Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 107.[1] Reactions of Diphenylphosphine with Molybdenumtungsten Dimetal Complexes; Crystal Structures of $[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(C_6H_4Me\text{-}4)\}(CO)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{11})]$ and $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ *

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Treatment of the compounds $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}R)]$ (R = H or Me) in CH_2Cl_2 with $PHPh_2$ affords the complexes $[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(C_6H_4Me\text{-}4)\}(CO)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}R)]$. The structure of the species with R = H was established by *X*-ray diffraction. The Mo–W bond [2.713(1) Å] is spanned by the PPh_2 group [Mo–P 2.439(3), W–P 2.360(3) Å], and in a transverse manner by the alkyne. However, the latter is twisted so that the *C*(OH) atom lies appreciably closer to the tungsten [μ-C–W 2.067(8) Å] than the molybdenum [μ-C–Mo 2.352(8) Å], whereas the $C(C_6H_4Me\text{-}4)$ atom is essentially symmetrically bridging [μ-C–Mo 2.224(9), μ-C–W 2.251(8) Å]. The molybdenum atom carries the $\eta^7\text{-}C_7H_7$ group (C–Mo av. 2.27 Å), and the tungsten atom is η^5 co-ordinated by the $C_2B_9H_{11}$ cage and a CO group. The reaction between $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ and $PHPh_2$ in CH_2Cl_2 gives the complex $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PHPh_2)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$. The latter on heating in toluene at 70 °C yields the compound $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$, the structure of which was established by *X*-ray diffraction. The Mo–W bond [2.708(1) Å] is bridged by the PPh_2 group [Mo–P 2.357(2), W–P 2.456(2) Å]. The tungsten atom is ligated by two CO groups, and η^5 co-ordinated by the C_2B_9 cage. In the open face of the latter a BH group in the α position to a CMe fragment forms a B–H⇀Mo exopolyhedral bond, while the boron atom β to the CMe groups in the pentagonal ring carries a $CH_2C_6H_4Me\text{-}4$ substituent. The molybdenum atom is ligated by a CO molecule and the indenyl group. The n.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, $^{11}B\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$) for the new compounds are reported and discussed.

We have previously reported the synthesis of the dimetal compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9R_2)]$ (**1a**; M = Mo, R = H), (**1b**; M = Mo, R = Me), and (**1c**; M = W, R = Me), C_9H_7 = indenyl.[2] These complexes were obtained by treating the salts $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9R_2)]$ (R = H or Me) with $[M(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (M = Mo or W) in CH_2Cl_2. Recently we have prepared the related compounds $[MMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9R_2)]$ (**2a**; M = Mo, R = H), (**2b**; M = W, R = H), and (**2c**; M = W, R = Me) and $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ (**3**). These products were isolated from reactions between the reagent $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)][BF_4]$ and the salts $[NEt_4][M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9R_2)]$ (M = Mo or W, R = H or Me) and $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{10}Me)]$, respectively.[3]

The dimetal complexes (**1**)—(**3**) are electronically unsaturated 32 c.v.e. (cluster valence-electron) species in which the metal–metal bonds are bridged both by an alkylidyne group and by an exopolyhedral B–H⇀M three-centre two-electron (3c–2e) bond. The carbaborane ligands thus adopt non-spectator roles in these products, a feature they share with many other dimetal compounds.[4] Moreover, as discussed further below, although bonding within the three-membered $\overline{M(\mu\text{-}CR)M'}$ rings is delocalised, it can be represented formally in different ways (see Scheme 1) in order to rationalise the observed n.m.r. or *X*-ray diffraction data for specific complexes.

Reactions of nucleophilic reagents with the compounds (**1**)—(**3**) are of interest by virtue of their unsaturation. We have studied a few reactions of this kind, employing tertiary phosphines,[2,3] diazoalkanes,[5] and alkynes.[6,7] Even allowing for the limited experimental work carried out so far, it is evident that products with unusual molecular structures can be obtained. In this paper we describe some reactions with diphenylphosphine, studied in the expectation that this phosphine would function as a precursor to μ-phosphido complexes, following initial co-ordination of a $PHPh_2$ ligand at one or other of the metal centres. Earlier work with PMe_3 revealed, for instance, that the site for addition of a phosphine varied, evidently being controlled by subtle steric or electronic effects. Thus treatment of compound (**1a**) with PMe_3 affords $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_{11})]$ (**1d**) in which the phosphine displaces a CO molecule ligating the tungsten atom. Similarly, compound (**2c**) with PMe_3 gives the species $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2d**) with the PMe_3 group ligating the tungsten atom and having a B–H ⇀ Mo bond. In contrast, (**1b**) and (**1c**) with PMe_3 yield the complexes $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**; M = Mo) and (**4b**; M = W). These products arise from addition of the phosphine to the $M(CO)(\eta^5\text{-}C_9H_7)$ group, without loss of CO but with a concomitant lifting of the B–H ⇀ M interaction. Interestingly, displacement of $N_2C(C_6H_4Me\text{-}4)_2$ from $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{N_2C(C_6H_4Me\text{-}4)_2\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**5a**) with PMe_3 gives $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}$

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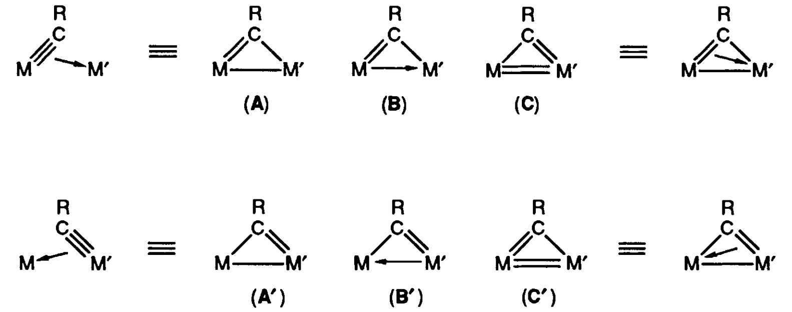
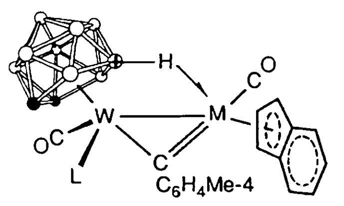
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

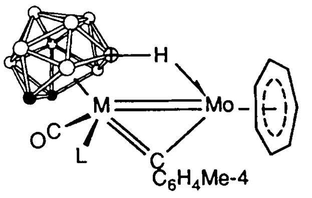


Scheme 1. M and M′ represent metal–ligand fragments, the ligands being omitted for clarity. In (**A**), (**B**), and (**C**) a C≡M group formally donates two, three, or four electrons, respectively, to a second metal centre (M′). However, in some of the dimetal species formed it is more satisfactory to invoke the alternative representations (**A′**), (**B′**), and (**C′**) as if a C≡M′ moiety formally acts as a donor, even though the product was obtained from a C≡M complex



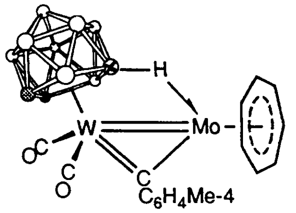
○BH ⊕B

	M	L	●
(**1a**)	Mo	CO	CH
(**1b**)	Mo	CO	CMe
(**1c**)	W	CO	CMe
(**1d**)	Mo	PMe_3	CH



○BH ⊕B

	M	L	●
(**2a**)	Mo	CO	CH
(**2b**)	W	CO	CH
(**2c**)	W	CO	CMe
(**2d**)	W	PMe_3	CMe



◍CH ●CMe ○BH ⊕B

(**3**)

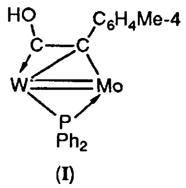
$C_9H_7)(\eta^5$-$C_2B_9H_9Me_2)]$ (**6a**) in which a $W(PMe_3)(\eta^5$-$C_9H_7)$ moiety is present, as in (**4b**). In contrast with the latter, however, in compound (**6a**) the B–H ⇀ W bond is maintained. Structurally similar to (**6a**) is the complex $[Mo_2(\mu$-CC_6H_4-Me-4$)(CO)_2\{P(OMe)_3\}(\eta^5$-$C_9H_7)(\eta^5$-$C_2B_9H_9Me_2)]$ (**6b**), obtained by treating $[NEt_4][Mo(\equiv CC_6H_4$Me-4$)(CO)\{P(OMe)_3\}$-$(\eta^5$-$C_2B_9H_9Me_2)]$ with $[Mo(CO)_2(NCMe)_2(\eta^5$-$C_9H_7)]$-$[BF_4]$.[3] Formation of (**6b**) in this manner involves migration of the $P(OMe)_3$ group from one molybdenum centre to the other. It is evident from these results that further studies of reactions between a variety of phosphorus donors and the dimetal compounds are warranted.

Results and Discussion

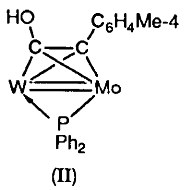
Treatment of compound (**2b**) in CH_2Cl_2 with $PHPh_2$ afforded a red complex (**7a**), isolated by column chromatography. It was not possible to define the structure of this species on the basis of microanalytical and spectroscopic data (Tables 1 and 2), although it was evident from the n.m.r. spectra that the product was not a simple $PHPh_2$ substitution derivative of (**2b**). In particular, the ^{13}C-$\{^1H\}$ n.m.r. spectrum revealed the absence of any resonance attributable to the μ-C nucleus of an alkylidyne group, and the ^1H spectrum did not display signals diagnostic of either a B–H ⇀ Mo bond, as present in the precursor, or the proton of a PH group of a $PHPh_2$ ligand. Fortunately, it was possible to grow crystals of compound (**7a**), and an *X*-ray diffraction study identified the complex as $[MoW(\mu$-$PPh_2)\{\mu$-$C(OH)C(C_6H_4$Me-4$)\}(CO)(\eta^7$-$C_7H_7)(\eta^5$-$C_2B_9H_{11})]$.

Data from the *X*-ray work are listed in Table 3, and the molecule is shown in Figure 1. The Mo–W bond [2.713(1) Å] is bridged by a PPh_2 group [Mo–P 2.439(3), W–P 2.360(3) Å], and unexpectedly it is also transversely spanned by a novel alkyne fragment $(HO)C\equiv C(C_6H_4$Me-4$)$. However, the ligated carbon atoms of the latter are distinctly asymmetrically linked to the metal atoms [Mo–C(4) 2.352(8), Mo–C(5) 2.224(9), W–C(4) 2.067(8), W–C(5) 2.251(8) Å]. These parameters suggest that the bridge structure (**I**) better represents the alkyne bonding than the form (**II**). Both (**I**) and (**II**) allow the tungsten and molybdenum centres to attain 18-electron valence shells, if the electron contributions from the η^7-C_7H_7, η^5-$C_2B_9H_{11}$, and CO groups are included. However, (**I**) better accords with the short W–C(4) distance [2.067(8) Å] and the relatively long Mo–C(4) separation [2.352(8) Å], whereas the W–C(5) [2.251(8) Å] and Mo–C(5) [2.224(9) Å] connectivities are very comparable. The μ-alkyne bonding depicted in (**I**) is of a type previously identified in several other molecules having heteroatom (O or N) substituents on the alkyne-carbon atoms,[8] and is intermediate between the commonly observed transverse mode and a structure in which the alkyne-carbon atoms lie parallel to the metal–metal bond.

As expected, the molybdenum atom carries the η^7-C_7H_7 ring. The tungsten is co-ordinated by a CO molecule [W–C(3)–O(3) 176(1)°], and by the open face of the *nido*-$C_2B_9H_{11}$ fragment. The B–H⇀Mo bridge present in the precursor (**2b**) is thus absent in compound (**7a**).



(**I**)

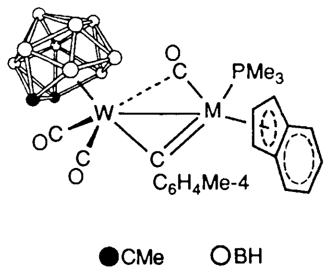


(**II**)

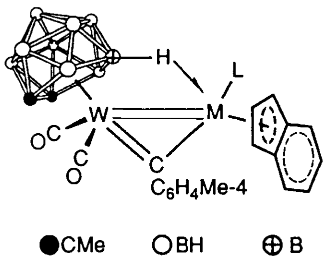
Table 1. Analytical[a] and physical data for the molybdenumtungsten complexes

	Compound[b]	Colour	Yield (%)	ν(CO)[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(**6c**)	$[MoW(\mu\text{-}CR)(CO)_2(PHPh_2)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Green	58	1 971s, 1 903s	45.8 (46.7)	4.7 (4.5)
(**7a**)	$[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(R)\}(CO)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{11})]$	Red	50	1 961s	44.3 (43.9)	4.8 (4.3)
(**7b**)	$[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(R)\}(CO)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$	Red	44	1 943s	44.1 (44.6)	4.9 (4.4)
(**8**)	$[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$	Purple	45	1 980s, 1 924s	45.8 (46.7)	4.7 (4.5)

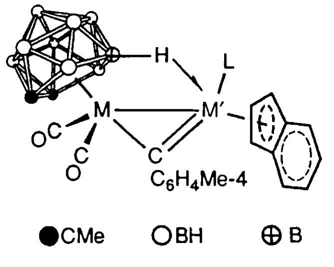
[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] Measured in CH_2Cl_2. All complexes show a broad band at *ca.* 2 560 cm^{-1} due to B–H.



	M
(**4a**)	Mo
(**4b**)	W



	M	L
(**5a**)	W	$N_2C(C_6H_4Me\text{-}4)_2$
(**5b**)	Mo	$N_2C(C_6H_4Me\text{-}4)_2$
(**5c**)	W	O

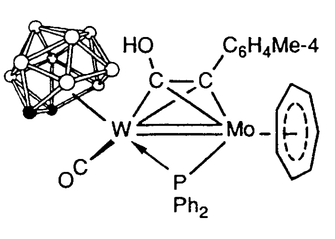


	M	M′	L
(**6a**)	W	W	PMe_3
(**6b**)	Mo	Mo	$P(OMe)_3$
(**6c**)	W	Mo	$PHPh_2$

Having identified complex (**7a**) by the *X*-ray analysis it was possible to interpret the n.m.r. data (Table 2). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a resonance at δ 125.2 p.p.m., in the range characteristic for a μ-PPh_2 group.[9] Moreover, the signal showed satellite peaks due to $^{183}W\text{-}^{31}P$ coupling (322 Hz) of the expected magnitude for a direct W–P bond. In the ^1H n.m.r. spectrum the expected signals are seen, including two resonances for the non-equivalent CH groups of the $C_2B_9H_{11}$ ligand at δ 2.55 and 2.84. Correspondingly, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the *C*H nuclei of the carbaborane cage display characteristic resonances at δ 42.7 and 44.3 p.p.m. In the ^1H n.m.r. spectrum of (**7a**) the C(OH) resonance is observed at δ 11.3, in the range expected.

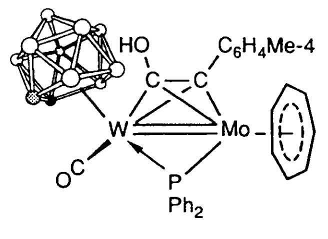
In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of compound (**7a**) the chemical shifts observed for the ligated carbon atoms of the μ-alkyne are of particular interest. These signals are seen at δ 193.1 and 85.5 p.p.m. The latter signal is in the normal range for an alkyne-carbon bridging a dimetal centre, whereas the former is in the chemical shift region for an alkyne co-ordinated to a single metal atom and donating an electron pair in a 'carbene-like' bonding mode.[10] These $^{13}C\text{-}\{^1H\}$ n.m.r. data are thus in accord with the *X*-ray diffraction results indicating a bonding mode of type (**I**) rather than (**II**) (see above) with the signal at 193.1 p.p.m. being assigned to the *C*(OH) nucleus and that at 85.5 p.p.m. to the CC_6H_4Me-4 group. Similar $^{13}C\text{-}\{^1H\}$ n.m.r. properties are displayed by the compound $[FeRu(\mu\text{-}Me\text{-}C_2NEt_2)(CO)_5(dab)]$ (dab = $Pr^iN{=}CHCH{=}NPr^i$) in which the alkyne is twisted with respect to the Fe–Ru bond, the *C*Me carbon being bonded to both metal atoms with the $CNEt_2$ carbon linked only to the iron. The $^{13}C\text{-}\{^1H\}$ n.m.r. resonances for the *C*Me and $CNEt_2$ nuclei occur at δ 88.7 and 232.9 p.p.m., respectively.[8b]

The reaction between compound (**3**) and $PHPh_2$ was also investigated. The product was the complex $[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(C_6H_4Me\text{-}4)\}(CO)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ (**7b**), characterised by the information given in Tables 1 and 2. The spectroscopic data for (**7b**) are very like those of (**7a**), and the two complexes evidently have similar structures. However, the n.m.r. spectra of (**7b**) revealed the existence of two isomers in solution, the relative intensities of the peaks corresponding to a ratio of 3:2. The existence of two isomers is not unexpected in view of the asymmetry introduced by the presence of CH and CMe groups in the carbaborane cage. The latter evidently adopts different configurations with respect to the OH and C_6H_4Me-4 substituents on the μ-alkyne. In one orientation the CMe and CC_6H_4Me-4 fragments would be cisoid, and in the other transoid. Interestingly, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (both isomers) the resonances for the ligated carbon atoms of the alkyne are widely disparate, as found for (**7a**). In the spectrum of (**7b**) the peaks at δ 191.8 and 196.2 p.p.m. are assigned to the *C*(OH) nuclei of both isomers, and those at 87.2 and 88.0 p.p.m. to the $C(C_6H_4Me\text{-}4)$ nuclei.



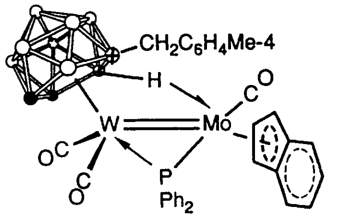
● CH ○ BH

(7a)



● CH ● CMe ○ BH

(7b)



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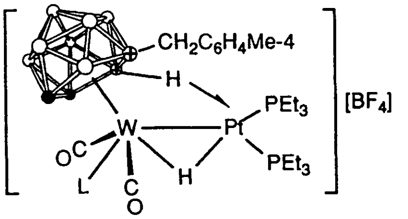
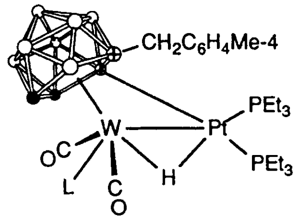




● CMe ○ BH ⊕ B

	L	
(9a)	PMe_3	(10a)
(9b)	CO	(10b)
(9c)	$CNBu^t$	(10c)

Although the mode of formation of the compounds (7) cannot be inferred with any certainty, previous results in this area suggest plausible intermediates (Scheme 2). It was mentioned earlier that treatment of (**2c**) with PMe_3 afforded the complex (**2d**) in which the phosphine is co-ordinated to the tungsten atom rather than the molybdenum centre. A similar attack of $PHPh_2$ on (**2b**) might afford the intermediate (**D**), having a bridging ketenyl group. The formation of the latter moiety by attack of CO on a μ-alkylidyne fragment has ample precedent.[11] A metal-assisted hydrogen transfer of the protonic hydrogen in the co-ordinated $PHPh_2$ molecule to the lone pair on the ketenyl oxygen atom, accompanied by migration of the resulting phosphido ligand into a site bridging the metal–metal bond *via* intermediate (**E**), could lead to compound (**7a**).

The reaction between $PHPh_2$ and the carbaboraneindenyl dimetal complex (**1b**) was next investigated, and was found to follow a very different course to those employing the carbaboranecycloheptatrienyl compounds (**2b**) or (**3**). The room-temperature reaction between (**1b**) and $PHPh_2$ in CH_2Cl_2 gave the simple substitution product $[MoW(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_2(PHPh_2)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6c**). This complex forms *via* displacement of CO from the molybdenum centre in (**1b**), and thus compound (**6c**) is structurally akin to (**6a**) and (**6b**) mentioned earlier. The presence of the $PHPh_2$ ligand in (**6c**) was confirmed by the ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra (Table 2). In the ^1H spectrum there is a diagnostic doublet resonance for the PH group at δ 5.89 with *J*(PH) 371 Hz, corresponding in intensity to a single proton. The $^{31}P\text{-}\{^1H\}$ spectrum shows a singlet signal at δ 24.4 p.p.m. This resonance is in the region for a co-ordinated $PHPh_2$ group, and moreover, the absence of $^{183}W\text{–}^{31}P$ satellite peaks establishes that the ligand is attached to the molybdenum rather than the tungsten centre.

The ^1H n.m.r. spectrum of complex (**6c**) shows a characteristic quartet resonance for the B–H→Mo group at δ −7.24 [*J*(BH) 79 Hz],[2,3,5] as well as two singlet signals for the non-equivalent CMe fragments of the carbaborane cage. Correspondingly, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum displays two peaks for the *C*Me nuclei at δ 64.9 and 64.4 p.p.m. and two signals for the C*Me* groups at δ 31.9 and 31.5 p.p.m. The $^{11}B\text{-}\{^1H\}$ n.m.r. spectrum of complex (**6c**) was also informative. The usual broad BH group signals were observed in the range δ −0.6 to −18.8 p.p.m., but in addition there was a peak for a unique boron atom at δ 17.5 p.p.m. In a fully coupled ^{11}B

Table 2. Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. data for the complexes[a]

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]	^{31}P (δ)[b,d]
(6c)	−7.24 [q, 1 H, BHMo, *J*(BH) 79], 2.03, 2.06 (s × 2, 6 H, CMe), 2.58 (Me-4), 4.71—4.76 (m, 2 H, C_9H_7), 5.35 (m, 1 H, C_9H_7), 5.89 [d, 1 H, PH, *J*(PH) 371], 6.82—7.48 (m, 18 H, C_6H_4, Ph, and C_9H_7)	367.8 [d, μ-C, *J*(PC) 8], 222.0, 216.3 (CO), 161.8 [$C^1(C_6H_4)$], 135.4—76.0 (C_6H_4, Ph, and C_9H_7), 64.9, 64.4 (*C*Me), 31.9, 31.5 (C*Me*), 21.2 (Me-4)	24.4
(7a)	2.41 (s, 3 H, Me-4), 2.55, 2.84 [s × 2, 2 H, $CH(C_2B_9H_{11})$], 5.10 (s, 7 H, C_7H_7), 7.01—8.18 (m, 14 H, C_6H_4 and Ph), 11.3 (s, 1 H, OH)	212.3 (CO), 193.1 (COH), 145.7—128.0 (C_6H_4 and Ph), 90.2 (C_7H_7), 85.5 ($\mathit{C}C_6H_4$Me-4), 44.3, 42.7 [$CH(C_2B_9H_{11})$], 21.2 (Me-4)	125.2 [*J*(WP) 322]
(7b)[e]	1.33, *1.38 (s × 2, 3 H, CMe), 2.40, *2.44 (s × 2, 3 H, Me-4), *3.18, 3.86 [s × 2, 1 H, $CH(C_2B_9H_{10}Me)$], 5.21 (s, 7 H, C_7H_7), 7.08—8.22 (m, 14 H, C_6H_4 and Ph), *8.72, 9.19 (s × 2, 1 H, OH)	*213.4 [d, CO, *J*(PC) 7], 213.1 [d, CO, *J*(PC) 4], *196.2, 191.8 (COH), 147.0—127.7 (C_6H_4 and Ph), *91.0, 90.9 (C_7H_7), 88.0, *87.2 ($\mathit{C}C_6H_4$-Me-4), *57.3, 56.3 (*C*Me), 55.1, *51.7 [CH-($C_2B_9H_{10}$Me)], *34.1, 33.1 (C*Me*), 21.7 (Me-4)	*125.5 [*J*(WP) 319] 131.3 [*J*(WP) 354]
(8)	−6.75 (br, 1 H, BHMo), −0.54, 0.82 [(AB), 2 H, CH_2, *J*(HH) 14], 2.02, 2.17 (s × 2, 6 H, CMe), 2.35 (s, 3 H, Me-4), 5.01 [t, 1 H, C_9H_7, *J*(HH) 4], 6.15 (m, 1 H, C_9H_7), 6.28, 6.82 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 6.42 (m, 1 H, C_9H_7), 6.99—7.84 (m, 14 H, Ph and C_9H_7)	240.2 [d, MoCO, *J*(PC) 7], 222.2 [d, WCO, *J*(PC) 24], 220.5 (WCO), 144.8—74.2 (C_6H_4, Ph, and C_9H_7), 65.2[f] (*C*Me), 38.5 ($\mathit{C}H_2C_6H_4$-Me-4), 34.8, 33.5 (C*Me*), 21.2 (Me-4)	169.8 [*J*(WP) 176]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at ambient temperatures. [b] In CD_2Cl_2. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$, measured in $(CD_3)_2CO$. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [e] Peaks asterisked due to the second, less-abundant isomer (see text). [f] Peak due to other *C*Me nucleus obscured by signals due to thf, added to solubilise the complex.

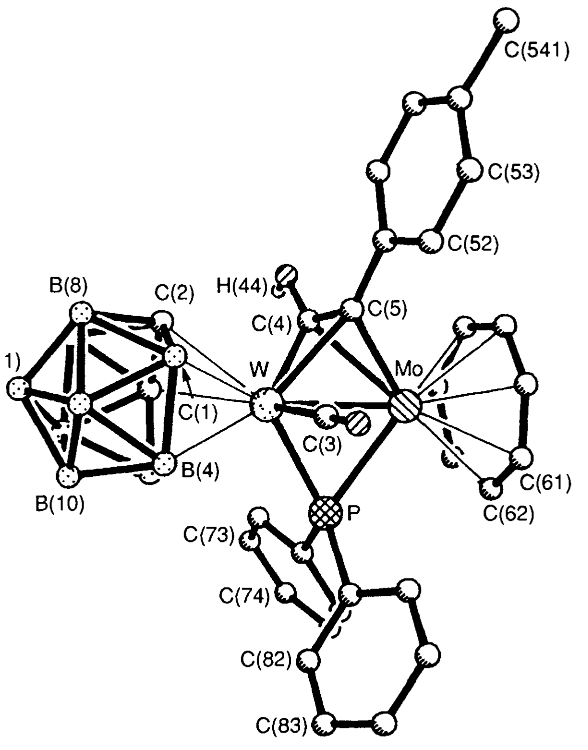


Figure 1. Molecular structure of $[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(C_6H_4\text{-}Me\text{-}4)\}(CO)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{11})]\cdot Me_2CO$ (**7a**) showing the atom numbering scheme

spectrum this resonance became a doublet [*J*(BH) 79 Hz]. These data are diagnostic for a B–H→Mo group. Thus for complex (**1b**) the corresponding signal is at δ 14.1 p.p.m., with *J*(BH) 84 Hz.[2]

The resonance for the μ-C nucleus of the *p*-tolylmethylidyne group in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**6c**) is seen as a doublet at 367.8 p.p.m. [*J*(PC) 8 Hz]. The relative deshielding of this signal is of interest, being comparable with the deshielding of the μ-C nuclei in the spectra of (**6a**) (δ 353.1) and (**6b**) (δ 380.5 p.p.m.). In contrast, the signals for the μ-C group in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**5a**) (δ 316.4), (**5b**) (δ 320.1), and (**5c**) (δ 302.8 p.p.m.) are appreciably less deshielded, as they are also in the spectra of the complexes (**2**), *e.g.* for (**2d**), δ(μ-C) = 312.5 p.p.m. A special feature of the structures of the species (**5**) is that *X*-ray diffraction data suggest the ligands L [$N_2C(C_6H_4Me\text{-}4)_2$ or O] function as 4e donors, and that some slippage of the indenyl group from η^5 to η^3 occurs.[5] Such an effect would be compensatory as far as electron donation to the metal centre of the $ML(\eta^5\text{-}C_9H_7)$ group is concerned. Thus the metal would acquire seven electrons whether the L and C_9H_7 groups respectively contributed either four and three, or two and five electrons. The μ-C resonances in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the dimetal compounds (**1**) and (**4**) are also relevant. These occur in the range δ 383.2—358.1 p.p.m., and stand in contrast with the less-deshielded resonance for the μ-C nucleus in the spectrum of compound (**3**) which is seen at δ 325.5 p.p.m.[2,3] It is thus apparent that the various compounds (**1**)—(**6**) may be divided into two groups, those which display μ-C $^{13}C\text{-}\{^1H\}$ n.m.r. signals in the range *ca.* 300—340 p.p.m. and those which are appreciably more deshielded with resonances in the range *ca.* 350—385 p.p.m. We suggest that these chemical shifts may be related to the bonding within the three-membered $\overline{M(\mu\text{-}C)M'}$ rings.

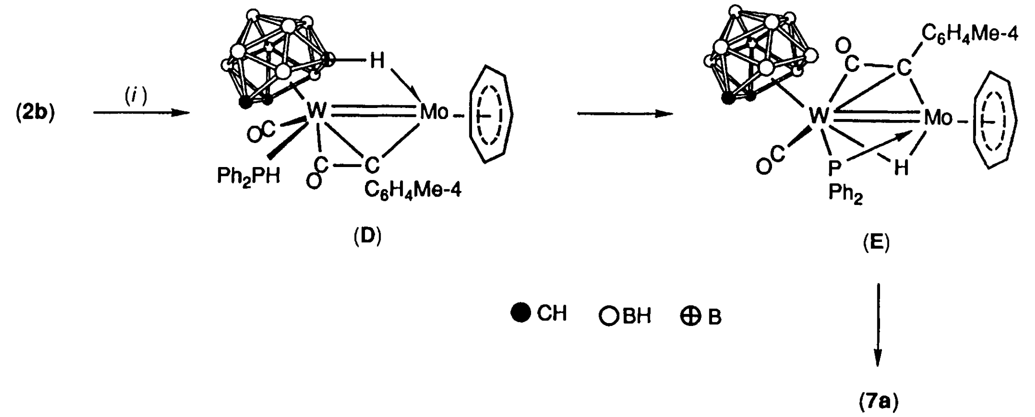
Although all the complexes are 32 c.v.e. species, it is proposed that those with μ-C resonances in the *ca.* 300—340 p.p.m. range attain formally 18-electron valence shells at both metal centres [Scheme 1, (**C**) or (**C′**)]. Those with μ-C signals at *ca.* 350—385 p.p.m. might have one metal centre with formally 16 electrons, with the other having an 18-electron valence shell [Scheme 1, (**A**) or (**A′**)]. Although more data are required to place these ideas on a firmer basis, earlier n.m.r. and *X*-ray diffraction studies have provided strong evidence that C≡M groups can function as two or four electron donors to a metal–ligand fragment.[12]

It seemed likely that compound (**6c**) would form a μ-PPh_2 complex on heating, and this proved to be so. In toluene at 70 °C it afforded a red species $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}$

Table 3. Selected internuclear distances (Å) and angles (°) for the complex $[MoW(\mu-PPh_2)\{\mu-C(OH)C(C_6H_4Me-4)\}(CO)(\eta^7-C_7H_7)(\eta^5-C_2B_9H_{11})]\cdot Me_2CO$ (**7a**)

W–Mo	2.713(1)	W–P	2.360(3)	W–C(1)	2.354(9)	W–C(2)	2.36(1)
W–B(3)	2.39(1)	W–B(4)	2.42(1)	W–B(5)	2.39(1)	W–C(3)	1.999(9)
W–C(4)	2.067(8)	W–C(5)	2.251(8)	Mo–P	2.439(3)	Mo–C(4)	2.352(8)
Mo–C(5)	2.224(9)	Mo–C(61)	2.27(1)	Mo–C(62)	2.32(1)	Mo–C(63)	2.29(1)
Mo–C(64)	2.20(2)	Mo–C(65)	2.29(1)	Mo–C(66)	2.31(1)	Mo–C(67)	2.24(1)
C(1)–C(2)	1.66(1)	C(2)–B(3)	1.68(2)	B(3)–B(4)	1.85(2)	B(4)–B(5)	1.70(2)
B(5)–C(1)	1.66(1)	C(3)–O(3)	1.12(1)	C(4)–O(4)	1.34(1)	O(4)–H(44)	0.7(1)
C(4)–C(5)	1.34(1)	C(61)–C(62)	1.38(2)	C(62)–C(63)	1.40(2)	C(63)–C(64)	1.39(2)
C(64)–C(65)	1.42(2)	C(65)–C(66)	1.38(2)	C(66)–C(67)	1.40(2)	C(67)–C(61)	1.35(2)

Mo–W–P	57.0(1)	Mo–W–C(3)	83.0(3)	P–W–C(3)	88.2(3)	Mo–W–C(4)	57.0(2)
P–W–C(4)	106.0(2)	Mo–W–C(5)	52.2(2)	P–W–C(5)	108.7(2)	W–Mo–P	54.2(1)
W–Mo–C(4)	47.5(2)	P–Mo–C(4)	95.3(2)	W–Mo–C(5)	53.1(2)	P–Mo–C(5)	106.9(2)
C(4)–Mo–C(5)	34.0(3)	W–P–Mo	68.8(1)	W–C(3)–O(3)	176(1)	W–C(4)–Mo	75.4(3)
W–C(4)–O(4)	141.2(7)	Mo–C(4)–O(4)	132.7(6)	W–C(4)–C(5)	79.5(5)	Mo–C(4)–C(5)	67.8(5)
O(4)–C(4)–C(5)	131.5(8)	C(4)–O(4)–H(44)	120(10)	W–C(5)–Mo	74.6(3)	W–C(5)–C(4)	64.6(5)
Mo–C(5)–C(4)	78.3(5)	C(61)–C(62)–C(63)	130(1)	C(62)–C(63)–C(64)	127(1)	C(63)–C(64)–C(65)	127(1)
C(64)–C(65)–C(66)	127(1)	C(65)–C(66)–C(67)	130(1)	C(66)–C(67)–C(61)	128(1)	C(67)–C(61)–C(62)	128(1)



Scheme 2. (*i*) + $PHPh_2$

$C_9H_7)\{\eta^5-C_2B_9H_8(CH_2C_6H_4Me-4)Me_2\}]$ (**8**). The presence of the μ-PPh_2 group was immediately apparent from the $^{31}P-\{^1H\}$ n.m.r. spectrum which showed a resonance at δ 169.8 p.p.m. [*J*(WP) 176 Hz], in the expected range.[9] Moreover, in the ^1H n.m.r. spectrum the appearance of a broad signal at δ −6.75 was strongly indicative of the presence of a B–H⇀Mo group. This was supported by the data from a fully coupled ^{11}B n.m.r. spectrum which displayed a doublet resonance at δ 16.7 p.p.m. [*J*(BH) 61 Hz] for a single boron nucleus. Other peaks occurred in the range δ 4.6 to −12.5 p.p.m., but the signal due to a single boron atom at +4.6 p.p.m. showed no $^1H-^{11}B$ coupling, a feature making it probable that it was linked to an exopolyhedral carbon atom. These data, coupled with the absence of any resonance for a μ-CC_6H_4Me-4 ligand in the $^{13}C-\{^1H\}$ n.m.r. spectrum, made an *X*-ray diffraction study on complex (**8**) a necessity in order to establish the structure.

Data from the *X*-ray diffraction work are summarised in Table 4, and the molecule is shown in Figure 2. It is immediately apparent that the pyrolysis of compound (**6c**) has produced another dimetal complex, but with an unexpected structure. The Mo–W bond [2.708(1) Å] is spanned by a PPh_2 group [Mo–P 2.357(2), W–P 2.456(2) Å], as expected. As indicated by the ^1H and ^{11}B n.m.r. data, discussed above, an exopolyhedral B–H⇀Mo 3c–2e bond is also present, and this linkage involves B(5), a boron atom adjacent to a CMe group in the open pentagonal face of the cage. The B(4) atom in the face carries a $CH_2C_6H_4Me$-4 substituent, thus accounting for the singlet resonance at δ 4.6 p.p.m. in the fully coupled ^{11}B n.m.r. spectrum, mentioned above. The molybdenum atom is co-ordinated by the indenyl group and a CO molecule, and the tungsten atom carries two terminal CO ligands and is ligated by the CCBBB ring of the *nido*-icosahedral C_2B_9 fragment in the usual manner.

Having established the structure of compound (**8**), the remaining n.m.r. data are readily interpreted. In the $^{13}C-\{^1H\}$ n.m.r. spectrum (Table 2) there are three CO resonances. A broad peak at δ 38.5 p.p.m. may be assigned to the *C*$H_2C_6H_4Me$-4 nucleus, based on the data obtained for other compounds having this structural feature.[13] The asymmetry of the molecule should result in the observation of two *C*Me and two C*Me* signals. The latter occur at 34.8 and 33.5 p.p.m., but only one *C*Me resonance is seen (δ 65.2 p.p.m.). However, the second peak is probably obscured by solvent peaks. The ^1H n.m.r. spectrum shows the two expected CMe resonances at δ 2.02 and 2.17, and also an AB pattern for the $BCH_2C_6H_4Me$-4 nuclei at δ −0.54 and 0.82 [*J*(HH) 14 Hz]. These peaks for the CH_2 group are unexpectedly shielded, since in other compounds containing a $BCH_2C_6H_4Me$-4 fragment the CH_2 resonances appear in the region δ *ca.* 2—3. However, inspection of the structure of compound (**8**) reveals that the tolyl ring of the $CH_2C_6H_4Me$-4 group is sterically constrained to adopt a site *anti* to the phenyl rings of the μ-PPh_2 ligand. Consequently the CH_2 protons are forced to lie in a cavity formed by the indenyl ring system and one of the phenyl rings of the PPh_2 group. It

Table 4. Selected internuclear distances (Å) and angles (°) for the complex $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (**8**)

W–Mo	2.708(1)	W–P	2.456(2)	W–C(1)	2.372(6)	W–C(2)	2.426(6)
W–B(3)	2.400(7)	W–B(4)	2.437(7)	W–B(5)	2.280(7)	W–C(5)	1.997(6)
W–C(6)	1.993(7)	Mo–P	2.357(2)	Mo–B(5)	2.491(7)	Mo–C(7)	1.939(7)
Mo–C(41)	2.437(7)	Mo–C(42)	2.340(7)	Mo–C(43)	2.308(7)	Mo–C(44)	2.284(6)
Mo–C(45)	2.390(6)	Mo–H	1.92(7)	C(1)–C(2)	1.653(9)	C(1)–B(5)	1.748(9)
C(2)–B(3)	1.719(9)	B(3)–B(4)	1.805(11)	B(4)–B(5)	1.822(10)	B(4)–C(10)	1.604(9)
B(5)–H	1.14(8)	C(5)–O(5)	1.145(8)	C(6)–O(6)	1.154(9)	C(7)–O(7)	1.162(8)
Mo–W–P	54.0(1)	Mo–W–C(5)	110.5(2)	Mo–W–C(6)	126.0(2)	C(5)–W–C(6)	81.8(3)
W–Mo–P	57.5(1)	W–Mo–B(5)	51.8(2)	P–Mo–B(5)	107.4(2)	W–Mo–C(7)	81.3(2)
W–Mo–H	77(2)	P–Mo–H	134(2)	B(5)–Mo–H	26(2)	W–P–Mo	68.4(1)
C(2)–C(1)–B(5)	108.6(5)	C(1)–C(2)–B(3)	110.4(5)	C(2)–B(3)–B(4)	109.9(5)	B(3)–B(4)–B(5)	101.5(5)
W–B(5)–Mo	69.0(2)	C(1)–B(5)–B(4)	109.4(5)	W–C(5)–O(5)	178.5(6)	W–C(6)–O(6)	178.6(6)
Mo–C(7)–O(7)	172.4(6)	B(4)–C(10)–C(11)	116.1(5)	Mo–H–B(5)	106.3(47)		

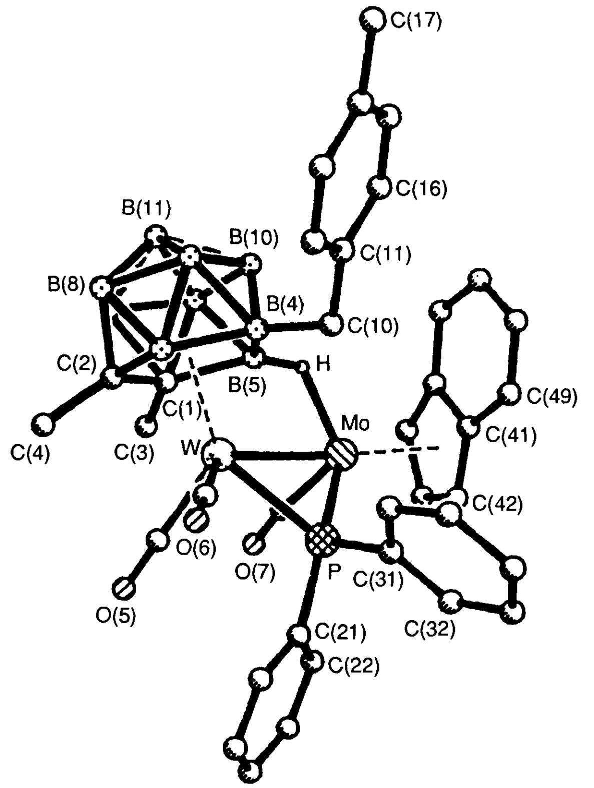


Figure 2. Molecular structure of $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (**8**) showing the atom numbering scheme

therefore seems probable that the unusually shielded ^1H n.m.r. chemical shifts observed for the CH_2 group arise *via* a through-space interaction with the fields generated by the aromatic ring systems.

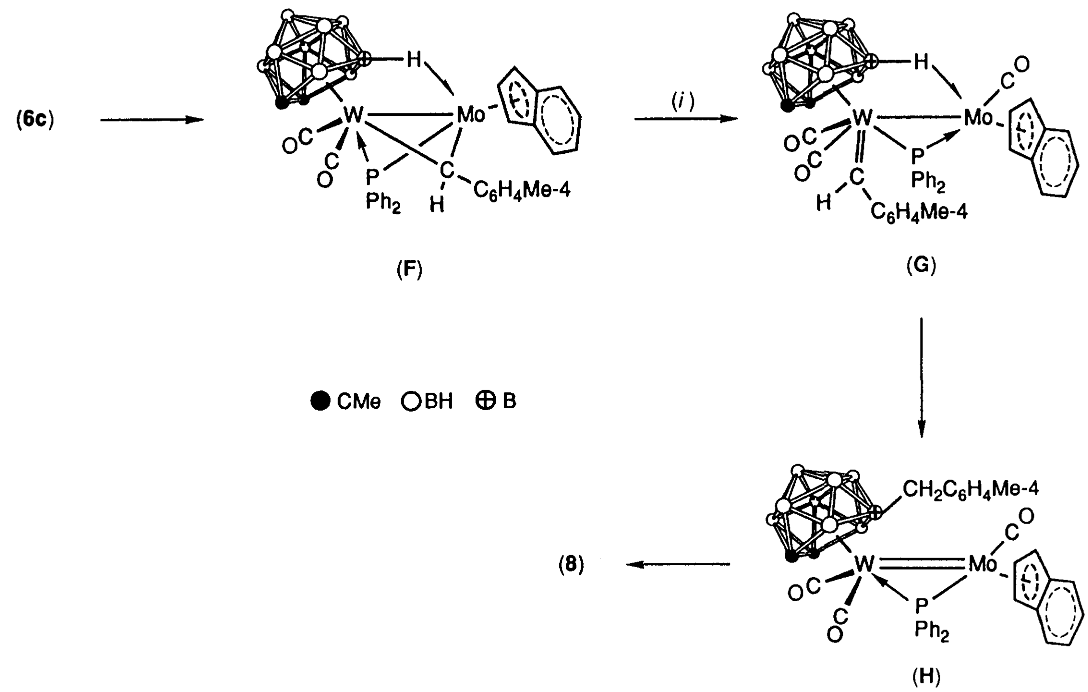
The mode of attachment of the carbaborane cage system to the dimetal fragment in compound (**8**) has precedent in the structures proposed for the tungstenplatinum salts $[WPt(\mu\text{-}H)(CO)_2L(PEt_3)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}][BF_4]$ (**9**), obtained by protonating the neutral species $[WPt(\mu\text{-}H)\{\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2\}(CO)_2L(PEt_3)_2]$ (**10a**; L = PMe_3), (**10b**; L = CO), and (**10c**; L = $CNBu^t$).[13a] Compound (**8**) is formed in somewhat less than 50% yield from (**6c**), which is not surprising since the former species contains three carbonyl groups and the latter two. Evidently a CO molecule is captured in what must be a complicated process. A possible pathway is indicated in Scheme 3. The intermediates suggested have precedent in earlier work. Thus the transfer of a hydrogen atom from a terminally bound $PHPh_2$ ligand to a μ-tolylmethylidyne group [intermediate (**F**)] occurs in the formation of $[WFe\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_3\{HB(pz)_3\}]$ [$HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate] from $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PHPh_2)\{HB(pz)_3\}]$.[14] The steps (**F**) ⟶ (**G**) ⟶ (**H**) are similar to those proposed to account for the formation of the species $[WPt(CO)_2(PEt_3)_2\{\eta^6\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ from the reaction between $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ and $[PtH(Me_2CO)(PEt_3)_2][BF_4]$.[13a] The final step (**H**) ⟶ (**8**) would allow the molybdenum atom to attain an 18-electron filled valence shell through formation of a B–H⇀Mo bond.

The work reported in this paper suggests that the complexes (**1a**)—(**1c**), (**2a**)—(**2c**), and (**3**) should undergo interesting reactions with many other donor molecules, particularly those with substrates wherein initial co-ordination of the donor can be followed by transfer of a hydrogen atom from the reactant onto another fragment ligating the dimetal system. The different reactivity patterns towards $PHPh_2$ shown by the compounds (**2b**) and (**3**) on the one hand, and (**1b**) on the other, is likely to be due to the presence or absence of CH *versus* CMe groups at the vertices of the cages leading to different steric and electronic effects. However, the possible influence of $\eta^7\text{-}C_7H_7$ *versus* $\eta^5\text{-}C_9H_7$ groups cannot be discounted and further experimental work is required.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. Light petroleum refers to that fraction of b.p. 40—60 °C. Alumina (BDH aluminium oxide, Brockman Activity II) and Florisil (Aldrich, 100—200 mesh) were used to pack chromatography columns (*ca.* 20 cm in length and 3.0 cm in diameter). The i.r. spectra were measured with a Perkin-Elmer FT1600 spectrophotometer, the n.m.r. spectra with JEOL JNM FX90Q, GX270, and GX400 instruments. The $^{11}B\text{-}\{^1H\}$ n.m.r. chemical shifts, measured in CD_2Cl_2, are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). The compounds (**1c**),[2] (**2b**),[3] and (**3**)[3] were prepared as previously described. Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Dimetal Compounds.—(*i*) Compound (**2b**) (0.33 g, 0.50 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and treated with $PHPh_2$ (0.20 cm^3, 1.15 mmol, excess), the mixture being stirred for 2 h. Solvent was reduced in volume *in vacuo* to



Scheme 3. (*i*) CO

ca. 2 cm^3, and transferred to the top of a chromatography column packed with Florisil. Elution with CH_2Cl_2–light petroleum (3:5) removed a trace of an unidentified red-brown fraction. Further elution with CH_2Cl_2 gave a red fraction which was collected. Solvent was reduced in volume *in vacuo* to *ca.* 2 cm^3, and light petroleum (10 cm^3) was added. Removal of the supernatant liquid with a syringe afforded red *microcrystals* of [$MoW(\mu$-$PPh_2)\{\mu$-$C(OH)C(C_6H_4Me$-$4)\}(CO)(\eta^7$-$C_7H_7)(\eta^5$-$C_2B_9H_{11})$] (**7a**) (0.21 g).

(*ii*) Similarly, compound (**3**) (0.34 g, 0.50 mmol) on treatment with $PHPh_2$ (0.20 cm^3, 1.15 mmol) gave red *microcrystals* of [$MoW(\mu$-$PPh_2)\{\mu$-$C(OH)C(C_6H_4Me$-$4)\}(CO)(\eta^7$-$C_7H_7)(\eta^5$-$C_2B_9H_{10}Me)$] (**7b**) (0.19 g).

(*iii*) In a similar manner to the synthesis of (**7a**), the compound (**1b**) (0.37 g, 0.50 mmol) was treated with $PHPh_2$ (0.10 cm^3, 0.57 mmol), and the mixture was stirred for 3 d. Chromatography on alumina, eluting with CH_2Cl_2, removed initially a trace of (**1b**), followed by a green fraction. Removal of solvent *in vacuo* gave green *microcrystals* of [$MoW(\mu$-CC_6H_4-Me-$4)(CO)_2(PHPh_2)(\eta^5$-$C_9H_7)(\eta^5$-$C_2B_9H_9Me_2)$] (**6c**) (0.26 g).

(*iv*) Compound (**6c**) (0.20 g, 0.22 mmol) was dissolved in toluene (10 cm^3) in a Schlenk tube fitted with a high-pressure stopcock. The vessel was partially evacuated, and heated to 70 °C for 3 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 3 cm^3) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (1:1), gradually changing to 100% CH_2Cl_2, removed a red fraction. Solvent was removed *in vacuo*, and the residue was crystallised from CH_2Cl_2–light petroleum (*ca.* 20 cm^3, 1:10) to give red *microcrystals* of [$MoW(\mu$-$PPh_2)(CO)_3(\eta^5$-$C_9H_7)\{\eta^5$-$C_2B_9H_8$-$(CH_2C_6H_4Me$-$4)Me_2\}$] (**8**) (0.93 g).

Crystal Structure Determinations.—Data were collected using a Nicolet R3m/V four-circle diffractometer (293 K, Mo-K_α *X*-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å), and were corrected for Lorentz, polarisation and *X*-ray absorption effects, the latter by an empirical method based upon azimuthal scan data.[15] The structures were solved by conventional heavy-atom methods, and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Except where otherwise noted, hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters (0.08; aromatic, CH_2 and OH), or a common refined isotropic thermal parameter (Me). Refinements by full-matrix least squares were performed on a DEC micro-Vax computer with the SHELXTL system of programs.[15] Scattering factors with corrections for anomalous dispersion were taken from ref. 16. Atom co-ordinates are given in Tables 5 and 6.

Crystals of (**7a**) were grown from acetone–thf (tetrahydrofuran)–light petroleum as deep red prisms (crystal dimensions *ca.* 0.30 × 0.25 × 0.25 mm). Of the 4 716 data collected (Wyckoff ω scans, $2\theta \leqslant 55°$), 3 998 had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement.

Crystal data. $C_{31}H_{36}B_9MoO_2PW{\cdot}C_3H_6O$, M = 906.8, orthorhombic, space group $P2_12_12_1$, a = 11.662(1), b = 16.987(2), c = 18.750(3) Å, U = 3 714.6(8) Å^3, Z = 4, D_c = 1.62 g cm^{-3}, $F(000)$ = 1 784, μ(Mo-K_α) = 35.7 cm^{-1}.

The carbaborane and hydroxyl hydrogen atoms were located from a low-angle difference electron-density synthesis and their positions were refined. The asymmetric unit contains one molecule of acetone which is hydrogen bonded to the hydroxyl proton H(44) and to the H(1) hydrogen atom of the carbaborane cage [O(90)···H(44) 2.09 and O(90)···H(1) 2.18 Å]. The space group is chiral and a Rogers' 'eta' refinement was used to confirm that the absolute configuration of the complex was correct.[17] Final R = 0.034 (R' = 0.033) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,3|F|^2]$. The final electron-density difference synthesis showed no peaks > 1.1 or < −0.8 e Å^{-3}.

Crystals of compound (**8**) were grown from an Et_2O–thf–hexane solvent mixture as deep red prisms (crystal dimensions *ca.* 0.50 × 0.43 × 0.40 mm). Of the 7 425 data collected (Wyckoff ω scans, $2\theta \leqslant 50°$), 4 845 had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement.

Crystal data. $C_{36}H_{40}B_9MoO_3PW$, M = 928.8, monoclinic,

Table 5. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**7a**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
W	90(1)	7 810(1)	2 014(1)
Mo	2 247(1)	8 271(1)	1 667(1)
P	1 684(2)	7 612(2)	2 768(1)
C(1)	−883(8)	6 618(5)	1 804(5)
C(2)	−1 568(8)	7 360(7)	1 422(5)
B(3)	−1 930(8)	8 053(6)	2 021(9)
B(4)	−1 429(9)	7 640(7)	2 880(6)
B(5)	−791(8)	6 767(7)	2 675(6)
B(6)	−1 817(12)	6 088(8)	2 332(9)
B(7)	−2 277(10)	6 468(7)	1 509(7)
B(8)	−2 976(9)	7 381(8)	1 670(7)
B(9)	−2 909(10)	7 555(8)	2 592(7)
B(10)	−2 198(10)	6 765(9)	2 989(8)
B(11)	−3 132(10)	6 592(8)	2 276(7)
C(3)	−22(9)	8 906(5)	2 396(5)
O(3)	−161(7)	9 515(4)	2 613(4)
C(4)	719(7)	7 772(6)	984(4)
O(4)	680(7)	7 330(4)	389(4)
C(5)	641(8)	8 553(5)	1 081(5)
C(51)	344(7)	9 211(6)	612(5)
C(52)	260(10)	9 979(6)	859(5)
C(53)	74(13)	10 585(6)	373(6)
C(54)	−69(12)	10 451(7)	−347(6)
C(55)	40(13)	9 697(7)	−584(5)
C(56)	242(9)	9 070(6)	−124(5)
C(541)	−220(15)	11 123(8)	−866(7)
C(61)	3 580(10)	9 121(9)	2 103(8)
C(62)	4 043(9)	8 382(11)	2 192(7)
C(63)	4 047(9)	7 733(8)	1 732(9)
C(64)	3 604(11)	7 699(9)	1 043(9)
C(65)	3 241(10)	8 337(10)	613(6)
C(66)	3 044(10)	9 100(9)	827(8)
C(67)	3 113(9)	9 436(7)	1 508(8)
C(71)	2 428(8)	6 661(6)	2 887(6)
C(72)	2 142(11)	6 047(7)	2 455(7)
C(73)	2 789(11)	5 353(7)	2 471(8)
C(74)	3 739(12)	5 291(9)	2 881(9)
C(75)	4 054(10)	5 922(9)	3 307(8)
C(76)	3 402(9)	6 613(8)	3 334(7)
C(81)	1 774(9)	8 081(6)	3 647(5)
C(82)	1 617(13)	7 651(8)	4 260(6)
C(83)	1 618(18)	8 020(8)	4 909(7)
C(84)	1 735(14)	8 830(8)	4 966(6)
C(85)	1 891(13)	9 246(7)	4 356(6)
C(86)	1 877(10)	8 890(6)	3 703(5)
O(90)	924(11)	5 782(5)	686(5)
C(91)	1 447(12)	5 354(8)	299(7)
C(92)	1 503(15)	4 506(9)	438(10)
C(93)	1 969(15)	5 646(11)	−343(9)

Table 6. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**8**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
W	755(1)	591(1)	1 913(1)
Mo	−398(1)	−729(1)	2 416(1)
P	−1 250(1)	601(1)	2 264(1)
C(1)	2 159(5)	−349(4)	1 517(3)
C(2)	2 688(5)	612(4)	1 492(3)
C(3)	1 721(6)	−784(4)	882(3)
C(4)	2 684(6)	1 102(5)	837(3)
B(3)	2 634(6)	1 077(5)	2 264(4)
B(4)	2 084(6)	344(5)	2 860(3)
B(5)	1 722(6)	−550(5)	2 327(3)
B(6)	3 021(7)	−977(6)	2 019(4)
B(7)	3 658(7)	−223(5)	1 496(4)
B(8)	3 949(7)	672(5)	1 961(4)
B(9)	3 581(6)	476(5)	2 783(4)
B(10)	2 995(7)	−554(5)	2 842(4)
B(11)	4 186(7)	−340(6)	2 315(4)
C(5)	132(6)	878(4)	1 000(3)
O(5)	−225(5)	1 025(4)	474(2)
C(6)	415(6)	1 798(4)	2 072(3)
O(6)	243(5)	2 499(3)	2 166(3)
C(7)	−691(6)	−946(4)	1 473(3)
O(7)	−972(4)	−1 127(3)	931(2)
C(10)	1 530(6)	577(5)	3 559(3)
C(11)	2 373(5)	807(4)	4 123(3)
C(12)	2 706(7)	1 626(4)	4 228(4)
C(13)	3 497(7)	1 834(5)	4 729(4)
C(14)	3 972(6)	1 253(5)	5 152(3)
C(15)	3 629(6)	443(5)	5 055(3)
C(16)	2 852(5)	206(5)	4 551(3)
C(17)	4 812(8)	1 497(7)	5 714(5)
C(21)	−2 327(5)	828(4)	1 601(3)
C(22)	−2 955(6)	189(5)	1 278(3)
C(23)	−3 668(6)	381(6)	728(3)
C(24)	−3 788(6)	1 194(6)	507(3)
C(25)	−3 186(6)	1 818(5)	831(3)
C(26)	−2 465(6)	1 656(5)	1 380(3)
C(31)	−1 834(5)	1 172(4)	2 972(3)
C(32)	−2 989(6)	1 052(5)	3 119(3)
C(33)	−3 469(7)	1 422(5)	3 664(4)
C(34)	−2 788(7)	1 933(5)	4 078(3)
C(35)	−1 634(7)	2 064(5)	3 939(3)
C(36)	−1 174(6)	1 686(4)	3 390(3)
C(41)	−1 137(6)	−1 171(4)	3 483(3)
C(42)	−2 043(6)	−1 118(5)	2 983(4)
C(43)	−1 832(6)	−1 722(5)	2 492(3)
C(44)	−773(6)	−2 104(4)	2 638(3)
C(45)	−324(6)	−1 779(4)	3 266(3)
C(46)	642(6)	−1 987(4)	3 674(4)
C(47)	764(7)	−1 626(5)	4 279(4)
C(48)	−49(9)	−1 051(5)	4 504(4)
C(49)	−959(8)	−795(5)	4 121(4)

space group $P2_1/n$, $a = 11.617(4)$, $b = 15.954(5)$, $c = 20.043(6)$ Å, $\beta = 91.98(3)°$, $U = 3\,712(2)$ Å^3, $Z = 4$, $D_c = 1.66$ g cm^{-3}, $F(000) = 1\,824$, $\mu(\text{Mo-}K_\alpha) = 35.7$ cm^{-1}.

The carbaborane and B–H→Mo hydrogen atoms were located from a low-angle difference electron-density synthesis. These atoms were included in the refinement but only the position of the B–H→Mo hydrogen atom was refined. Final $R = 0.031$ ($R' = 0.032$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,5|F|^2]$. The final electron-density difference synthesis showed no peaks >0.52 or <-0.42 e Å^{-3}.

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

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