Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 103.[1] Carbaborane Molybdenum and Tungsten Dimetal Complexes

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Treatment of the complex $[\mathrm{Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)}][\mathrm{BF_4}]$ ($\mathrm{C_9H_7}$ = indenyl) with the salts $[\mathrm{NEt_4}][\mathrm{W(\equiv CC\equiv CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)}]$ and $[\mathrm{NEt_4}][\mathrm{Mo(\equiv CC_6H_4Me\text{-}4)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_2B_9H_9Me_2)}]$ in $\mathrm{CH_2Cl_2}$ affords, respectively, the dimetal compounds $[\mathrm{MoW(\mu\text{-}CC\equiv CBu^t)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)}]and[\mathrm{Mo_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_9H_7(\eta^5\text{-}C_2B_9H_9Me_2)}]$. Similarly, reactions between the salts $[\mathrm{NEt_4}][\mathrm{M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)}]$ (M = Mo or W, R = $\mathrm{C_6H_4Me\text{-}4}$, R′ = H; M = W, R = $\mathrm{C_6H_4Me\text{-}4}$ or $\mathrm{C_6H_4Me\text{-}2}$, R′ = Me; M = W, R = $\mathrm{C\equiv CBu^t}$, R′ = Me) and $[\mathrm{Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)}][\mathrm{BF_4}]$ yield the dimetal complexes $[\mathrm{MMo(\mu\text{-}CR)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9R'_2)}]$ (M = W, R = $\mathrm{C_6H_4Me\text{-}4}$, $\mathrm{C_6H_4Me\text{-}2}$, or $\mathrm{C\equiv CBu^t}$, R′ = Me; M = Mo or W, R = $\mathrm{C_6H_4Me\text{-}4}$, R′ = H). The compounds $[\mathrm{MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)}]$ and $[\mathrm{MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)}]$ have also been prepared using the reagents $[\mathrm{NEt_4}][\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{10}Me)}]$ and $[\mathrm{NEt_4}][\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)}]$. All the dimetal compounds have structures in which the metal–metal bonds are bridged by an alkylidyne group and by a B–H→Mo three-centre two-electron bond. The latter involves a boron atom lying in the face of the *nido*-carbaborane fragment which is co-ordinated to the other metal centre in the η^5 (for $\mathrm{C_2B_9H_9R'_2}$) or η^6 (for $\mathrm{C_2B_{10}H_{10}Me_2}$) bonding mode. The n.m.r. data (^{1}H, ^{13}C-{^{1}H}, ^{11}B-{^{1}H}, ^{11}B, and ^{31}P-{^{1}H}) for the new compounds are reported and discussed in the context of the structures proposed.

The alkylidyne-molybdenum and -tungsten salts $[\mathrm{NEt_4}][\mathrm{M(\equiv CR)(CO)L(\eta^5\text{-}C_2B_9H_9R'_2)}]$[**1**; M = Mo or W, R = alkyl or aryl, L = CO or $\mathrm{P(OMe)_3}$, R′ = H or Me] and $[\mathrm{NEt_4}][\mathrm{W(\equiv CR)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)}]$ (**2**; R = $\mathrm{C_6H_4Me\text{-}4}$ or $\mathrm{C_6H_3Me_2\text{-}2,6}$) are versatile reagents for the synthesis of complexes with bonds between these metals and other transition elements.[2] The di- and poly-nuclear metal compounds isolated are of interest both on account of their reactivity, and because of the different ways in which the resulting structures may be viewed. Thus products obtained employing the species (**1**) may be classed as *closo*-icosahedral carbametallaboranes in which molybdenum or tungsten atoms fill the pentagonal faces of *nido*-$\mathrm{C_2B_9H_9R'_2}$ fragments while being simultaneously linked to other metal–ligand moieties. Alternatively, since there is a parallelism in the electronic behaviour of η^5-$\mathrm{C_2B_9H_9R'_2}$ and η^5-$\mathrm{C_5R'_5}$ groups, resulting in certain similarities in their co-ordination behaviour,[3] some of the new compounds reported may be viewed as analogues of known di- or poly-nuclear metal complexes containing cyclopentadienyl groups. However, the carbaborane ligands frequently adopt a non-spectator role in the various syntheses, bridging the metal–metal bonds formed *via* exopolyhedral B–H→M or B–M linkages. This feature gives rise to a distinctly different chemistry from that observed with polynuclear metal complexes containing η^5-$\mathrm{C_5R'_5}$ ligands. Consequently, with the alkylidynecarbametallaborane reagents, many unusual reactions have been observed.

In one facet of this research several dimetal compounds have been prepared containing Mo–W or W–W bonds.[4] In this paper we describe further examples of such products.

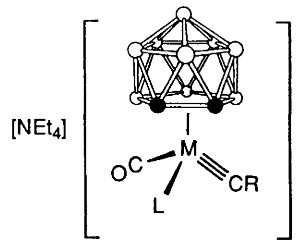
Results and Discussion

The synthesis of certain of the dimetal compounds described below necessitated the initial preparation of the hitherto unreported salts $[\mathrm{NEt_4}][\mathrm{M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)}]$ (**1b**; M = Mo, R = $\mathrm{C_6H_4Me\text{-}4}$, R′ = H), (**1j**; M = W, R = $\mathrm{C\equiv CBu^t}$, R′ = Me), and $[\mathrm{NEt_4}][\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{10}Me)}]$ (**3**). Data characterising these mononuclear metal species are given in Tables 1 and 2, and they were obtained using the following procedures.

Complex (**1b**) was prepared by treating $[\mathrm{Mo(\equiv CC_6H_4Me\text{-}4)(O_2CCF_3)(CO)_2(py)_2}]$ (py = pyridine) in thf (tetrahydrofuran) with $\mathrm{Na_2[C_2B_9H_{11}]}$ in the same solvent. Following addition of $\mathrm{NEt_4Cl{\cdot}H_2O}$, and column chromatography of the mixture on alumina, the product was isolated as a red oil, from which crystals of (**1b**) were obtained by washing with $\mathrm{Et_2O}$. The i.r. spectrum shows two CO stretching bands at 1 976 and 1 896 cm^{-1}, which may be compared with those observed[5] for the anion of (**1a**) at 1 965 and 1 880 cm^{-1}. In the ^{13}C-{^{1}H} n.m.r. spectrum of (**1b**) the diagnostic resonance for the ligated alkylidyne-carbon is at δ 301.2 p.p.m. That for the tungsten analogue (**1a**) is at δ 293.9 p.p.m.

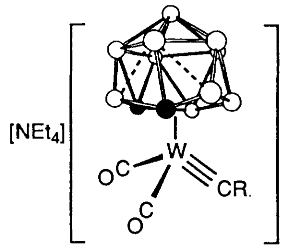
Complex (**1j**) was synthesised from $[\mathrm{W(\equiv CC\equiv CBu^t)(O_2CCF_3)(CO)_2(NC_5H_4Me\text{-}4)_2}]$ and $\mathrm{Na_2[C_2B_9H_9Me_2]}$ in thf, followed by addition of $\mathrm{NEt_4Cl{\cdot}H_2O}$. As expected, there are two CO bands (1 968 and 1 886 cm^{-1}) in the i.r. spectrum. The frequencies observed are lower than those found in the spectrum of the cyclopentadienyl analogue $[\mathrm{W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)}]$ [$\nu_{\mathrm{max.}}$(CO) at 1 988 and 1 929 cm^{-1}],[6a] as expected, since in (**1j**) the $\mathrm{W(CO)_2}$ group is part of an anion. In the ^{13}C-{^{1}H} n.m.r. spectrum (Table 2) the resonance for the C≡W group is at δ 269.0 p.p.m. [*J*(WC) 212 Hz] which may be compared with the corresponding signal in the spectrum of $[\mathrm{W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)}]$ at δ 266.7 p.p.m. [*J*(WC) 226 Hz]. The presence of the $\mathrm{C\equiv CBu^t}$ substituent attached to the alkylidyne-carbon atom in the latter, and in (**1j**), results in the resonance for the C≡W group being appreciably less deshielded than those observed in the spectra of alkylidynetungsten compounds in which the ligated carbon atoms carry alkyl or aryl groups, *e.g.* (**1a**) or (**1b**) discussed above.

The complex (**3**) was prepared from $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)(O_2CCF_3)(CO)_2(py)_2}]$ and $\mathrm{Na_2[C_2B_9H_{10}Me]}$ in thf, followed by addition of $\mathrm{NEt_4Cl{\cdot}H_2O}$. The data obtained for (**3**) (Tables 1 and 2) are in agreement with the formulation proposed.



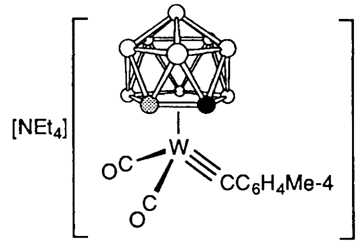
○BH

	M	L	R	●
(**1a**)	W	CO	C_6H_4Me-4	CH
(**1b**)	Mo	CO	C_6H_4Me-4	CH
(**1c**)	W	CO	Me	CMe
(**1d**)	W	CO	C_6H_4Me-4	CMe
(**1e**)	Mo	CO	C_6H_4Me-4	CMe
(**1f**)	Mo	$P(OMe)_3$	C_6H_4Me-4	CMe
(**1g**)	W	CO	C_6H_4Me-2	CMe
(**1h**)	W	CO	$C_6H_3Me_2$-2,6	CMe
(**1i**)	W	CO	Ph	CMe
(**1j**)	W	CO	$C\equiv CBu^t$	CMe



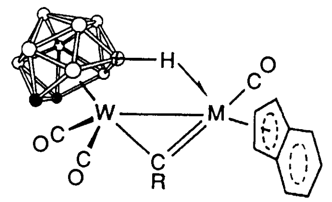
●CMe ○BH

	R
(**2a**)	C_6H_4Me-4
(**2b**)	$C_6H_3Me_2$-2,6



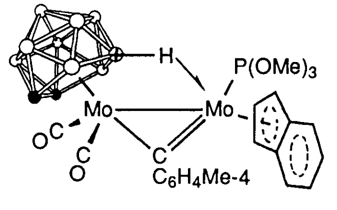
○BH ◎CH ●CMe

(**3**)



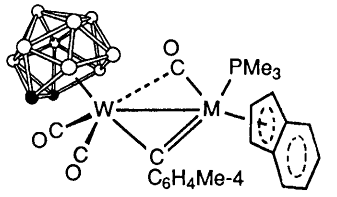
○BH ⊕B

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



●CMe ○BH ⊕B

(**4e**)



●CMe ○BH

	M
(**4f**)	Mo
(**4g**)	W

Several dimetal compounds containing Mo–W or Mo–Mo bonds were next prepared using as precursors some of the reagents (**1**), and the complexes (**2a**) and (**3**). Treatment of (**1j**) in CH_2Cl_2 with $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ ($\eta^5\text{-}C_9H_7$ = indenyl) afforded the green crystalline complex $[MoW(\mu\text{-}CC\equiv CBu^t)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**) characterised by the data given in Tables 1—3. Compound (**4a**) is closely related to the previously reported species $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9R'_2)]$ (**4b**; M = Mo, R′ = Me), (**4c**; M = Mo, R′ = H), and (**4d**; M = W, R′ = Me).[4a] Examination of the n.m.r. data for (**4a**) revealed that in solution this species exists as a mixture of two isomers in the ratio *ca.* 4:1. Similar behaviour is shown by compound (**4b**).[4a] Thus in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4a**) two alkylidyne-carbon resonances are observed at δ 357.0 and 348.3 p.p.m. for the minor and major isomers, respectively. The spectrum of (**4b**) shows corresponding peaks at 390.8 and 381.7 p.p.m. It is noteworthy that the signals for the μ-C nuclei of the isomers of (**4a**) are appreciably less deshielded than those of the isomers of (**4b**). As mentioned above, a similar effect is observed with the mononuclear metal alkylidyne complexes when the group $C\equiv CBu^t$ replaces C_6H_4Me-4 in the CR fragment, and the phenomenon is also found with trimetal complexes with capping μ_3-CR groups.[6]

In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4a**) resonances for the alkynyl carbon nuclei are seen at δ 157.6 ($C\equiv \mathit{C}Bu^t$) and 99.0 p.p.m. ($\mathit{C}\equiv CBu^t$) for the major isomer, and at δ 160.8 ($C\equiv \mathit{C}Bu^t$) and 100.6 p.p.m. ($\mathit{C}\equiv CBu^t$) for the minor isomer. These assignments are based on arguments presented earlier employing fully coupled ^{13}C n.m.r. spectra.[6] The extent of the deshielding of the resonances for the $C\equiv \mathit{C}Bu^t$ nuclei in the isomers of (**4a**) is unprecedented for an unco-ordinated alkyne and must arise through interaction of orbitals of π symmetry in the Mo(μ-C)W ring with the π orbitals of the C≡C bond. What seems apparent

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

Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$	Analysis (%)	
				C	H
(1b) $[NEt_4][Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$	Red	74	1 976s, 1 896vs	[c] 46.0 (46.4)	7.0 (7.4)
(1j) $[NEt_4][W(\equiv CC{\equiv}CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	60	1 968s, 1 886vs	[d] 39.8 (40.4)	6.8 (7.1)
(3) $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{10}Me)]$	Red	82	1 962s, 1 878vs	[e] 41.0 (40.7)	6.0 (6.5)
(4a) $[MoW(\mu\text{-}CC{\equiv}CBu^t)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Green	65	2 006vs, 1 957s (sh)	38.3 (37.7)	4.5 (4.3)
(4e) $[Mo_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Green	44	1 975vs, 1 910s	41.7 (41.6)	5.4 (5.1)
(5a) $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	29	1 995vs, 1 935s	36.2 (36.5)	4.5 (4.2)
(5b) $[MoW(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	27	1 995vs, 1 935s	35.4 (36.3)	4.5 (4.2)
(5c) $[MoW(\mu\text{-}CC{\equiv}CBu^t)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	51	1 994vs, 1 939s	36.0 (35.5)	5.5 (4.6)
(5d) $[Mo_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{11})]$	Red	69	2 009vs, 1 950s	39.0 (39.7)	4.5 (4.4)
(5e) $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{11})]$	Red	72	2 000vs, 1 937s	35.1 (34.4)	4.2 (3.8)
(5f) $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$	Red	66	1 998vs, 1 937s	34.6 (35.5)	5.0 (4.0)
(5g) $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	79	1 996vs	38.3 (39.4)	5.0 (5.0)
(6) $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$	Red	29	2 032s, 1 995vs	35.3 (35.9)	4.6 (4.3)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. All complexes show a broad band at *ca.* 2 550 cm^{-1} due to B–H. [c] N, 2.5 (2.7%). [d] N, 1.8 (2.2%). [e] N, 2.3 (2.3%).

is that the relative shielding of the μ-C resonance in (**4a**), with respect to that in (**4b**), and the substantial deshielding of the C≡*C*Bu^t resonance in the former, are related phenomena.

The presence of six CO resonances in the spectrum of (**4a**) (Table 2) is in agreement with the presence of the two isomers. As with (**4b**)—(**4d**), the nature of the isomerism is unclear but probably relates to different orientations of the Mo(CO)(η^5-C_9H_7) fragment with respect to the $\overline{Mo(\mu\text{-}C)W}$ ring, or to the B–H⟶Mo bond involving a boron atom α rather than β to the carbons in the $\overline{CCBBB}$ pentagonal face of the cage.[4a] One anomaly in the ^{13}C-{^1H} n.m.r. spectrum is the presence of four C*Me* signals (two for each isomer) and only two broad signals due to the *C*Me carbons at δ 67.8 and 67.4 p.p.m. There should, of course, be four such signals. The explanation is almost certainly that the *C*Me signals coincide.

The presence of the B–H⟶Mo exopolyhedral bond in (**4a**) is clearly revealed in the ^1H n.m.r. spectrum by a shielded resonance at δ −7.58. As expected, this signal is a quartet due to ^{11}B–^1H coupling (73 Hz).[4a] The corresponding signal in the spectrum of (**4b**) is at δ −7.98 [*J*(BH) 84 Hz]. These *J*(BH) values are lower than those observed (*ca.* 130—160 Hz) for two-centre two-electron B–H bonds,[7a] and mirror the reduction in ^1H–^{13}C coupling found for C–H⟶M linkages *versus* C–H bonds.[7b]

The ^{11}B-{^1H} n.m.r. spectrum of compound (**4a**) shows diagnostic resonances at δ 16.8 (major isomer) and 15.8 p.p.m. (minor isomer) for the B–H⟶Mo groups in the two species. In a fully coupled ^{11}B spectrum the peak due to the major isomer is a doublet [*J*(BH) 73 Hz], as expected for this assignment, while the signal due to the minor isomer was too weak to be resolved. The structure of (**4b**) has been established by *X*-ray diffraction, and this study revealed that the B–H⟶Mo bond involved the boron atom in the pentagonal face of the cage which is β to the carbon atoms.[4a] It seems very likely therefore that this is the configuration adopted also by the major isomer of (**4a**).

The reaction between (**1f**) and $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ afforded the dimetal complex $[Mo_2(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4e**). This species is formulated as having a $Mo\{P(OMe)_3\}(\eta^5\text{-}C_9H_7)$ fragment, implying migration of the $P(OMe)_3$ ligand from one molybdenum centre to the other during reaction. Firm evidence supporting this conclusion is derived from the ^{13}C-{^1H} n.m.r. data, with resonances for the $Mo(CO)_2$ group at δ 223.6 and 224.8 p.p.m., neither signal showing ^{31}P–^{13}C coupling. If a $Mo(CO)\{P(OMe)_3\}$ group were present ^{31}P–^{13}C coupling would be observed, as is seen in the ^{13}C-{^1H} n.m.r. spectra of the precursor (**1f**) [δ 244.3 p.p.m., *J*(PC) 22 Hz], or the dimetal species $[MoAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)\{P(OMe)_3\}(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ [δ 240.8 p.p.m., *J*(PC) 27 Hz].[8] Migration of the $P(OMe)_3$ group in the formation of (**4e**) is related to the migration of PMe_3 ligands from tungsten to cobalt or rhodium centres in the synthesis of certain mixed-metal complexes using the ketenyl complex $[W\{\eta^2\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ as a precursor.[9]

The ^{13}C-{^1H} n.m.r. spectrum of compound (**4e**) shows a diagnostic resonance for the μ-C nucleus at δ 380.5 p.p.m., which appears as a doublet [*J*(PC) 13 Hz] due to coupling with the transoid $P(OMe)_3$ ligand. The CMe groups of the C_2B_9 cage in (**4e**) are non-equivalent, as they are in (**4a**)—(**4d**), since there is no plane of symmetry through the metal atoms, the B–H⟶M bond, and the midpoint of the cage C–C bond. Thus each CMe group in compound (**4e**) gives rise to two signals [δ 68.3 and 67.3 (*C*Me), and 31.0 and 30.7 p.p.m. (C*Me*)]. In agreement, the ^1H n.m.r. spectrum displays two CMe resonances at δ 1.80 and 2.12.

The presence of the B–H⟶Mo group in (**4e**) is unequivocally established by the appearance of the quartet signal in the ^1H n.m.r. spectrum at δ −6.60 [*J*(BH) 73 Hz], and by the doublet resonance in the fully coupled ^{11}B spectrum at δ 18.7 p.p.m.

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

Compound	$^{1}H^{b}$ (δ)	$^{13}C^{c}$ (δ)
(1b)	[d]1.14 (br m, 12 H, $CH_2\mathit{Me}$), 2.17 (s, 3 H, Me-4), 3.16 [q, 8 H, $C\mathit{H}_2Me$, *J*(HH) 7], 7.12, 7.46 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	301.2 (C≡Mo), 229.6 (CO), 143.9 [$C^1(C_6H_4)$], 138.7, 128.5, 128.2 (C_6H_4), 52.4 ($\mathit{C}H_2Me$), 43.2 [br, CH ($C_2B_9H_{11}$)], 21.2 (Me-4), 7.2 ($CH_2\mathit{Me}$)
(1j)	1.29 (s, 9 H, Bu^t), 1.35 [t of t, 12 H, $CH_2\mathit{Me}$, *J*(HH) 7, *J*(NH) 2], 2.01 (s, 6 H, CMe), 3.25 [q, 8 H, $C\mathit{H}_2Me$, *J*(HH) 7]	269.0 [C≡W, *J*(WC) 212], 228.6 [CO, *J*(WC) 181], 99.2 ($\mathit{C}{\equiv}CBu^t$), 91.0 ($C{\equiv}\mathit{C}Bu^t$), 63.0 (br, *C*Me), 53.4 ($\mathit{C}H_2Me$), 30.5 ($C\mathit{Me}_3$), 30.2 (C*Me*), 29.2 ($\mathit{C}Me_3$), 8.5 ($CH_2\mathit{Me}$)
(3)	[d]1.23 [t of t, 12 H, $CH_2\mathit{Me}$, *J*(HH) 7, *J*(NH) 2], 1.87 (s, 3 H, CMe), 2.26 (s, 3 H, Me-4), 3.12 [q, 8 H, $C\mathit{H}_2Me$, *J*(HH) 7], 7.09, 7.37 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	296.5 [C≡W, *J*(WC) 199], 226.5 (CO), 148.7 [$C^1(C_6H_4)$], 137.9, 128.7, 127.7 (C_6H_4), 66.3 (br, *C*Me), 51.6 ($\mathit{C}H_2Me$), 46.1 [br, *C*H ($C_2B_9H_{11}$)], 32.8 (C*Me*), 21.2 (Me-4), 7.2 ($CH_2\mathit{Me}$)
(4a)	−7.58 [q, 1 H, BHMo, *J*(BH) 73], 1.55 (s, 9 H, Bu^t), 1.86, 2.03 (s × 2, 6 H, CMe), 5.80—6.18 (m, 3 H, C_9H_7), 6.66—7.60 (m, 4 H, C_9H_7)	[e]357.0*, 348.3 (μ-C), 231.5*, 228.2 (MoCO), 222.5, 220.8*, 213.7*, 211.7 (WCO), 160.8*, 157.6 ($C{\equiv}\mathit{C}Bu^t$), 130.1—113.9 (C_9H_7), 100.6*, 99.0 ($\mathit{C}{\equiv}CBu^t$), 94.6—77.3 (C_9H_7), 67.8, 67.4 (br, *C*Me), 33.4*, 31.5, 31.0*, 30.6 (C*Me*), 30.4 ($C\mathit{Me}_3$), 29.2*, 29.0 ($\mathit{C}Me_3$)
(4e)	−6.60 [q, 1 H, BHMo, *J*(BH) 73], 1.80, 2.12 (s × 2, 6 H, CMe), 3.22 [d, 9 H, OMe, *J*(PH) 11], 4.48, 4.86, 5.65 (m × 3, 3 H, C_9H_7), 6.96—7.74 (m, 8 H, C_6H_4, C_9H_7)	380.5 [d, μ-C, *J*(PC) 13], 224.8, 223.6 (CO), 157.9 [$C^1(C_6H_4)$], 136.7, 128.6 (C_6H_4), 128.2—124.8 (C_9H_7), 124.7 (C_6H_4), 116.5—75.3 (C_9H_7), 68.3, 67.3 (*C*Me), 52.8 (OMe), 31.0, 30.7 (C*Me*), 21.2 (Me-4)
(5a)	1.97 (s, 6 H, CMe), 2.53 (s, 3 H, Me-4), 5.33 (s, 7 H, C_7H_7), 7.02, 7.42 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	324.8 [μ-C, *J*(WC) 115], 216.6 [CO, *J*(WC) 163], 161.3 [$C^1(C_6H_4)$], 135.7, 128.7, 121.4 (C_6H_4), 88.7 (C_7H_7), 65.4 (*C*Me), 31.0 (C*Me*), 21.3 (Me-4)
(5b)	1.93, 2.01, 2.14 (s × 3, 9 H, Me-2 and CMe), 5.26 (s, 7 H, C_7H_7), 6.95—7.55 (m, 4 H, C_6H_4)	324.8 (μ-C), 222.2, 212.5 (CO), 162.7 [$C^1(C_6H_4)$], 130.6, 129.6, 126.3, 125.4, 121.1 (C_6H_4), 88.8 (C_7H_7), 68.1, 67.3 (*C*Me), 31.0 (br, 2 × C, C*Me*), 20.7 (Me-2)
(5c)	1.62 (s, 9 H, Bu^t), 1.95 (s, 6 H, CMe), 5.49 (s, 7 H, C_7H_7)	293.7 [μ-C, *J*(WC) 114], 216.6 [CO, *J*(WC) 162], 137.1 ($C{\equiv}\mathit{C}Bu^t$), 98.8 ($\mathit{C}{\equiv}CBu^t$), 89.7 (C_7H_7), 65.8 (*C*Me), 31.8 ($C\mathit{Me}_3$), 31.1 (C*Me*), 30.4 ($\mathit{C}Me_3$)
(5d)	2.54 (s, 3 H, Me-4), 2.73 [br s, 2 H, CH ($C_2B_9H_{11}$)], 5.24 (s, 7 H, C_7H_7), 7.15, 7.44 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	336.9 (μ-C), 221.1 (CO), 158.9 [$C^1(C_6H_4)$], 136.0, 128.9, 121.4 (C_6H_4), 89.2 (C_7H_7), 40.5 [CH ($C_2B_9H_{11}$)], 21.4 (Me-4)
(5e)	2.57 (s, 3 H, Me-4), 2.93 [br s, 2 H, CH ($C_2B_9H_{11}$)], 5.31 (s, 7 H, C_7H_7), 7.10, 7.47 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	323.5 (μ-C), 213.7 [CO, *J*(WC) 161], 161.1 [$C^1(C_6H_4)$], 135.8, 128.7, 121.5 (C_6H_4), 88.7 (C_7H_7), 37.9 [CH ($C_2B_9H_{11}$)], 21.4 (Me-4)
(5f)	[f]1.81, (s, 3 H, CMe), 2.54 (s, 3 H, Me-4), 3.31 [br, 1 H, CH ($C_2B_9H_{10}Me$)], 5.25 (s, 7 H, C_7H_7), 7.03, 7.13 (m × 2, 2 H, C_6H_4), 7.46 [d, 2 H, C_6H_4, *J*(HH) 8]	325.5 (μ-C), 217.1, 213.6 (CO), 161.0 [$C^1(C_6H_4)$], 135.5, 128.8, 121.1 (br, C_6H_4), 88.4 (C_7H_7), 56.9 (*C*Me), 49.1 [CH ($C_2B_9H_{10}Me$)], 34.0 (C*Me*), 21.1 (Me-4)
(5g)	1.45 [d, 9 H, MeP, *J*(PH) 9], 1.76, 1.81 (s × 2, 6 H, CMe), 2.49 (s, 3 H, Me-4), 5.08 (s, 7 H, C_7H_7), 6.64, 7.18, 7.29, 7.40 [d × 4, 4 H, C_6H_4, *J*(HH) 8]	312.5 (μ-C), 241.9 [d, CO, *J*(PC) 9], 162.9 [$C^1(C_6H_4)$], 134.1, 129.1, 127.9, 124.8, 121.0 (C_6H_4), 87.5 (C_7H_7), 64.6, 58.8 (*C*Me), 32.0, 30.6 (C*Me*), 24.2 [d, MeP, *J*(PC) 36], 21.3 (Me-4)
(6)	[f]1.57, 1.98 (s, 6 H, CMe), 2.53 (s, 3 H, Me-4), 5.30 (s, 7 H, C_7H_7), 6.71, 7.05, 7.43, 7.48 [d × 4, 4 H, C_6H_4, *J*(HH) 8]	[g]322.7 (μ-C), 208.1, 195.4 (CO), 159.8 [$C^1(C_6H_4)$], 135.3, 128.3, 128.1, 120.3, 119.5 (C_6H_4), 89.1 (C_7H_7), 85.1, 63.5 (*C*Me), 34.9 (2 × C*Me*), 20.9 (Me-4)

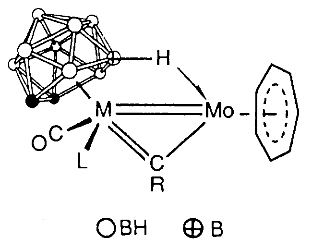
[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at ambient temperatures unless otherwise stated. [b] In CD_2Cl_2 unless otherwise stated. Proton resonances for B–H groups occur as broad unresolved signals in the range δ 0—3. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$, measured in CD_2Cl_2–CH_2Cl_2. [d] Signal due to $C\mathit{H}(C_2B_9H_{10}Me)$ obscured by $C\mathit{H}_2Me$ resonance of NEt_4^+. [e] Resonances asterisked are due to a minor isomer (*ca.* 20%), see text. [f] Measured at −60 °C. [g] Measured at −30 °C.

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

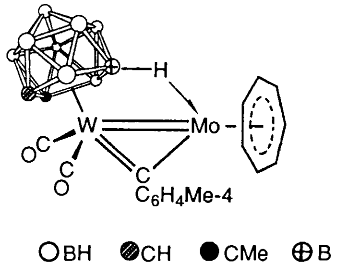
Compound[b]	^{11}B (δ)
(1b)	−8.8, −12.4, −13.0, −19.0, −22.5, −24.0 (BH)
(1j)	−7.1, −11.2, −14.0, −15.9, −20.3 (BH)
(3)	−7.7, −9.9, −13.5, −16.5, −19.7 (BH)
(4a)	16.8 [BHMo, *J*(BH) 73], 15.8* (BHMo), −6.1 to −11.6 (br, BH)
(4e)	18.7 [BHMo, *J*(BH) 73], −8.5 to −13.1 (br, BH)
(5a)	11.5 [BHMo, *J*(BH) 79], −8.1 to −12.7 (BH)
(5b)	11.5 [BHMo, *J*(BH) 79], −8.1 to −12.6 (br, BH)
(5c)	12.5 [BHMo, *J*(BH) 79], −8.1 to −12.2 (br, BH)
(5d)	17.0 [BHMo, *J*(BH) 73], −8.9, −13.0, −16.6, −23.9 (BH)
(5e)	10.1 [BHMo, *J*(BH) 79], −8.9, −12.4, −16.2, −17.1, −24.0 (BH)
(5f)	11.7 [BHMo, *J*(BH) 77], −7.1, −10.4, −11.8, −15.4, −17.0 (BH)
(5g)	1.7 [BHMo, *J*(BH) 86], −6.6, −8.1, −10.3, −13.0, −14.2, −16.2 (BH)
(6)	17.4 [BHMo, *J*(BH) 73], 1.4, −5.1, −8.1, −11.6, −16.7 (BH)

[a] Hydrogen-1 decoupled, chemical shifts (δ) are in p.p.m., positive to high frequency of $BF_3{\cdot}EtO$ (external). Coupling constants are in Hz. Measurements were made in CD_2Cl_2. [b] For complexes (4)—(6) the ^1H–^{11}B coupling constants were measured from fully coupled ^{11}B n.m.r. spectra.

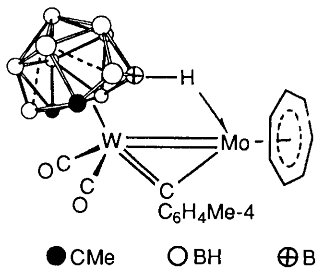
[*J*(BH) 73 Hz]. As expected, the ^{31}P-{^1H} n.m.r. spectrum shows a sharp singlet at δ 172.1 p.p.m. Compound (**4e**) showed no evidence of existing in more than one isomeric form; the steric demands of the $P(OMe)_3$ ligand probably prevents the Mo{$P(OMe)_3$}(η^5-C_9H_7) group from adopting different orientations with respect to the remainder of the molecule. It almost certainly has a structure with the B–H→Mo linkage involving the β-boron of the $\overline{CCB\mathit{B}B}$ ring. *X*-Ray diffraction



M	L	R	●
(5a) W	CO	C_6H_4Me-4	CMe
(5b) W	CO	C_6H_4Me-2	CMe
(5c) W	CO	C≡CBu^t	CMe
(5d) Mo	CO	C_6H_4Me-4	CH
(5e) W	CO	C_6H_4Me-4	CH
(5g) W	PMe_3	C_6H_4Me-4	CMe



(5f)



(6)

studies on the structurally related complexes [W_2(μ-CC_6H_4-Me-4)$(CO)_2$L(η^5-C_9H_7)(η^5-$C_2B_9H_9Me_2$)] [L = O or $N_2C(C_6H_4Me\text{-}4)_2$], which contain WL($\eta^5$-$C_9H_7$) groups similar to the Mo{$P(OMe)_3$}(η^5-C_9H_7) fragment in (**4e**), revealed B–H⇀W bonds employing the boron atom β to the carbon atoms in the CCB*B*B ring.[4b] These ditungsten compounds have ^1H and ^{13}C-{^1H} n.m.r. resonances very similar to those of (**4e**). Thus for [W_2(μ-CC_6H_4Me-4)$(CO)_2${N_2C-$(C_6H_4Me\text{-}4)_2$}(η^5-C_9H_7)(η^5-$C_2B_9H_9Me_2$)] the ^1H n.m.r. resonance for the B–H⇀W group is at δ −6.92, and in the ^{13}C-{^1H} n.m.r. spectrum the signals for the CMe groups are at δ 63.3 and 59.9 (*C*Me) and 30.8 and 30.6 p.p.m. (C*Me*).

Treatment of the reagents (**1d**), (**1g**), and (**1j**) with a slight excess of the complex [Mo$(CO)_2$(NCMe)(η^7-C_7H_7)][BF_4] in CH_2Cl_2 gives respectively, the dimetal complexes [MoW(μ-CR)$(CO)_2$(η^7-C_7H_7)(η^5-$C_2B_9H_9Me_2$)] (**5a**; R = C_6H_4Me-4), (**5b**; R = C_6H_4Me-2), and (**5c**; R = C≡CBu^t), data for which are given in Tables 1—3. All three compounds show two CO stretching bands in their i.r. spectra (Table 1), and in addition (**5c**) has a band at 2 142 cm^{-1} which may be ascribed to the C≡CBu^t group. The compounds (**5a**) and (**5c**) are very similar to the complexes (**4b**) and (**4a**), respectively, except that a Mo(η^7-C_7H_7) unit in the first two species replaces a Mo(CO)-(η^5-C_9H_7) fragment in the last two. In both pairs of complexes a three-centre two-electron B–H⇀Mo bond is present. However, the resonance for this group is not apparent in the ^1H n.m.r. spectrum of (**5a**) or (**5c**), probably because the signal is too broad. Nevertheless, the fully coupled ^{11}B n.m.r. spectra of (**5a**) and (**5c**) (Table 3) provide unequivocal evidence for the presence of the B–H⇀Mo bonds with doublet signals [*J*(BH) 79 Hz] corresponding in intensity to one boron nucleus at δ 11.5 for (**5a**) and at δ 12.5 p.p.m. for (**5c**).

In the ^{13}C-{^1H} n.m.r. spectra of compounds (**5a**) and (**5c**) resonances for the μ-C nuclei occur at δ 324.8 and 293.7 p.p.m. respectively. These signals are appreciably less deshielded than the corresponding peaks of (**4a**) (348.3 p.p.m., major isomer), (**4e**) (380.5 p.p.m.) (Table 2), and (**4b**) (381.7 p.p.m.).[4a] The electronically unsaturated dimetal complex [NEt_4][WFe(μ-CC_6H_4Me-2)$(CO)_5$(η^5-$C_2B_9H_9Me_2$)] displays the μ-C resonance in the ^{13}C-{^1H} n.m.r. spectrum at δ 387.9 p.p.m.[10] This chemical shift is more similar to those found for (**4a**), (**4b**), and (**4e**) than for (**5a**) and (**5c**). The difference in chemical shifts of the μ-C nuclei between the two types of complexes (**4**) and (**5**) may well reflect different electron distributions within the three-membered alkylidyne-carbon dimetal ring systems.[11] The alkylidyne-carbon shifts for the species (**5**) are in the range observed for electronically saturated dimetal complexes with 34 valence electrons, while the shifts for the complexes (**4**) correspond to those observed for electronically unsaturated dimetal compounds with 32 valence electrons. Both types of compound are ostensibly electronically unsaturated, having 32 valence electrons rather than the 34 required to give each metal centre a filled shell. However, we have chosen to represent the complexes (**4a**)—(**4d**) with formulations implying that the tungsten atoms have 16-electron configurations and the molybdenum atoms have 18 electrons, while the species (**5**) are represented as 'saturated' dimetal compounds with both metal centres having a filled shell. It is of interest that the ^{183}W–^{13}C couplings (*ca.* 115 Hz) associated with the μ-C resonances of (**5a**) and (**5c**) are appreciably greater than that observed (98 Hz) for the complex (**4b**),[4a] implying stronger μ-C–W bonds in (**5a**) and (**5c**), as depicted in the structural formula shown.

None of the complexes (**5a**)—(**5c**) shows any evidence for the existence of isomers. Moreover, the ^1H and ^{13}C-{^1H} n.m.r. spectra of (**5a**) and (**5c**) reveal that in each compound the cage CMe groups are equivalent. Thus for (**5a**) the ^1H n.m.r. spectrum displays a single cage CMe resonance at δ 1.97, and correspondingly the ^{13}C-{^1H} n.m.r. spectrum shows one set of peaks at δ 65.4 (*C*Me) and 31.0 p.p.m. (C*Me*). The equivalence of the two CMe groups in (**5a**) and (**5c**) is in accord with the presence of a plane of symmetry in these molecules, as would occur if the B–H⇀Mo bonds involved the boron atom which is β to the carbon atoms in the pentagonal face of the cage ligating the tungsten atom, and there was free rotation of the η^7-C_7H_7 ring.

The n.m.r. data for compound (**5b**) are more complex, reflecting the asymmetry introduced by the presence of the C_6H_4Me-2 group. Thus in contrast with the ^{13}C-{^1H} n.m.r. spectra of (**5a**) and (**5c**), which display only one CO resonance, the spectrum of (**5b**) shows two CO peaks (Table 2). In the complexes (**4b**) and (**4d**) *X*-ray diffraction studies showed[4a] that the C_6H_4Me-4 rings are essentially at right angles to the plane defined by the M(μ-C)W fragments. Similarly in [MoFe(μ-$CC_6H_3Me_2$-2,6)$(CO)_5$-(η-C_5H_5)][11] and [NEt_4][WFe(μ-$CC_6H_3Me_2$-2,6)$(CO)_5$(η^5-$C_2B_9H_9Me_2$)][10] the planes defined by the carbon atoms of the $C_6H_3Me_2$-2,6 groups are approximately orthogonal to the M(μ-C)Fe rings, a feature which is probably sterically imposed. It is thus highly probable that in (**5b**) also the arene fragment adopts a similar configuration. The presence of the Me-2 substituent would then make the two CO ligands non-equivalent and would thereby account for the two carbonyl resonances observed. Moreover, even if as seems probable the B–H⇀Mo bond in (**5b**) involves the central boron atom CCB*B*B, as in (**5a**) and (**5c**), the CMe groups of the η^5-$C_2B_9H_9Me_2$ ligand will be inequivalent. In agreement, the ^{13}C-{^1H} n.m.r. spectrum shows two *C*Me resonances at δ 68.1 and 67.3 p.p.m. The appearance of only one C*Me* peak at δ 31.0 p.p.m. is almost certainly due to the coincidental overlap of two resonances, since the signal is broad. In support of this conclusion the ^1H n.m.r. spectrum displays three signals at δ 1.93, 2.01, and 2.14 due to the two cage CMe groups and the Me-2 substituent on the arene ring.

The reaction between [Mo(CO)$_2$(NCMe)(η^7-C_7H_7)][BF$_4$] and (**1b**) afforded the complex [Mo$_2$(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C_7H_7)(η^5-$C_2B_9H_{11}$)] (**5d**), and the related species [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C_7H_7)(η^5-$C_2B_9H_{11}$)] (**5e**) was similarly prepared using (**1a**). Compounds (**5d**) and (**5e**) are characterised by the data given in the Tables. The presence of the B–H⇀Mo groups is clearly revealed by the resonances observed in the ^{11}B n.m.r. spectra at δ 17.0 for (**5d**) and 10.1 p.p.m. for (**5e**), both appearing as doublets due to ^{11}B–^1H coupling. Peaks in the ^1H and ^{13}C-{^1H} n.m.r. spectra are in accord with the structures proposed, although like the other compounds of type (**5**) a high-field ^1H resonance due to the B–H⇀Mo group could not be discerned. As with the other products containing η^7-C_7H_7 groups, there are diagnostic resonances for this ligand in the ^1H n.m.r. [δ 5.24 for (**5d**) and 5.31 for (**5e**)] and the ^{13}C-{^1H} n.m.r spectra [δ 89.2 for (**5d**) and 88.7 p.p.m. for (**5e**)].

Treatment of compound (**3**) in CH_2Cl_2 with [Mo(CO)$_2$(NCMe)(η^7-C_7H_7)][BF$_4$] gives the red complex [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C_7H_7)(η^5-$C_2B_9H_{10}Me$)] (**5f**). This species almost certainly has a similar structure to that of (**5a**). However, due to the lower symmetry of the C_2B_9 cage the molecule has no plane of symmetry. The n.m.r. data for (**5f**) vary with temperature probably as a result of some restriction in rotation about the μ-C–C$_6$H$_4$Me-4 bond. In the room-temperature ^1H n.m.r. spectrum the aromatic protons *ortho* to the alkylidyne-carbon give rise to a broad signal, and in the ^{13}C-{^1H} n.m.r. spectrum there is a corresponding broadening of the resonance at δ 121.1 p.p.m. due to the *ortho* carbons. In the ^1H n.m.r. spectrum measured at −60 °C there is a doublet at δ 7.46 [*J*(HH) 8 Hz], due presumably to coincident signals of the two aromatic protons *meta* to the alkylidyne-carbon and two second-order multiplets at δ 7.03 and 7.13 attributable to the two *ortho* protons. This pattern corresponds to the arene ring lying orthogonal to the Mo(μ-C)W ring. In contrast, the ^1H n.m.r. spectra of (**5a**), (**5c**), and (**5d**) all display a typical (AB)$_2$ pattern for the protons of the C$_6$H$_4$Me-4 group. This difference in behaviour can be accounted for in two ways. Either the aromatic C$_6$H$_4$Me-4 groups of (**5a**), (**5c**), and (**5d**) are undergoing free rotation at room temperature or they too are undergoing a form of restricted rotation, which is unobservable by n.m.r. spectroscopy due to the higher symmetry of these molecules.

The reaction between compound (**2a**) and [Mo(CO)$_2$(NCMe)(η^7-C_7H_7)][BF$_4$] affords the dimetal compound [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C_7H_7)(η^6-$C_2B_{10}H_{10}Me_2$)] (**6**). As with the complexes (**5**), a diagnostic peak for the B–H⇀Mo group is observed in the ^{11}B n.m.r. spectrum at δ 17.4 p.p.m. [*J*(BH) 73 Hz]. However, no high-field resonance is seen in the ^1H n.m.r. spectrum, a feature due presumably to a poor signal-to-noise ratio so that the expected quartet due to this single proton is not seen. Complex (**6**), like other dimetal species containing the η^6-$C_2B_{10}H_{10}Me_2$ ligand,[12] displays dynamic behaviour in solution as revealed by the n.m.r. data. In the ^1H n.m.r. spectrum measured at room temperature the signals due to the CMe group (δ 1.57 and 1.98) are broad, as are those at δ 6.71 and 7.05, due presumably to the C$_6$H$_4$ protons *ortho* to the alkylidyne unit. In the ^{13}C-{^1H} n.m.r. spectrum, recorded at ambient temperatures, there are two resonances for the W(CO)$_2$ group (δ 208.8 and 196.8 p.p.m.) but both peaks are broad, as are signals seen at δ 120.6 [C^2(C$_6$H$_4$Me-4)] and at 87.0 and 64.5 p.p.m. (*C*Me). Measurement of the ^1H n.m.r. spectrum at −60 °C and the ^{13}C-{^1H} spectrum at −30 °C gives the data listed in Table 2. All the peaks measured under these conditions are sharp. In the ^1H n.m.r. spectrum there are four doublets for the C$_6$H$_4$ protons, and in the ^{13}C-{^1H} n.m.r. spectrum there are six resonances for the C$_6$H$_4$ ring carbons and two peaks for the *C*Me nuclei (δ 85.1 and 63.5 p.p.m.). Two signals for the C*Me* groups might have been anticipated but only one (δ 34.9 p.p.m.) is observed. It is, however, at an intensity corresponding to two ^{13}C nuclei and so evidently the C*Me* resonances are coincident. High-temperature ^1H n.m.r. measurements in [$^2H_8$]toluene revealed a coalescence of the two cage C*Me* signals at *ca.* 40 °C, with a reasonably sharp peak appearing at 100 °C. Likewise, at the latter temperature, the C$_6$H$_4$ proton signals have the customary (AB)$_2$ pattern.

More than one dynamic process is probably involved for compound (**6**) in solution. An *X*-ray crystallographic study on [NEt$_4$][WFe(μ-CC$_6$H$_3$Me$_2$-2,6)(CO)$_4$(η^6-$C_2B_{10}H_{10}Me_2$)][12] revealed that the B–H⇀Fe bond utilises the boron atom β to the CMe groups in the η^6-CBCB*B*B face of the cage ligating the tungsten. Moreover, since the atoms in the face are not coplanar the two C–W ring distances are appreciably different [2.19(1) and 2.51(1) Å]. This arrangement almost certainly occurs in compound (**6**) in the solid state and at low temperatures in solution, but at ambient temperatures the cage is non-rigid and the two CMe groups begin to equivalence with coalescence reached at *ca.* 40 °C. This fluxionality is probably associated with diamond–square–diamond transformations within the docosahedral framework, as discussed previously for other dimetal compounds containing η^6-$C_2B_{10}H_{10}Me_2$ groups.[12] The C$_6$H$_4$Me-4 ring meanwhile probably lies orthogonal to the Mo(μ-C)W plane at low temperatures, displaying four doublets in the aromatic region of the ^1H n.m.r. spectrum. In the crystal structure of [NEt$_4$][WFe(μ-CC$_6$H$_3$Me$_2$-2,6)(CO)$_4$(η^6-$C_2B_{10}H_{10}Me_2$)] the xylyl ring is at 92.4° to the W(μ-C)Fe plane.[12] For (**6**), in solution at room temperature, the non-rigidity of the cage affects the C$_6$H$_4$ ring, and the aromatic ^1H signals broaden. At 100 °C the cage CMe groups are exchanging rapidly on the n.m.r. time-scale, and so the ^1H n.m.r. spectrum under these conditions displays one signal for the CMe groups and an (AB)$_2$ pattern for the C$_6$H$_4$ protons. Coalescence of the cage methyl signals is in accord with the boron β to the CMe groups being involved in the B–H⇀Mo bond. Unfortunately, the ^{11}B-{^1H} n.m.r. spectrum was not sufficiently well resolved in the region of innocent cage BH groups to allow satisfactory two-dimensional ^{11}B-{^1H} n.m.r. spectra to be recorded. Such data if available might have confirmed the B^β–H⇀Mo interaction proposed which, however, is very likely in view of earlier results.[12]

Reactions between the complexes (**4b**) or (**4d**) and PMe$_3$ leads to addition of the phosphine to the M(CO)(η^5-C_9H_7) fragment with a consequential lifting of the B–H⇀M interaction and affording, respectively, the complexes [MW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(PMe$_3$)(η^5-C_9H_7)(η^5-$C_2B_9H_9Me_2$)] (**4f**; M = Mo) and (**4g**; M = W).[4a] It was, therefore, of interest to investigate the reaction between one of the compounds of type (**5**) and PMe$_3$ to determine whether the phosphine would co-ordinate at the molybdenum atom or whether a CO co-ordinated to the tungsten atom would be replaced. Treatment of (**5a**) *with PMe*$_3$

at ambient temperatures afforded the complex $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(5g)**, data for which are given in Tables 1—3. Examination of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (see Experimental section) established that a $WPMe_3$ group was present. The singlet peak (δ −21.1 p.p.m.) showed strong $^{183}W\text{–}^{31}P$ coupling (410 Hz). The magnitude of this coupling is indicative of the presence of a direct W–P bond as exists in the tricarbonyl compound **(4g)** [δ −20.3 p.p.m., *J*(WP) 368 Hz] and in $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ [δ −26.3 p.p.m., *J*(WP) 408 Hz].[4] The latter dicarbonyl species has a $B\text{–}H\rightharpoonup W(PMe_3)(\eta^5\text{-}C_9H_7)$ group akin to the $B\text{–}H\rightharpoonup Mo(\eta^7\text{-}C_7H_7)$ fragment in **(5g)**. The ^1H, $^{13}C\text{-}\{^1H\}$, and ^{11}B n.m.r. data are in agreement with the formulation proposed. The ^1H and $^{13}C\text{-}\{^1H\}$ spectra show that the cage CMe groups are non-equivalent as a result of the asymmetry introduced by changing the $W(CO)_2$ group in **(5a)** for the $W(CO)(PMe_3)$ moiety in **(5g)**. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum shows a diagnostic resonance for the μ-C nucleus at δ 312.5 p.p.m., and a single CO peak at δ 241.9 p.p.m. which is a doublet [*J*(PC) 9 Hz]. The ^{11}B n.m.r. spectrum had a doublet resonance at δ 1.7 p.p.m. [*J*(BH) 86 Hz], as required by the presence of the $B\text{–}H\rightharpoonup Mo$ bridge linkage.

The new compounds described herein extend the range of dimetal complexes containing tungsten–molybdenum bonds with bridging alkylidyne groups. Moreover, in all the new species the carbaborane ligands display exopolyhedral $B\text{–}H\rightharpoonup Mo$ bonding.

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 used in chromatography columns (*ca.* 20 cm in length and 3.0 cm in diameter) was BDH aluminium oxide (Brockman Activity II). The n.m.r. spectra were recorded with JEOL JNM FX90Q, GX270, and GX400 spectrometers, and the i.r. spectra with Nicolet MX5 and Perkin-Elmer FT1600 spectrometers. The $^{31}P\text{-}\{^1H\}$ n.m.r. chemical shifts (δ) are positive to high frequency of 85% H_3PO_4 (external). The complexes $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$[13] and $[Mo(CO)_2(NCMe)(\eta^7\text{-}C_7H_7)][BF_4]$[14] were prepared as described previously. The reagents $[M(\equiv CC_6H_4Me\text{-}4)(O_2CCF_3)(CO)_2(py)_2]$ (M = Mo or W) were synthesised by the method used to obtain $[W(\equiv CC_6H_4Me\text{-}4)(O_2CCF_3)(CO)_2(tmen)]$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine).[6a,15] The salts $Na_2[C_2B_9H_9Me_2]$, $Na_2[C_2B_9H_{11}]$,[16] and $Na_2[C_2B_{10}H_{10}Me_2]$[17] were prepared in thf by literature methods. The salt $Na_2[C_2B_9H_{10}Me]$ was obtained from $C_2B_{10}H_{11}Me$ in a similar procedure to that used for $Na_2[C_2B_9H_9Me_2]$. The reagents **(1a)**, **(1d)**, **(1f)**, **(1g)**,[5,8,10] and **(2a)**[12] were synthesised by methods previously described.

The compound $[W(\equiv CC\equiv CBu^t)(O_2CCF_3)(CO)_2(NC_5H_4Me\text{-}4)_2]$, required for the synthesis of the salt **(1j)**, was prepared as follows. A thf (50 cm^3) solution of $HC\equiv CBu^t$ (4.0 cm^3, 32.5 mmol) at −40 °C was treated dropwise with $LiBu^n$ (20.3 cm^3 of a 1.6 mol dm^{-3} solution in hexane), and the mixture was stirred and allowed to warm slowly to room temperature during which time butane was evolved. Stirring was continued, and a portion of the resulting solution was titrated against 0.1 mmol dm^{-3} HCl to determine the molarity of the $Li(C\equiv CBu^t)$ formed. A suspension of $[W(CO)_6]$ (3.52 g, 10.0 mmol) in Et_2O–thf (100 cm^3, 10:1) was cooled to −40 °C and stirred. One equivalent of the $Li(C\equiv CBu^t)$ reagent (*ca.* 22—24 cm^3) was added dropwise and the mixture was warmed to room temperature and stirred for 1 h to generate $Li[W\{C(O)C\equiv CBu^t\}(CO)_5]$ *in situ*. The resulting orange solution was cooled to −78 °C, and $(CF_3CO)_2O$ (1.5 cm^3, 10.6 mmol) in thf (20 cm^3) was added dropwise over 15 min. The mixture became red, and CO was evolved. On warming to 0 °C, 4-methylpyridine (7 cm^3, excess) was added and mixture was stirred for 2 h at room temperature, CO being released. Solvent was removed *in vacuo*, and orange residue was dissolved in CH_2Cl_2 (25 cm^3) and chromatographed. Elution with CH_2Cl_2 gave a yellow eluate from which solvent was removed *in vacuo*. Crystallisation of the solid from CH_2Cl_2–light petroleum (*ca.* 50 cm^3, 1:3) afforded yellow *microcrystals* of $[W(\equiv CC\equiv CBu^t)(O_2CCF_3)(CO)_2(NC_5H_4Me\text{-}4)_2]$ (4.62 g, 73%) (Found: C, 43.0; H, 4.0; N, 4.4. $C_{23}H_{23}F_3N_2O_4W$ requires C, 43.7; H, 3.7; N, 4.2%), $\nu_{max.}$(CO) at 1 995s, 1 913vs, and 1 716m cm^{-1} in CH_2Cl_2. N.m.r. (in CD_2Cl_2): ^1H, δ 1.24 (s, 9 H, Bu^t), 2.39 (s, 6 H, Me-4), 7.17, and 8.57 [$(AB)_2$, 8 H, C_5H_4N, *J*(AB) 7]; $^{13}C\text{-}\{^1H\}$, δ 245.7 [C≡W, *J*(WC) 206], 223.1 [CO, *J*(WC) 170], 160.9 [q, CF_3CO_2, *J*(FC) 37], 151.7, 151.4, 126.6 (C_5H_4N), 116.4 [q, CF_3, *J*(FC) 290], 96.9 [$C\equiv CBu^t$, *J*(WC) 60 Hz], 80.6 ($C\equiv CBu^t$), 30.9 (CMe_3), 28.0 (CMe_3), and 21.4 p.p.m. (Me-4).

Analytical and physical data for the other new compounds are given in Table 1.

Preparation of the Mononuclear Molybdenum and Tungsten Alkylidyne Complexes.—(*i*) The compound $[Mo(\equiv CC_6H_4Me\text{-}4)(O_2CCF_3)(CO)_2(py)_2]$ (2.10 g, 3.99 mmol) was dissolved in thf (50 cm^3) and treated with $Na_2[C_2B_9H_{11}]$ (4.0 mmol) in thf (*ca.* 50 cm^3). The mixture was stirred for 4 h, and then $NEt_4Cl\cdot H_2O$ (1 g, excess) was added, with stirring continued for 10 min. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 (10 cm^3), and the mixture was chromatographed. Elution of the column with CH_2Cl_2 removed a red band. Removal of solvent *in vacuo* afforded a red oil which was sufficiently pure for use in synthesis. Washing the oil several times with Et_2O eventually gave red *microcrystals* of $[NEt_4][Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ **(1b)** (1.53 g).

(*ii*) In a similar synthesis, the compound $[W(\equiv CC\equiv CBu^t)(O_2CCF_3)(CO)_2(NC_5H_4Me\text{-}4)_2]$ (2.53 g, 4.00 mmol) in thf (50 cm^3) was treated with $Na_2[C_2B_9H_9Me_2]$ (4.0 mmol) in thf (50 cm^3). The salt $NEt_4Cl\cdot H_2O$ (1 g) was added, yielding red *microcrystals* of $[NEt_4][W(\equiv CC\equiv CBu^t)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(1j)** (1.50 g).

(*iii*) As in the preparation of **(1b)**, the compound $[W(\equiv CC_6H_4Me\text{-}4)(O_2CCF_3)(CO)_2(py)_2]$ (2.46 g, 4.00 mmol) in thf (50 cm^3) was treated with $Na_2[C_2B_9H_{10}Me]$ (4.0 mmol) in thf (50 cm^3). Following addition of $NEt_4Cl\cdot H_2O$ (1.0 g), red *microcrystals* of $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{10}Me)]$ **(3)** (2.03 g) were obtained.

Preparation of the Dimetal Compounds.—(*i*) Compound **(1j)** (0.25 g, 0.40 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (0.20 g, 0.46 mmol) was added. The mixture was stirred for 1 h. Solvent was reduced in volume *in vacuo* to *ca.* 10 cm^3, and the solution chromatographed. The column was eluted with CH_2Cl_2–light petroleum, initially in 3:1 proportion but increasing to pure CH_2Cl_2. The solvent was removed *in vacuo* from the green eluate and the residue was crystallised from CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1:10) at 25 °C to yield green *microcrystals* of $[MoW(\mu\text{-}CC\equiv CBu^t)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(4a)** (0.19 g).

(*ii*) In a similar experiment, compound **(1f)** (0.16 g, 0.41 mmol) in CH_2Cl_2 (25 cm^3) was treated with $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (0.20 g, 0.46 mmol) giving green *microcrystals* of $[Mo_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **(4e)** (0.13 g). $^{31}P\text{-}\{^1H\}$ N.m.r. (CD_2Cl_2): δ 172.1 (s) p.p.m.

(*iii*) The complexes **(5a)**—**(5f)** and **(6)** were all prepared by the procedure described above for the synthesis of **(4a)**, using the following combinations of reagents.

(*a*) The complex [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C$_7$H$_7$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**5a**) (0.08 g) was obtained from (**1d**) (0.25 g, 0.39 mmol) and [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] (0.17 g, 0.46 mmol).

(*b*) The reagents (**1g**) (0.25 g, 0.39 mmol) and [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] (0.17 g, 0.46 mmol) yielded [MoW(μ-CC$_6$H$_4$Me-2)(CO)$_2$(η^7-C$_7$H$_7$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**5b**) (0.07 g).

(*c*) For [MoW(μ-CC≡CBu^t)(CO)$_2$(η^7-C$_7$H$_7$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**5c**) (0.14 g), the salt (**1j**) (0.25 g, 0.40 mmol) was treated with [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] (0.17 g, 0.46 mmol).

(*d*) Compound (**1b**) (0.21 g, 0.41 mmol) and [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] (0.17 g, 0.46 mmol) gave [Mo$_2$(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C$_7$H$_7$)(η^5-C$_2$B$_9$H$_{11}$)] (**5d**) (0.16 g).

(*e*) Similarly, treatment of compound (**1a**) (0.24 g, 0.40 mmol) with [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] (0.17 g, 0.46 mmol) afforded [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C$_7$H$_7$)(η^5-C$_2$B$_9$H$_{11}$)] (**5e**) (0.19 g).

(*f*) Similarly, compound (**3**) (0.25 g, 0.40 mmol) and [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] (0.17 g, 0.46 mmol) afforded [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C$_7$H$_7$)(η^5-C$_2$B$_9$H$_{10}$Me)] (**5f**) (0.18 g).

(*g*) The complex [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^7-C$_7$H$_7$)(η^6-C$_2$B$_{10}$H$_{10}$Me$_2$)] (**6**) (0.08 g) was obtained from (**2a**) (0.25 g, 0.39 mmol) and [Mo(CO)$_2$(NCMe)(η^7-C$_7$H$_7$)][BF$_4$] (0.17 g, 0.46 mmol).

Reaction with Trimethylphosphine.—Complex (**5a**) (0.23 g, 0.33 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3) and treated with PMe$_3$ (3.3 cm^3 of a 0.10 mol dm^{-3} solution in Et$_2$O), and the mixture was stirred for 24 h. The resulting solution was reduced in volume *in vacuo* to *ca.* 5 cm^3 and chromatographed. Elution with CH$_2$Cl$_2$ removed a red eluate. Solvent was removed *in vacuo* and the residue was crystallised from CH$_2$Cl$_2$–light petroleum (*ca.* 10 cm^3, 1:10) to give red *microcrystals of* [MoW(μ-CC$_6$H$_4$Me-4)(CO)(PMe$_3$)(η^7-C$_7$H$_7$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**5g**) (0.20 g). ^{31}P-{^{1}H} N.m.r. (CD$_2$Cl$_2$): δ −21.1 p.p.m. [J(WP) 410 Hz].

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