Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 114.¹ Ditungsten–Digold Compounds having two W(\equiv CC₆H₄Me-4)-(CO)₂(η^5 -C₂B₉H₉Me₂) Fragments linked by AuP(Ph)₂(CH₂)_n(Ph)₂PAu (n = 2-6) Groups*

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Treatment of 1 equivalent of the reagent [NEt₄][W(\equiv CR)(CO)₂(η^5 -C₂B₉H₉Me₂)] (R = C₆H₄Me-4), in the presence of TIBF₄, with 0.5 equivalent of the compounds [Au₂Cl₂(μ -Ph₂P(CH₂)_nPPh₂)] (n = 2-6) in CH₂Cl₂ affords the complexes [W₂Au₂(μ -CR)₂(μ -Ph₂P(CH₂)_nPPh₂)(CO)₄(η^5 -C₂B₉H₉Me₂)₂]. The crystal structure of the species with n = 4 has been determined by X-ray crystallography, confirming that the molecule has two RC=W(CO)₂(η^5 -C₂B₉H₉Me₂) fragments bridged by an AuP(Ph)₂CH₂CH₂CH₂CH₂(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 [W₂Au₂(μ -CR)₂(μ -Z or *E*-Ph₂PCH=CHPPh₂)(CO)₄(η^5 -C₂B₉H₉Me₂)₂] have been prepared from reactions between the gold compounds [Au₂Cl₂(μ -Z or *E*-Ph₂-PCH=CHPPh₂)] (cod = cycloocta-1,5-diene) to the complexes [W₂Au₂(μ -CR)₂(μ -Ph₂P(CH₂)_nPPh₂)(CO)₄(η^5 -C₂B₉H₉Me₂)₂]. The NMR data (¹H, ¹³C-{¹H}, ³¹P-{¹H} and ¹¹B-{¹H}) for the new complexes are reported and discussed.

Salts of the anionic alkylidyne metal complexes [M(=CR)- $(CO)_2(\eta^5 - C_2 B_9 H_9 R'_2)]^-$ (M = W or Mo; R = alkyl, aryl or alkynyl; $\mathbf{R}' = \mathbf{M}\mathbf{e}$ or \mathbf{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(PPh₃)₂]- $[W(\equiv CR)(CO)_2(\eta^5 - C_2B_9H_9Me_2)]$ (R = C₆H₄Me-4) and [AuCl(PPh₃)] in thf (tetrahydrofuran) in the presence of TlPF₆.³ The structure of the product, $[WAu(\mu-CR)(CO)_2$ - $(PPh_3)(\eta^5-C_2B_9H_9Me_2)$] 1, was established by X-ray crystallography, a study which revealed that the tungsten-gold bond was semibridged by the *p*-tolylmethylidyne group $[\mu$ -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 [NEt₄][WAuCl(μ -CR)(CO)₂(η ⁵-C₂B₉H₉Me₂)] 2,^{4a} $[N(PPh_{3})_{2}][W_{2}Au(\mu-CR)_{2}(CO)_{4}(\eta^{5}-C_{2}B_{9}H_{9}Me_{2})_{2}] \qquad 3,^{3} \\ [W_{2}Au(\mu-CR)_{2}(CO)_{4}(\eta^{5}-C_{2}B_{9}H_{9}Me_{2})(\eta-C_{5}H_{5})] \ 4, [WPtAu \begin{array}{l} (\mu_{3}\text{-}CR)(CO)_{2}(PMe_{2}Ph)_{3}(\eta^{5}\text{-}C_{2}B_{9}H_{9}Me_{2})] \ \textbf{5} \ \text{and} \ [W_{2}PtAu-(\mu-CR)(\mu_{3}\text{-}CR)(CO)_{4}(cod)(\eta^{5}\text{-}C_{2}B_{9}H_{9}Me_{2})(\eta-C_{5}H_{5})] \ \textbf{6} \\ (cod = cycloocta-1,5\text{-diene})^{4b} \ \text{exemplify the diverse nature of} \end{array}$ the products that have been obtained.

In this paper we describe the synthesis of ditungsten-digold compounds in which two AuW(μ -CR)(CO)₂(η^5 -C₂B₉H₉Me₂) moieties are linked by bidentate Ph₂P(CH₂)_nPPh₂ (n = 2-6) or Ph₂PCH=CHPPh₂ 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 metalligand fragments to afford a new class of chain-like metal species.

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



Results and Discussion

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

Table 1 Analytical^a and physical data for the complexes

		Yield		Analysis (%)	
Compound ^b	Colour	(%)	$v_{max}(CO)^{c}/cm^{-1}$	С	Н
7a $[W_2Au_2(\mu-CR)_2{\mu-Ph_2P(CH_2)_2PPh_2}(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$	Orange	61	2005vs, 1936vs	36.1	4.2
				(36.1)	(3.8)
7b $[W_2Au_2(\mu-CR)_2\{\mu-Ph_2P(CH_2)_3PPh_2\}(CO)_4(\eta^3-C_2B_9H_9Me_2)_2]$	Brown	18	2003vs, 1935vs	36.2	3.9
				(36.4)	(3.9)
7c $[W_2Au_2(\mu-CR)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}(CO)_4(\eta^3-C_2B_9H_9Me_2)_2]$	Red	40	2003vs, 1935vs	37.8	4.0
	YieldColour $(\%)$ $v_{max}(CO)^c/cm^{-1}$ C $_{2})_{2}$ Orange612005vs, 1936vs36.1 $_{2})_{2}$ Brown182003vs, 1935vs36.2 $_{2})_{2}$ Red402003vs, 1935vs37.8 $_{2})_{2}$ Red312002vs, 1933vs37.9 $_{2})_{2}$ Brown412003vs, 1934vs37.1 $_{2})_{2}$ Brown412003vs, 1934vs37.1 $_{2})_{2}$ Orange131975vs (br), 1913s (vbr), 36.4 $_{1884m}(sh)$ (36.1Me_{2})_{2}Ochre452005vs, 1936vs35.8Brown35 ⁴ 1942vs (br), 1846m (vbr), 33.91806m (vbr)(34.9)Beige42 ⁴ 1948vs, 1938s (sh), 1844m(vbr), 1791m (br)Beige45 ⁴ Beige45 ⁴ 1949vs (br), 1846m (vbr), 36.51796m (vbr)(35.8)1796m (vbr)(35.8)Tan31 ⁴ 1949vs (br), 1843m (vbr), 1798m (vbr)	(36.8)	(4.0)		
7d $[W_2Au_2(\mu-CR)_2\{\mu-Ph_2P(CH_2)_5PPh_2\}(CO)_4(\eta^3-C_2B_9H_9Me_2)_2]$	Red	31	2002vs, 1933vs	37.9	4.3
	_			(37.2)	(4.1)
$7e \left[W_{2}Au_{2}(\mu-CR)_{2} \left\{ \mu-Ph_{2}P(CH_{2})_{6}PPh_{2} \right\} (CO)_{4}(\eta^{3}-C_{2}B_{9}H_{9}Me_{2})_{2} \right]$	Brown	41	2003vs, 1934vs	37.1	4.6
	_			(37.6)	(4.1)
8a $[W_2Au_2(\mu-CR)_2(\mu-Z-Ph_2PCH=CHPPh_2)(CO)_4(\eta^3-C_2B_9H_9Me_2)_2]$	Orange	13	1975vs (br), 1913s (vbr),	36.4	4.6
			1884m (sh)	(36.1)	(3.7)
8b $[W_2Au_2(\mu-CR)_2(\mu-E-Ph_2PCH=CHPPh_2)(CO)_4(\eta^3-C_2B_9H_9Me_2)_2]$	Ochre	45	2005vs, 1936vs	35.8	3.7
	-			(36.1)	(3.7)
9a $[W_2Pt_2Au_2(\mu_3-CR)_2{\mu-Ph_2P(CH_2)_2PPh_2}(CO)_4(cod)_2-$	Brown	35	^a 1942vs (br), 1846m (vbr),	33.9	3.8
$(\eta^3 - C_2 B_9 H_9 M e_2)_2$			1806m (vbr)	(34.9)	(3.8)
9b $[W_2Pt_2Au_2(\mu_3-CR)_2\{\mu-Ph_2P(CH_2)_3PPh_2\}(CO)_4(cod)_2$ -	Beige	42	^a 1945vs (br), 1844m (vbr),	35.4	3.9
$(\eta^3 - C_2 B_9 H_9 M e_2)_2$			1788m (vbr)	(35.2)	(3.9)
9c $[W_2Pt_2Au_2(\mu_3-CR)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}(CO)_4(cod)_2-$	Beige	41	^a 1948vs, 1938s (sh), 1844m		
$(\eta^3 - C_2 B_9 H_9 M e_2)_2]^e$			(vbr), 1791m (br)		
9d $[W_2Pt_2Au_2(\mu_3-CR)_2\{\mu-Ph_2P(CH_2)_5PPh_2\}(CO)_4(cod)_2-$	Beige	45	^a 1949vs (br), 1846m (vbr),	36.5	4.0
$(\eta^{3}-C_{2}B_{9}H_{9}Me_{2})_{2}$	_		1796m (vbr)	(35.8)	(4.3)
9e $[W_2Pt_2Au_2(\mu_3-CR)_2\{\mu-Ph_2P(CH_2)_6PPh_2\}(CO)_4(cod)_2-(\eta^5-C_2B_9H_9Me_2)_2]^e$	Tan	31	" 1949vs (br), 1843m (vbr), 1798m (vbr)		

^a Calculated values are given in parentheses. ^b $R = C_6H_4$ Me-4. ^c Measured in CH₂Cl₂ unless otherwise stated. All the complexes show a broad band in the range 2500–2550 cm⁻¹ due to v(BH). ^d Measured in thf. ^e Satisfactory microanalytical data not available.



species with AuP(Ph)₂(CH₂)_n(Ph)₂PAu chains, 0.5 equivalent of the digold compounds $[Au_2Cl_2\{\mu-Ph_2P(CH_2)_nPPh_2\}]$ was added to CH₂Cl₂ solutions of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ (R = C₆H₄Me-4), with TlBF₄ present to remove the chloride as TlCl. Column chromatography on alumina separated the ditungsten-digold compounds $[W_2Au_2-(\mu-CR)_2\{\mu-Ph_2P(CH_2)_nPPh_2\}(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$ (n = 27a, 37b, 47c, 57d, or 67e) 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 Ph₂P(CH₂)_nPPh₂ from gold by the RC=W group of $[W(\equiv CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]^-$ 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 $[Au_2Cl_2(\mu-cis- \text{ or } trans-Ph_2PCH=CHPPh_2)]$, afforded the species $[W_2Au_2(\mu-CR)_2(\mu-Ph_2PCH=CHPPh_2)(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$ 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 $(\eta^{5}-C_{2}B_{9}H_{9}Me_{2})(OC)_{2}W \equiv CC_{6}H_{4}Me-4$ fragments are bridged by an AuP(Ph)₂CH₂CH₂CH₂CH₂(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 $\beta\text{-}CH_2$ groups in the PCH₂CH₂CH₂CH₂CH₂P 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 threemembered 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" for the complexes

- Compound 1H^b (δ) 2.20 (s, 12 H, CMe), 2.32 (s, 6 H, Me-4), 2.84 (s, 4 H, 7a CH₂), 7.13 [half of (AB)₂, 4 H, C₆H₄, J(AB) 8], 7.46-7.60 (m, 24 H, Ph and C₆H₄) 1.96 (m, 2 H, β-CH₂), 2.12 (s, 12 H, CMe), 2.32 (s, 6 7h
 - H, Me-4), 2.81 (m, 4 H, α-CH₂), 7.10 [half of (AB)₂, 4 H, C₆H₄, J(AB) 8], 7.42-7.55 (m, 24 H, Ph and C₆H₄)
- 7c 1.81 (m, 4 H, β-CH₂), 2.20 (s, 12 H, CMe), 2.34 (s, 6 H, Me-4), 2.59 (m, 4 H, α-CH₂), 7.17 [half of (AB)₂, 4 H, C₆H₄, J(AB) 8], 7.49–7.65 (m, 24 H, Ph and C₆H₄)
- 1.64 (m, 6 H, β and γ -CH₂), 2.16 (s, 12 H, CMe), 2.31 (s, 6 H, Me-4), 2.55 (m, 4 H, α -CH₂), 7.12 [half of 7d (AB)₂, 4 H, C₆H₄, J(AB) 8], 7.34–7.67 (m, 24 H, Ph and C_6H_4)
- 7e 1.42 (m, 4 H, γ-CH₂), 1.63 (m, 4 H, β-CH₂), 2.19 (s, 12 H, CMe), 2.34 (s, 6 H, Me-4), 2.59 (m, 4 H, α -CH₂), 7.16 [half of (AB)₂, 4 H, C₆H₄, J(AB) 8], 7.49–7.69 (m, 24 H, Ph and C_6H_4) 1.97, * 1.98 (s, 12 H, CMe), 2.27, * 2.29 (s, 6 H, Me-4)
- 8a 6.77, 7.06 [(AB)₂, 8 H, C₆H₄, J(AB) 8], *6.83, *7.09 [(AB)₂, 8 H, C₆H₄, 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] 8b
 - 2.17 (s, 12 H, CMe), 2.32 (s, 6 H, Me-4), 7.10 [half of (AB)₂, 4 H, C₆H₄, J(AB) 8], 7.53–7.63 (m, 26 H, CH=CH, Ph and C_6H_4)
- 1.78 (m, 4 H, CH₂ of cod), 2.14, 2.18, 2.35 (s × 3, 18 H, CMe and Me-4), 2.55 (m, 4 H, CH₂ of cod), 2.74 (m, 4 H, CH₂), 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, C₆H₄, J(AB) 8], 7.44–7.51 (m, 20 H, Ph) 96 ^d
 - $1.72 (m, 2 H, \beta$ -CH₂), 1.87 (m, 4 H, CH₂ of cod), 2.14, 2.17, 2.33 (s \times 3, 18 H, CMe and Me-4), 2.46 (m, 8 H, CH₂ of cod), 2.61 (m, 4 H, CH₂ of cod), 2.76 (m, 4 H, α-CH₂), 4.59, 4.68, 5.18, 5.44 (m × 4, 8 H, CH of cod), 7.03, 7.13 [(AB)₂, 8 H, C₆H₄, J(AB) 8], 7.19-7.76 (m, 20 H, Ph)
 - 1.58 (m, 4 H, β-CH₂), 1.89 (m, 4 H, CH₂ of cod), 2.14, 2.20, 2.34 (s \times 3, 18 H, CMe and Me-4), 2.47 (m, 8 H, α -CH₂ and CH₂ 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, C₆H₄, J(AB) 8], 7.35-7.68 (m, 20 H, Ph)
- 9d 4 1.51 (m, 6 H, β- and γ-CH₂), 1.90 (m, 4 H, CH₂ of cod), 2.14, 2.19, 2.31 (s × 3, 18 H, CMe and Me-4), 2.47 (m, 8 H, α-CH₂ and CH₂ of cod), 4.63, 4.77, 5.22, 5.43 (m \times 4, 8 H, CH of cod), 7.08, 7.17 [(AB)₂, 8 H, C₆H₄, J(AB) 8], 7.35–7.65 (m, 20 H, Ph) 9e⁴
 - 1.35 (m, 4 H, γ-CH₂), 1.51 (m, 4 H, β-CH₂), 1.90 (m, 4 H, CH₂ of cod), 2.14, 2.22, 2.35 (s × 3, 18 H, CMe and Me-4), 2.47 (m, 8 H, α -CH₂ and CH₂ 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, C₆H₄, J(AB) 8], 7.23–7.55 (m, 20 H. Ph)

¹³C^c (δ)

292.8 [(AXX'), µ-C, |J(AX) + J(AX')| 25], 219.1 [CO, J(WC) 162], 149.0 $[C^{1}(C_{6}H_{4})]$, 142.3-127.8 (Ph and $C_{6}H_{4}$), 66.5 (CMe), 31.1 (CMe), 24.6 $[(AXX'), CH_{2}, |J(AX) + AX')|$ 38], 22.0 (Me-4)

²295.5 (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 [C¹(C₆H₄)], 142.3–127.4 (Ph and C₆H₄), *66.8, 66.6 (CMe), 31.2, * 30.9 (CMe), 29.6 [(AXX'), α -CH₂, |J(AX) + J(AX')| 46], 22.0, *21.9 (Me-4), 21.4 [t, β-CH₂, J(PC) 5]

*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 [C¹(C₆H₄)], 142.2–129.0 (Ph and C₆H₄), 66.6, ⁺66.4 (CMe), 31.2, * 30.9 (CMe), 28.3 [d, α-CH₂, J(PC) 33], 27.5 [(AXX'), β- CH_2 , |J(AX) + J(AX')| 23], 22.0, *21.1 (Me-4)

 CH_2 , $[p(RA) + J(RA)]_{2,2}$, 22.0, 21.1 (Me-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 [C¹(C₆H₄)], 142.2–129.3 (Ph and C₆H₄), 66.6, *66.2 (CMe), 32.3 [t, γ-CH₂, J(PC) 16], 31.2, *30.9 (CMe), 28.4 [d, α-CH₂, J(PC) 33], 25.5 [d, β-CH₂, J(PC) 5], *22.7, 22.0 (Me-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 [C¹(C₆H₄)], 142.1–129.4 (Ph and C₆H₄), 66.6, *65.4 (CMe), 31.2 (CMe), 30.7 [d, γ-CH₂, J(PC) 16], 28.4 [d, α-CH₂, J(PC) 33], 26.0 [d, β-CH₂, J(PC) 3], 22.0, *21.0 (Me-4)

|J(AX) + J(AX')| 62], 138.5–127.8 (Ph and C₆H₄), 64.7, * 59.6 (CMe), 31.1, 30.8 (CMe), *21.9, 21.4 (Me-4)

293.1 [(AXX'), μ-C, |J(AX) + J(AX')| 26], 219.1 [CO, J(WC) 162], 148.9 $[C^{1}(C_{6}H_{4})], 142.4 [C^{4}(C_{6}H_{4})], 141.9 [(AXX'), CH=CH, |J(AX) + J(AX')]$ 50], 134.1–127.0 (Ph and C₆H₄), 66.8 (CMe), 31.2 (CMe), 22.0 (Me-4)

290.4 [d, μ₃-C, *J*(PC) 14], 231.5, 219.1 (CO), 153.5 [C¹(C₆H₄)] 136.4–124.5 (Ph and C₆H₄), 106.5, 106.2, 99.6, 93.8 (CH of cod) 66.3, 64.8 (CMe), 32.4 [t, γ-CH₂, J(PC) 16], 31.0, 30.8, 30.5 (CH₂ of cod), 30.2 (br, CMe), 28.7 [d, α-CH₂, J(PC) 32], 28.4 (CH₂ of cod), 25.3 [d, β-CH₂, J(PC) 5], 21.2 (Me-4)

289.8 [d, μ_3 -C, J(PC) 15, J(PtC) 571], 231.4, 219.6 (CO), 153.5 [C¹(C₆H₄)], 136.4–124.5 Ph and C₆H₄), 106.7, 106.1, 99.7, 93.6 (CH of cod), 66.3, 64.9 (CMe), 32.0, 30.9 (CH₂ of cod), 30.7 [d, γ -CH₂, J(PC) 16], 30.5, 30.2 (CH₂ of cod), 30.0 (CMe), 28.7 [d, α -CH₂, J(PC) 32], 25.8 [d, β -CH₂, J(PC) 3], 21.2 (Me-4)

^a Chemical shifts δ in ppm, coupling constants in Hz, measurements at ambient temperatures in CD₂Cl₂. Asterisked peaks are due to minor isomer (see text). ^b Resonances for B-H protons are not resolved, due to ¹¹B-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 SiMe₄ (δ 0.0). ^d Some CH₂(cod) signals are obscured by other peaks. Signals due to CH groups of cod ligands show ¹⁹⁵Pt satellite peaks in ¹H spectra [J(PtH) ca. 45-75 Hz], and also in ¹³C-{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-C¹ (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 $[175(1)^{\circ}]$ observed for $[WPt(\mu-CC_{6}H_{3}Me_{2}-2,6)(\mu-\sigma,\eta^{5}-C_{2}B_{9} H_8Me_2)(CO)_2(PEt_3)].^{5b}$

The tungsten atoms in compound 7c carry two essentially terminally bound CO groups. The nido-icosahedral 7,8-C2B9-H₉Me₂ 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 squarepyramidal 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°

9a 4

9c d

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(μ -CR)(CO)₂(η^{5} -C₂B₉H₉-Me₂) moieties.

The NMR data (Tables 2 and 3) for compound 7c are in

Table 3	Boror	n-11 and phosphorus-31 NM	R data ^a for the complexes
Comp	ound	¹¹ B ^b (δ)	³¹ P ^c (δ)
7a		-2.9 (3 B), -5.8 (6 B),	55.3 (s)
7b		-2.8 (3 B), -5.8 (6 B),	51.4 (s)
7c		-7.5 (6 B), -9.6 (3 B) -2.8 (3 B), -5.8 (6 B),	53.9 (s)
7d		-7.4 (6 B), -8.1 (3 B) -2.8 (3 B), -5.8 (6 B).	53.0 (s)
70		-7.5 (6 B), -9.8 (3 B) 27 (3 P) 57 (6 P)	52 5 (c)
/e		-7.6 (6 B), -9.6 (3 B)	55.5 (8)
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,
9b		-1.5 (3 B), -6.8 (11 B),	48.6 [s, J (PtP) 110],
9c		-9.6 (4 B) -1.4 (3 B), -6.7 (11 B),	* 48.0 [s, J(PtP) 100] 50.7 [s, J(PtP) 96,
9d		-9.7 (4 B) -1.2 (3 B), -6.8 (11 B),	J(WP) 22] 49.8 [s, J(PtP) 99]
Qe		-9.4 (4 B) -1.1 (3 B) -6.7 (11 B)	50 4 [s 1(PtP) 95
		-9.8 (4 B)	J(WP) 11]

^{*a*} Chemical shifts δ in ppm, coupling constants in Hz, measurements in CD₂Cl₂ at ambient temperatures. ^{*b*} Hydrogen-1 decoupled, chemical shifts are positive to high frequency of BF₃-Et₂O (external). In fully coupled ¹¹B-¹H spectra, J(HB) values are *ca.* 115-135 Hz. ^{*c*} Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H₃PO₄ (external). Asterisked peaks are due to a second isomer.

accord with the structure established by the X-ray diffraction study. The ³¹P-{¹H} NMR spectrum revealed the expected singlet resonance which occured at δ 53.9. For the precursor [Au₂Cl₂{ μ -Ph₂P(CH₂)₄PPh₂}] the ³¹P signal is at δ 30.2 (see Experimental section). The ¹¹B-{¹H} NMR spectrum of 7c, and the other compounds of similar type, displayed four broad peaks (Table 3). In fully coupled ¹¹B 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

Signals in the ¹H NMR spectrum of compound 7c were as expected. However, a duplication of certain peaks in the ¹³C-{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 ³¹P-¹³C coupling (27 Hz) and there were ¹⁸³W satellite peaks [J(WC) 146 Hz]. In the ¹³C-{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 ¹³C 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 ³¹P-¹³C couplings are larger, *e.g.* 59 Hz for [WPt(μ -CC₆H₄Me-4)(CO)₂(PMe₂Ph)₂-(n-C₅H₅)],⁹ than that (27 Hz) found for the major isomer of 7c

 $(\eta-C_3H_5)$],⁹ than that (27 Hz) found for the major isomer of 7c. The ¹³C-{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 ³¹P-¹³C 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 CH₂ backbone.

In contrast with the four compounds 7b-7e, the ${}^{13}C{-}{^{1}H}$ 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)
WB(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)	PC(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–Ć(20)–W	86.6(4)	Au - C(20) - C(21)	110.4(6)	WC(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)
WC(11)-O(11)	180(1)	P-C(31)-C(32)	119.9(7)	PC(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 $[W_2Au_2(\mu-CR)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$ 7c showing the crystallographic numbering scheme

isomer only. An X-ray diffraction study of $[Au_2Cl_2(\mu-Ph_2-PCH_2CH_2PPh_2)]$, 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 CH₂ units in the chain, the AuPPh₂ groups carrying the bulky RC=W(CO)₂(η^5 -C₂B₉H₉-Me₂) fragments are constrained to one conformer. It is noteworthy that the crystal structure of **7c** reveals a transoid arrangement of Au-P groups. A ¹³C-{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 AuPPh₂ groups with respect to the CH₂ backbone seems probable. With **7b**, having three CH₂ 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 [NEt₄]-[W(\equiv CR)(CO)₂(η^5 -C₂B₉H₉Me₂)] and the species [Au₂Cl₂(μ -Ph₂PCH₂PPh₂)] afforded 3 as its [NEt₄]⁺ salt rather than a product structurally similar to the complexes 7. An X-ray crystal structure study¹¹ on [Au₂Cl₂(μ -Ph₂PCH₂PPh₂)] revealed a sterically crowded molecule, making it unlikely that the two Cl⁻ ligands could be successfully replaced by [W(\equiv CR)(CO)₂(η^5 -C₂B₉H₉Me₂)]⁻ 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 [Au₂Cl₂(μ -Me₂PCH₂-CH₂PMe₂)] and [NEt₄][W(\equiv CR)(CO)₂(η^5 -C₂B₉H₉Me₂)] occurred only slowly and surprisingly yielded the tetraethyl-ammonium salt of 3, instead of an analogue of 7a, despite Me₂PCH₂CH₂PMe₂.

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, ¹³C-{¹H}, and ³¹P-{¹H} NMR spectra (Tables 2 and 3). The absence of any ³¹P-¹³C coupling on the alkylidyne carbon resonance (δ 303.3) of the minor isomer may indicate that in this species steric constraints about the two AuPPh₂ units, due to the proximity of the bulky $W(CO)_2(\eta^5 - C_2B_9H_9Me_2)$ 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 [W2Pt2Au2(µ3-CR)2-91 $\{\mu - Ph_2P(CH_2)_2PPh_2\}(CO)_4(cod)_2(\eta^5 - C_2B_9H_9Me_2)_2\}$ 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 ${}^{13}C{}^{1H}$ data discussed below. The ¹H NMR spectra were as expected, although in some cases not all the CH₂ 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 ¹⁹⁵Pt–¹H coupling (*ca.* 45–75 Hz). In the spectrum of **9a** two of the four CH(cod) multiplets overlap.

The ${}^{13}C-{}^{1}H$ 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 CH₂ chains, were appreciably more soluble, and their ${}^{13}C-{}^{1}H$ 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 CH₂(cod) groups, the former showing ¹⁹⁵Pt-¹³C 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 ¹³C-{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 ¹³C-{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 ¹⁹⁵Pt satellite bands [*J*(PtC) 571 Hz]. In the ¹³C-{¹H} NMR spectrum of [WPtAu(μ_3 -CC₆H₄Me-4)(CO)₂(PPh₃)(cod)(η^5 -C₂B₉H₉Me₂)],¹³ a compound structurally similar to **5** but having Au(PPh₃) 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 Ph₂P(CH₂)_nPPh₂ chain. What remains at issue is whether the µ3-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(μ_3 -CR)(CO)₂(PMe₃)₃(η -C₅H₅)][PF₆], 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 ³¹P- $\{^{1}H\}$ 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 ¹⁹⁵Pt satellites. The ${}^{31}PAu_{-}^{195}Pt$ coupling (72–99 Hz) is too large for a three-bond value. Moreover, the ${}^{31}P-{}^{1}H$ NMR spectrum of [WPtAu(μ_3 -CR)(CO)₂(PMe₃)₃(η -C₅H₅)][PF₆] shows no Me₃³¹PAu-¹⁹⁵Pt 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(PPh₃) 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 -CW₂Cu atoms.¹⁵

The ³¹P-{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 ¹⁹⁵Pt-³¹P 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 ³¹P-{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 ³¹P-{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 ¹³C-{¹H} NMR spectrum of 9b could not be measured. The apparent presence of only one species in the ${}^{31}P-{}^{1}H$ 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 ³¹P resonance.

During the course of the work described herein some reactions were investigated between the compounds 7 and $[Pt(nb)(P-Me_2Ph)_2]$ (nb = norbornene), generated *in situ* from $[Pt(nb)_3]$ and two equivalents of PMe₂Ph. 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 Ph₂P(CH₂)_nPPh₂ ligands from the gold centres in 7a or 7e by free PMe₂Ph 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 [NEt₄][W(\equiv CR)(CO)₂(η^5 -C₂B₉H₉Me₂)],^{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 CH₂Cl₂ 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 ³¹P-{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 = 5and 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 [W₂Au₂(µ-CR)₂{µ-Ph₂P(CH₂)_n- PPh_2 (CO)₄(η^5 -C₂B₉H₉Me₂)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 CH₂Cl₂ (20 cm³) solution containing [NEt₄][W(=CR)- $(CO)_2(\eta^5-C_2B_9H_9Me_2)$] (0.50 g, 0.79 mmol) and TlBF₄ (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 TICI was observed. The mixture was filtered through a Celite plug (ca. 3 cm) and solvent was removed in vacuo. The residue was dissolved in CH₂Cl₂-light petroleum (5 cm³, 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 CH₂Cl₂-light petroleum (ca. 40 cm³, 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 $(3 \times 15 \text{ cm}^3)$ and dried in vacuo. Further elution of the chromatography column with CH₂Cl₂ gave a second brown fraction which, after removal of solvent in vacuo, was identified by IR spectroscopy as [NEt₄][W₂Au(µ- $CR_{2}(CO)_{4}(\eta^{5}-C_{2}B_{9}H_{9}Me_{2})_{2}$] (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 TlBF₄.

Synthesis of the Complexes $[W_2Au_2(\mu-CR)_2(\mu-Ph_2PCH=CHPPh_2)(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$.—A CH₂Cl₂ (20 cm³) solution containing a mixture of $[NEt_4][W(=CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ (0.25 g, 0.40 mmol) and TIBF₄ (0.13 g, 0.45 mmol) was treated with $[Au_2Cl_2(\mu-Z-Ph_2PCH=CHPPh_2)]$ (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 CH₂Cl₂–light petroleum (5 cm³, 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 orangebrown band. Removal of solvent *in vacuo* from the eluate afforded a brown solid which was crystallised from CH₂Cl₂–light petroleum (30 cm³, 1:15) to yield orange *microcrystals* of $[W_2Au_2(\mu-CR)_2(\mu-Z-Ph_2PCH=CHPPh_2)(CO)_4(\eta^5-C_2B_9H_9-$

Table 5 Data for crystal structure analysis of compound 7c

Malagular formula	
	$C_{56}\Pi_{72}Au_{2}B_{18}O_{4}\Gamma_{2}W_{2}C\Pi_{2}CI_{2}$
Mi Crustal system	1912.J
Space group	$P2_1/c$ (no. 14)
a/A	16.7386(12)
b/A	14.1585(10)
c/\mathbf{A}	15.6820(9)
β/°	90.828(5)
$U/Å^3$	3709.2(4)
Z	2
$D_c/\mathrm{Mg}\mathrm{m}^{-3}$	1.712
F(000)	1816
$\mu(Mo-K\alpha)/cm^{-1}$	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/°)	$1.15 + 0.34 \tan\theta$
2θ range/°	3.0-40.0
Radiation	Mo-K α ($\bar{\lambda} = 0.710~73~\text{\AA}$)
Observed data	3000
$[F \ge 4.0\sigma(F)]$	
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,	0.95, -0.60
minimum)/e Å ⁻³	

 Me_{2} [2] 8a (0.045 g), washed with light petroleum (3 × 10 cm³) and dried *in vacuo*. Elution of the chromatography column with neat CH₂Cl₂ led to the recovery of [NEt₄][W₂Au(μ -CR)₂-(CO)₄(η ⁵-C₂B₉H₉Me₂)₂] (*ca.* 0.13 g), formed as a by-product.

The compound $[W_2Au_2(\mu-CR)_2(\mu-E-Ph_2PCH=CHPPh_2)-(CO)_4(\eta^5-C_2B_9H_9Me_2)_2]$ **8b** (0.16 g) was similarly obtained from $[NEt_4][W(=CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ (0.40 mmol), $[Au_2Cl_2(\mu-E-Ph_2PCH=CHPPh_2)]$ (0.20 mmol) and TIBF₄ (0.45 mmol).

Synthesis of the Complexes [W₂Pt₂Au₂(µ₃-CR)₂{µ-Ph₂P- $(CH_2)_n PPh_2$ (CO)₄ (cod)₂ (η^5 -C₂B₉H₉Me₂)₂].—In a representative synthesis of this type of compound a three-necked roundbottom flask (100 cm³) was charged with thf (20 cm³) and maintained at 0 °C while the solvent was saturated with C₂H₄. 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 cm³, 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 CH₂Cl₂-light petroleum (25 cm³, 1:4) to yield microcrystals of $[W_2Pt_2Au_2(\mu_3-CR)_2\{\mu-Ph_2P(CH_2)_2PPh_2\}$ - $(CO)_4(cod)_2(\eta^5-C_2B_9H_9Me_2)_2$] **9a** (0.046 g), after washing with light petroleum (2 \times 10 cm³) 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 ($0.164 \times 0.360 \times 0.443$ 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 6 Atomic positional parameters (fractional coordinates, × 10⁶) for compound 7c with estimated standard deviations in parentheses

Atom	x	у	Ζ	Atom	x	у	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)
Р	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 $[F \ge 4.0\sigma(F), R_{int} = 0.033]$. Systematic absences (h0l, l = 2n + 1)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-PC¹⁹ 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 $\times 10^{-2}$. Hydrogen atomic positions were calculated (C-H 0.96 and B-H 1.10 Å) and not refined. The minimised quantity was $\sum w ||F_0| - |F_c||^2$ 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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