Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 99.[1] Synthesis of the Cluster Compounds [MWCoAu-(μ-CC$_6$H$_4$Me-4)(μ_3-CR)(CO)$_4$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (M = Mo or W, R = C$_6$H$_4$Me-4; M = W, R = Me); Crystal Structure of the Complex [MoWCoAu-(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)-(η^5-C$_2$B$_9$H$_9$Me$_2$)]·CH$_2$Cl$_2$ *

Nicholas Carr, M. Concepción Gimeno, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The trimetal complexes [MWAu(μ-CC$_6$H$_4$Me-4)$_2$(CO)$_4$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (M = Mo or W), with molecular structures based on a MAuW spine and each metal–metal bond bridged by a *p*-tolylmethylidyne group, react with [Co(η-C$_2$H$_4$)$_2$(η-C$_5$Me$_5$)] in CH$_2$Cl$_2$ at room temperature to afford the tetranuclear metal compounds [MWCoAu(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$-(η-C$_5$H$_5$)(η-C$_5$Me$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)]. An *X*-ray diffraction study on the molybdenum-containing product revealed a structure with the Co(η-C$_5$Me$_5$) fragment co-ordinated to the 4-MeC$_6$H$_4$C=W(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$) group of the precursor. The cobalt atom is also bonded to the gold, so the metal core consists of a WCoAu triangle [W–Co 2.597(2), W–Au 2.826(1), and Co–Au 2.580(2) Å] spiked by the molybdenum [Mo–Au 2.763(2) Å]. The *p*-tolylmethylidyne ligands asymmetrically bridge the metal sites. One group spans the Mo–Au bond [μ-C–Au 2.11(1) and μ-C–Mo 1.90(2) Å], and the other the WCoAu triangle [μ-C–Au 2.30(1), μ-C–Co 1.86(1), and μ-C–W 1.97(1) Å]. The Mo, W, and Co atoms are co-ordinated by the η-C$_5$H$_5$, η^5-C$_2$B$_9$H$_9$Me$_2$, and η-C$_5$Me$_5$ groups, respectively. The Mo and W atoms each carry two CO ligands, but one of these attached to tungsten semi-bridges the W–Co bond [W–C–O 163(1)°]. The reaction between [Co(η-C$_2$H$_4$)$_2$(η-C$_5$Me$_5$)] and [W$_2$Au(μ-CMe)(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] affords a mixture of two isomeric products. Their structures correspond to the alternative possibilities of addition of a Co(η-C$_5$Me$_5$) fragment to either the MeC=W(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$) or the 4-MeC$_6$H$_4$C=W(CO)$_2$(η-C$_5$H$_5$) group in the precursor, but the former isomer predominates. The spectroscopic (i.r. and n.m.r.) properties of the new compounds are reported and discussed.

In the preceding paper[1] we described the synthesis of the trimetal compounds [MWAu(μ-CR)(μ-CR')(CO)$_4$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**1**; M = W, R = R' = C$_6$H$_4$Me-4 or Me; R = Me, R' = C$_6$H$_4$Me-4; M = Mo, R = R' = C$_6$H$_4$Me-4). These neutral complexes are related to the gold salts [W$_2$Au(μ-CC$_6$H$_4$Me-4)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$][PF$_6$] (**2**)[2a] and [N(PPh$_3$)$_2$]-[W$_2$Au(μ-CC$_6$H$_4$Me-4)$_2$(CO)$_4$(η^5-C$_2$B$_9$H$_9$Me$_2$)$_2$] (**3**)[2b] by virtue of an isolobal mapping of the C$_5$H$_5$$^-$ ligand with the *nido*-icosahedral fragment η^5-C$_2$B$_9$H$_9$Me$_2$$^{2-}$. Moreover, since Au$^{\mathrm{I}}$ and Pt^0 are isoelectronic, the compounds (**1**)—(**3**) are structurally akin to the earlier reported[3] compound [W$_2$Pt(μ-CC$_6$H$_4$Me-4)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (**4**).

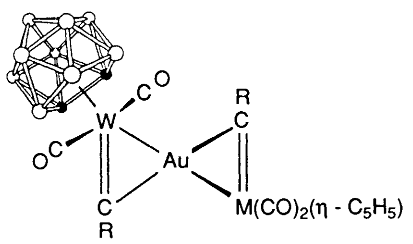
The ditungstenplatinum complex (**4**), as well as related molecules in which the tungsten atom is replaced by molybdenum, or the platinum by nickel, have been used as reagents for preparing numerous polynuclear metal compounds containing bonds between dissimilar transition elements.[4] This has been possible because the C=W bonds present in (**4**) function as sites for the attachment of co-ordinatively unsaturated metal–ligand fragments. The question naturally arises as to whether the species (**1**) can also be used as precursors for the synthesis of metal cluster compounds. However, there is an important and interesting structural difference between the unsaturated sites in the compounds (**1**) and (**4**). In the latter, which has two η-C$_5$H$_5$ groups, the two C=W units are identical, whereas in the former the corresponding C=M (M = Mo or W) fragments differ, due to the asymmetry introduced by having an η-C$_5$H$_5$ and an η^5-C$_2$B$_9$H$_9$Me$_2$ ligand present in the same molecule. Consequently, upon addition of a metal–ligand fragment to the compounds (**1**), one or other of the C=W and C=M groups is likely to be the preferred site for attack. Indeed, in a preliminary test of this possibility, in the preceding paper[1] we showed that addition of Pt(PMe$_2$Ph)$_2$ or Pt(cod) (cod = cyclo-octa-1,5-diene) groups to the compounds (**1**) occurs at the 4-MeC$_6$H$_4$C=W(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$) end of these molecules to afford, respectively, the tetranuclear metal complexes [W$_2$PtAu(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$(cod)(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**5a**) and [MWPtAu(μ-CR')(μ_3-CR)(CO)$_4$-(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**5b**; M = W, R = R' = C$_6$H$_4$Me-4), (**5c**; R = Me, R' = C$_6$H$_4$Me-4), and (**5d**; M = Mo, R = R' = C$_6$H$_4$Me-4). In this paper we report studies on addition of the Co(η^5-C$_5$Me$_5$) fragment to species of type (**1**).

Results and Discussion

At room temperature in CH$_2$Cl$_2$, the compounds (**1a**) and (**1d**) react with 1 equivalent of [Co(η-C$_2$H$_4$)$_2$(η-C$_5$Me$_5$)] to afford, respectively, in essentially quantitative yield, the tetranuclear metal compounds [MWCoAu(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**6a**; M = W) and (**6b**; M = Mo). In a similar reaction, complex (**1c**) and [Co(η-C$_2$H$_4$)$_2$(η-C$_5$Me$_5$)] gave a chromatographically separable mixture of two isomeric products [W$_2$CoAu(μ-CC$_6$H$_4$Me-

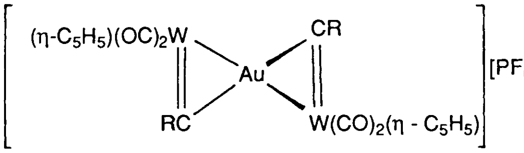
---

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

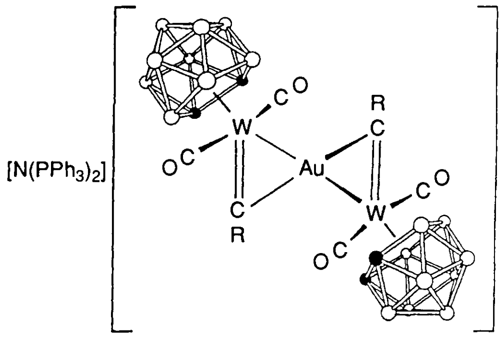


○ BH ● CMe

	M	R	R′
(**1a**)	W	C_6H_4Me - 4	C_6H_4Me - 4
(**1b**)	W	Me	Me
(**1c**)	W	Me	C_6H_4Me - 4
(**1d**)	Mo	C_6H_4Me - 4	C_6H_4Me - 4



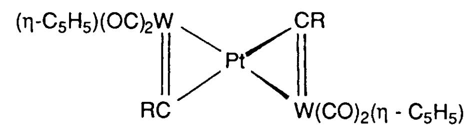
(**2**)



○BH ● CMe

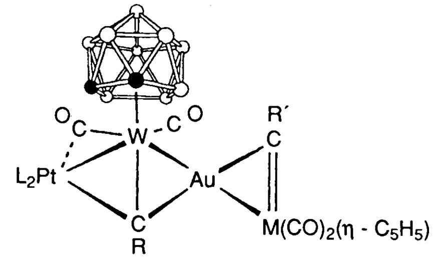
(**3**)

R = C_6H_4Me - 4



(**4**)

R = C_6H_4Me - 4



○BH ● CMe

	M	R	R′	L_2
(**5a**)	W	C_6H_4Me-4	C_6H_4Me-4	cod
(**5b**)	W	C_6H_4Me-4	C_6H_4Me-4	2 PMe_2Ph
(**5c**)	W	Me	C_6H_4Me-4	2 PMe_2Ph
(**5d**)	Mo	C_6H_4Me-4	C_6H_4Me-4	2 PMe_2Ph

4) (μ_3-CMe)(CO)$_4$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**6c**) and [W$_2$CoAu(μ-CMe)(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**7**). These species were formed in the ratio (**6c**):(**7**) of *ca.* 4:1. Data for these new cluster compounds are given in Tables 1 and 2, but discussion is deferred until the results of an *X*-ray diffraction study on (**6b**) are reported. The results are summarised in Table 3, and the structure is shown in the Figure.

It is immediately apparent that as a result of the reaction between the cobalt compound and (**1d**) a Co(η-C$_5$Me$_5$) fragment has added to the 4-MeC$_6$H$_4$C$\equiv$W(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$) group of the trimetal complex. The reaction has thus followed a similar pattern to those between the species (**1**) and the platinum moieties Pt(cod) or Pt(PMe$_2$Ph)$_2$.[1] In (**6b**), however, the structure is not based on a four-metal-atom chain since there is a Co–Au bond, as discussed further below. Hence the core of the molecule is a metal-atom triangle WCoAu with an external Au–Mo linkage.

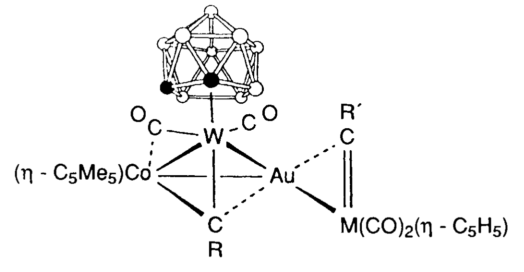
The structure has several unusual features. Both *p*-tolylmethylidyne ligands occupy asymmetrically bridging sites with respect to the metal atoms they ligate. Thus the atom C(15) bridging the Mo–Au bond [Mo–C(15) 1.90(2), Au–C(15) 2.11(1) Å] lies perceptibly closer to the Mo atom. As a result the angle Mo–C(15)–C(16) [155(1)°] is significantly larger than the angle Au–C(15)–C(16) [118(1)°]. A similar structural feature has been observed in the molecules [WPt(μ-CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(PEt$_3$)(μ-σ:η^5-C$_2$B$_9$H$_8$Me$_2$)],[5a] [WRu(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)],[5b] and [WAu(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)(η^5-C$_2$B$_9$H$_9$Me$_2$)],[2b] having W–μ-C–C^1 (arene ring) angles of 175(1), 152.6(5), and 163(2)°, respectively. Moreover, the Mo–μ-C and Au–μ-C distances in (**6b**) are very similar to the W–μ-C [1.88(3) Å] and Au–μ-C [2.19(3) Å] separations in [WAu(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)(η^5-C$_2$B$_9$H$_9$Me$_2$)].[2b] Furthermore, the M–μ-C (M = Mo or W) distances in all the above dimetal compounds are only slightly longer than the C$\equiv$W separation [1.826(7) Å] in the salt [PPh$_4$][W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)].[6] Hence the C$\equiv$M bonds are little changed by formation of W–Pt, W–Ru, and M–Au (M = Mo or W) bonds in the polynuclear metal species.

The C(7) atom asymmetrically spans the WCoAu triangle [W–C(7) 1.97(1), Co–C(7) 1.86(1), and Au–C(7) 2.30(1) Å]; thus the interaction with the gold atom is weak. The W–C(7) and Co–C(7) distances may be compared with those found [W–μ-C 1.913(7) and Co–μ-C 1.939(8) Å] in the dimetal compound [WCo(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)].[7] However, whereas in the latter species the W–Co bond is 2.758(1) Å, in (**6b**) it is much shorter [2.597(2) Å]. It is apparent that there is

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

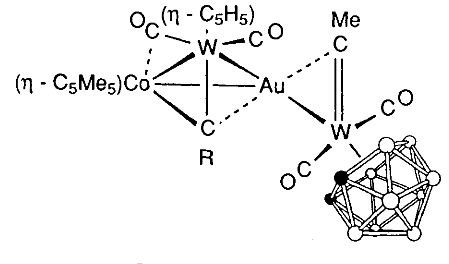
Compound[b]	Yield (%)	$\nu_{max.}$(CO)[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(6a) [$W_2CoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)$]	86	2 010m, 1 948s, 1 780wbr	36.3 (36.0)	3.9 (3.8)
(6b) [$MoWCoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)$]	92	2 017m, 1 957s, 1 780wbr	37.1 (37.0)	4.0 (4.2)
(6c) [$W_2CoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)$]	55	2 004m, 1 945s, 1 769wbr	32.6 (32.3)	3.8 (3.7)
(7) [$W_2CoAu(\mu\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)$]	15	1 994m, 1 948m, 1 924w, 1 848wbr	32.0 (32.3)	3.6 (3.7)

[a] Calculated values are given in parentheses. [b] All compounds are brown in colour. [c] Measured in CH_2Cl_2. A broad weak band is observed in all the spectra near 2 550 cm^{-1} due to ν(BH).



○ BH ● CMe

	M	R	R′
(6a)	W	C_6H_4Me - 4	C_6H_4Me - 4
(6b)	Mo	C_6H_4Me - 4	C_6H_4Me - 4
(6c)	W	Me	C_6H_4Me - 4



○BH ● CMe

(7) R = C_6H_4Me - 4

appreciable electron delocalisation within the C(7)WCo ring in **(6b)**, and the tungsten–cobalt distance may correspond to a W=Co bond. It is noteworthy that in the complex [PPh_4][$WCo_2(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)$] the W–Co distances (average 2.768 Å) are significantly longer.[8]

The other metal–metal distances in **(6b)** are 2.763(2) (Mo–Au), 2.826(1) (W–Au), and 2.580(2) Å (Co–Au). In [$WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)$] the W–Au bond length is 2.780(8) Å,[2b] similar to that in **(6b)**. Moreover, since the radii of Mo and W are the same, the Mo–Au separation is as might be expected. However, the Co–Au bond length is relatively short, and may well reflect some degree of multiple bonding between these two metal centres. It may be noted that the Co–Au distances in [$Co_3Au(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)(CO)_7(PPh_3)$] are in the range 2.638—2.847 Å,[9] and are more typical.

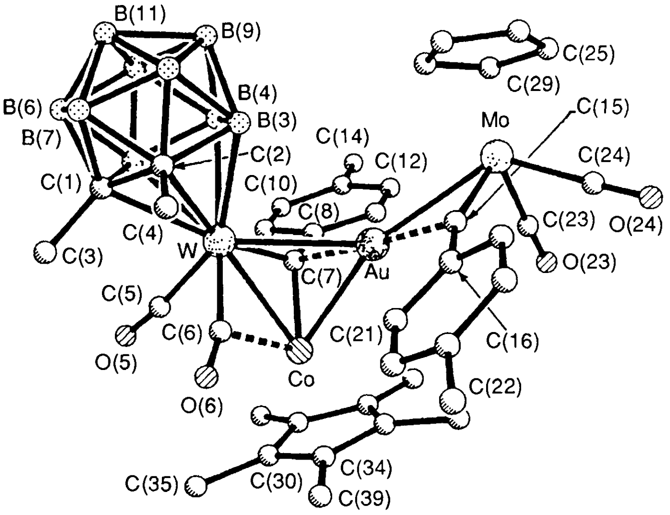


Figure. The molecular structure of the complex [$MoWCoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)$]·$CH_2Cl_2$ **(6b)**, showing the crystallographic numbering scheme

In summary, although the overall co-ordination geometry around the Au atom is one in which it is ligated by five atoms these interactions vary. Thus the Au atom appears to be relatively weakly bonded to C(7) and C(15), while the linkage to the Co atom is very strong, and those to the Mo and W linkages are as expected. In metal-cluster terminology the MoWCoAu core of **(6b)** may be classed as being of the 'spiked-triangle' type. However, attempts to assign valence-electron counts to the individual metal centres do not lead to satisfactory results.

The molybdenum and tungsten atoms in compound **(6b)** each carry two CO groups but C(6)O(6) semi-bridges the W–Co bond [W–C(6)–O(6) 163(1)°, W–C(6) 1.99(2), Co–C(6) 2.30 (1) Å]. As expected, the Mo, W, and Co atoms are co-ordinated, respectively, by the C_5H_5, $C_2B_9H_9Me_2$, and C_5Me_5 ligands.

Having established the structure of **(6b)** it follows that **(6a)** and **(6c)** have similar structures because of similarities in the spectroscopic properties of the three species. All show in their i.r. spectra three CO stretching bands (Table 1), with one of these

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	$^1H^b(\delta)$	$^{13}C^c(\delta)$
(6a)	1.14 (s, 15 H, C_5Me_5), 1.99 (s, 6 H, CMe), 2.26, 2.44 (s × 2, 6 H, Me-4), 5.41 (s, 5 H, C_5H_5), 7.13 (mbr, 4 H, C_6H_4), 7.27, 7.36 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	347.2, 288.2 (μ-C), 265.1 (μ-CO), 215.6, 212.3, 210.2 (CO), 158.1, 141.9 [$C^1(C_6H_4)$], 136.7—123.5 (C_6H_4), 97.4, 94.2 (C_5H_5 and C_5Me_5), 64.5, 62.3 (*C*Me), 29.6, 28.9 (C*Me*), 21.7, 21.2 (Me-4), 8.2 (C_5Me_5)
(6b)	1.22 (s, 15 H, C_5Me_5), 2.07 (s, 6 H, CMe), 2.37, 2.51 (s × 2, 6 H, Me-4), 5.42 (s, 5 H, C_5H_5), 7.23 (mbr, 4 H, C_6H_4), 7.32, 7.42 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7]	348.7, 298.3 (μ-C), 264.9 (μ-CO), 226.4, 223.7, 210.1 (CO), 158.1, 144.5 [$C^1(C_6H_4)$], 136.7—123.4 (C_6H_4), 97.4, 95.9 (C_5H_5 and C_5Me_5), 64.6, 62.4 (*C*Me), 29.6, 29.0 (C*Me*), 21.7, 21.2 (Me-4), 8.3 (C_5Me_5)
(6c)	1.38 (s, 15 H, C_5Me_5), 2.01, 2.10, 2.31 (s × 3, 9 H, CMe and Me-4), 4.45 (s, 3 H, μ-CMe), 5.58 (s, 5 H, C_5H_5), 7.18 (mbr, 4 H, C_6H_4)	355.7, 291.7 (μ-C), 266.0 (μ-CO), 215.6, 213.3, 210.9 (CO), 147.3 [$C^1(C_6H_4)$], 142.5, 129.6, 129.1 (C_6H_4), 97.3, 93.5 (C_5H_5 and C_5Me_5), 64.0, 62.1 (*C*Me), 44.5 (μ-C*Me*), 29.3, 28.9 (C*Me*), 21.7 (Me-4), 8.4 (C_5Me_5)
(7)	1.30 (s, 15 H, C_5Me_5), 1.99, 2.14, 2.19 (s × 3, 9 H, CMe and Me-4), 2.45 (s, 3 H, μ-CMe), 5.65 (s, 5 H, C_5H_5), 6.99—7.35 (m, 4 H, C_6H_4)	352.1, 313.6 (μ-C), 243.5 (μ-CO), 221.4, 218.6, 211.4 (CO), 151.0 [$C^1(C_6H_4)$], 137.1, 128.1, 122.1 (C_6H_4), 96.8, 94.2 (C_5H_5 and C_5Me_5), 64.2, 64.1 (*C*Me), 40.7 (μ-C*Me*), 29.8, 29.6 (C*Me*), 21.1 (Me-4), 8.6 (C_5Me_5)

[a] Chemical shifts in p.p.m., coupling constants in Hz, measurements in CD_2Cl_2. [b] Resonances for B–H protons are not resolved due to $^{11}B-^1H$ coupling, and very broad weak signals are observed in the range δ 0—5. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (δ 0.0 p.p.m.).

Table 3. Selected internuclear distances (Å) and angles (°) for [MoWCoAu(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)$(CO)_4$(η-C_5H_5)(η-C_5Me_5)(η^5-$C_2B_9H_9Me_2$)]·CH_2Cl_2 (**6b**) with estimated standard deviations in parentheses

Mo–Au	2.763(2)	W–Au	2.826(1)	Co–Au	2.580(2)	Co–W	2.597(2)
Au–C(7)	2.30(1)	Au–C(15)	2.11(1)	W–B(3)	2.43(2)	W–B(4)	2.39(2)
W–B(5)	2.34(2)	W–C(1)	2.42(2)	W–C(2)	2.48(1)	W–C(5)	2.04(2)
W–C(6)	1.99(2)	W–C(7)	1.97(1)	Mo–C(15)	1.90(2)	Mo–C(23)	1.99(2)
Mo–C(24)	1.98(2)	Co–C(6)	2.30(1)	Co–C(7)	1.86(1)	C(5)–O(5)	1.11(2)
C(6)–O(6)	1.16(2)	C(23)–O(23)	1.16(2)	C(24)–O(24)	1.12(2)	C(1)–C(2)	1.63(2)
C(2)–B(3)	1.70(3)	B(3)–B(4)	1.82(3)	B(4)–B(5)	1.75(3)	B(5)–C(1)	1.71(2)
C(7)–C(8)	1.48(2)	C(15)–C(16)	1.47(2)	C(1)–C(3)	1.54(3)	C(2)–C(4)	1.51(2)
Mo–C(C_5H_5)(mean)	2.34(2)	Co–C(C_5Me_5)(mean)	2.11(2)				

W–Au–Mo	143.4(1)	W–Au–Co	57.2(1)	Mo–Au–Co	154.7(1)
W–Au–C(7)	43.8(3)	Mo–Au–C(7)	132.4(4)	Co–Au–C(7)	44.3(4)
W–Au–C(15)	138.5(4)	Mo–Au–C(15)	43.3(4)	Co–Au–C(15)	139.3(4)
C(7)–Au–C(15)	175.7(6)	Au–W–Co	56.6(1)	Au–W–C(5)	128.9(4)
Co–W–C(5)	73.5(4)	Au–W–C(6)	82.2(5)	Co–W–C(6)	58.3(4)
C(5)–W–C(6)	81.1(7)	Au–W–C(7)	53.7(4)	Co–W–C(7)	45.4(4)
C(5)–W–C(7)	84.2(6)	C(6)–W–C(7)	103.4(6)	Au–Mo–C(15)	49.8(4)
Au–Mo–C(23)	81.0(6)	C(15)–Mo–C(23)	101.4(7)	Au–Mo–C(24)	124.9(6)
C(15)–Mo–C(24)	82.3(7)	C(23)–Mo–C(24)	84.3(7)	Au–Co–W	66.2(1)
Au–Co–C(6)	82.7(5)	W–Co–C(6)	47.6(4)	Au–Co–C(7)	59.7(5)
W–Co–C(7)	49.2(4)	W–C(5)–O(5)	173(2)	W–C(6)–O(6)	163(1)
Co–C(6)–O(6)	123(1)	W–C(6)–Co	74.1(5)	Au–C(7)–W	82.5(4)
Au–C(7)–Co	76.0(4)	W–C(7)–Co	85.3(6)	W–C(7)–C(8)	137(1)
Co–C(7)–C(8)	133.5(1)	Au–C(15)–Mo	86.9(5)	Au–C(15)–C(16)	118(1)
Mo–C(15)–C(16)	155(1)	Mo–C(23)–O(23)	177(2)	Mo–C(24)–O(24)	177(1)

absorptions (*ca.* 1 780 cm^{-1}) being characteristic for a bridging group. This band is presumably due to a CO ligand bridging the W–Co bond, which although semi-bridging in the solid-state structure of (**6b**) may be more symmetrically bridging in solution.

The $^{13}C-\{^1H\}$ n.m.r. spectra are also informative (Table 2). Each compound displays four CO resonances, as expected, with one of the signals having a chemical shift (δ *ca.* 265 p.p.m.) diagnostic for a bridging carbonyl group.[10] Two resonances for the ligated carbon nuclei of the alkylidyne groups are seen in each spectrum. These are at δ 347.2 and 288.2 for (**6a**), 348.7 and 298.3 for (**6b**), and 355.7 and 291.7 p.p.m. for (**6c**). Based on earlier results,[7,11] it is tempting to assign the less deshielded resonance in each pair to the alkylidyne carbon bridging the WCoAu triangle, and the more deshielded peak to the alkylidyne-carbon atom edge-bridging the M–Au (M = Mo or W) bond. However, the asymmetry in the bonding of the alkylidyne ligands, revealed by the *X*-ray diffraction study on (**6b**), makes such an assignment unsafe. Thus if the structure of these molecules is regarded as one in which one alkylidyne group edge-bridges a WCoAu triangle while the other is essentially terminally bound to a Mo or W atom then it becomes reasonable to attribute the less deshielded resonance in each pair to the terminally bound group, and the more deshielded peak to the group edge-bridging the WCoAu triangle. This would lead to the opposite assignment to that inferred by regarding the structures as having one triply bridging and one edge-bridging alkylidyne ligand. Interestingly, the resonance at δ 347.2 p.p.m. in the spectrum of (**6a**) is of similar chemical shift to that

Table 4. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**6b**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	4 911(1)	5 926(1)	2 627(1)	C(11)	6 834(10)	8 198(12)	5 024(8)
W	5 440(1)	7 505(1)	1 987(1)	C(12)	6 331(10)	7 410(14)	4 880(8)
Mo	3 879(1)	5 455(1)	3 274(1)	C(13)	6 059(9)	7 009(12)	4 199(8)
Co	6 224(1)	5 899(2)	2 488(1)	C(14)	7 174(11)	8 654(14)	5 741(9)
Cl(1)	9 012(15)	6 305(18)	640(12)	C(15)	3 940(8)	5 005(10)	2 408(7)
Cl(2)	10 236(20)	6 840(23)	1 173(19)	C(16)	3 688(10)	4 440(11)	1 749(8)
Cl(2′)	10 433(26)	5 099(54)	885(25)	C(17)	2 995(12)	3 981(14)	1 545(9)
O(5)	7 088(7)	8 027(10)	2 043(7)	C(18)	2 755(12)	3 389(14)	947(9)
O(6)	5 496(7)	5 917(9)	875(6)	C(19)	3 199(13)	3 326(14)	536(9)
O(23)	5 315(8)	4 461(11)	4 372(7)	C(20)	3 864(13)	3 832(17)	710(10)
O(24)	3 135(8)	3 366(10)	3 225(7)	C(21)	4 094(11)	4 406(14)	1 306(9)
B(3)	4 151(11)	8 040(16)	1 806(10)	C(22)	2 922(15)	2 616(15)	−121(10)
B(4)	4 862(11)	8 815(14)	2 433(10)	C(23)	4 796(11)	4 825(13)	3 955(9)
B(5)	5 422(10)	9 266(13)	1 961(10)	C(24)	3 419(10)	4 115(13)	3 259(8)
B(6)	4 860(12)	10 083(15)	1 271(11)	C(25)	3 287(13)	6 095(14)	4 033(10)
B(7)	4 134(11)	9 333(15)	681(11)	C(26)	2 795(11)	6 219(15)	3 312(11)
B(8)	3 598(11)	8 836(16)	1 132(12)	C(27)	3 116(12)	6 873(14)	2 980(10)
B(9)	3 882(12)	9 277(16)	2 009(12)	C(28)	3 787(11)	7 191(12)	3 458(10)
B(10)	4 724(15)	10 063(15)	2 081(11)	C(29)	3 888(12)	6 699(14)	4 102(9)
B(11)	3 930(13)	10 066(17)	1 298(13)	C(30)	7 116(10)	5 275(13)	2 219(10)
C(1)	5 042(9)	8 831(12)	1 123(8)	C(31)	7 361(9)	5 558(13)	2 958(10)
C(2)	4 306(8)	8 126(11)	1 031(7)	C(32)	6 953(10)	4 988(13)	3 287(10)
C(3)	5 484(10)	8 693(14)	618(8)	C(33)	6 464(10)	4 383(13)	2 774(10)
C(4)	4 024(10)	7 357(13)	455(9)	C(34)	6 554(10)	4 535(13)	2 117(9)
C(5)	6 513(10)	7 785(12)	2 013(8)	C(35)	7 408(12)	5 645(14)	1 676(10)
C(6)	5 538(9)	6 396(12)	1 365(9)	C(36)	7 984(10)	6 281(15)	3 288(10)
C(7)	5 949(8)	6 965(10)	2 939(7)	C(37)	7 101(11)	4 985(15)	4 053(10)
C(8)	6 248(8)	7 364(10)	3 664(7)	C(38)	5 940(13)	3 601(14)	2 889(11)
C(9)	6 772(9)	8 173(11)	3 818(8)	C(39)	6 189(12)	3 958(13)	1 447(11)
C(10)	7 064(10)	8 549(12)	4 484(9)	C(40)	9 685(30)	5 602(35)	714(37)

observed for the edge-bridging *p*-tolylmethylidyne carbon nucleus in $[WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (δ 341.0 p.p.m.)[7] while the peak at δ 288.2 p.p.m. has a shift comparable with that (δ 294.3 p.p.m.) observed for the $C(C_6H_4Me\text{-}4)Mo$ group in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of compound (**5d**).[1]

A solution to the problem of assigning the alkylidyne-carbon signals in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the complexes (**6a**)—(**6c**) would have been possible if one of the resonances in the spectrum of (**6b**) had displayed ^{183}W satellite peaks. The observation of $^{183}W\text{-}^{13}C$ coupling on a μ-C resonance would have defined the signal as being due to C(7) in the Figure. Unfortunately no ^{183}W satellites were observed on either the peak at δ 348.7 or that at 298.3 p.p.m. If such coupling is observed it is *ca.* 150 Hz, but it is not unusual for these signals to be too weak to be seen, as is evidently the case for (**6b**).

As mentioned above, the reaction between (**1c**) and $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$ afforded, in addition to (**6c**), an isomeric complex (**7**). Data for the latter are in agreement with this species having the molecular structure shown, resulting from a $Co(\eta\text{-}C_5Me_5)$ fragment having added to the $4\text{-}MeC_6H_4C\equiv W(CO)_2(\eta\text{-}C_5H_5)$ group of (**1c**). The i.r. spectrum of compound (**7**) displays four CO bands, one of which (1 848 cm^{-1}) is in the region indicative of a semi-bridging carbonyl ligand. It is noteworthy, however, that this peak is to considerably higher frequency than those for the bridging CO groups in the complexes (**6a**)—(**6c**) indicating that the bridging is less pronounced in complex (**7**). In agreement with this deduction, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of compound (**7**) the resonance for the semi-bridging CO ligand (δ 243.5 p.p.m.) is less deshielded than the peaks (*ca.* δ 265 p.p.m.) for this group in the spectra of the complexes (**6a**)—(**6c**). Resonances in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**7**) at δ 352.1 and 313.6 p.p.m. may be assigned to the two alkylidyne-carbon nuclei. Other peaks in the spectra are in agreement with the structure proposed.

The formation of complex (**7**), albeit in appreciably less amount than its isomer (**6c**), evidently results from some activation of the $4\text{-}MeC_6H_4C\equiv W(CO)_2(\eta\text{-}C_5H_5)$ unit in (**1c**), in contrast with (**1a**) or (**1d**). Further studies are required to establish whether under appropriate conditions it is possible to obtain cluster compounds resulting from addition of metal–ligand fragments to both the $C\equiv W$ and the $C\equiv M$ groups of the compounds (**1**).

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C, and all solvents were freshly distilled over appropriate drying agents. Chromatography columns were of alumina (Brockman, activity II), and all compounds were handled using Schlenk-tube techniques under oxygen-free nitrogen. The compounds $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$[12] and (**1**)[1] were prepared as described previously. The instrumentation used for spectroscopic measurements has been described earlier.[4]

Synthesis of the Tetranuclear Metal Complexes.—(*i*) A CH_2Cl_2 (20 cm^3) solution of complex (**1a**) (0.11 g, 0.10 mmol) was treated with $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$ (0.03 g, 0.10 mmol), and the mixture was stirred for 4 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 2:3) and chromatographed. Elution with the same solvent mixture afforded a brown eluate. Removal of solvent *in vacuo* gave brown *microcrystals* of $[W_2CoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6a**) (0.11 g).

(*ii*) The compound (**1d**) (0.10 g, 0.10 mmol) in CH_2Cl_2 (20 cm^3) was treated with $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$ (0.03 g, 0.10 mmol), and the mixture was stirred for 3 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 2:3) and chromatographed. Elution with the same solvent mixture removed a brown fraction which, following evaporation of solvent *in vacuo*, gave brown *microcrystals* of $[MoWCoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6b**) (0.11 g).

(*iii*) In a similar experiment, the compounds (**1c**) (0.10 g, 0.10 mmol) and $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$ (0.03 g, 0.10 mmol) in CH_2Cl_2 (20 cm^3) gave two fractions upon chromatography. The first eluate, after removal of solvent *in vacuo*, gave brown *microcrystals* of $[W_2CoAu(\mu\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**7**) (0.02 g). The second fraction yielded brown *microcrystals* of $[W_2CoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6c**) (0.07 g).

Crystal-structure Determination of Compound (**6b**).—Crystals of (**6b**) were grown from CH_2Cl_2–light petroleum (1:4) as dark brown prisms, and contained 1 molecule of CH_2Cl_2 per asymmetric unit. A crystal of dimensions *ca.* 0.2 × 0.3 × 0.7 mm was sealed in a Lindemann capillary tube under nitrogen. Diffracted intensities were measured (θ—2θ scans) at 298 K in the range $4 \leqslant 2\theta \leqslant 50°$ on a Siemens R3m/V four-circle diffractometer. Of 7 386 unique data, 4 719 had $F \geqslant 6\sigma(F)$, and only these were used in the solution and refinement of the structure, after correction for Lorentz, polarisation, and *X*-ray absorption effects. The latter correction was based on a semi-empirical method using azimuthal scan data.[13]

Crystal data. $C_{39}H_{49}AuB_9CoMoO_4W{\cdot}CH_2Cl_2$, M = 1 299.7, monoclinic, space group $P2_1/n$ (no. 14), a = 18.806(6), b = 13.302(3), c = 20.317(6) Å, β = 110.13(2)°, U = 4 772(2) Å^3, Z = 4, D_c = 1.81 g cm^{-3}, $F(000)$ = 2 328, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, $\mu(Mo\text{-}K_\alpha)$ = 61.4 cm^{-1}.

The structure was solved by conventional heavy-atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atoms were included at calculated positions (C–H 0.96 and B–H 1.10 Å)[14] with refined isotropic thermal parameters for hydrogens attached to boron atoms, and fixed isotropic thermal parameters (*ca.* $1.2U_{equiv.}$ of the parent carbon atom) for all remaining hydrogens. The CH_2Cl_2 molecule of crystallisation was disordered with one Cl atom occupying two sites (*ca.* 50% occupancy). Refinement by blocked-cascade least squares led to R = 0.049 (R' = 0.050) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,5|F|^2]$ giving a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 1.73$ or $\leqslant -1.54$ e Å^{-3}. All calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[13] Scattering factors with corrections for anomalous dispersion were taken from ref. 15. Atomic co-ordinates for (**6b**) are listed in Table 4.

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

Acknowledgements

We thank the Spanish Consejo Superior de Investigaciones Científicas for a Fellowship (to M. C. G.) and the U.S.A.F. Office of Scientific Research (Grant 86-0125) for partial support.

References

1 Part 98, M. C. Gimeno and F. G. A. Stone, preceding paper.

2 (*a*) G. A. Carriedo, J. A. K. Howard, K. Marsden, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1589; (*b*) M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, and F. G. A. Stone, *ibid.*, 1987, 61.

3 T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 763.

4 S. J. Davies, J. A. K. Howard, M. U. Pilotti, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, 2289; S. J. Davies, J. A. K. Howard, R. J. Musgrove, and F. G. A. Stone, *ibid.*, p. 2269 and refs. therein.

5 (*a*) D. D. Devore, J. A. K. Howard, J. C. Jeffery, M. U. Pilotti, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, 303; (*b*) M. Green, J. A. K. Howard, A. N. de M. Jelfs, O. Johnson, and F. G. A. Stone, *ibid.*, 1987, 73.

6 O. Johnson, J. A. K. Howard, M. Kapan, and G. M. Reisner, *J. Chem. Soc., Dalton Trans.*, 1988, 2903.

7 J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, N. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2075.

8 F-E. Baumann, J. A. K. Howard, R. J. Musgrove, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1891.

9 J. C. Jeffery, T. M. Walters, and K. D. V. Weerasuria, unpublished work.

10 B. E. Mann and B. F. Taylor, '^{13}C NMR Data for Organometallic Compounds,' Academic Press, London, 1981.

11 J. A. Abad, E. Delgado, M. E. Garcia, M. J. Grosse-Ophoff, I. J. Hart, J. C. Jeffery, M. S. Simmons, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 41; S. J. Davies and F. G. A. Stone, *ibid.*, 1989, 785.

12 S. A. Frith and J. L. Spencer, *Inorg. Synth.*, 1985, **23**, 19.

13 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-Ray System, revision 5.1, 1985.

14 P. Sherwood, BHGEN, a program for the calculation of idealised H-atom positions for a *nido*-icosahedral carbaborane fragment, Bristol University, 1986.

15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 8*th December* 1989; *Paper* 9/05254B