Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 109.[1] Reactions of Tungsten–Molybdenum Dimetal Compounds bearing Carbaborane Ligands with Alkynes; Crystal Structure of $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(\eta\text{-}C_7H_7)]$ *

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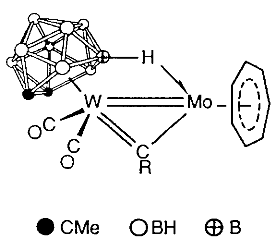
Treatment of the compounds $[MoW(\mu\text{-}CR)(CO)_2(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ in thf (tetrahydrofuran) with the alkynes MeC≡CMe or EtC≡CEt affords the complexes $[MoW(\mu\text{-}CR)(CO)(\eta\text{-}R'C_2R')(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ ($R = C_6H_4Me$-4, $R' = Me$; $R = C{\equiv}CBu^t$, $R' = Me$ or Et). Similar reactions between $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ and MeC≡CMe or PhC≡CPh yield the related species $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}R'C_2R')(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ ($R' = Me$ or Ph). The reaction of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ with MeC≡CMe in toluene at 100 °C gives a novel dimetal complex $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(\eta\text{-}C_7H_7)]$, the structure of which was established by X-ray diffraction. The Mo–W bond [2.922(1) Å] is symmetrically bridged by a $\mu\text{-}C_4Me_4$ fragment, the carbon atoms of which are linked to both metal atoms in the η^4 fashion. The molybdenum atom carries the $\eta\text{-}C_7H_7$ ligand, and the tungsten atom is ligated by a $CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2$ fragment. In the latter the $CH(C_6H_4Me\text{-}4)$ moiety forms a bridge between the tungsten [W–C 2.226(8) Å] and a boron atom [B–C 1.54(1) Å] in the pentagonal face of the cage. This boron atom is in the β site (BβBCC) with respect to the carbon atoms, and all the atoms of the ring are bonded to the tungsten, but the connectivities are somewhat asymmetric [2.227(9)–2.472(9) Å]. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR data for the new compounds are reported and discussed.

The Mo–W bonds in the compounds $[MoW(\mu\text{-}CR)(CO)_2(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ ($R = C_6H_4Me$-4 **1a** or $C{\equiv}CBu^t$ **1b**), $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ **1c**, and $[MoW(\mu\text{-}CR)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ ($\eta^5\text{-}C_9H_7$ = indenyl, $R = C_6H_4Me$-4 **2a** or $C{\equiv}CBu^t$ **2b**) are bridged both by alkylidyne groups and by B–H→Mo three-centre two-electron linkages.[2] These structural features, and the fact that the complexes are electronically unsaturated with 32 c.v.e.s (cluster valence electrons), make them potentially interesting as precursors for the synthesis of other molybdenum–tungsten species.[3] The presence of the activated B–H→Mo and μ-CR groups in proximity at the dimetal centres can lead to novel reactions on treatment with substrate molecules. Thus compound **2a** with EtC≡CEt in toluene solution affords the complex $[MoW\{\mu\text{-}\sigma,\eta\text{-}CH(C_6H_4Me\text{-}4)\text{-}C_2B_9H_8Me_2\}(CO)_3(\eta\text{-}EtC_2Et)(\eta^5\text{-}C_9H_7)]$ **3**, the structure of which has been established by X-ray diffraction.[3a] The metal–metal separation [2.604(1) Å] is sufficiently short to imply a Mo=W bond.

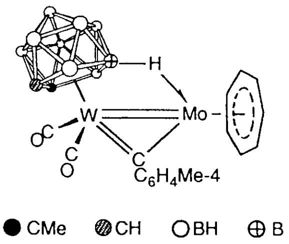
In this paper we extend the studies with alkynes, describing reactions of the species **1** with MeC≡CMe, EtC≡CEt and PhC≡CPh.

Results and Discussion

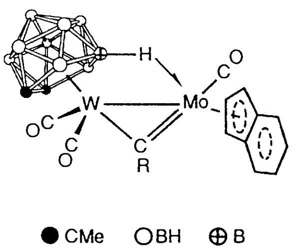
Heating a mixture of compound **1a** in thf (tetrahydrofuran) at 65 °C with but-2-yne affords the complex $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **4a**, in which the alkyne has displaced a CO group ligating the tungsten atom. The IR spectrum (Table 1) shows, as expected, only one



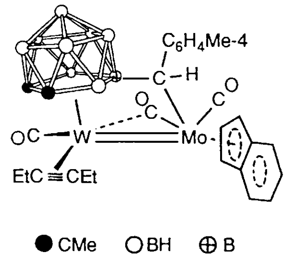
	R
1a	C_6H_4Me-4
1b	$C{\equiv}CBu^t$



1c



	R
2a	C_6H_4Me-4
2b	$C{\equiv}CBu^t$



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* 2(η^7)-Cycloheptatrienyl[1(7,8,9,10,11-η)-7,8-dimethyl-7,8-dicarba-*nido*-undecaboran-10-yl(*p*-tolyl)methyl-1κ*C*][μ-(2,3,4,5-η:2,3,4,5-η)-3,4-dimethylhexa-3-ene-2,5-diylidene]molybdenumtungsten (*Mo–W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical[a] and physical data for the molybdenum–tungsten complexes

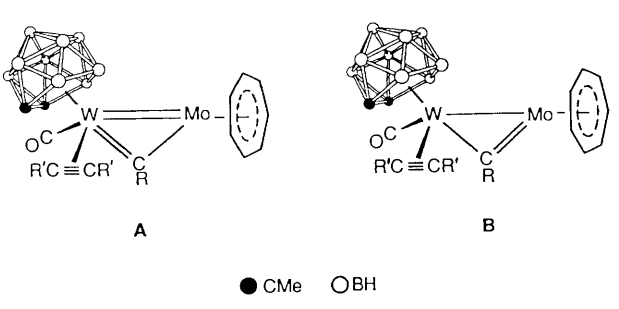
Compound[b]	Yield (%)	$\nu_{max}(CO)^c$/cm^{-1}	Analysis (%) C	Analysis (%) H
4a $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	27	2000	40.5 (41.1)	4.5 (5.0)
4b $[MoW(\mu\text{-}CC{\equiv}CBu^t)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	48	1995	39.1 (39.1)	4.6 (5.3)
4c $[MoW(\mu\text{-}CC{\equiv}CBu^t)(CO)(\eta\text{-}EtC_2Et)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$	41	2012	41.8 (40.9)	5.1 (5.6)
4d $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$	60	2028	38.5 (39.3)	4.9 (4.7)
4e $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}PhC_2Ph)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$	65	2026	47.0 (47.9)	5.1 (4.5)
5 $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(\eta\text{-}C_7H_7)]$	20		43.6 (43.7)	5.3 (5.6)

[a] Calculated values are given in parentheses. [b] All complexes are tan in colour, except **5** which is red. [c] Measured in CH_2Cl_2. All spectra show a broad band at *ca.* 2550 cm^{-1} due to B–H.

Table 2 Hydrogen-1 and carbon-13 NMR data[a] for the complexes

Compound	^1H (δ)	$^{13}C^b$ (δ)
4a	1.82, 2.04 (s × 2, 6 H, CMe), 2.51 (s, 3 H, Me-4), 3.08, 3.36 (s × 2, 6 H, C_2Me_2), 5.09 (s, 7 H, C_7H_7), 6.74, 7.36 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	379.0 (μ-C), 201.6 (CO), 161.5 [$C^1(C_6H_4)$], 150.4 (*C*$_2$Me$_2$), 134.5, 128.1 (C_6H_4), 126.6 (*C*$_2$Me$_2$), 120.2 (C_6H_4), 91.4 (C_7H_7), 65.6, 64.7 (*C*Me), 29.9, 29.3 (C*Me*), 25.2, 21.3, 20.4 (C$_2$*Me*$_2$ and Me-4)
4b[c]	1.56 (s, 9 H, Bu^t), 2.25, 2.34 (s × 2, 6 H, CMe), 3.05, 3.32 (s × 2, 6 H, C_2Me_2)	351.5 (μ-C), 201.6 (CO), 162.7 (C≡*C*Bu^t), 153.6, 126.5 (*C*$_2$Me$_2$), 98.5 (*C*≡CBu^t), 91.5 (C_7H_7), 68.7 64.5 (*C*Me), 31.4 (C*Me*$_3$), 31.0 (*C*Me$_3$), 30.1, 30.0 (C*Me*), 25.0, 21.1 (C$_2$*Me*$_2$)
4c	1.43 [t, 3 H, CH$_2$*Me*, *J*(HH) 8], 1.57 (s, 9 H, Bu^t), 1.69 [t, 3 H, CH$_2$*Me*, *J*(HH) 7], 2.31, 2.39 (s × 2, 6 H, CMe), 2.87–3.04 (m, 1 H, C*H*$_2$Me), 3.29–3.58 (m, 2 H, C*H*$_2$Me), 4.48–4.66 (m, 1 H, C*H*$_2$Me), 5.33 (s, 7 H, C_7H_7)	351.1 [μ-C, *J*(WC) 139], 202.6 [CO, *J*(WC) 162], 162.1 (C≡*C*Bu^t), 159.4 [*C*$_2$Et$_2$, *J*(WC) 46], 130.4 (*C*$_2$Et$_2$), 98.8 [*C*≡CBu^t, *J*(WC) 20], 91.8 (C_7H_7) 68.8, 64.4 (*C*Me), 36.0 (*C*H$_2$Me), 31.5 (C*Me*$_3$) 31.3 (*C*Me$_3$), 31.2 (*C*H$_2$Me), 30.6, 30.3 (*C*Me), 15.6, 15.2 (CH$_2$*Me*)
4d	[d]0.87 (br s, 3 H, CMe), 2.54 (s, 3 H, Me-4), 3.00, 3.51 (s × 2, 6 H, C_2Me_2), 4.02 (br s, 1 H, CH), 5.21 (s, 7 H, C_7H_7), 6.58, 7.02 [d × 2, 2 H, C_6H_4, *J*(HH) 8], 7.37 [d, 2 H, C_6H_4, *J*(HH) 8]	382.4 (μ-C), 200.0 (CO), 160.6 [$C^1(C_6H_4)$], 150.9 (*C*$_2$Me$_2$), 136.4 (C_6H_4), 129.7 (*C*$_2$Me$_2$), 129.0, 120.6 (C_6H_4), 91.0 (C_7H_7), 65.7 (*C*Me), 57.3 (CH), 30.8 (*C*Me), 23.8, 22.6 (C$_2$*Me*$_2$), 21.3 (Me-4)
4e	1.30 (s, 3 H, CMe), 2.57 (s, 3 H, Me-4), 2.79 (br s, 1 H, CH), 5.04 (s, 7 H, C_7H_7), 6.98 (br m, 2 H, C_6H_4), 7.42–7.65 (m, 10 H, Ph), 8.15 [d, 2 H, C_6H_4, *J*(HH) 7]	377.5 (μ-C), 200.4 (CO), 161.6 [$C^1(C_6H_4)$], 147.0 (*C*$_2$Ph$_2$), 140.2, 138.6 [C^1(Ph)], 135.4 (C_6H_4), 132.8 (*C*$_2$Ph$_2$), 131.0, 130.0, 129.7, 129.4, 128.9, 128.2, 119.9 (Ph and C_6H_4), 92.7 (C_7H_7), 61.5 (*C*Me), 59.0 (CH), 31.2 (C*Me*), 21.1 (Me-4)
5	[e] 1.18 [s, 3 H, CMe ($C_2B_9H_8Me_2$)], 1.82, 1.84 [s × 2, 6 H, C(Me)C(*Me*)C(*Me*)C(Me)], 2.21 2.31, 2.47, 2.67 [s × 4, 12 H, Me-4, CMe ($C_2B_9H_8Me_2$), and C(*Me*)C(Me)C(Me)C(*Me*)], 5.09 (br s, 7 H, C_7H_7), 6.38, 6.82 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	211.4 [*C*(Me)C(Me)C(Me)*C*(Me), *J*(WC) 99], 141.4 [$C^1(C_6H_4)$], 133.8, 128.2, 127.9 (C_6H_4), 86.7 [C(Me)*C*(Me)*C*(Me)C(Me)], 85.8 (C_7H_7), 85.4 [C(Me)*C*(Me)*C*(Me)C(Me)], 77.0 [vbr, *C*(H)C_6H_4Me-4], 71.0, 68.4 [*C*Me ($C_2B_9H_8Me_2$)], 30.9, 30.4 [C*Me* ($C_2B_9H_8Me_2$)], 27.4, 27.2 [C(*Me*)C(Me)C(Me)C(*Me*)], 20.6 (Me-4), 17.1, 13.9 [C(Me)C(*Me*)C(*Me*)C(Me)]

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measurements in CD_2Cl_2 at ambient temperatures unless otherwise stated. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [c] Measured in $CDCl_3$. [d] Measured at −60 °C. [e] Resonance due to BC(*H*)C_6H_4-Me-4 not observed.

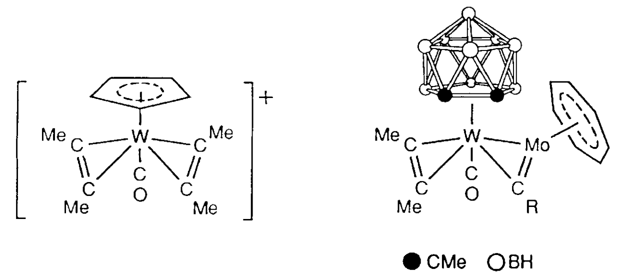


	R	R'
4a	C_6H_4Me-4	Me
4b	C≡CBu^t	Me
4c	C≡CBu^t	Et

carbonyl stretching band, and this is observed at 2000 cm^{-1}. The ^1H NMR spectrum (Table 2) displays the resonances for the C_6H_4Me-4 and C_7H_7 groups, as well as two signals for the non-equivalent CMe groups of the $C_2B_9H_9Me_2$ cage at δ 1.82 and 2.04, and two peaks due to the non-equivalent Me substituents of the alkyne at δ 3.08 and 3.36. There is no high-field resonance indicating the presence of a B–H→Mo linkage. By itself the absence of the signal is insufficient evidence for the absence of a B–H→Mo group since the quartet signals [*J*(BH) *ca.* 80 Hz] for this moiety are often weak.[2a] Indeed, no resonance for a B–H→Mo group is seen in the ^1H NMR spectrum of compound **1a**. However, the ^{11}B-{^1H} NMR spectrum of **4a** showed no deshielded resonance for a B–H→Mo group as observed in the spectrum of the precursor **1a** at δ 11.5. The ^{11}B-{^1H} NMR spectrum of **4a** did, however, display five broad overlapping signals in the range δ −2.4 to −11.7, as expected for BH groups not involved in exopolyhedral bonding.

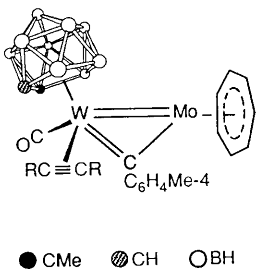
The ^{13}C-{^1H} NMR spectrum of compound **4a** showed a diagnostic signal for the μ-C nucleus of the bridging alkylidyne group at δ 379.0. This signal is relatively deshielded, as found for the μ-C nuclei in other structurally related electronically unsaturated dimetal species, in which the metal atoms do not attain 18-electron valence shells.[2a,4] The ^{13}C-{^1H} NMR spectrum also shows peaks at δ 126.6 and 150.4, due to the ligated carbon atoms of the alkyne. The latter chemical shift is relatively deshielded and is in the region expected if the MeC≡CMe group were donating more than two electrons to the tungsten centre,[5] a feature we shall refer to later.

Treatment of compound **1b** with either MeC≡CMe or EtC≡CEt affords the complexes [MoW(μ-CC≡CBu^t)(CO)(η-

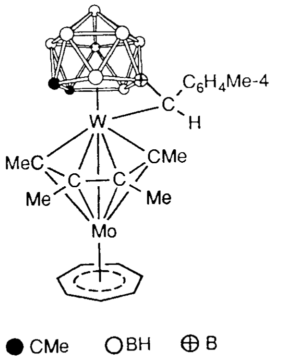


4a or **4b**

Scheme 1 R = C_6H_4Me-4 or C≡CBu^t



	R
4d	Me
4e	Ph



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$R'C_2R')(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R′ = Me **4b** or Et **4c**), respectively. Data characterising these products are given in Tables 1 and 2. The spectroscopic features are very similar to those for complex **4a**, except for features arising from the substitution of the C≡CBu^t fragment for the C_6H_4Me-4 group. In the ^{13}C-{^{1}H} NMR spectra of **4b** and **4c** the ligated carbons of the alkylidyne groups give rise to signals at δ 351.5 and 351.1, respectively. These peaks are significantly more deshielded than the corresponding resonance observed (δ 293.7) in the spectrum of the precursor **1b**.[2a]

The ^{13}C-{^{1}H} NMR spectrum of complex **4c** was of sufficiently good quality to display ^{183}W satellite peaks on the resonances for the CO and μ-C groups, and on one of the Et*C*≡*C*Et carbons, and also surprisingly on the *C*≡CBu^t nucleus as well (Table 2). The alkynyl carbons of the hex-3-yne give rise to signals at δ 159.4 [*J*(WC) 46 Hz] and 130.4. The latter shows no ^{183}W–^{13}C coupling, which suggests that it is probably less than 10 Hz.

We referred above to the observation of two distinct Me*C*≡*C*Me resonances in the ^{13}C-{^{1}H} NMR spectrum of compound **4a**. Moreover, in the ^{13}C-{^{1}H} NMR spectra of all three complexes **4a**–**4c** the two resonances for the ligated carbon atoms of the alkyne ligands are relatively disparate. This phenomenon has been previously observed in the spectrum of the salt $[W(CO)(\eta\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][PF_6]$ which displays signals for the MeC_2Me nuclei at δ 142.2 and 160.4.[6] The observation of two peaks for the alkyne carbons in the salt, and in the complexes **4**, implies that the alkyne molecules are not rotating on the NMR time-scale at room temperature. However, for the salt $[W(CO)(\eta\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][PF_6]$ site exchange of the MeC_2Me nuclei becomes fast at 155 °C.[6]

The chemical shifts observed for the ligand carbon atoms of the alkyne in the ^{13}C-{^{1}H} NMR spectra of the compounds **4** and the salt $[W(CO)(\eta\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][PF_6]$ are of interest. The two resonances for the latter (see above) occur towards the lower and the upper ends of the range (*ca.* δ 140–180) of chemical shifts anticipated for a co-ordinated alkyne donating three electrons to a metal centre, based on empirical correlations discussed elsewhere.[5] If each MeC_2Me molecule donates three electrons, the metal atom in the cation would attain an 18-electron valence shell. In the case of the compounds **4a**–**4c** the peak observed in each pair of signals at *ca.* δ 127–130 is in the range expected for an alkyne donating two electrons to a metal centre, while the resonance at *ca.* δ 150–159 corresponds to the expected value for an alkyne donating three electrons to a metal atom. The empirical correlation between alkyne carbon chemical shifts and the number of electrons donated to the metal by the alkyne[5] is therefore ambiguous for the compounds **4**.

A satisfactory valence-electron count for the metal atoms in the compounds **3** and **4a**–**4c** depends on what assumptions are made regarding not only the number of electrons donated by the alkyne molecules, but also the number contributed to the metal centres by the $\eta^5\text{-}C_2B_9H_9Me_2$, $\eta^5\text{-}C_9H_7$ or $\eta\text{-}C_7H_7$ ligands, and whether the metal–metal linkages are single or double bonds. Normally the $\eta^5\text{-}C_2B_9H_9Me_2$, $\eta^5\text{-}C_9H_7$ and $\eta\text{-}C_7H_7$ groups are formally four-, five- and seven-electron donors, respectively. However, ring 'slippage' could lead to an η^3 bonding mode for the carbaborane cage, an η^3 co-ordination for the C_9H_7 group, and an η^5 mode for the C_7H_7 ring. Indeed there is evidence from X-ray diffraction data that in complex **3** the carbaborane cage is η^3 co-ordinated to the tungsten atom.[3a]

The hex-3-yne ligand in complex **3** shows signals at δ 172.0 and 178.2 in its ^{13}C-{^{1}H} NMR spectrum, typical of a three-electron donor ligand even though only one alkyne group is present. This seeming anomally can be explained by involving resonance between a four-electron donor EtC≡CEt and a slipped cage donating two electrons to the W atom, and a two-electron donor EtC≡CEt and an η^5 carbaborane cage donating four electrons. Such a situation would leave the W atom with a 16-electron valence shell, assuming a Mo=W double bond, and two electrons contributed by the CO group.

The representations **A** and **B** shown for the compounds **4a**–**4c** assumes electron-pair donation by the alkynes. In **A** the presence of μ-C=W and Mo=W bonds would result in 18- and 16-valence-electron counts at the W and Mo atoms, respectively. In **B** both metal centres have formally 16-valence-electron shells. Irrespective of whether representation **A** or **B** is preferred, and the former seems intuitively more satisfying, these dimetal compounds are 30 c.v.e. species. However, if the alkyne molecules contribute four electrons, the complexes **4** are less unsaturated with 32 c.v.e., and a different canonical form for the Mo(μ-C)W ring systems would be required.

It is interesting to note the structural relationship between the cation of the salt $[W(CO)(\eta\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][PF_6]$ and the compounds **4a** and **4b** depicted in Scheme 1. This isolobal relationship arises through mapping between the groups $\eta\text{-}C_5H_5^-$ and $\eta^5\text{-}C_2B_9H_9Me_2^{2-}$, and between the fragments CMe and $Mo(\eta^7\text{-}C_7H_7)$, resulting from similarities in frontier orbitals and electron counts.[7]

Reactions between complex **1c** and the alkynes MeC≡CMe and PhC≡CPh were next investigated. We have previously observed that compounds containing the ligand $\eta^5\text{-}C_2B_9H_{10}Me$ in some instances afford reaction products in higher yield than those obtained employing analogous reagents containing the more bulky $\eta^5\text{-}C_2B_9H_9Me_2$ group.[2a] This observation is borne out by the fact that complex **1c** reacts with MeC≡CMe and with PhC≡CPh to give, respectively, the compounds $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}RC_2R)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ (R = Me **4d** or Ph **4e**) in appreciably higher yield than the species **4a**–**4c**. The complexes **4d** and **4e** were characterised by the data given in Tables 1 and 2. As with compounds **4a**–**4c** alternative representations of the electron distribution within the dimetal systems are possible with **4d** and **4e**. We have chosen a representation with the Mo and W atoms having 16- and 18-valence-electron shells, respectively, with the alkynes donating an electron pair. Although the spectroscopic properties of **4d** and **4e** are essentially similar to those of **4a**–**4c**, there are two aspects of interest. First, both the complexes **4d** and **4e** are formed as single isomeric species. One might have expected formation of a mixture of two diastereomers as the ligand η^5-

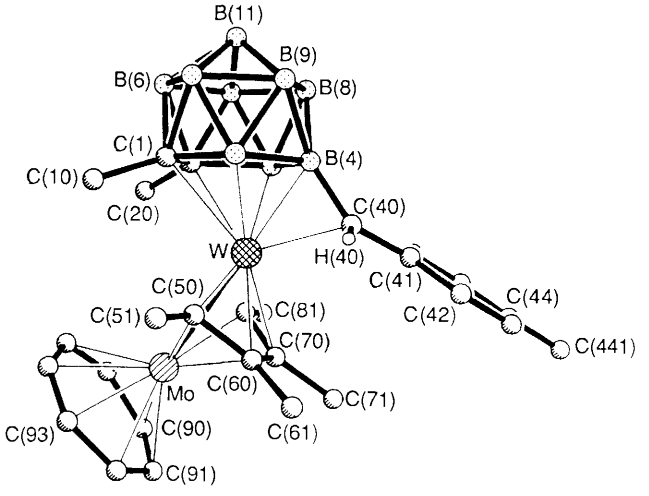

Fig. 1 The structure of the molecule $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(\eta\text{-}C_7H_7)]$ **5**, showing the atom labelling scheme

$C_2B_9H_{10}Me$ has no plane of symmetry and the two CO groups in the precursor **1c** are inequivalent.[2a] In the absence of X-ray crystallographic data it is impossible to say which isomer is formed, or indeed if the isomer formed is the same for **4d** and **4e**. The second point of interest is that the compounds **4d** and **4e** show a fluxional process resulting in certain signals of the C_6H_4Me-4 group in the ^1H NMR spectrum being broad at room temperature. Thus the complex **4d** displays a broad signal at δ 6.76 and a doublet at δ 7.37 due to the C_6H_4 aromatic protons at ambient temperatures and three doublets of relative intensity 1 : 1 : 2 at δ 6.58, 7.02 and 7.37 in the spectrum measured at −60 °C. This is indicative of restrictive rotation of the C_6H_4Me-4 group. It is, however, not apparent why the complexes **4d** and **4e** show this behaviour and compound **4a** containing the more bulky η^5-$C_2B_9H_9Me_2$ cage does not. One possibility is that the C_6H_4Me-4 group in complex **4a** is undergoing restricted rotation, but that the resonances for the aromatic protons are coincident in the ^1H NMR spectrum. This possibility is strengthened by the observation that in the ^{13}C-$\{^1H\}$ NMR spectrum the C_6H_4 signal at δ 120.2 is broader than that of the resonance at δ 128.1.

During the formation of complex **4a** from the reactants at 65 °C formation of trace amounts of a red species was observed. When the reaction was repeated in toluene at 100 °C using an excess of MeC≡CMe, or when compound **4a** was treated with MeC≡CMe, the same product was isolated. The latter was identified as the compound $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4\text{-}Me\text{-}4)C_2B_9H_8Me_2\}(\eta\text{-}C_7H_7)]$ **5** by the data given in Tables 1 and 2, and by an X-ray diffraction study. The results of the latter are summarised in Table 3, and the structure of the molecule is shown in Fig. 1.

Compound **5** contains no CO group, thus explaining the absence of any carbonyl stretching band in the IR spectrum. The complex contains a Mo–W bond [2.922(1) Å] spanned by a C(Me)C(Me)C(Me)C(Me) group, formed by a combination of two but-2-yne molecules. The μ-C_4Me_4 fragment formally contributes six electrons to the dimetal system. As expected, the molybdenum atom carries the C_7H_7 ring, the carbon atoms of which are disordered (see Experimental section). The tungsten atom is ligated by a $CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2$ group such that the $CH(C_6H_4Me$-4) moiety forms a bridge between the tungsten [W–C(40) 2.226(8) Å] and a boron atom [B(4)–C(40) 1.54(1) Å] in the pentagonal face of the cage. This boron atom is in the β site ($\overline{B\mathit{B}BCC}$) with respect to the carbon atoms, and all the atoms of the ring are bonded to the tungsten. However, the connectivities are somewhat different with W–B(4) [2.227(9) Å] being the shortest distance. This type of cage–metal bonding has been observed previously in $[Rh\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_{10}\}(CO)(PPh_3)]$[8a] and in $[NEt_4][Mo\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(CO)_3]$.[8b] The W–C(40) distance in compound **5** [2.226(8) Å] is similar to those found (average 2.238 Å) in several complexes in which tungsten is bonded to a primary alkyl group.[9] There have been no reports of W–C distances involving secondary alkyl groups as exists in complex **5**. Interestingly, the W–C(40) separation is appreciably shorter than the corresponding distance in the aforementioned rhodium compound $[Rh\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_{10}\}(CO)(PPh_3)]$ [2.374(3) Å]. In the latter the Rh–C distance is outside the normal σ bond range.[8a] The bonding of the $CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2$ fragment in compound **5** contrasts with that found for this moiety in complex **3** where it spans the metal–metal bond.[3a]

Compound **5** is electronically unsaturated with 30 c.v.e.s, and yet the Mo–W separation is appreciably longer than those found in the compound **2a** [2.657(2) Å],[2b] **3** [2.604(1) Å],[3a] $[MoW(\mu\text{-}PPh_2)\{\mu\text{-}C(OH)C(C_6H_4Me\text{-}4)\}(CO)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{11})]$ [2.713(1) Å] and $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ [2.708(1) Å],[3c] all of which have 32 c.v.e.s. Indeed, the Mo–W distance [2.922(1) Å] in compound **5** is comparable with those found in the electronically saturated (48 c.v.e.) trimetal complex $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ [2.881(3) and 2.867(3) Å][10] and the electronically saturated (34 c.v.e.) dimetal compound $[MoW\{\mu\text{-}C(C_6H_4\text{-}OMe\text{-}2)C(Me)O\}(CO)_4(\eta\text{-}C_5H_5)_2]$ [2.935(1) Å].[11] In the trimetal anionic complex there are two exopolyhedral B–H⇀Mo bonds so that formally the η^5-$C_2B_9H_9Me_2$ cage ligating the W atom donates eight electrons to the Mo_2W triangle. It would appear that the metal–metal distances in these complexes are strongly influenced by the steric and bonding requirements of the bridging ligands. Hence an electronically unsaturated dimetal compound like **5** can have metal–metal distances corresponding to single bonds, and conversely electronically saturated dimetal compounds (34 c.v.e.), *e.g.* $[MnW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)O\}(CO)_5(\eta\text{-}C_5H_5)]$ [2.696(1) Å],[11] can have very short metal–metal separations, as if a multiple bond were present.

The attachment of the μ-C_4Me_4 group to the dimetal centre in complex **5** is of particular interest. All four carbon atoms in the chain are coplanar and are bonded to both metal atoms. The W–C distances to the outer carbons [C(50) and C(80)] are 1.985(8) and 1.999(8) Å, and to the inner carbons [C(60) and C(70)] are 2.270(9) and 2.279(8) Å. The Mo–C distances to the outer carbons are 2.222(8) and 2.224(8) Å, and to the inner carbons 2.239(7) and 2.243(7) Å. Thus the μ-C_4Me_4 ligand is tilted very slightly such that the outer carbons C(50) and C(80) are perceptibly closer to the W atom and the inner carbons C(60) and C(70) are slightly nearer the Mo atom. The angle between the Mo–W vector and the plane defined by C(50)C(60)C(70)C(80) is 81.4°, so the bonding is essentially symmetrical.

There are many known dimetal compounds in which a C_4R_4 (R = alkyl or aryl) fragment spans a metal–metal bond,[12] but in general the μ-C_4R_4 moiety bridges asymmetrically, displaying a pronounced lean towards one metal atom. These structures may therefore be formally described as metallacyclopentadiene species which are η^5 bonded to a second metal centre *via* the four carbon atoms and the metal–metal bond. Recently, however, several compounds have been described as having structures akin to complex **5** with a μ-C_4R_4 group symmetrically linked to two metal atoms in an η^4 bonding mode. These include several polynuclear niobium species reported by Cotton and Shang,[13] and the ditungsten complex $[W_2Cl_4(\mu\text{-}C_4Me_4)(\eta\text{-}C_5H_4Me)_2]$ described by Green and Mountford.[14]

Having established the molecular structure of complex **5** the NMR data (Table 2) can be readily interpreted. The ^{13}C-$\{^1H\}$ NMR spectrum shows a very deshielded resonance at δ 211.4 displaying ^{183}W satellites [*J*(WC) 99 Hz]. We assign this signal

Table 3 Selected internuclear distances (Å) and angles (°) for the complex $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(\eta^7\text{-}C_7H_7)]\cdot CH_2Cl_2$ **5**

Mo–W	2.922(1)	Mo–C(50)	2.222(8)	Mo–C(60)	2.239(7)	Mo–C(70)	2.243(7)
Mo–C(80)	2.224(8)	Mo–C(C_7H_7)	2.30*	W–C(1)	2.472(9)	W–C(2)	2.465(8)
W–B(3)	2.338(9)	W–B(4)	2.227(9)	W–B(5)	2.342(9)	W–C(40)	2.226(8)
W–C(50)	1.985(8)	W–C(60)	2.270(9)	W–C(70)	2.279(8)	W–C(80)	1.999(8)
C(1)–C(2)	1.59(1)	C(1)–B(5)	1.68(1)	C(1)–C(10)	1.50(1)	C(2)–C(20)	1.54(1)
C(2)–B(3)	1.66(1)	B(3)–B(4)	1.83(1)	B(4)–B(5)	1.81(1)	B(4)–C(40)	1.54(1)
C(40)–H(40)	0.96(8)	C(40)–C(41)	1.49(1)	C(50)–C(60)	1.49(1)	C(60)–C(70)	1.46(1)
C(70)–C(80)	1.49(1)	C(50)–C(51)	1.51(1)	C(60)–C(61)	1.51(1)	C(70)–C(71)	1.52(1)
C(80)–C(81)	1.50(1)						

Mo–W–C(40)	140.9(2)	Mo–W–C(50)	49.4(2)	Mo–W–C(60)	49.1(2)	C(40)–W–C(60)	94.5(3)
C(50)–W–C(60)	40.4(3)	Mo–W–C(70)	49.2(2)	C(40)–W–C(70)	94.2(3)	C(50)–W–C(70)	73.5(3)
C(60)–W–C(70)	37.4(3)	Mo–W–C(80)	49.5(2)	C(40)–W–C(80)	113.9(3)	C(50)–W–C(80)	96.4(3)
C(60)–W–C(80)	73.2(3)	C(70)–W–C(80)	40.0(3)	Mo–W–C(50)	42.8(2)	W–Mo–C(60)	50.1(2)
C(50)–Mo–C(60)	39.1(3)	W–Mo–C(70)	50.3(2)	C(50)–Mo–C(70)	70.1(3)	C(60)–Mo–C(70)	38.0(3)
W–Mo–C(80)	43.1(2)	C(50)–Mo–C(80)	83.9(3)	C(60)–Mo–C(80)	69.8(3)	C(70)–Mo–C(80)	38.9(3)
W–C(40)–B(4)	69.8(4)	W–C(40)–C(41)	119.2(5)	W–C(40)–H(40)	104(5)	B(4)–C(40)–H(40)	118(6)
B(4)–C(40)–C(41)	129.6(7)	C(41)–C(40)–H(40)	108(6)	W–C(50)–Mo	87.8(3)	W–C(50)–C(60)	80.1(4)
Mo–C(50)–C(60)	71.1(4)	W–C(60)–Mo	80.8(3)	W–C(60)–C(50)	59.5(4)	Mo–C(60)–C(50)	69.8(4)
W–C(60)–C(70)	71.7(5)	Mo–C(60)–C(70)	71.2(4)	C(50)–C(60)–C(70)	120.7(7)	W–C(70)–Mo	80.5(3)
W–C(70)–C(60)	71.0(5)	Mo–C(70)–C(60)	70.9(4)	W–C(70)–C(80)	59.8(4)	Mo–C(70)–C(80)	69.9(4)
C(60)–C(70)–C(80)	120.4(7)	W–C(80)–Mo	87.4(3)	W–C(80)–C(70)	80.2(4)	Mo–C(80)–C(70)	71.3(4)

* Mo–C(η-C_7H_7) distances 2.27(2)–2.34(2) Å.

to the outer carbons [C(50) and C(80)] of the μ-C_4Me_4 moiety, which give rise to accidentally coincident peaks. The signals at δ 27.2 and 27.4 are assigned to the Me groups attached to these carbons. The very deshielded peak due to C(50) and C(80) suggests that they are 'alkylidene like' in character. The similar carbon atoms in $[W_2Cl_4(\mu\text{-}C_4Me_4)(\eta\text{-}C_5H_4Me)_2]$ are also relatively deshielded (δ 185.4).[14] The inner carbons [C(60) and C(70)] give rise to separate resonances at δ 85.4 and 86.7. It is noteworthy that these signals are very much more shielded than the peak for C(50) and C(80). Moreover, the Me groups bonded to these inner carbons give rise to signals (δ 13.9 and 17.1) which are also more shielded that the resonances for the Me substituents attached to the outer carbons. A broad peak at δ 77.0 can be assigned to the *C*H(C_6H_4Me-4) nucleus. The corresponding resonance in the spectrum of $[NEt_4][Mo\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(CO)_3]$ is at δ 80.0.[8b] In the ^1H NMR spectrum of **5** there was no sign of a resonance for the C*H*(C_6H_4Me-4) proton, probably because it is too broad, or hidden by the broad η-C_7H_7 signal. Nevertheless, the hydrogen H(40) was located in the X-ray diffraction study.

The $^{11}B\text{-}\{^1H\}$ NMR spectrum shows a deshielded resonance at δ 9.0 due to the *B*C(H)C_6H_4Me-4 nucleus. This peak remained a singlet in a fully coupled ^{11}B spectrum indicating that it was not due to a BH group. The resonance for the corresponding boron nucleus in $[NEt_4][Mo\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(CO)_3]$ occurs at δ 8.7.[8b] The $^{11}B\text{-}\{^1H\}$ NMR spectrum of **5** also shows peaks at δ −10.2, −4.7, −1.2, 5.7 and 6.8. These resonances are due to the BH fragments. However, the signals at δ 5.7 and 6.8 are sufficiently deshielded to be ascribed to B–H⇀Mo bonds. This was disproved by the coupled ^{11}B spectrum which revealed ^{11}B–^1H coupling constants of 138 and 134 Hz, respectively. These values are typical for two-centre two-electron B–H bonds, whereas the *J*(BH) values for B–H⇀M bridges are typically *ca.* 80–90 Hz.

There was evidence that compound **5** undergoes dynamic behaviour in solution. When the $^{13}C\text{-}\{^1H\}$ NMR spectrum is measured at −60 °C the peaks at δ 13.7 and 17.2 due to the inner C*Me* groups become broad, as do the resonances at δ 30.4 and 30.9 for the cage C*Me* fragments. The outer *C*Me groups of the μ-C_4Me_4 moiety also give rise to a broad signal at δ 211.8, while a sharper but still relatively broad signal for the B*C*(H)C_6H_4Me-4 nucleus is seen at δ 76.8. The nature of the dynamic process causing these features is not known, but may be due to a rotation of the $\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2$ ligand. It seems unlikely that a 'flipping' of the μ-C_4Me_4 group is occurring from towards W to leaning towards Mo since the outer *C*(Me)C(Me)C(Me)*C*(Me) carbon nuclei are so very deshielded, in accord with a symmetrical disposition of the ligand.

It is interesting to contrast the behaviour of compound **1a** when treated with MeC≡CMe with that of **2a** treated with EtC≡CEt. In the latter reaction none of the CO ligands is displaced, although one of these groups migrates to the Mo atom in compound **3**. More interestingly in the formation of the latter the bridging *p*-tolylmethylidyne group in **2a** inserts into the activated B–H⇀Mo bond. This may occur because the alkyne initially acts as a two-electron donor in an associative manner giving a saturated 34 c.v.e. species $[MoW(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_3(\eta\text{-}EtC_2Et)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$, and then the alkyne becomes a four-electron donor providing the driving force for insertion of the μ-CC_6H_4Me-4 group into the B–H bond. The loss of the B–H⇀Mo linkages in the formation of the compounds **4** is surprising unless it is accepted, contrary to the evidence from ^{13}C NMR chemical shifts, that the alkyne molecules present in the products are functioning as four-electron donors. The reaction of compound **4a** with an excess of MeC≡CMe to afford the complex **5** is particularly interesting, and may imply an intermediate with a B–H⇀Mo bridge into which the alkylidyne group inserts.

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.* 15 cm in length and 2 cm in diameter) was BDH aluminium oxide (Brockman Activity II). The NMR spectra were recorded with JEOL JNM FX90Q, GX270 and GX400 spectrometers, IR spectra with a Perkin-Elmer FT600 spectrometer, and $^{11}B\text{-}\{^1H\}$ NMR spectra in CD_2Cl_2 [chemical shifts are positive to high frequency of $BF_3\cdot Et_2O$ (external)]. The compounds **1** were prepared as previously described.[2a] Analytical data for the new compounds are given in Table 1.

Table 4 Atomic positional parameters (fractional coordinates × 10^4) for compound **5** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1499(1)	3109(1)	6719(1)	C(51)	2750(8)	1576(6)	7578(7)
Mo	1332(1)	1868(1)	5323(1)	C(60)	2721(6)	2497(4)	6090(6)
C(1)	462(6)	2765(4)	7951(6)	C(61)	3873(6)	2453(5)	6203(7)
C(10)	326(7)	1933(5)	8000(7)	C(70)	2138(6)	2970(4)	5318(6)
C(2)	−232(6)	3242(4)	7096(6)	C(71)	2713(8)	3378(5)	4632(7)
C(20)	−1041(6)	2832(5)	6327(7)	C(80)	1019(6)	3090(5)	5255(6)
B(3)	311(7)	4044(5)	6882(7)	C(81)	379(7)	3527(5)	4425(6)
B(4)	1551(7)	4077(5)	7742(7)	C(90)	607(20)	1612(8)	3693(11)
B(5)	1564(7)	3208(6)	8418(7)	C(90A)	1184(40)	1501(18)	3710(23)
B(6)	−565(8)	3239(6)	8256(8)	C(91)	1642(22)	1358(14)	3910(19)
B(7)	−663(8)	4068(6)	7558(8)	C(91A)	1916(24)	1139(20)	4229(29)
B(8)	482(9)	4586(6)	7981(9)	C(92)	2100(12)	866(12)	4727(20)
B(9)	1284(9)	4047(6)	8954(8)	C(92A)	1952(22)	706(16)	5093(27)
B(10)	591(9)	3231(6)	9084(8)	C(93)	1662(19)	588(10)	5498(17)
B(11)	−81(9)	4068(7)	8835(9)	C(93A)	1233(32)	592(14)	5658(20)
C(40)	2507(6)	4078(5)	7264(6)	C(94)	689(21)	718(11)	5739(13)
C(41)	2801(6)	4607(4)	6540(6)	C(94A)	258(31)	905(19)	5481(24)
C(42)	3852(6)	4738(5)	6540(6)	C(95)	−146(15)	1159(12)	5242(18)
C(43)	4149(7)	5206(5)	5865(7)	C(95A)	−237(19)	1329(17)	4791(33)
C(44)	3457(7)	5569(5)	5161(6)	C(96)	−170(13)	1531(11)	4304(20)
C(45)	2419(6)	5456(4)	5170(6)	C(96A)	66(26)	1643(13)	3886(24)
C(46)	2105(6)	4981(4)	5847(6)	C(01)	6803(12)	886(9)	6875(10)
C(441)	3785(8)	6079(5)	4405(7)	Cl(1)	8068(3)	606(3)	7241(4)
C(50)	2207(6)	2126(4)	6828(6)	Cl(2)	6606(3)	1827(3)	6973(3)

Synthesis of the Alkynedimetal Compounds.—The compound **1a** (0.35 g, 0.51 mmol) was dissolved in thf (*ca.* 20 cm^3) in a Schlenk tube (100 cm^3) fitted with a high-pressure stopcock, and $MeC\equiv CMe$ (0.20 cm^3, 2.50 mmol) was added. The reaction vessel was sealed under a partial vacuum and heated at 65 °C for *ca.* 15 h. Solvent was removed *in vacuo* and after dissolving the residue in CH_2Cl_2 (3 cm^3) the solution was chromatographed. Elution with the same solvent removed a brown fraction which was reduced in volume *in vacuo* to *ca.* 3 cm^3. Addition of light petroleum (*ca.* 20 cm^3), cooling to −20 °C, and removal of supernatant liquid with a syringe afforded tan coloured *microcrystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **4a** (0.10 g).

The other alkyne dimetal compounds were made in a similar manner. (*a*) The complex $[MoW(\mu\text{-}CC\equiv CBu^t)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **4b** (0.17 g) was obtained from the reagent **1b** (0.34 g, 0.50 mmol) and $MeC\equiv CMe$ (0.20 cm^3, 2.5 mmol). (*b*) Treatment of **1b** (0.34 g, 0.50 mmol) with $EtC\equiv CEt$ (0.30 cm^3, 2.6 mmol) gave *microcrystals* of the complex $[MoW(\mu\text{-}CC\equiv CBu^t)(CO)(\eta\text{-}EtC_2Et)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **4c** (0.15 g). (*c*) The reaction between compound **1c** (0.34 g, 0.50 mmol) and $MeC\equiv CMe$ (0.20 cm^3, 2.5 mmol) afforded *microcrystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ **4d** (0.21 g). (*d*) The complex $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}PhC_2Ph)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_{10}Me)]$ **4e** (0.27 g) was isolated from the reaction between the reagent **1c** (0.34 g, 0.50 mmol) and $PhC\equiv CPh$ (0.20 g, 1.1 mmol).

Reaction between $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}MeC_2Me)(\eta\text{-}C_7H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ *and But-2-yne.*—Compound **4a** (0.35 g, 0.49 mmol) was dissolved in toluene (10 cm^3) and $MeC\equiv CMe$ (0.20 cm^3, 2.5 mmol) was added. The Schlenk tube, fitted with a high-pressure stopcock, was sealed under reduced pressure, and heated at 100 °C overnight. A small amount of brown precipitate believed to be polybut-2-yne was usually produced. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 3 cm^3) and chromatographed. Elution with the same solvent removed a red fraction. The solvent was reduced in volume *in vacuo* to *ca.* 3 cm^3 and light petroleum (*ca.* 5 cm^3) was added affording red *microcrystals* of $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2\}(\eta\text{-}C_7H_7)]$ **5** (0.07 g).

Crystal Structure Determination.—Crystals of compound **5** were grown as dark red prisms from CH_2Cl_2–hexane (1:10) solutions. Diffracted intensities were collected (Wyckoff ω scans) at room temperature from a crystal of dimensions *ca.* 0.20 × 0.25 × 0.30 mm, sealed under nitrogen in a glass capillary tube, on a Siemens R3m/V four-circle diffractometer. Of the 5677 unique reflections ($2\theta \leqslant 50°$), 4078 had $F \geqslant 4.0\sigma(F)$, and only these were used for structure solution and refinement, after the data had been corrected for Lorentz, polarisation, and X-ray absorption effects. The latter was based on a semi-empirical method using azimuthal scan data.[15]

Crystal data. $C_{27}H_{34}B_9MoW{\cdot}CH_2Cl_2$, $M = 820.5$, monoclinic, space group $P2_1/n$, $a = 13.270(2)$, $b = 17.882(3)$, $c = 13.826(2)$ Å, $\beta = 101.47(2)°$, $U = 3218(1)$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 1596$, Mo-Kα X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\ 73$ Å, μ(Mo-Kα) = 42.2 cm^{-1}.

The metal atoms were located by direct methods, and successive Fourier difference syntheses were used to locate all the other atoms except the hydrogen atoms. All non-hydrogen atoms, except the C atoms of the C_7H_7 ring, were given anisotropic thermal parameters, with the hydrogen atoms of the C_6H_4Me-4, μ-C_4Me_4 and $C_2B_9H_8Me_2$ groups included in calculated positions (C–H 0.96 and B–H 1.10 Å).[16] The atom H(40) was located and fully refined. All hydrogens were refined with fixed isotropic thermal parameters [$U_{iso} = 0.08$ Å^2 for CH and 1.2 U_{iso}(B) for BH], except for those of the C_7H_7 ring which were not generated. The carbon atoms of the C_7H_7 ring were disordered, and the refinement led to establishment of a 70:30 site occupancy. Refinement by full-matrix least squares on a Digital μ-Vax computer using the SHELXTL Plus system of programs[15] converged at $R = 0.038$ ($R' = 0.037$). A weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0004|F_o|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 0.90$ or $\leqslant -0.94$ e Å^{-3}. Scattering factors with corrections for anomalous dispersion were taken from ref. 17. Atomic coordinates are listed in Table 4.

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

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