Polyhedron Vol. 11, No. 22, pp. 2841–2848, 1992
Printed in Great Britain

0277–5387/92 $5.00+.00

(CARBORANE)RHODIUM–GOLD COMPLEXES

JUSTIN E. GOLDBERG and F. GORDON A. STONE*

Department of Chemistry, Baylor University, Waco, TX 76798-7348, U.S.A.

(*Received* 17 *July* 1992; *accepted* 3 *August* 1992)

Abstract—Treatment of the reagent $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})]$ in CH_2Cl_2, in the presence of $TlBF_4$, with half an equivalent of the digold compounds $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ ($n = 2$–6) affords the complexes $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$. The compounds $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (n = 3 or 6) have similarly been prepared. Reactions between the digold complexes $[Au_2Cl_2(\mu\text{-}Z$ or $E\text{-}Ph_2PCH{=}CHPPh_2)]$ and the salts $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}7,n\text{-}C_2B_9H_{11})]$ (n = 8 or 9) give the four isomeric dirhodium–digold complexes $[Rh_2Au_2(\mu\text{-}Z$ or $E\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,n\text{-}C_2B_9H_{11})_2]$. The NMR data for the new compounds are reported and discussed in terms of the formulations proposed.

In studies on compounds having bonds between dissimilar metal atoms, we have employed the salts $[NEt_4][Rh(CO)(L)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (**1a**, L = PPh_3, R = H; **1b**, L = CO, R = Me; **1c**, L = PPh_3, R = Me) to prepare complexes in which rhodium is bonded to rhenium,[1a] cobalt,[1b] iridium,[1b] platinum[1c,d] and gold.[1e,f] This approach to compounds with heteronuclear metal–metal bonds was prompted by the recognition that the anion of the salt **1a** is isolobally mapped[2] with $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$, and that the latter has been employed as a useful synthon for preparing mixed-metal compounds for some 30 years.[3] The reagent **1d** is an isomer of **1a**,[4] having an $\eta^5\text{-}7,9\text{-}C_2B_9H_{11}$ ligand instead of the $\eta^5\text{-}7,8\text{-}C_2B_9H_{11}$ group present in the former species.† We have recently studied reactions between **1d** and the platinum compounds $[PtCl(R)(L)_2]$ (R = H, Me or Ph; L = PEt_3, PMe_2Ph or PPh_3) and have thereby obtained a variety of Rh—Pt complexes.[1d] In this paper we extend our work with **1d** describing a series of new Rh—Au compounds. Earlier work with the reagents **1a**–**1c** afforded several Rh—Au complexes, including the compounds **2**–**4**.[1e,f]

RESULTS AND DISCUSSION

The reaction between $[AuCl(PPh_3)]$ and **1d** in THF, in the presence of $TlBF_4$ to remove chloride as insoluble TlCl, afforded the complex $[RhAu(CO)(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})]$ (**2d**), characterized by the data given in Tables 1 and 2. Compound **2d** (Fig. 1) is an isomer of **2a**.[1e] Both species show a single, very strong band in their IR spectra for the CO ligand (**2a**, 1998; **2d**, 1993 cm^{-1}), and the $^{31}P\{^1H\}$ NMR spectra reveal two resonances for the PRh and PAu groups. Those for **2d** occur at δ 36.4 [PRh, J(RhP) 132 Hz] and 33.2 (PAu). The corresponding data for **2a** are δ 35.9 [PRh, J(RhP) 123 Hz] and δ 35.3 [PAu, J(RhP) 12 Hz], which are clearly very similar.

The $^{13}C\{^1H\}$ NMR spectrum of **2d** was informative with signals for the CO group at δ 192.5 [J(RhC) 73, J(PC) 14 and 8 Hz], and for the cage-carbon nuclei at δ 51.9 and 49.1. The observance of two $CH(C_2B_9H_{11})$ peaks is consistent both with the ^1H NMR data (δ 1.96 and 2.19) and with the data for **2a** (δ 44.3 and 44.0 in the $^{13}C\{^1H\}$, and δ 1.91 and 2.52 in the ^1H NMR spectrum), and is as expected given the asymmetry of the rhodium centre. Whether the carborane ligand is rotating about an axis through the rhodium atom and the centroid of the open pentagonal face, or whether

---

* Author to whom correspondence should be addressed.

† In the salt **1a** a rhodium atom forms, with a $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ dianion, a *closo*-1,2-dicarba-3-rhodadodecaborane structure. Similarly, in **1d** a $[nido\text{-}7,9\text{-}C_2B_9H_{11}]^{2-}$ dianion forms a *closo*-1,7-dicarba-2-rhodacarborane icosahedral framework. However, in the formulae in this paper the carborane groups are designated as $\eta^5\text{-}7,n\text{-}C_2B_9H_{11}$ (n = 8 or 9) in order to emphasize their pentahapto ligand properties, in which they formally act as four-electron donors.

Table 1. Analytical[a] and physical data for the rhodium–gold complexes

Compound	Colour	Yield (%)	$\nu_{max}(CO)^b$ (cm^{-1})	Analysis (%) C	H
2d $[RhAu(CO)(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11}]$	Yellow	90	1993 vs	47.3 (47.6)	4.2 (4.2)
3c $[WRhAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$	Orange	56	2016 vs, 1993 m (sh), 1954 s	38.1 (38.2)	3.4 (3.4)
5a $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$	Cream	65	1993 vs	43.8 (44.3)	4.5 (4.2)
5b $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$	Cream	64	1989 vs	44.3 (44.6)	4.4 (4.2)
5c $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$	Yellow	78	2002 vs	45.0 (44.6)	4.8 (4.2)
5d $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$	Cream	67	1992 vs	45.3 (44.9)	4.7 (4.3)
5e $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$	Beige	61	1990 vs	45.9 (45.2)	4.6 (4.4)
5f $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$	Cream	58	1993 vs	46.3 (45.5)	4.7 (4.5)
5g $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$	Yellow	76	2000 vs	45.8 (45.5)	4.6 (4.5)
6a $[Rh_2Au_2(\mu\text{-}E\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$	Beige	32	1992 vs	44.4 (44.4)	4.3 (4.1)
6b $[Rh_2Au_2(\mu\text{-}Z\text{-}Ph_2PCH{=}CHPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$	Beige	54	1987 vs	45.1 (44.4)	4.3 (4.1)
6c $[Rh_2Au(\mu\text{-}E\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]^c$	Beige		2002 vs		
6d $[Rh_2Au_2(\mu\text{-}Z\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$	Orange	71	1999 vs	44.1 (44.4)	4.3 (4.1)

[a] Calculated values are given in parentheses.

[b] Measured in CH_2Cl_2. All spectra show a broad band in the range 2500–2550 cm^{-1} due to ν(BH).

[c] Satisfactory microanalytical data not available.

Table 2. ^1H, ^{13}C and ^{31}P NMR data[a] for the rhodium–gold complexes

Compound	$^1H^b$ (δ)	$^{13}C^c$ (δ)	$^{31}P^d$ (δ)
2d	1.96, 2.19 [s × 2, 2H, $CH(C_2B_9H_{11})$], 7.22–7.60 (m, 30H, Ph)	192.5 [d of d of d, CO, J(RhC) = 73, J(PC) = 14 and 8], 135.0–128.0 (Ph), 51.9, 49.1 ($C_2B_9H_{11}$)	36.4 [d, br, PRh, J(RhP) = 132], 33.2 (s, br, PAu)
3c	1.68, 2.18 [s × 2, 2H, $CH(C_2B_9H_{11})$], 2.30 (s, 3H, Me-4), 5.59 (s, 5H, C_5H_5), 7.01, 7.21 [(AB)$_2$, 4H, C_6H_4, J(AB) = 8], 7.30–7.60 (m, 15H, Ph)	283.4 [μ-C, J(WC) = 152], 213.6 [WCO, J(WC) = 180], 193.3 [d of d, RhCO, J(RhC) = 74, J(PC) = 14], 148.7 [$C^1(C_6H_4)$, J(WC) = 31], 141.9–128.6 (Ph and C_6H_4), 92.6 (C_5H_5), 50.0 ($C_2B_9H_{11}$), 21.9 (Me-4)	37.1 [d, PRh, J(RhP) = 132]
5a	2.05 [s, 4H, $CH(C_2B_9H_{11})$], 2.45 (m, br, 4H, CH_2), 7.19–7.56 (m, 50H, Ph)	[e] 135.0–127.0 (Ph), 51.5, 48.7 ($C_2B_9H_{11}$), 24.5 [(AXX′), CH_2, |J(AX) + J(AX′)| = 36]	36.2 [d of d, vbr, PRh, J(RhP) = 132 and 30], 32.6 (s, br, PAu)
5b	1.75 (m, 2H, β-CH_2), 1.99, 2.09 [s × 2, 4H, $CH(C_2B_9H_{11})$], 2.52 (m, 4H, α-CH_2), 7.22–7.61 (m, 50H, Ph)	192.6 [d of d of d, CO, J(RhC) = 75, J(PC) = 14 and 7], 135.0–128.7 (Ph), 52.0, 48.9 ($C_2B_9H_{11}$), 29.1 [(AXX′), α-CH_2, |J(AX) + J(AX′)| = 45], 20.8 [t, β-CH_2, J(PC) = 5]	36.0 [d, PRh, J(RhP) = 132], 28.2 (s, PAu)

5c	1.91 (m, 2H, β-CH$_2$), 1.98, 2.54 [s × 2, 4H, CH(C$_2$B$_9$H$_{11}$)], 2.64 (m, 4H, α-CH$_2$), 7.22–7.53 (m, 50H, Ph)	191.6 [d of d, CO, J(RhC) = 72, J(PC) = 18], 134.4–128.9 (Ph), 44.5, 43.9 (C$_2$B$_9$H$_{11}$), 29.2 [(AXX′), α-CH$_2$, $\lvert J$(AX)+J(AX′)$\rvert$ = 42], 21.1 [t, β-CH$_2$, J(PC) = 5]	36.5 [d, br, PRh, J(RhP) = 124], 31.3 [d, PAu, J(RhP) = 11]
5d	1.53 (m, 4H, β-CH$_2$), 1.98 [s, 2H, CH(C$_2$B$_9$H$_{11}$)], 2.15 (m, 4H, α-CH$_2$), 2.20 [s, 2H, CH(C$_2$B$_9$H$_{11}$)], 7.24–7.58 (m, 50H, Ph)	192.7 [d of d of d, CO, J(RhC) = 74, J(PC) = 14 and 8], 135.2–128.7 (Ph), 51.9, 49.2 (C$_2$B$_9$H$_{11}$), 28.4 [d, α-CH$_2$, J(PC) = 33], 27.3 [(AXX′), β-CH$_2$, $\lvert J$(AX+J(AX′)$\rvert$ = 23]	36.4 [d, br, PRh, J(RhP) = 132], 30.7 (s, br, PAu)
5e	1.40 (m, 4H, β-CH$_2$), 1.54 (m, 2H, γ-CH$_2$), 1.95 [s, 2H, CH(C$_2$B$_9$H$_{11}$)], 2.19 [m, 6H, α-CH$_2$ and CH(C$_2$B$_9$H$_{11}$)], 7.24–7.58 (m, 50H, Ph)	192.8 [d of d of d, CO, J(RhC) = 74, J(PC) = 14 and 8], 135.1–128.7 (Ph), 51.9, 49.1 (C$_2$B$_9$H$_{11}$), 31.8 [t, γ-CH$_2$, J(PC) = 15], 28.2 [d, α-CH$_2$, J(PC) = 33], 25.3 [d, β-CH$_2$, J(PC) = 5]	36.1 [d, br, PRh, J(RhP) = 132], 30.0 (s, br, PAu)
5f	1.31 (m, br, 4H, γ-CH$_2$), 1.41 (m, br, 4H, β-CH$_2$), 1.97 [s, 2H, CH(C$_2$B$_9$H$_{11}$)], 2.21 [m, br, 6H, α-CH$_2$ and CH(C$_2$B$_9$H$_{11}$)], 7.24–7.61 (m, 50H, Ph)	192.8 [d of d of d, CO, J(RhC) = 74, J(PC) = 14 and 8], 135.2–128.7 (Ph), 51.9, 49.2 (C$_2$B$_9$H$_{11}$), 30.6 [d, γ-CH$_2$, J(PC) = 15], 28.5 [d, α-CH$_2$, J(PC) = 32], 25.9 [d, β-CH$_2$, J(PC) = 5]	36.3 [d, br, PRh, J(RhP) = 132], 30.6 (s, br, PAu)
5g	1.34 (m, br, 4H, γ-CH$_2$), 1.51 (m, br, 4H, β-CH$_2$), 1.92 [s, 2H, CH(C$_2$B$_9$H$_{11}$)], 2.29 (m, br, 4H, α-CH$_2$), 2.52 [s, 2H, CH(C$_2$B$_9$H$_{11}$)], 7.28–7.60 (m, 50H, Ph)	191.7 [d of d, CO, J(RhC) = 72, J(PC) = 18], 134.6–128.9 (Ph), 44.3, 43.8 (C$_2$B$_9$H$_{11}$), 30.5 [d, γ-CH$_2$, J(PC) = 15], 28.8 [d, α-CH$_2$, J(PC) = 33], 25.9 [d, β-CH$_2$, J(PC) = 5]	36.6 [d, br, PRh, J(RhP) = 122], 33.4 [d, PAu, J(RhP) = 11]
6a	1.97, 2.10 [s × 2, 4H, CH(C$_2$B$_9$H$_{11}$)], 7.19–7.59 (m, 52H, Ph and CH═CH)	192.4 [d of d of d, CO, J(RhC) = 74, J(PC) = 14 and 8], 142.4 [(AXX′), CH═CH, $\lvert J$(AX)+J(AX′)$\rvert$ = 52], 135.2–128.7 (Ph), 51.8, 49.1 (C$_2$B$_9$H$_{11}$)	36.2 [d, br, PRh, J(RhP) = 132], 29.5 (s, br, PAu)
6b	1.86, 2.29 [s × 2, 4H, CH(C$_2$B$_9$H$_{11}$)], 6.76 [(AA′XX′), 2H, CH═CH, J(AX) = 39, J(AX′) = 17, J(AA′) = 3, J(XX′) = 17], 7.16–7.55 (m, 50H, Ph)	193.3 [d of d, CO, J(RhC) = 72, J(PC) = 15], 135.8 [(AXX′), CH═CH, $\lvert J$(AX)+J(AX′)$\rvert$ = 47], 134.9–128.6 (Ph), 52.4, 48.3 (C$_2$B$_9$H$_{11}$)	35.7 [d, PRh, J(RhP) = 130], 23.1 [d, PAu, J(RhP) = 15]
6c	1.97, 2.62 [s × 2, 4H, CH(C$_2$B$_9$H$_{11}$)], 7.22–7.57 (m, 52H, Ph and CH═CH)	191.3 [d of d, CO, J(RhC) = 72, J(PC) = 18], 143.0 [(AXX′), CH═CH, $\lvert J$(AX)+J(AX′)$\rvert$ = 56], 136.0–128.0 (Ph), 44.8, 44.1 (C$_2$B$_9$H$_{11}$)	36.7 [d, br, PRh. J(RhP) = 123], 32.7 (s, PAu)
6d	1.89, 2.69 [s × 2, 4H, CH(C$_2$B$_9$H$_{11}$)], 6.74 [(AA′XX′), 2H, CH═CH, J(AX) = 36, J(AX′) = 16, J(AA′) = 8, J(XX′) = 16], 7.24–7.56 (m, 50H, Ph)	192.0 [d of d, CO, J(RhC) = 72, J(PC) = 18], 135.4 [(AXX′), CH═CH, $\lvert J$(AX)+J(AX′)$\rvert$ = 56], 135.1–128.9 (Ph), 45.2, 44.3 (C$_2$B$_9$H$_{11}$)	36.5 [d, PRh, J(RhP) = 122], 26.8 (s, br, PAu)

---

[a] Chemical shifts δ in ppm, coupling constants in Hz, measurements at ambient temperatures in CD$_2$Cl$_2$.

[b] Resonances for B—H protons occur as unresolved broad weak signals in the range δ 0–3.

[c] Hydrogen-1 decoupled, chemical shifts are positive to the high frequency of SiMe$_4$.

[d] Hydrogen-1 decoupled, chemical shifts are positive to the high frequency of 85% H$_3$PO$_4$ (external).

[e] Resonance for CO ligands not observed due to weak spectrum and multiplicity of signal.

it is rigid on the NMR time-scale, will make no difference to the asymmetry of the CH vertices with respect to the $Rh(CO)(PPh_3)Au$ fragment. This is because there is no position the cage may adopt which will allow a plane of mirror symmetry to be drawn through the molecule, so as to make the CH vertices equivalent. They must always be inequivalent, although their signals may sometimes be accidentally coincident. What is noteworthy is that in the $^{13}C\{^{1}H\}$ NMR spectrum of **2a** the signal at δ 44.3 appears as a doublet [J(XC) 5 Hz], presumably due either to ^{103}Rh or ^{31}PRh coupling. However, both CH signals for **2d** are singlets. This slight difference possibly arises from the fact that the 7,9 cage is known to adopt a slightly distorted geometry, with one of the boron atoms in the pentagonal coordinating face lying out of the plane of the remaining four atoms.[1d,4] This slight distortion, relative to the geometry of the 7,8 cage where no similar distortion has been observed, may be sufficient to remove the slight coupling.

What is more unexpected, and thus even more noteworthy, is the fact that in **2d** the signal for the CO group is a doublet-of-doublet-of-doublets, whereas in **2a** it is the more expected doublet-of-doublets. This is a feature which is observed again later in relation to the compounds **5**; the 7,9 species always shows an extra ^{31}PAu coupling to the CO group. We propose that this extra observable coupling is due to a very subtle shift in the position of the CO ligand, making it more *transoid* to the Au—P vector, and thus increasing the magnitude of the ^{31}PAu coupling to the point where it becomes resolved and hence observable. Indeed, it seems reasonable to assume that this subtle repositioning of the CO group is a further consequence of the slightly distorted 7,9 cage. Furthermore, that distortion, resulting in a slight shifting of the ligands relative to one another, may also account for the fact that the signal for the PAu group in **2a** is a doublet, due to ^{103}Rh coupling, whereas in **2d** the comparable PAu signal is a broad singlet. This difference between the 7,8 and 7,9 systems will again become apparent when we discuss compounds **5**, where the same subtle variations are observed.

In view of the earlier synthesis of the trimetal complex **3a**,[1e] from the reaction between **1a** and $[WAuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, in the presence of $TlBF_4$, the corresponding reaction between **1d** and the tungsten–gold species was investigated. In this manner the complex $[WRhAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ (**3c**) was prepared (Fig. 1). The latter was fully characterized by the data given in Tables 1 and 2, and, as expected, these data are very similar to those of its isomer **3a** containing the $\eta^5\text{-}7,8\text{-}C_2B_9H_{11}$ ligand.

The synthesis of **3c** from $[WAuCl(\mu\text{-}CC_6H_4Me\text{-}4)$

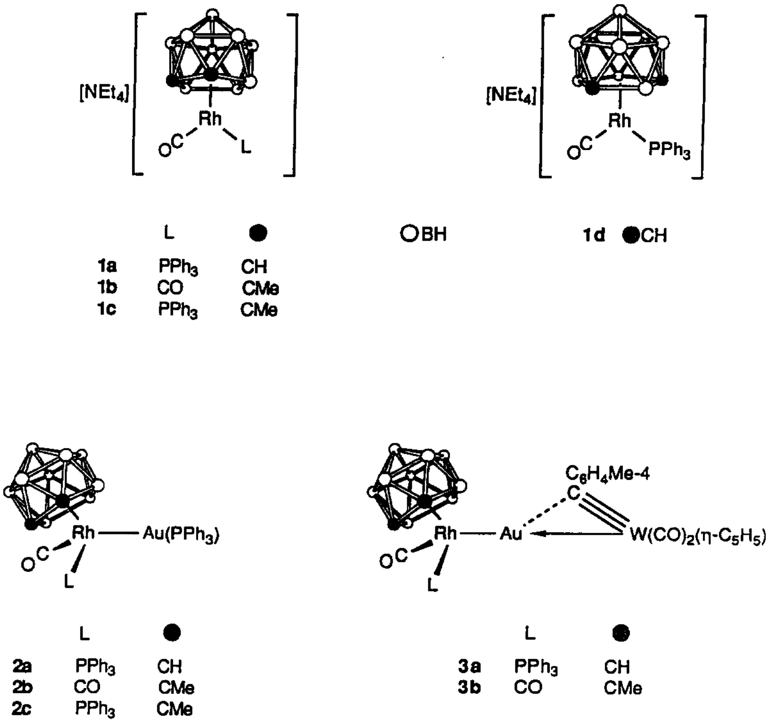


Fig. 1.

$(CO)_2(\eta\text{-}C_5H_5)]$ and **1d** also afforded small quantities of **2d** and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$. These two by-products evidently form via the decomposition of **3c** since solutions of the latter were observed to decompose slowly to give the same two species. The isomeric compound **3a** is more stable, and its structure was confirmed by X-ray diffraction.[1e]

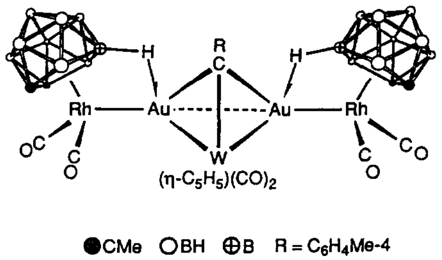
We have recently employed the digold compounds $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ ($n = 2$–6) and $[Au_2Cl_2\{\mu\text{-}Z$ or $E\text{-}Ph_2PCH{=}CHPPh_2\}]$ as precursors for the synthesis of ditungsten–digold complexes, in which two $RC\equiv W(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9Me_2)$ ($R = C_6H_4Me\text{-}4$) groups are bridged by $AuP(Ph)_2(CH_2)_n(Ph)_2PAu$ or $AuP(Ph)_2CH{=}CH(Ph)_2PAu$ units.[5] It was of interest, therefore, to determine if reactions between **1d** and the same digold compounds would afford complexes of the types $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$ and $[Rh_2Au_2(\mu\text{-}Z$ or $E\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$, in which two $Rh(CO)(PPh_3)(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})$ fragments are similarly held together by the $AuP(Ph)_2(CH_2)_n(Ph)_2PAu$ or $AuP(Ph)_2CH{=}CH(Ph)_2PAu$ moieties.

Treatment of a CH_2Cl_2 solution of **1d** with half an equivalent of the chlorogold complexes $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$, in the presence of excess $TlBF_4$, afforded the compounds $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$ [$n = 2$ (**5a**), 3 (**5b**), 4 (**5d**), 5 (**5e**) and 6 (**5f**)]. In similar syntheses, employing the reagent **1a**, the complexes $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ [$n = 3$ (**5c**) and 6 (**5g**)] were obtained. The pairs of compounds **5b** and **5c**, and **5f** and **5g**, are isomers, differing only in the disposition of the CH vertices in the *nido*-η^5-$C_2B_9H_{11}$ ligands. Data characterizing all the compounds **5** are summarized in Tables 1 and 2, and are in agreement with the formulations shown for **5a**, **5b** and **5d**–**5f** (Fig. 2). Structural formulae for **5c** and **5g** are not displayed because of their close similarities with those of **5b** and **5f**, respectively.

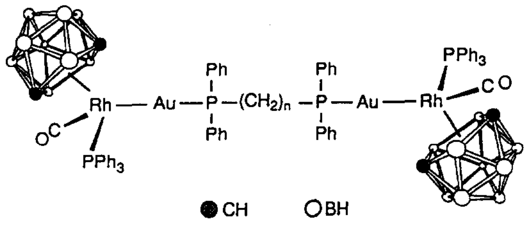
All the species **5** show a single CO stretching band in their IR spectra in the range 1989–2002 cm^{-1}. The NMR data (Table 2) were informative in supporting the structures proposed. The $^{31}P\{^1H\}$ NMR spectra of the complexes showed two resonances for the PRh and PAu groups, respectively. The latter signals were generally broad singlets, in the range δ 28.2–33.4. However, the spectra of **5c** and **5g** were sufficiently resolved for the PAu resonances to appear as doublets, due to weak $^{103}RhAu^{31}P$ coupling (11 Hz); the change from the 7,9- to the 7,8-cage seeming to make the difference, as was discussed earlier. The PRh resonances of **5b**–**5f** occur as broad doublets [$J(RhP)$ 122–132] at *ca* δ 36.5. That of **5a**, however, was a doublet-of-doublets with couplings of 132 and 30 Hz, respectively. We ascribe the former to the anticipated $^{103}Rh{-}^{31}PPh_3$ single bond coupling. Since the PAu resonance is a singlet the 30 Hz value cannot be the result of a three-bond $^{31}PPh_3RhAu^{31}PPh_2$ coupling, and must also be due to a $^{103}Rh{-}^{31}PPh_3$ interaction. The observation of this second, but weak, $^{103}Rh{-}^{31}P$ coupling may be caused by a spatial $^{103}Rh{-}{-}{-}Rh^{31}P$ effect, arising through a folding of the relatively short $P(CH_2)_2$ chain so as to bring the $Rh(CO)(PPh_3)(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})$ groups into proximity with one another. Unfortunately, it was not possible to grow crystals of **5a** for an X-ray diffraction study.

With the exception of **5a**, the $^{13}C\{^1H\}$ NMR spectra of all the complexes showed a single resonance for the CO ligand. The absence of the expected signal in the spectrum of **5a** is attributed to measurements being made on a weak solution, resulting from the relative insolubility of the compound, together with the anticipated multiplicity of the resonance, thereby leading to the peaks being lost in the noise. For the other compounds, the CO resonances are seen at *ca* δ 192, appearing either as a doublet-of-doublets [$J(RhC)$ *ca* 75, $J(PC)$ *ca* 14 and 8 Hz] for the complexes containing the 7,9-carborane ligand, or as a doublet-of-doublets [$J(RhC)$ *ca* 72, $J(PC)$ *ca* 18 Hz] for the 7,8 analogues. As was mentioned earlier for **2a** vs **2d**, this difference is attributed to the distortions of the η^5-7,9-$C_2B_9H_{11}$ ligand being sufficient to force the CO group more *transoid* relative to the PAu moiety, thus increasing the $^{31}PAuRh^{13}CO$ coupling. All the complexes **5** show the expected two diagnostic peaks for the non-equivalent carborane cage CH nuclei. Interestingly, the signals for the species **5c** (δ 44.5 and 43.9) and **5g** (δ 44.3 and 43.8), which contain η^5-7,8-$C_2B_9H_{11}$ groups, are less widely separated than those (δ *ca* 52 and 49) for the molecules **5** which have η^5-7,9-$C_2B_9H_{11}$ ligands. The assignments for the CH_2 groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra (Table 2) were made in part on the basis of those for the structurally related complexes $[W_2Au_2(\mu\text{-}CC_6H_4Me\text{-}4)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)_2]$.[5]

Solutions of the compounds **5** slowly (several hours) decompose to give the compound **2a** or **2d**, depending on which η^5-$C_2B_9H_{11}$ group they contain. The species with the longer CH_2 chains and having the η^5-7,8-$C_2B_9H_{11}$ cage system appeared marginally more stable in solution. However, in contrast, the reaction between **1a** and $[Au_2Cl_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]$ did not afford an isomer of **5a**, only decomposition products being observed.



4



	n
5a	2
5b	3
5d	4
5e	5
5f	6

Fig. 2.

Reactions between the salts **1a** and **1d** and the compounds $[Au_2Cl_2(\mu\text{-}Z$ or $E\text{-}Ph_2PCH{=}CHPPh_2)]$ were next investigated, and in this manner the four isomeric complexes $[Rh_2Au_2(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,n\text{-}C_2B_9H_{11})_2]$ ($n = 8$ or 9) (**6**) were prepared; data for which are given in Tables 1 and 2. Only the species **6a** and **6b**, containing *nido*-η^5-7,9-$C_2B_9H_{11}$ ligands, are displayed (Fig. 3), since **6c** and **6d** with *nido*-η^5-7,8-$C_2B_9H_{11}$ groups are structurally so similar. Compound **6c**, with a *trans*-$Ph_2PCH{=}CHPh_2$ group and an η^5-7,8-$C_2B_9H_{11}$ cage, was relatively unstable in solution, decomposing to give **2a**. Hence, a pure sample for microanalysis was not obtained. The NMR data for **6c**, and all the other compounds **6**, displayed the expected resonances in accord with the structures proposed. As expected, based on the earlier discussion, in the $^{13}C\{^1H\}$ NMR spectra, the signals for the CO ligands in **6c** and **6d**, both of which contain the 7,8-carborane group, appeared as a doublet-of-doublets. As was also expected, that for the CO group of **6a**, containing the 7,9 cage, was a doublet-of-doublet-of-doublets. However, for **6b**, although it also contains the 7,9-$C_2B_9H_{11}$ group, the signal for the CO ligands was the more simple doublet-of-doublets. Possibly, in this case, the constraints of the sterically more rigid and thus more demanding *cis*-alkene forces the PAu group into a position such that the $^{31}PAuRh^{13}C$ coupling is now too small to be resolved, or is possibly zero. In fact, it is noteworthy that, in this complex only, the signal for the PAu group appears as a doublet, due to $^{103}Rh{-}^{31}P$ coupling (15 Hz), whereas for **6a**, **c** and **d** the resonance is observed as a broad singlet. Clearly, in these compounds, with less steric freedom than those containing alkane chains, there is not just an effect caused by the change of the carborane cage, but also one due to the steric constraints imposed by the alkene group.

EXPERIMENTAL

Light petroleum refers to that fraction of b.p. 40–60°C, and all solvents were freshly distilled over appropriate drying agents prior to use. Chromatography columns *ca* 15 cm long and 3 cm in diameter were packed with silica (70–230 mesh). Celite pads, used to remove TlCl by filtration, were *ca* 3 cm thick. All experiments were carried out under nitrogen using Schlenk-tube techniques. The NMR measurements were made using a Bruker AMX 360 MHz spectrometer and IR spectra were recorded with a Bruker IFS 25 instrument. The reagents $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}7,n\text{-}C_2B_9H_{11})]$ ($n = 8$ or 9),[4] $[AuCl(PPh_3)]$,[6] $[WAuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$,[1e] $[Au_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}]$[5] and $[Au_2Cl_2(\mu\text{-}Ph_2PCH{=}CHPPh_2)]$[5] were prepared by procedures described previously.

Synthesis of the complex $[RhAu(CO)(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})]$

A mixture containing **1d** (0.10 g, 0.15 mmol), $[AuCl(PPh_3)]$ (0.075 g, 0.15 mmol) and $TlBF_4$ (0.047 g, 0.16 mmol) in THF (20 cm^3) was stirred for *ca* 30 min, after which time an IR spectrum indicated that the reaction was complete. The mixture was filtered through Celite, and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (*ca* 3 cm^3) and chromatographed on silica at −10°C. Elution with the same solvent removed a yellow band. Evaporation of the solvent *in vacuo*, followed by crystallization of the residue from CH_2Cl_2–light petroleum (*ca* 20 cm^3, 1 : 10), gave yellow crystals of $[RhAu(CO)(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})]$ (**2d**) (0.14 g).

Synthesis of the complex $[WRhAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$

A mixture of **1d** (0.15 g, 0.23 mmol), $[WAuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.15 g, 0.23 mmol) and $TlBF_4$ (0.073 g, 0.25 mmol) was stirred in CH_2Cl_2 (25 cm^3) for *ca* 30 min, after which time the resulting brown slurry was filtered through Celite. The solvent was removed *in vacuo* and the residue was adsorbed on silica by addition of *ca* 2 g of the latter, followed by *ca* 10 cm^3 of CH_2Cl_2. After the removal of solvent *in vacuo*, all solid material was transferred to the top of a silica chromatography column held at −10°C. Elution with CH_2Cl_2–light petroleum (2 : 3) removed an orange fraction, which was shown by IR spectroscopy to contain both $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and the desired product. The complex $[WRhAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ (**3c**) (0.15 g) was isolated microanalytically-pure by crystallization from CH_2Cl_2–light petroleum (*ca* 20 cm^3, 1 : 10), washing with light petroleum (3 × 10 cm^3) and drying *in vacuo*. Small amounts of **2d** were also observed in the product mixtures and identified by NMR spectroscopy.

Synthesis of the complexes $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$

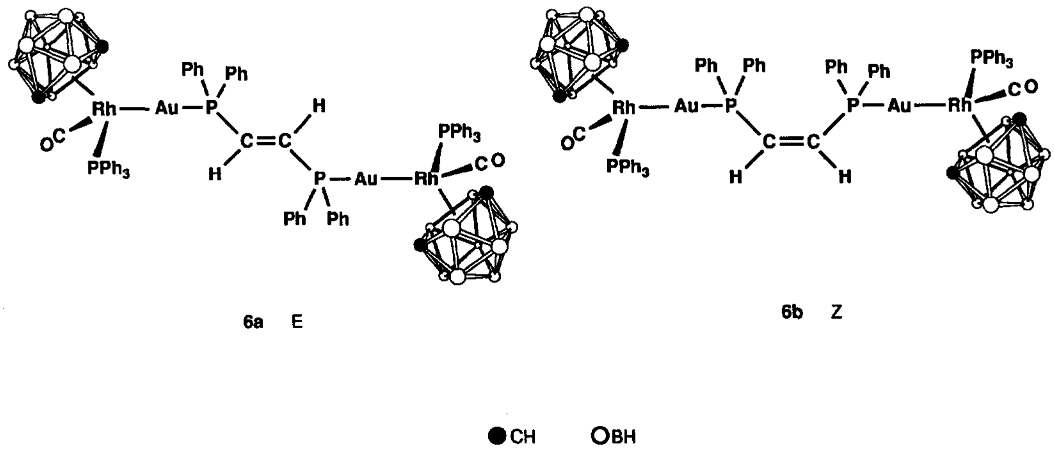
A similar procedure was used to prepare all these compounds, therefore, only that for one complex (**5d**) is given in detail. A CH_2Cl_2 (15 cm^3) solution of **1d** (0.10 g, 0.15 mmol) and $TlBF_4$ (0.050 g, 0.17 mmol) was treated with $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}]$ (0.068 g, 0.075 mmol) and the mixture was stirred for 30 min. The resulting cloudy yellow solution was filtered through Celite. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (5 cm^3), and the solution chromatographed on silica at −10°C. Elution with the same solvent afforded a pale yellow eluate. The removal of the solvent *in vacuo* and crystallization of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1 : 4) gave $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})_2]$ (**5d**) (0.095 g) as a yellow powder, which was washed with light petroleum (2 × 10 cm^3) and dried *in vacuo*.

Synthesis of the compounds $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$

A mixture of **1a** (0.10 g, 0.15 mmol) and $TlBF_4$ (0.050 g, 0.17 mmol) in CH_2Cl_2 (15 cm^3) was added to $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}]$ (0.067 g, 0.075 mmol) and the reactants were stirred for *ca* 15 min. The cloudy pale orange solution was filtered through Celite, and the solvent was removed *in vacuo* from the yellow filtrate. The residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on silica at −10°C. Elution with CH_2Cl_2 gave a bright yellow fraction. The removal of the solvent *in vacuo*, followed by crystallization of the solid from CH_2Cl_2–light petroleum (*ca* 10 cm^3, 1 : 5), gave yellow microcrystals of $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$(**5c**) (0.11 g), washed with light petroleum (2 × 10 cm^3) and dried *in vacuo*. The complex $[Rh_2Au_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**5g**) was similarly prepared from **1a** and $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}]$.

Synthesis of the complexes $[Rh_2Au_2(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})_2]$

The complexes **6** were all prepared by a similar method, and therefore only that for **6d** is given in detail. A CH_2Cl_2 (15 cm^3) solution of **1a** (0.10 g, 0.15 mmol) was treated successively with $TlBF_4$ (0.050 g, 0.17 mmol) and $[Au_2Cl_2(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)]$ (0.066 g, 0.075 mmol). The mixture was stirred for 30 min, and then filtered



6a E

6b Z

● CH ○ BH

Fig. 3.

through Celite. The solvent was removed *in vacuo* from the orange solution, and the residue was redissolved in CH_2Cl_2 (*ca* 4 cm^3) and chromatographed at -10°C in the usual manner. Eluting with the same solvent gave an orange eluate, from which the solvent was removed *in vacuo*. The residue was recrystallized from CH_2Cl_2–light petroleum (*ca* 20 cm^3, 1 : 5) to give microcrystals of $[Rh_2Au_2(\mu\text{-}Z\text{-}Ph_2PCH{=}CHPPh_2)(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**6d**) (0.10 g), washed with light petroleum (2×10 cm^3) and dried *in vacuo*.

Acknowledgements—We thank the Robert A. Welch Foundation for support (Grant AA-1201) and the U.K. Science and Engineering Research Council for the award of a research studentship (to J. E. G.).

REFERENCES

1. (a) M. U. Pilotti, F. G. A. Stone and I. Topaloğlu, *J. Chem. Soc., Dalton Trans.* 1991, 1621; (b) J. R. Fernandez, G. F. Helm, J. A. K. Howard, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* 1990, 1747; (c) J. E. Goldberg, J. A. K. Howard, H. Müller, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* 1990, 3055; (d) J. E. Goldberg, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* 1992, in press; (e) N. Carr, M. C. Gimeno, J. E. Goldberg, M. U. Pilotti, F. G. A. Stone and I. Topaloğlu, *J. Chem. Soc., Dalton Trans.* 1990, 2253; (f) M. U. Pilotti, F. G. A. Stone and I. Topaloğlu, *J. Chem. Soc., Dalton Trans.* 1991, 1355.
2. (a) R. Hoffmann, *Angew. Chem., Int. Edn Engl.* 1982, **21**, 711; (b) F. G. A. Stone, *Angew. Chem., Int. Edn Engl.* 1984, **23**, 89.
3. R. B. King, P. M. Treichel and F. G. A. Stone, *Chem. Ind.* 1961, 747.
4. J. A. Walker, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.* 1985, **24**, 2688.
5. J. E. Goldberg, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* 1992, in press.
6. R. Usón and A. Laguna, *Organomet. Synth.* 1986, **3**, 325.