Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 114.[1] Ditungsten–Digold Compounds having two $W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ Fragments linked by $AuP(Ph)_2(CH_2)_n(Ph)_2PAu$ (n = 2–6) Groups*

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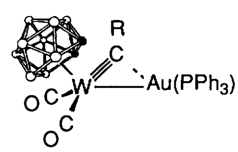
Treatment of 1 equivalent of the reagent $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4), in the presence of $TlBF_4$, with 0.5 equivalent of the compounds $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (n = 2–6) in CH_2Cl_2 affords the complexes $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$. The crystal structure of the species with n = 4 has been determined by X-ray crystallography, confirming that the molecule has two $RC\equiv W(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ fragments bridged by an $AuP(Ph)_2CH_2CH_2CH_2CH_2(Ph)_2PAu$ unit, with a centre of inversion at the midpoint of the chain of methylene groups. The W–Au bonds [2.798(1) Å] are asymmetrically bridged by the *p*-tolylmethylidyne ligands [W–μ-C 1.870(9), Au–μ-C 2.194(9) Å]. In a similar manner, the compounds $[W_2Au_2(\mu\text{-}CR)_2(\mu\text{-}Z$ or $E\text{-}Ph_2PCH{=}CHPPh_2)(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ have been prepared from reactions between the gold compounds $[Au_2Cl_2(\mu\text{-}Z$ or $E\text{-}Ph_2PCH{=}CHPPh_2)]$ and the salt $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$. Addition of $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene) to the complexes $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ affords the chain cluster compounds $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_4(cod)_2(\eta^5\text{-}C_2B_9H_9Me_2)_2]$. The NMR data ($^1H$, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$ and $^{11}B\text{-}\{^1H\}$) for the new complexes are reported and discussed.

Salts of the anionic alkylidyne metal complexes $[M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]^-$ (M = W or Mo; R = alkyl, aryl or alkynyl; R′ = Me or H) afford a variety of structurally interesting di- or tri-nuclear mixed-metal compounds upon treatment with low-valent metal species.[2] One of the first reactions of this type investigated was that between $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4) and $[AuCl(PPh_3)]$ in thf (tetrahydrofuran) in the presence of $TlPF_6$.[3] The structure of the product, $[WAu(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **1**, was established by X-ray crystallography, a study which revealed that the tungsten–gold bond was semibridged by the *p*-tolylmethylidyne group [μ-C–W 1.88(3), μ-C–Au 2.19(3) Å]. Following this initial study several other compounds have been isolated having W–Au bonds and bridging *p*-tolylmethylidyne groups, and with the W atoms ligated by *nido*-icosahedral $C_2B_9H_9Me_2$ fragments. The complexes $[NEt_4][WAuCl(\mu\text{-}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **2**,[4a] $[N(PPh_3)_2][W_2Au(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **3**,[3] $[W_2Au(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)(\eta\text{-}C_5H_5)]$ **4**, $[WPtAu(\mu_3\text{-}CR)(CO)_2(PMe_2Ph)_3(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5** and $[W_2PtAu(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)(\eta^5\text{-}C_2B_9H_9Me_2)(\eta\text{-}C_5H_5)]$ **6** (cod = cycloocta-1,5-diene)[4b] exemplify the diverse nature of the products that have been obtained.

In this paper we describe the synthesis of ditungsten–digold compounds in which two $AuW(\mu\text{-}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ moieties are linked by bidentate $Ph_2P(CH_2)_nPPh_2$ (n = 2–6) or $Ph_2PCH{=}CHPPh_2$ ligands. The primary motive for preparing these complexes was to establish whether the W(μ-CR)Au groups at the ends of these molecules would ligate other metal–ligand fragments to afford a new class of chain-like metal species.



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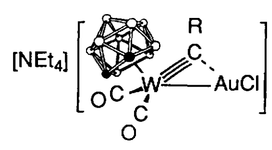

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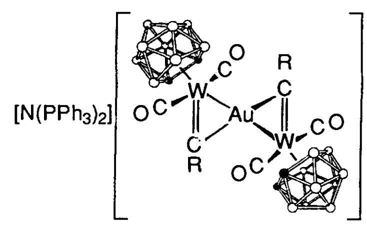

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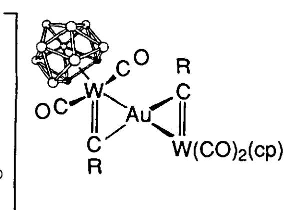

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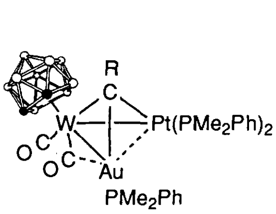

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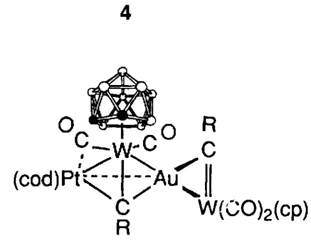


6

R = C_6H_4Me–4, cp = η–C_5H_5
○BH ●CMe

Results and Discussion

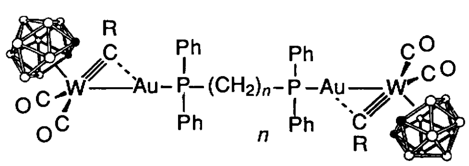
The method of synthesis of the desired complexes was based on that employed earlier to obtain complex **1**.[3] To prepare

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

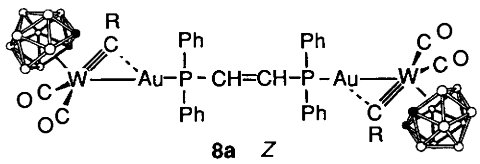
Table 1 Analytical[a] and physical data for the complexes

Compound[b]	Colour	Yield (%)	$\nu_{max}(CO)$[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
7a $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Orange	61	2005vs, 1936vs	36.1 (36.1)	4.2 (3.8)
7b $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Brown	18	2003vs, 1935vs	36.2 (36.4)	3.9 (3.9)
7c $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Red	40	2003vs, 1935vs	37.8 (36.8)	4.0 (4.0)
7d $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Red	31	2002vs, 1933vs	37.9 (37.2)	4.3 (4.1)
7e $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Brown	41	2003vs, 1934vs	37.1 (37.6)	4.6 (4.1)
8a $[W_2Au_2(\mu\text{-}CR)_2(\mu\text{-}Z\text{-}Ph_2PCH{=}CHPPh_2)(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Orange	13	1975vs (br), 1913s (vbr), 1884m (sh)	36.4 (36.1)	4.6 (3.7)
8b $[W_2Au_2(\mu\text{-}CR)_2(\mu\text{-}E\text{-}Ph_2PCH{=}CHPPh_2)(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Ochre	45	2005vs, 1936vs	35.8 (36.1)	3.7 (3.7)
9a $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_4(cod)_2\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Brown	35	[d] 1942vs (br), 1846m (vbr), 1806m (vbr)	33.9 (34.9)	3.8 (3.8)
9b $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(CO)_4(cod)_2\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Beige	42	[d] 1945vs (br), 1844m (vbr), 1788m (vbr)	35.4 (35.2)	3.9 (3.9)
9c $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}(CO)_4(cod)_2\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)_2]$[e]	Beige	41	[d] 1948vs, 1938s (sh), 1844m (vbr), 1791m (br)		
9d $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}(CO)_4(cod)_2\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Beige	45	[d] 1949vs (br), 1846m (vbr), 1796m (vbr)	36.5 (35.8)	4.0 (4.3)
9e $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(CO)_4(cod)_2\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)_2]$[e]	Tan	31	[d] 1949vs (br), 1843m (vbr), 1798m (vbr)		

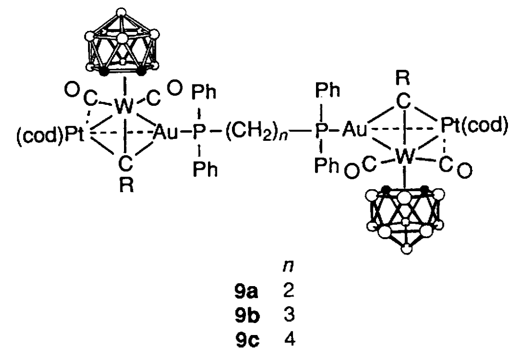
[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] Measured in CH_2Cl_2 unless otherwise stated. All the complexes show a broad band in the range 2500–2550 cm^{-1} due to ν(BH). [d] Measured in thf. [e] Satisfactory microanalytical data not available.



	n
7a	2
7b	3
7c	4
7d	5
7e	6



8a *Z*
8b *E*



	n
9a	2
9b	3
9c	4
9d	5
9e	6

R = C_6H_4Me–4
○ BH ● CMe

species with $AuP(Ph)_2(CH_2)_n(Ph)_2PAu$ chains, 0.5 equivalent of the digold compounds $[Au_2Cl_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ was added to CH_2Cl_2 solutions of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4), with $TlBF_4$ present to remove the chloride as TlCl. Column chromatography on alumina separated the ditungsten–digold compounds $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ (*n* = 2 **7a**, 3 **7b**, 4 **7c**, 5 **7d**, or 6 **7e**) from the trimetal complex **3**, formed in variable amounts (*ca.* 15–50%) as its $[NEt_4]^+$ salt. The latter species evidently results from displacement of $Ph_2P(CH_2)_nPPh_2$ from gold by the RC≡W group of $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ during the reaction pathway. It was observed that those preparations of the compounds **7** which proceeded in relatively poor yield are those in which a high proportion of the $[NEt_4]^+$ salt of **3** was formed.

A similar procedure to that used to obtain the complexes **7**, employing the chlorogold reagents $[Au_2Cl_2(\mu\text{-}cis\text{-}$ or $trans\text{-}Ph_2PCH{=}CHPPh_2)]$, afforded the species $[W_2Au_2(\mu\text{-}CR)_2(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8**. Again the $[NEt_4]^+$ salt of **3** was formed in these reactions. Data identifying the several new compounds of types **7** and **8** are summarised in Tables 1–3.

Before discussing the spectroscopic data the results of an X-ray diffraction study on complex **7c** are described. Selected internuclear distances and angles are given in Table 4 and the structure of the molecule is shown in Fig. 1. As expected, two $(\eta^5\text{-}C_2B_9H_9Me_2)(OC)_2W{\equiv}CC_6H_4Me$-4 fragments are bridged by an $AuP(Ph)_2CH_2CH_2CH_2CH_2(Ph)_2PAu$ unit. The two halves of the molecule are symmetry related about a centre of inversion at the midpoint of the bond joining the two β-CH_2 groups in the $PCH_2CH_2CH_2CH_2P$ chain. The Au–P separations [2.291(2) Å] may be compared with that [2.27(1) Å] found in **1**.[3] Moreover, the dimensions of the W(μ-C)Au three-membered rings in **7c** [W–Au 2.798(1), W–C(20) 1.870(9), Au–C(20) 2.194(9) Å] and in **1** [W–Au 2.780(8), W–μ-C 1.88(3), Au–μ-C 2.19(3) Å] are very comparable. Thus the *p*-tolylmethylidyne ligands in **7c** semibridge the W–Au bonds in a similar fashion to that observed in **1**. This semibridging, seen also with alkylidyne groups in some tungsten–ruthenium[5a] and

Table 2 Hydrogen-1 and carbon-13 NMR data[a] for the complexes

Compound	^1H[b] (δ)	^{13}C[c] (δ)
7a	2.20 (s, 12 H, CMe), 2.32 (s, 6 H, Me-4), 2.84 (s, 4 H, CH_2), 7.13 [half of $(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.46–7.60 (m, 24 H, Ph and C_6H_4)	292.8 [(AXX′), μ-C, |*J*(AX) + *J*(AX′)| 25], 219.1 [CO, *J*(WC) 162], 149.0 [$C^1(C_6H_4)$], 142.3–127.8 (Ph and C_6H_4), 66.5 (*C*Me), 31.1 (C*Me*), 24.6 [(AXX′), CH_2, |*J*(AX) + AX′)| 38], 22.0 (Me-4)
7b	1.96 (m, 2 H, β-CH_2), 2.12 (s, 12 H, CMe), 2.32 (s, 6 H, Me-4), 2.81 (m, 4 H, α-CH_2), 7.10 [half of $(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.42–7.55 (m, 24 H, Ph and C_6H_4)	*295.5 (μ-C), 292.6 [d, μ-C, *J*(PC) 26], *221.1 [CO, *J*(WC) 164], 219.6 [CO, *J*(WC) 163], *149.0, 148.4 [$C^1(C_6H_4)$], 142.3–127.4 (Ph and C_6H_4), *66.8, 66.6 (*C*Me), 31.2, *30.9 (C*Me*), 29.6 [(AXX′), α-CH_2, |*J*(AX) + *J*(AX′)| 46], 22.0, *21.9 (Me-4), 21.4 [t, β-CH_2, *J*(PC) 5]
7c	1.81 (m, 4 H, β-CH_2), 2.20 (s, 12 H, CMe), 2.34 (s, 6 H, Me-4), 2.59 (m, 4 H, α-CH_2), 7.17 [half of $(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.49–7.65 (m, 24 H, Ph and C_6H_4)	*295.5 (μ-C), 292.4 [d, μ-C, *J*(PC) 27, *J*(WC) 146], *221.5 (CO), 219.7 [CO, *J*(WC) 163], 149.1, *148.4 [$C^1(C_6H_4)$], 142.2–129.0 (Ph and C_6H_4), 66.6, *66.4 (*C*Me), 31.2, *30.9 (C*Me*), 28.3 [d, α-CH_2, *J*(PC) 33], 27.5 [(AXX′), β-CH_2, |*J*(AX) + *J*(AX′)| 23], 22.0, *21.1 (Me-4)
7d	1.64 (m, 6 H, β- and γ-CH_2), 2.16 (s, 12 H, CMe), 2.31 (s, 6 H, Me-4), 2.55 (m, 4 H, α-CH_2), 7.12 [half of $(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.34–7.67 (m, 24 H, Ph and C_6H_4)	*295.5 (μ-C), 292.6 [d, μ-C, *J*(PC) 27], *221.4 (CO), 219.9 [CO, *J*(WC) 163], 149.1, *148.4 [$C^1(C_6H_4)$], 142.2–129.3 (Ph and C_6H_4), 66.6, *66.2 (*C*Me), 32.3 [t, γ-CH_2, *J*(PC) 16], 31.2, *30.9 (C*Me*), 28.4 [d, α-CH_2, *J*(PC) 33], 25.5 [d, β-CH_2, *J*(PC) 5], *22.7, 22.0 (Me-4)
7e	1.42 (m, 4 H, γ-CH_2), 1.63 (m, 4 H, β-CH_2), 2.19 (s, 12 H, CMe), 2.34 (s, 6 H, Me-4), 2.59 (m, 4 H, α-CH_2), 7.16 [half of $(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.49–7.69 (m, 24 H, Ph and C_6H_4)	*295.5 (μ-C), 292.6 [d, μ-C, *J*(PC) 27], *221.7 (CO), 219.9 [CO, *J*(WC) 162], 149.1, *148.5 [$C^1(C_6H_4)$], 142.1–129.4 (Ph and C_6H_4), 66.6, *65.4 (*C*Me), 31.2 (C*Me*), 30.7 [d, γ-CH_2, *J*(PC) 16], 28.4 [d, α-CH_2, *J*(PC) 33], 26.0 [d, β-CH_2, *J*(PC) 3], 22.0, *21.0 (Me-4)
8a	1.97, *1.98 (s, 12 H, CMe), 2.27, *2.29 (s, 6 H, Me-4), 6.77, 7.06 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], *6.83, *7.09 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 9], 7.34–7.55 (m, 20 H, Ph), 7.73, *7.74 [(AA′XX′), 2 H, CH=CH, *J*(AX) 21, *J*(AX′) 21, *J*(AA′) 42, *J*(XX′) 21]	* 303.3 (μ-C), 303.1 [(AXX′), μ-C, |*J*(AX) + *J*(AX′)| 34], 222.2 [CO, *J*(WC) 165], *220.4 (CO), 155.5 [(AXX′), $C^1(C_6H_4)$, |*J*(AX) + *J*(AX′)| 8], *155.0 [(AXX′), $C^1(C_6H_4)$, |*J*(AX) + *J*(AX′)| 7], 147.1, *147.0 [(AXX′), CH=CH, |*J*(AX) + *J*(AX′)| 62], 138.5–127.8 (Ph and C_6H_4), 64.7, *59.6 (*C*Me), 31.1, * 30.8 (C*Me*), *21.9, 21.4 (Me-4)
8b	2.17 (s, 12 H, CMe), 2.32 (s, 6 H, Me-4), 7.10 [half of $(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.53–7.63 (m, 26 H, CH=CH, Ph and C_6H_4)	293.1 [(AXX′), μ-C, |*J*(AX) + *J*(AX′)| 26], 219.1 [CO, *J*(WC) 162], 148.9 [$C^1(C_6H_4)$], 142.4 [$C^4(C_6H_4)$], 141.9 [(AXX′), CH=CH, |*J*(AX) + *J*(AX′)| 50], 134.1–127.0 (Ph and C_6H_4), 66.8 (*C*Me), 31.2 (C*Me*), 22.0 (Me-4)
9a[d]	1.78 (m, 4 H, CH_2 of cod), 2.14, 2.18, 2.35 (s × 3, 18 H, CMe and Me-4), 2.55 (m, 4 H, CH_2 of cod), 2.74 (m, 4 H, CH_2), 4.65 (m, 4 H, CH of cod), 5.16, 5.47 (m × 2, 4 H, CH of cod), 7.08, 7.14 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 7.44–7.51 (m, 20 H, Ph)	
9b[d]	1.72 (m, 2 H, β-CH_2), 1.87 (m, 4 H, CH_2 of cod), 2.14, 2.17, 2.33 (s × 3, 18 H, CMe and Me-4), 2.46 (m, 8 H, CH_2 of cod), 2.61 (m, 4 H, CH_2 of cod), 2.76 (m, 4 H, α-CH_2), 4.59, 4.68, 5.18, 5.44 (m × 4, 8 H, CH of cod), 7.03, 7.13 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 7.19–7.76 (m, 20 H, Ph)	
9c[d]	1.58 (m, 4 H, β-CH_2), 1.89 (m, 4 H, CH_2 of cod), 2.14, 2.20, 2.34 (s × 3, 18 H, CMe and Me-4), 2.47 (m, 8 H, α-CH_2 and CH_2 of cod), 4.66, 4.79, 5.24, 5.44 (m × 4, 8 H, CH of cod), 7.11, 7.18 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 7.35–7.68 (m, 20 H, Ph)	
9d[d]	1.51 (m, 6 H, β- and γ-CH_2), 1.90 (m, 4 H, CH_2 of cod), 2.14, 2.19, 2.31 (s × 3, 18 H, CMe and Me-4), 2.47 (m, 8 H, α-CH_2 and CH_2 of cod), 4.63, 4.77, 5.22, 5.43 (m × 4, 8 H, CH of cod), 7.08, 7.17 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 7.35–7.65 (m, 20 H, Ph)	290.4 [d, μ_3-C, *J*(PC) 14], 231.5, 219.1 (CO), 153.5 [$C^1(C_6H_4)$] 136.4–124.5 (Ph and C_6H_4), 106.5, 106.2, 99.6, 93.8 (CH of cod) 66.3, 64.8 (*C*Me), 32.4 [t, γ-CH_2, *J*(PC) 16], 31.0, 30.8, 30.5 (CH_2 of cod), 30.2 (br, C*Me*), 28.7 [d, α-CH_2, *J*(PC) 32], 28.4 (CH_2 of cod), 25.3 [d, β-CH_2, *J*(PC) 5], 21.2 (Me-4)
9e[d]	1.35 (m, 4 H, γ-CH_2), 1.51 (m, 4 H, β-CH_2), 1.90 (m, 4 H, CH_2 of cod), 2.14, 2.22, 2.35 (s × 3, 18 H, CMe and Me-4), 2.47 (m, 8 H, α-CH_2 and CH_2 of cod), 4.67, 4.78, 5.25, 5.44 (m × 4, 8 H, CH of cod), 7.11, 7.19 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 7.23–7.55 (m, 20 H, Ph)	289.8 [d, μ_3-C, *J*(PC) 15, *J*(PtC) 571], 231.4, 219.6 (CO), 153.5 [$C^1(C_6H_4)$], 136.4–124.5 Ph and C_6H_4), 106.7, 106.1, 99.7, 93.6 (CH of cod), 66.3, 64.9 (*C*Me), 32.0, 30.9 (CH_2 of cod), 30.7 [d, γ-CH_2, *J*(PC) 16], 30.5, 30.2 (CH_2 of cod), 30.0 (C*Me*), 28.7 [d, α-CH_2, *J*(PC) 32], 25.8 [d, β-CH_2, *J*(PC) 3], 21.2 (Me-4)

[a] Chemical shifts δ in ppm, coupling constants in Hz, measurements at ambient temperatures in CD_2Cl_2. Asterisked peaks are due to minor isomer (see text). [b] Resonances for B–H protons are not resolved, due to ^{11}B–^1H coupling, and occur as very broad, weak signals in the range δ 0–3. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (δ 0.0). [d] Some CH_2(cod) signals are obscured by other peaks. Signals due to CH groups of cod ligands show ^{195}Pt satellite peaks in ^1H spectra [*J*(PtH) *ca.* 45–75 Hz], and also in $^{13}C-\{^1H\}$ spectra [*J*(PtC) *ca.* 105–145 Hz], where the solubility of the complex allowed the latter spectra to be measured (see text).

platinum complexes,[5b] results in a widening of the W-μ-C-C^1 (aryl) angle. In compound **7c** this angle [W–C(20)–C(21) 161.7(7)°] is very close to that found previously in **1** [163(2)°], and both are appreciably less than the corresponding angle [175(1)°] observed for [$WPt(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(CO)_2(PEt_3)$].[5b]

The tungsten atoms in compound **7c** carry two essentially terminally bound CO groups. The *nido*-icosahedral 7,8-$C_2B_9H_9Me_2$ cages ligating the tungsten atoms form *closo*-1,2-dicarba-3-tungstadodecaborane structures with the metal atoms. Since the open pentagonal face of the cage may be regarded as occupying three co-ordination sites, the cage, together with the two CO groups, the gold atom, and the alkylidyne carbon atom give a seven-co-ordinate tungsten. However, overall the ligands about the metal atom adopt a distorted square-pyramidal or 'four-legged piano stool' arrangement. The distance between the tungsten atoms and the centroids of the pentagonal rings is 1.919 Å. The W–B(1,2,3) and W–C(1,3) distances are given in Table 4. A least-squares planes program verified the planarity of the open face of the *nido*-$C_2B_9H_9Me_2$ cage [ring C(1)–C(3)–B(1)–B(2)–B(3) deviation 0.017 Å], and within the pentagonal ring the average bond angle is 108°.

The mean P–C bond length is 1.81(1) Å, and all other determined bond distances are internally consistent and in good agreement with other experimental values.[6] The phosphorus atoms are tetrahedrally co-ordinated with an average Au–P–C angle (112°) slightly larger than ideality and an average C–P–C bond angle (107°) discernibly less than ideal. These differences can be attributed to steric hindrance caused by the bulkiness of the $AuW(\mu-CR)(CO)_2(\eta^5-C_2B_9H_9-Me_2)$ moieties.

The NMR data (Tables 2 and 3) for compound **7c** are in accord with the structure established by the X-ray diffraction study. The $^{31}P-\{^1H\}$ NMR spectrum revealed the expected singlet resonance which occured at δ 53.9. For the precursor $[Au_2Cl_2\{\mu-Ph_2P(CH_2)_4PPh_2\}]$ the ^{31}P signal is at δ 30.2 (see Experimental section). The $^{11}B-\{^1H\}$ NMR spectrum of **7c**, and the other compounds of similar type, displayed four broad peaks (Table 3). In fully coupled ^{11}B spectra these resonances become doublets with *J*(HB) values (*ca.* 115–135 Hz) expected for BH cage vertices undisturbed by exopolyhedral B–H→M bonding.[7]

Table 3 Boron-11 and phosphorus-31 NMR data[a] for the complexes

Compound	$^{11}B^b$ (δ)	$^{31}P^c$ (δ)
7a	−2.9 (3 B), −5.8 (6 B), −7.2 (6 B), −9.6 (3 B)	55.3 (s)
7b	−2.8 (3 B), −5.8 (6 B), −7.5 (6 B), −9.6 (3 B)	51.4 (s)
7c	−2.8 (3 B), −5.8 (6 B), −7.4 (6 B), −8.1 (3 B)	53.9 (s)
7d	−2.8 (3 B), −5.8 (6 B), −7.5 (6 B), −9.8 (3 B)	53.0 (s)
7e	−2.7 (3 B), −5.7 (6 B), −7.6 (6 B), −9.6 (3 B)	53.5 (s)
8a	−4.0 (3 B), −7.0 (6 B), −8.3 (6 B), −10.7 (3 B)	*42.5 (s), 40.1 (s)
8b	−2.7 (3 B), −5.7 (6 B), −7.3 (6 B), −9.5 (3 B)	53.8 (s)
9a	−1.4 (3 B), −6.5 (11 B), −10.7 (4 B)	51.5 [s, *J*(PtP) 72, *J*(WP) 32]
9b	−1.5 (3 B), −6.8 (11 B), −9.6 (4 B)	48.6 [s, *J*(PtP) 110], *48.0 [s, *J*(PtP) 100]
9c	−1.4 (3 B), −6.7 (11 B), −9.7 (4 B)	50.7 [s, *J*(PtP) 96, *J*(WP) 22]
9d	−1.2 (3 B), −6.8 (11 B), −9.4 (4 B)	49.8 [s, *J*(PtP) 99]
9e	−1.1 (3 B), −6.7 (11 B), −9.8 (4 B)	50.4 [s, *J*(PtP) 95, *J*(WP) 11]

[a] Chemical shifts δ in ppm, coupling constants in Hz, measurements in CD_2Cl_2 at ambient temperatures. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3\cdot Et_2O$ (external). In fully coupled $^{11}B-^1H$ spectra, *J*(HB) values are *ca.* 115–135 Hz. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external). Asterisked peaks are due to a second isomer.

Signals in the ^1H NMR spectrum of compound **7c** were as expected. However, a duplication of certain peaks in the $^{13}C-\{^1H\}$ NMR spectrum indicated the presence in solution of *ca.* 10% of a minor isomer. Thus two resonances were seen for μ-C nuclei for the minor and major isomer at δ 295.5 and 292.4, respectively. The latter signal was a doublet due to $^{31}P-^{13}C$ coupling (27 Hz) and there were ^{183}W satellite peaks [*J*(WC) 146 Hz]. In the $^{13}C-\{^1H\}$ NMR spectrum of **1** the μ-C resonance is at δ 292.9 with *J*(PC) 28 Hz. These chemical shifts correlate with the semibridging nature of the *p*-tolylmethylidyne groups. When these ligands span heteronuclear metal–metal bonds more symmetrically the ^{13}C NMR resonances are appreciably more deshielded (δ *ca.* 325–380).[5b,8] Moreover, in dimetal complexes with symmetrically bridging alkylidyne fragments, and with the ligated carbon atoms attached to a metal atom carrying a phosphine, the $^{31}P-^{13}C$ couplings are larger, *e.g.* 59 Hz for $[WPt(\mu-CC_6H_4Me-4)(CO)_2(PMe_2Ph)_2-(\eta-C_5H_5)]$,[9] than that (27 Hz) found for the major isomer of **7c**.

The $^{13}C-\{^1H\}$ NMR spectra of compounds **7b**, **7d** and **7e** also display duplicate resonances indicating the presence of isomers. Whereas with **7d** and **7e** the relative peak intensities showed that one of the isomers was present in small amounts (*ca.* 10%), the spectrum of **7b** revealed two isomers in *ca.* 4:3 ratio. In the spectrum of each compound two signals are seen for μ-C nuclei of the two isomers at δ 292.6 and 295.5. Whereas the resonance for the principal isomer (Table 2) shows $^{31}P-^{13}C$ coupling, the signal for the less-abundant isomer does not, presumably due to weaker μ-C–Au bonding in the latter species. This same feature is shown by the spectrum of **7c**. The existence of isomers is attributed to the presence of rotamers, resulting from different conformations of the CH_2 backbone.

In contrast with the four compounds **7b**–**7e**, the $^{13}C-\{^1H\}$ NMR spectrum of **7a** showed peaks corresponding to one

Table 4 Selected internuclear distances (Å) and angles (°) for the complex $[W_2Au_2(\mu-CC_6H_4Me-4)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$ **7c**

Au–W	2.798(1)	Au–P	2.291(2)	Au–C(20)	2.194(9)	W–B(1)	2.40(1)
W–B(2)	2.42(1)	W–B(3)	2.37(1)	W–C(1)	2.422(8)	W–C(3)	2.44(1)
W–C(10)	1.98(1)	W–C(11)	2.00(2)	W–C(20)	1.870(9)	B(1)–C(3)	1.68(1)
B(1)–B(2)	1.78(2)	B(1)–B(6)	1.78(2)	B(1)–B(7)	1.76(2)	B(2)–B(3)	1.77(1)
B(2)–B(7)	1.75(2)	B(2)–B(8)	1.73(2)	B(3)–C(1)	1.71(1)	B(3)–B(4)	1.74(2)
B(3)–B(8)	1.75(2)	B(4)–C(1)	1.70(1)	B(4)–B(5)	1.73(2)	B(4)–B(8)	1.75(2)
B(4)–B(9)	1.75(2)	B(5)–C(1)	1.73(2)	B(5)–C(3)	1.74(2)	B(5)–B(6)	1.76(2)
B(5)–B(9)	1.74(2)	B(6)–C(3)	1.71(2)	B(6)–B(7)	1.72(2)	B(6)–B(9)	1.73(2)
B(7)–B(8)	1.74(2)	B(7)–B(9)	1.74(2)	B(8)–B(9)	1.72(2)	C(1)–C(3)	1.64(1)
P–C(31)	1.804(8)	P–C(41)	1.807(8)	P–C(51)	1.829(8)	C(10)–O(10)	1.17(2)
C(11)–O(11)	1.14(2)	C(1)–C(2)	1.56(1)	C(3)–C(4)	1.56(1)	C(20)–C(21)	1.43(1)
C(24)–C(27)	1.49(2)	C(51)–C(52)	1.50(1)	C(91)–Cl(1)	1.78(2)	C(91)–Cl(2)	1.78(2)
W–Au–P	161.1(1)	W–Au–C(20)	41.9(2)	Au–W–C(20)	51.5(3)	P–Au–C(20)	155.6(2)
C(10)–W–C(11)	84.5(6)	C(10)–W–C(20)	97.4(5)	C(11)–W–C(20)	78.4(5)	Au–W–C(10)	70.2(3)
Au–W–C(11)	117.7(4)	Au–C(20)–W	86.6(4)	Au–C(20)–C(21)	110.4(6)	W–C(20)–C(21)	161.7(7)
Au–P–C(31)	117.0(3)	Au–P–C(41)	109.5(3)	Au–P–C(51)	109.1(3)	W–C(10)–O(10)	176(1)
W–C(11)–O(11)	180(1)	P–C(31)–C(32)	119.9(7)	P–C(41)–C(42)	119.5(6)	P–C(51)–C(52)	111.6(6)

	Distances		Angles	
Ring	Mean	Range	Mean	Range
C(21)–C(26)	1.38(1)	1.37–1.39	120(2)	117.4–121.9
C(31)–C(36)	1.37(1)	1.36–1.38	120(1)	118.5–121.9
C(41)–C(46)	1.37(1)	1.35–1.39	120(2)	116.9–123.8

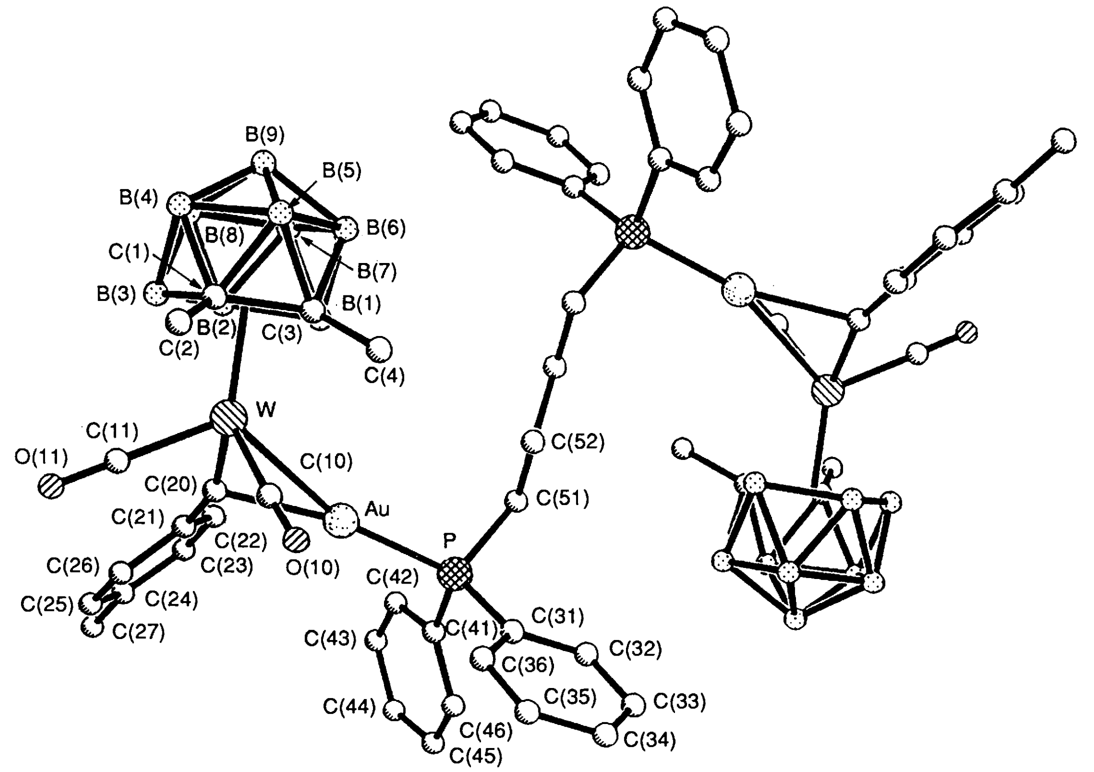


Fig. 1 The molecular structure of the complex $[W_2Au_2(\mu\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **7c** showing the crystallographic numbering scheme

isomer only. An X-ray diffraction study of $[Au_2Cl_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]$, the precursor to **7a**, showed that in this molecule the two halves point away from one another.[10] It is possible that in **7a**, with only two CH_2 units in the chain, the $AuPPh_2$ groups carrying the bulky $RC{\equiv}W(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ fragments are constrained to one conformer. It is noteworthy that the crystal structure of **7c** reveals a transoid arrangement of Au–P groups. A $^{13}C\text{-}\{^1H\}$ NMR study of the crystals recovered from the X-ray work showed that they were of the major isomer. With the longer chains in **7b**–**7e** the existence of rotamers resulting from different orientations of the $AuPPh_2$ groups with respect to the CH_2 backbone seems probable. With **7b**, having three CH_2 groups in the chain, two conformers are apparently almost equally favoured.

The importance of steric effects in these syntheses is further indicated by the observation that the reaction between $[NEt_4][W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ and the species $[Au_2Cl_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ afforded **3** as its $[NEt_4]^+$ salt rather than a product structurally similar to the complexes **7**. An X-ray crystal structure study[11] on $[Au_2Cl_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ revealed a sterically crowded molecule, making it unlikely that the two Cl^- ligands could be successfully replaced by $[W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ moieties without breakdown of the five-atom AuPCPAu chain. Electronic effects also apparently play a part in the nature of the products isolated. Thus the reaction between $[Au_2Cl_2(\mu\text{-}Me_2PCH_2CH_2PMe_2)]$ and $[NEt_4][W({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ occurred only slowly and surprisingly yielded the tetraethylammonium salt of **3**, instead of an analogue of **7a**, despite $Me_2PCH_2CH_2PMe_2$ being less bulky than $Ph_2PCH_2CH_2PPh_2$.

The NMR data for the two compounds **8** are in accord with the assigned structures, but **8a** with a *cis*-CH=CH group exists in solution as an isomeric mixture (*ca.* 4:1), a feature revealed in the ^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ NMR spectra (Tables 2 and 3). The absence of any $^{31}P\text{-}^{13}C$ coupling on the alkylidyne carbon resonance (δ 303.3) of the minor isomer may indicate that in this species steric constraints about the two $AuPPh_2$ units, due to the proximity of the bulky $W(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ groups, weaken the Au–μ-C bonds.

We have carried out preliminary work to establish whether the compounds **7** can be used as precursors to other polynuclear mixed-metal complexes by addition of metal–ligand fragments to the C≡W groups at both ends of the molecule. Because of earlier success in building chains based on combining Pt(cod) fragments with C≡W groups,[12] reactions between the complexes **7** and $[Pt(cod)_2]$ were investigated. Addition of **7a** to an ethylene-saturated thf solution of $[Pt(cod)_2]$ at 0 °C followed by warming to room temperature, afforded $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_4(cod)_2(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **9a**. Similar syntheses employing **7b**–**7e** with $[Pt(cod)_2]$ yielded the hexanuclear metal complexes **9b**–**9e**. Data characterising the compounds **9** are given in Tables 1–3. Although satisfactory microanalytical data were not obtained for **9c** or **9e** the spectroscopic properties of these two species were very similar to those of **9a**, **9b** and **9d**, leaving little doubt that they have similar structures.

The IR spectra of the compounds **9** show three broad CO stretching bands, one of which (*ca.* 1800 cm^{-1}) suggests the presence of semibridging carbonyl ligands, in agreement with $^{13}C\text{-}\{^1H\}$ data discussed below. The ^1H NMR spectra were as expected, although in some cases not all the CH_2 signals of the cod ligands were resolved. In the structures proposed the four CH groups of the cod ligands would be inequivalent. Accordingly, the spectra of **9b**–**9e** show four distinct multiplets in the range δ 4.59–5.44 for these groups, all displaying $^{195}Pt\text{-}^1H$ coupling (*ca.* 45–75 Hz). In the spectrum of **9a** two of the four CH(cod) multiplets overlap.

The $^{13}C\text{-}\{^1H\}$ NMR spectra of compounds **9a**–**9c** could not be measured because these were relatively insoluble, and a poor signal-to-noise ratio prevented observation of all the peaks, particularly those due to the CO and μ_3-CR groups. However, complexes **9d** and **9e**, with the longer CH_2 chains, were appreciably more soluble, and their $^{13}C\text{-}\{^1H\}$ NMR spectra could be successfully recorded (Table 2). As in the ^1H NMR spectra, and as expected based on the proposed structures, four signals were seen (Table 2) for both the CH(cod) and CH_2(cod) groups, the former showing $^{195}Pt-^{13}C$ coupling (*ca.* 105–145 Hz) of the expected magnitude.[12] In the CO region two resonances were observed for both compounds at δ *ca.* 231 and 219. The chemical shift of the former signal suggests that it is due to a semibridging CO group. It may be compared with the CO peak seen at δ 235.4 in the $^{13}C-\{^1H\}$ NMR spectrum of **6**, the other three resonances in this spectrum occurring at δ 215.7, 212.7 and 212.1.[4b]

The μ_3-C resonances in the $^{13}C-\{^1H\}$ NMR spectra of compounds **9d** and **9e** occur at δ 290.4 and 289.8, respectively, to be compared with the corresponding signals in the spectra of **5** and **6** at δ 290.7 and 284.9 respectively.[4b] The peaks for **9d** and **9e** appear as doublets [*J*(PC) *ca.* 15 Hz], while the spectrum of **9e** was of sufficient quality to measure ^{195}Pt satellite bands [*J*(PtC) 571 Hz]. In the $^{13}C-\{^1H\}$ NMR spectrum of $[WPtAu(\mu_3-CC_6H_4Me-4)(CO)_2(PPh_3)(cod)(\eta^5-C_2B_9H_9Me_2)]$,[13] a compound structurally similar to **5** but having $Au(PPh_3)$ and Pt(cod) groups, the μ_3-C resonance is at δ 291.1 with *J*(PC) 15 and *J*(PtC) 595 Hz, data very similar to those for **9e**.

There can be little doubt that all the complexes **9** have the same basic structure in which two μ_3-CWPtAu fragments terminate a $Ph_2P(CH_2)_nPPh_2$ chain. What remains at issue is whether the μ_3-CWPtAu groups adopt a *closo*-trimetallatetrahedrane structure or a 'butterfly' arrangement with Pt and Au atoms at the wing-tip positions, and the C–W linkage forming the body of the butterfly. The latter configuration occurs in $[WPtAu(\mu_3-CR)(CO)_2(PMe_3)_3(\eta-C_5H_5)][PF_6]$, the structure of which has been established by X-ray crystallography.[14] Unfortunately, despite persistent efforts, it was not possible to grow crystals of any of the compounds **9** of suitable quality for an X-ray diffraction study. However, the data from the $^{31}P-\{^1H\}$ NMR spectra suggest that in these molecules there is a Pt–Au connectivity. The spectra (Table 3) of **9a** and **9c**–**9e** show a singlet resonance at δ *ca.* 50, with ^{195}Pt satellites. The $^{31}PAu-^{195}Pt$ coupling (72–99 Hz) is too large for a three-bond value. Moreover, the $^{31}P-\{^1H\}$ NMR spectrum of $[WPtAu(\mu_3-CR)(CO)_2(PMe_3)_3(\eta-C_5H_5)][PF_6]$ shows no $Me_3{}^{31}PAu-^{195}Pt$ coupling.[14] We conclude, therefore, that there is a degree of direct Pt–Au bonding in the compounds **9**, the AuP groups providing one valence electron and three valence orbitals in cluster bonding, as does the $Cu(PPh_3)$ moiety in $[W_2Cu(\mu_3-CR)(CO)_4(PPh_3)(\eta-C_5H_5)_2]$ which has a *closo* structure for the core μ_3-CW_2Cu atoms.[15]

The $^{31}P-\{^1H\}$ NMR spectrum of compound **9b** differed from those of the other complexes in showing two singlet resonances at δ 48.0 and 48.6 of approximately equal intensity, with $^{195}Pt-^{31}P$ couplings of 100 and 110 Hz, respectively. This may be explained by the presence of a chromatographically inseparable mixture of two sets of diastereoisomers. As has been discussed previously in other chain systems,[12b] the μ-C≡W groups in the species **7** are prochiral and approach of the Pt(cod) reagent from one side or the other would give rise to a chiral μ_3-C centre. Since **9b** has two such chiral groups this results in the possibility of a mixture of two diastereoisomeric pairs. It is noteworthy that the observed ratio of isomers from the $^{31}P-\{^1H\}$ NMR data approaches the theoretically expected value of 1:1. It is to be expected that the chemical shift difference for the two isomeric pairs would be greater in the $^{31}P-\{^1H\}$ than in the ^1H NMR spectrum and this, together with the broadness of the observed signals in the latter due to overlapping peaks, might account for the observation of duplicate resonances in the former spectrum only. As mentioned above, unfortunately a satisfactory $^{13}C-\{^1H\}$ NMR spectrum of **9b** could not be measured. The apparent presence of only one species in the $^{31}P-\{^1H\}$ NMR spectra of **9c**–**9e** may be due to the greater separation of the chiral centres resulting in the two sets of peaks being unresolved. Moreover, conformer constraints imposed on **7a**, discussed above, may favour only one face for approach of the Pt(cod) groups, leading to the formation of only one set of diastereoisomers for **9a**, and therefore the observation of a single ^{31}P resonance.

During the course of the work described herein some reactions were investigated between the compounds **7** and $[Pt(nb)(PMe_2Ph)_2]$ (nb = norbornene), generated *in situ* from $[Pt(nb)_3]$ and two equivalents of PMe_2Ph. Both **7a** and **7e** reacted with $[Pt(nb)(PMe_2Ph)_2]$ to give the previously reported compound **5**.[4b] Evidently these reactions proceed with displacement of the $Ph_2P(CH_2)_nPPh_2$ ligands from the gold centres in **7a** or **7e** by free PMe_2Ph present in the mixtures, thus affording the kinetically more stable product **5**. Despite this result, it is likely that the compounds **7** can be used as precursors to more complex cluster species *via* addition of metal–ligand fragments to the RC≡W groups. In this manner new types of metal clusters should be accessible, provided the ligands attached to the metal fragments do not dissociate and attack the gold centres.

Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C, and all solvents were freshly distilled over appropriate drying agents before use. Chromatography columns *ca.* 15 cm long and 3 cm in diameter were packed with alumina (Brockman activity II), and all experiments were done under oxygen-free nitrogen using Schlenk-tube techniques. The NMR measurements were made using a Bruker AMX 360 spectrometer and IR spectra were recorded with a Bruker IFS 25 spectrophotometer. The reagents $[NEt_4][W(\equiv CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$,[3,13] $[Pt(cod)_2]$ and $[Pt(nb)_3]$[16] were prepared by procedures described earlier.

The compounds $[Au_2Cl_2\{\mu-Ph_2P(CH_2)_nPPh_2\}]$ (n = 2–6) and $[Au_2Cl_2(\mu-Ph_2PCH=CHPPh_2)]$ were prepared in quantitative yield by treating [AuCl(tht)] (tht = tetrahydrothiophene)[17] in CH_2Cl_2 with 0.5 equivalent of the appropriate bidentate phosphine. Addition of light petroleum or trituration with diethyl ether affords the desired products, which were dried *in vacuo*. The compounds $[Au_2Cl_2\{\mu-Ph_2P(CH_2)_nPPh_2\}]$ [n = 2 and 6) and $[Au_2Cl_2(\mu-Ph_2PCH=CHPPh_2)]$ have been obtained previously by alternative syntheses.[18] The $^{31}P-\{^1H\}$ NMR spectra display singlet resonances at δ 31.9 (for n = 2, lit.,[18b] δ 31.5), 27.2 (for n = 3), 30.2 (for n = 4), 30.0 (for n = 5 and 6), and at δ 13.2 and 29.6 for the *cis* and *trans* isomers of $[Au_2Cl_2(\mu-Ph_2PCH=CHPPh_2)]$, respectively.

Synthesis of the Complexes $[W_2Au_2(\mu-CR)_2\{\mu-Ph_2P(CH_2)_nPPh_2\}(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$.—In a typical preparation, $[Au_2Cl_2\{\mu-Ph_2P(CH_2)_6PPh_2\}]$ (0.36 g, 0.39 mmol) was added to a CH_2Cl_2 (20 cm^3) solution containing $[NEt_4][W(\equiv CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ (0.50 g, 0.79 mmol) and $TlBF_4$ (0.25 g, 0.87 mmol), and the mixture was stirred for *ca.* 40 min. The colour changed from orange to brown and a grey precipitate of TlCl was observed. The mixture was filtered through a Celite plug (*ca.* 3 cm) and solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 3:2) and chromatographed at −20 °C. Elution with the same solvent mixture yielded an orange-brown fraction which was collected. Removal of solvent *in vacuo* gave a red-brown residue which was crystallised from CH_2Cl_2–light petroleum (*ca.* 40 cm^3, 1:20) to afford brown *microcrystals* of $[W_2Au_2(\mu-CR)_2\{\mu-Ph_2P(CH_2)_6PPh_2\}(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$ **7e** (0.30 g), washed with light petroleum (3 × 15 cm^3) and dried *in vacuo*. Further elution of the chromatography column with CH_2Cl_2 gave a second brown fraction which, after removal of solvent *in vacuo*, was identified by IR spectroscopy as $[NEt_4][W_2Au(\mu-CR)_2(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$ (*ca.* 0.15 g), the tetraethylammonium salt of **3**.

A similar procedure was used to obtain the compounds **7a** (0.43 g), **7b** (0.065 g), **7c** (0.14 g) and **7d** (0.27 g). The quantities of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ employed were 0.79, 0.40, 0.40 and 0.95 mmol, respectively, together with, in each synthesis, 0.5 equivalent of the appropriate $[Au_2Cl_2\{\mu-Ph_2P(CH_2)_nPPh_2\}]$ compound and excess of $TlBF_4$.

Synthesis of the Complexes $[W_2Au_2(\mu\text{-}CR)_2(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$.—A CH_2Cl_2 (20 cm^3) solution containing a mixture of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.25 g, 0.40 mmol) and $TlBF_4$ (0.13 g, 0.45 mmol) was treated with $[Au_2Cl_2(\mu\text{-}Z\text{-}Ph_2PCH{=}CHPPh_2)]$ (0.17 g, 0.20 mmol), and the mixture was stirred for *ca.* 30 min. After filtration through a Celite pad (*ca.* 3 cm), solvent was removed *in vacuo*. The brown residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 3:2) and chromatographed at −20 °C. Elution with the same solvent mixture gave initially a trace of an unidentified yellow fraction. Further elution removed an orange-brown band. Removal of solvent *in vacuo* from the eluate afforded a brown solid which was crystallised from CH_2Cl_2–light petroleum (30 cm^3, 1:15) to yield orange *microcrystals* of $[W_2Au_2(\mu\text{-}CR)_2(\mu\text{-}Z\text{-}Ph_2PCH{=}CHPPh_2)(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8a** (0.045 g), washed with light petroleum (3 × 10 cm^3) and dried *in vacuo*. Elution of the chromatography column with neat CH_2Cl_2 led to the recovery of $[NEt_4][W_2Au(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ (*ca.* 0.13 g), formed as a by-product.

The compound $[W_2Au_2(\mu\text{-}CR)_2(\mu\text{-}E\text{-}Ph_2PCH{=}CHPPh_2)(CO)_4(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8b** (0.16 g) was similarly obtained from $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.40 mmol), $[Au_2Cl_2(\mu\text{-}E\text{-}Ph_2PCH{=}CHPPh_2)]$ (0.20 mmol) and $TlBF_4$ (0.45 mmol).

Synthesis of the Complexes $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_4(cod)_2(\eta^5\text{-}C_2B_9H_9Me_2)_2]$.—In a representative synthesis of this type of compound a three-necked round-bottom flask (100 cm^3) was charged with thf (20 cm^3) and maintained at 0 °C while the solvent was saturated with C_2H_4. The compound $[Pt(cod)_2]$ (0.050 g, 0.12 mmol) was added, and the solution was stirred for *ca.* 5 min under an atmosphere of C_2H_4 to labilise cod ligands from platinum.[16] Complex **7a** (0.099 g, 0.06 mmol) was added, and the mixture was warmed slowly to room temperature with stirring. Infrared spectral measurements revealed that the reaction was complete in *ca.* 20 min, after which period solvent was removed *in vacuo*. The brown residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 3:2) and chromatographed at −20 °C using the same solvent mixture. Continued elution, increasing the proportion of CH_2Cl_2 to light petroleum to 7:2, afforded a brown fraction. Removal of solvent *in vacuo* gave a brown residue which was crystallised from CH_2Cl_2–light petroleum (25 cm^3, 1:4) to yield *microcrystals* of $[W_2Pt_2Au_2(\mu_3\text{-}CR)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_4(cod)_2(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **9a** (0.046 g), after washing with light petroleum (2 × 10 cm^3) and drying *in vacuo*.

A similar procedure was used to prepare the compounds **9b** (0.084 g), **9c** (0.054 g), **9d** (0.090 g), and **9e** (0.041 g) from $[Pt(cod)_2]$ (2 equivalents) and the complexes **7b**, **7c**, **7d** and **7e**, respectively.

Crystal Structure Determination.—Crystals of compound **7c** were grown by slow diffusion of a dichloromethane solution into layered light petroleum. The X-ray measurements were obtained from a clear red rectangular crystal (0.164 × 0.360 × 0.443 mm). Crystal data and relevant parameters are summarized in Table 5. The final cell parameters were determined at high angles. The 3809 collected reflections (*h* 0–15, *k* 0–13, *l* −16 to 16) showed a slow decay of −0.1145% h^{-1} which

Table 5 Data for crystal structure analysis of compound **7c**

Molecular formula	$C_{56}H_{72}Au_2B_{18}O_4P_2W_2\cdot CH_2Cl_2$
M	1912.3
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	16.7386(12)
b/Å	14.1585(10)
c/Å	15.6820(9)
β/°	90.828(5)
U/Å^3	3709.2(4)
Z	2
D_c/Mg m^{-3}	1.712
$F(000)$	1816
μ(Mo-Kα)/cm^{-1}	72.49
T/K	292
Diffractometer	Enraf–Nonius CAD4-F
Scan type	ω–2θ
Scan speed/° min^{-1}	0.43–3.44
Scan range (ω/°)	1.15 + 0.34 tanθ
2θ range/°	3.0–40.0
Radiation	Mo-Kα ($\bar{\lambda}$ = 0.710 73 Å)
Observed data [$F \geqslant 4.0\sigma(F)$]	3000
Data-to-parameter ratio	7.2:1
R, R' (R_{all})	0.0296, 0.0352 (0.0462)
R_{int}	0.033
S	1.03
Residual density (maximum, minimum)/e Å^{-3}	0.95, −0.60

Table 6 Atomic positional parameters (fractional coordinates, × 10^6) for compound **7c** with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Au	2341(1)	−54(1)	4149(1)	C(23)	4307(7)	1555(8)	5727(7)
W	2453(1)	1235(1)	2803(1)	C(24)	5078(6)	1434(8)	5476(7)
P	1819(1)	−1103(2)	5104(1)	C(25)	5206(7)	1183(9)	4643(8)
C(1)	1688(6)	1970(6)	1661(5)	C(26)	4584(7)	1029(9)	4076(7)
C(2)	1938(7)	1501(7)	808(6)	C(27)	5760(7)	1571(11)	6088(8)
C(3)	1077(6)	1464(6)	2325(6)	C(31)	1580(5)	−2269(6)	4710(5)
C(4)	719(7)	478(7)	2102(7)	C(32)	1144(6)	−2877(7)	5203(6)
B(1)	1219(7)	1850(8)	3328(7)	C(33)	999(7)	−3794(7)	4959(6)
B(2)	1965(7)	2750(8)	3291(6)	C(34)	1291(7)	−4099(8)	4194(7)
B(3)	2262(7)	2763(7)	2213(6)	C(35)	1728(7)	−3489(9)	3696(8)
B(4)	1459(7)	3133(7)	1579(7)	C(36)	1857(6)	−2581(7)	3949(6)
B(5)	695(7)	2317(8)	1630(8)	C(41)	2508(5)	−1251(5)	5992(5)
B(6)	397(7)	2261(9)	2701(7)	C(42)	2774(6)	−473(7)	6430(5)
B(7)	951(8)	3055(8)	3294(8)	C(43)	3321(6)	−507(6)	7072(6)
B(8)	1601(8)	3608(8)	2600(7)	C(44)	3628(6)	−1357(6)	7327(6)
B(9)	651(9)	3333(9)	2255(8)	C(45)	3368(6)	−2159(7)	6913(7)
C(10)	2438(9)	−67(8)	2351(7)	C(46)	2816(6)	−2113(6)	6242(7)
O(10)	2393(8)	−826(7)	2056(6)	C(51)	904(5)	−609(6)	5544(5)
C(11)	3500(9)	1332(9)	2212(8)	C(52)	301(5)	−382(7)	4856(5)
O(11)	4100(6)	1385(8)	1876(6)	C(91)	4183(9)	3855(9)	4377(9)
C(20)	3177(5)	1027(6)	3704(6)	Cl(1)	4756(7)	3963(9)	3435(7)
C(21)	3808(5)	1162(6)	4315(5)	Cl(2)	3569(7)	4863(8)	4531(6)
C(22)	3679(6)	1431(7)	5144(5)				

constituted a maximum correction of 1.119 18. After the intensity data were corrected for Lorentz and polarisation effects, an empirical absorption correction (maximum, minimum transmission factors = 0.6026, 0.9993) was made. From the remaining independent data (3441), 3000 were observed [$F \geqslant 4.0\sigma(F)$, $R_{int} = 0.033$]. Systematic absences ($h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$) yielded the space-group assignment.

The structure was solved by the heavy-atom Patterson (Au, W, P) and Fourier methods and refined using the SHELXTL-PC [19] package of programs. The structural model was refined by the blocked full-matrix least-squares method. After applying a secondary extinction correction [$g = 1.5(2) \times 10^{-4}$ e^{-2}] and anisotropic refinement for all non-hydrogen atoms, the R factors stabilised with an average shift/error value of 2.0×10^{-2}. Hydrogen atomic positions were calculated (C–H 0.96 and B–H 1.10 Å) and not refined. The minimised quantity was $\Sigma w||F_o| - |F_c||^2$ and the weighting scheme was $w^{-1} = \sigma^2(F) + 0.0018 F^2$. The final Fourier difference map showed the highest peak to be 0.95 e Å^{-3} in the vicinity of the Au atom. Elsewhere only random fluctuations were observed. Atomic scattering factors were taken from ref. 20. Final atomic positional parameters for non-hydrogen atoms are given in Table 6.

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

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