Alkylidyne(carbaborane) Complexes of the Group 6 Metals. Part 8.[1] Proton-induced Alkylidyne Ligand Coupling at Dimetal Centres†

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Protonation ($HBF_4{\cdot}Et_2O$) of equimolar mixtures of the compounds $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) and $[NEt_4][W(\equiv CC\equiv CBu^t)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ in CH_2Cl_2 at −78 °C affords the dimetal complexes $[MW\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[=C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$. The ditungsten compound was also obtained by protonating equimolar mixtures of $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ and $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$, and the species $[W_2\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[=C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ was similarly prepared by treating equimolar mixtures of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[NEt_4][W(\equiv CC\equiv CBu^t)(CO)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})]$ with $HBF_4{\cdot}Et_2O$. The structure of $[MoW\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[=C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ has been established by X-ray diffraction. The Mo–W bond [3.031(2) Å] is bridged by a $C(Bu^t)CC[=C(H)C_6H_4Me\text{-}4]$ unit [average C–C 1.40(3) Å]. All three carbon atoms of the chain ligate the Mo atom but only two carbons of the $C(Bu^t)CC$ fragment ligate the W atom. The latter is also co-ordinated by the *nido*-icosahedral $7,8\text{-}C_2B_9H_{11}$ cage and two CO groups, and the Mo atom is co-ordinated by a C_5H_5 ring and two CO ligands, as expected. Solutions of the compounds $[MW\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[=C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,8\text{-}$ or $\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ slowly (days) convert into new species of formulation $[MW\{\mu\text{-}\eta^3:\eta^2,\eta^5\text{-}C(H)(C_6H_4Me\text{-}4)CC[C(H)(Bu^t)(7,8\text{-}$ or $7,9\text{-}C_2B_9H_{10})]\}(CO)_4(\eta\text{-}C_5H_5)]$, a process accelerated by refluxing in tetrahydrofuran. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR data of the new compounds are reported and discussed in relation to the structures proposed.

Protonation of salts of the anionic complexes $[M(\equiv CR)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]^-$ (M = W or Mo, R = alkyl or aryl, R′ = Me or H) is proving to be a rich field for investigation. A variety of different products have been isolated depending on the particular salt employed, the acids used for protonation, and the nature of the substrate molecules added to the reaction mixtures.[1,2]

One segment of this area of study involves the synthesis of dimetal species by treating the salts with $HBF_4{\cdot}Et_2O$ in the presence of the compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = alkyl, aryl or alkynyl).[3] We have previously shown that treatment of a mixture of $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ **1a** and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 at −78 °C with $HBF_4{\cdot}Et_2O$ affords the ditungsten compound $[W_2(\mu\text{-}CMe)(CO)_3\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\text{-}10\text{-}Me_2\text{-}7,8\}(\eta\text{-}C_5H_5)]$ **2a**.[3a] In contrast, addition of $HBF_4{\cdot}Et_2O$ to equimolar quantities of **1a** and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ gives the compound $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)(\eta\text{-}C_5H_5)]$ **3a**, a reaction which proceeds with loss of a $C(H)C_6H_4Me\text{-}4$ fragment at some stage. Loss of both a BH vertex and a $C(H)C_6H_4Me\text{-}4$ group has been observed upon treatment of mixtures of $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}7,9\text{-}C_2B_{10}H_{10}Me_2)]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$. The product of this reaction is $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)(\eta\text{-}C_5H_5)]$ **4**. The latter is an isomer of **3a**, with no connectivity between the carbon atoms in the open pentagonal C_2B_3 face of the *nido*-C_2B_9 fragment ligating the tungsten atom. Complex **4** is the more stable isomer, since it forms quantitatively when **3a** is heated in toluene.[3a] Related to these studies has been the recent observation that treatment of equimolar mixtures of **1a** and $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$ affords $[W_2(\mu\text{-}CC\equiv CBu^t)(CO)_4\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\text{-}10\text{-}Me_2\text{-}7,8\}(\eta\text{-}C_5H_5)]$ **5**.[3d] Moreover, the latter, upon refluxing in thf (tetrahydrofuran), releases CO and forms $[W_2(\mu\text{-}CC\equiv CBu^t)(CO)_3\{\eta^5\text{-}7,8\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\text{-}10\text{-}Me_2\text{-}7,8\}(\eta\text{-}C_5H_5)]$ **2b**.

The pathway to the products of the type **2**, several of which are now known,[3a,b] probably involves an alkylidenetungsten intermediate $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, formed upon addition of $HBF_4{\cdot}Et_2O$ to **1a**. Insertion of the alkylidene ligand of this intermediate into the cage B–H bond would afford the $BCH_2C_6H_4Me\text{-}4$ group found in the products, while co-ordination of the C≡W linkage of a $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ substrate molecule to the electronically unsaturated tungsten centre would generate the W–W bond bridged by the alkylidyne moiety. Formation of **5** and its thermolysis to give **2b** indicates that generation of the exopolyhedral $B\text{–}H\rightharpoonup W$ three-centre two-electron bonds in molecules of structural type **2** occurs as the last step in the reaction sequence.

Protonation studies on salts of the anionic complexes $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]^-$, containing CH rather than CMe vertices, have been limited thus far,[2,3] but those reactions investigated have not afforded products in which an alkylidene fragment has inserted into a cage B–H bond to form a BCH_2R group. Thus addition of $HBF_4{\cdot}Et_2O$ to a mixture of **1b** and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ yields the ditungsten compound $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ **3b**, the overall stoichiometry implying release of a C(H)Me ligand at some stage in the reaction profile. The product of this reaction might have been the μ-alkyne-(μ-hydrido)-ditungsten complex $[W_2(\mu\text{-}H)(\mu\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$, because we have previously observed that treatment of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$ yields $[W_2(\mu\text{-}H)(\mu\text{-}MeC_2Me)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$,[4] and protonation of **1b** with $HBF_4{\cdot}Et_2O$ yields $[PPh_4][W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}\text{-}$

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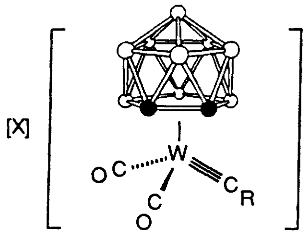
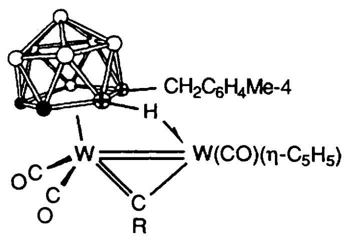
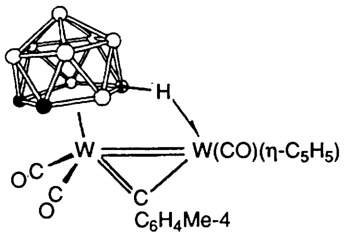
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



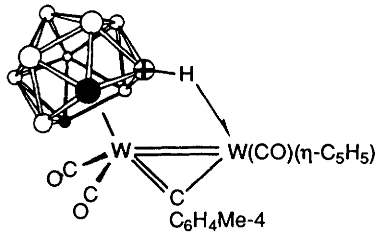
	X	R	●
1a	NEt_4	C_6H_4Me-4	CMe
1b	PPh_4	C_6H_4Me-4	CH
1c	NEt_4	C_6H_4Me-4	CH
1d	NEt_4	$C\equiv CBu^t$	CH
1e	NEt_4	$C\equiv CBu^t$	CMe



	R	●
2a	Me	CMe
2b	$C\equiv CBu^t$	CMe

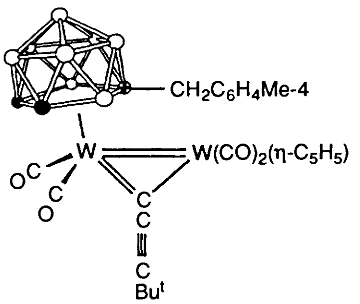


	●
3a	CMe
3b	CH

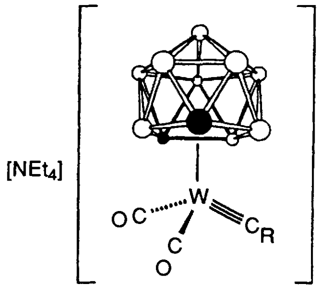


	●
4	CMe

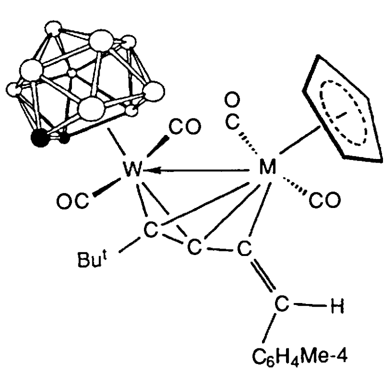
○BH ⊕B



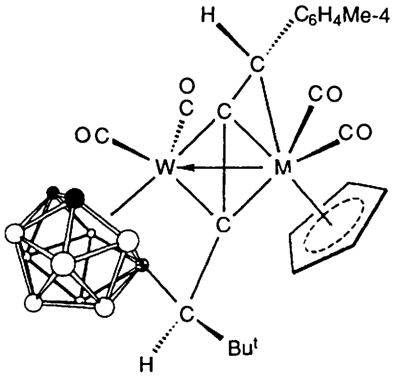
	●
5	CMe



	R	●
6	$C\equiv CBu^t$	CH



	M
7a	W
7b	Mo



	M
8a	W
8b	Mo

●CH ○BH ⊕B

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

	Compound[b]	Yield (%)	$\nu_{max}(CO)$[c]/cm^{-1}	Analysis (%)	
				C	H
1d	$[NEt_4][W(\equiv CC\equiv CBu^t)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$	62	[d] 1975s, 1899s	[e] 38.3 (38.3)	7.1 (6.8)
6	$[NEt_4][W(\equiv CC\equiv CBu^t)(CO)_2(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})]$	58	[f] 1977s, 1894s	[g] 38.1 (38.3)	7.0 (6.8)
7a	$[W_2\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[{=}C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$	17	2028w, 2003s, 1996s, 1965m, 1955m	36.5 (35.7)	4.6 (3.8)
7b	$[MoW\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[{=}C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$	31	2031m, 1966s, 1968s, 1955m (br)	39.5 (39.7)	4.4 (4.2)
7c	$[W_2\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[{=}C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$	20	2026w, 2002s, 1956s (br)	35.8 (35.7)	4.5 (3.8)
8a	$[W_2\{\mu\text{-}\eta^3:\eta^2,\eta^5\text{-}C(H)(C_6H_4Me\text{-}4)CC[C(H)(Bu^t)(7,8\text{-}C_2B_9H_{10})]\}(CO)_4(\eta\text{-}C_5H_5)]$	81	2031s, 1968s, 1942s, 1852m	35.2 (35.7)	3.9 (3.8)
8b	$[MoW\{\mu\text{-}\eta^3:\eta^2,\eta^5\text{-}C(H)(C_6H_4Me\text{-}4)CC[C(H)(Bu^t)(7,8\text{-}C_2B_9H_{10})]\}(CO)_4(\eta\text{-}C_5H_5)]$	32	2033s, 1974s, 1948s, 1858m	39.5 (39.7)	4.4 (4.2)
8c	$[W_2\{\mu\text{-}\eta^3:\eta^2,\eta^5\text{-}C(H)(C_6H_4Me\text{-}4)CC[C(H)(Bu^t)(7,9\text{-}C_2B_9H_{10})]\}(CO)_4(\eta\text{-}C_5H_5)]$	73	2034s, 1968s, 1859w	35.4 (35.7)	3.9 (3.8)

[a] Calculated values are given in parentheses. [b] Compounds **1d** and **6** are orange, the others are red. [c] Measured in CH_2Cl_2. All complexes show a broad band of medium intensity at *ca.* 2550 cm^{-1} due to B–H. [d] $\nu_{max}(C\equiv C)$ at 2131w cm^{-1}. [e] N, 2.3 (2.4%). [f] $\nu_{max}(C\equiv C)$ at 2127w cm^{-1}. [g] N, 2.4 (2.4%).

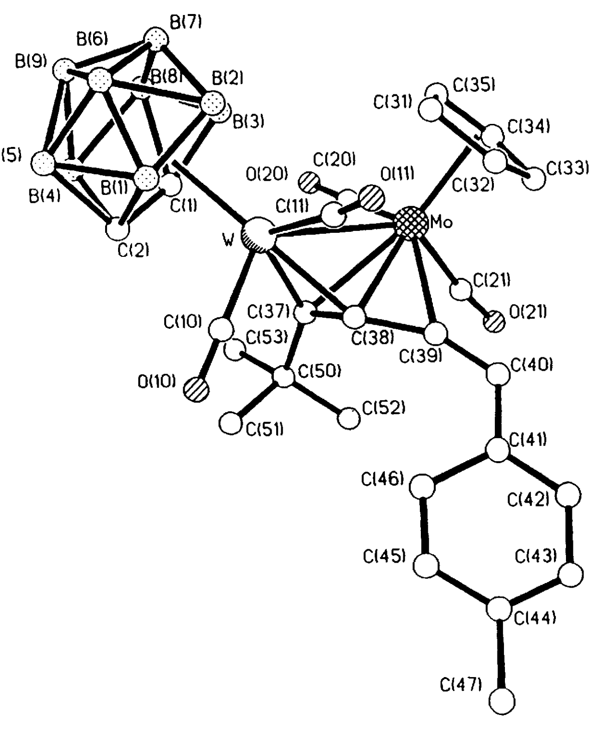


Fig. 1 Molecular structure of $[MoW\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[{=}C(H)C_6H_4Me4]\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ **7b**, showing the crystallographic atom labelling scheme

$(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$.[3c] Both these ditungsten compounds arise *via* a coupling of alkylidyne groups, probably *via* the intermediacy of μ-vinyl species, as discussed later.

The nature of the products obtained by protonating salts of the type **1** in the presence of the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ appears to depend critically on whether CMe or CH vertices are present in the cages of the carbaborane reagent. Further studies on species containing $\eta^5\text{-}C_2B_9H_{11}$ ligands are merited, therefore, in order to delineate the scope of this field. Herein we describe protonations of mixtures of **1c**, **1d** or **6** and the compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = W or Mo, R = $C_6H_4Me\text{-}4$; M = W, R = $C\equiv CBu^t$). Neither of the reagents **1d** or **6** has been previously reported, the latter being an isomer of the former, but containing the $\eta^5\text{-}7,9\text{-}C_2B_9H_{11}$ *nido*-icosahedral fragment instead of the more common $\eta^5\text{-}7,8\text{-}C_2B_9H_{11}$ moiety. Both **1d** and **6** are related to the salt **1e**, which also contains a $W\equiv CC\equiv CBu^t$ group, and has been shown to form cluster compounds readily.[5]

Results and Discussion

Protonation of equimolar mixtures of compounds **1c** and $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4\cdot Et_2O$ in CH_2Cl_2 at −78 °C afforded the ditungsten compound $[W_2\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[{=}C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ **7a**. Unexpectedly the same product was obtained by protonating mixtures of **1d** and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, and in both syntheses ^1H NMR studies, discussed below, revealed that it was formed as a mixture of two isomers. Treatment of equimolar mixtures of **1d** and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4\cdot Et_2O$ yielded $[MoW\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[{=}C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ **7b**, and a similar protonation of a mixture of **6** and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ gave $[W_2\{\mu\text{-}\eta^3:\eta^2\text{-}C(Bu^t)CC[{=}C(H)C_6H_4Me\text{-}4]\}(CO)_4(\eta^5\text{-}7,9\text{-}C_2B_9H_{11})(\eta\text{-}C_5H_5)]$ **7c**. The latter is an isomer of **7a**, with a *nido*-$7,9\text{-}C_2B_9H_{11}$ icosahedral fragment ligating a tungsten atom in place of an $\eta^5\text{-}7,8\text{-}C_2B_9H_{11}$ group. Data for **7a**–**7c** are given in Tables 1 and 2.

Discussion of the spectroscopic properties of the compounds **7** is deferred until the results of X-ray diffraction studies are described. Data were obtained from crystals of both **7a** and **7b**, which were isostructural, but those for the latter afforded a better structural solution (*R* 0.0858) than those for the former (*R* 0.100). Accordingly, only the results for **7b** are discussed herein. Significant bond distances and angles for **7b** are listed in Table 3 and the structure is shown in Fig. 1. The molecule has an unusual structure with the Mo–W bond [3.031(2) Å] bridged by three carbon atoms such that two are bonded to the tungsten [C(37)–W 2.16(2), C(38)–W 2.13(2) Å], and three to the molybdenum [C(37)–Mo 2.41(2), C(38)–Mo 2.25(2), C(39)–Mo 2.34(2) Å]. Atom C(37) carries the Bu^t group, and C(39) a $C(H)C_6H_4Me\text{-}4$ fragment. The C(39)–C(40) separation [1.32(3) Å] is comparable with that found for the C=C bond in $[RhPt\{\sigma\text{-}C(C_6H_4Me\text{-}4){=}C(C_6H_4Me\text{-}4)H\}(CO)(PEt_3)(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ [1.34(1) Å].[6] As expected, the Mo atom carries two CO ligands and the C_5H_5 ring, and the W atom is ligated by two CO groups and the *nido*-$7,8\text{-}C_2B_9H_{11}$ fragment in the usual manner.

The Mo–W separation in compound **7b** may be compared with that found [2.922(1) Å] in $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)\text{-}7,8\text{-}C_2B_9H_8Me_2\}(\eta^7\text{-}C_7H_7)]$[7] in which the metal–metal bond is bridged by four carbon atoms. More-

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

Compound	^{1}H(δ)	^{13}C[b](δ)
1d	1.28 (s, 9 H, Bu^t), 1.34 [t of t, 12 H, CH$_2Me$, J(HH) 7, J(NH) 2], 2.50 (s br, 2 H, CH of C$_2$B$_9$H$_{11}$), 3.22 [q, 8 H, CH_2Me, J(HH) 7]	264.3 [C≡W, J(WC) 214], 226.4 [CO, J(WC) 182], 99.4 (C≡CBu^t), 90.4 (C≡CBu^t), 53.2 [t, CH$_2$N, J(NC) 4], 35.8 (br, CH), 30.2 (CMe_3), 28.9 (CMe$_3$), 7.8 (CH$_2Me$)
6	1.25 (s, 9 H, Bu^t), 1.36 [t of t, 12 H, CH$_2Me$, J(HH) 7, J(NH) 2], 1.48 (s br, 2 H, CH of C$_2$B$_9$H$_{11}$), 3.24 [q, 8 H, CH_2Me, J(HH) 7]	263.5 [C≡W, J(WC) 210], 226.0 [CO, J(WC) 187], 99.8 [C≡CBu^t, J(WC) 53], 90.1 [C≡CBu^t, J(WC) 12], 53.2 [t, CH$_2$N, J(NC) 3], 41.3 (br, CH), 30.1 (CMe_3), 28.9 (CMe$_3$), 7.8 (CH$_2Me$)
7a[c]	* 1.24, 1.32 (s, 9 H, Bu^t), * 2.39, 2.41 (s, 3 H, Me-4), * 2.66, * 3.19, 3.40, 3.75 (br, s × 2, 2 H, CH of C$_2$B$_9$H$_{11}$), 5.54, * 5.78 (s, 5 H, C$_5$H$_5$), * 6.17, 6.20 [s, 1 H, C(H)C$_6$H$_4$Me-4], * 7.21, * 7.25 [(AB)$_2$, C$_6$H$_4$, J(AB) 9], 7.26 (s, 4 H, C$_6$H$_4$)	[d] 214.9, 213.1, 208.3, 207.3 (CO), 161.7 (CC=C), 138.2, 133.4, 130.3, 127.5 (C$_6$H$_4$), 120.9 (CC=C), 94.6, 90.3 (CBu^t and CC=C), 90.2 (C$_5$H$_5$), 42.8 (CMe$_3$), 38.9, 38.7 (C$_2$B$_9$H$_{11}$), 34.5 (CMe_3), 21.0 (Me-4)
7b	1.35 (s, 9 H, Bu^t), 2.40 (s, 3 H, Me-4), 3.28, 3.82 (br, s × 2, 2 H, CH of C$_2$B$_9$H$_{11}$), 5.47 (s, 5 H, C$_5$H$_5$), 6.32 [s, 1 H, C(H)C$_6$H$_4$Me-4], 7.25 (s, 4 H, C$_6$H$_4$)	227.2, 220.7, 213.3, 205.5 (CO), 162.8 (CC=C), 138.2, 132.2, 129.8, 126.7 (C$_6$H$_4$), 119.9 (CC=C), 97.0, 93.3 (CBu^t and CC=C), 90.7 (C$_5$H$_5$), 44.1 (CMe$_3$), 39.4, 38.9 (C$_2$B$_9$H$_{11}$), 33.8 (CMe_3), 21.0 (Me-4)
7c[e]	1.29 (s, 9 H, Bu^t), 2.39 (s, 3 H, Me-4), 2.44, 2.72 (br, s × 2, 2 H, CH of C$_2$B$_9$H$_{11}$), 5.48 (s, 5 H, C$_5$H$_5$), 6.23 [s, 1 H, C(H)C$_6$H$_4$Me-4], 7.24, 7.25 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	
8a	0.95 (s, 9 H, Bu^t), 2.36 (s, 3 H, Me-4), 2.70 [s br, 1 H, C(H)Bu^t], 2.80, 4.25 (br, s × 2, 2 H, CH of C$_2$B$_9$H$_{10}$), 5.69 (s, 5 H, C$_5$H$_5$), 7.20, 7.40 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 7], 8.58 [s, 1 H, C(H)C$_6$H$_4$Me-4]	222.5, 214.7, 205.2, 203.3 [CO, J(WC) 143, 158, 177 and 154], 139.6, 132.9, 129.6, 129.5 (C$_6$H$_4$), 96.8 [C(H)C$_6$H$_4$Me-4], 94.0 (μ-C$_2$), 93.3 (C$_5$H$_5$), 92.0 (μ-C$_2$), 50.0 [br, C(H)Bu^t], 42.5, 40.2 (C$_2$B$_9$H$_{10}$), 39.3 (CMe$_3$), 28.9 (CMe_3), 21.5 (Me-4)
8b	0.93 (s, 9 H, Bu^t), 2.36 (s, 3 H, Me-4), 2.58 [s br, 1 H, C(H)Bu^t], 2.79, 4.25 (br, s × 2, 2 H, CH of C$_2$B$_9$H$_{10}$), 5.62 (s, 5 H, C$_5$H$_5$), 7.21, 7.42 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8], 7.92 [s, 1 H, C(H)C$_6$H$_4$Me-4]	[f] 221.3, 219.6, 216.7, 215.8 (CO), 139.6, 131.9, 129.4 (C$_6$H$_4$), 97.9 [C(H)C$_6$H$_4$Me-4], 96.8 (μ-C$_2$), 95.7 (C$_5$H$_5$), 90.7 (μ-C$_2$), 42.2, 40.2 (C$_2$B$_9$H$_{10}$), 39.0 (CMe$_3$), 28.5 (CMe_3), 21.3 (Me-4)
8c	0.91 (s, 9 H, Bu^t), 1.08, 1.99 (br, s × 2, 2 H, CH of C$_2$B$_9$H$_{10}$), 2.36 (s, 3 H, Me-4), 2.84 [s, br, 1 H, C(H)Bu^t], 5.75 (s, 5 H, C$_5$H$_5$), 7.26 [s, 1 H, C(H)C$_6$H$_4$Me-4], 7.21, 7.36 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 7]	218.1, 215.6, 205.7, 202.3 [CO, J(WC) 151, 164, 180 and 154], 139.6, 132.5, 129.4, 129.1 (C$_6$H$_4$), 93.4 (C$_5$H$_5$), 92.2 [C(H)C$_6$H$_4$Me-4], 92.0, 83.4 (μ-C$_2$), 52.9, 50.5 (C$_2$B$_9$H$_{10}$), 49.8 [br, C(H)Bu^t], 39.4 (CMe$_3$), 28.9 (CMe_3), 21.5 (Me-4)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measurements at ambient temperatures in CD$_2$Cl$_2$ unless otherwise stated. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe$_4$ (0.0 ppm). [c] Peaks in the ^{1}H NMR spectrum marked with an asterisk are due to the minor isomer (see text). Some signals due to the second isomer were also observed in the ^{13}C NMR spectrum but poor signal-to-noise ratio made assignments unsatisfactory. [d] Measured in (CD$_3$)$_2$CO. [e] Relative insolubility of complex inhibited measurements of ^{13}C NMR spectrum. [f] Signal for C(H)Bu^t nucleus not observed. Observation of three instead of the customary four resonances for C$_6$H$_4$ group due to overlap of two peaks at δ 129.4, as revealed by the relative intensity.

Table 3 Selected internuclear distances (Å) and angles (°) for the complex [MoW{μ-η^3:η^2-C(Bu^t)CC[=C(H)C$_6$H$_4$Me-4]}(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)(η^5-C$_5$H$_5$)] **7b**

W–Mo	3.031(2)	W–C(1)	2.36(2)	W–C(2)	2.42(2)	W–B(1)	2.27(3)
W–B(2)	2.38(3)	W–B(3)	2.41(2)	W–C(10)	1.94(2)	W–C(11)	1.96(2)
W–C(37)	2.16(2)	W–C(38)	2.13(2)	Mo–C(20)	1.98(2)	Mo–C(21)	1.99(3)
Mo–C(31)	2.29(4)	Mo–C(32)	2.30(3)	Mo–C(33)	2.28(2)	Mo–C(34)	2.16(3)
Mo–C(35)	2.25(3)	Mo–C(37)	2.41(2)	Mo–C(38)	2.25(2)	Mo–C(39)	2.34(2)
C(1)–C(2)	1.57(4)	C(1)–B(3)	1.61(3)	C(1)–B(4)	1.67(3)	C(1)–B(8)	1.76(4)
C(2)–B(1)	1.88(4)	C(2)–B(4)	1.61(4)	C(2)–B(5)	1.76(4)	B(1)–B(2)	1.66(4)
B(1)–B(5)	1.90(3)	B(1)–B(6)	1.76(4)	B(2)–B(3)	1.71(5)	B(2)–B(6)	1.82(4)
B(2)–B(7)	1.86(5)	B(3)–B(7)	1.66(4)	B(3)–B(8)	1.69(4)	B(4)–B(5)	1.79(4)
B(4)–B(8)	1.89(4)	B(4)–B(9)	1.82(4)	B(5)–B(6)	1.80(4)	B(5)–B(9)	1.91(5)
B(6)–B(7)	1.82(5)	B(6)–B(9)	1.81(5)	B(7)–B(8)	1.66(5)	B(7)–B(9)	1.65(5)
B(8)–B(9)	1.72(5)	C(10)–O(10)	1.19(3)	C(11)–O(11)	1.19(3)	C(20)–O(20)	1.20(2)
C(21)–O(21)	1.19(3)	C(37)–C(38)	1.42(4)	C(37)–C(50)	1.54(4)	C(38)–C(39)	1.38(3)
C(39)–C(40)	1.32(3)	C(40)–C(41)	1.39(4)	C(44)–C(47)	1.60(5)	C(50)–C(51)	1.49(4)
C(50)–C(52)	1.46(4)	C(50)–C(53)	1.53(4)				

Mo–W–C(10)	126.3(6)	Mo–W–C(11)	81.4(7)	C(10)–W–C(11)	84.2(9)	C(37)–W–C(10)	89.6(9)
C(37)–W–C(11)	114.6(9)	C(38)–W–C(10)	78.5(9)	C(38)–W–C(11)	76.6(9)	W–Mo–C(20)	88.8(8)
W–Mo–C(21)	134.5(8)	C(20)–Mo–C(21)	82(1)	W–C(10)–O(10)	179(2)	W–C(11)–O(11)	170(2)
C(37)–Mo–C(20)	76(1)	C(37)–Mo–C(21)	89.6(9)	C(38)–Mo–C(20)	111(1)	C(38)–Mo–C(21)	98(1)
C(39)–Mo–C(20)	137(1)	C(39)–Mo–C(21)	80(1)	Mo–C(20)–O(20)	175(3)	Mo–C(21)–O(21)	173(2)
W–C(37)–Mo	82.8(8)	W–C(38)–Mo	87.4(9)	C(50)–C(37)–Mo	132(2)	C(50)–C(37)–W	144(1)
C(38)–C(37)–C(50)	127(2)	C(38)–C(37)–W	69(1)	C(38)–C(37)–Mo	66(1)	C(37)–C(38)–C(39)	131(2)
C(37)–C(38)–W	72(1)	C(39)–C(38)–W	146(2)	C(37)–C(38)–Mo	78(1)	C(39)–C(38)–Mo	76(1)
C(38)–C(39)–C(40)	153(2)	C(40)–C(39)–Mo	137(2)	C(38)–C(39)–Mo	69(1)	C(39)–C(40)–C(41)	126(2)
C(40)–C(41)–C(42)	119(2)						

over, it is interesting that the metal–metal distance found in the X-ray diffraction study of **7a** [3.015(2) Å], mentioned above, is also similar to those in the ditungsten compounds [W$_2${μ-θ^3-C(H)C(H)CMe$_2$}(CO)$_9$] [3.189(1) Å] and [W$_2${μ-η^3:η^3-C(Me)C(Me)C(H)C(H)CMe$_2$}(CO)$_8$] [3.049(1) Å][8] in which chains of three and four carbon atoms bridge the W–W bonds, respectively. The presence of Mo(W)→W donor bonds invoked for **7a** and **7b** would allow both dimetal centres to attain 18-electron valence shells. The C(37)–C(38) [1.42(4) Å] and C(38)–C(39) [1.38(3) Å] distances in **7b** are comparable with those found [average 1.35(2) Å] for the μ-allenyl fragment $C(Bu^t){=}C{=}CH$ present in $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3{:}\eta^5\text{-}C(H)CC(Bu^t)C(O)C_2B_9H_8Me_2\}(CO)_8]$, the product of the reaction between **1e** and $[Fe_2(CO)_9]$.[5d]

The distance between the tungsten atom and the centroid of the base of the *nido*-$C_2B_9H_{11}$ cage in compound **7b** is 1.884 Å and that between the molybdenum atom and the centroid of the η-C_5H_5 ring is 1.954 Å. The W–C(1,2) and W–B(1,2,3) bond lengths are listed in Table 3. The planarities of the open face of the *nido*-$C_2B_9H_{11}$ cage [ring C(1)–C(2)–B(1)–B(2)–B(3), deviation 0.025 Å], the η-C_5H_5 ring (deviation 0.013 Å) and the phenyl ring (deviation 0.018 Å) have been verified by the use of a least-squares planes program. The mean C–C bond distances and angles in the η-C_5H_5 and phenyl rings are: 1.35 Å, 108°; and 1.38 Å, 120°, respectively. The mean carbonyl bond distance of 1.19 Å and all other experimentally determined bond distances are internally consistent and in agreement with other observed values.[9]

Since the NMR data (Table 2) for compound **7c** show features in common with those of **7a** and **7b** it would seem certain that **7c** has a similar structure but with an η^5-7,9-$C_2B_9H_{11}$ ligand instead of the η^5-7,8-$C_2B_9H_{11}$ group. A puzzling result, however, was the observation that the ^1H NMR spectrum of **7a**, in contrast with that of **7b** or **7c**, revealed duplicate peaks, indicating the presence of two isomers. Relative peak intensities in the spectrum of **7a** indicated an isomer ratio of *ca.* 7:3. Some resonances due to the second isomer were also seen in the ^{13}C-$\{^1H\}$ NMR spectrum, but this spectrum displayed weak signals due to the low solubility of the compound, and so few peaks for the minor isomer were observed.

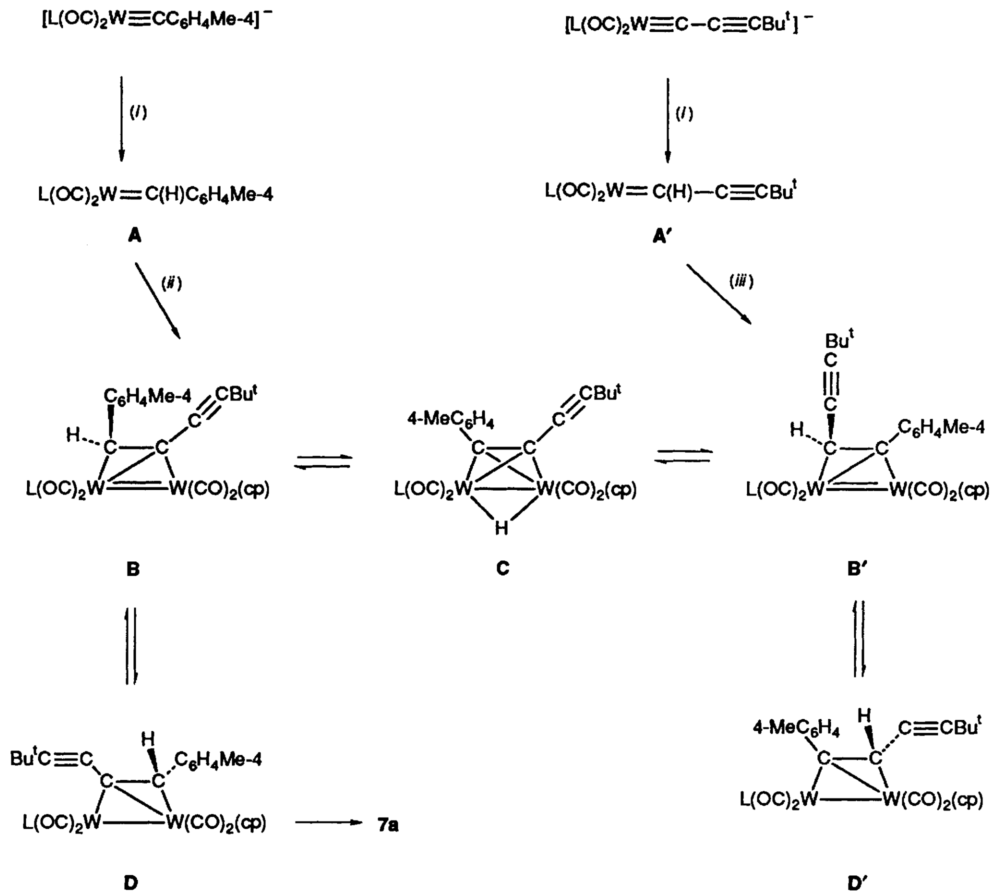
Careful chromatography of samples of compound **7a**, with slow elution of the column with CH_2Cl_2–light petroleum (1:9), enabled a partial separation of the two isomers. However, ^1H NMR measurements on solutions of either fraction showed that the equilibrium mixture was re-established within minutes. The nature of the isomerism is not clear at the present time, but it is evident that the two species are structurally very similar. Perhaps they differ in the conformation of their $W(CO)_2(\eta^5\text{-}C_2B_9H_{11})$ fragments with respect to the remainder of the molecule. Rotation of the $W(CO)_2(\eta^5\text{-}C_2B_9H_{11})$ group about an axis through the W atom and the C(37)C(38)Mo triangle (Fig. 1) could give different conformers in which the carbaborane cage is either cisoid or transoid to the C_5H_5 ring, the latter conformation being found in the solid state for **7b**. The inability to detect isomers of the latter from its ^1H NMR spectrum might be due to their rapid interconversion on the NMR time-scale, or to one isomer being so favoured over the other that resonances due to the minor species are not detected in the spectrum above the signal-to-noise ratio.

The resonances observed in the ^1H and ^{13}C-$\{^1H\}$ NMR spectra of the complexes **7** are in agreement with their structures. Thus the ^{13}C-$\{^1H\}$ NMR spectrum of **7b** shows four CO resonance at δ 227.2, 220.7, 213.3 and 205.5, corresponding to the four different environments of these ligands. A relatively deshielded peak at δ 162.8 is ascribed to C(38) (Fig. 1). The resonance for the central carbon in the μ_3-$C(Bu^t)CCH$ group of $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3{:}\eta^5\text{-}C(H)CC(Bu^t)C(O)C_2B_9H_8Me_2\}(CO)_8]$ is at δ 163.1.[5d] A resonance in the ^{13}C-$\{^1H\}$ NMR spectrum of **7b** at δ 119.9 is assigned to the $\mathit{C}(H)C_6H_4Me$-4 nucleus. In the spectrum of $[RhPt\{\sigma\text{-}C(C_6H_4Me\text{-}4){=}C(C_6H_4Me\text{-}4)H\}(CO)(PEt_3)(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ the corresponding resonance is at δ 127.5.[6] Satisfactory assignments may also be made for the other resonances in the ^{13}C-$\{^1H\}$ NMR spectrum, including the diagnostic signals at δ 39.4 and 38.9 for the carbaborane cage CH groups. In the spectrum of **3b** these occur at δ 39.1 and 40.0.[3c] In the ^1H NMR spectrum of **7b** a singlet peak for one hydrogen at δ 6.32 is assigned to the vinyl group proton $C{=}C(\mathit{H})C_6H_4Me$-4. The resonance for the corresponding proton in the above-mentioned rhodium–platinum compound occurs at δ 6.20.[6] Other peaks in the ^1H NMR spectrum of **7b** are as expected, including resonances for the carbaborane cage CH groups at δ 3.28 and 3.82. Both signals are broad due to the proximity of the quadrupolar ^{11}B nuclei. The ^{11}B-$\{^1H\}$ NMR spectra of the compounds were uninformative showing broad unresolved peaks in the range δ 0.28 to −20.1.

As mentioned above, compound **7a** could be obtained either by protonating mixtures of **1c** and $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$, or by protonating mixtures of **1d** and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$. This observation suggests that these reactions proceed *via* a common intermediate which subsequently yields **7a**. Based on results previously reported,[1,2] a probable pathway is indicated in Scheme 1. Protonation of **1c** or **1d** would afford the alkylidene species **A** and **A′**, respectively, in which the tungsten centres are electronically unsaturated. Addition of the C≡W groups of the molecules $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or $C\equiv CBu^t$) to these metal centres followed by C–C bond formation would give μ-vinyl intermediates of the type **B** and **B′**.[4,10] The well established process of pivoting of vinyl groups at dimetal centres[11] would account for conversion of **B** into **D**. Such a process would be facilitated in a 32-valence-electron dimetal species of type **B**. Slippage of the four-carbon chain of **D** across the W–W bond could afford the product **7a**. Pivoting of the vinyl group in **B′** to give **D′** is also possible, but both of these intermediates contain a $C(H)C\equiv CBu^t$ group not the $C(H)C_6H_4Me$-4 fragment found in **7a** by the X-ray diffraction analysis. Therefore, the conversion of **B′** into **B** *via* the μ-alkyne-μ-hydrido-ditungsten species **C** is proposed in order to facilitate migration of the hydrogen atom between adjacent μ-C atoms. Such an isomerisation has been observed previously in the facile interconversion of μ-$C(H){=}C(H)C_6H_4Me$-4 into μ-$C(C_6H_4Me\text{-}4){=}CH_2$ groups at W–Fe dimetal centres.[12] Moreover, it should be noted that **C** is closely related structurally to the cationic complex $[W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]^+$ [4] and the anionic complex $[W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$ mentioned earlier.[3c,13] Thus the steps **A′** ⟶ **B′** ⟶ **C** ⟶ **B** ⟶ **D** would account for the observation that protonation of mixtures of **1d** and $[W(\equiv C_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ afford the same product as is obtained by protonation of mixtures of **1c** and $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$.

During studies on the compounds **7** it was observed that in solution they slowly afforded the complexes $[MW\{\mu\text{-}\eta^3{:}\eta^2,\eta^5\text{-}C(H)(C_6H_4Me\text{-}4)CC[C(H)(Bu^t)(7,8\text{-}C_2B_9H_{10})]\}(CO)_4(\eta\text{-}C_5H_5)]$ (M = W **8a** or Mo **8b**) and $[W_2\{\mu\text{-}\eta^3{:}\eta^2,\eta^5\text{-}C(H)(C_6H_4Me\text{-}4)CC[C(H)(Bu^t)(7,9\text{-}C_2B_9H_{10})]\}(CO)_4(\eta\text{-}C_5H_5)]$ **8c**. The transformation of **7a** into **8a** in CH_2Cl_2 at room temperature was complete in 10 d, while **7c** converted completely into **8c** under the same conditions in 3 d. As expected, heating solutions of the complexes accelerated the process, and **7b** afforded **8b** after refluxing a thf solution of the former for 6 h, but the yield of the latter was reduced by some decomposition. Data characterising the complexes **8** are given in Tables 1 and 2.

Persistent attempts to grow crystals of one or other of the compounds **8** of suitable quality for an X-ray diffraction study were met with little success, although data from a crystal of **8a** allowed a crude analysis of the structure which was in full agreement with the NMR spectral interpretations. The ^{13}C-$\{^1H\}$ NMR spectrum of **8a** (Table 2) displays four resonances for the four non-equivalent CO ligands and each signal has ^{183}W–^{13}C satellite peaks. The C_6H_4 and C_5H_5 rings show the usual resonances, as do the two non-equivalent cage CH vertices. A broad signal at δ 50.0 is assigned to the $B\mathit{C}(H)Bu^t$ nucleus. The chemical shift is somewhat less deshielded than that (δ 77.0) for the $B\mathit{C}(H)C_6H_4Me$-4 group in $[MoW(\mu\text{-}C_4Me_4)\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)\text{-}7,8\text{-}C_2B_9H_8Me_2\}(\eta^7\text{-}C_7H_7)]$,[7] but this is to be expected since in the latter species the BC carbon is bonded to the tungsten whereas in **8a** it is part of a μ-C_4 chain. Resonances in the spectrum of **8a** at δ 96.8, 94.0 and 92.0 may be ascribed to the other three carbon nuclei of the C_4 chain which bridge the metal–metal bond. The results of a distortionless enhancement by polarisation transfer (DEPT)



Scheme 1 cp = η-C_5H_5, L = η^5-7,8-$C_2B_9H_{11}$. (*i*) $HBF_4\cdot Et_2O$; (*ii*) [W(≡CC≡CBu^t)$(CO)_2$(cp)]; (*iii*) [W(≡CC_6H_4Me-4)$(CO)_2$(cp)]

experiment allowed unambiguous assignment of the resonance due to the *C*H(C_6H_4Me-4) nucleus as the peak at δ 96.8.

The ^1H NMR spectrum of compound **8a** was also informative. Two diagnostic broad signals, each with intensity corresponding to a single proton, are seen for the cage CH groups at δ 2.80 and 4.25. A somewhat less broad peak for one hydrogen at δ 2.70 is assigned to the C(*H*)Bu^t nucleus and a sharp signal due to one hydrogen at δ 8.58 to the C(*H*)C_6H_4-Me-4 nucleus. Other signals were as expected.

Formation of the species **8** from the complexes **7** involves a major reorganisation of the attachment of the C(Bu^t)CC[=C(H)C_6H_4Me-4] fragment to the dimetal system. The CBu^t group has inserted into a cage B–H bond with cleavage of its linkage to the tungsten atom. At the other end of the bridging organic moiety the vinyl group has become co-ordinated to the M$(CO)_2$(η-C_5H_5) unit. Even so, in the complexes **8**, as in their precursors **7**, the W$(CO)_2$(η^5-$C_2B_9H_{11}$) fragment is ligated by two of the carbon atoms of the bridging organic system and the M$(CO)_2$(η-C_5H_5) fragment by three of the carbon atoms. The migration process which produces the BC(H)(Bu^t)C system is novel, but several reactions involving C_2B_9M cages have been identified which afford molecules containing BC(H)(C_6H_4-Me-4)M (M = Mo,[14] W,[7] Ru[15] and Rh[16]) units. The non-spectator role of cage B–H groups is a feature of this developing field,[17] and the reactions reported in this paper provide further examples of the novel molecular structures obtained.

Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C, and all solvents were freshly distilled over appropriate drying agents before use. Chromatography columns *ca.* 15 cm long and 2 cm in diameter were packed with alumina (Brockmann activity II), and all experiments were done under oxygen-free nitrogen using Schlenk-tube techniques. The NMR measurements were made using a Bruker AMX 360 spectrometer and IR spectra were recorded with a Bruker IFS 25 spectrophotometer. The reagents [W(≡CR)$(CO)_2$(η-C_5H_5)] (R = C_6H_4Me-4[18a] or C≡CBu^t[18b]), [W(≡CC≡CBu^t)(O_2CCF_3)$(CO)_2$(NC_5H_4Me-4$)_2$],[5a] Na_2[7,8- or 7,9-$C_2B_9H_{11}$][19] and [NEt_4][W(≡CC_6H_4Me-4)$(CO)_2$(η^5-7,8-$C_2B_9H_{11}$)][20] were obtained by procedures previously described. Tetrafluoroboric acid was an 85% solution of $HBF_4\cdot Et_2O$ in Et_2O as supplied by Aldrich. Microanalytical data for the new compounds are given in Table 1.

Synthesis of the Complexes [NEt_4][W(≡CC≡CBu^t)$(CO)_2$(η^5-$C_2B_9H_{11}$)].—The compound [W(≡CC≡CBu^t)(O_2CCF_3)$(CO)_2$-(NC_5H_4Me-4$)_2$] (2.50 g, 4.0 mmol) was treated with a thf (40 cm^3) solution of Na_2[7,8-$C_2B_9H_{11}$] (5.0 mmol), generated *in situ* from [$NHMe_3$][7,8-$C_2B_9H_{12}$] (0.96 g, 5.0 mmol) and NaH (23 mmol in an oil dispersion). The mixture was stirred for 4 h, following which [NEt_4]Cl·H_2O (0.79 g, 4.3 mmol) was added and the stirring continued for 1 h. Solvent was removed *in vacuo*, and the residue was taken up in CH_2Cl_2 (40 cm^3) and filtered through a Celite pad (*ca.* 3 × 3 cm). Solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2 (10 cm^3) and chromatographed. Elution of the column with the same solvent removed an orange fraction. Removal of all volatile material *in vacuo*, followed by crystallisation of the residue from CH_2Cl_2–Et_2O (20 cm^3, 1:4) gave orange *microcrystals* of [NEt_4][W(≡CC≡CBu^t)$(CO)_2$(η^5-7,8-$C_2B_9H_{11}$)] **1d** (1.47 g).

Compound **6** (0.68 g) was similarly prepared from [W(≡CC≡CBu^t)(O_2CCF_3)$(CO)_2$(NC_5H_4Me-4$)_2$] (1.25 g, 2.0 mmol) and Na_2[7,9-$C_2B_9H_{11}$] (2.5 mmol in 30 cm^3 thf) following addition of [NEt_4]Cl·H_2O (0.39 g, 2.2 mmol).

Preparation of the Dimetal Complexes [MW{μ-η^3:η^2-C(Bu^t)CC[=C(H)C_6H_4Me-4]}$(CO)_4$(η^5-$C_2B_9H_{11}$)(η-C_5H_5)].—(*i*) A mixture of compounds **1c** (0.14 g, 0.24 mmol) and $[W(\equiv CC\equiv CBu^t)(CO)_2(\eta-C_5H_5)]$ (0.94 g, 0.24 mmol) in CH_2Cl_2 (25 cm^3) at −78 °C was treated with $HBF_4{\cdot}Et_2O$ (45 μl, 0.24 mmol). The mixture was slowly warmed (*ca.* 1 h) to room temperature and stirred for 2 h. Alumina (*ca.* 3 g) was added and all volatile material was removed *in vacuo*. The resulting powder was transferred to the top of a chromatography column which was eluted with CH_2Cl_2–light petroleum (2:3). An orange-red fraction was collected and following removal of solvent *in vacuo* red *microcrystals* of $[W_2\{\mu-\eta^3:\eta^2-C(Bu^t)CC[=C(H)C_6H_4Me-4]\}(CO)_4(\eta^5-7,8-C_2B_9H_{11})(\eta-C_5H_5)]$ **7a** (0.035 g) were isolated. Using a similar procedure, protonation of a mixture of **1d** and $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ gave **7a**, also a mixture of isomers (see Results and Discussion).

(*ii*) A mixture of compounds **1d** (0.15 g, 0.24 mmol) and $[Mo(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ (0.78 g, 0.24 mmol) in CH_2Cl_2 (25 cm^3) at −78 °C was treated with $HBF_4{\cdot}Et_2O$ (45 μl, 0.24 mmol). By using work-up procedures similar to those for **7a**, red *microcrystals* of $[MoW\{\mu-\eta^3:\eta^2-C(Bu^t)CC[=C(H)-C_6H_4Me-4]\}(CO)_4(\eta^5-7,8-C_2B_9H_{11})(\eta-C_5H_5)]$ **7b** (0.06 g) were obtained.

Table 4 Data for crystal structure analysis of compound **7b**

Molecular formula	$C_{26}H_{33}B_9MoO_4W$
M	786.6
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	10.442(2)
b/Å	19.583(4)
c/Å	16.438(3)
β/°	103.34(3)
U/Å^3	3271(1)
Z	4
D_c/Mg m^{-3}	1.597
$F(000)$	1528
μ(Mo-Kα)/cm^{-1}	39.93
T/K	292
Diffractometer	Enraf-Nonius CAD4-F
Scan type	ω–2θ
Scan speed/° min^{-1}	0.49–3.44
Scan range, ω/°	1.30 + 0.34 tanθ
2θ range/°	3.0–40.0
Radiation	Mo-Kα ($\bar{\lambda}$ = 0.710 73 Å)
Observed data [$F \geqslant 4.0\sigma(F)$]	2342
Refined parameters	366
Data-to-parameter ratio	6.4:1
R,R'	0.0858, 0.0921
R_{int}	0.043
S	1.14
Residual density/e Å^{-3}	2.38, −1.89

(*iii*) The compound $[W_2\{\mu-\eta^3:\eta^2-C(Bu^t)CC[=C(H)C_6H_4-Me-4]\}(CO)_4(\eta^5-7,9-C_2B_9H_{11})(\eta-C_5H_5)]$ **7c** (0.042 g) was similarly prepared from **6** (0.15 g, 0.24 mmol), $[W(\equiv CC_6H_4-Me-4)(CO)_2(\eta-C_5H_5)]$ (0.10 g, 0.24 mmol) and $HBF_4{\cdot}Et_2O$ (45 μl, 0.24 mmol).

Formation of the Complexes $[MW\{\mu-\eta^3:\eta^2,\eta^5-C(H)(C_6H_4-Me-4)CC[C(H)(Bu^t)(C_2B_9H_{10})]\}(CO)_4(\eta-C_5H_5)]$.—(*i*) A CH_2Cl_2 (20 cm^3) solution of compound **7a** (0.12 g, 0.14 mmol) was stirred for 10 d, after which time IR measurements revealed that no further change in the composition of the mixture was taking place. Alumina (*ca.* 3 g) was added, and all volatile material was removed *in vacuo*. The resulting powder was applied to the top of a chromatography column which was eluted with CH_2Cl_2–light petroleum (1:4). A deep red fraction was collected, which after removal of solvent *in vacuo* afforded red *microcrystals* of $[W_2\{\mu-\eta^3:\eta^2,\eta^5-C(H)(C_6H_4Me-4)CC-[C(H)(Bu^t)(7,8-C_2B_9H_{10})]\}(CO)_4(\eta-C_5H_5)]$ **8a** (0.097 g). In a similar experiment, **7c** (0.20 g, 0.23 mmol) in CH_2Cl_2 (20 cm^3) after 3 d gave $[W_2\{\mu-\eta^3:\eta^2,\eta^5-C(H)(C_6H_4Me-4)CC[C(H)-(Bu^t)(7,9-C_2B_9H_{10})]\}(CO)_4(\eta-C_5H_5)]$ **8c** (0.15 g).

(*ii*) The compound **7b** (0.12 g, 0.15 mmol) was dissolved in thf (40 cm^3) and heated under reflux for 6 h. After cooling to room temperature, alumina (*ca.* 3 g) was added, and all volatile material was removed *in vacuo*. The powder obtained was transferred to the top of a chromatography column, which was eluted with CH_2Cl_2–light petroleum (1:4). The deep red fraction collected was evaporated *in vacuo* to give red *microcrystals* of $[MoW\{\mu-\eta^3:\eta^2,\eta^5-C(H)(C_6H_4Me-4)CC[C(H)-(Bu^t)(7,8-C_2B_9H_{10})]\}(CO)_4(\eta-C_5H_5)]$ **8b** (0.038 g).

Crystal Structure and Refinement.—The dark red single crystal (0.338 × 0.051 × 0.204 mm) used in the structural analysis was selected on the basis of optical homogeneity. The intensities were measured using the ω–2θ technique in the 2θ range of 3.0–40.0° (*h* 0–10, *k* 0–18, *l* −15 to 15). Table 4 lists the experimental and statistical summaries. The monitored standard reflections measured as a function of time (every 2 h) revealed a slow decay of −0.0396% h^{-1} which constituted a maximum correction of 1.042 58. Lorentz and polarisation corrections and a numerical absorption correction (transmission factors, maximum and minimum = 1.000, 0.8080) were applied to the 3396 collected reflections of which 3042 were

Table 5 Atomic positional parameters (fractional coordinates × 10^4) for compound **7b** with estimated standard deviations in parentheses

Atom	x	y	z
W	1161(1)	2226(1)	4230(1)
Mo	4129(2)	2308(1)	4502(1)
C(1)	473(20)	2373(11)	2770(14)
C(2)	−719(24)	2058(17)	3074(17)
B(1)	−884(25)	2688(14)	3906(16)
B(2)	179(34)	3323(16)	3934(22)
B(3)	990(26)	3099(13)	3179(13)
B(4)	−1050(26)	2402(14)	2161(21)
B(5)	−2091(25)	2609(17)	2848(16)
B(6)	−1498(25)	3415(17)	3320(20)
B(7)	−157(30)	3685(22)	2858(21)
B(8)	157(29)	3126(15)	2170(20)
B(9)	−1428(35)	3303(18)	2240(21)
C(10)	183(19)	1567(11)	4732(14)
O(10)	−419(17)	1155(12)	5028(13)
C(11)	1561(21)	2643(13)	5346(14)
O(11)	1612(21)	2927(10)	5993(11)
C(20)	3921(28)	2265(16)	3274(11)
O(20)	3724(20)	2281(17)	2526(10)
C(21)	5543(21)	1633(15)	4485(19)
O(21)	6477(20)	1283(12)	4506(15)
C(31)	3762(26)	3404(19)	4886(24)
C(32)	4597(27)	3090(16)	5572(19)
C(33)	5786(22)	2885(13)	5384(13)
C(34)	5580(23)	3114(15)	4640(18)
C(35)	4510(24)	3423(14)	4317(15)
C(37)	2504(19)	1426(12)	4061(15)
C(38)	2706(19)	1602(12)	4923(16)
C(39)	3821(19)	1576(14)	5564(13)
C(40)	4500(22)	1373(12)	6305(14)
C(41)	4110(22)	874(14)	6796(15)
C(42)	4970(23)	654(11)	7475(15)
C(43)	4639(23)	161(12)	7994(15)
C(44)	3370(29)	−106(15)	7845(17)
C(45)	2489(27)	124(16)	7145(19)
C(46)	2813(23)	599(15)	6600(18)
C(47)	2897(33)	−652(20)	8435(23)
C(50)	2590(22)	708(14)	3702(18)
C(51)	1397(30)	358(19)	3843(29)
C(52)	3762(27)	324(16)	4109(21)
C(53)	2269(44)	659(20)	2744(18)

independent. After averaging ($R_{int} = 0.043$), 2342 reflections with $F \geqslant 4.0\sigma(F)$ were included in the structural analysis. The space-group assignment was made according to systematic absences ($h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$).

The heavy-atom Patterson method was employed to locate the tungsten and molybdenum atoms, thus the phase problem was solved. Fourier difference mapping determined the positional coordinates of all other non-hydrogen atoms. The block full-matrix least-squares method was used to refine[21] the model. Anisotropic refinement of all non-hydrogen atoms yielded a final reliability factor of 0.0858. This relatively high value is probably a result of the small crystal size. Initially all cage atoms were treated as boron atoms until sufficient data became available to allow a distinction to be made between carbon and boron atoms on the basis of bond lengths. In general C–C are shorter than B–B separations in complexes of this type. Hydrogen-atom positions were calculated (C–H 0.96 and B–H 1.10 Å) and allowed to ride on their respective bonding atoms with fixed isotropic thermal parameters; 366 parameters were refined where $\Sigma w||F_o| - |F_c||^2$ was minimised, $w^{-1} = [\sigma^2(F_o) + 0.0119|F_o|^2]$. The 'goodness-of-fit' value (S) was 1.14. A final Fourier difference map displayed some electron density in the vicinity of the heavy metal atoms which is quite normal. Elsewhere, the density map was virtually featureless. Atomic scattering factors were taken from the ref. 22. Final non-hydrogen atom positions according to the numbering scheme in Fig. 1 are listed in Table 5.

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

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