub>2</sub>(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)]. However, the <sup>31</sup>P-{<sup>1</sup>H}, <sup>11</sup>B-{<sup>1</sup>H}, and <sup>11</sup>B n.m.r. data suggest that this product exists as a *ca.* 1:1 mixture of two isomers (**5b**) and (**5c**), rather than as (**5b**) only, the analogue of (**5a**). Thus the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum of (**5a**) (Table 2) shows two resonances for a RhPPh<sub>3</sub> and a AuPPh<sub>3</sub>

\* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.



group, each a doublet as expected. Unexpectedly, the spectrum of  $[\text{RhAu}(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  also shows two peaks; these signals correspond to two AuPPh<sub>3</sub> groups in slightly different environments. Although there was no evidence in the  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectra for a mixture of isomers, a proton-coupled  $^{11}\text{B}$  spectrum was revealing in showing a doublet resonance at  $\delta -1.5$  p.p.m. [ $J(\text{BH})$  76 Hz], and several broad overlapping peaks in the range  $-4.4$  to  $-16.0$  p.p.m. The signal at  $\delta -1.5$  p.p.m. suggests<sup>5,6</sup> the presence of a species having a B-H→M three-centre two-electron bond, as depicted in (5c). The coupling of 76 Hz is typical for such a linkage, and may be compared with that for a two-centre two-electron B-H bond which is *ca.* 130 Hz. The presence of the B-H→Au group in (5c) might have been expected to reveal itself in the  $^1\text{H}$  n.m.r. spectrum by the presence of a quartet resonance ( $^{11}\text{B}\text{-}^1\text{H}$  coupling) in the range  $\delta -0.2$  to  $-12.0$  p.p.m.<sup>5-7</sup> However, these high-field signals are often broad and weak, and sometimes are not observed, as discussed further below.

Although the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of  $[\text{RhAu}(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  clearly reveals the presence of two



species containing AuPPh<sub>3</sub> groups, as mentioned above, the  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectra did not indicate the existence of two isomers. In the  $^1\text{H}$  spectrum there was only one CMe resonance, and correspondingly in the  $^{13}\text{C}\{-^1\text{H}\}$  spectrum there was only one CMe and one CMe peak. This pattern is as expected either for (5b) or for (5c), provided that the latter has a symmetrical structure with the B-H→Au bond involving the boron atom in the face of the  $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$  ligand which is  $\beta$  to the CMe groups.<sup>5,6</sup> However, the similarity in the structures of (5b) and (5c) could well lead to a coincidence of the  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. signals due to the CMe groups in these species.

The reaction between the salt (1a) and the compound  $[\text{WAuCl}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (6)<sup>8</sup> was next investigated. In  $\text{CH}_2\text{Cl}_2$ , in the presence of TIBF<sub>4</sub>, these reagents afford the trimetal compound  $[\text{WRhAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_3(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  (7a) in essentially quantitative yield. Data for this complex are listed in Tables 1 and 2, and the structure was established by X-ray diffraction. The results of the latter study are summarised in Table 3, and the molecular structure is shown in Figure 1.

The molecule has a bent W-Au-Rh spine [W-Au-Rh 156.9(1)°, W-Au 2.732(1) and Rh-Au 2.640(1) Å]. The W-Au separation may be compared with those in the complexes  $[\text{W}_2\text{Au}(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  [2.752(1) Å]<sup>9a</sup> and  $[\text{WAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  [2.780(8) Å].<sup>9b</sup> In the latter the  $\mu\text{-C-Au}$  and  $\mu\text{-C-W}$  distances are 2.19(3) and 1.88(3) Å, respectively, and are thus very similar to the corresponding bond lengths in (7a) [C(3)-Au 2.13(1) and C(3)-W 1.90(1) Å]. In both (7a) and  $[\text{WAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ , and in struc-

**Table 1.** Analytical<sup>a</sup> and physical data for the complexes

Compound	Colour	Yield (%)	$\nu_{\max}(\text{CO})^b/\text{cm}^{-1}$	Analysis (%)	
				C	H
(1b) [NEt <sub>4</sub> ][Rh(CO) <sub>2</sub> ( $\eta^5$ -C <sub>2</sub> B <sub>9</sub> H <sub>9</sub> Me <sub>2</sub> )]	Brown	70	2 013vs, 1 946vs	36.5 (37.4)	8.2 (7.9)
(5a) [RhAu(CO)(PPh <sub>3</sub> ) <sub>2</sub> ( $\eta^5$ -C <sub>2</sub> B <sub>9</sub> H <sub>9</sub> Me <sub>2</sub> )]	Green	93	1 998s	48.0 (47.6)	4.2 (4.2)
(5b), (5c) [RhAu(CO) <sub>2</sub> (PPh <sub>3</sub> )( $\eta^5$ -C <sub>2</sub> B <sub>9</sub> H <sub>9</sub> Me <sub>2</sub> )] <sup>d</sup>	Yellow	90	2 048vs, 1 996s	36.2 (37.0)	4.4 (3.9)
(7a) [WRhAu( $\mu$ -CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>3</sub> (PPh <sub>3</sub> )( $\eta$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -C <sub>2</sub> B <sub>9</sub> H <sub>9</sub> Me <sub>2</sub> )]	Orange	92	2 011vs, 1 996s, 1 947m	38.2 (38.2)	4.0 (3.4)
(7b) [WRhAu( $\mu$ -CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>4</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -C <sub>2</sub> B <sub>9</sub> H <sub>9</sub> Me <sub>2</sub> )] <sup>e</sup>	Orange		2 056s, 2 008s, 1 951m		
(8) [WRh <sub>2</sub> Au <sub>2</sub> ( $\mu_3$ -CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>6</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -C <sub>2</sub> B <sub>9</sub> H <sub>9</sub> Me <sub>2</sub> ) <sub>2</sub> ]	Orange	91 <sup>f</sup>	2 060vs, 2 037s, 2 008vs, 1 986s	21.5 (22.3)	3.2 (2.9)
(9a) [WMnAu( $\mu$ -CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>7</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )]	Orange-red	82	2 057w, 2 005m, 1 951s	29.4 (30.0)	1.9 (1.5)
(9b) [WCoAu( $\mu$ -CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>6</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )]	Orange	86	2 050w, 2 011m, 1 977w, 1 955s	29.5 (29.4)	1.8 (1.6)

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub>; medium to weak broad bands observed at ca. 2 560 cm<sup>-1</sup> in the spectra of compounds (1), (5), (7), and (8) are due to B-H absorptions. <sup>c</sup> N, 3.5 (3.1%). <sup>d</sup> Isomers, see text. <sup>e</sup> Not isolated free of compound (8). However, i.r. bands in CO region could be measured from mixtures containing (8), since latter could be isolated pure and its spectrum measured. <sup>f</sup> Yield of mixture of compounds (7b) and (8), based on rhodium. From this mixture (8) can be recovered (see text) in ca. 79% yield.

**Table 2.** Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. data<sup>a</sup> for the complexes

Compound	<sup>1</sup> H(δ) <sup>b</sup>	<sup>13</sup> C(δ) <sup>c</sup>	<sup>31</sup> P(δ) <sup>d</sup>
(5a)	1.91, 2.52 (s × 2, 2 H, CH), 7.21—7.59 (m, 30 H, Ph)	191.5 [d of d, CO, <i>J</i> (RhC) 72, <i>J</i> (PC) 18], 134.3—128.9 (Ph), 44.3 [d, C(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> ), <i>J</i> (PC) 5], 44.0 [C(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> )]	35.9 [d, PRh, <i>J</i> (RhP) 123], 35.3 [d, PAu, <i>J</i> (RhP) 12]
(5b), (5c)	2.36 (s, 6 H, CMe), 7.40—7.56 (m, 15 H, Ph)	186.2 [d, CO, <i>J</i> (RhC) 70], 133.2—128.4 (Ph), 70.0 (CMe), 30.4 (Me)	39.0 [d, PAu, <i>J</i> (RhP) 28], 38.5 [d, PAu, <i>J</i> (RhP) 28]
(7a)	2.23 (s, 2 H, CH), 2.26 (s, 3 H, Me-4), 5.62 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.96—7.35 (m, 19 H, C <sub>6</sub> H <sub>4</sub> and Ph)	284.3 [ $\mu$ -C, <i>J</i> (WC) 151], 214.0, 213.8 [WCO, <i>J</i> (WC) 176 and 181 respectively], 191.3 [d of d, RhCO, <i>J</i> (RhC) 81, <i>J</i> (PC) 18], 134.0—128.5 (C <sub>6</sub> H <sub>4</sub> and Ph), 92.0 (C <sub>5</sub> H <sub>5</sub> ), 44.1, 43.3 [C(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> )], 21.5 (Me-4)	36.1 [d, PRh, <i>J</i> (RhP) 125]
(7b) <sup>e</sup>	2.34 (s, 3 H, Me-4), 2.37 (s, 6 H, CMe), 5.75 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 7.15, 7.47 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (AB) 8]	289.1 (br, $\mu$ -C), 213.6 [WCO, <i>J</i> (WC) 173], 186.5 [d, RhCO, <i>J</i> (RhC) 71], 150.5 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 140.1, 130.6, 128.8 (C <sub>6</sub> H <sub>4</sub> ), 91.3 (C <sub>5</sub> H <sub>5</sub> ), 70.2 (br, CMe), 30.9 (CMe), 21.5 (Me-4)	
(8)	2.32, 2.40 (s × 2, 12 H, CMe), 2.42 (s, 3 H, Me-4), 5.91 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 7.17, 7.57 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (AB) 8]	289.3 (br, $\mu$ -C), 205.9 [WCO, <i>J</i> (WC) 164], 186.0 [d, RhCO, <i>J</i> (RhC) 71], 185.7 [d, RhCO, <i>J</i> (RhC) 66], 148.8 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 139.9, 130.5, 128.5 (C <sub>6</sub> H <sub>4</sub> ), 89.6 (C <sub>5</sub> H <sub>5</sub> ), 72.1, 71.2 (br, CMe), 30.9, 30.8 (CMe), 21.0 (Me-4)	
(9a)	2.30 (s, 3 H, Me-4), 5.83 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 7.12, 7.52 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (AB) 8]	285.2 ( $\mu$ -C), 220.7 (br, MnCO), 215.0 [WCO, <i>J</i> (WC) 182], 147.9 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 141.8, 130.0, 129.1 (C <sub>6</sub> H <sub>4</sub> ), 92.3 (C <sub>5</sub> H <sub>5</sub> ), 21.7 (Me-4)	
(9b)	2.31 (s, 3 H, Me-4), 5.82 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 7.14, 7.57 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (AB) 8]	285.6 ( $\mu$ -C), 213.0 [WCO, <i>J</i> (WC) 178], 209 (br, CoCO), 148.1 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 142.4, 130.7, 129.2 (C <sub>6</sub> H <sub>4</sub> ), 92.4 (C <sub>5</sub> H <sub>5</sub> ), 21.8 (Me-4)	

<sup>a</sup> Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures. <sup>b</sup> Measured in CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe<sub>4</sub>. Measurements in CD<sub>2</sub>Cl<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H<sub>3</sub>PO<sub>4</sub> (external). <sup>e</sup> Data taken from the spectrum of a mixture of compounds (7b) and (8), see text.

turally related species, there are alternative ways of regarding the bonding in the W( $\mu$ -C)Au rings to account for the asymmetric bridging of the metal-metal bond by the *p*-tolylmethylidyne ligand, while also maintaining reasonable electron counts at the two metal centres.<sup>1,9b</sup> The formulation depicted for (7a) implies a W→Au donor bond which with the Rh-Au bond would give the gold(i) centre the commonly found 14-electron shell. The weaker  $\mu$ -C-Au interaction could provide a mechanism for a transfer of electron density from the gold to the  $\pi^*$  orbitals of the C≡W system. In complexes containing  $\mu$ -C(aryl) ligands spanning heteronuclear metal-metal bonds involving molybdenum or tungsten the asymmetry in the bonding is reflected in the M(Mo or W)- $\mu$ -C-C<sup>1</sup>(aryl) angles. The larger this angle the more asymmetric is the bonding, and as a result the C≡M linkage tends to retain its triple-bond

character. Using this criterion, the degree of asymmetry in the bridge bonding in (7a) [W-C(3)-C(4) 156(1)°] is very similar to that of the  $\mu$ -CC<sub>6</sub>H<sub>4</sub>Me-4 ligand bridging the Mo-Au bond in [MoWCoAu( $\mu$ -CC<sub>6</sub>H<sub>4</sub>Me-4)( $\mu_3$ -CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>4</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] [Mo- $\mu$ -C-C<sup>1</sup> 155(1)°].<sup>1</sup> A greater degree of asymmetry in the bridge system occurs in [WAu( $\mu$ -CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(PPh<sub>3</sub>)( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] [163(2)°]<sup>9b</sup> and [WPt( $\mu$ -CC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(CO)<sub>2</sub>(PEt<sub>3</sub>)( $\mu$ - $\sigma$ : $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Me<sub>2</sub>)] [175(1)°].<sup>6b</sup>

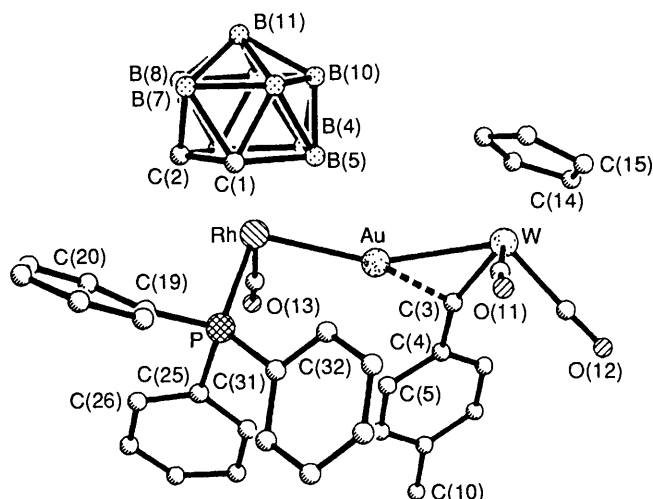
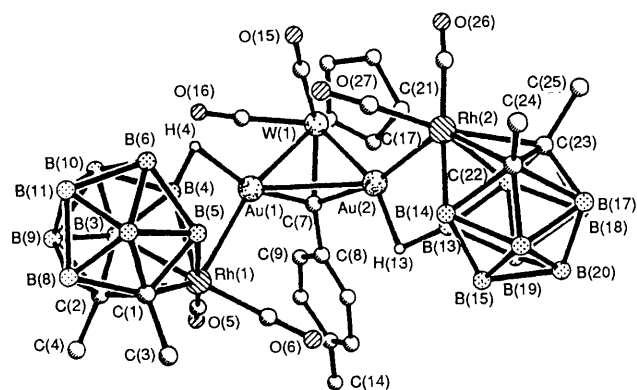
As expected, there is a PPh<sub>3</sub> group co-ordinated to the Rh atom in (7a) [Rh-P 2.340(3) Å], as well as a CO and an  $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> ligand. The W atom carries a C<sub>5</sub>H<sub>5</sub> ring and two carbonyl groups. All the carbonyl ligands are essentially linearly bound to their respective metal centres.

The spectroscopic data for compound (7a) are in agreement

**Table 3.** Selected internuclear distances (Å) and angles (°) for the complex  $[\text{WRhAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_3(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$  (**7a**), with estimated standard deviations in parentheses

Au-W	2.732(1)	Au-Rh	2.640(1)	W-C(3)	1.90(1)	Au-C(3)	2.13(1)
W-C(11)	1.99(2)	W-C(12)	1.98(2)	W-C(C <sub>5</sub> H <sub>5</sub> )*	2.33(2)	Rh-P	2.340(3)
Rh-C(13)	1.85(1)	Rh-C(1)	2.24(1)	Rh-C(2)	2.30(1)	Rh-B(3)	2.24(2)
Rh-B(4)	2.27(1)	Rh-B(5)	2.28(1)	P-C(Ph)*	1.83(1)	C(1)-C(2)	1.65(2)
C(2)-B(3)	1.66(2)	B(3)-B(4)	1.86(2)	B(4)-B(5)	1.81(2)	C(1)-B(5)	1.73(2)
B(5)-B(6)	1.80(2)	C(1)-B(6)	1.71(2)	B(6)-B(7)	1.78(2)	C(1)-B(7)	1.77(2)
C(2)-B(7)	1.70(2)	B(7)-B(8)	1.76(2)	C(2)-B(8)	1.67(2)	B(3)-B(8)	1.79(2)
B(8)-B(9)	1.80(2)	B(3)-B(9)	1.80(2)	B(4)-B(9)	1.81(2)	B(9)-B(10)	1.79(2)
B(4)-B(10)	1.79(2)	B(5)-B(10)	1.77(2)	B(6)-B(10)	1.74(2)	B(6)-B(11)	1.78(2)
B(7)-B(11)	1.75(2)	B(8)-B(11)	1.76(2)	B(9)-B(11)	1.79(2)	B(10)-B(11)	1.78(2)
C(11)-O(11)	1.16(2)	C(12)-O(12)	1.14(2)	C(13)-O(13)	1.14(2)		
W-Au-Rh	156.9(1)	Au-Rh-P	97.2(1)	Au-Rh-C(13)	79.0(4)	P-Rh-C(13)	88.4(4)
Au-W-C(3)	51.0(4)	Au-W-C(11)	81.0(4)	Au-W-C(12)	124.4(4)	Au-C(3)-W	85.1(4)
C(3)-Au-W	44.0(3)	W-C(11)-O(11)	175(1)	W-C(12)-O(12)	177(1)	Rh-C(13)-O(13)	172(1)
W-C(3)-C(4)	156(1)	Au-C(3)-C(4)	119(1)				

\* Average distances between W and C atoms of C<sub>5</sub>H<sub>5</sub> ring, and between P and C<sup>1</sup> atoms of Ph rings, respectively.

**Figure 1.** The molecular structure of the complex  $[\text{WRhAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_3(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$  (**7a**), showing the crystallographic numbering scheme**Figure 2.** The molecular structure of  $[\text{WRh}_2\text{Au}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)_2]$  (**8**), showing the crystallographic numbering scheme for one of the two independent molecules

with the structure found by X-ray diffraction. The i.r. spectrum (Table 1) displays three carbonyl bands in the terminal region, and correspondingly the  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectrum (Table 2) shows three CO resonances. The signal for the  $\mu\text{-CC}_6\text{H}_4\text{Me-4}$  nucleus occurs at  $\delta$  284.3 p.p.m., a chemical shift reflecting

the asymmetric spanning of the W-Au bond by the *p*-tolylmethylidyne group.<sup>6b</sup> Other peaks in the  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectra are as expected.

Treatment of compound (**6**) with the salt (**1b**) in  $\text{CH}_2\text{Cl}_2$ , in the presence of  $\text{TIBF}_4$ , afforded a mixture of two compounds  $[\text{WRhAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$  (**7b**) and  $[\text{WRh}_2\text{Au}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)_2]$  (**8**) formed in the ratio *ca.* 2:3. It was not possible to separate (**7b**) from (**8**) by column chromatography, but crystallisation of mixtures allowed pure samples of (**8**) to be obtained. Indeed, the nature of the latter species only became apparent after an X-ray diffraction study, described below. Data for the two compounds are listed in Tables 1 and 2. Complex (**7b**) appears to be an analogue of (**7a**), although the possibility that it contains a B-H→Au fragment cannot be entirely eliminated. A  $^{11}\text{B}$  n.m.r. spectrum of a mixture of (**7b**) and (**8**) revealed a diagnostic resonance for a B-H→metal linkage at  $\delta$  7.5 p.p.m. [ $J(\text{BH})$  79 Hz]. However, this signal can be attributed to the B-H→Au groups present in (**8**) (see below), and thus if (**7b**) also contains a similar moiety the  $^{11}\text{B}$  resonances for the B-H→Au linkages in the two species must be coincident.

The X-ray diffraction study on compound (**8**) revealed an asymmetric unit containing two structurally similar but crystallographically independent molecules, the results for one of which are summarised in Table 4. The structure of this molecule is shown in Figure 2, from which it is evident that the core is based on a  $\text{W}\text{Au}_2$  triangle capped by a *p*-tolylmethylidyne group. Each gold atom is linked to a  $\text{Rh}(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)$  fragment *via* both a Rh-Au bond and a B-H→Au three-centre two-electron bond. The  $\text{Au}(1)\cdots\text{Au}(2)$  separation [2.969(2) Å] may well represent little or no direct metal-metal bonding, this distance being influenced by the orbital and steric requirements of the bridging  $4\text{-MeC}_6\text{H}_4\text{C}\equiv\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  fragment<sup>10</sup> rather than a need to establish a Au-Au bond.

The other metal-metal separations in compound (**8**) are  $\text{Au}(1)\text{-W}(1)$  2.755(2),  $\text{Au}(2)\text{-W}(1)$  2.744(2),  $\text{Au}(1)\text{-Rh}(1)$  2.715(2), and  $\text{Au}(2)\text{-Rh}(2)$  2.718(3) Å. The Au-W distances are very similar to those of the Au-W bond in (**7a**) and in related molecules, discussed above. However, the Au-Rh bonds in (**8**) are somewhat longer than the Au-Rh linkage in (**7a**). This is probably due to the presence of the B-H→Au bridges in (**8**). Although the atoms H(4) and H(13) were not located in the X-ray diffraction study, the sites assigned are in accord with those calculated using the steric-potential-energy-minimisation technique.<sup>11</sup> Moreover, the  $\text{Au}(1)\text{-B}(4)$  [2.35(3) Å] and  $\text{Au}(2)\text{-B}(13)$  [2.38(3) Å] distances strongly imply a bonding interaction

**Table 4.** Selected internuclear separations (Å) and angles (°) for  $[\text{WRh}_2\text{Au}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)_2]$  (**8**) (one of two independent molecules) with estimated standard deviations in parentheses

Au(1)⋯Au(2)	2.969(2)	Au(1)–W(1)	2.755(2)	Au(1)–Rh(1)	2.715(2)	Au(1)–B(4)	2.35(3)
Au(1)–H(4)	1.84*	Au(1)–C(7)	1.98(3)	Au(2)–W(1)	2.744(2)	Au(2)–Rh(2)	2.718(3)
Au(2)–B(13)	2.38(3)	Au(2)–H(13)	1.85*	Au(2)–C(7)	2.13(2)	W(1)–C(7)	2.02(2)
W(1)–C(15)	2.01(3)	W(1)–C(16)	1.98(3)	Rh(1)–C(5)	1.86(3)	Rh(1)–C(6)	1.87(2)
Rh(2)–C(26)	1.89(2)	Rh(2)–C(27)	1.89(3)	C(5)–O(5)	1.19(4)	C(6)–O(6)	1.18(3)
C(15)–O(15)	1.16(3)	C(16)–O(16)	1.18(3)	C(26)–O(26)	1.11(3)	C(27)–O(27)	1.16(4)
B(4)–H(4)	1.33*	B(13)–H(13)	1.32*	B(3)–B(4)	1.83(4)	B(3)–C(2)	1.80(4)
B(4)–B(5)	1.82(5)	B(5)–C(1)	1.75(4)	C(1)–C(2)	1.62(3)	B(12)–B(13)	1.81(5)
B(12)–C(23)	1.80(4)	B(13)–B(14)	1.76(5)	B(14)–C(22)	1.79(3)	C(22)–C(23)	1.60(4)
Au(2)–Au(1)–W(1)	57.1(1)	Au(2)–Au(1)–Rh(1)	114.9(1)	W(1)–Au(1)–Rh(1)	162.5(1)		
Au(2)–Au(1)–C(7)	45.6(6)	W(1)–Au(1)–C(7)	47.1(5)	Au(1)–Au(2)–W(1)	57.5(1)		
Au(1)–Au(2)–Rh(2)	126.9(1)	W(1)–Au(2)–Rh(2)	121.5(1)	Au(1)–Au(2)–C(7)	41.6(7)		
W(1)–Au(2)–C(7)	47.0(5)	Au(1)–W(1)–Au(2)	65.4(1)	Au(1)–W(1)–C(7)	45.7(7)		
Au(2)–W(1)–C(7)	50.2(6)	Au(1)–Rh(1)–C(5)	88.6(7)	Au(1)–Rh(1)–C(6)	93.4(7)		
C(5)–Rh(1)–C(6)	94(1)	Au(2)–Rh(2)–C(26)	92(1)	Au(2)–Rh(2)–C(27)	87(1)		
C(26)–Rh(2)–C(27)	91(1)	Rh(1)–C(5)–O(5)	176(2)	Rh(1)–C(6)–O(6)	175(3)		
W(1)–C(15)–O(15)	177(2)	W(1)–C(16)–O(16)	177(2)	Rh(2)–C(26)–O(26)	175(2)		
Rh(2)–C(27)–O(27)	177(2)	Au(1)–C(7)–W(1)	93(1)	Au(1)–C(7)–W(1)	87(1)		
Au(2)–C(7)–W(1)	83(1)	Au(1)–C(7)–C(8)	125(2)	Au(2)–C(7)–C(8)	117(1)		
W(1)–C(7)–C(8)	139(2)						

\* Calculated position for hydrogen atom, see text and ref. 11.

between these atoms. Both B(4) and B(13) are in  $\beta$  positions with respect to the carbon atoms in the face of the  $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$  ligand. It is noteworthy that in (**7a**) the Au⋯B(4) and Au⋯B(5) separations are 2.97 and 2.85 Å, respectively, in accord with the absence of any B–H→Au interaction in this compound. The *p*-tolylmethylidene group caps the W(1)Au(1)Au(2) triangle with bond distances [C(7)–W(1) 2.02(2), C(7)–Au(1) 1.98(3), and C(7)–Au(2) 2.13(2) Å] very similar to those found for this ligand in the salt  $[\text{WPtAu}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PMe}_3)_3(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$  [ $\mu\text{-C-W}$  2.01(4) and  $\mu\text{-C-Au}$  2.21(4) Å].<sup>12</sup> The tungsten and rhodium atoms in (**8**) each carry two terminally bound carbonyl ligands. The W atom carries the  $\text{C}_5\text{H}_5$  ring, and the Rh atoms are ligated by the  $\text{C}_2\text{B}_9\text{H}_9\text{Me}_2$  cages in the usual  $\eta^5$  manner.<sup>2</sup>

As mentioned above, it was possible to obtain pure samples of compound (**8**) for spectroscopic studies. A proton-coupled <sup>11</sup>B n.m.r. spectrum revealed a diagnostic doublet resonance at  $\delta$  7.5 p.p.m. [ $J(\text{BH})$  79 Hz] for the B–H→Au group. The remainder of the spectrum showed broad overlapping peaks in the range –4.4 to –16.0 p.p.m. corresponding to the other boron nuclei. The <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum (Table 2) showed a characteristic resonance for the  $\mu_3\text{-C}$  alkylidene-carbon nucleus at  $\delta$  289.3 p.p.m. Other signals in the <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum, and the peaks in the <sup>1</sup>H n.m.r. spectrum, are in accord with the structure established by X-ray diffraction.

The mode of formation of compound (**8**) is of interest. It was established that (**7b**) is not an intermediate in the synthesis of (**8**). Mixtures of (**7b**) and (**8**) in  $\text{CH}_2\text{Cl}_2$  or in thf, when stirred for several hours, did not show any conversion of the former into the latter. However, a clue to the mode of formation of (**8**) was found when the synthesis of these compounds was carried out in thf rather than in  $\text{CH}_2\text{Cl}_2$ . The synthesis proceeds much more slowly in the former solvent, and significantly the presence of  $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  was observed. The latter appears to form by dissociation of compound (**6**), one of the reagents used in the preparation of (**7b**) and (**8**). This dissociative process would also release a AuCl fragment, which could add<sup>9a,12</sup> to the unsaturated W( $\mu\text{-C}$ )Au ring in (**7b**) to afford a species  $[\text{WRhAu}_2\text{Cl}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ . Replacement of Cl in the latter by the anion of (**1b**) would then yield complex (**8**) (see Scheme).

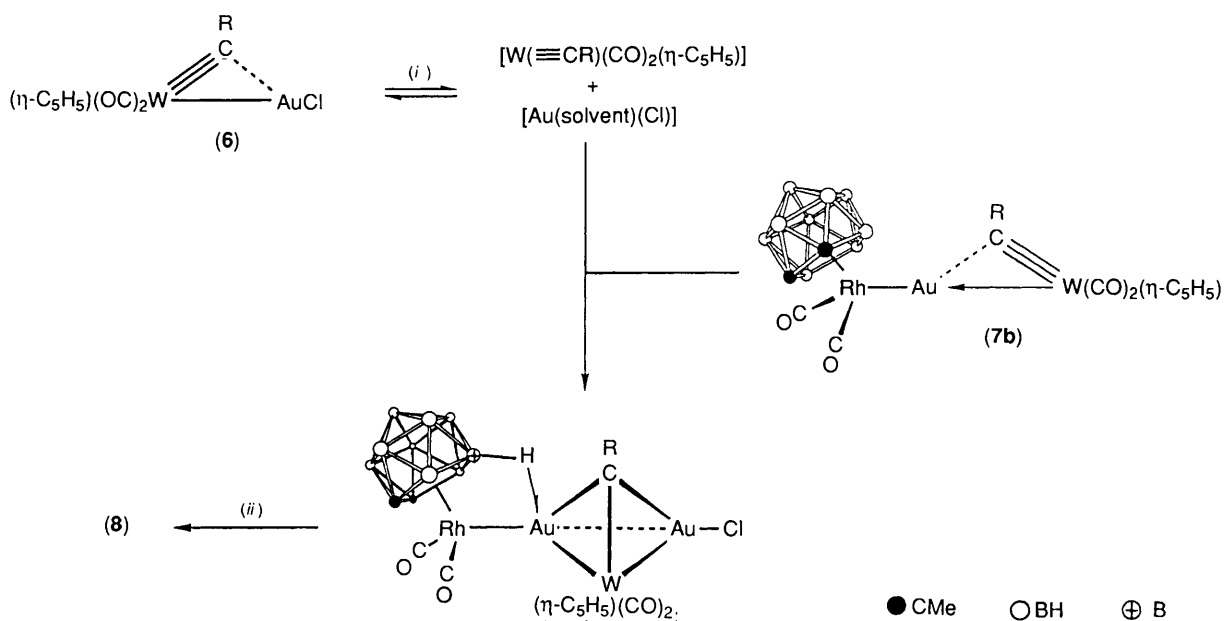
Isolobal mapping between metal–ligand fragments can provide a useful guide to the synthesis of organometallic complexes.<sup>13,14</sup> In this context, anions of the salts (**1**) are isolobal with the species  $[\text{Mn}(\text{CO})_5]^-$  or  $[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ . Both the manganese and the iron complexes are formally  $[\text{ML}_5]^-$  ( $d^8$  metal, L = an electron-pair donor) fragments. The  $\text{C}_5\text{H}_5$  ring in the iron anion is regarded as tridentate and carries a uninegative charge.<sup>13</sup> The coordination mode of *nido*-icosahedral  $\text{C}_2\text{B}_9\text{H}_9\text{R}_2$  (R = H or Me) cages in metal complexes is also tridentate, but in contrast with  $\text{C}_5\text{H}_5$  these carbaborane ligands formally carry a dinegative charge. From this it follows that the anions  $[\text{Rh}(\text{CO})\text{L}(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{R}_2)]^-$  are also  $[\text{ML}_5]^-$  ( $d^8$ ) fragments, and hence a complex such as (**5a**) can be mapped with the long known compound  $[(\text{OC})_5\text{Mn-Au}(\text{PPh}_3)]$ .<sup>15</sup>

Illustrating these relationships (Experimental section), treatment of compound (**6**) with  $\text{Na}[\text{Mn}(\text{CO})_5]$  affords the trimetal complex  $[\text{WMnAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$  (**9a**), characterised by the data given in Tables 1 and 2. Moreover, the anion  $[\text{Co}(\text{CO})_4]^-$  ( $\text{ML}_4$ ,  $d^{10}$ ) has a frontier orbital containing an electron pair, in common with  $[\text{Mn}(\text{CO})_5]^-$  or the anions (**1**), so treatment of (**6**) with  $[\text{N}(\text{PPh}_3)_2][\text{Co}(\text{CO})_4]$  yields  $[\text{WCoAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$  (**9b**) (Tables 1 and 2). On the basis of the metal–ligand fragments comprising the complexes (**9**) they may be mapped with the rhodium–gold–tungsten compound (**7a**).

The results described in this paper further illustrate the versatility of the salts (**1**) in the synthesis of complexes containing heteronuclear metal–metal bonds.<sup>3</sup> Moreover, as far as we are aware, compound (**8**), and very probably the isomer (**5c**) also, provide the first examples of species containing three-centre two-electron B–H→Au bonds. Recently exopolyhedral B–H→Cu bonding, supporting metal–metal linkages, has been identified in the compounds  $[\text{N}(\text{PPh}_3)_2][\text{M}_2\text{Cu}_2(\mu\text{-CO})_4(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})_2]$  (M = Mo or W),<sup>7</sup> and it is therefore probable that B–H→Ag systems will also exist. Further studies involving the complexes (**1**) are continuing.

## Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C.



Scheme. R = C<sub>6</sub>H<sub>4</sub>Me-4. (i) solvent = thf or CH<sub>2</sub>Cl<sub>2</sub>; (ii) + (1b)

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free atmosphere. Alumina (Brockman activity II) was used for chromatography (2 × 15 cm columns). The complexes [NEt<sub>4</sub>][Rh(CO)(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)],<sup>2a</sup> [AuCl(PPh<sub>3</sub>)],<sup>16</sup> [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>],<sup>17</sup> Ti<sub>2</sub>[C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>],<sup>4</sup> and [WAuCl(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)],<sup>1</sup> were prepared as described previously. Analytical and other data for the new compounds are given in Table 1. The i.r. spectra were measured with a Perkin-Elmer FT 1600 spectrophotometer, and n.m.r. spectra were recorded with JEOL JNM FX90Q, GX270, and GX400 spectrometers. The <sup>11</sup>B-{<sup>1</sup>H} n.m.r. spectra were measured in CD<sub>2</sub>Cl<sub>2</sub>, and chemical shifts are positive to high frequency of BF<sub>3</sub>·Et<sub>2</sub>O (external).

**Synthesis of the Salt** [NEt<sub>4</sub>][Rh(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)].—A thf (20 cm<sup>3</sup>) solution of [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>] (0.50 g, 1.29 mmol) was treated with Ti<sub>2</sub>[7,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>] (1.47 g, 2.58 mmol), and the mixture was stirred for 30 min at room temperature. The salt NEt<sub>4</sub>Cl (0.50 g, 3.02 mmol) was added, and stirring was continued for 30 min. The mixture was filtered through a Celite pad (ca. 4 cm), solvent was removed *in vacuo*, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and chromatographed. Elution with CH<sub>2</sub>Cl<sub>2</sub>-EtOH (1:1), followed by removal of solvent *in vacuo*, afforded a brown-black residue. The latter was crystallised from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O (1:4, 10 cm<sup>3</sup>) to afford brown microcrystals of [NEt<sub>4</sub>][Rh(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (1b) (0.81 g).

**Synthesis of the Dimetal Compounds** [RhAu(CO)(PPh<sub>3</sub>)L(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R<sub>2</sub>)] (L = PPh<sub>3</sub>, R = H; L = CO, R = Me).—(i) The compounds (1a) (0.10 g, 0.15 mmol), [AuCl(PPh<sub>3</sub>)] (0.075 g, 0.15 mmol), and TIBF<sub>4</sub> (0.19 g, 0.66 mmol) were dissolved in thf (20 cm<sup>3</sup>), and the mixture was stirred at room temperature until an i.r. spectrum revealed that all of the reagent (1a) had been consumed. The mixture was then filtered through a Celite plug (ca. 3 cm), solvent was removed *in vacuo*, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and chromatographed. Elution with the same solvent mixture afforded a yellow eluate. Removal of solvent *in vacuo*, followed by crystallisation from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (ca. 20 cm<sup>3</sup>, 1:20) gave green-yellow microcrystals of [RhAu(CO)(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (5a) (0.14 g), which were washed with light petroleum (2 × 10 cm<sup>3</sup>) and dried *in vacuo*.

(ii) Treatment of compound (1b) (0.20 g, 0.44 mmol) with [AuCl(PPh<sub>3</sub>)] (0.22 g, 0.44 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) in the presence of TIBF<sub>4</sub> (0.13 g, 0.45 mmol) afforded a yellow mixture which was filtered through Celite (ca. 4 cm). Solvent was removed *in vacuo*, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (3 cm<sup>3</sup>, 1:2) and chromatographed. Elution with the same solvent mixture, followed by removal of solvent *in vacuo* from the eluate, gave yellow microcrystals of [RhAu(CO)<sub>2</sub>(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (5b), (5c) (0.31 g).

**Reactions between the Compound** [WAuCl(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] and the Salts [NEt<sub>4</sub>][Rh(CO)L(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R<sub>2</sub>)] (R = H, L = PPh<sub>3</sub>; R = Me, L = CO).—(i) A mixture of compound (6) (0.13 g, 0.20 mmol), the salt (1a) (0.13 g, 0.20 mmol), and TIBF<sub>4</sub> (0.07 g, 0.24 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) for 20 min. The suspension was then filtered through a Celite pad (ca. 1 cm), and the resulting solution was evaporated *in vacuo*. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (5 cm<sup>3</sup>, 2:3) and chromatographed. Elution with the same solvent mixture afforded an orange eluate. Removal of solvent *in vacuo* gave orange microcrystals of [WRhAu(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>3</sub>(PPh<sub>3</sub>)(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (7a) (0.23 g).

(ii) The compounds (6) (0.13 g, 0.20 mmol), (1b) (0.10 g, 0.22 mmol), and TIBF<sub>4</sub> (0.07 g, 0.24 mmol) were stirred together in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) for 30 min. The resulting suspension was filtered through a Celite pad (ca. 1 cm), and the solution evaporated to dryness *in vacuo*. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (6 cm<sup>3</sup>, 2:3) and chromatographed. Elution with the same solvent mixture gave an orange eluate, which upon removal of solvent *in vacuo* gave orange microcrystals shown by n.m.r. spectroscopy to be a ca. 2:3 mixture of [WRhAu(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (7b) and [WRh<sub>2</sub>Au<sub>2</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>6</sub>(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)<sub>2</sub>] (8). Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (6 cm<sup>3</sup>, 1:2) gave bright orange microcrystals of (8) (0.13 g).

If the reaction is carried out in thf over a period of 24 h, with a work up as described above, the same mixture is obtained. However, monitoring of the reaction by i.r. spectroscopy revealed the formation of [W(≡CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)], presumably by dissociation of (6).

**Table 5.** Atomic positional parameters (fractional co-ordinates,  $\times 10^4$ ) with estimated standard deviations in parentheses for complex (7a)

Atom	x	y	z	Atom	x	y	z
Au	-321(1)	3 479(1)	1 775(1)	C(11)	2 706(12)	3 765(11)	2 302(10)
W	2 117(1)	4 344(1)	1 220(1)	C(12)	3 177(12)	3 442(12)	625(10)
Rh	-2 423(1)	3 464(1)	2 631(1)	C(13)	-3 219(11)	2 665(10)	1 594(8)
P	-2 547(3)	1 754(2)	3 213(2)	C(14)	3 122(17)	5 806(13)	476(14)
O(11)	3 136(11)	3 498(12)	2 936(9)	C(15)	3 794(15)	5 995(13)	1 261(17)
O(12)	3 772(10)	2 947(10)	245(9)	C(16)	2 898(29)	6 198(13)	1 876(13)
O(13)	-3 788(10)	2 270(8)	942(6)	C(17)	1 677(18)	6 116(12)	1 358(17)
B(3)	-3 487(12)	4 823(11)	2 522(10)	C(18)	1 848(16)	5 898(12)	543(12)
B(4)	-1 747(12)	5 224(10)	2 224(9)	C(19)	-3 300(10)	1 771(9)	4 241(8)
B(5)	-740(12)	4 979(11)	3 151(10)	C(20)	-4 576(10)	1 976(10)	4 282(9)
B(6)	-953(14)	5 897(12)	4 052(10)	C(21)	-5 125(12)	2 035(11)	5 057(9)
B(7)	-2 639(16)	5 558(12)	4 307(10)	C(22)	-4 418(14)	1 902(13)	5 809(10)
B(8)	-3 650(14)	5 773(12)	3 409(11)	C(23)	-3 187(15)	1 716(14)	5 789(9)
B(9)	-2 585(13)	6 272(12)	2 588(10)	C(24)	-2 603(12)	1 677(11)	5 008(8)
B(10)	-913(14)	6 349(12)	3 023(10)	C(25)	-3 556(11)	531(9)	2 525(8)
B(11)	-2 073(14)	6 699(11)	3 714(10)	C(26)	-4 904(13)	87(12)	2 580(10)
C(1)	-1 862(11)	4 533(9)	3 894(8)	C(27)	-5 654(17)	-771(14)	1 952(13)
C(2)	-3 410(11)	4 501(10)	3 538(8)	C(28)	-5 062(20)	-1 160(13)	1 314(10)
C(3)	719(10)	3 113(10)	705(8)	C(29)	-3 703(21)	-785(13)	1 278(11)
C(4)	88(10)	2 191(9)	79(7)	C(30)	-2 956(17)	70(13)	1 893(10)
C(5)	-1 022(14)	1 360(12)	222(10)	C(31)	-1 027(10)	1 311(9)	3 516(7)
C(6)	-1 552(15)	447(13)	-382(11)	C(32)	151(11)	2 125(9)	3 707(8)
C(7)	-1 041(13)	341(12)	-1 162(9)	C(33)	1 320(11)	1 805(11)	4 015(8)
C(8)	10(13)	1 203(10)	-1 337(8)	C(34)	1 276(11)	746(11)	4 106(9)
C(9)	571(12)	2 111(11)	-729(9)	C(35)	99(12)	-95(11)	3 891(9)
C(10)	-1 631(16)	-650(13)	-1 810(10)	C(36)	-1 054(11)	181(9)	3 610(9)

**Synthesis of the Compounds** [WMAu( $\mu$ -CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>n</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (M = Mn,  $n = 7$ ; M = Co,  $n = 6$ ).—(i) A mixture of compound (6) (0.13 g, 0.20 mmol) and Na[Mn(CO)<sub>5</sub>] (0.05 g, 0.20 mmol) was stirred in thf (25 cm<sup>3</sup>) for 20 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (10 cm<sup>3</sup>, 2:3) and chromatographed. Elution with the same solvent mixture gave an orange-red solution. Removal of solvent *in vacuo* afforded orange microcrystals of [WMnAu( $\mu$ -CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (9a) (0.13 g).

(ii) The compounds (6) (0.13 g, 0.20 mmol), [N(PPh<sub>3</sub>)<sub>2</sub>][Co(CO)<sub>4</sub>] (0.14 g, 0.20 mmol), and TIBF<sub>4</sub> (0.07 g, 0.24 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (25 cm<sup>3</sup>) for 20 min. The resulting suspension was filtered through Celite (*ca.* 1 cm), after which solvent was removed *in vacuo*. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (5 cm<sup>3</sup>, 2:3) and chromatographed. Elution with the same solvent mixture, followed by removal of solvent *in vacuo* from an orange eluate, gave orange microcrystals of [WCoAu( $\mu$ -CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>6</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (9b) (0.13 g).

**Crystal Structure Determinations.**—(a) [WRhAu( $\mu$ -CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>3</sub>(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)( $\eta$ <sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (7a). Crystals of (7a) were grown as orange prisms by diffusion of light petroleum into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. Diffracted intensities were recorded ( $\theta$ —2 $\theta$  scans) at 298 K from a crystal of dimensions *ca.* 0.05  $\times$  0.40  $\times$  0.70 mm on a Nicolet P2<sub>1</sub> four-circle diffractometer. Of the 6 815 unique data ( $4 \leq 2\theta \leq 50^\circ$ ), 5 845 had  $F \geq 6\sigma(F)$ , and only these were used in the solution and refinement of the structure, after correction for Lorentz, polarisation, and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.<sup>18</sup>

**Crystal data.** C<sub>36</sub>H<sub>38</sub>AuB<sub>9</sub>O<sub>3</sub>PRhW,  $M = 1 130.7$ , triclinic,  $a = 10.395(2)$ ,  $b = 12.355(2)$ ,  $c = 15.556(2)$  Å,  $\alpha = 94.42(1)$ ,  $\beta = 94.32(1)$ ,  $\gamma = 104.13(1)^\circ$ ,  $U = 1 922.4(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.95$  g cm<sup>-3</sup>,  $F(000) = 1 072$ , space group  $P\bar{1}$  (no. 2), Mo-K $\alpha$  X-radiation (graphite monochromator),  $\lambda = 0.710 69$  Å,  $\mu(\text{Mo-K}\alpha) = 73.4$  cm<sup>-1</sup>.

The molecular structure of compound (7a) was solved, and all non-hydrogen atoms located, by conventional heavy-atom and difference-Fourier syntheses. Hydrogen atoms were included at calculated positions (B-H 1.10 and C-H 0.96 Å)<sup>19</sup> with fixed isotropic thermal parameters (*ca.* 1.2  $U_{\text{equiv}}$  of the parent boron or carbon atom). All other atoms were given anisotropic thermal parameters. Initially all cage atoms were treated as being boron atoms until sufficient data became available to allow a distinction to be made between C and B atoms on the basis of thermal parameters and bond lengths. In general C-C linkages are *ca.* 1.65 Å or less, and B-B separations *ca.* 1.70 Å or more. Refinement by blocked-cascade least squares led to  $R = 0.070$  ( $R' = 0.066$ ), and a weighting scheme of the form  $w^{-1} = [\sigma^2(F) + 0.000 5|F|^2]$  gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks  $\geq 3.7$  or  $\leq -5.3$  e Å<sup>-3</sup>, the largest lying close to the metal atoms.

(b) [WRh<sub>2</sub>Au<sub>2</sub>( $\mu_3$ -CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>6</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)( $\eta$ <sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)<sub>2</sub>].0.5CH<sub>2</sub>Cl<sub>2</sub> (8). Crystals of compound (8) were grown as orange plates from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum. The complex crystallised with two chemically identical molecules and a molecule of CH<sub>2</sub>Cl<sub>2</sub> per asymmetric unit. A crystal of suitable dimensions (*ca.* 0.80  $\times$  0.80  $\times$  0.10 mm) was sealed under nitrogen in a Lindemann tube. Data collection was as for (7a). Of 16 027 unique reflections, 10 748 had  $F \geq 4\sigma(F)$ , and only these were used in the solution and refinement of the structure, after corrections for Lorentz, polarisation, and X-ray absorption effects.<sup>18</sup>

**Crystal data.** C<sub>27</sub>H<sub>42</sub>Au<sub>2</sub>B<sub>18</sub>O<sub>6</sub>Rh<sub>2</sub>W.0.5CH<sub>2</sub>Cl<sub>2</sub>,  $M = 1 483.3$ , triclinic,  $a = 13.528(3)$ ,  $b = 13.650(4)$ ,  $c = 26.08(2)$  Å,  $\alpha = 75.83(4)$ ,  $\beta = 82.62(4)$ ,  $\gamma = 77.48(2)^\circ$ ,  $U = 4 543(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.17$  g cm<sup>-3</sup>,  $F(000) = 2 740$ , space group  $P\bar{1}$  (no. 2),  $\mu(\text{Mo-K}\alpha) = 98.0$  cm<sup>-1</sup>.

The molecular structure of compound (8) was solved by direct methods. Only the metal atoms were initially located, the light atoms being subsequently located from successive Fourier difference syntheses. Refinement by blocked-cascade least

**Table 6.** Atomic positional parameters (fractional co-ordinates,  $\times 10^4$ ) with estimated standard deviations in parentheses for complex (8)

Atom	x	y	z	Atom	x	y	z
Au(1)	6 439(1)	2 327(1)	5 084(1)	Au(3)	2 312(1)	2 236(1)	973(1)
Au(2)	7 873(1)	2 860(1)	4 144(1)	Au(4)	1 306(1)	2 340(1)	12(1)
W(1)	5 811(1)	3 211(1)	4 082(1)	W(2)	232(1)	2 573(1)	964(1)
Rh(1)	7 304(1)	971(1)	5 929(1)	Rh(3)	3 272(1)	3 716(1)	1 087(1)
Rh(2)	8 907(1)	4 432(1)	3 920(1)	Rh(4)	2 637(1)	1 483(1)	-710(1)
O(5)	6 457(13)	-676(12)	5 620(9)	O(32)	1 348(12)	4 635(13)	1 659(8)
O(6)	9 388(14)	594(17)	5 329(10)	O(33)	2 638(14)	4 984(15)	15(8)
O(15)	5 809(12)	5 208(10)	4 496(7)	O(42)	-1 291(12)	2 799(14)	113(8)
O(16)	3 895(14)	2 836(16)	4 873(9)	O(43)	491(11)	4 872(10)	512(7)
O(26)	7 219(13)	5 825(15)	3 304(9)	O(53)	3 967(13)	409(15)	190(8)
O(27)	7 813(14)	4 980(15)	4 938(9)	O(54)	1 788(15)	-440(14)	-598(9)
B(3)	5 852(19)	1 443(19)	6 413(14)	B(21)	4 704(17)	2 948(18)	716(11)
B(4)	6 355(18)	2 513(17)	5 962(10)	B(22)	4 043(18)	2 028(18)	1 160(11)
B(5)	7 672(31)	2 355(23)	6 100(13)	B(23)	3 751(20)	2 480(17)	1 793(12)
B(6)	6 595(22)	3 384(21)	6 318(14)	B(24)	4 766(18)	1 421(20)	1 676(13)
B(7)	7 539(27)	2 576(25)	6 770(14)	B(25)	5 045(22)	2 271(24)	2 018(13)
B(8)	7 123(25)	1 561(22)	7 232(14)	B(26)	5 779(18)	3 112(21)	1 583(13)
B(9)	5 839(22)	1 621(23)	7 066(13)	B(27)	5 926(19)	2 809(18)	960(12)
B(10)	5 478(20)	2 726(22)	6 526(14)	B(28)	5 393(18)	1 643(20)	1 030(13)
B(11)	6 189(24)	2 823(20)	7 014(13)	B(29)	5 993(18)	1 832(23)	1 555(12)
B(12)	9 677(22)	3 508(21)	3 320(14)	B(30)	3 116(20)	3 037(18)	-855(11)
B(13)	9 663(21)	2 772(17)	4 001(14)	B(31)	1 675(15)	3 156(17)	-854(12)
B(14)	10 188(19)	3 457(17)	4 356(12)	B(32)	1 609(17)	2 380(17)	-1 328(11)
B(15)	10 953(17)	2 334(17)	4 135(17)	B(33)	1 336(23)	3 793(23)	-1 506(14)
B(16)	11 534(18)	3 415(21)	4 095(13)	B(34)	2 025(22)	3 069(18)	-1 975(12)
B(17)	11 590(20)	4 107(21)	3 444(14)	B(35)	3 317(19)	3 039(21)	-1 996(11)
B(18)	11 008(18)	3 503(18)	3 055(13)	B(36)	3 480(27)	3 724(23)	-1 517(12)
B(19)	10 594(21)	2 392(23)	3 516(13)	B(37)	2 352(23)	4 144(18)	-1 198(11)
B(20)	11 755(22)	2 796(22)	3 598(14)	B(38)	2 449(22)	4 185(20)	-1 891(13)
C(1)	7 835(17)	1 337(18)	6 658(11)	C(28)	4 466(14)	3 494(15)	1 680(9)
C(2)	6 845(17)	809(17)	6 845(11)	C(29)	4 925(15)	3 786(15)	1 093(9)
C(3)	8 922(20)	700(20)	6 748(12)	C(30)	4 131(18)	4 337(19)	2 001(11)
C(4)	6 912(19)	-316(19)	7 109(11)	C(31)	5 122(16)	4 887(16)	819(10)
C(5)	6 823(17)	-57(17)	5 742(10)	C(32)	2 073(18)	4 314(17)	1 443(11)
C(6)	8 567(16)	707(16)	5 549(10)	C(33)	2 857(15)	4 541(16)	404(10)
C(7)	6 770(15)	1 908(15)	4 399(9)	C(34)	1 321(15)	1 424(16)	756(10)
C(8)	7 091(15)	796(15)	4 339(9)	C(35)	1 498(14)	274(14)	865(9)
C(9)	6 315(16)	271(16)	4 290(10)	C(36)	2 284(17)	-350(17)	1 166(10)
C(10)	6 476(18)	-722(18)	4 283(11)	C(37)	2 308(18)	-1 417(19)	1 294(11)
C(11)	7 537(19)	-1 274(19)	4 245(12)	C(38)	1 696(17)	-1 835(17)	1 073(11)
C(12)	8 308(17)	-799(18)	4 308(11)	C(39)	1 025(18)	-1 240(19)	740(11)
C(13)	8 063(16)	277(16)	4 349(10)	C(40)	844(15)	-151(15)	664(10)
C(14)	7 756(23)	-2 351(23)	4 175(14)	C(41)	1 829(25)	-3 070(26)	1 218(15)
C(15)	5 791(16)	4 472(16)	4 354(10)	C(42)	-731(16)	2 773(16)	394(10)
C(16)	4 629(20)	2 954(19)	4 589(12)	C(43)	389(14)	4 049(14)	666(9)
C(17)	5 897(19)	2 620(19)	3 302(11)	C(44)	-945(17)	1 757(17)	1 494(11)
C(18)	4 901(21)	2 781(21)	3 521(13)	C(45)	-1 254(20)	2 842(20)	1 493(12)
C(19)	4 563(20)	3 958(21)	3 499(13)	C(46)	-503(20)	3 127(21)	1 762(12)
C(20)	5 439(19)	4 396(19)	3 270(12)	C(47)	268(18)	2 215(18)	1 907(11)
C(21)	6 270(18)	3 529(19)	3 160(11)	C(48)	-29(18)	1 424(18)	1 763(11)
C(22)	10 618(14)	4 510(15)	3 888(9)	C(49)	2 859(15)	1 996(15)	-1 637(9)
C(23)	10 269(15)	4 575(15)	3 314(9)	C(50)	3 685(15)	2 373(15)	-1 367(9)
C(24)	10 768(19)	5 439(20)	4 054(12)	C(51)	3 112(19)	1 065(19)	-1 861(12)
C(25)	10 068(19)	5 552(19)	2 902(12)	C(52)	4 752(18)	1 682(18)	-1 327(11)
C(26)	7 876(18)	5 328(17)	3 517(10)	C(53)	3 478(19)	826(19)	-148(12)
C(27)	8 244(18)	4 793(18)	4 548(11)	C(54)	2 113(16)	287(17)	-631(10)
Cl(1)	8 752(10)	-694(11)	2 696(6)				
Cl(2)	8 480(10)	1 304(11)	2 938(5)				
C(55)	7 786(34)	406(25)	2 840(18)				

squares, with anisotropic thermal parameters for all non-hydrogen atoms, including the carbon atom of the  $\text{CH}_2\text{Cl}_2$  molecule but not the other carbon atoms, led to  $R = 0.070$  ( $R' = 0.062$ ). A weighting scheme of the form  $w^{-1} = [\sigma^2(F) + 0.0005|F|^2]$  gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks  $\geq 2.0$  or  $\leq -2.8 \text{ e } \text{\AA}^{-3}$ . The hydrogen atoms of the B-H→Au linkages were included at calculated positions<sup>11</sup> with fixed isotropic

thermal parameters (*ca.*  $1.2 U_{\text{equiv}}$  of the parent boron atom), all other hydrogen atoms being omitted.

For compounds (7a) and (8) calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.<sup>18</sup> Scattering factors with corrections for anomalous dispersion were taken from ref. 20. Atomic co-ordinates for (7a) and (8) are listed in Tables 5 and 6 respectively.



Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

### Acknowledgements

We thank the USAF Office of Scientific Research (Grant 86-0125) for support, the Turkish Government and the University of Ege for a Scholarship (to I. T.), the Spanish Consejo Superior de Investigaciones Científicas for a Fellowship (to M. C. G.), and Dr. I. J. Hart for the initial synthesis of compound (**1b**).

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Received 20th December 1989; Paper 9/05479K