Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 98.[1] Tri- and Tetra-nuclear Metal Compounds with Ethylidyne or *p*-Tolylmethylidyne Groups, and having both Cyclopentadienyl and Carbaborane Ligands

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

The trimetal compounds [MWAu(μ-CR)(μ-CR′)(CO)$_4$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (M = Mo or W, R = R′ = C$_6$H$_4$Me-4; M = W, R = R′ = Me; R = Me, R′ = C$_6$H$_4$Me-4) have been prepared by treating the complexes [MAuCl(μ-CR′)(CO)$_2$(η-C$_5$H$_5$)] (M = Mo or W, R′ = C$_6$H$_4$Me-4; M = W, R′ = Me) with the reagents [NEt$_4$][W($\equiv$CR)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] (R = C$_6$H$_4$Me-4 or Me) in CH$_2$Cl$_2$ in the presence of TlBF$_4$. The trimetal compounds react with [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) or [Pt(PMe$_2$Ph)$_2$(nb)] (nb = norbornene = bicyclo[2.2.1]heptene) to afford, respectively, the 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$_2$)] 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$_2$)] (M = W, R = R′ = C$_6$H$_4$Me-4; R = Me, R′ = C$_6$H$_4$Me-4; M = Mo, R = R′ = C$_6$H$_4$Me-4). The cod complex was prepared by an alternative method, by treating [NEt$_4$][WPt(μ-CC$_6$H$_4$Me-4)(CO)$_2$(cod)(η^5-C$_2$B$_9$H$_9$Me$_2$)] with [WAuCl(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)], in the presence of TlBF$_4$. Addition of an excess of PMe$_2$Ph in thf (tetrahydrofuran) to [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$_2$)] in the same solvent results in displacement of both cod and W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$) groups, and formation of the trimetal complex [WPtAu(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_2$Ph)$_3$(η^5-C$_2$B$_9$H$_9$Me$_2$)]. The i.r. and n.m.r. (^{1}H and ^{13}C-{^{1}H}) data for the compounds are reported and discussed.

In earlier papers[2] in this series we have described how polynuclear metal complexes with molecular structures based on chains or rings of metal atoms, and with the metal–metal bonds bridged by alkylidyne groups, may be prepared. The procedures leading to these products employ as synthons the trimetal complexes [M$_2$M′(μ-CR)$_2$(CO)$_4$L$_2$] (M = W or Mo, M′ = Pt or Ni, R = alkyl or aryl, L = η-C$_5$H$_5$ or η-C$_5$Me$_5$) of which some twenty such species are known.[3] The paradigm molecule for this chemistry is the complex [W$_2$Pt(μ-CC$_6$H$_4$Me-4)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (**1**),[4] and the isoelectronic relationship between Pt^0 and Au$^{\text{I}}$ led to the synthesis of the related gold salt [W$_2$Au(μ-CC$_6$H$_4$Me-4)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$][PF$_6$] (**2**).[5a] This product was obtained by treating [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] with [AuCl(tht)] (tht = tetrahydrothiophene) in the presence of TlPF$_6$. Compound (**1**) can be obtained from the same tungsten reagent and [Pt(C$_2$H$_4$)$_3$], the latter being generated *in situ* from [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) and ethylene.[4]

Recently a new dimension has been added to these studies, based on the isolobal relationship existing between the groups η-C$_5$H$_5$ and η^5-C$_2$B$_9$H$_9$Me$_2$.† A series of anionic complexes [W($\equiv$CR)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)]$^-$ (R = alkyl or aryl) has been prepared,[6,7] which are mapped isolobally with the neutral compounds [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)]. Moreover, the C$\equiv$W bonds in the carbaborane species will co-ordinate metal–ligand fragments[8] in a manner similar to that observed for these linkages in their cyclopentadienyl analogues. Thus in the context of the work described in this paper the reaction between [AuCl(tht)] and 2 equivalents of [N(PPh$_3$)$_2$][W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] afforded the salt [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**).[6] The relationship between the salts (**2**) and (**3**) is self-evident, following replacement of η-C$_5$H$_5$ groups in the former with η^5-C$_2$B$_9$H$_9$Me$_2$ ligands in the latter. Also relevant is the mapping of the salt [WAu(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)][PF$_6$] (**4**)[5b] with the neutral complex [WAu(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**5**).[6] The compounds (**4**) and (**5**) were prepared by a similar methodology. Namely, treatment of [AuCl(PPh$_3$)], in the presence of TlPF$_6$, with [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] or [N(PPh$_3$)$_2$][W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] affords the complexes (**4**) and (**5**), respectively.

The successful synthesis of the salts (**2**) and (**3**), and the above-mentioned relationship between η-C$_5$H$_5$ and η^5-C$_2$B$_9$H$_9$Me$_2$ groups, raises the interesting possibility of preparing neutral trimetal compounds of formulation [MWAu(μ-CR)(μ-CR′)(CO)$_4$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**6**; M = W or Mo, R or R′ = alkyl or aryl). Such complexes are likely to be useful starting points for the synthesis of polynuclear metal complexes, using the methods developed previously.[2] This paper describes the preparation of compounds of type (**6**).

Results and Discussion

The trimetal compounds [MWAu(μ-CR)(μ-CR′)(CO)$_4$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**6a**; M = W, R = R′ = C$_6$H$_4$Me-4), (**6b**; M = W, R = R′ = Me), (**6c**; M = W, R = Me, R′ = C$_6$H$_4$Me-4), and (**6d**; M = Mo, R = R′ = C$_6$H$_4$Me-4) were obtained by employing the dimetal complexes [MAuCl(μ-CR′)(CO)$_2$(η-C$_5$H$_5$)] (**7a**; M = W, R′ = C$_6$H$_4$Me-4), (**7b**; M =

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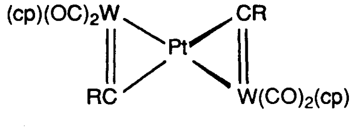
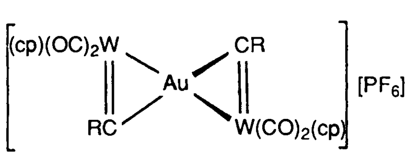
† In this paper, and in others in this series, a tungsten atom forms with a [*nido*-7,8-C$_2$B$_9$H$_9$Me$_2$]$^{2-}$ anion a *closo*-1,2-dicarba-3-tungstadodecaborane structure. However, in the formulae the carbaborane group is designated as η^5-C$_2$B$_9$H$_9$Me$_2$ in order to emphasise its pentahapto ligand properties in which it formally acts as a four-electron donor, as opposed to the five-electron donor η-C$_5$H$_5$ group.



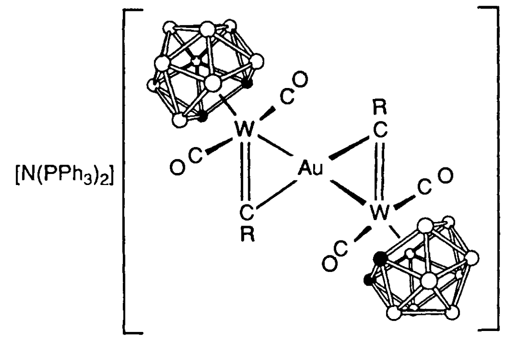
(1)

cp = η^5-C_5H_5, R = C_6H_4Me - 4



(2)

cp = η^5-C_5H_5, R = C_6H_4Me - 4



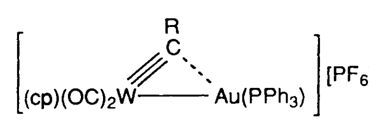
○ BH ● CMe R = C_6H_4Me - 4

(3)

Mo, R′ = C_6H_4Me-4), and (**7c**; M = W, R′ = Me) as precursors. The latter are themselves new species, and these reagents were synthesised by treating the gold complex [AuCl(tht)] with the compounds $[M(\equiv CR')(CO)_2(\eta$-$C_5H_5)]$ (M = W, R′ = C_6H_4Me-4 or Me; M = Mo, R′ = C_6H_4Me-4).

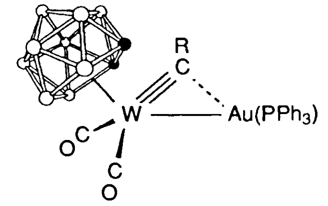
The compounds (**7a**)—(**7c**) were characterised by microanalysis and by their spectroscopic properties (Tables 1 and 2). Structurally they are similar to the recently reported[9] complex $[WAu(C_6F_5)(\mu$-CC_6H_4Me-$4)(CO)_2(\eta$-$C_5H_5)]$ (**7d**) which was obtained by treating $[W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)]$ with $[Au(C_6F_5)(tht)]$. They show two strong bands in their i.r. spectra in the CO region (Table 1). For (**7a**) and (**7b**) diagnostic resonances for the μ-*C*C_6H_4Me-4 nuclei occur in the ^{13}C-$\{^1H\}$ n.m.r. spectra (Table 2) at δ 285.9 and 296.8 p.p.m., respectively. Complex (**7c**) was unstable in solution and its spectrum could not be measured. It is noteworthy that in the spectrum of (**7d**) the μ-C resonance occurs at δ 287.4 p.p.m.[9] The relatively shielded chemical shifts observed for the alkylidyne-carbon nuclei in all three compounds suggests that the ligand asymmetrically bridges the metal–metal bond.[10] This structural feature has been established by *X*-ray diffraction for the complex (**5**) and in the ^{13}C-$\{^1H\}$ n.m.r. spectrum of this species the μ-C resonance occurs at δ 292.9 p.p.m.,[6] a shift very similar to those observed in the spectra of the compounds (**7**).

The trimetal compounds (**6**) were prepared in high yield by addition of the reagents $[NEt_4][W(\equiv CR)(CO)_2(\eta^5$-$C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4 or Me)[6,7] to CH_2Cl_2 solutions of the relevant species (**7a**), (**7b**), or (**7c**), the reactions being carried out in the presence of $TlBF_4$ to remove chloride as insoluble TlCl. Data for the compounds (**6**) are given in Tables 1 and 2, and are in accord with the formulations proposed.



(4)

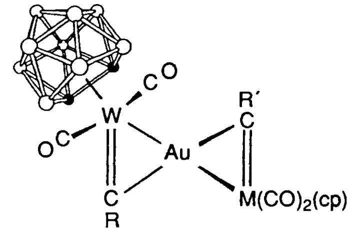
R = C_6H_4Me - 4



○ BH ● CMe

(5)

R = C_6H_4Me - 4



○ BH ● CMe

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

All four compounds (**6**) show four terminal CO stretching bands in their i.r. spectra, in agreement with their asymmetric structures. In contrast, the more symmetrical complexes (**2**) and (**3**) both display two CO absorptions in their i.r. spectra.[5a,6] In the ^{13}C-$\{^1H\}$ n.m.r. spectra of the complexes (**6**), however, only two CO resonances are observed. This must be due to site exchange of these ligands on the n.m.r. time-scale, a process which probably involves rotation of the $M(CO)_2(\eta$-$C_5H_5)$ and $W(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$ groups so as to equivalence the two CO ligands at each metal site, thereby leading to the observation of two peaks in the spectrum. The ^{13}C-$\{^1H\}$ n.m.r. spectra were informative in showing for each complex two signals for μ-C nuclei. Thus for (**6b**) these resonances occur at δ 305.7 and 301.0 p.p.m., and display ^{183}W–^{13}C satellite peaks with *J*(WC) values of 138 and 147 Hz, respectively. Moreover, resonances at δ 41.8 and 41.4 p.p.m. may be ascribed to the two μ-C*Me* groups. Peaks for the carbon nuclei present in the η^5-$C_2B_9H_9Me_2$ ligand were seen at δ 65.5 (*C*Me) and 30.4 p.p.m. (C*Me*).[7] The appearance of two rather than four signals may be attributed to rotation of the $W(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$ moiety on the n.m.r. time-scale, as discussed above. The ^1H n.m.r. spectrum of (**6b**) shows as expected one peak for the CMe groups present in the carbaborane fragment, two peaks for the μ-CMe ligands, and one resonance for the η-C_5H_5 ring.

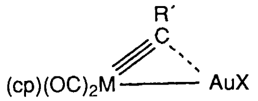
As mentioned earlier, compound (**1**) and several structurally related species are important reagents for the synthesis of polynuclear metal complexes. The C=M (M = W or Mo) groups present in this type of trimetal compound readily add metal–

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

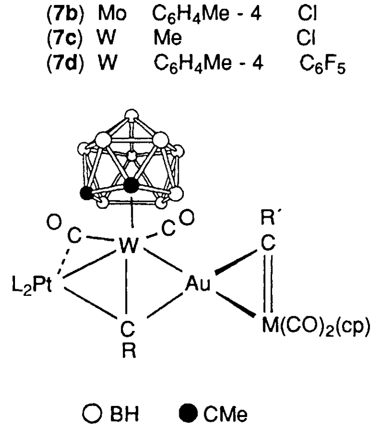
Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$	Analysis (%) C	Analysis (%) H
(6a) $[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	86	2 021s, 1 998vs, 1 962s, 1 931m	31.7 (31.4)	3.3 (3.1)
(6b) $[W_2Au(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Orange	73	2 023vs, 1 997s, 1 960s, 1 929m	22.3 (21.4)	2.9 (2.7)
(6c) $[W_2Au(\mu\text{-}CMe)(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Orange	70	2 019s, 2 000vs, 1 958s, 1 932m	26.8 (26.8)	3.0 (2.9)
(6d) $[MoWAu(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	80	2 029s, 1 998vs, 1 977vs, 1 932m	34.2 (34.1)	3.5 (3.4)
(7a) $[WAuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$	Red	91	2 011s, 1 953s	28.4 (28.2)	2.3 (1.9)
(7b) $[MoAuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$	Orange-red	90	2 022s, 1 968s	32.6 (32.6)	2.6 (2.2)
(7c) $[WAuCl(\mu\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)]$	Yellow	87	2 022s, 1 957s	19.7 (19.2)	1.8 (1.4)
(8a) $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)]$	Purple-red	65[c]	2 015m, 1 952s, 1 787w,br	31.2 (31.5)	3.2 (3.3)
(8b) $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)]$	Brown	78	1 992m, 1 925s, 1 832w,br	35.0 (34.2)	3.9 (3.6)
(8c) $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)]$	Brown	68	1 992m, 1 924s, 1 830br,w	31.7 (31.2)	3.6 (3.5)
(8d) $[MoWPtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_2Ph)_2\text{-}(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Green	61	1 996m, 1 926s, 1 813w,br	36.0 (36.2)	4.2 (3.8)
(11a) $[WPtAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_3(\eta^5\text{-}C_2B_9H_9Me_2)]$	Green	52	1 893m, 1 814m,br	33.8 (33.6)	4.1 (4.1)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. All complexes containing $\eta^5\text{-}C_2B_9H_9Me_2$ ligands show a broad band in the range 2 500—2 550 cm^{-1} due to ν(BH). [c] Synthesis from complexes (**7a**) and (**9**) gives *ca.* 80% yield (see text).

ligand fragments to build up chain and ring structures.[2] The synthesis of the complexes (**6**) raises the interesting possibility of employing these species as precursors to cluster compounds containing ligated $\eta^5\text{-}C_2B_9H_9Me_2$ groups. The non-spectator role often played by the latter in this new chemistry[8] provides a further impetus to such studies. Accordingly, we have carried out some preliminary studies in this area, which have led to the synthesis of the tetranuclear metal compounds described below.



	M	R′	X
(**7a**)	W	C_6H_4Me - 4	Cl
(**7b**)	Mo	C_6H_4Me - 4	Cl
(**7c**)	W	Me	Cl
(**7d**)	W	C_6H_4Me - 4	C_6F_5



	M	R	R′	L_2
(**8a**)	W	C_6H_4Me - 4	C_6H_4Me - 4	cod
(**8b**)	W	C_6H_4Me - 4	C_6H_4Me - 4	2 PMe_2Ph
(**8c**)	W	Me	C_6H_4Me - 4	2 PMe_2Ph
(**8d**)	Mo	C_6H_4Me - 4	C_6H_4Me - 4	2 PMe_2Ph

Treatment of an ethylene-saturated thf (tetrahydrofuran) solution of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) with 1 equivalent of (**6a**) in the same solvent yielded the purple-red product $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4\text{-}(cod)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8a**) in *ca.* 60% yield. Data characterising this species are given in the Tables. Compound (**8a**) could have two possible structures: that shown involving addition of a Pt(cod) fragment to the $RC{=}W(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ group of (**6a**), or alternatively a structure resulting from addition of the Pt(cod) moiety to the $R'C{=}W(CO)_2(\eta\text{-}C_5H_5)$ group. Although an *X*-ray diffraction study on (**8a**) has not been carried out, the structure depicted was established by an alternative synthesis. This involved treating compound (**7a**) with the complex $[NEt_4][WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**9**), the anion of which was previously isolated[7] as the $[P(CH_2Ph)Ph_3]^+$ salt. In this reaction $TlBF_4$ was added in order to remove Cl from (**7a**) as insoluble TlCl. The yield of (**8a**) by this route is *ca.* 80%. This synthesis must proceed *via* addition of a cationic $[(\eta\text{-}C_5H_5)(OC)_2W(\mu\text{-}CC_6H_4Me\text{-}4)Au]^+$ species to the C=W bond in the anion of (**9**). Since in the latter the Pt(cod) fragment is attached to the W atom carrying the $\eta^5\text{-}C_2B_9H_9Me_2$ ligand this must also be the situation in the product (**8a**). A band at 1 787 cm^{-1} in the i.r. spectrum of (**8a**) suggests the presence of an asymmetrically bridging CO ligand. A similar band is observed at 1 693 cm^{-1} in the spectrum of the structurally related compound (**9**), the lower frequency being due to the anionic nature of this complex.[7]

Reactions between $[Pt(PMe_2Ph)_2(nb)]$ (nb = bicyclo-[2.2.1]heptene), generated *in situ* from $[Pt(nb)_3]$ and PMe_2Ph, and the complexes (**6a**), (**6c**), and (**6d**) afforded, respectively, the tetranuclear metal compounds $[MWPtAu(\mu\text{-}CR')(\mu_3\text{-}CR)\text{-}(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8b**; M = W, R = R′ = C_6H_4Me-4), (**8c**; M = W, R = Me, R′ = C_6H_4Me-4), and (**8d**; M = Mo, R = R′ = C_6H_4Me-4). Data for these species are listed in Tables 1 and 2, and are in agreement with the formulations proposed. The $^{13}C\text{-}\{^1H\}$ n.m.r. data are of interest. For each complex, as expected, two resonances are observed for the bridging alkylidyne-carbon nuclei. For the

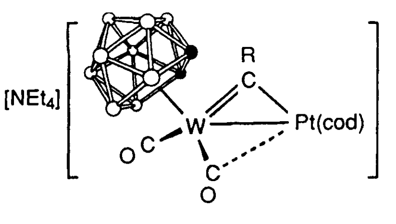
Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	$^1H^b(\delta)$	$^{13}C^c(\delta)$
(6a)[d]	2.19 (s, 6 H, CMe), 2.36, 2.37 (s × 2, 6 H, Me-4), 5.76 (s, 5 H, C_5H_5), 7.17—7.65 (m, 8 H, C_6H_4)	296.9, 289.9 (μ-C), 219.1, 211.6 (CO), 148.0, 147.7 [$C^1(C_6H_4)$], 142.3, 141.4, 130.3, 129.4, 129.1 (C_6H_4), 93.0 (C_5H_5), 65.7 (*C*Me), 30.5 (C*Me*), 21.9, 21.8 (Me-4)
(6b)	2.18 (s, 6 H, CMe), 2.62, 2.81 (s × 2, 6 H, μ-CMe), 5.75 (s, 5 H, C_5H_5)	305.7 [μ-C, *J*(WC) 138], 301.0 [μ-C, *J*(WC) 147], 218.4 [CO, *J*(WC) 165], 210.9 [CO, *J*(WC) 182], 92.6 (C_5H_5), 65.5 (*C*Me), 41.8, 41.4 (μ-C*Me*), 30.4 (C*Me*)
(6c)	2.12 (s, 6 H, CMe), 2.34 (s, 3 H, Me-4), 2.85 (s, 3 H, μ-CMe), 5.84 (s, 5 H, C_5H_5), 7.18, 7.53 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	305.0 [μ-C, *J*(WC) 138], 291.7 [μ-C, *J*(WC) 152], 218.0 [CO, *J*(WC) 161], 212.2 [CO, *J*(WC) 181], 147.9 [$C^1(C_6H_4)$], 142.6, 130.4, 129.3 (C_6H_4), 93.0 (C_5H_5), 65.6, 65.3 (*C*Me), 41.4 (μ-C*Me*), 30.3 (C*Me*), 21.7 (Me-4)
(6d)	2.16 (s × 2, 6H, CMe), 2.35 (s, 6 H, Me-4), 5.70 (s, 5 H, C_5H_5), 7.19—7.60 (m, 8 H, C_6H_4)	301.1 297.2 (μ-C), 223.4, 219.7 (CO), 148.2, 145.4 [$C^1(C_6H_4)$], 143.4, 141.9, 131.2, 130.3, 129.6, 129.3 (C_6H_4), 94.8 (C_5H_5), 66.2 (*C*Me), 30.6 (C*Me*), 21.8, 21.7 (Me-4)
(7a)	2.32 (s, 3 H, Me-4), 5.85 (s, 5 H, C_5H_5), 7.13, 7.57 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	285.9 (μ-C), 212.8 (CO), 149.6 [$C^1(C_6H_4)$], 142.2, 128.9 (C_6H_4), 92.0 (C_5H_5), 21.4 (Me-4)
(7b)	2.35 (s, 3 H, Me-4), 5.79 (s, 5 H, C_5H_5), 7.15, 7.66 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	296.8 (μ-C), 223.7 (CO), 146.6 [$C^1(C_6H_4)$], 131.3, 129.3 (C_6H_4), 93.7 (C_5H_5), 21.6 (Me-4)
(7c)[e]	2.59 (s, 3 H, CMe), 5.77 (s, 5 H, C_5H_5)	
(8a)	2.00 [mbr, 8 H, CH_2(cod)], 2.07, 2.23, 2.32, 2.39 (s × 4, 12 H, CMe and Me-4), 4.00—5.40 [m, 4 H, CH(cod)], 5.62 (s, 5 H, C_5H_5), 7.13—7.19 (m, 8 H, C_6H_4)	284.9 (μ-C), 282.1 (μ_3-C), 235.4, 215.7, 212.7, 212.1 (CO), 150.9, 147.7 [$C^1(C_6H_4)$], 141.2—125.5 (C_6H_4), 105.7 (br), 99.3, 94.8 [CH(cod)],[f] 93.6 (C_5H_5), 67.7, 64.2 (*C*Me), 31.0, 30.2, 29.8, 29.6, 29.4, 28.9 [*C*Me and CH_2(cod)], 21.6, 20.8 (Me-4)
(8b)	1.01 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 40], 1.10 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 38], 1.50 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 23], 1.90 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 23], 2.18, 2.19, 2.24, 2.32 (s × 4, 12 H, CMe and Me-4), 6.81—7.44 (m, 18 H, Ph and C_6H_4)	295.1 (μ-C), 290.2 [d, μ_3-C, *J*(PC) 60], 221.4, 220.2, 219.9, 215.0 (CO), 159.8, 149.9 [$C^1(C_6H_4)$], 139.8—123.5 (Ph and C_6H_4), 93.6 (C_5H_5), 65.3, 65.2 (*C*Me), 30.9, 30.8 (C*Me*), 21.8, 20.9 (Me-4), 17.7 [d, MeP, *J*(PC) 29], 16.9 [d, MeP, *J*(PC) 31], 15.6 [d, MeP, *J*(PC) 28], 15.2 [d, MeP, *J*(PC) 27]
(8c)	1.05 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 38], 1.13 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 39], 1.60 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 24], 1.85 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 24], 1.85 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 23], 2.14, 2.22, 2.28 (s × 3, 9 H, CMe and Me-4), 2.63 (s, 3 H, μ-CMe), 5.46 (s, 5 H, C_5H_5), 6.94—7.75 (m, 14 H, Ph and C_6H_4)	303.9 (μ-C), 289.4 [d, μ_3-C, *J*(PC) 61], 220.6, 219.5, 219.2, 213.6 (CO), 159.6 [$C^1(C_6H_4)$], 134.5—123.5 (Ph and C_6H_4), 93.5 (C_5H_5), 64.6, 64.3 (*C*Me), 41.0 (μ-C*Me*), 30.5, 30.3 (C*Me*), 20.7 (Me-4), 17.0 [d, MeP, *J*(PC) 24], 16.5 [d, MeP, *J*(PC) 31], 16.1 [d, MeP, *J*(PC) 29], 15.5 [d, MeP, *J*(PC) 32]
(8d)	1.01 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 40], 1.07 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 38], 1.49 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 23], 1.87 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 22], 2.19, 2.21, 2.26, 2.34 (s × 4, 12 H, CMe and Me-4), 5.16 (s, 5 H, C_5H_5), 6.88—7.46 (m, 18 H, Ph and C_6H_4)	303.7 [d, μ_3-C, *J*(PC) 64], 294.3 (μ-C), 233.9 [d, WCO, *J*(PC) 12], 225.3, 219.8, 219.5 (CO), 158.5, 149.8 [$C^1(C_6H_4)$], 139.5—124.9 (Ph and C_6H_4), 95.2 (C_5H_5), 65.2, 65.0 (*C*Me), 30.6, 30.5 (C*Me*), 21.5, 20.7 (Me-4), 17.2, 16.5, 15.7, 15.0 (m × 4, MeP)
(11a)	0.88 [d, 3 H, MePPt, *J*(PH) 9, *J*(PtH) 37], 1.04 [d, 3 H, MePPt, *J*(PH) 9, *J*(PtH) 30], 1.60 [d, MePPt, *J*(PH) 8, *J*(PtH) 23], 1.78 [d, 3 H, MePPt, *J*(PH) 8, *J*(PtH) 23], 1.87 [d, 6 H, MePAu, *J*(PH) 10], 2.19, 2.27, 2.37 (s × 3, 9 H, CMe and Me-4), 6.88—7.70 (m, 19 H, Ph and C_6H_4)	290.7 [d of d, μ_3-C, *J*(PC) 56, 20], 225.4, 224.4 (CO), 161.4 [$C^1(C_6H_4)$], 133.8—123.0 (Ph and C_6H_4), 66.0, 65.7 (*C*Me), 32.0, 30.0 (C*Me*), 20.8 (Me-4), 17.9 [d, MePPt, *J*(PC) 29, *J*(PtC) 44], 16.7, 16.3, 15.8, 15.3, 14.8 (m × 5, MePPt and MePAu)

[a] Chemical shifts in p.p.m., coupling constants in Hz, measurements at room temperature in CD_2Cl_2 unless otherwise stated. [b] For complexes containing the η^5-$C_2B_9H_9Me_2$ ligand the resonances for the 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.). [d] Measured in $CDCl_3$. [e] Instability of complex in solution prevented measurement of ^{13}C-{^1H} spectrum. [f] These signals show ^{195}Pt satellite peaks, with *J*(PtC) *ca.* 105—137 Hz.

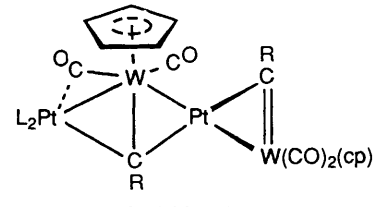
compounds **(8a)**—**(8c)** the more shielded signal is assigned to the μ_3-C nucleus, on the basis of earlier studies.[2,11] In agreement with this assignment, the resonances at δ 290.2 and 289.4 p.p.m. for **(8b)** and **(8c)**, respectively, appear as doublets. This feature may be attributed to ^{31}P–^{13}C coupling (*ca.* 60 Hz) with a transoid PMe_2Ph ligand on the platinum atom. In the ^{13}C-{^1H} n.m.r. spectrum of the compound [$W_2Pt_2(\mu$-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)$(CO)_4(PMePh_2)_2(\eta$-$C_5H_5)_2$] **(10a)**,[2e] which is structurally related to **(8b)**, the μ_3-C resonance (δ 252.8 p.p.m.) is also a doublet with *J*(PC) 51 Hz.

In contrast with the data for compounds **(8b)** and **(8c)**, in the ^{13}C-{^1H} n.m.r. spectrum of **(8d)** it is the more deshielded



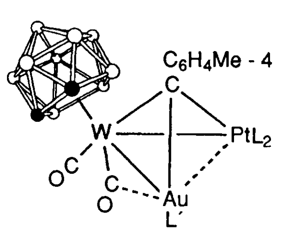
○ BH ● CMe

(9)



$R = C_6H_4Me$ - 4

	L_2
(10a)	2 PMe_2Ph
(10b)	cod



● CMe ○ BH

	L_2	L′
(11a)	2 PMe_2Ph	PMe_2Ph
(11b)	cod	PPh_3

resonance at δ 303.7 p.p.m. which displays ^{31}P–^{13}C coupling (64 Hz), and this signal must be assigned to the μ_3-C nucleus. However, the substitution of a molybdenum atom for tungsten could influence the values of the chemical shifts of **(8d)** compared with those of **(8b)** or **(8c)**. Moreover, the presence of the η^5-$C_2B_9H_9Me_2$ ligand in the complexes **(8)** clearly effects the chemical shifts observed for the μ-C and μ_3-C groups. This is evident from a comparison of the resonances for the alkylidyne-carbon nuclei in the spectra of the two pairs of compounds **(8a)** (μ-C, 284.9; μ_3-C, 282.1) and (**10b**, one isomer) (μ-C, 310.6; μ_3-C, 251.7), and **(8b)** (μ-C, 295.1; μ_3-C, 290.2) and **(10a)** (μ-C, 311.8; μ_3-C, 252.8 p.p.m.).[2e] Thus for complexes in which the carbaborane cage ligates tungsten the difference between the chemical shifts for μ-C and μ_3-C groups is appreciably smaller than that observed for analogous species containing the η-C_5H_5 ligand.

The compounds **(8)** all display four CO peaks in their ^{13}C-{^{1}H} spectra, indicating that these groups do not undergo site exchange on the n.m.r. time-scale. This is in contrast with the behaviour of the complexes **(6)**, discussed above. In their i.r. spectra the complexes **(8)** show three CO absorptions (Table 1); that at lowest frequency may be assigned to an asymmetrically bridging group. The compounds **(10)** show a similar band pattern in the CO region.[2e] It is noteworthy that in the ^{13}C-{^{1}H} n.m.r. spectrum of **(8d)** the CO resonance at δ 233.9 is a doublet [*J*(PC) 12 Hz]. This is in accord with this signal being due to a CO ligand semi-bridging the W–Pt bond.

The ^{31}P-{^{1}H} n.m.r. spectra of the complexes **(8b)**—**(8d)** were measured (see Experimental section). For each compound the expected two doublet resonances were observed, and in addition the signals showed ^{195}Pt satellite peaks.

It was anticipated that treatment of **(8a)** with PMe_2Ph in excess would afford complex **(8b)** by displacement of the cod group. In practice only a trace of **(8b)** was obtained *via* this reaction. The main products were [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] and [WPtAu(μ_3-CC_6H_4Me-4)$(CO)_2(PMe_2Ph)_3$(η^5-$C_2B_9H_9Me_2$)] **(11a)**. The latter complex, characterised by microanalysis and spectroscopic data (Tables 1 and 2), is structurally similar to the previously reported[7] species [WPtAu(μ_3-CC_6H_4Me-4)$(CO)_2(PPh_3)$(cod)(η^5-$C_2B_9H_9Me_2$)] **(11b)**. Compound **(11b)** was prepared by treating the $[P(CH_2Ph)Ph_3]^+$ salt of the anion of **(9)** with [AuCl(PPh_3)] and $TlPF_6$.

Formation of compound **(11a)** results from displacement of both the cod and the W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5) groups from **(8a)** by PMe_2Ph ligands; a result further supporting the proposed structure of the latter with the 4-MeC_6H_4C≡W$(CO)_2$-(η-C_5H_5) group ligating the gold atom. Displacement of alkylidynemetal groups from gold with tertiary phosphines has been previously observed.[5]

The spectroscopic data for **(11a)** are in agreement with the formulation given. Two CO bands (1 893 and 1 814 cm^{-1}) are observed in the i.r. spectrum. In the spectrum of **(11b)** the corresponding bands are seen at 1 948 and 1 795 cm^{-1}, suggesting that in this species only one CO ligand semi-bridges a metal–metal bond. Both **(11a)** and **(11b)** show, in their ^{13}C-{^{1}H} n.m.r. spectra, diagnostic resonances for the μ_3-C nuclei. For **(11a)** the signal is a doublet of doublets at δ 290.7 p.p.m. [*J*(PC) 56 and 20 Hz], and the corresponding signal in the spectrum of **(11b)** is a doublet at δ 291.1 p.p.m. [*J*(PC) 15 Hz]. The ^{31}P-{^{1}H} n.m.r. spectrum of **(11a)** has resonances at δ 27.5 (PAu), −3.3 and −12.2 p.p.m. (PPt). This assignment is firmly based on the observation of ^{195}Pt satellite peaks on the last two signals (see Experimental section).

Isolation of the complexes **(6)** and **(8)** suggests interesting possibilities for their future use as reagents for the synthesis of polynuclear metal compounds. The presence of the C=M (M = Mo or W) groups in these species should facilitate addition of a variety of metal–ligand fragments thereby affording new mixed-metal complexes.[2,12]

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C, and all solvents were freshly distilled over appropriate drying agents prior to use. Chromatography was carried out on alumina (Brockman, activity II), and all compounds were handled using Schlenk-tube techniques under oxygen-free nitrogen. The reagents [AuCl(tht)],[13] [M(≡CR′)$(CO)_2$(η-C_5H_5)] (M = W, R′ = C_6H_4Me-4 or Me; M = Mo, R′ = C_6H_4Me-4),[14] $[NEt_4]$[W(≡CR)$(CO)_2$(η^5-$C_2B_9H_9Me_2$)] (R = C_6H_4Me-4 or Me),[6,7] [Pt$(cod)_2$], and [Pt$(nb)_3$][15] were prepared by published procedures. The instrumentation used for the spectroscopic measurements has been described in previous parts of this series.[2] Phosphorus-31 n.m.r. chemical shifts, measured in CD_2Cl_2, are positive to high frequency of 85% H_3PO_4 (external). Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Complexes [MAuCl(μ-CR′)$(CO)_2$(η-C_5H_5)] **(7)**.—(*i*) A CH_2Cl_2 (20 cm^3) solution of [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] (0.08 g, 0.20 mmol) was treated with [AuCl(tht)] (0.06 g, 0.20 mmol). After stirring the mixture for 30 min solvent was removed *in vacuo*. The residue was washed with light petroleum (3 × 15 cm^3), and crystallised from CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1:10) to give red *microcrystals* of [WAuCl(μ-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] **(7a)** (0.11 g).

(*ii*) In a similar experiment a CH_2Cl_2 (20 cm^3) solution of $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.06 g, 0.20 mmol) was treated with $[AuCl(tht)]$ (0.06 g, 0.20 mmol) to give red *microcrystals* of $[MoAuCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (**7b**) (0.09 g).

(*iii*) Using the same procedure as that described above for (**7a**), the compound $[WAuCl(\mu\text{-}CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (**7c**) (0.10 g) was obtained from $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.06 g, 0.20 mmol) and $[AuCl(tht)]$ (0.06 g, 0.20 mmol).

Synthesis of the Complexes $[MWAu(\mu\text{-}CR)(\mu\text{-}CR')(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6**).—(*i*) A CH_2Cl_2 (25 cm^3) solution of complex (**7a**) (0.13 g, 0.20 mmol) was treated with $TlBF_4$ (0.07 g, 0.25 mmol), and the mixture was stirred for 5 min before addition of the salt $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.13 g, 0.20 mmol). The reactants were stirred for 15 min, and the mixture was filtered through a Celite pad (*ca.* 2 cm). Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 2:3) and chromatographed on alumina. Elution with the same solvent mixture afforded a red eluate. Removal of solvent *in vacuo* gave red *microcrystals* of $[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6a**) (0.19 g).

(*ii*) Similarly, complex (**7c**) (0.11 g, 0.20 mmol) and $TlBF_4$ (0.07 g, 0.25 mmol) in CH_2Cl_2 (25 cm^3) with $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.11 g, 0.20 mmol) yielded orange *microcrystals* of $[W_2Au(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6b**) (0.14 g).

(*iii*) Treatment of complex (**7a**) (0.13 g, 0.20 mmol) and $TlBF_4$ (0.07 g, 0.25 mmol) in CH_2Cl_2 (25 cm^3) with $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.11 g, 0.20 mmol) afforded orange *microcrystals* of $[W_2Au(\mu\text{-}CMe)(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6c**) (0.15 g), after the same work-up procedures as used for (**6a**).

(*iv*) Compound $[MoWAu(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6d**) (0.16 g) was similarly prepared as red *microcrystals* from (**7b**) (0.11 g, 0.20 mmol), $TlBF_4$ (0.07 g, 0.25 mmol), and $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (0.13 g, 0.20 mmol).

Reactions of the Complexes $[MWAu(\mu\text{-}CR)(\mu\text{-}CR')(CO)_4(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$.—(*i*) A cold (0 °C) thf (10 cm^3) solution of complex (**6a**) (0.11 g, 0.10 mmol) was added to an ethylene-saturated thf solution (0 °C) of $[Pt(cod)_2]$ (0.05 g, 0.12 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 (10 cm^3, 1:1) and chromatographed on alumina. Elution with the same solvent mixture removed a trace of (**6a**), and this was followed by a red fraction. Removal of solvent *in vacuo* from the latter gave purple-red *microcrystals* of $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8a**) (0.09 g).

Complex (**8a**) was also prepared by an alternative procedure. A thf (25 cm^3) solution of (**7a**) (0.06 g, 0.10 mmol) was treated with $TlBF_4$ (0.03 g, 0.12 mmol) and the mixture was stirred for 15 min. Compound (**9**) (0.09 g, 0.10 mmol) was then added, and the reactants were stirred for 15 min, after which time the mixture was filtered through a Celite pad (*ca.* 1 cm). Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture gave a purple-red eluate. Removal of solvent *in vacuo* gave *microcrystals* of (**8a**) (0.11 g, 80%).

(*ii*) A thf (20 cm^3) solution of $[Pt(PMe_2Ph)_2(nb)]$ (0.10 mmol) was prepared *in situ* from $[Pt(nb)_3]$ (0.05 g, 0.10 mmol) and PMe_2Ph (0.20 mmol, 1 cm^3 of a 0.20 mol dm^{-3} solution in thf). This mixture was treated with complex (**6a**) (0.11 g, 0.10 mmol). After stirring the reactants for 2 h, solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 2:3), and the product was isolated by chromatography. Elution of the column with the same solvent mixture, followed by removal of solvent *in vacuo*, gave brown *microcrystals* of $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8b**) (0.11 g). $^{31}P\text{-}\{^1H\}$ N.m.r.: δ −5.5 [d, *J*(PP) 6, *J*(PtP) 4 027] and −15.8 p.p.m. [d, *J*(PP) 6, *J*(PtP) 2 824 Hz].

(*iii*) In a similar synthesis, $[Pt(PMe_2Ph)_2(nb)]$ (0.10 mmol) and (**6c**) (0.10 g, 0.10 mmol) afforded brown *microcrystals* of $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8c**) (0.10 g). $^{31}P\text{-}\{^1H\}$ N.m.r.: δ −7.2 [d, *J*(PP) 4, *J*(PtP) 4 060] and −16.2 p.p.m. [d, *J*(PP) 4, *J*(PtP) 2 802 Hz].

(*iv*) Treatment of a thf (20 cm^3) solution of $[Pt(PMe_2Ph)_2(nb)]$ (0.10 mmol), prepared *in situ* from $[Pt(nb)_3]$ and PMe_2Ph as described above, with compound (**6d**) (0.10 g, 0.10 mmol) afforded, after chromatography, green *microcrystals* of $[MoWPtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8d**) (0.09 g). $^{31}P\text{-}\{^1H\}$ N.m.r.: δ −12.2 [d, *J*(PP) 6, *J*(PtP) 4 118] and −15.5 p.p.m. [d, *J*(PP) 6, *J*(PtP) 2 754 Hz]. This reaction also yields a trace of $[Mo_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$[2b] and the trimetal complex (**11a**), separated by chromatography and identified by i.r. spectroscopy.

Reaction between $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ *and* PMe_2Ph.—A thf (20 cm^3) solution of complex (**8a**) (0.14 g, 0.10 mmol) was treated with PMe_2Ph (0.30 mmol, 1.5 cm^3 of a 0.20 mol dm^{-3} solution in thf), and the mixture was stirred for 30 min. 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 fast-running orange fraction which was identified by i.r. spectroscopy as $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.02 g, *ca.* 50%). This was followed by a brown eluate which by i.r. and ^1H n.m.r. spectroscopy was shown to contain a trace (*ca.* 8 mg) of complex (**8b**). Further elution of the chromatography column with CH_2Cl_2–light petroleum (3:1) afforded a green eluate. Removal of solvent *in vacuo* and crystallisation from CH_2Cl_2–light petroleum (20 cm^3, 1:4) gave green *microcrystals* of $[WPtAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_3(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**11a**) (0.07 g). $^{31}P\text{-}\{^1H\}$ N.m.r.: δ 27.5 (s, PAu), −3.3 [s, PPt, *J*(PPt) 4 131], and −12.2 p.p.m. [s, PPt, *J*(PPt) 2 855 Hz].

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