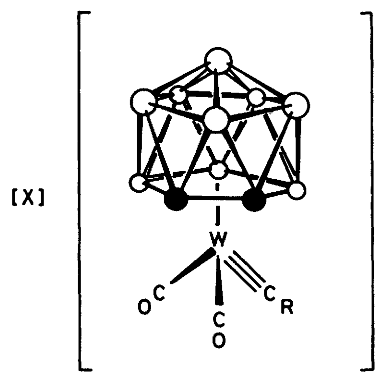
In memory of S. M. Nelson and T. A. Stephenson

Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 67.[1] Reactions of the Salts [X][W(≡CR)(CO)$_2$-(η^5-$C_2B_9H_9Me_2$)][X = P(CH$_2$Ph)Ph$_3$, R = C_6H_4Me-4; X = NEt$_4$, R = Ph] with Bis(cyclo-octa-1,5-diene)platinum *

Franz-Erich Baumann, Judith A. K. Howard, Owen Johnson, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The salts [X][W(≡CR)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)] [X = NEt$_4$, R = Ph; X = P(CH$_2$Ph)Ph$_3$ or PPh$_4$, R = C_6H_4Me-4] have been prepared, and an *X*-ray diffraction study has been carried out on the tetraphenylphosphonium compound. There are two very similar crystallographically independent anions, together with their associated counter ions, in the asymmetric unit of the structure. In the anion the tungsten atom carries two terminally bound carbonyl ligands (W–CO mean 2.019 Å, W–C–O mean 176.9°), a *p*-tolylmethylidyne ligand [W≡CC$_6$H$_4$Me-4 mean 1.83(3) Å], and the η^5-7,8-$C_2B_9H_9Me_2$ cage [mean W–ligated cage atoms, 2.424 Å (mean of 10)]. Treatment of the species [X][W(≡CR)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)] [X = P(CH$_2$Ph)Ph$_3$, R = C_6H_4Me-4; X = NEt$_4$, R = Ph] in thf (tetrahydrofuran) with [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) affords the complexes [P(CH$_2$Ph)Ph$_3$][PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(cod)(η^5-$C_2B_9H_9Me_2$)] (**2a**) and [NEt$_4$][PtW(μ-CPh)-(CO)$_2$(cod)(η^5-$C_2B_9H_9Me_2$)] (**2b**), respectively. The cod ligand in the compounds (**2**) may be displaced with tertiary phosphines, but crystalline products were not obtained. Moreover, protonation of (**2**) led to decomposition. However, treatment of (**2a**) with [AuCl(PPh$_3$)] and TlPF$_6$, and (**2b**) with the gold reagent and KPF$_6$, in thf, affords the trimetal compounds [AuPtW(μ_3-CR)-(CO)$_2$(PPh$_3$)(cod)(η^5-$C_2B_9H_9Me_2$)] (R = C_6H_4Me-4 or Ph), which were fully characterised. The n.m.r. data (^{1}H, ^{13}C-{^{1}H}, ^{195}Pt-{^{1}H}, and ^{31}P-{^{1}H}) for the complexes are reported.

We have previously described the synthesis of the salt [N(PPh$_3$)$_2$][W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)] (**1a**). Treatment of (**1a**) with [AuCl(PPh$_3$)], [RhCl(PPh$_3$)$_3$], [Rh(PPh$_3$)$_2$L$_2$][PF$_6$] [L$_2$ = cod (cyclo-octa-1,5-diene) or nbd (norborna-2,5-diene)], [Ru(CO)(NCMe)$_2$(η-C$_5$H$_5$)][BF$_4$], or [M(CO)$_2$(NCMe)$_2$(η^5-C$_9$H$_7$)][BF$_4$] (M = Mo or W, η^5-C$_9$H$_7$ = indenyl) affords neutral dimetal compounds in which the metal–metal bonds (Au–W, Rh–W, Ru–W, Mo–W, or W–W) are bridged by a *p*-tolylmethylidyne group.[2] These results suggested the possibility that the C≡W bond present in (**1a**) would combine with neutral metal–ligand fragments to afford anionic polynuclear metal complexes which might have interesting properties. Preliminary studies revealed that in such reactions (**1a**) generally afforded products difficult to crystallise. This led us to prepare the related salts [X][W(≡CR)-(CO)$_2$(η^5-$C_2B_9H_9Me_2$)] [(**1b**), X = NEt$_4$, R = Ph; (**1c**), X = P(CH$_2$Ph)Ph$_3$, R = C$_6$H$_4$Me-4; (**1d**), X = PPh$_4$, R = C$_6$H$_4$Me-4] in the expectation that changing the cation or the alkylidyne group would yield more tractable complexes. This strategy has been partially successful in reactions with zero-valent platinum complexes described herein. Moreover, the availability of crystals of (**1d**) has allowed an *X*-ray diffraction study to be made on this species. Single-crystal *X*-ray diffraction studies on the neutral compounds [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)][3] and [W(≡CC$_6$H$_4$Me-4)(CO)$_2${B(pz)$_4$}] [B(pz)$_4$ = tetrakis(pyrazol-1-yl)borate][4] have been reported, and in view of the extensive ligating properties of the C≡W groups in compounds of this type knowledge of the structures of these reagents is important.



	X	R
(**1a**)	N(PPh$_3$)$_2$	C$_6$H$_4$Me-4
(**1b**)	NEt$_4$	Ph
(**1c**)	P(CH$_2$Ph)Ph$_3$	C$_6$H$_4$Me-4
(**1d**)	PPh$_4$	C$_6$H$_4$Me-4

○ BH ● CMe

Results and Discussion

Treatment of a thf (tetrahydrofuran) solution of [W(≡CPh)-Br(CO)$_4$] with Na$_2$[7,8-$C_2B_9H_9Me_2$], followed by addition of NEt$_4$Cl, affords [NEt$_4$][W(≡CPh)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)] (**1b**) in *ca.* 70% yield. The salts (**1c**) and (**1d**) were prepared similarly, using the reagents [P(CH$_2$Ph)Ph$_3$]Cl and PPh$_4$Cl,

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

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

	Compound	Colour	Yield (%)	$\nu_{max.}(CO)^{b}/cm^{-1}$	Analysis (%) C	H
(**1b**)	$[NEt_4][W(\equiv CPh)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$	Red-orange	70	1 964s, 1 880vs	[c] 38.3 (40.7)	6.6 (6.6)
(**1c**)	$[P(CH_2Ph)Ph_3][W(\equiv CC_6H_4Me-4)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$	Orange	73	1 960s, 1 876vs	54.3 (54.7)	5.5 (5.2)
(**1d**)	$[PPh_4][W(\equiv CC_6H_4Me-4)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$	Orange	71	1 959s, 1 874vs	54.7 (54.2)	5.3 (5.0)
(**2a**)	$[P(CH_2Ph)Ph_3][PtW(\mu-CC_6H_4Me-4)(CO)_2(cod)(\eta^5-C_2B_9H_9Me_2)]$	Orange-red	82	1 916sv, 1 693m br	47.6 (48.7)	5.0 (5.0)
(**2b**)	$[NEt_4][PtW(\mu-CPh)(CO)_2(cod)(\eta^5-C_2B_9H_9Me_2)]$	Red-orange	68	[d] 1 920s, 1 711m br	[e] 36.5 (37.7)	5.6 (5.7)
(**4a**)	$[AuPtW(\mu_3-CC_6H_4Me-4)(CO)_2(PPh_3)(cod)(\eta^5-C_2B_9H_9Me_2)]$	Black	25	1 948vs, 1 795m br	36.4 (38.0)	4.0 (4.0)
(**4b**)	$[AuPtW(\mu_3-CPh)(CO)_2(PPh_3)(cod)(\eta^5-C_2B_9H_9Me_2)]$	Black	90	1 948s, 1 804m br	37.8 (37.5)	3.7 (3.8)

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] N, 2.2 (2.3%). [d] In thf. [e] N, 1.5 (1.5%).

Table 2. Selected bond distances (Å) and interbond angles (°) for one of the crystallographically independent molecules of $[PPh_4][W(\equiv CC_6H_4Me-4)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ (**1d**)[a]

W(1)–C(1)	1.955 [2.020]	W(1)–C(2)	2.023 [2.077]	W(1)–C(50)	1.82(3) [1.84(3)]	C(50)–C(51)	1.46(3) [1.48(3)]
C(1)–O(1)	1.124 [1.132]	C(2)–O(2)	1.100 [1.134]	W(1)–cage[b]	2.427(8) [2.421(9)]	P(1)–C(Ph)	1.79(1) [1.79(1)]

W(1)–C(1)–O(1)	176.2 [174.8]	W(1)–C(2)–O(2)	178.5 [178.2]	W(1)–C(50)–C(51)	171(2) [166(2)]
C(1)–W(1)–C(50)	88.9(8) [83.6(9)]	C(2)–W(1)–C(50)	81.2(9) [83.2(9)]	C(1)–W(1)–C(2)	90.7 [87.8]

[a] Values in square brackets refer to the corresponding parameter in the second crystallographically independent molecule. Estimated standard deviations (e.s.d.s) appear in parentheses only where the positions of all atoms involved were refined without constraints. No e.s.d.s are given for parameters involving constrained (geometrically or positionally) atoms. [b] Mean value from W to ligated cage atoms.

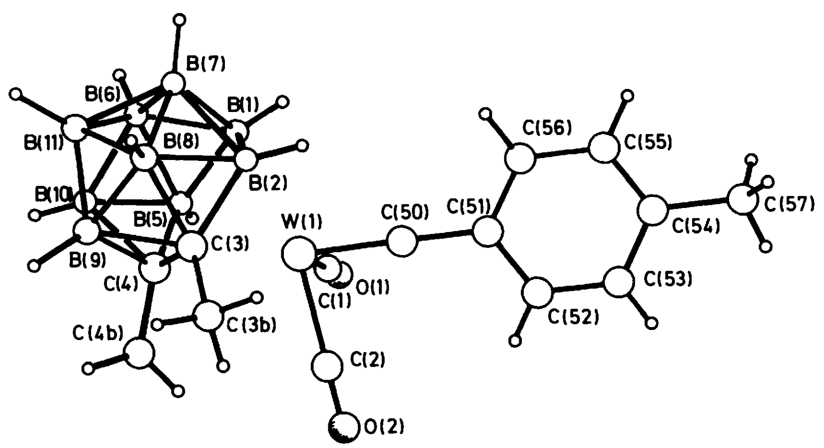


Figure. The molecular structure of one of the two crystallographically independent anions of $[PPh_4][W(\equiv CC_6H_4Me-4)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ (**1d**) showing the atom-numbering scheme

respectively. Some data for these species are given in Table 1. The i.r. spectra of the salts are characterised by the appearance of two bands in the carbonyl stretching region. For comparison, the spectrum of (**1a**) has these bands at 1 956 and 1 874 cm^{-1}.[2a] In the $^{13}C-\{^1H\}$ n.m.r. spectrum of (**1b**) the resonance for the ligated carbon of the CPh group occurs at δ 297.3 p.p.m., with ^{183}W satellite peaks [J(WC) 199 Hz]. The corresponding signal in the spectrum of (**1a**) is seen at 298.3 p.p.m. with J(WC) 198 Hz.[2a]

Of the four salts (**1a**)—(**1d**), only (**1d**) gave crystals of suitable quality for *X*-ray analysis. The results are summarised in Table 2, and the structure of the anion is shown in the Figure. There are two crystallographically independent anions and their associated cations in the asymmetric unit, and the poor agreement between some of the corresponding structural parameters we attribute to a less than satisfactory least-squares refinement due to the presence of a pseudo-inversion centre. Nevertheless, the gross features of the two anions are essentially the same. The short W(1)–C(50) separation [1.82(3) and W(1′)–C(50′), 1.84(3) Å] compares well with that in the neutral species $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ [1.82(2) Å].[3] The carbonyl ligands attached to tungsten [W(1)–C(1) 1.955, W(1)–C(2) 2.023, W(1′)–C(1′) 2.020, and W(1′)–C(2′) 2.077 Å] are all terminally bound [W(1)–C(1)–O(1) 176.2, W(1)–C(2)–O(2) 178.5, W(1′)–C(1′)–O(1′) 174.8, and W(1′)–C(2′)–O(2′), 178.2°].

Table 3. Hydrogen-1, carbon-13, and platinum-195 n.m.r. data[a] for the complexes

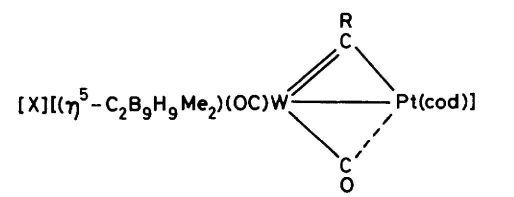
Compound	$^{1}H(\delta)$[b]	$^{13}C(\delta)$[c]	$^{195}Pt(\delta)$[d]
(**2a**)	1.30—1.52 [m, 8 H, CH_2(cod)], 2.02 (s, 3 H, CMe), 2.30 (s, 3 H, Me-4), 2.34 (s br, 3 H, CMe), 4.52 [d, 2 H, CH_2Ph, *J*(PH) 14], 4.55—4.91 [m, 2 H, CH(cod)], 5.54—5.76 [m, 2 H, CH(cod)], 6.86—7.84 (m, 24 H, C_6H_4 and Ph)	[e,f] 314.3 [μ-C, *J*(PtC) 741, *J*(WC) 145], 238.6 [CO, *J*(WC) 170, *J*(PtC) 122], 155.9 [$C^1(C_6H_4)$], 133.9, 127.8, 122.5 (C_6H_4), 104.2, 93.8 [CH(cod)], 72.8 [*C*Me, *J*(PtC) 142], 61.9 (*C*Me), 33.0 [C*Me*, *J* (PtC) 15], 30.6, 30.0 (CH_2, cod), 29.3 (C*Me*), 21.3 (Me-4)	499.1 [*J*(WPt) 283]
(**2b**)	1.20 [t of t, 12 H, CH_2*Me*, *J*(HH) 7, *J*(NH) 2], 1.70—2.18 [m br, 8 H, CH_2(cod)], 2.07 (s, 6 H, CMe), 3.08 [q, 8 H, *CH*$_2$Me, *J*(HH) 8], 4.30—5.60 [m, 4 H, CH(cod)], 6.23—7.07 (m, 5 H, Ph)	[f] 312.8 [μ-C, *J*(PtC) 739, *J*(WC) 140], 238.6 [CO, *J*(WC) 171, *J*(PtC) 122], 159.3 [C^1(Ph)], 127.3, 124.3, 122.3 (Ph), 104.6, 94.3 [CH(cod)], 62.1 (*C*Me), 59.5 [*C*Me, *J*(PtC) 115], 52.4 (*C*H$_2$Me), 30.6, 30.1 [CH_2(cod)], 29.4 [C*Me*, *J*(PtC) 50], 28.2 (C*Me*), 7.7 (CH_2*Me*)	498.1 [*J*(WPt) 273]
(**4a**)	0.88—2.10 [m br, 8 H, CH_2(cod)], 2.15 (s, 6 H, CMe), 2.36 (s, 3 H, Me-4), 4.46—5.08 [m, 4 H, CH(cod)], 7.06—7.22 (m, 4 H, C_6H_4), 7.42—7.76 (m, 15 H, Ph)	291.1 [d, μ_3-C, *J*(PC) 15, *J*(PtC) 595, *J*(WC) 139], 231.3 [CO, *J*(WC) 150], 218.9 [CO, *J*(WC) 162], 153.5 [$C^1(C_6H_4)$, *J*(PtC) 24], 136.3 (C_6H_4), 134.4 [d, *J*(PC) 12, Ph], 132.9 (C_6H_4 or Ph), 129.9 [d, *J*(PC) 12, Ph], 128.5, 124.4 (C_6H_4 or Ph), 106.3, 106.0, 99.4, 93.6 [CH(cod)], 66.6, 65.3 (*C*Me), 31.3, 30.6, 30.1, 29.8 [CH_2(cod) and C*Me*], 21.2 (Me-4)	886.7 [d *J*(PtP) 100]
(**4b**)	0.79—2.58 [m br, 8 H, CH_2(cod)], 2.15 (s, 6 H, CMe), 4.44—5.76 [m, 4 H, CH(cod)], 7.04—7.26 (m, 5 H, μ-CPh), 7.40—7.76 (m, 15 H, PPh_3)	290.2 [d, μ_3-C, *J*(PC) 15, *J*(PtC) 591], 231.1, 218.5 (CO), 156.3 [C^1(Ph), *J*(PtC) 22], 134.7—124.2 (Ph), 106.1 [CH(cod), 2 × C], 99.5, 93.6 [CH(cod)], 66.7 [*C*Me, *J*(PtC) 12], 65.4 [d, *C*Me, *J*(PC) 5], 31.5, 30.8, 30.1, 29.9, 29.5 (CH_2 and C*Me*)	868.3 [d, *J*(PtP) 98, *J*(WPt) 235]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, and measurements at room temperature unless otherwise stated. [b] Measured in CD_2Cl_2. Proton resonances for B–H groups occur as broad unresolved signals in the range δ 0—3. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2 at room temperature unless otherwise stated. Signals due to CH groups of cod ligands show ^{195}Pt satellite peaks with *J*(PtC) 90—150 Hz. [d] Hydrogen-1 decoupled, δ values are to high frequency of Ξ (^{195}Pt) = 21.4 MHz. [e] Peaks due to $[P(CH_2Ph)Ph_3]^+$ cation observed but not listed. [f] Measured at −40 °C.

As mentioned in the Introduction, we wished to investigate reactions of the salts (**1**) with neutral metal complexes having labile ligands in order to obtain anionic di- or poly-nuclear metal compounds with bridging alkylidyne groups. Previous work employing the compounds $[W(\equiv CR)(CO)_2L]$ {R = C_6H_4Me-4, Ph, or Me; L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]} as building blocks in the synthesis of compounds with heteronuclear metal–metal bonds afforded neutral products.[5] The isolation of anionic species offers the possibility of observing new reactivity patterns. Since in earlier studies we had shown that $[Pt(cod)_2]$ reacts very readily with the W≡C bonds in the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)]$ (R = C_6H_4Me-4 or Ph, R′ = H or Me),[6] the zero-valent platinum reagent was used in our initial studies with the compounds (**1**).

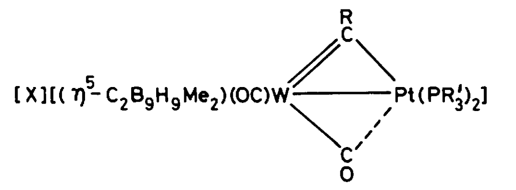
Treatment of (**1c**) with $[Pt(cod)_2]$ in thf at 0 °C afforded the complex $[P(CH_2Ph)Ph_3][PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2a**). The salt $[NEt_4][PtW(\mu\text{-}CPh)(CO)_2(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2b**) was similarly obtained from (**1b**). The compounds (**2**) were characterised by the data given in Tables 1 and 3. Both complexes showed two carbonyl stretching bands in their i.r. spectra; one occurs at relatively low frequency [1 693 cm^{-1} for (**2a**), 1 711 cm^{-1} for (**2b**)] implying strongly that one of the CO groups semi-bridges the metal–metal bond. This is supported by the ^{13}C-{^1H} n.m.r. data, measured at −40 °C. Although for each complex only one CO resonance is observed (Table 3), due to site-exchange of the carbonyl ligands, there are ^{195}Pt satellite peaks on this signal [*J*(PtC) 122 Hz], representing a time-averaged interaction with the platinum.

The ^{13}C-{^1H} n.m.r. spectra are informative in several other respects. There are characteristic resonances for the bridging alkylidyne-carbon nuclei [δ 314.3 (**2a**), and 312.8 p.p.m. (**2b**)], and the signals show ^{195}Pt and ^{183}W satellite peaks. Moreover,

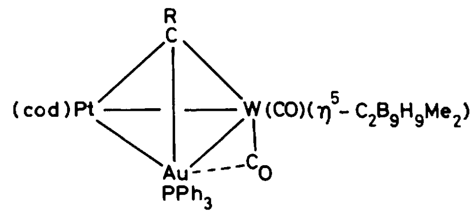


	X	R
(**2a**)	$P(CH_2Ph)Ph_3$	C_6H_4Me - 4
(**2b**)	NEt_4	Ph

the magnitude of the observed coupling constants are as expected for the presence of a Pt(μ-CR)W (R = alkyl or aryl) fragment in these species.[6] Interestingly, the spectra show only two resonances for the CH groups and two resonances for the CH_2 groups of the cod ligand, a situation which persists for (**2b**) even when the spectrum was measured at −80 °C. It is probable that in the anions of (**2a**) and (**2b**) the platinum atom lies in a pseudo-square planar environment. Hence in a static structure of (**2**) the four CH groups would be non-equivalent, as would the CH_2 groups, leading to the observation of four resonances for either moiety. Similar dynamic behaviour in a complex containing the asymmetric fragment $(\eta^5\text{-}C_2B_9H_9Me_2)(OC)_2$-W≡$CC_6H_4Me$-4 has been observed previously with $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$.[2a] In the latter the Rh–W bond is semi-bridged by a CO group, yet the ^{13}C-{^1H} n.m.r. spectrum shows only one carbonyl resonance. Moreover, the ^{31}P-{^1H} n.m.r. spectrum of the rhodium–tungsten compound displays only one resonance, whereas an



X	R	PR'_3
(**3a**) $P(CH_2Ph)Ph_3$	C_6H_4Me-4	$PMePh_2$
(**3b**) NEt_4	Ph	$PMePh_2$
(**3c**) NEt_4	Ph	PMe_2Ph



R

(**4a**) C_6H_4Me-4

(**4b**) Ph

X-ray diffraction study revealed that the PPh_3 groups were non-equivalent in the crystal. The n.m.r. data for the rhodium–tungsten complex have been explained in terms of rotation of the carbaborane–tungsten fragment about an axis through the rhodium and the mid-point of the μ-C–W bond *via* an intermediate having two semi-bridging CO groups. Such a mechanism equivalences the two CO and two PPh_3 sites. A similar process with the compounds (**2**) would lead to the appearance of one CO resonance, and two CH and two CH_2 signals for the cod group in the ^{13}C-{^1H} n.m.r. spectrum.

It is interesting to compare the reactions between (**1b**) or (**1c**) and [Pt(cod)$_2$] with those between the platinum reagent and the complexes [W(≡CR)(CO)$_2$(η-$C_5R'_5$)], mentioned above. With the latter both cod ligands are displaced producing trimetal compounds [PtW_2(μ-CR)$_2$(CO)$_4$(η-$C_5R'_5$)$_2$], and even using a 1:1 ratio of reactants dimetal species [PtW(μ-CR)(CO)$_2$(cod)(η-$C_5R'_5$)] are not observed.[6] Our inability to isolate dianionic complexes [PtW_2(μ-CR)$_2$(CO)$_4$(η^5-$C_2B_9H_9Me_2$)$_2$]$^{2-}$ (R = C_6H_4Me-4) may not be due to the bulky nature of the carbaborane ligand since it has been possible to characterise the isoelectronic trimetal monoanion [AuW_2(μ-CC_6H_4-Me-4)$_2$(CO)$_4$(η^5-$C_2B_9H_9Me_2$)$_2$]$^-$ as its [N(PPh$_3$)$_2$]$^+$ salt.[2a]

Attempts were made to displace the cod ligand in the complexes (**2**) with tertiary phosphines, but unfortunately crystalline products could not be isolated. Nevertheless, spectroscopic studies on the dark red oils formed indicated that these were the desired compounds. Treatment of (**2a**) in thf at 0 °C with precisely two equivalents of $PMePh_2$ afforded a product formulated as [P(CH$_2$Ph)Ph$_3$][PtW(μ-CC_6H_4Me-4)(CO)$_2$(PMePh$_2$)$_2$(η^5-$C_2B_9H_9Me_2$)] (**3a**) [$\nu_{max.}$(CO) at 1 887s and 1 722m br cm^{-1} (in thf)] on the basis of ^{13}C-{^1H}, ^{31}P-{^1H}, and ^{195}Pt-{^1H} n.m.r. measurements. Thus the ^{13}C-{^1H} spectrum had characteristic peaks for the various ligands: δ 325.3 [d, μ-C, *J*(PC) 54, *J*(PtC) 649, *J*(WC) 143], 241.7 [CO, *J*(WC) 163, *J*(PtC) 34], 160.2 [d, C^1(C$_6$H$_4$Me-4), *J*(PC) 7, *J*(PtC) 27], 139.1 [d, C^1(Ph), *J*(PC) 44, *J*(PtC) 30], 138.9 [d, C^1(Ph), *J*(PC) 39, *J*(PtC) 18], 60.3, 56.0 (*C*Me), 29.5, 28.3 (C*Me*), 21.1 (Me-4), 12.9 [d, MeP, *J*(PC) 22, *J*(PtC) 25], and 12.3 p.p.m. [d, MeP, *J*(PC) 25, *J*(PtC) 29 Hz]. The ^{31}P-{^1H} spectrum showed two resonances, corresponding to the non-equivalent $PMePh_2$ groups: δ 11.6 [d, *J*(PP) 17, *J*(PtP) 3 291] and 6.9 p.p.m. [d, *J*(PP) 17, *J*(PtP) 3 689, *J*(WP) 23 Hz]. The ^{195}Pt-{^1H} spectrum had a single resonance at δ 189 p.p.m., appearing as a doublet of doublets [*J*(PPt) 3 689 and 3 291 Hz].

Similarly, addition of $PMePh_2$ and PMe_2Ph to (**2b**) gave red oils formulated as [NEt$_4$][PtW(μ-CPh)(CO)$_2$(L)$_2$(η^5-$C_2B_9H_9Me_2$)] [(**3b**), L = $PMePh_2$; (**3c**), L = PMe_2Ph)]. Spectroscopic data for these species are as expected for the structures shown, and are summarised in the Experimental section. Solutions of the complexes (**3**) in CH_2Cl_2 decompose after 1—2 h. Use of other tertiary phosphines also failed to yield crystalline products.

It was hoped that the protonation of the salts (**2**) would afford stable neutral complexes. However, treatment of (**2a**) in CH_2Cl_2 with $HBF_4 \cdot Et_2O$, or with 40% aqueous HBF_4, did not afford an isolable product, although there was i.r. evidence [$\nu_{max.}$(CO) at 2 021 and 1 920 cm^{-1}] for formation of a neutral species. In view of this result, and the isolobal relationship existing between H^+ and [Au(PPh$_3$)]$^+$, the complexes (**2**) were treated with the latter species, which was generated *in situ*. Reaction between (**2a**) in thf and a mixture of [AuCl(PPh$_3$)] and $TlPF_6$ affords the black crystalline trimetal complex [AuPtW(μ$_3$-CC_6H_4Me-4)(CO)$_2$(PPh$_3$)(cod)(η^5-$C_2B_9H_9Me_2$)] (**4a**). A similar reaction involving (**2b**) in thf with [AuCl(PPh$_3$)] and KPF_6 gave [AuPtW(μ$_3$-CPh)(CO)$_2$(PPh$_3$)(cod)(η^5-$C_2B_9H_9Me_2$)] (**4b**). Compounds (**4a**) and (**4b**) are characterised by the data given in Tables 1 and 3.

The ^{13}C-{^1H} n.m.r. spectra of the complexes (**4**) are structurally informative. Resonances for the μ$_3$-C nuclei occur at δ 291.1 (**4a**) and 290.2 p.p.m. (**4b**), and these are seen as doublets due to ^{31}P–^{13}C coupling (15 Hz). Moreover, these signals have ^{195}Pt satellite peaks [*J*(PtC) ~590 Hz]. Both spectra show two CO resonances, and hence these ligands are not undergoing site-exchange on the n.m.r. time-scale at room temperature, as observed with the precursors (**2**). Moreover, for (**4a**) the CO peaks showed ^{183}W–^{13}C coupling, but no ^{195}Pt–^{13}C coupling. This result, taken with observation of a band in the i.r. at 1 795 cm^{-1}, indicating a semi-bridging CO ligand, suggests that this group is associated with the Au–W rather than the Pt–W bond. In contrast with (**2**), the cod ligands in (**4a**) and (**4b**) show four CH and four CH_2 resonances in their ^{13}C-{^1H} n.m.r. spectra in accord with a rigid structure. Evidence for the *closo*-trimetallatetrahedrane structure for (**4**), rather than a butterfly arrangement of the core atoms, is provided by the observation of ^{31}PAu–^{195}Pt coupling in both the ^{31}P-{^1H} and ^{195}Pt-{^1H} n.m.r. spectra [100 Hz for (**4a**), and 98 Hz for (**4b**)]. These values represent two rather than three bond couplings. No Me$_3$^{31}PAu–^{195}Pt coupling is observed in the ^{31}P-{^1H} n.m.r. spectrum of [AuPtW(μ$_3$-CC_6H_4Me-4)(CO)$_2$(PMe$_3$)$_3$(η-C_5H_5)][PF$_6$] which was shown by *X*-ray analysis to have a 'butterfly' arrangement for the μ$_3$-CAuPtW core with the gold and platinum atoms at the wing-tip positions.[7]

The *closo* structures proposed for (**4**) (44 cluster valence electrons) imply that the Au(PPh$_3$) groups employ one valence electron and three valence orbitals in cluster bonding, identifying these fragments[8] with CH^{2+}. A similar situation applies to the Cu(PPh$_3$) group in [CuW$_2$(μ$_3$-CC_6H_4Me-4)(CO)$_4$(PPh$_3$)(η-C_5H_5)$_2$].[9]

Addition of an excess of $PMePh_2$ to a dark brown CH_2Cl_2 solution of (**4a**) immediately afforded a red solution, the ^{31}P-{^1H} n.m.r. spectrum of which shows signals corresponding to various phosphine–gold cations and of the anion of (**3a**). Treatment of [CuW$_2$(μ$_3$-CC_6H_4Me-4)(CO)$_4$(PPh$_3$)(η-C_5H_5)$_2$] with PPh_3 leads to a similar decomposition affording [W(≡CC$_6$-

H_4Me-4)$(CO)_2(\eta$-$C_5H_5)$] and unidentified copper-containing species.[9]

It should be mentioned in passing that the ^{11}B-{^1H} n.m.r. spectra of the new compounds described herein were measured. However, only broad unresolved signals were observed in the range *ca.* δ −6 to −17 p.p.m. [relative to $BF_3 \cdot Et_2O$ (external)]. No characteristic resonance was observed for a unique boron involved in B–H ⇀ M or B–M (M = Pt or Au) bonding.[2] The η^5-$C_2B_9H_9Me_2$ ligand thus conforms to the normal pentahapto co-ordination to the tungsten.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. Light petroleum refers to that fraction of b.p. 40—60 °C. Brockman activity II alumina was used for chromatography. The compounds [W(≡CPh)Br$(CO)_4$],[10] Na_2[7,8-$C_2B_9H_9Me_2$],[11] Na[W(≡CC_6H_4Me-4)$(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$],[2a] [Pt$(cod)_2$],[12] and [AuCl(PPh_3)][13] were prepared by literature methods. Analytical and other data for the new compounds are given in Table 1. Phosphorus-31 n.m.r. chemical shifts (δ) are in p.p.m. to high frequency of 85% H_3PO_4 (external).

Preparation of the Salts [X][W(≡CR)$(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$][X = NEt_4, R = Ph; X = P$(CH_2Ph)Ph_3$ *or* PPh_4, R = C_6H_4Me-4].—(*i*) A thf (20 cm^3) solution of [W(≡CPh)Br$(CO)_4$] (3.24 g, 6.98 mmol) at *ca.* −25 °C was treated slowly with 10-cm^3 portions (*via* a syringe) of a thf solution (80 cm^3) of Na_2[7,8-$C_2B_9H_9Me_2$] (7.73 mmol). The mixture assumes a dark red colour, and the CO evolved was removed with a slow stream of nitrogen. The mixture was warmed to room temperature (1 h), excess NEt_4Cl (1.1 g, ~11 mmol) was added, and the reagents were stirred for 1 h. The mixture was then passed through a Celite pad (*ca.* 2 × 3 cm), and solvent was removed *in vacuo* affording a red oil. The latter was treated with CH_2Cl_2 (75 cm^3) and chromatographed (2 × 7 cm column). Elution with the same solvent gave a red-orange eluate which was reduced in volume to *ca.* 10 cm^3 and cooled to 0 °C. Diethyl ether (40 cm^3) was slowly added, while the solution was well stirred. Red-orange *microcrystals* of [NEt_4][W(≡CPh)$(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$] (**1b**) (3.0 g) were collected, washed with Et_2O (2 × 10 cm^3), and dried *in vacuo*. Carbon-13 n.m.r. (CD_2Cl_2–CH_2Cl_2): δ 297.3 [≡CPh, *J*(WC) 199], 227.4 [CO, *J*(WC) 184 Hz], 151.7 [C^1(Ph)], 128.5, 128.1, 127.7 (Ph), 62.3 (br, *C*Me), 53.1 (N*C*H_2Me), 29.9 (C*Me*), and 7.9 p.p.m. (NCH_2*Me*).

(*ii*) A thf (*ca.* 80 cm^3) solution of Na[W(≡CC_6H_4Me-4)$(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$] (6.9 mmol) was treated with a slight excess of [P$(CH_2Ph)Ph_3$]Cl (3.3 g, 7.0 mmol), and the mixture was stirred rapidly for 1 h. The precipitate obtained was removed by filtration through a Celite pad. The resulting solution was evaporated *in vacuo*, and the dark red oil dissolved in CH_2Cl_2 (*ca.* 20 cm^3) and chromatographed. Elution with the same solvent gave an orange eluate, brown decomposition products remaining on the top of the column. The eluate was concentrated to *ca.* 5—10 cm^3, cooled to 0 °C, and Et_2O (30—50 cm^3) slowly added with vigorous stirring. An oil forms initially, but after several hours bright orange *microcrystals* of [P$(CH_2Ph)Ph_3$][W(≡CC_6H_4Me-4)$(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$] (**1c**) (4.32 g) are produced.

The salt [PPh_4][W(≡CC_6H_4Me-4)$(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$] (**1d**) was similarly prepared using PPh_4Cl. Large red crystals of (**1d**) may be obtained by dissolving some of the initially formed *microcrystals* in CH_2Cl_2, with a layer of the mother-liquor above this solution. Cooling to −20 °C affords red crystals after *ca.* 2 d, and these may be recovered, washed with Et_2O, and dried *in vacuo*.

Synthesis of the Complexes [X][PtW(μ-CR)$(CO)_2$(cod)$(\eta^5$-$C_2B_9H_9Me_2)$][X = P$(CH_2Ph)Ph_3$, R = C_6H_4Me-4; X = NEt_4, R = Ph].—The procedure for the preparation of both compounds is the same, and that for (**2a**) is described. The complexes [Pt$(cod)_2$] (0.42 g, 1.02 mmol) and (**1c**) (0.86 g, 1.01 mmol) were placed in a Schlenk tube, and thf (10 cm^3) was added. The mixture was stirred at 0 °C for *ca.* 5 h under a slow stream of nitrogen. Diethyl ether (70 cm^3) was then added slowly over a period of *ca.* 3 h. If possible the solution should be seeded to avoid formation of an oil. Moreover, an oily product is obtained if the Et_2O is added rapidly. The brick-red powder formed upon addition of the ether was filtered off, and the *microcrystals* were washed with Et_2O (3 × 10 cm^3) and then dried *in vacuo* to give [P$(CH_2Ph)Ph_3$][PtW(μ-CC_6H_4Me-4)$(CO)_2$(cod)$(\eta^5$-$C_2B_9H_9Me_2)$] (**2a**) (0.63 g). Some oily material remaining in the Schlenk tube was treated with thf (10 cm^3), the filtrate from the first fraction added, and the mixture treated slowly with Et_2O (50 cm^3). This procedure afforded additional *microcrystals* (0.34 g) of (**2a**).

Reactions with $PMePh_2$ *and* PMe_2Ph. The general procedure involved treating the salts (**2**) in thf (*ca.* 5 cm^3) at 0 °C with exactly two equivalents of the tertiary phosphines. After stirring (30 min) i.r. measurements indicated complete conversion. After removing solvent *in vacuo*, the dark red oil remaining was used for the i.r. and n.m.r. studies since attempts to purify further by fractional crystallisation or column chromatography failed. Unless precisely two equivalents of phosphine are used, the resulting products contain free $PMePh_2$ or PMe_2Ph, the n.m.r. signals of which interfere with those of the complexes.

Data for (**3a**) are given in the text. For [NEt_4][PtW(μ-CPh)$(CO)_2(PMePh_2)_2(\eta^5$-$C_2B_9H_9Me_2)$] (**3b**), $\nu_{max.}$(CO) at 1 890s and 1 720m br cm^{-1} (in thf); n.m.r.: ^{13}C-{^1H}, δ 323.2 [d, μ-C, *J*(PC) 52, *J*(PtC) 650] and 241.7 p.p.m. [CO, *J*(PtC) 37 Hz]; ^{31}P-{^1H} (CD_2Cl_2), δ 11.4 [d, *J*(PP) 12, *J*(PtP) 3 300] and 6.31 p.p.m. [d, *J*(PP) 12, *J*(PtP) 3 668, *J*(WP) 13 Hz]; ^{195}Pt-{^1H} (CD_2Cl_2), δ 161.1 p.p.m. [*J*(PPt) 3 668 and 3 300 Hz]. For [NEt_4][PtW(μ-CPh)$(CO)_2(PMe_2Ph)(\eta^5$-$C_2B_9H_9Me_2)$] (**3c**), $\nu_{max.}$(CO) at 1 888s and 1 708m br cm^{-1} (in thf); n.m.r.: ^{13}C-{^1H}, δ 325.9 [d, μ-C, *J*(PC) 58] and 239.4 p.p.m. [CO, *J*(PtC) 29 Hz]; ^{31}P-{^1H} (PhCl–CD_2Cl_2), δ −5.7 [d, *J*(PP) 8, *J*(PtP) 3 060] and −6.8 p.p.m. [d, *J*(PP) 8, *J*(PtP) 3 735, *J*(WP) 17 Hz]; ^{195}Pt-{^1H} (PhCl–CD_2Cl_2), δ 207.9 p.p.m. [d of d, *J*(PPt) 3 735 and 3 060 Hz].

Preparation of the Complexes [AuPtW$(\mu_3$-CR)$(CO)_2(PPh_3)$(cod)$(\eta^5$-$C_2B_9H_9Me_2)$] (R = C_6H_4Me-4 *or* Ph).—(*i*) A Schlenk tube was charged with (**2a**) (0.58 g, 0.50 mmol), [AuCl(PPh_3)] (0.25 g, 0.50 mmol), and $TlPF_6$ (0.41 g, 1.2 mmol), and thf (5 cm^3) was added. The mixture was stirred for 1 h under a slow stream of nitrogen. At this stage i.r. monitoring of the mixture may reveal the presence of unreacted (**2a**), in which case stirring is continued until the latter is consumed. Solvent was removed *in vacuo*, and the dark brown residue extracted with CH_2Cl_2 (2 × 5 cm^3) and the extracts chromatographed using the same solvent. The brown eluate was then reduced in volume to *ca.* 5—10 cm^3, and portions (4 × 10 cm^3) of light petroleum added until the solution became turbid. Cooling to −20 °C for *ca.* 15 h then afforded black *microcrystals* of [AuPtW$(\mu_3$-CC_6H_4Me-4)$(CO)_2(PPh_3)$(cod)$(\eta^5$-$C_2B_9H_9Me_2)$] (**4a**) (0.75 g). Phosphorus-31 n.m.r. (CD_2Cl_2): δ 52.9 p.p.m. [*J*(PtP) 100 Hz].

(*ii*) A mixture of (**2b**) (0.057 g, 0.06 mmol), [AuCl(PPh_3)] (0.031 g, 0.06 mmol), and KPF_6 (0.10 g, 0.50 mmol) in thf (3 cm^3) was stirred at 0 °C. After 2 h, solvent was removed *in vacuo*, and the brown residue extracted with CH_2Cl_2 (2 × 5 cm^3) and the extracts chromatographed. Elution with the same solvent mixture gave a brown eluate, which was concentrated *in vacuo*

Table 4. Atomic co-ordinates ($\times 10^4$) for $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1d**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)*	2 295	3 532	1 944	W(1′)	7 706(1)	6 478(1)	8 048(1)
C(1)†	1 575	2 629	687	C(1′)	8 381	7 414	9 381
O(1)†	1 178	2 064	−21	O(1′)	8 836	7 941	10 084
C(2)†	3 070	4 657	1 017	C(2′)	6 933	5 349	9 037
O(2)†	3 475	5 260	498	O(2′)	6 524	4 713	9 558
C(50)	1 221(18)	4 292(21)	2 138(25)	C(50′)	8 896(19)	5 862(21)	7 971(27)
C(52)	191(7)	5 283(9)	1 294(7)	C(52′)	9 610(7)	4 461(8)	8 503(8)
C(53)	−697(7)	5 772(9)	1 342(7)	C(53′)	10 488(7)	3 972(8)	8 505(8)
C(54)	−1 497(7)	5 750(9)	2 242(7)	C(54′)	11 435(7)	4 170(8)	7 764(8)
C(55)	−1 408(7)	5 241(9)	3 096(7)	C(55′)	11 505(7)	4 858(8)	7 023(8)
C(56)	−520(7)	4 753(9)	3 048(7)	C(56′)	10 627(7)	5 347(8)	7 022(8)
C(51)	280(7)	4 774(9)	2 148(7)	C(51′)	9 680(7)	5 149(8)	7 762(8)
C(57)	−2 465(7)	6 282(9)	2 294(7)	C(57′)	12 392(7)	3 637(8)	7 766(8)
B(1)	1 884(5)	2 332(6)	3 231(6)	B(1′)	8 059(6)	7 707(6)	6 781(6)
B(2)	2 516(5)	3 670(6)	3 836(6)	B(2′)	7 607(6)	6 334(6)	6 139(6)
C(3)	3 777(5)	3 950(6)	3 125(6)	C(3′)	6 303(6)	5 935(6)	6 783(6)
C(4)	3 990(5)	2 962(6)	2 181(6)	C(4′)	5 966(6)	6 873(6)	7 726(6)
B(5)	2 861(5)	1 899(6)	2 132(6)	B(5′)	6 970(6)	8 008(6)	7 811(6)
B(6)	2 732(5)	1 484(6)	3 436(6)	B(6′)	7 114(6)	8 447(6)	6 514(6)
B(7)	2 510(5)	2 564(6)	4 492(6)	B(7′)	7 497(6)	7 407(6)	5 493(6)
B(8)	3 703(5)	3 614(6)	4 405(6)	B(8′)	6 384(6)	6 263(6)	5 499(6)
B(9)	4 657(5)	3 192(6)	3 356(6)	B(9′)	5 343(6)	6 586(6)	6 514(6)
B(10)	4 072(5)	1 886(6)	2 747(6)	B(10′)	5 792(6)	7 907(6)	7 146(6)
B(11)	3 861(5)	2 272(6)	4 180(6)	B(11′)	6 087(6)	7 543(6)	5 708(6)
C(3b)	4 419(5)	5 101(6)	3 036(6)	C(3b′)	5 796(6)	4 767(6)	6 892(6)
C(4b)	4 793(5)	3 188(6)	1 168(6)	C(4b′)	5 101(6)	6 597(6)	8 693(6)
P(1)	7 567(3)	587(3)	2 650(3)	P(1′)	2 387(4)	9 432(3)	7 343(3)
C(12)	5 351(5)	−243(5)	3 478(7)	C(12′)	4 590(6)	10 130(5)	6 553(7)
C(13)	4 367(5)	−1 043(5)	3 451(7)	C(13′)	5 620(6)	10 865(5)	6 526(7)
C(14)	4 342(5)	−2 017(5)	2 760(7)	C(14′)	5 725(6)	11 884(5)	7 145(7)
C(15)	5 301(5)	−2 192(5)	2 096(7)	C(15′)	4 800(6)	12 167(5)	7 790(7)
C(16)	6 285(5)	−1 392(5)	2 123(7)	C(16′)	3 771(6)	11 432(5)	7 816(7)
C(11)	6 310(5)	−418(5)	2 814(7)	C(11′)	3 665(6)	10 413(5)	7 198(7)
C(22)	8 770(5)	−753(7)	3 110(7)	C(22′)	1 217(5)	10 639(7)	6 652(6)
C(23)	9 690(5)	−1 212(7)	2 976(7)	C(23′)	327(5)	11 119(7)	6 678(6)
C(24)	10 564(5)	−950(7)	2 175(7)	C(24′)	−532(5)	11 028(7)	7 525(6)
C(25)	10 518(5)	−229(7)	1 507(7)	C(25′)	−500(5)	10 455(7)	8 346(6)
C(26)	9 597(5)	231(7)	1 640(7)	C(26′)	390(5)	9 974(7)	8 319(6)
C(21)	8 723(5)	−31(7)	2 442(7)	C(21′)	1 248(5)	10 066(7)	7 473(6)
C(32)	8 519(9)	1 671(7)	4 527(6)	C(32′)	1 347(6)	8 144(5)	5 577(5)
C(33)	8 710(9)	2 518(6)	5 393(6)	C(33′)	1 199(6)	7 255(5)	4 751(5)
C(34)	8 102(9)	3 307(6)	5 555(6)	C(34′)	1 956(6)	6 597(5)	4 550(5)
C(35)	7 304(9)	3 249(6)	4 849(6)	C(35′)	2 861(6)	6 827(5)	5 175(5)
C(36)	7 113(9)	2 402(6)	3 982(6)	C(36′)	3 009(6)	7 716(5)	6 001(5)
C(31)	7 721(9)	1 613(6)	3 821(6)	C(31′)	2 252(6)	8 375(5)	6 202(5)
C(42)	6 842(8)	578(6)	675(5)	C(42′)	3 154(7)	9 286(6)	9 304(5)
C(43)	6 742(8)	1 030(6)	−217(5)	C(43′)	3 164(7)	8 734(6)	10 149(5)
C(44)	7 309(8)	2 079(6)	−292(5)	C(44′)	2 395(7)	7 766(6)	10 226(5)
C(45)	7 976(8)	2 677(6)	525(5)	C(45′)	1 617(7)	7 350(6)	9 458(5)
C(46)	8 075(8)	2 225(6)	1 416(5)	C(46′)	1 607(7)	7 901(6)	8 614(5)
C(41)	7 508(8)	1 175(6)	1 492(5)	C(41′)	2 375(7)	8 869(6)	8 537(5)

* Position fixed for origin definition. † Positions of atoms C(1), O(1), C(2), O(2), C(1′), O(1′), C(2′), O(2′) were fixed during refinement.

to *ca.* 1 cm^3 and treated with light petroleum (20 cm^3). On cooling to −20 °C for 2—3 d black *microcrystals* of $[AuPtW(\mu_3\text{-}CPh)(CO)_2(PPh_3)(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4b**) were formed. Concentration of the mother-liquor and treatment with more light petroleum gives additional crystals of (**4b**) (combined yield 68 mg). Phosphorus-31 n.m.r.: δ 53.2 p.p.m. [*J*(PtP) 98 Hz].

Crystal-structure Determination of Compound (**1d**).—Crystals of compound (**1d**) grow as transparent red spheroids from CH_2Cl_2–Et_2O. That chosen for study had dimensions *ca.* 0.4 × 0.4 × 0.2 mm, and was sealed in a Lindemann tube under nitrogen. Diffracted intensities were collected (ω–2θ scans) in the range $2.9 \leqslant 2\theta \leqslant 50°$ at 298 K on a Nicolet *P3m* four-circle diffractometer. Of 5 256 unique intensities, 4 777 had $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in (I) based on counting statistics. Only these data were used in final refinement of the structure, after all the data had been corrected for Lorentz and polarisation effects, and an empirical correction applied for *X*-ray absorption.[14]

Crystal data for (**1d**). $[P(C_6H_5)_4]^+[C_{14}H_{22}B_9O_2W]^-$, M = 842.9, triclinic, a = 12.395(2), b = 13.120(4), c = 12.533(4) Å, α = 101.10(3), β = 82.04(2), γ = 104.48(2)°, U = 1 928(1) Å^3, D_c = 1.46 g cm^{-3}, Z = 2, F(000) = 840, space group $P1$ (no. 1), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 31.33 cm^{-1}.

Structure solution and refinement. The structure was solved by heavy-atom methods; all non-hydrogen atoms were located from difference Fourier calculations. All refinements, by blocked-cascade least-squares techniques, were performed on a Data General S230 'Eclipse' computer with the SHELXTL suite of programs.[14]

The asymmetric unit of this structure consists of two enantiomeric formula units related by a non-crystallographic pseudo-centre of inversion in the non-centrosymmetric space group $P1$. This pseudo-symmetry led to severe problems during structure refinement by least squares: poorly defined molecular geometry, disparity between the distances of equivalent bonds in the two molecules, and disparate thermal parameters for pseudo-equivalent atoms in each formula unit. The refinement strategy ultimately adopted was the use of rigid-group constraints during least-squares refinement.

For the cations, tetrahedral geometry was imposed at each phosphorus atom. The eight P–C(phenyl) bond distances were made equivalent, and this value allowed to refine. The phenyl groups of the cations were constrained to be regular hexagons (C–C 1.395 Å); the phenyl hydrogens (generated geometrically, C–H 0.96 Å) were allowed to ride on the supporting ring-carbon atom, with a fixed isotropic thermal parameter (*ca.* $1.2U_{iso}$ of the parent carbon atom).

For the anion, a well determined carbaborane cage from a previous structure,[2b] with hydrogen atoms generated geometrically (C–H 0.96; B–H 1.10 Å),[15] was used as a rigid group. The five atoms forming the open pentagonal face of this idealised cage were least-squares fitted to the corresponding five atoms in the poorly determined cages of the two anions. The distances between tungsten and the ligated cage atoms in each anion were allowed to refine after initially equivalencing the ten W–B (or C) interatomic distances to the same value and error range. This value refined as 2.424(6) Å and the ten W–B(C) values fall in the range 2.38—2.48 Å. The boron and carbon atoms of the rigid carbaborane cage were refined with isotropic thermal parameters, while the hydrogens had fixed isotropic thermal parameters [H(B) 0.06 and H(Me) 0.07 Å^2]. The carbonyl ligands were unstable during least-squares refinement, and were therefore included in fixed positions (U_{iso} = 0.05 Å^2) determined from a difference Fourier synthesis.

The C_6H_4Me-4 ring carbon atoms were refined as rigid groups with individual isotropic thermal parameters. The Me-4 carbon atom and all the C_6H_4Me-4 hydrogen atoms were included in calculated positions (C–C 1.52, C–H 0.96 Å), the latter with fixed isotropic thermal parameters [H(phenyl) 0.06 and H(Me) 0.07 Å^2]. The W–C and C–C_6H_4Me-4 distances in the two anions were tied to common refined parameters.

The weighting scheme applied was of the form $w^{-1} = [\sigma^2(F_o) + 0.000\,4|F_o|^2]$. The final difference Fourier synthesis showed residual peaks <1.5 e Å^{-3} close to the tungsten atoms. Scattering factors for W were taken from ref. 16, while those for all other atoms are included in the programs of ref. 14. Rigid-group least-squares refinement converged at $R = 0.053$ ($R' = 0.055$). Atom co-ordinates are listed in Table 4.

Acknowledgements

We thank the Deutscher Akademischer Austauschdienst for the award of a NATO Fellowship (to F-E. B), and the S.E.R.C. for support.

References

1 Part 66, M. J. Attfield, J. A. K. Howard, A. N. de M. Jelp, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2219.
2 (*a*) M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 61; (*b*) M. Green, J. A. K. Howard, A. N. de M. Jelfs, O. Johnson, and F. G. A. Stone, *ibid.*, p. 73; (*c*) M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *ibid.*, p. 81.
3 E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.
4 M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 187.
5 F. G. A. Stone, *Pure Appl. Chem.*, 1986, **58**, 529.
6 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.*, 1982, 763; G. P. Elliott, J. A. K. Howard, T. Mise, I. Moore, C. M. Nunn, and F. G. A. Stone, *ibid.*, 1986, 2091.
7 G. A. Carriedo, J. A. K. Howard, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1984, 2545.
8 D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **232**, 171.
9 M. Müller-Gliemann, S. V. Hoskins, A. G. Orpen, A. L. Ratermann, and F. G. A. Stone, *Polyhedron*, 1986, **5**, 791.
10 E. O. Fischer, U. Schubert, and H. Fischer, *Inorg. Synth.*, 1979, **19**, 172.
11 M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862; M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *ibid.*, p. 879.
12 J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213.
13 R. Uson, A. Laguna, and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.
14 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-ray system, Cambridge, 1976; updated Göttingen, 1981.
15 P. Sherwood, local programs for Eclipse S230 Data General Computer, Bristol, 1986.
16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 8th December 1987; *Paper* 6/2354