Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 104.[1] Trimetal Molybdenum and Tungsten Complexes containing η^5-$C_2B_9H_9R'_2$ (R'= H or Me) Ligands; Crystal Structure of $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ *

Stephen J. Dossett, Ian J. Hart, Massimino U. Pilotti, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

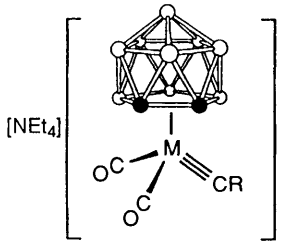
Solutions of the salts $[NEt_4][M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]$ (M = Mo or W, R = C_6H_4Me-4 or $C\equiv CBu^t$, R' = H or Me), in thf (tetrahydrofuran) at room temperature, react with the compound $[Mo(CO)_3(NCMe)_3]$ to afford the trimetal complexes $[NEt_4][Mo_2M(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_9R'_2)]$ (M = W, R = C_6H_4Me-4, R' = H or Me; M = Mo, R = C_6H_4Me-4, R' = H; M = W, R = $C\equiv CBu^t$, R' = Me). A single-crystal *X*-ray diffraction study was carried out on the PMe_3 derivative $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$. The metal triangle [Mo–Mo 2.968(3), Mo–W 2.881(3) and 2.867(3) Å] in the anion is capped on one side by the *p*-tolylmethylidyne group [μ_3-C–Mo av. 2.26(2), μ_3-C–W 2.01(2) Å], and is bridged on the other by the $C_2B_9H_9Me_2$ cage. The latter is η^5 co-ordinated to the tungsten atom and linked to the molybdenum atoms *via* two exopolyhedral B–H$\rightharpoonup$Mo bonds. The bond to one molybdenum centre involves a BH fragment α to a CMe group in the CCBBB face of the cage, while the bond to the other molybdenum centre employs a BH fragment β to the CMe groups. Moreover, the molybdenum atom linked to the cage *via* the β BH group carries the PMe_3 ligand [Mo–P 2.489(7) Å]. This metal atom is also ligated by two terminally bound CO groups, and by a CO molecule that asymmetrically bridges to the other molybdenum [Mo–C–O 156(2) and 124(2)°]. The latter is co-ordinated by three CO groups, and the tungsten atom by two CO molecules. In the formation of $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ there was n.m.r. evidence for the formation of a second isomer (*ca.* 15%) in which the PMe_3 group occupies a different site. Attempts to protonate the salts $[NEt_4][Mo_2M(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_9R'_2)]$ in order to obtain stable neutral complexes were unsuccessful, but treatment of $[NEt_4][Mo_2W(\mu_3\text{-}CC\equiv CBu^t)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ in thf with $[AuCl(PPh_3)]$ in the presence of $TlPF_6$ gives $[Mo(CO)_6]$ and the dimetal complex $[WAu(\mu\text{-}CC\equiv CBu^t)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$. The latter reacts with $[Pt(nb)(PMe_2Ph)_2]$ (nb = bicyclo[2.2.1]heptene) to afford the trimetal complex $[WPtAu(\mu_3\text{-}CC\equiv CBu^t)(CO)_2(PPh_3)(PMe_2Ph)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$. 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.

In a series of papers[1,2] we have demonstrated that salts of the tungsten complexes $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]^-$ (R = alkyl or aryl, R' = H or Me) and the molybdenum species $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)L(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ [L = CO or $P(OMe_3)_3$] are useful precursors for the synthesis of compounds with heteronuclear metal–metal bonds. The C$\equiv$M (M = Mo or W) groups in these anionic complexes act as donors towards low-valent metal–ligand fragments. However, an intriguing aspect of this synthetic procedure is the frequency with which the *nido*-icosahedral η^5-$C_2B_9H_9R'_2$ cages bonded to the tungsten or molybdenum centres adopt a non-spectator role. Often this takes the form of cage slippage so as to form exopolyhedral B–H$\rightharpoonup$metal bonds.[1] However, further transformations frequently occur, thereby affording products having molecular structures of hitherto unknown type.[3]

The alkylidyne(carbaborane)-tungsten and -molybdenum reagents display both similarities and differences compared with those observed with the isolobal and neutral compounds $[M(\equiv CR)(CO)_2L]$ {M = Mo or W, R = alkyl or aryl, L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]}.[4] The L groups in the latter reagents remain co-ordinated to one metal centre in the reaction products, whereas with the anionic alkylidyne metal compounds containing η^5-$C_2B_9H_9R'_2$ fragments the carbaborane cage may ligate one or more metal centres in the final products depending upon whether the cage adopts a spectator or non-spectator role. This is well illustrated in reactions with $[Co_2(CO)_8]$. Treatment of the species $[M(\equiv CR)(CO)_2L]$ with $[Co_2(CO)_8]$ affords a family of trimetal complexes $[MCo_2(\mu_3\text{-}CR)(CO)_8L]$.[5] In the latter the alkylidyne ligands cap the metal triangles, the vertices of which comprise one $M(CO)_2L$ and two $Co(CO)_3$ fragments. In contrast, reactions of $[Co_2(CO)_8]$ with salts of the anionic complexes $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ afford two types of trimetal compound. In one type the cage ligand adopts a spectator role, while in the other it does not. For example, $[Co_2(CO)_8]$ and the salt $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1a**) afford the complex $[NEt_4][WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2a**) as the final product. However, the latter forms *via* the intermediacy of the octacarbonyl species $[NEt_4][WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2b**).[6] Moreover, treatment of (**2a**) with CO regenerates (**2b**). It is evident that the structure of the anion

---

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



○BH

	M	R	●
(1a)	W	C_6H_4Me-4	CMe
(1b)	W	C_6H_4Me-4	CH
(1c)	Mo	C_6H_4Me-4	CH
(1d)	W	$C{\equiv}CBu^t$	CMe

of (**2b**) is related to that of the compounds $[\mathrm{MCo_2(\mu_3\text{-}CR)(CO)_8L}]$ by interchanging the $\eta^5\text{-}C_2B_9H_9Me_2$ *nido* cage in the former by L groups in the latter.

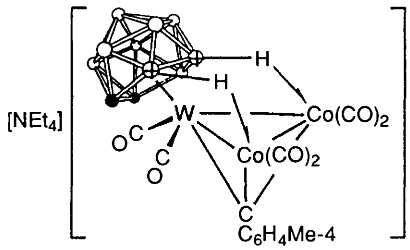
We have previously reported reactions between the compounds $[\mathrm{Mo(CO)_3(NCMe)_3}]$ and $[\mathrm{M({\equiv}CR)(CO)_2L}]$ [M = Mo or W, R = aryl, L = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, or $\mathrm{HB(pz)_3}$].[7] The products are trimetal species of formulation $[\mathrm{MoM_2(\mu\text{-}CR)_2(\mu\text{-}CO)_2(CO)_4L_2}]$, but interestingly these complexes adopt one of two alternative structures in the solid state. Thus the reaction between $[\mathrm{Mo(CO)_3(NCMe)_3}]$ and $[\mathrm{W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)}]$ yields $[\mathrm{MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2}]$ (**3a**) which *X*-ray diffraction studies revealed has the structure (**A**). In contrast, $[\mathrm{Mo(CO)_3(NCMe)_3}]$ and $[\mathrm{Mo({\equiv}CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)}]$ afford $[\mathrm{Mo_3(\mu\text{-}CC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2}]$ (**3b**) which in the crystal has structure (**B**).[7] Moreover, in solution compounds of the type $[\mathrm{MoM_2(\mu\text{-}CR)_2(\mu\text{-}CO)_2(CO)_4L_2}]$ exist as an equilibrium mixture of the isomeric forms (**A**) and (**B**), the proportion of each isomer depending on the nature of R and L. These interesting results prompted us to investigate the reactions between $[\mathrm{Mo(CO)_3(NCMe)_3}]$ and the reagents $[\mathrm{NEt_4}][\mathrm{M({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)}]$ (**1a**; M = W, R = C_6H_4Me-4, R′ = Me), (**1b**; M = W, R = C_6H_4Me-4, R′ = H), (**1c**; M = Mo, R = C_6H_4Me-4, R′ = H), and (**1d**; M = W, R = $C{\equiv}CBu^t$, R′ = Me), in order to make a comparison with the $[\mathrm{M({\equiv}CR)(CO)_2L}]$ systems.

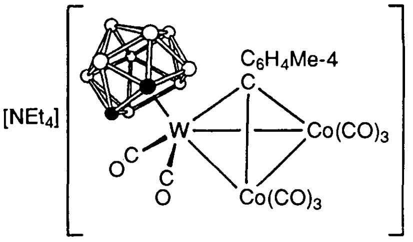
Results and Discussion

Treatment of thf (tetrahydrofuran) solutions of the salts $[\mathrm{NEt_4}][\mathrm{M({\equiv}CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)}]$ (**1**) at room temperature with $[\mathrm{Mo(CO)_3(NCMe)_3}]$ affords the trimetal complexes $[\mathrm{NEt_4}][\mathrm{Mo_2M(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_9R'_2)}]$ (**4a**; M = W, R = C_6H_4Me-4, R′ = Me), (**4b**; M = W, R = C_6H_4Me-4, R′ = H), (**4c**; M = Mo, R = C_6H_4Me-4, R′ = H), and (**4d**; M = W, R = $C{\equiv}CBu^t$, R′ = Me). Data characterising these products are listed in Tables 1—3.

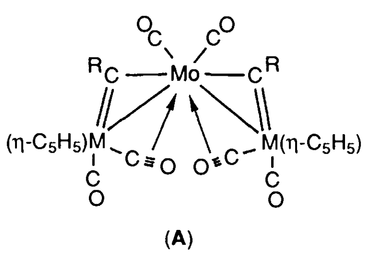
The reaction between (**1d**) and $[\mathrm{Mo(CO)_3(NCMe)_3}]$ was investigated because it has been shown previously[5c,8] that addition of low-valent metal fragments to the compounds $[\mathrm{M({\equiv}CC{\equiv}CBu^t)(CO)_2L}]$ [M = Mo or W, L = $\eta\text{-}C_5H_5$ or $\mathrm{HB(pz)_3}$] can occur either at the C≡M bond or at the C≡C linkage, depending on the nature of L. Generally with L = $\eta\text{-}C_5H_5$ addition at the C≡M group occurs, while with the more bulky L = $\mathrm{HB(pz)_3}$ group complexation occurs *via* the C≡C bonds.

The presence of the exopolyhedral B–H⇀Mo bonds in the species (**4a**)—(**4d**) was revealed by ^{1}H n.m.r. spectroscopy and by fully coupled ^{11}B n.m.r. measurements. The ^{1}H spectra of each of the complexes (**4b**)—(**4d**) displayed (Table 2) two high-field quartet resonances [*J*(BH) *ca.* 90 Hz] diagnostic for exopolyhedral B–H⇀Mo bonds. The appearance of two signals in each spectrum arises because the B–H⇀Mo groups are not equivalent since they involve boron atoms α or β with respect to the carbon atoms in the pentagonal CCBBB face of the cage ligand. The spectrum of (**4a**) was less well resolved, but a broad peak corresponding to two protons was observed

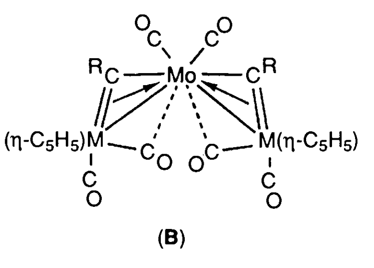




(**2a**) ● CMe ○ BH ⊕B (**2b**)

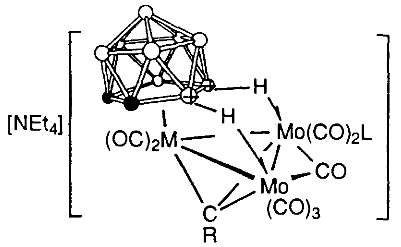


(**A**)



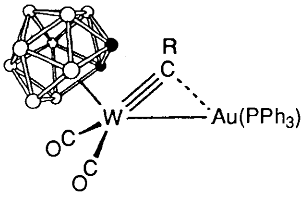
(**B**)

	M	R
(3a)	W	C_6H_4Me-4
(3b)	Mo	$C_6H_3Me_2$-2,6



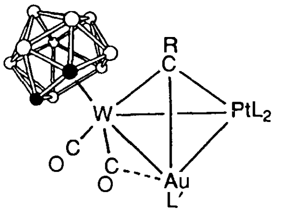
○ BH ⊕ B

	M	R	L	●
(**4a**)	W	C_6H_4Me-4	CO	CMe
(**4b**)	W	C_6H_4Me-4	CO	CH
(**4c**)	Mo	C_6H_4Me-4	CO	CH
(**4d**)	W	$C{\equiv}CBu^t$	CO	CMe
(**4e**)	W	C_6H_4Me-4	PMe_3	CMe
(**4f**)	W	$C{\equiv}CBu^t$	dppm	CMe



● CMe ○ BH

	R
(**5a**)	$C{\equiv}CBu^t$
(**5b**)	C_6H_4Me-4



● CMe ○ BH

	R	L_2	L′
(**6a**)	$C{\equiv}CBu^t$	$(PMe_2Ph)_2$	PPh_3
(**6b**)	C_6H_4Me-4	$(PMe_2Ph)_2$	PMe_2Ph
(**6c**)	C_6H_4Me-4	cod	PPh_3

at δ −8.7 to −10.3. For the complex $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (C_9H_7 = indenyl), in which the presence of a $B{-}H{\rightharpoonup}Mo$ bond was confirmed by *X*-ray crystallography, the ^1H n.m.r. spectrum reveals a quartet signal at δ −7.98 [*J*(BH) 84 Hz].[9] In the ^1H n.m.r. spectrum of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_{11})]$ the corresponding resonance for the $B{-}H{\rightharpoonup}Mo$ group is at δ −9.45. The data for these two dimetal compounds compare well with those for the complexes (**4a**)—(**4d**). The presence of the two $B{-}H{\rightharpoonup}Mo$ linkages in these species was further confirmed by the appearance of two deshielded peaks in the $^{11}B\text{-}\{^1H\}$ n.m.r. spectra, the remaining boron nuclei giving rise to broad signals in the range δ *ca.* −3 to −20 p.p.m. (Table 3). In fully coupled ^{11}B spectra these $B{-}H{\rightharpoonup}Mo$ resonances become doublets, due to $^1H\text{-}^{11}B$ coupling (*ca.* 90 Hz).

The triply bridging alkylidyne ligands in the compounds (**4a**)—(**4c**) are revealed in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Table 2) by resonances at δ 311.5, (**4a**), 310.4, (**4b**), and 328.8 p.p.m., (**4c**). In the spectrum of $[Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ the μ_3-C signal is appreciably less deshielded at δ 257.0 p.p.m.[10] However, in the spectrum of $[NEt_4][MoFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\sigma'{:}\eta^5\text{-}C_2B_9H_7Me_2)(CO)_8]$ the μ_3-C resonance is at δ 314.0 p.p.m.[11] being comparable in chemical shift with the values found for (**4a**)—(**4c**). It is generally observed that if a carbaborane cage is present in a complex the alkylidyne carbon resonance is more deshielded than if a cyclopentadienyl group ligates one of the metal centres.

The data for compound (**4d**) are of special interest since they establish the structure shown, rather than one in which the C≡C bond in the precursor (**1d**) ligates the two molybdenum atoms. The resonances for $CC{\equiv}CBu^t$ nuclei are at δ 269.2 ($\mathit{C}C{\equiv}CBu^t$), 127.5 ($CC{\equiv}\mathit{C}Bu^t$), and 101.6 p.p.m. ($C\mathit{C}{\equiv}CBu^t$). These assignments are based on the $^{13}C\text{-}\{^1H\}$ n.m.r. shifts observed in the spectra of other trimetal compounds containing $\mu_3\text{-}CC{\equiv}CBu^t$ groups, derived from reactions between the reagent $[W({\equiv}CC{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ and low-valent metal fragments.[5c,8] Moreover, the resonance for the μ_3-C nucleus of (**4d**) is unambiguous since the signal shows $^{183}W\text{-}^{13}C$ coupling (112 Hz). The product (**4d**) is thus a species in which the C≡W bond of (**1d**) formally bridges a dimolybdenum fragment. In this respect the reaction is similar to that between $[W({\equiv}CC{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ which gives $[Mo_2W(\mu_3\text{-}CC{\equiv}CBu^t)(CO)_6(\eta\text{-}C_5H_5)_3]$, rather than that between $[W({\equiv}CC{\equiv}CBu^t)(CO)_2\{HB(pz)_3\}]$ and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ which yields $[Mo_2\{\mu\text{-}Bu^tC_2C{=}W(CO)_2[HB(pz)_3]\}(CO)_4(\eta\text{-}C_5H_5)_2]$.[5c,8] The latter species results from formal addition of a dimolybdenum fragment to the C≡C group of the precursor. That the reactivity pattern of compound (**1d**) is more similar to that of $[W({\equiv}CC{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ than $[W({\equiv}CC{\equiv}CBu^t)(CO)_2\{HB(pz)_3\}]$ is probably related to the fact that the $HB(pz)_3$ ligand (cone angle 184°) is more sterically demanding than $\eta^5\text{-}C_2B_9H_9Me_2$ (cone angle *ca.* 140°) or $\eta\text{-}C_5H_5$ (cone angle 100°).[12]

In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of compounds (**4a**), (**4c**), and (**4d**) there are nine CO resonances as expected. In the spectrum of (**4b**) there are eight peaks but the resonance at δ 217.4 p.p.m. corresponds in intensity to two CO groups. The signal in each spectrum at *ca.* 235 p.p.m. has a chemical shift indicative of a μ-CO ligand. In support of this conclusion, the i.r. spectra of (**4a**)—(**4d**) show a CO band at *ca.* 1830 cm^{-1}.

Since the two $B{-}H{\rightharpoonup}Mo$ linkages in the complexes (**4**) involve boron atoms in different environments in the pentagonal face of the cage, the CR′ (R′ = H or Me) fragments are non-equivalent. In agreement, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4a**) the two cage CMe moieties give rise to four resonances at δ 66.9 and 58.3 (*C*Me) and at 32.9 and 32.7 p.p.m. (C*Me*). The spectrum of compound (**4d**), which also has two CMe groups, shows a similar pattern, while the spectra of (**4b**) and (**4c**) each display two CH resonances.

The anions of the complexes (**4a**)—(**4d**) have structures closely related to that of the anion of the salt (**2a**).[6] As mentioned earlier, compound (**2a**) forms *via* the intermediacy of the species (**2b**). No evidence was obtained in the present work, however, for trimetal complexes of formulation $[MMo_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_{10}(\eta^5\text{-}C_2B_9H_9R'_2)]$ (M = Mo or W, R = C_6H_4Me-4 or $C{\equiv}CBu^t$, R′ = H or Me), structurally analogous to (**2b**), with the carbaborane ligand adopting a spectator role. Solutions of the complexes (**4a**)—(**4d**) did not react readily with CO under mild conditions (1 bar, 10^5 Pa), as does (**2a**).

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

Compound[b]	Colour	Yield (%)	$\nu_{\mathrm{max.}}(\mathrm{CO})^c$/cm^{-1}	Analysis(%)		
				C	H	N
(4a) $[\mathrm{NEt_4}][\mathrm{Mo_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)}]$	Brown	44	2 025m, 1 975vs, 1 942s, 1 870w(br), 1 821w(br)	33.9 (34.1)	4.5 (4.1)	1.6 (1.4)
(4b) $[\mathrm{NEt_4}][\mathrm{Mo_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_{11})}]$	Brown	45	2 026m, 1 981vs, 1 960s, 1 913m(br), 1 829w(br)	32.5 (32.6)	4.1 (3.9)	1.5 (1.4)
(4c) $[\mathrm{NEt_4}][\mathrm{Mo_3(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_{11})}]$	Brown	51	2 026m, 1 981vs, 1 955s, 1 938s, 1 925m(br), 1 864w(br), 1 822w(br)	34.5 (35.8)	4.4 (4.2)	1.8 (1.6)
(4d) $[\mathrm{NEt_4}][\mathrm{Mo_2W(\mu_3\text{-}CC{\equiv}CBu^t)(\mu\text{-}CO)(CO)_8\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)}]$	Brown	38	2 028m, 1 978vs, 1 931s, 1 836m	32.7 (33.2)	4.8 (4.4)	1.5 (1.4)
(4e) $[\mathrm{NEt_4}][\mathrm{Mo_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_7(PMe_3)\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)}]$	Brown	90	1 996m, 1 945vs, 1 910m, 1 894m, 1 826w, 1 768w	34.4 (34.8)	4.4 (4.8)	1.7 (1.3)
(4f) $[\mathrm{NEt_4}][\mathrm{Mo_2W(\mu_3\text{-}CC{\equiv}CBu^t)(\mu\text{-}CO)(CO)_7\text{-}(dppm)(\eta^5\text{-}C_2B_9H_9Me_2)}]$	Brown	34	1 975s, 1 935vs, 1 894s, 1 806m, 1 725m	46.3 (45.7)	4.9 (4.9)	1.3 (1.0)
(5a) $[\mathrm{WAu(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)}]$	Red	54	2 077vs, 1 937s	39.6 (40.3)	3.4 (4.3)	
(6a) $[\mathrm{WPtAu(\mu_3\text{-}CC{\equiv}CBu^t)(CO)_2(PPh_3)(PMe_2\text{-}Ph)_2(\eta^5\text{-}C_2B_9H_9Me_2)}]$	Green	68	1 905s, 1 814m	38.4 (39.6)	4.8 (4.3)	

[a] Calculated values are given in parentheses. [b] R = $\mathrm{C_6H_4Me}$-4. [c] Measured in $\mathrm{CH_2Cl_2}$, all complexes show broad weak $\nu_{\mathrm{max.}}(\mathrm{BH})$ *ca.* 2 560 cm^{-1}.

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

Compound	^{1}H (δ)	^{13}C[b] (δ)
(4a)	−10.3 to −8.7 (br, 2 H, B–H–Mo), 1.30 [t of t, NCH$_2$*Me*, 12 H, *J*(HH) 7, *J*(NH) 2], 2.24, 2.35, 2.44, (s × 3, 9 H, Me-4 and CMe), 3.13 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7], 7.22, 7.48 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 8]	311.5 (μ_3-C), 235.6 (μ-CO), 222.6, 220.8, 220.6, 220.3, 214.7, 213.2, 210.6, 209.4 (CO), 160.6 [C^1(C$_6$H$_4$)], 135.6, 128.4, 127.8 (C$_6$H$_4$), 66.9, 58.3 (*C*Me), 54.0 (N*C*H$_2$Me), 32.9, 32.7 (C*Me*), 21.3 (Me-4), 2.8 (NCH$_2$*Me*)
(4b)	−9.70 [q, 1 H, B–H–Mo, *J*(BH) 85], −9.24 [q, 1 H, B–H–Mo, *J*(BH) 92], 1.33 [t of t, 12 H, NCH$_2$*Me*, *J*(HH) 7, *J*(NH) 2], 2.48 (s, 3 H, Me-4), 3.16 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7], 3.38, 3.44 (s × 2, 2 H, CH), 7.27, 7.51 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 8]	310.4 (μ_3-C), 236.4 (μ-CO), 221.0, 217.8, 217.4,[c] 214.3, 213.6, 209.1, 208.7 (CO), 160.5 [C^1(C$_6$H$_4$)], 135.6, 128.4, 127.9 (C$_6$H$_4$), 53.0 (N*C*H$_2$Me), 40.7, 27.5 (CH), 21.3 (Me-4), 7.7 (NCH$_2$*Me*)
(4c)	−10.68 [q, 1 H, B–H–Mo, *J*(BH) 91], −9.92 [q, 1 H, B–H–Mo, *J*(BH) 90], 1.26 (br, 12 H, NCH$_2$*Me*), 2.37 (s, 3 H, Me-4), 3.11 (br, 8 H, NC*H*$_2$Me), 3.26 (s, 1 H, CH), 7.24, 7.46 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 8]	328.8 (μ_3-C), 236.5 (μ-CO), 227.6, 225.8, 221.1, 215.6, 213.9, 209.3, 208.8, 201.6 (CO), 158.0 [C^1(C$_6$H$_4$)], 135.7, 129.2, 128.0 (C$_6$H$_4$), 53.1 (N*C*H$_2$Me), 44.5, 30.4 (CH), 21.3 (Me-4), 7.8 (NCH$_2$*Me*)
(4d)	−9.58 [q, 1 H, B–H–Mo, *J*(BH) 92], −9.48 [q, 1 H, B–H–Mo, *J*(BH) 92], 1.31 [t of t, 12 H, NCH$_2$*Me*, *J*(HH) 7, *J*(NH) 2], 1.43 (s, 9 H, Bu^t), 2.31, 2.40 (s × 2, 6 H, CMe), 3.17 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7]	269.2 [μ_3-C, *J*(WC) 112], 232.2 (μ-CO), 222.7, 218.7, 218.6, 218.0, 217.6, 212.7, 211.8, 208.1 (CO), 127.5 (C≡*C*Bu^t), 101.6 (*C*≡CBu^t), 67.8, 59.2 (*C*Me), 53.2 (N*C*H$_2$Me), 33.5, 33.0 (C*Me*), 32.0 (C*Me*$_3$), 30.2 (*C*Me$_3$), 7.9 (NCH$_2$*Me*)
(4e)[d]	−10.3 to −8.7 (br, 2 H, B–H–Mo), 1.22 [t of t, 12 H, NCH$_2$*Me*, *J*(HH) 7, *J*(NH) 2], 1.42, 1.49* [d × 2, 9 H, PMe, *J*(PH) 9], 2.18, 2.26, 2.35 (s × 3, 9 H, Me-4 and CMe), 3.05 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7], 7.11, 7.35 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 8]	310.4 (μ_3-C), 253.9, 253.7*, 226.1, 225.9, 225.7, 225.2, 224.7, 223.8, 223.6, 222.2, 221.9, 218.3, 218.2, 206.7* [d, MoCO, *J* (PC) 27], 203.8 [d, MoCO, *J*(PC) 22], 162.0 [C^1(C$_6$H$_4$)], 133.8, 128.9, 127.4 (C$_6$H$_4$), 66.3, 57.3 (*C*Me), 33.1, 32.7*, 32.5 (C*Me*), 21.2 (Me-4), 19.1, 18.9* [d × 2, MeP, *J*(PC) 28], 7.8 (CH$_2$*Me*)
(4f)[e]	−8.50 (br, 1 H, B–H–Mo), −6.78 [q, 1 H, B–H–Mo, *J*(BH) 86], 1.24 [t of t, 12 H, NCH$_2$*Me*, *J*(HH) 7, *J*(NH) 2], 1.61 (s, 9 H, Bu^t), 2.09, 2.24 (s × 2, 6 H, CMe), 3.12 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7], 4.01 (m, 2 H, PCH$_2$P), 6.58—8.19 (m, 20 H, Ph)	270.2 (μ_3-C), 259.0 (μ-CO), 228.0, 227.6,[f] 222.5, 222.4, 221.0 (CO), 137.4—127.8 (Ph), 124.1 (C≡*C*Bu^t), 103.4 (*C*≡CBu^t), 65.7, 57.5 (*C*Me), 53.3 (*C*H$_2$Me), 48.7 [d of d, PCH$_2$P, *J*(PC) 22 and 17], 33.2 (C*Me*), 32.7 (C*Me* and C*Me*$_3$), 30.2 (*C*Me$_3$), 7.7 (NCH$_2$*Me*)
(5a)	1.34 (s, 9 H, Bu^t), 2.02 (s, 6 H, CMe), 7.0—7.7 (m, 15 H, Ph)	250.7 [d, μ-C, *J*(PC) 30], 218.1 [d, CO, *J*(PC) 19], 134.4—127.3 (Ph), 104.6 (C≡*C*Bu^t), 98.7 (*C*≡CBu^t), 61.8 (*C*Me), 35.1 (C*Me*), 30.2 (C*Me*$_3$), 29.5 (*C*Me$_3$)
(6a)	1.13 (s, 9 H, Bu^t), 1.74—1.86 (m, 12 H, MeP), 2.24 (s, 6 H, CMe), 7.02—7.58 (m, 25 H, Ph)	252.2 [d of d, μ_3-C, *J*(PC) 60 and 20, *J*(PtC) 510], 229.8 [d, CO, *J*(PC) 6, *J*(PtC) 31], 222.5 (CO), 138.6—127.5 (Ph), 130.3 (C≡*C*Bu^t), 100.9 [*C*≡CBu^t, *J*(PtC) 56], 65.0, 64.9 (*C*Me), 30.4, 29.6 (C*Me*), 29.3 (C*Me*$_3$), 29.0 (*C*Me$_3$), 16.3 [d, MeP, *J*(PC) 27], 15.3 [d, MeP, *J*(PC) 30], 14.4 [d, MeP, *J*(PC) 35], 13.9 [d, MeP, *J*(PC) 21]

[a] Chemical shifts are in p.p.m., coupling constants in Hz, measurements in $\mathrm{CD_2Cl_2}$ at ambient temperatures. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $\mathrm{SiMe_4}$. [c] Peak corresponds in intensity to two CO groups. [d] Peaks asterisked are due to minor isomer (see text). [e] In some spectra peaks due to a minor isomer (*ca.* 5%) were observed. [f] Peak corresponds in intensity to three CO groups.

In a further attempt to lift the B–H⇀Mo interactions in these species, compound **(4a)** was treated with 2 equivalents of $\mathrm{PMe_3}$. This reaction resulted in displacement of one of the carbonyl groups ligating a molybdenum atom by a $\mathrm{PMe_3}$ group, thereby affording the compound $[\mathrm{NEt_4}][\mathrm{Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)}]$. Several

Table 3. Boron-11 and phosphorus-31 n.m.r. data[a] for the complexes

Compound	$^{11}B^{b}$ (δ)	$^{31}P^{c}$ (δ)
(4a)	23.9 [d, B–H–Mo, J(BH) 91], 18.1 [d, B–H–Mo, J(BH) 98], −4.3, −9.2, −11.0, −11.8 (br, BH)	
(4b)	23.0 [d, B–H–Mo, J(BH) 85], 13.0 [d, B–H–Mo, J(BH) 92], −6.1, −9.6, −11.9, −13.3, −18.4, −21.0 (br, BH)	
(4c)	25.2 [d, B–H–Mo, J(BH) 91], 13.1 [d, B–H–Mo, J(BH) 90], −6.3, −8.6, −12.3, −17.8, −21.2 (br, BH)	
(4d)	23.6 [d, B–H–Mo, J(BH) 92], 14.1 [d, B–H–Mo, J(BH) 92], −2.0 to −3.5 (br, BH)	
(4e)[d]	26.5* (B–H–Mo), 24.2 [d, B–H–Mo, J(BH) 85], 19.4 [d, B–H–Mo, J(BH) 92], −4.8 to −19.0 (vbr, BH)	−4.08, −4.62*
(4f)	26.4 [d, B–H–Mo, J(BH) 86], 19.0 (br, B–H–Mo), −5.4, −7.8, −9.2, −14.0 (br, BH)	14.9 [d, J(PP) 32], −14.6 [d, J(PP) 32]
(5a)	−4.0, −7.4, −9.2, −11.6 (br, BH)	53.1 (s)
(6a)[e]	−2.6, −8.6, −11.7 (br, BH)	51.6 (s, br, PAu), 1.5 [d, PPt, J(PP) 8, J(PtP) 3 876], −10.1 [d of d, PPt, J(PP) 8 and 4, J(PtP) 3 093]

[a] Chemical shifts in p.p.m., coupling constants in Hz, measurements in CD_2Cl_2 at ambient temperatures. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external); J(BH) values measured from fully coupled ^{11}B spectra. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [d] Peaks due to minor isomer are asterisked (see text). [e] $^{195}Pt\text{-}\{^1H\}$ N.m.r.: δ 351.9 p.p.m. [d of d, J(PPt) 3 096 and 3 873, J(WPt) 226 Hz], chemical shift to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz.

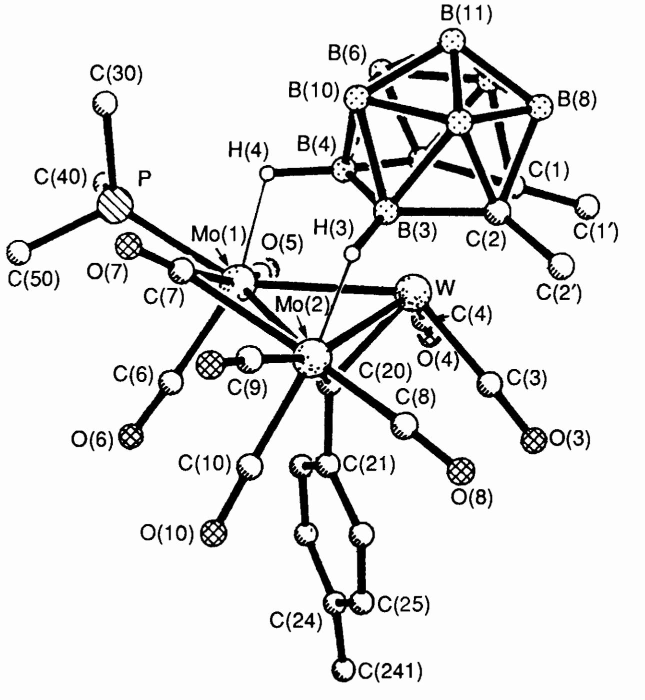


Figure. The structure of the complex anion of the salt $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(4e)**

isomers of this formulation are possible depending on which CO group in the precursor **(4a)** is substituted by the PMe_3 ligand. At the individual Mo atoms the terminal CO sites are not equivalent. Moreover, the two $Mo(CO)_3$ groups are not symmetrically related since one Mo atom is ligated by an α BH group in the face of the cage, and the other by a β BH group. As discussed below, n.m.r. data revealed that two isomers of $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ are formed, in a ratio of *ca.* 85:15 based on relative peak intensities in the $^{31}P\text{-}\{^1H\}$ spectrum. Probably the most likely form of isomerism corresponds to PMe_3 substitution at one or other of the non-equivalent molybdenum centres, rather than CO displacement at alternative sites at one metal centre.

It was possible to grow single crystals of the isomer assumed to be the major species, and carry out an *X*-ray diffraction study. The results are summarised in Table 4, and the structure of the anion is shown in the Figure. It is evident that this PMe_3-substituted product **(4e)** is the isomer with a $Mo(CO)_2(PMe_3)$ group linked to a β BH fragment in the $\overline{\mathrm{CCB}B\mathrm{B}}$ face of the cage. Moreover the PMe_3 ligand occupies a site on Mo(1) which is cisoid to H(4). Although not located in the electron-density difference map, the atoms H(3) and H(4) are in sites predicted using the steric-potential-energy-minimisation technique.[13]

The core of the anion is formed by the Mo_2W triangle [Mo–Mo 2.968(3), W–Mo(1) 2.881(3), W–Mo(2) 2.867(3) Å]. The Mo–Mo separation is within the range (*ca.* 2.95—3.10 Å) generally found in complexes in which molybdenum–molybdenum single bonds are spanned by organic groups.[14] In complex **(3b)**, which has structure **(B)**, the Mo–Mo bonds [2.802(1) Å] are shorter, but this species is electronically unsaturated.[7a] The Mo–W distances in **(4e)** may be compared with those in $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$[2.657(2) Å][9] and in **(3a)** [2.938(1) Å] which has structure **(A)**.[7b]

The *p*-tolylmethylidyne group in **(4e)** caps the metal triangle [Mo(1)–C(20) 2.24(2), Mo(2)–C(20) 2.29(2), W–C(20) 2.01(2) Å], but lies somewhat closer to the tungsten. The Mo(1)–Mo(2) bond is asymmetrically bridged by a carbonyl group [Mo(1)–C(7)–O(7) 156(2), Mo(2)–C(7)–O(7) 124(2)°; Mo(1)–C(7) 2.05(3), Mo(2)–C(7) 2.52(2) Å]. In agreement, the i.r. spectrum displays a weak absorption at 1768 cm^{-1}. The remaining carbonyl ligands in **(4e)** are essentially terminally bound to their respective metal centres [M(Mo or W)–C–O 177 ± 1°] with the possible exception of C(10)–O(10) [Mo(2)–C(10)–O(10) 173°].

Having established the structure of complex **(4e)**, the n.m.r. data (Tables 2 and 3) are readily interpretable. However, as mentioned above, there was evidence for the presence of a minor isomer (*ca.* 15%). Thus the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed two singlet resonances at δ −4.08 and −4.62 p.p.m., the former being more intense. The absence of $^{183}W\text{–}^{31}P$ coupling on these peaks confirms that they are due to $MoPMe_3$ groups rather than a $WPMe_3$ fragment.

The reaction between dppm ($Ph_2PCH_2PPh_2$) and **(4d)** was also investigated, in an attempt to form a complex in which the dppm group bridges two metal centres. In practice, the complex $[NEt_4][Mo_2W(\mu_3\text{-}CC{\equiv}CBu^t)(\mu\text{-}CO)(CO)_7(dppm)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(4f)** was obtained in which the diphenylphos-

Table 4. Selected internuclear distances (Å) and angles (°) for the complex $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(4e)**

W–Mo(1)	2.881(3)	W–Mo(2)	2.867(3)	W–C(1)	2.36(2)	W–C(2)	2.38(2)
W–B(3)	2.30(2)	W–B(4)	2.31(2)	W–B(5)	2.34(3)	W–C(3)	1.96(2)
W–C(4)	2.02(2)	W–C(20)	2.01(2)	Mo(1)–Mo(2)	2.968(3)	Mo(1)–P(1)	2.489(7)
Mo(1)–B(4)	2.58(2)	Mo(1)–H(4)	1.85[a]	Mo(1)–C(5)	2.00(2)	Mo(1)–C(6)	2.01(2)
Mo(1)–C(7)	2.05(3)	Mo(1)–C(20)	2.24(2)	Mo(2)–B(3)	2.55(2)	Mo(2)–H(3)	1.85[a]
Mo(2)–C(7)	2.52(2)	Mo(2)–C(8)	1.93(2)	Mo(2)–C(9)	1.95(2)	Mo(2)–C(10)	1.94(3)
Mo(2)–C(20)	2.29(2)	C(1)–C(2)	1.62(3)	C(1)–B(5)	1.75(3)	C(2)–B(3)	1.76(3)
B(3)–B(4)	1.84(4)	B(4)–B(5)	1.68(4)	C–O[b]	1.14(3)		
Mo(1)–W–Mo(2)	62.2(1)	Mo(1)–W–C(3)	133.4(6)	Mo(2)–W–C(3)	90.0(8)	Mo(1)–W–C(4)	92.1(6)
Mo(2)–W–C(4)	135.5(6)	C(3)–W–C(4)	83(1)	Mo(1)–W–C(20)	50.8(5)	Mo(2)–W–C(20)	52.6(5)
C(3)–W–C(20)	82.6(8)	C(4)–W–C(20)	82.9(8)	W–Mo(1)–Mo(2)	58.7(1)	W–Mo(1)–P	151.3(2)
Mo(2)–Mo(1)–P	135.4(2)	W–Mo(1)–H(4)	77.9(1)	Mo(2)–Mo(1)–H(4)	101.2(1)	P–Mo(1)–H(4)	74.6(2)
W–Mo(1)–C(5)	88.1(6)	Mo(2)–Mo(1)–C(5)	141.4(7)	P–Mo(1)–C(5)	83.2(7)	H(4)–Mo(1)–C(5)	89.1(6)
W–Mo(1)–C(6)	121.1(7)	Mo(2)–Mo(1)–C(6)	89.4(7)	P–Mo(1)–C(6)	86.7(7)	H(4)–Mo(1)–C(6)	161.0(7)
C(5)–Mo(1)–C(6)	92.4(9)	W–Mo(1)–C(7)	107.8(6)	Mo(2)–Mo(1)–C(7)	56.8(7)	P–Mo(1)–C(7)	78.6(7)
H(4)–Mo(1)–C(7)	85.8(6)	C(5)–Mo(1)–C(7)	161.8(9)	C(6)–Mo(1)–C(7)	86.9(9)	W–Mo(1)–C(20)	44.1(5)
Mo(2)–Mo(1)–C(20)	49.9(5)	P–Mo(1)–C(20)	163.3(5)	C(5)–Mo(1)–C(20)	93.1(8)	C(6)–Mo(1)–C(20)	77.1(8)
C(7)–Mo(1)–C(20)	104.4(8)	W–Mo(2)–Mo(1)	59.1(1)	W–Mo(2)–H(3)	78.4(1)	Mo(1)–Mo(2)–H(3)	96.3(1)
W–Mo(2)–C(7)	96.1(6)	Mo(1)–Mo(2)–C(7)	42.8(6)	H(3)–Mo(2)–C(7)	83.5(5)	W–Mo(2)–C(8)	96.1(6)
Mo(1)–Mo(2)–C(8)	151.3(7)	H(3)–Mo(2)–C(8)	91.9(6)	C(7)–Mo(2)–C(8)	165.9(9)	W–Mo(2)–C(9)	156.4(6)
Mo(1)–Mo(2)–C(9)	121.9(7)	H(3)–Mo(2)–C(9)	78.1(6)	C(7)–Mo(2)–C(9)	79.3(9)	C(8)–Mo(2)–C(9)	86.7(9)
W–Mo(2)–C(10)	121.9(7)	Mo(1)–Mo(2)–C(10)	94.6(7)	H(3)–Mo(2)–C(10)	159.7(7)	C(7)–Mo(2)–C(10)	93.1(9)
C(8)–Mo(2)–C(10)	86(1)	C(9)–Mo(2)–C(10)	81.7(9)	W–Mo(2)–C(20)	44.2(5)	Mo(1)–Mo(2)–C(20)	48.4(5)
C(7)–Mo(2)–C(20)	89.5(7)	C(8)–Mo(2)–C(20)	104.3(8)	C(9)–Mo(2)–C(20)	156.9(8)	C(10)–Mo(2)–C(20)	78.8(8)
W–C(3)–O(3)	176(2)	W–C(4)–O(4)	177(2)	Mo(1)–C(5)–O(5)	177(2)	Mo(1)–C(6)–O(6)	178(2)
Mo(1)–C(7)–Mo(2)	80.4(8)	Mo(1)–C(7)–O(7)	156(2)	Mo(2)–C(7)–O(7)	124(2)	Mo(2)–C(8)–O(8)	177(2)
Mo(2)–C(9)–O(9)	177(2)	Mo(2)–C(10)–O(10)	173(2)	W–C(20)–Mo(1)	85.1(7)	W–C(20)–Mo(2)	83.2(7)
Mo(1)–C(20)–Mo(2)	81.7(6)	W–C(20)–C(21)	134(1)	Mo–C(20)–C(21)	128(1)	Mo(2)–C(20)–C(21)	127(1)

[a] Parameter fixed, see text. [b] Average distance.

phinomethane molecule functions as a monodentate ligand. Data characterising **(4f)** are given in Tables 1—3.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed two resonances, both doublets [*J*(PP) 32 Hz], at δ −14.6 and 14.9 p.p.m. Since for the free ligand the $^{31}P\text{-}\{^1H\}$ resonance is at δ −22.0 p.p.m.,[15] it is probable that the signal at −14.6 p.p.m. is due to the un-coordinated PPh_2 moiety and that at 14.9 p.p.m. to the $MoPPh_2$ group. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of **(4f)** is in agreement with the structure proposed. The μ_3-C resonance is seen at 270.2 p.p.m., and a signal at 259.0 p.p.m. may be ascribed to the μ-CO ligand. The latter peak is more deshielded than the corresponding resonance of the precursor **(4d)** (δ 232.2 p.p.m.). This would be expected if in **(4f)** the ligand were more fully bridging. In agreement, in the i.r. spectrum of **(4f)** there is a band at 1 725 cm^{-1}, whereas the lowest-frequency CO absorption in the spectrum of **(4d)** is at 1 836 cm^{-1}. The terminally bound CO groups of **(4f)** display resonances in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum which overlap, so that only five signals are seen. However, as expected, the *C*Me groups give rise to two peaks at δ 65.7 and 57.5 p.p.m. The C*Me* groups should also give rise to two signals. One is clearly observed at δ 33.2 p.p.m., but the other peak (32.7 p.p.m.) overlaps with that for methyl groups of the CMe_3 moiety.

In the ^1H n.m.r. spectrum of compound **(4f)** there are the expected two resonances for the exopolyhedral B–H⇀Mo bonds. That at δ −6.78 is a quartet [*J*(BH) 86 Hz], but that seen at −8.50 is broad, probably as a result of $^1H\text{-}^{31}P$ coupling. The cage CMe groups give rise to two resonances (δ 2.09 and 2.24), in agreement with asymmetry of the complex.

Attempts to protonate the complexes **(4)** with $HBF_4{\cdot}Et_2O$ did not yield tractable products. Monitoring the protonations by i.r. spectroscopy showed that initially new complexes were formed, but attempts to isolate these species led to decomposition with formation of $[Mo(CO)_6]$. However, an interesting reaction was observed on treatment of **(4d)** with $[Au(PPh_3)]^+$. The latter is isolobal with the H^+, and can be generated *in situ* from $[AuCl(PPh_3)]$ and $TlPF_6$ in thf. The dimetal complex $[WAu(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(5a)** was formed, together with $[Mo(CO)_6]$. Release of molybdenum hexacarbonyl in this reaction implies that the B–H⇀Mo bonds in **(4d)**, and probably in the other complexes also, are easily broken. This may explain our inability to isolate stable products on protonation.

Compound **(5a)** was also prepared by a more logical route. Treatment of **(1d)** in thf with $[AuCl(PPh_3)]$ and $TlPF_6$ affords **(5a)** in 50—60% yield. Complex **(5a)** is an analogue of the previously prepared species $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(5b)**,[16] and the two compounds have similar spectroscopic properties. In the i.r. spectrum of **(5a)** the CO absorptions are seen at 2 007 and 1 937 cm^{-1}, while for **(5b)** these peaks occur at 2 002 and 1 933 cm^{-1}. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of **(5a)** the resonance for the μ-C nucleus is a doublet at δ 250.7 p.p.m. [*J*(PC) 30 Hz]. For **(5b)** the corresponding data are δ 292.9 [*J*(PC) 28 Hz]. In the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of **(5a)** the resonance for the PPh_3 group is at δ 53.1 p.p.m., to be compared with that 56.1 p.p.m. in the spectrum of **(5b)**.

Treatment of complex **(5a)** in thf with $[Pt(nb)(PMe_2Ph)_2]$ (nb = bicyclo[2.2.1]heptene), prepared *in situ* from $[Pt(nb)_3]$ and PMe_2Ph, afforded the trimetal complex $[WPtAu(\mu_3\text{-}CC{\equiv}CBu^t)(CO)_2(PPh_3)(PMe_2Ph)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(6a)**. This synthesis was prompted by the earlier preparation of the related complexes $[WPtAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2L_2(L')(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**6b**; L = L′ = PMe_2Ph) and (**6c**; L_2 = cod = cycloocta-1,5-diene, L′ = PPh_3). The species **(6b)** and **(6c)** were prepared by different routes. The former by treatment of the cluster complex $[W_2PtAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ with PMe_2Ph,[2b] and the latter by treating the salt $[P(CH_2Ph)Ph_3][WPt(\mu\text{-}CC_6H_4\text{-}$

$\mathrm{Me\text{-}4)(CO)_2(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]}$ with $\mathrm{[AuCl(PPh_3)]}$ in thf, in the presence of $\mathrm{TlPF_6}$.[17]

Data for compound (**6a**) are given in Tables 1—3. In the i.r. spectrum there are two CO bands at 1 905 and 1 814 cm^{-1}. Corresponding bands appear in the spectra of (**6b**) (1 893 and 1 814 cm^{-1}) and (**6c**) (1 948 and 1 795 cm^{-1}). The absorption at lowest frequency in each spectrum can be attributed to a semi-bridging carbonyl group. In the $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**6a**) the diagnostic signal for the μ_3-C group is seen at δ 252.2 p.p.m. as a doublet of doublets [J(PC) 60 and 20 Hz] with ^{195}Pt satellite peaks [J(PtC) 510 Hz]. In the spectrum of (**6b**) the resonance is at δ 290.7 p.p.m. [J(PC) 56 and 20 Hz],[2b] and in (**6c**) it is at 290.2 p.p.m. [J(PC) 15, J(PtC) 591 Hz]. The more shielded signal observed with (**6a**) is consistent with the presence of the $\mathrm{C{\equiv}CBu^t}$ group.[5c,8] There are two CO resonances in the spectrum of (**6a**), as expected. These occur at 229.8 and 222.5 p.p.m., and the former signal is a doublet [J(PC) 6 Hz] with ^{195}Pt satellite peaks [J(PtC) 31]. These couplings are in accord with the presence of a weakly semi-bridging CO ligand, as mentioned above. The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**6a**) (Table 3) is also in agreement with the structure proposed. The broad singlet at δ 51.6 p.p.m. can be ascribed to the $\mathrm{AuPPh_3}$ group. The signal is broad due to both quadrupolar effects of the Au atom and to unresolved $^{31}\mathrm{P}$–$^{31}\mathrm{P}$ coupling with the transoid $\mathrm{PMe_2Ph}$ group of the $\mathrm{Pt(PMe_2Ph)_2}$ moiety. The latter gives rise to two signals, a doublet at 1.5 p.p.m. [J(PP) 8, J(PtP) 3 876 Hz] and a doublet of doublets at −10.1 p.p.m. [J(PP) 8 and 4, J(PtP) 3 093 Hz]. The appearance of $^{195}\mathrm{Pt}$–$^{31}\mathrm{P}$ satellite peaks on these signals confirms that they are due to the $\mathrm{Pt(PMe_2Ph)_2}$ fragment. In the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**6b**) the resonances for the $\mathrm{Pt(PMe_2Ph)_2}$ moiety are at δ −3.3 [J(PPt) 4 131] and −12.2 p.p.m. [J(PPt) 2 855 Hz].[2b]

The new compounds reported herein further demonstrate the versatile role that can be played by the $\eta^5\text{-}\mathrm{C_2B_9H_9R'_2}$ (R′ = H or Me) ligands in complexes containing heteronuclear metal–metal bonds. Moreover, the compounds (**4a**)—(**4d**), prepared using the reagents (**1**), are structurally very different from the products (**3**) isolated employing the species $\mathrm{[M({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]}$ (M = W, R = $\mathrm{C_6H_4Me\text{-}4}$; M = Mo, R = $\mathrm{C_6H_3Me_2\text{-}2,6}$) as precursors.

Experimental

The experimental procedures and the instrumentation used to characterise the new compounds have been described previously.[1,2] The reagents $\mathrm{[Mo(CO)_3(NCMe)_3]}$,[18] $\mathrm{[AuCl(PPh_3)]}$,[19] and the salts (**1**)[1,16,17] were prepared as described earlier. The compound $\mathrm{[Pt(nb)(PMe_2Ph)_2]}$ was prepared *in situ* by adding 2 equivalents of $\mathrm{PMe_2Ph}$ to $\mathrm{[Pt(nb)_3]}$.[20] Light petroleum refers to that fraction of b.p. 40—60 °C. Alumina (BDH aluminium oxide, Brockman Activity II) or Kieselgel-60 were used for chromatography columns. Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Trimetal Complexes $\mathrm{[NEt_4][Mo_2M(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_9R'_2)]}$ (M = W, R = $\mathrm{C_6H_4Me\text{-}4}$, R′ = H *or* Me; R = $\mathrm{C{\equiv}CBu^t}$, R′ = Me; M = Mo, R = $\mathrm{C_6H_4\text{-}Me\text{-}4}$, R′ = H).—(*a*) Compound (**1a**) (0.63 g, 0.99 mmol) in thf (25 cm^3) was treated with $\mathrm{[Mo(CO)_3(NCMe)_3]}$ (1.0 g, 3.7 mmol) in excess, and the mixture was stirred for 1 h. Solvent was removed *in vacuo*, the residue was dissolved in $\mathrm{CH_2Cl_2}$ (*ca.* 10 cm^3), and the solution was chromatographed on Kieselgel (2 × 15 cm column) at −20 °C. Elution with $\mathrm{CH_2Cl_2}$ removed a brown fraction. Solvent was removed *in vacuo* to afford brown *microcrystals* of $\mathrm{[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]}$ (**4a**) (0.45 g), recrystallised from $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$ (*ca.* 10 cm^3, 1:10) at ambient temperatures.

(*b*) In a similar experiment, compound (**1b**) (0.61 g, 1.01 mmol) and $\mathrm{[Mo(CO)_3(NCMe)_3]}$ (1.0 g, 3.7 mmol) in thf (25 cm^3) yielded brown *microcrystals* of $\mathrm{[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_{11})]}$ (**4b**) (0.45 g).

(*c*) Brown *microcrystals* of the salt $\mathrm{[NEt_4][Mo_3(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_2B_9H_{11})]}$ (**4c**) (0.48 g) were obtained by the method employed to prepare compound (**4a**), using the reagents (**1c**) (0.52 g, 1.00 mmol) and $\mathrm{[Mo(CO)_3(NCMe)_3]}$ (1.0 g, 3.7 mmol) in thf (25 cm^3).

(*d*) Similarly, the compounds (**1d**) (0.62 g, 0.99 mmol) and $\mathrm{[Mo(CO)_3(NCMe)_3]}$ (1.0 g, 3.7 mmol) afforded brown *microcrystals* of $\mathrm{[NEt_4][Mo_2W(\mu_3\text{-}CC{\equiv}CBu^t)(\mu\text{-}CO)(CO)_8\text{-}(\eta^5\text{-}C_2B_9H_9Me_2)]}$ (**4d**) (0.38 g).

Reactions with Phosphines.—(*a*) Compound (**4a**) (0.51 g, 0.50 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) was treated with $\mathrm{PMe_3}$ (1.0 mmol) in excess, and the reaction mixture was stirred for 24 h. The volume of solvent was reduced *in vacuo* to *ca.* 5 cm^3, and the solution was chromatographed on alumina (2 × 15 cm column). Elution with $\mathrm{CH_2Cl_2}$ gave a dark brown eluate. Solvent was removed *in vacuo*, and the residue was crystallised from $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$ (10 cm^3, 1:10) to yield brown *microcrystals* of $\mathrm{[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]}$ (**4e**) (0.48 g).

(*b*) In a similar experiment, compound (**4d**) (0.50 g, 0.49 mmol) and dppm (0.21 g, 0.55 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) afforded brown *microcrystals* of $\mathrm{[NEt_4][Mo_2W(\mu_3\text{-}CC{\equiv}CBu^t)\text{-}(\mu\text{-}CO)(CO)_7(dppm)(\eta^5\text{-}C_2B_9H_9Me_2)]}$ (**4f**) (0.23 g).

Reactions with $\mathrm{[AuCl(PPh_3)]}$.—(*a*) Compound (**4d**) (0.51 g, 0.50 mmol) in thf (*ca.* 20 cm^3) was treated with $\mathrm{[AuCl(PPh_3)]}$ (0.25 g, 0.51 mmol), followed by $\mathrm{TlPF_6}$ (0.18 g, 0.52 mmol). The mixture was stirred for 1 h, after which solvent was removed *in vacuo*. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (10 cm^3) and chromatographed on alumina (2 × 15 cm column) at −20 °C. Elution with $\mathrm{CH_2Cl_2}$–light petroleum (1:2) removed substantial amounts of $\mathrm{[Mo(CO)_6]}$, identified by i.r. spectroscopy. Elution with $\mathrm{CH_2Cl_2}$–light petroleum (2:1) removed a red band. Solvent was removed *in vacuo*, the residue was dissolved in the minimum of $\mathrm{CH_2Cl_2}$ (*ca.* 0.5 cm^3), and light petroleum (*ca.* 10 cm^3) was added. Cooling the solution to *ca.* −78 °C and removal of supernatant liquid with a syringe gave red *microcrystals* of $\mathrm{[WAu(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]}$ (**5a**) (0.08 g).

(*b*) In a similar manner, the salt (**1d**) (0.31 g, 0.50 mmol) in thf (10 cm^3) was treated with $\mathrm{[AuCl(PPh_3)]}$ (0.25 g, 0.51 mmol) and $\mathrm{TlPF_6}$ (0.18 g, 0.52 mmol) yielding red *microcrystals* of (**5a**) (0.25 g).

Synthesis of the Trimetal Complex $\mathrm{[WPtAu(\mu_3\text{-}CC{\equiv}CBu^t)(CO)_2(PPh_3)(PMe_2Ph)_2(\eta^5\text{-}C_2B_9H_9Me_2)]}$.—The complex $\mathrm{[Pt(nb)_3]}$ (0.12 g, 0.25 mmol) was dissolved in thf (10 cm^3) and treated with $\mathrm{PMe_2Ph}$ (2.5 cm^3 of a 0.20 mol dm^{-3} solution in thf, 0.50 mmol) to prepare $\mathrm{[Pt(nb)(PMe_2Ph)_2]}$ *in situ.* This reagent was then treated with a thf (*ca.* 10 cm^3) solution of compound (**5a**) (0.23 g, 0.25 mmol), and the mixture was stirred for 1 h. Solvent was removed *in vacuo*, the residue dissolved in $\mathrm{CH_2Cl_2}$ (*ca.* 5 cm^3), and the resulting solution chromatographed on alumina (2 × 15 cm column). Elution with $\mathrm{CH_2Cl_2}$–light petroleum (1:1) gradually increasing to pure $\mathrm{CH_2Cl_2}$ afforded a green eluate. Solvent was removed *in vacuo*, the product was dissolved in $\mathrm{CH_2Cl_2}$ (*ca.* 2 cm^3) and light petroleum (*ca.* 15 cm^3) added. Cooling to −20 °C gave green *microcrystals* of $\mathrm{[WPtAu(\mu_3\text{-}CC{\equiv}CBu^t)(CO)_2(PPh_3)\text{-}(PMe_2Ph)_2(\eta^5\text{-}C_2B_9H_9Me_2)]}$ (**6a**) (0.24 g) after removal of supernatant liquid with a syringe.

Crystal Structure Determination.—Crystals of compound (**4e**) grow as black prisms by diffusion of light petroleum into a

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

Atom	x	y	z
W	253(1)	8 184(1)	765(1)
Mo(1)	2 100(1)	6 984(1)	1 127(1)
Mo(2)	730(2)	8 078(1)	1 896(1)
P	3 022(5)	5 507(4)	1 148(3)
C(1)	−1 591(17)	7 904(15)	305(9)
C(1′)	−1 914(21)	8 566(15)	−115(10)
C(2)	−1 865(17)	8 017(14)	937(9)
C(2′)	−2 393(18)	8 819(17)	1 149(10)
B(3)	−910(18)	7 340(16)	1 325(11)
B(4)	−108(21)	6 705(16)	814(12)
B(5)	−511(20)	7 087(17)	208(11)
B(6)	−1 121(21)	6 103(18)	434(12)
B(7)	−2 103(21)	6 850(22)	114(14)
B(8)	−2 965(24)	7 420(23)	573(12)
B(9)	−2 511(22)	7 077(20)	1 198(13)
B(10)	−1 399(21)	6 245(16)	1 155(13)
B(11)	−2 599(21)	6 343(19)	671(14)
C(3)	60(18)	9 445(16)	825(11)
O(3)	−63(14)	10 187(12)	894(9)
C(4)	1 227(18)	8 512(16)	112(10)
O(4)	1 766(13)	8 732(13)	−236(7)
C(5)	2 784(20)	7 008(15)	386(9)
O(5)	3 205(19)	7 002(12)	−27(7)
C(6)	3 670(22)	7 411(16)	1 454(9)
O(6)	4 570(12)	7 622(13)	1 639(8)
C(7)	1 638(18)	6 575(16)	1 879(10)
O(7)	1 575(19)	6 091(13)	2 225(9)
C(8)	−93(17)	9 143(15)	2 080(9)
O(8)	−542(13)	9 804(11)	2 188(7)
C(9)	457(19)	7 713(15)	2 634(10)
O(9)	329(17)	7 539(14)	3 069(8)
C(10)	2 177(22)	8 587(18)	2 218(9)
O(10)	2 974(13)	8 909(12)	2 459(7)
C(20)	1 835(17)	8 429(12)	1 149(7)
C(21)	2 803(16)	9 147(15)	1 103(8)
C(22)	3 762(16)	9 033(13)	752(8)
C(23)	4 589(17)	9 709(15)	676(8)
C(24)	4 509(19)	10 506(18)	943(10)
C(25)	3 525(17)	10 579(15)	1 287(9)
C(26)	2 667(22)	9 942(16)	1 362(11)
C(241)	5 354(22)	11 235(18)	830(12)
C(30)	1 946(20)	4 627(14)	1 241(10)
C(40)	3 851(22)	5 144(17)	565(11)
C(50)	4 143(25)	5 316(16)	1 669(12)
N	−1 366(18)	2 963(13)	1 853(8)
C(61)	−114(46)	2 629(35)	1 983(20)
C(62)	424(37)	2 129(28)	1 569(16)
C(63)	−2 171(30)	2 164(20)	1 751(13)
C(64)	−2 374(29)	1 525(20)	2 183(13)
C(65)	−1 488(32)	3 547(24)	1 332(14)
C(66)	−2 594(35)	3 907(27)	1 277(17)
C(67)	−1 835(32)	3 390(22)	2 329(14)
C(68)	−1 246(26)	4 253(19)	2 445(12)

CH_2Cl_2 solution of the complex at room temperature. That chosen for study had dimensions *ca.* 0.50 × 0.20 × 0.20 mm, and was sealed in a Lindemann tube under nitrogen. Diffracted intensities were measured (θ—2θ scans) at 298 K in the range $2.9 \leqslant 2\theta \leqslant 50°$ on a Nicolet R3m/V four-circle diffractometer. Of 7 449 unique reflections, 3 716 had $F \geqslant 6\sigma(F)$, and only these were used in the solution and refinement of the structure, after corrections for Lorentz, polarisation and *X*-ray absorption effects. The latter correction was based on a semiempirical method using azimuthal scan data.[21]

Crystal data. $C_{31}H_{51}B_9Mo_2NO_8PW$, $M = 1\,069.7$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.975(6)$, $b = 15.385(7)$, $c = 24.95(2)$ Å, $\beta = 90.45(5)°$, $U = 4\,213(4)$ Å^3, $D_c = 1.69$ g cm^{-3}, $Z = 4$, $F(000) = 1\,280$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,73$ Å, $\mu(\text{Mo-}K_\alpha) = 61.4$ cm^{-1}.

The structure was solved by first locating the metal atoms by direct methods and then all other atoms except hydrogens were found in subsequent difference Fourier syntheses. The non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of the C and N atoms in the NEt_4^+ cation. All hydrogen atoms were included at calculated positions (C–H 0.96 and B–H 1.10 Å).[22] Except for H(3) and H(4), which were located using the steric-potential-energy-minimisation technique,[13] all hydrogens were refined with fixed isotropic thermal parameters [$U_{iso} = 0.08$ Å^2 for C*H* and 1.2 U_{iso} (B) for B*H*]. Refinement by full-matrix least squares led to $R = 0.074$ ($R' = 0.068$). A weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0007|F_o|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 1.0$ or $\leqslant -1.4$ e Å^{-3}, except near the W (2.9 and 3.1 e Å^{-3}, at 1.07 Å), Mo(1) (1.6 e Å^{-3} at 1.09 Å), and Mo(2) (1.7 e Å^{-3} at 1.02 Å) atoms. Calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[21] Scattering factors with corrections for anomalous dispersion were taken from ref. 23. Atomic co-ordinates are listed in Table 5.

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

Acknowledgements

We thank the S.E.R.C. for research studentships (to S. J. D. and M. U. P.) and the USAF Office of Scientific Research (Grant 86–0125) for partial support.

References

1 Part 103, S. J. Dossett, I. J. Hart, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, preceding paper.

2 (*a*) N. Carr, M. C. Gimeno, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1990, 2247, 2617; (*b*) M. C. Gimeno and F. G. A. Stone, *ibid.*, p. 2239 and refs. therein.

3 F. G. A. Stone, *Adv. Organomet. Chem.*, 1990, **31**, 53.

4 F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89; *ACS Symp. Ser.*, 1983, **211**, 383; *Pure Appl. Chem.*, 1986, **58**, 529.

5 (*a*) M. J. Chetcuti, P. A. M. Chetcuti, J. C. Jeffery, R. M. Mills, P. Mitrprachachon, S. J. Pickering, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 699; (*b*) M. D. Bermudez, E. Delgado, G. P. Elliott, N. H. Tran-Huy, F. Major-Real, F. G. A. Stone, and M. J. Winter, *ibid.*, 1987, 1235; (*c*) I. J. Hart, A. F. Hill, and F. G. A. Stone, *ibid.*, 1989, 2261 and refs. therein.

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

7 (*a*) S. J. Dossett, A. F. Hill, J. A. K. Howard, B. A. Nasir, T. P. Spaniol, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, 1871; (*b*) G. A. Carriedo, J. A. K. Howard, K. Marsden, F. G. A. Stone, and P. Woodward, *ibid.*, 1984, 1589.

8 S. J. Etches, I. J. Hart, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, 2281.

9 M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 81.

10 M. Green, S. J. Porter, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 513.

11 D. D. Devore, C. Emmerich, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, 797.

12 S. Trofimenko, J. C. Calabrese, and J. S. Thompson, *Inorg. Chem.*, 1987, **26**, 1507; T. P. Hanusa, *Polyhedron*, 1982, **2**, 663.

13 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

14 W. I. Bailey, M. H. Chisholm, F. A. Cotton, and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 5764; J. A. Beck, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 195 and refs. therein.

15 M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 1697.

16 M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 61.

17 F-E. Baumann, J. A. K. Howard, O. Johnson, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2661.

18 D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

19 R. Uson and A. Laguna, *Organomet. Synth.*, 1986, **3**, 325.

20 L. Crascall and J. L. Spencer, *Inorg. Synth.*, in the press; J. L. Spencer, *ibid.*, 1979, **19**, 213.

21 G. M. Sheldrick, SHELXTL PLUS programs used with the Nicolet *X*-ray system.

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

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

Received 10*th May* 1990; *Paper* 0/02067B