Alkylidyne(carbaborane) Complexes of the Group 6 Metals. Part 4.[1] Formation of Unsaturated Dimetal Species, including 'Reverse' Polytopal Isomerisation, and Reactions with Trimethylphosphine†

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Treatment of a mixture of $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9\text{-}7,8\text{-}Me_2)]$ and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at −78 °C affords the dimetal complex $[W_2(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}Et\text{-}7,8\text{-}Me_2\}]$, which with PMe_3 gives $[W_2(\mu\text{-}CMe)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}Et\text{-}7,8\text{-}Me_2\}]$. Mixtures of the salts $[X][WI(CO)_3\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-}Me_2\}]$ (X = NMe_3Ph or $AsPh_4$, R = C_6H_4Me-4) and the compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = W or Mo) in CH_2Cl_2 react with $AgBF_4$ to yield the dimetal complexes $[MW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$ and $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$. The corresponding reaction between a mixture of $[AsPh_4][WI(CO)_3\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-}Me_2\}]$ (R = C_6H_4Me-4) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$, in the presence of $TlBF_4$, affords equal amounts of the two isomers $[W_2(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-}Me_2\}]$ and $[W_2(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}7,8\text{-}Me_2\}]$. The latter product is the result of a polytopal rearrangement of the cage CMe groups in the precursor. This isomerisation also occurs in the formation of the complexes $[W_2(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}7,8\text{-}Me_2\}]$ (R = Me or C_6H_4Me-4) from reactions of $AgBF_4$ with mixtures of $[X][WI(CO)_3\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-}Me_2\}]$ and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$. Some reactions of the dimetal compounds containing $\eta^5\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}Me_2$ groups with PMe_3 have been studied, and the crystal structure of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$ has been determined by X-ray crystallography. The W–W bond [2.798(1) Å] is spanned essentially symmetrically by the *p*-tolylmethylidyne group [μ-C–W (average) 2.03 Å]. One W atom carries the C_5H_5 ring, a CO group and the PMe_3 ligand [W–P 2.478(3) Å]. The other W atom is co-ordinated by two CO groups and a *nido*-$2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2$ icosahedral fragment. The NMR data (^1H, $^{13}C\text{-}\{^1H\}$, $^{11}B\text{-}\{^1H\}$, ^{11}B, and $^{31}P\text{-}\{^1H\}$) for the new compounds are reported and discussed.

We have recently reported studies on protonation of the alkylidyne(carbaborane)tungsten salts $[X][W(\equiv CR)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9\text{-}7,8\text{-}Me_2)]$ **1** (X = NEt_4, PPh_4, *etc.*; R = C_6H_4-Me-4 or Me), carried out in the presence and absence of substrate molecules.[1,2] Thus, treatment of the reagents **1** with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 affords the complexes $[W(CO)_4\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}7,8\text{-}Me_2\}]$ (R = Me **2a** or C_6H_4Me-4 **2b**), the yields of which are increased if solutions containing the reactants are saturated with CO during protonation. Similarly, treatment of mixtures of compound **1b** and PhC≡CPh with $HBF_4{\cdot}Et_2O$ gives the complex $[W(CO)_2(\eta\text{-}PhC_2Ph)_2\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}7,8\text{-}Me_2\}]$ **2c**. Above *ca.* −20 °C, however, the latter releases a molecule of CO to yield $[W(CO)(\eta\text{-}PhC_2Ph)_2\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}7,8\text{-}Me_2\}]$ **3**.[2]

In contrast with the results obtained using $HBF_4{\cdot}Et_2O$, addition of aqueous HI to the reagents **1** (X = PPh_4) in CH_2Cl_2 at −78 °C affords the salts $[PPh_4][WI(CO)_3\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-}Me_2\}]$ **4**. In these products the CMe groups no longer occupy adjacent vertices in the WC_2B_9 icosahedron, as a result of a polytopal rearrangement of the cage which occurs at an unprecedentedly low temperature.[1] Treatment of **4b** with $AgBF_4$ in the presence of PhC≡CPh yields the alkyne complex $[W(CO)_2(\eta\text{-}PhC_2Ph)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$ **5**.

The isolobal relationship between PhC≡CPh and the molecules $RC\equiv M(CO)_2(\eta\text{-}C_5H_5)$ (M = W or Mo, R = C_6H_4-Me-4 or Me) prompted us to prepare novel di- or tri-nuclear metal complexes, using the synthetic strategies which afforded the alkyne complexes **3** and **5**. The former method, *i.e.* protonation of mixtures containing the reagents $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and the salts **1** with $HBF_4{\cdot}Et_2O$, produced several dimetal compounds containing bridging alkylidyne ligands.[3] In this paper we report further experiments of this type, as well as results obtained *via* the second synthetic route, employing the salts **4**, the compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$, and $AgBF_4$ or $TlBF_4$ as halide-abstracting agents.

Results and Discussion

Treatment of a mixture of the reagents **1a** (X = NEt_4) 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, after column chromatography on alumina,

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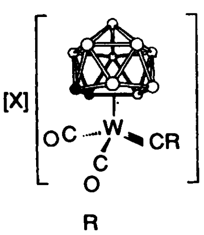
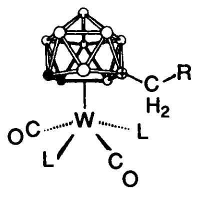
† In several of the compounds described a tungsten atom forms with a $[nido\text{-}7,8\text{-}C_2B_9H_9Me_2]^{2-}$ anion a *closo*-1,2-dicarba-3-tungstadodecaborane structure. This leads to formulations such as $[closo\text{-}1,2\text{-}Me_2\text{-}8\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}3\text{-}(\eta\text{-}PhC_2Ph)_2\text{-}3,3\text{-}(CO)_2\text{-}3,1,2\text{-}WC_2B_9H_8]$ **3** and $[NEt_4][closo\text{-}1,8\text{-}Me_2\text{-}11\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2\text{-}I\text{-}2,2,2\text{-}(CO)_3\text{-}2,1,8\text{-}WC_2B_9H_8]$ **4**. However, the use of this numbering scheme leads to an impossibly complex nomenclature for the new dimetal compounds reported in this paper. For these species we treat the cages as *nido* 11-vertex ligands with numbering as for an icosahedron from which the twelfth vertex has been removed.

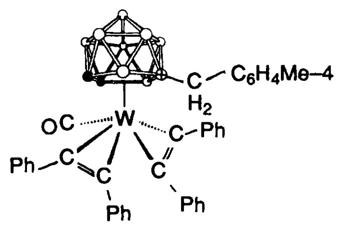
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



	R
1a	Me
1b	C_6H_4Me-4



	R	L
2a	Me	CO
2b	C_6H_4Me-4	CO
2c	C_6H_4Me-4	PhCCPh



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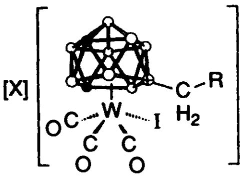
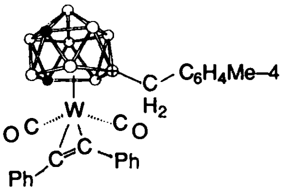


	R
4a	Me
4b	C_6H_4Me-4



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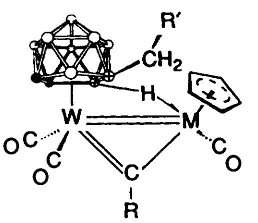
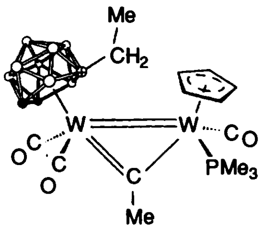
○BH ⊕B ●CMe
X = NEt_4, NMe_3Ph, PPh_4, $AsPh_4$, *etc.*



	M	R	R′
6a	W	Me	Me
6b	W	Me	C_6H_4Me-4
6c	Mo	C_6H_4Me-4	C_6H_4Me-4



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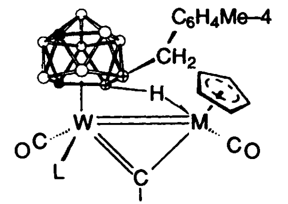
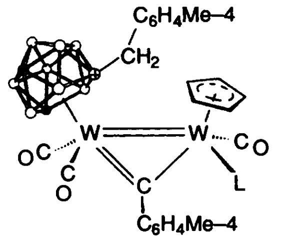


	M	L	R
8a	W	CO	C_6H_4Me-4
8b	W	CO	Me
8c	W	PMe_3	C_6H_4Me-4
8d	Mo	CO	C_6H_4Me-4
8e	Mo	PMe_3	C_6H_4Me-4



	L
9a	CO
9b	PMe_3

○BH ⊕B ●CMe

the ditungsten compound $[W_2(\mu\text{-CMe})(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-Et-}7,8\text{-Me}_2\}]$ **6a**, characterised by the data given in Tables 1–3. Complex **6a** is an analogue of the recently reported species **6b**, similarly obtained by adding $HBF_4{\cdot}Et_2O$ to an equimolar mixture of **1b** (X = NEt_4) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$.[3] In the ^1H NMR spectrum of **6a** there is a diagnostic quartet signal for the three-centre two-electron B–H ⇀ W bond at δ −7.97 [*J*(BH) 74 Hz]. Correspondingly, in the $^{11}B\text{-}\{^1H\}$ NMR spectrum there is a deshielded resonance for one boron nucleus at δ 19.6 which in a fully coupled spectrum is a doublet [*J*(HB) 74 Hz]. The NMR data for **6b** are very similar: ^1H, δ −7.85 [*J*(BH) 82 Hz]; and ^{11}B, δ 19.8 [*J*(HB) 82 Hz].

Compound **6a** reacts with PMe_3 to give $[W_2(\mu\text{-CMe})(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-Et-}7,8\text{-Me}_2\}]$ **7**, which does not contain an exopolyhedral B–H ⇀ W bond. The assignment to compound **7**, of a structure in which the PMe_3 group is bonded to the cyclopentadienyl-carrying metal, is based on close correlation of its colour and NMR spectra with those of $[W_2(\mu\text{-CC}_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$ **9b**, discussed later. In particular, it is noted that the $^{31}P\text{-}\{^1H\}$ spectrum reveals very strong coupling to tungsten [*J*(WP) 394 Hz], and that the $^{13}C\text{-}\{^1H\}$ NMR spectrum contains a singlet–doublet–singlet pattern for the carbonyl resonances. These signals occur at δ 239.6, 230.0 and 224.0 respectively, with a small $^{31}P\text{–}^{13}C$ coupling of 10 Hz for the central resonance indicating a cisoid relationship between carbonyl and phosphine ligands. These and other data characterising complex **7** are listed in Tables 1–3, and are fully consistent with the structure shown.

Reactions of the salts **4** were next investigated. Addition of $AgBF_4$ to an equimolar mixture of **4b** (X = NMe_3Ph) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 afforded, after stirring the reagents for several days, the compound $[W_2(\mu\text{-CC}_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4\text{-}Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$ **8a**, in essentially quantitative yield, together with trace amounts of $[W_2(\mu\text{-CC}_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$ **9a**. Compound **9a** was subsequently isolated in high yield (*ca.* 70%) by reduction of the reaction time to *ca.* 30 min and chromatography of the product mixture at low temperatures. It was thus shown to be an intermediate in the synthesis of **8a** since its solutions decompose quantitatively, with loss of CO, to afford **8a** within 5 d. This conversion, although not reversible by treatment of **8a** with CO gas at room temperature, was sufficiently slow to allow full characterisation of **9a**.

Data characterising compounds **8a** and **9a** are listed in Tables 1–3; the $^{11}B\text{-}\{^1H\}$ NMR spectra are especially informative. For **8a** there are resonances at δ 26.9 and 3.4, each corresponding in intensity to a single boron nucleus, and these signals may be assigned to the B–H ⇀ W and BCH_2 groups respectively. In agreement, the signal at δ 26.9 becomes a doublet [*J*(HB) 80 Hz] in a fully coupled ^{11}B spectrum, while that at δ 3.4 remains a singlet. The ^{11}B NMR spectrum of **9a** on the other hand shows no evidence for the presence of a B–H ⇀ W group, but a singlet resonance at δ 8.4 is diagnostic for the BCH_2 fragment. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **8a** and **9a** are also in

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

				$\nu_{max}{}^{b}$/cm^{-1}		Analysis (%)	
	Compound	Colour	Yield (%)	CO	BH	C	H
6a	$[W_2(\mu\text{-CMe})(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-Et-}7,8\text{-Me}_2\}]$	Green	40	1997s, 1944vs, 1919w (sh)	2564w (br)	26.6 (26.2)	3.7 (4.0)
7	$[W_2(\mu\text{-CMe})(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-Et-}7,8\text{-Me}_2\}]$	Purple	32	1931s, 1812m (br)	2559w (br)	28.3 (28.2)	4.8 (4.5)
8a	$[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$	Green	76	2001s, 1947s, 1921w (sh)	2580w (br)	38.3 (38.0)	4.2 (4.0)
8b	$[W_2(\mu\text{-CMe})(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$	Green-grey	36	1998s, 1942s, 1916w (sh)	2576w (br)	31.9 (32.7)	3.9 (3.9)
8c	$[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$	Green	93	1908m, 1872s (br)	2580w (br)	38.7 (38.6)	5.6 (4.8)
8d	$[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$	Green	84	2004s, 1951s, 1925w (sh)	2582w (br)	42.6 (42.2)	4.5 (4.4)
8e	$[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$	Green	94	1911m, 1872s (br)	2580w (br)	43.4 (42.7)	5.9 (5.3)
9a	$[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$	Dark grey	70	2028s, 1974s, 1950w (sh), 1914w	2577w (br)	38.4 (38.2)	4.2 (3.9)
9b	$[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$	Purple	97	1970m, 1938s, 1825m	2571w (br)	38.3 (38.8)	4.4 (4.6)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2.

agreement with the formulations proposed. Hence, in the ^1H NMR spectrum of **8a** there is a quartet resonance at δ −8.48 [J(BH) 80 Hz] due to the B–H ⇀ W group, and an AB pattern attributable to the two protons of the CH_2B group at δ 0.18 and 0.42 [J(AB) 14 Hz], as found in the spectra of other complexes containing this structural feature.[1] The AB pattern for the CH_2B group of **9a** is seen in the ^1H NMR spectrum at δ 1.64 and 1.77 [J(AB) 15 Hz].

A mixture of the salt **4b** (X = $AsPh_4$) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 upon treatment with $TlBF_4$ gave after *ca.* 18 h the compound $[W_2(\mu\text{-CMe})(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$ **8b**, together with an equal amount of complex **6b**; these species being separable by column chromatography. The two products are polytopal isomers. Interestingly, if $AgBF_4$ is used to effect halide abstraction instead of $TlBF_4$, compound **6b** is the only reaction product. Furthermore, this observation is not unique, a similar transformation being observed if a mixture of the reagents **4a** (X = NMe_3Ph) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 is treated with $AgBF_4$. The product of this reaction is compound **6a**, previously prepared from **1a** (X = NEt_4), $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$, and $HBF_4{\cdot}Et_2O$.[3] Synthesis of the compounds **6** from the precursors **4** requires rearrangement of the cage topology from 2,8-C_2B_9 to the conformation of the original starting materials **1** (7,8-C_2B_9). Not only is this transformation unusually facile, but it involves reunion of the carbon vertices of the icosahedral cage, in direct contrast with the commonly observed trends of polytopal isomerisation.[4] We have observed[1] this phenomenon once before through treatment of the salts **4** with excess of $AgBF_4$ in the presence of CO to afford a 1:1 mixture of the species $[W(CO)_4\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-Me}_2\}]$ (R = Me or C_6H_4Me-4) and their isomers **2a** and **2b**, respectively. The mechanism of these novel isomerisations is unknown, as are the respective roles played by $AgBF_4$ *versus* $TlBF_4$. With the former reagent removal of I^- is observed to be faster than when the thallium salt is used, and this may allow sufficient time for a *hyper-closo* intermediate to undergo a polytopal rearrangement before addition of a substrate molecule [CO or $RC\equiv W(CO)_2(\eta\text{-}C_5H_5)$] at the electronically unsaturated tungsten centre.

Treatment of compound **8a** with PMe_3 affords $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$ **8c**. The latter retains its exopolyhedral B–H ⇀ W linkage as revealed by a quartet resonance in the ^1H NMR spectrum at δ −10.13 [J(BH) 80 Hz], with a corresponding doublet signal in the fully coupled ^{11}B spectrum at δ 28.6 [J(HB) 80 Hz]. The ^{31}P-{^1H} NMR spectrum shows a singlet at δ −16.25 with ^{183}W satellites [J(WP) 303 Hz], indicating a direct W–P bond. Loss of a molecule of CO in the formation of **8c** is revealed by its ^{13}C-{^1H} NMR spectrum, which displays only two signals in the carbonyl region, at δ 236.8 and 221.4. The former resonance is a doublet, showing the small ^{31}P–^{13}C coupling (12 Hz) associated with a cisoid arrangement of carbonyl and phosphine ligands.

The molybdenum–tungsten compound $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$ **8d** was prepared by adding $AgBF_4$ to a mixture of **4b** (X = NMe_3Ph) and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 and allowing the reaction to proceed for 30 min. Complex **8d** is an isomer of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}7,8\text{-Me}_2\}]$ **6c**, previously prepared by treating a mixture of **1b** (X = NEt_4) and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$.[3] Like compound **8a**, complex **8d** reacts with PMe_3, to yield $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-Me}_2\}]$ **8e**. Data fully characterising compounds **8d** and **8e** are given in Tables 1–3. The ^{31}P-{^1H} NMR spectrum of **8e** shows conclusively that the PMe_3 group ligates the W rather than the Mo atom, since the singlet resonance at δ −18.43 exhibits strong ^{183}W-^{31}P coupling (301 Hz). This result serves to confirm the structural assignment for **8c**, as the NMR spectra of compounds **8c** and **8e** clearly show these compounds to be analogues. As expected, the ^1H NMR spectra of **8d** and **8e** show characteristic peaks at δ −7.72 [J(BH) 70 Hz] and −9.42 [J(BH) 70 Hz] respectively, for the B–H ⇀ Mo groups. In the ^{11}B NMR spectra the signals for these groups are at δ 24.6 (**8d**) and 26.4 (**8e**) with J(HB) 70 Hz, while those for the BCH_2 fragments are at δ 4.3 (**8d**) and 4.4 (**8e**).

As mentioned above, the isolation of compound **9a** is possible because its conversion into **8a** by loss of CO and formation of a B–H ⇀ W bridge is slow, requiring about 5 d in solution for completion. In contrast, compound **8d** forms very rapidly with visible evolution of CO gas, and there was no evidence for a molybdenum–tungsten species analogous to **9a**. The fourth CO ligand in compound **9a** makes this species unique among complexes of this general type.[3,5]

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

Compound	^{1}H[b] (δ)	^{13}C[c] (δ)
6a	−7.97 [br q, 1 H, BHW, *J*(BH) 74], −1.13, −0.97 [q of AB, 2 H, BCH$_2$, *J*(HH$_A$) 7, *J*(HH$_B$) 7, *J*(AB) 15], 0.10 [d of d, 3 H, CH$_2$*Me*, *J*(HH) 7 and 7], 2.10, 2.39 (s × 2, 6 H, CMe), 4.86 (s, 3 H, μ-CMe), 5.76 (s, 5 H, C$_5$H$_5$)	380.3 [s, μ-C, *J*(WC) 80 and 137], 224.2 [s, CO, *J*(WC) 141], 217.2 [s, CO, *J*(WC) 213], 214.2 [s, CO, *J*(WC) 152], 93.2 (C$_5$H$_5$), 68.7, 63.5 (s × 2, br, *C*Me), 50.2 (μ-C*Me*), 36.8, 31.8 (C*Me*), 26.4 (m, vbr, BCH$_2$), 14.8 (CH$_2$*Me*)
7	0.58 (br s, 3 H, CH$_2$*Me*), 1.37 [d, 9 H, MeP, *J*(PH) 10], 1.57 (br m, 2 H, BCH$_2$), 1.70, 2.26 (s × 2, 6 H, CMe), 5.03 (s, 3 H, μ-CMe), 5.73 (s, 5 H, C$_5$H$_5$)	367.3 (μ-*C*Me), 239.6 (CO), 230.0 [d, CO, *J*(PC) 10], 224.4 (CO), 98.0 (C$_5$H$_5$), 66.3, 63.6 (s × 2, br, *C*Me), 52.3 (μ-C*Me*), 31.4 (C*Me*), 30.1 (m, vbr, BCH$_2$), 29.9 (C*Me*), 21.4 [d, MeP, *J*(PC) 37], 15.8 (CH$_2$*Me*)
8a	−8.48 [br q, 1 H, BHW, *J*(BH) 80], 0.18, 0.42 [AB, 2 H, BCH$_2$, *J*(AB) 14], 1.83, 1.89, 2.18, 2.55 (s × 4, 12 H, CMe and Me-4), 5.69 (s, 5 H, C$_5$H$_5$), 6.42, 6.72, 6.82, 7.36 [(AB)$_2$ × 2, 8 H, C$_6$H$_4$, *J*(AB) 8]	372.9 [s, μ-C, *J*(WC) 82 and 137], 223.1 [s, CO, *J*(WC) 134], 214.3 [s, CO, *J*(WC) 214], 213.2 [s, CO, *J*(WC) 153], 163.0 [C^1(μ-C*C*$_6$H$_4$)], 143.0 [C^1(C$_6$H$_4$)], 136.5, 134.9 [C^4(C$_6$H$_4$)], 128.4,[d]128.3, 119.4 [C^{2,3}(C$_6$H$_4$)], 93.5 (C$_5$H$_5$), 69.7 (br, *C*Me), 63.9 (*C*Me), 42.8 (m, vbr, BCH$_2$), 37.6, 28.8 (C*Me*), 21.2, 21.0 (Me-4)
8b	−8.43 [br q, 1 H, BHW, *J*(BH) 71], 0.07, 0.56 [AB, 2 H, BCH$_2$, *J*(AB) 15], 1.79, 1.84 (s × 2, 6 H, CMe), 2.18 (s, 3 H, Me-4), 4.85 (s, 3 H, μ-CMe), 5.84 (s, 5 H, C$_5$H$_5$), 6.28, 6.80 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 7]	380.5 (μ-C), 224.4, 214.5, 213.4 (CO), 142.6 [C^1(C$_6$H$_4$)], 133.4 [C^4(C$_6$H$_4$)], 128.4, 128.3 [C^{2,3}(C$_6$H$_4$)], 92.9 (C$_5$H$_5$), 69.3 (br, *C*Me), 63.1 (*C*Me), 50.0 (μ-C*Me*), 41.3 (m, vbr, BCH$_2$), 37.5, 28.8 (C*Me*), 21.0 (Me-4)
8c	−10.13 [br q, 1 H, BHW, *J*(BH) 80], 1.07, 1.29 [AB, 2 H, BCH$_2$, *J*(AB) 15], 1.39 [d, 9 H, MeP, *J*(PH) 10], 1.71 (s, 3 H, CMe), 2.19, 2.26 (s × 2, 6 H, Me-4), 2.54 (s, 3 H, CMe), 5.41 (s, 5 H, C$_5$H$_5$), 6.45, 6.68, 6.83, 7.28 [(AB)$_2$ × 2, 8 H, C$_6$H$_4$, *J*(AB) 8]	366.5 (μ-C), 236.8 [d, CO, *J*(PC) 12], 221.4 (CO), 163.7 [C^1(μ-C*C*$_6$H$_4$)], 144.8 [C^1(C$_6$H$_4$)], 135.2, 132.8 [C^4(C$_6$H$_4$)], 128.7, 128.1, 127.5, 121.3 [C^{2,3}(C$_6$H$_4$)], 92.9 (C$_5$H$_5$), 68.2 (br, *C*Me), 62.8 (*C*Me), 42.5 (m, vbr, BCH$_2$), 36.2, 29.1 (C*Me*), 21.1, 21.0 (Me-4), 18.6 [d, MeP, *J*(PC) 31]
8d	−7.72 [br q, 1 H, BHMo, *J*(BH) 70], 0.08, 0.44 [AB, 2 H, BCH$_2$, *J*(AB) 14], 1.82 (s, 3 H, CMe), 1.99, 2.18 (s × 2, 6 H, Me-4), 2.52 (s, 3 H, CMe), 5.66 (s, 5 H, C$_5$H$_5$), 6.40, 6.73, 6.82, 7.34 [(AB)$_2$ × 2, 8 H, C$_6$H$_4$, *J*(AB) 8]	388.3 [s, μ-C, *J*(WC) 92], 226.1 (MoCO), 222.8 [s, WCO, *J*(WC) 131], 211.5 [s, WCO, *J*(WC) 156], 161.9 [C^1(μ-C*C*$_6$H$_4$)], 143.0 [C^1(C$_6$H$_4$)], 136.6, 133.4 [C^4(C$_6$H$_4$)], 128.5, 128.4, 128.3, 119.1 [C^{2,3}(C$_6$H$_4$)], 96.1 (C$_5$H$_5$), 71.6 (br, *C*Me), 64.1 (*C*Me), 41.9 (m, vbr, BCH$_2$), 36.9, 28.7 (C*Me*), 21.3, 21.0 (Me-4)
8e	−9.42 [br q, 1 H, BHMo, *J*(BH) 70], 1.14, 1.28 [AB, 2 H, BCH$_2$, *J*(AB) 15], 1.43 [d, 9 H, MeP, *J*(PH) 9], 1.71 (s, 3 H, CMe), 2.18, 2.32 (s × 2, 6 H, Me-4), 2.50 (s, 3 H, CMe), 5.37 (s, 5 H, C$_5$H$_5$), 6.43, 6.68, 6.82, 7.28 [(AB)$_2$ × 2, 8 H, C$_6$H$_4$, *J*(AB) 7]	384.0 (μ-C), 237.1 [d, WCO, *J*(PC) 12, *J*(WC) 128], 232.5 (MoCO), 162.4 [C^1(μ-C*C*$_6$H$_4$)], 144.7 [C^1(C$_6$H$_4$)], 135.2, 132.8 [C^4(C$_6$H$_4$)], 128.7, 128.1, 127.7, 121.0 [C^{2,3}(C$_6$H$_4$)], 95.2 (C$_5$H$_5$), 69.7 (br, *C*Me), 63.5 (*C*Me), 41.7 (m, vbr, BCH$_2$), 35.3, 28.9 (C*Me*), 21.2, 21.0 (Me-4), 18.6 [d, MeP, *J*(PC) 32]
9a	0.67, 1.62 (s × 2, 6 H, CMe), 1.64, 1.77 [AB, 2 H, BCH$_2$, *J*(AB) 15], 2.24, 2.59 (s × 2, 6 H, Me-4), 5.71 (s, 5 H, C$_5$H$_5$), 6.44, 6.72, 6.91, 7.30 [(AB)$_2$ × 2, 8 H, C$_6$H$_4$, *J*(AB) 7]	380.4 [s, μ-C, *J*(WC) 79 and 104], 223.8 [s, CO, *J*(WC) 143], 219.4 [s, CO, *J*(WC) 165], 216.2 [s, CO, *J*(WC) 165], 214.3 [s, CO, *J*(WC) 171], 166.4 [C^1(μ-C*C*$_6$H$_4$)], 143.1 [C^1(C$_6$H$_4$)], 136.1, 133.3 [C^4(C$_6$H$_4$)], 128.7, 128.6, 127.4, 121.6 [C^{2,3}-(C$_6$H$_4$)], 95.9 (C$_5$H$_5$), 72.8 (br, *C*Me), 66.5 (*C*Me), 31.6 (m, vbr, BCH$_2$), 29.5, 29.4, 28.9, 21.0 (C*Me* and Me-4)
9b	[e] 0.98, 1.10*, 2.25*, 1.33 (s × 2, 6 H, CMe), 1.53, 1.57* [d, 9 H, MeP, *J*(PH) 11], 2.23*, 2.29 (s, 3 H, Me-4), 2.49, 2.92 [AB, 2 H, BCH$_2$, *J*(AB) 13], 2.54 (s, 3 H, Me-4), 5.72, 5.76* (s, 5 H, C$_5$H$_5$), 6.19, 6.26* [d, 1 H, C$_6$H$_4$, *J*(HH) 8], 6.62, 6.83* [d, 1 H, C$_6$H$_4$, *J*(HH) 8], 6.69*, 6.91*, 7.05, 7.12 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 8], 7.71, 7.33 [d × 2, 2 H, C$_6$H$_4$, *J*(HH) 8]	[e] 353.1 (μ-C), 236.6 (CO), 230.5 [d, CO, *J*(PC) 9], 222.9 (CO), 162.9, 161.8* [C^1(μ-C*C*$_6$H$_4$)], 145.5, 144.4* [C^1(C$_6$H$_4$)], 135.1*, 134.8, 132.9, 132.6* [C^4(C$_6$H$_4$)], 128.8, 128.6*, 128.3, 128.2* [C^{2,3}(C$_6$H$_4$)], 127.6, 127.3*, 126.8, 126.5, 121.4*, 118.7 [C^{2,3,5,6}(C$_6$H$_4$)], 96.3, 95.8* (C$_5$H$_5$), 62.5 (*C*Me), 59.8 (br, *C*Me), 31.1 (m, vbr, BCH$_2$), 30.9, 30.1*, 29.1 (C*Me*), 22.9 [d, MeP, *J*(PC) 36], 21.2, 21.1*, 21.0 (Me-4)

[a] Chemical shifts δ in ppm, coupling constants in Hz, measurements at room temperature in CD$_2$Cl$_2$ unless otherwise stated. [b] Proton resonances for terminal B–H groups occur as broad unresolved signals in the range δ *ca.* −2 to +3. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe$_4$. [d] Extra intensity and width of this peak suggests coincidence of two signals. [e] Spectrum recorded at −60 C. Peaks due to minor isomer (relative proportion 2:5) indicated by asterisk, see text. Note that in some cases major and minor isomer resonances are coincident, or are too weak to be observed.

Compound **9a** reacts with PMe$_3$ to afford [W$_2$(μ-CC$_6$H$_4$Me-4)(CO)$_3$(PMe$_3$)(η-C$_5$H$_5$){η^5-2,8-C$_2$B$_9$H$_8$-10-(CH$_2$C$_6$H$_4$Me-4)-2,8-Me$_2$}] **9b** in essentially quantitative yield. Examination of the ^{1}H, ^{13}C-{^{1}H}, ^{11}B-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of this product revealed that it was formed as an equilibrium mixture of two isomers, in the ratio 2:5 based on relative peak intensities from the ^{31}P-{^{1}H} spectrum. We suggest that the isomerism results from different configurations of the W(CO)(PMe$_3$)(η-C$_5$H$_5$) fragment with respect to the remainder of the molecule.[6] Both isomers display fluxionality such that resonances in the ^{1}H and ^{13}C NMR spectra are broad and unresolved when recorded at ambient temperatures. However, when measurements are made at −60 C limiting low-temperature spectra are obtained. Under these conditions, the ^{1}H and ^{13}C-{^{1}H} NMR spectra indicate non-equivalent aromatic hydrogen and carbon atoms for one C$_6$H$_4$ ring of each isomer. This implies that rotation about one of the C–C^1(C$_6$H$_4$) bonds is restricted, but does not in itself give a clue as to which of the two *p*-tolyl rings in each isomer is responsible.

In the ^{1}H NMR spectrum of compound **9b** there is no signal for an exopolyhedral B–H → W bond, but an AB pattern for a BCH$_2$ group of the major isomer is seen at δ 2.49 and 2.92 with *J*(AB) 13 Hz. In the ^{11}B-{^{1}H} NMR spectrum this BCH$_2$ group resonates at δ 7.8 for the major, and at δ 6.2 for the minor isomer. In the ^{13}C-{^{1}H} NMR spectrum there is a very broad peak at δ 31.1 which may be ascribed to overlapping signals for the BCH$_2$ moiety of both isomers. The resonance seen at δ 353.1 may be ascribed to the ligated carbon of the bridging alkylidyne group; the signal being due either to the major isomer or to an overlap of peaks due to both isomers. The resonance is relatively deshielded, although less so than those for the μ-C nuclei of the other complexes (range δ 366.5–388.3, Table 2). These chemical shifts are typical for dimetal compounds with bridging alkylidyne groups and which are electronically unsaturated

Table 3 Boron-11 and phosphorus-31 NMR data[a] for the complexes

Compound	$^{11}B^{b}$ (δ)	$^{31}P^{c}$ (δ)
6a	19.6 [s, 1 B, BHW, J(BH) 74], 6.6 (s, 1 B, BCH_2), −3.2, −4.4, −7.4, −9.2, −11.2, −12.7, −14.2 (1 B × 7)	
7	12.3 (s, 1 B, BCH_2), −4.9, −6.6, −7.2 (1 B × 3), −8.7 (2 B), −9.8, −11.8, −13.4 (1 B × 3)	−22.15 [s, J(WP) 394]
8a	26.9 [s, 1 B, BHW, J(BH) 80], 3.4 (s, 1 B, BCH_2), −6.3 (2 B), −9.2 (3 B), −12.0, −15.3 (1 B × 2)	
8b	26.3 [s, 1 B, BHW, J(BH) 71], 2.8 (s, 1 B, BCH_2), −6.1 (2 B), −9.4 (3 B), −12.2, −16.0 (1 B × 2)	
8c	28.6 [s, 1 B, BHW, J(BH) 80], 4.0 (s, 1 B, BCH_2), −5.9 (1 B), −8.3 (2 B), −10.2 (3 B), −15.2 (1 B)	−16.25 [s, J(WP) 303]
8d	24.6 [s, 1 B, BHMo, J(BH) 70], 4.3 (s, 1 B, BCH_2), −5.9 (1 B), −7.0, −8.9 (2 B × 2), −11.0, −14.8 (1 B × 2)	
8e	26.4 [s, 1 B, BHMo, J(BH) 70], 4.4 (s, 1 B, BCH_2), −6.2 (1 B), −8.3 (2 B), −9.6 (3 B), −14.5 (1 B)	−18.43 [s, J(WP) 301]
9a	8.4 (s, 1 B, BCH_2), −1.6, −2.8 (1 B × 2), −6.9 (br, 4 B), −12.5, −15.0 (1 B × 2)	
9b[d]	7.8, 6.2* (s, 1 B, BCH_2), −1.9 to −17.6 (m, br, 8 B)	−19.78* [s, J(WP) 390], −22.86 [s, J(WP) 390]

[a] Chemical shifts δ in ppm, coupling constants in Hz, measurements in CD_2Cl_2 at ambient temperature. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). The J(BH) values were obtained from fully coupled ^{11}B NMR spectra. [c] Hydrogen-1 decoupled, chemical shifts to high frequency of 85% H_3PO_4 (external). [d] Peaks for minor isomer indicated by asterisk, see text.

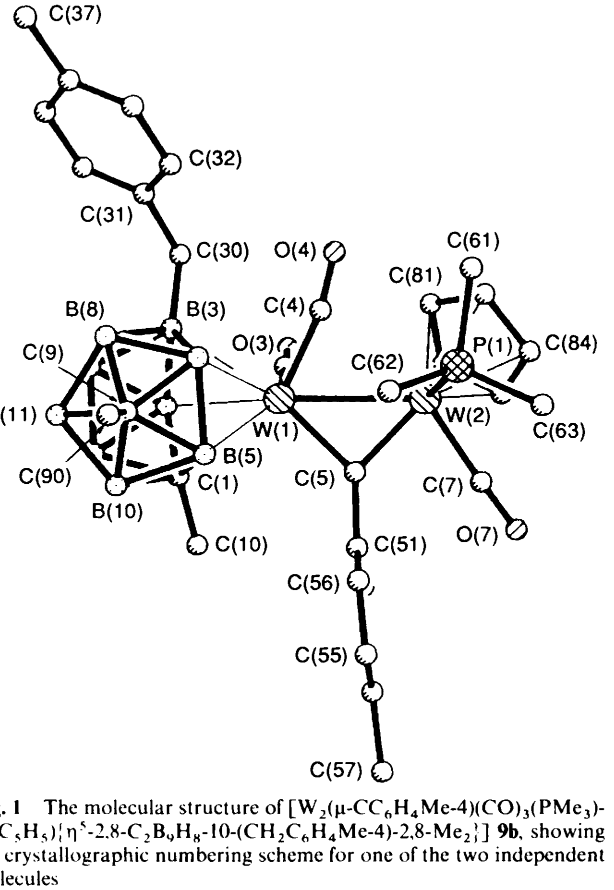


Fig. 1 The molecular structure of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$ **9b**, showing the crystallographic numbering scheme for one of the two independent molecules

with 32 cluster valence electrons (c.v.e.s).[6b,7] In the carbonyl region of the spectrum, a singlet–doublet–singlet pattern at δ 236.6, 230.5 [J(PC) 9 Hz] and 222.9 indicates significant structural similarity to complex 7, mentioned earlier. Furthermore, the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows that in both isomers the phosphine ligand is bound strongly to tungsten, leading to $^{183}W\text{-}^{31}P$ coupling of 390 Hz. This figure is comparable with that for complex **7**, but contrasts markedly with those of compounds **8c** and **8e** (*ca.* 300 Hz). However, these data leave some ambiguity as to the structure of the purple complexes **7** and **9b**, since they do not show beyond doubt which tungsten atom bears the phosphine ligand.

In order to define the structure of compound **9b** unequivocally and thereby reveal the structure of complex **7**, an X-ray crystallographic study of the former species was carried out. The asymmetric unit contains two similar but crystallographically independent molecules, minor differences being associated with the orientations of the bridging tolyl ring and the MeP groups. The significant bond distances and angles are listed in Table 4 and the structure of molecule 1 is shown in Fig. 1. Since the structural parameters are so similar, only the data for this molecule are discussed.

The W–W bond [2.798(1) Å] is spanned essentially symmetrically by the *p*-tolylmethylidyne group [W(1)–C(5) 2.06(1), W(2)–C(5) 2.00(1) Å]. In compound **6b** the W–W separation [2.651(1) Å] is shorter, and the μ-C distances are 1.95(1) and 2.03(1) Å.[3] The shorter metal–metal bond in **6b**, compared with **9b**, is probably due to the effect of the B–H ⇀ W bond in the former, since both are electronically unsaturated 32 c.v.e. species.

The X-ray data reveal that W(2) carries the C_5H_5 ring, the PMe_3 ligand [W–P 2.478(3) Å], and a terminally bound carbonyl group, W(2)–C(7)–O(7) 178(1)°. The W–P distance is typical for a W–PMe_3 group (2.485 Å).[8] The W(1) atom is co-ordinated by two CO groups, W(1)–C(3)–O(3) 178(1) and W(1)–C(4)–O(4) 168(1)°, with the latter slightly bent towards W(2). Several of the dimetal compounds described in this paper display IR bands for CO groups below 1900 cm⁻¹, indicating semi-bridging of the metal–metal bonds by these ligands. The metal atom W(1) is also co-ordinated by the *nido*-2,8-C_2B_9 fragment, previously observed by X-ray diffraction in the alkyne complex $[W(CO)_2(\eta\text{-}PhC_2Me)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$,[1] which is isolobally mapped with compound **9b**. In the latter the exopolyhedral $CH_2C_6H_4Me$-4 group is linked to a boron in the lower pentagonal ring of the cage [B(3)–C(30) 1.62(2) Å]. Examination of the molecular structure of **9b** not only proves that the PMe_3 ligand is bonded to the cyclopentadienyl-bearing tungsten atom, but indicates which C–C¹(C_6H_4) bond is likely to have restricted rotation.

Table 4 Selected internuclear distances (Å) and angles (°) for [$W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}$] **9b**

Molecule 1

W(1)–W(2)	2.798(1)	W(2)–P(1)	2.478(3)	W(1)–C(3)	2.00(1)	W(1)–C(4)	1.93(1)
W(2)–C(7)	1.97(2)	C(3)–O(3)	1.13(2)	C(4)–O(4)	1.18(2)	C(7)–O(7)	1.14(2)
W(1)–C(5)	2.06(1)	W(2)–C(5)	2.00(1)	C(5)–C(51)	1.48(1)	W(1)–C(1)	2.46(1)
W(1)–B(2)	2.39(1)	W(1)–B(3)	2.46(2)	W(1)–B(4)	2.36(2)	W(1)–B(5)	2.34(1)
W(2)–C(cp)	2.364*	P(1)–C	1.792*	C(1)–C(10)	1.55(2)	C(9)–C(90)	1.52(2)
B(3)–C(30)	1.62(2)	C(30)–C(31)	1.52(2)	C(1)–B(2)	1.70(2)	C(1)–B(5)	1.69(2)
C(1)–B(6)	1.72(2)	C(1)–B(10)	1.69(2)	B(2)–B(3)	1.79(2)	B(2)–B(6)	1.80(2)
B(2)–B(7)	1.78(2)	B(3)–B(4)	1.82(2)	B(3)–B(7)	1.77(2)	B(3)–B(8)	1.80(2)
B(4)–B(5)	1.83(2)	B(4)–B(8)	1.78(2)	B(4)–C(9)	1.72(2)	B(5)–C(9)	1.74(2)
B(5)–B(10)	1.78(2)	B(6)–B(7)	1.72(2)	B(6)–B(10)	1.73(2)	B(6)–B(11)	1.73(2)
B(7)–B(8)	1.77(2)	B(7)–B(11)	1.79(2)	B(8)–C(9)	1.68(2)	B(8)–B(11)	1.77(2)
C(9)–B(10)	1.69(2)	C(9)–B(11)	1.69(2)	B(10)–B(11)	1.75(2)		

W(1)–C(3)–O(3)	178(1)	W(1)–C(4)–O(4)	168(1)	W(2)–C(7)–O(7)	178(1)
W(2)–W(1)–C(3)	87.3(4)	W(2)–W(1)–C(4)	65.9(4)	C(3)–W(1)–C(4)	86.3(5)
W(2)–W(1)–C(1)	141.5(3)	W(2)–W(1)–B(2)	157.2(4)	W(2)–W(1)–B(3)	146.6(3)
W(2)–W(1)–B(4)	129.2(3)	W(2)–W(1)–B(5)	125.8(3)	W(2)–W(1)–C(5)	45.6(3)
C(3)–W(1)–C(5)	109.8(5)	C(4)–W(1)–C(5)	106.7(5)	B(3)–C(30)–C(31)	114(1)
W(1)–W(2)–P(1)	100.2(1)	W(1)–W(2)–C(7)	122.0(4)	P(1)–W(2)–C(7)	85.3(4)
W(1)–W(2)–C(5)	47.3(3)	P(1)–W(2)–C(5)	98.6(3)	C(7)–W(2)–C(5)	74.7(5)
W(1)–C(5)–W(2)	87.1(4)	W(1)–C(5)–C(51)	136.9(7)	W(2)–C(5)–C(51)	135.8(8)
W(1)–C(1)–C(10)	112.4(8)	W(1)–B(3)–C(30)	115.1(8)		

Molecule 2

W(1A)–W(2A)	2.803(1)	W(2A)–P(1A)	2.477(4)	W(1A)–C(3A)	1.99(1)	W(1A)–C(4A)	1.95(1)
W(2A)–C(7A)	1.95(2)	C(3A)–O(3A)	1.15(2)	C(4A)–O(4A)	1.16(2)	C(7A)–O(7A)	1.17(2)
W(1A)–C(5A)	2.08(1)	W(2A)–C(5A)	2.00(1)	C(5A)–C(51A)	1.47(1)	W(1A)–C(1A)	2.45(1)
W(1A)–B(2A)	2.44(2)	W(1A)–B(3A)	2.45(2)	W(1A)–B(4A)	2.33(1)	W(1A)–B(5A)	2.33(1)
W(2A)–C(cp)	2.375*	P(1A)–C	1.796*	C(1A)–C(10A)	1.54(2)	C(9A)–C(90A)	1.51(2)
B(3A)–C(30A)	1.61(2)	C(30A)–C(31A)	1.53(2)	C(1A)–B(2A)	1.70(2)	C(1A)–B(5A)	1.69(2)
C(1A)–B(6A)	1.72(2)	C(1A)–B(10A)	1.69(2)	B(2A)–B(3A)	1.82(2)	B(2A)–B(6A)	1.77(2)
B(2A)–B(7A)	1.78(2)	B(3A)–B(4A)	1.84(2)	B(3A)–B(7A)	1.75(2)	B(3A)–B(8A)	1.78(2)
B(4A)–B(5A)	1.79(2)	B(4A)–B(8A)	1.81(2)	B(4A)–C(9A)	1.75(2)	B(5A)–C(9A)	1.71(2)
B(5A)–B(10A)	1.79(2)	B(6A)–B(7A)	1.77(2)	B(6A)–B(10A)	1.74(2)	B(6A)–B(11A)	1.77(2)
B(7A)–B(8A)	1.72(2)	B(7A)–B(11A)	1.78(2)	B(8A)–C(9A)	1.72(2)	B(8A)–B(11A)	1.74(2)
C(9A)–B(10A)	1.71(2)	C(9A)–B(11A)	1.71(2)	B(10A)–B(11A)	1.78(3)		

W(1A)–C(3A)–O(3A)	178(1)	W(1A)–C(4A)–O(4A)	169(1)	W(2A)–C(7A)–O(7A)	178(1)
W(2A)–W(1A)–C(3A)	85.5(4)	W(2A)–W(1A)–C(4A)	66.4(4)	C(3A)–W(1A)–C(4A)	83.7(5)
W(2A)–W(1A)–C(1A)	140.0(3)	W(2A)–W(1A)–B(2A)	154.4(3)	W(2A)–W(1A)–B(3A)	148.1(3)
W(2A)–W(1A)–B(4A)	131.1(3)	W(2A)–W(1A)–B(5A)	127.2(4)	W(2A)–W(1A)–C(5A)	45.5(3)
C(3A)–W(1A)–C(5A)	112.6(5)	C(4A)–W(1A)–C(5A)	105.4(5)	B(3A)–C(30A)–C(31A)	117.1(9)
W(1A)–W(2A)–P(1A)	100.2(1)	W(1A)–W(2A)–C(7A)	122.1(4)	P(1A)–W(2A)–C(7A)	84.8(4)
W(1A)–W(2A)–C(5A)	47.7(3)	P(1A)–W(2A)–C(5A)	93.2(3)	C(7A)–W(2A)–C(5A)	74.6(5)
W(1A)–C(5A)–W(2A)	86.8(4)	W(1A)–C(5A)–C(51A)	135.7(7)	W(2A)–C(5A)–C(51A)	137.4(8)
W(1A)–C(1A)–C(10A)	111.3(8)	W(1A)–B(3A)–C(30A)	115.6(8)		

* Average distance between W and C atoms of C_5 ring, and between P and C atoms of PMe_3 respectively.

Hence we suggest that spinning about C(30)–C(31) is facile and occurs rapidly in solutions cooled to −60 °C, whereas the close approach of C(10) and C(7)–O(7) towards the bridging *p*-tolylmethylidyne group restricts rotation of the latter about C(5)–C(51). Thus the $\mu\text{-}CC_6H_4$ aromatic ring is believed to be responsible for broadening of the peaks in the ambient-temperature ^1H and ^{13}C NMR spectra.

Potentially, species such as **6** or **8** may be formed as diastereoisomers, since the cage and the metal centre carrying the C_5H_5 group are chiral, yet only one isomer is observed for each complex. This is believed to be due to steric constraints imposed by the B–H ⟶ M bridge system which provide a strong thermodynamic preference for one particular conformation. Since **9b** contains no such linkage it exists in two isomeric forms. However, if careful recrystallisation of the various products is not carried out many of these compounds do show traces of NMR-detectable species, probably diastereoisomers, with similar chemical shifts to those of the major product. Once pure, all the complexes **6** and **8** show no tendency to isomerise.

Formation of the PMe_3 complexes described in this paper illustrates three different types of reaction observed previously with dimetal compounds structurally related to the species **6**, **8a** and **8d**. In reactions of the first type a CO molecule is substituted at the carbaborane-bearing metal atom, which may be molybdenum or tungsten. This process occurs in the synthesis of compounds **8c** and **8e**, and the B–H ⟶ M interaction is sustained in the product. Similar behaviour has been observed previously in the preparation of [$MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$] ($C_9H_7$ = indenyl)[5] and [$MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta^7\text{-}C_7H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9\text{-}7,8\text{-}Me_2)$].[6b] In reactions of the second type the B–H ⟶ M three-centre two-electron bonds are lifted by addition of the PMe_3 group to the metal atom (Mo or W) bearing the $\eta\text{-}C_5H_5$ ligand or a related group ($\eta^5\text{-}C_9H_7$). This process is observed in the synthesis of compound **7**, and in the preparation of the species [$MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9\text{-}7,8\text{-}Me_2)$] (M = Mo or W).[5] In the third category of reaction, a CO molecule at the $\eta\text{-}C_5H_5$-bearing metal atom is substituted by a PMe_3 molecule. This is observed in the synthesis of the compounds **9b** and [MoW(μ-

$\mathrm{CMe)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4\text{-}Me\text{-}4)\text{-}7,8\text{-}Me_2\}]}$, or $\mathrm{[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]}$.[3] The different types of reaction observed with $\mathrm{PMe_3}$ do not appear to follow a recognisable pattern, nor is one particular reactivity greatly favoured over the others, which demonstrates the subtle electronic and steric balance operating in these unsaturated dimetal species.

It is evident from the work described in this paper, and that reported previously,[3] that it is possible to prepare many dimetal compounds of the Group 6 metals containing the $\mathrm{C_2B_9H_8(CH_2R)Me_2}$ cage system. However, whereas the exopolyhedral $\mathrm{CH_2R}$ group is invariably bonded to a boron atom in the metal-ligating pentagonal ring of the *nido*-$\mathrm{C_2B_9}$ fragment, the C vertices of this fragment may both lie in this $\overline{\mathrm{CCBBB}}$ ring, or one of the carbons may occupy a site in the second layer of cage atoms. With this topology there is no C–C connectivity.

Fortunately, it is possible to distinguish by $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ NMR spectroscopy between polytopal isomers such as **6b** and **8b**, or **6c** and **8d**. The $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ NMR spectra of the species **6** display two resonances for the non-equivalent CMe nuclei which are reasonably sharp and of equal intensity. In contrast, the signals for the non-equivalent CMe nuclei of complexes of type **8** consist of a singlet adjacent to a very broad peak. The latter may be tentatively assigned to the upper-ring carbon atom, the signal broadened and weakened in intensity by the effect of five adjacent quadrupolar boron nuclei.

As unsaturated 32 c.v.e. dimetal species, the complexes reported in this paper were expected to show interesting chemical reactivity beyond the syntheses described with $\mathrm{PMe_3}$. Many novel compounds have been obtained through reactions of related dimetal species with substrates such as alkynes, secondary phosphines and diazoalkanes, leading to C–C or B–C bond-forming and hydrogen migration.[9] Furthermore, when heated at 80 °C in toluene for 3 h the 32 c.v.e. complex $\mathrm{[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9\text{-}7,8\text{-}Me_2)]}$ undergoes a polytopal rearrangement to give $\mathrm{[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,9\text{-}C_2B_9H_9\text{-}7,9\text{-}Me_2)]}$,[3] in which the cage carbon atoms are no longer adjacent to one another, but remain co-ordinated to the W atom.

Unfortunately, the compounds reported herein display very limited chemical reactivity and show no tendency to isomerise, even under prolonged heating (toluene, 80 °C). This is probably due to steric crowding around the metal centres, exacerbated by the $\mathrm{CH_2R}$ substituent on the cage. Nevertheless, these species provide further evidence for the applicability of isolobal theory to designed synthesis,[10] and demonstrate that unsaturated dimetallacarbaborane systems can show unusual rearrangement behaviour.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. The NMR spectra were recorded with JEOL JNM GX270 and GX400 spectrometers, the IR spectra with a Perkin-Elmer FT1600 spectrometer. Chromatography columns of given dimensions were charged with alumina (Brockman activity III). The compounds $\mathrm{[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]}$ ($\mathrm{M = Mo}$ or W, $\mathrm{R = C_6H_4Me\text{-}4}$; M = W, R = Me),[11] $\mathrm{[X][W(\equiv CR)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9\text{-}7,8\text{-}Me_2)]}$ ($\mathrm{X = PPh_4}$ or $\mathrm{NEt_4}$, $\mathrm{R = C_6H_4Me\text{-}4}$ or Me),[12] and $\mathrm{[X][WI(CO)_3\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-}Me_2\}]}$ ($\mathrm{X = NEt_4}$, $\mathrm{NMe_3Ph}$, or $\mathrm{AsPh_4}$; $\mathrm{R = C_6H_4Me\text{-}4}$ or Me)[1] were obtained using procedures reported earlier. The reagent $\mathrm{HBF_4{\cdot}Et_2O}$ consisted of an 85% solution in diethyl ether as supplied by Aldrich Chemicals.

Synthesis of the Dimetal Compounds.—(*i*) A mixture of compound **1a** ($\mathrm{X = NEt_4}$) (0.16 g, 0.29 mmol) and $\mathrm{[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]}$ (0.095 g, 0.29 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) at −78 °C was treated with $\mathrm{HBF_4{\cdot}Et_2O}$ (50 μl, 0.29 mmol) and stirred vigorously. The reaction mixture rapidly darkened from yellow to brown *via* red, and was allowed to warm to room temperature over *ca.* 30 min. After stirring for 90 min, alumina (*ca.* 3 g) was added to the mixture and solvent was removed *in vacuo*. The resulting powder was transferred to the top of the alumina-packed chromatography column (2 × 12 cm) which was eluted with $\mathrm{CH_2Cl_2}$–hexane (3:7), to separate a dark green fraction. This fraction was collected and solvent reduced *in vacuo* to *ca.* 5 cm^3 whereupon cooling to −78 °C and removal of the supernatant *via* a syringe yielded dark green *microcrystals* of $\mathrm{[W_2(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}Et\text{-}7,8\text{-}Me_2\}]}$ **6a** (0.085 g). A number of minor products, predominantly orange and brown, remained adsorbed on the alumina and could not be isolated.

(*ii*) A $\mathrm{CH_2Cl_2}$ (20 cm^3) solution of compound **6a** (0.085 g, 0.11 mmol) was treated with $\mathrm{PMe_3}$ (20 μl, 0.19 mmol) and stirred for 12 h, during which time the green reaction mixture became red-brown. Solvent was removed *in vacuo* and the residue redissolved in $\mathrm{CH_2Cl_2}$–hexane (2 cm^3, 2:3), for chromatography on alumina. Elution of the column (2 × 15 cm) with the same solvent mixture separated four bands. The first (green) was a trace of starting compound and the second (pink) also only contained a trace of material, so could not be identified. The third (purple) was collected, stripped of solvent *in vacuo*, and recrystallised from $\mathrm{CH_2Cl_2}$–hexane (5 cm^3, 1:4) at −78 °C, to yield purple *microcrystals* of $\mathrm{[W_2(\mu\text{-}CMe)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}Et\text{-}7,8\text{-}Me_2\}]}$ **7** (0.030 g). The fourth fraction (orange) was a second unidentified trace of a by-product.

(*iii*) (*a*) A mixture of compound **4b** ($\mathrm{X = NMe_3Ph}$) (0.20 g, 0.25 mmol) and $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]}$ (0.14 g, 0.25 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (20 cm^3) and treated with $\mathrm{AgBF_4}$ (0.049 g, 0.25 mmol). The mixture was stirred at room temperature for 5 d before removal of solvent *in vacuo*. A $\mathrm{CH_2Cl_2}$–hexane mixture (3 cm^3, 1:4) was added to the residue and the resulting slurry transferred to a chromatography column (2 × 15 cm) *via* a syringe. Elution of the column at −20 °C with the same solvent mixture separated two fractions. The first was collected and solvent removed *in vacuo* to isolate a dark green powder which was recrystallised carefully from $\mathrm{CH_2Cl_2}$–hexane (5 cm^3, 1:10) at −78 °C. Removal, *via* a syringe, of the pale yellow supernatant containing a trace of $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]}$ yielded dark green *microcrystals* of $\mathrm{[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]}$ **8a** (0.17 g). The second fraction was a trace of the intermediate compound **9a**.

(*b*) In a similar experiment a mixture of compounds **4b** ($\mathrm{X = NMe_3Ph}$) (0.20 g, 0.25 mmol) and $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]}$ (0.14 g, 0.25 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (20 cm^3) and treated with $\mathrm{AgBF_4}$ (0.049 g, 0.25 mmol). The solution darkened considerably and gentle evolution of gas was observed. After 30 min solvent was removed *in vacuo* and $\mathrm{CH_2Cl_2}$–hexane (3 cm^3, 1:4) added to the residue for transfer to the top of a chromatography column (2 × 15 cm), cooled at −20 °C. Elution with the same solvent mixture afforded a grey band from which solvent was rapidly removed *in vacuo*. Recrystallisation of the resultant powder from $\mathrm{CH_2Cl_2}$–hexane (3 × 5 cm^3, 1:10) at −78 °C removed traces of compound **8a**, and afforded dark grey *microcrystals* of $\mathrm{[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]}$ **9a** (0.16 g). Solid samples of **9a** are stable under an inert atmosphere for several days, but its solutions decompose quantitatively to compound **8a** within 5 d at ambient temperatures.

(*iv*) A mixture of the salt **4b** ($\mathrm{X = AsPh_4}$) (0.15 g, 0.14 mmol) and $\mathrm{[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]}$ (0.05 g, 0.15 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (20 cm^3) and treated with $\mathrm{TlBF_4}$ (0.042 g, 0.14 mmol). The resulting solution was stirred for 18 h, during which time a bright yellow precipitate appeared and the mixture turned from dark orange to brown-green. The suspension was filtered through a Celite plug (2 × 2 cm) before removal of solvent *in vacuo*. The residue was treated with CH_2Cl_2–hexane (3 cm^3, 1:4) and the resulting slurry transferred to the top of a chromatography column (2 × 15 cm). Elution of the column with the same solvent mixture separated two green fractions, the first slightly darker than the second. Each was collected, stripped of solvent *in vacuo*, and recrystallised from CH_2Cl_2–hexane (5 cm^3, *ca.* 1:20). Thus from the former fraction were isolated dark green *microcrystals* of $[W_2(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$ **8b** (0.040 g), and from the latter fraction dark green *microcrystals* of the previously reported[3] isomeric compound **6b** (0.040 g).

(*v*) A CH_2Cl_2 solution (20 cm^3) of compound **8a** (0.10 g, 0.11 mmol) was treated with an excess of PMe_3 (40 μl, 0.39 mmol), and the mixture was stirred for 2 d, during which time it darkened slightly. Solvent was removed *in vacuo*, and the residue was chromatographed (2 × 12 cm column). Elution of the column with CH_2Cl_2–hexane (1:4) afforded a single fraction from which solvent was removed *in vacuo*. Recrystallisation of the product from CH_2Cl_2–hexane (20 cm^3, 1:10) at −78 °C yielded dark green *microcrystals* of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$ **8c** (0.10 g).

(*vi*) In a similar procedure to (*iiib*) above, a mixture of compounds **4b** (X = NMe_3Ph) (0.20 g, 0.25 mmol) and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.081 g, 0.25 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and treated with $AgBF_4$ (0.049 g, 0.25 mmol). As the solution was stirred a colour change was observed, from orange to green, along with the precipitation of a pale solid and the gentle evolution of CO. After 30 min solvent was removed *in vacuo* and the residue chromatographed (2 × 15 cm column) at −20 °C. Elution with CH_2Cl_2–hexane (1:4) isolated one fraction, from which solvent was again removed *in vacuo* to afford a green powder. Recrystallisation from CH_2Cl_2–hexane (10 cm^3, 1:6) at −78 °C and removal of a minor brown by-product in the supernatant yielded dark green *microcrystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4Me\text{-}4)\text{-}2,8\text{-}Me_2\}]$ **8d** (0.17 g).

(*vii*) A solution of compound **8d** (0.06 g, 0.075 mmol) in CH_2Cl_2 (20 cm^3) was treated with an excess of PMe_3 (40 μl, 0.39 mmol), as for (*v*) above. The mixture was stirred for 4 d

Table 5 Atomic positional parameters (fractional coordinates × 10^4) for compound **9b**, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	4 705(1)	804(1)	1 583(1)	C(5)	3 414(9)	428(5)	1 849(4)
W(2)	2 457(1)	1 088(1)	1 556(1)	C(51)	3 268(6)	−80(3)	2 153(3)
P(1)	1 544(3)	649(2)	747(1)	C(52)	3 379	−12	2 669
C(3)	5 121(11)	1 547(6)	1 935(5)	C(53)	3 165	−469	2 962
O(3)	5 345(9)	1 974(4)	2 119(4)	C(54)	2 839	−995	2 740
C(4)	4 014(10)	1 256(5)	1 008(5)	C(55)	2 728	−1 064	2 224
O(4)	3 764(7)	1 510(4)	629(4)	C(56)	2 943	−606	1 930
C(7)	1 457(11)	592(6)	1 850(5)	C(57)	2 585(15)	−1 494(7)	3 066(6)
O(7)	849(8)	319(5)	2 017(4)	C(61)	1 319(16)	1 063(7)	166(5)
C(1)	6 183(9)	131(5)	1 978(4)	C(62)	2 281(14)	61(6)	571(6)
C(10)	5 999(10)	−92(6)	2 491(4)	C(63)	165(12)	378(10)	719(6)
B(2)	6 697(12)	791(6)	1 895(5)	C(81)	2 740(11)	2 105(4)	1 482(6)
B(3)	6 401(11)	994(6)	1 247(5)	C(82)	2 650	1 968	1 979
B(4)	5 520(12)	415(6)	946(5)	C(83)	1 558	1 742	1 961
B(5)	5 373(10)	−100(6)	1 432(5)	C(84)	972	1 740	1 453
B(6)	7 585(12)	170(7)	1 955(6)	C(85)	1 703	1 964	1 157
B(7)	7 710(12)	684(6)	1 518(5)	W(1A)	8 593(1)	1 789(1)	4 261(1)
B(8)	6 978(11)	433(6)	929(5)	W(2A)	10 739(1)	1 382(1)	4 215(1)
C(9)	6 372(9)	−175(5)	1 066(4)	P(1A)	10 226(3)	489(2)	3 738(1)
C(90)	6 165(11)	−637(6)	667(4)	C(3A)	9 330(11)	2 102(6)	4 927(5)
B(10)	6 742(12)	−382(7)	1 672(5)	O(3A)	9 727(8)	2 274(4)	5 317(4)
B(11)	7 716(12)	−60(7)	1 369(6)	C(4A)	8 954(9)	1 053(6)	4 591(4)
C(30)	6 516(10)	1 644(5)	1 057(4)	O(4A)	8 987(7)	615(4)	4 791(3)
C(31)	6 882(7)	1 687(4)	559(3)	C(7A)	11 477(11)	1 584(6)	3 667(5)
C(32)	6 145	1 538	114	O(7A)	11 947(8)	1 700(5)	3 350(4)
C(33)	6 508	1 554	−338	C(1A)	7 197(10)	2 486(5)	3 849(5)
C(34)	7 607	1 720	−345	C(10A)	7 757(11)	2 971(5)	3 608(6)
C(35)	8 344	1 869	100	B(2A)	7 275(13)	2 478(6)	4 478(6)
C(36)	7 981	1 853	552	B(3A)	6 989(12)	1 763(6)	4 678(5)
C(37)	7 997(14)	1 705(7)	−842(6)	B(4A)	6 846(10)	1 338(6)	4 102(5)
B(5A)	7 010(10)	1 820(6)	3 612(5)	C(52A)	8 944	1 898	2 810
B(6A)	6 050(13)	2 734(7)	4 063(6)	C(53A)	8 856	2 192	2 359
B(7A)	5 913(13)	2 273(7)	4 561(6)	C(54A)	9 362	2 726	2 354
B(8A)	5 628(12)	1 600(6)	4 316(5)	C(55A)	9 956	2 964	2 800
C(9A)	5 695(10)	1 646(5)	3 694(5)	C(56A)	10 044	2 670	3 250
C(90A)	4 968(10)	1 246(5)	3 329(5)	C(57A)	9 272(15)	3 031(8)	1 851(6)
B(10A)	5 897(12)	2 333(6)	3 518(6)	C(61A)	8 732(12)	354(7)	3 515(6)
B(11A)	5 042(13)	2 178(7)	3 956(7)	C(62A)	10 698(14)	467(8)	3 148(6)
C(30A)	7 261(10)	1 537(7)	5 248(5)	C(63A)	10 711(19)	−161(7)	4 019(7)
C(31A)	6 311(6)	1 231(4)	5 434(3)	C(81A)	11 730(8)	766(3)	4 875(4)
C(32A)	6 231	638	5 417	C(82A)	12 483	975	4 583
C(33A)	5 365	365	5 590	C(83A)	12 552	1 576	4 641
C(34A)	4 579	685	5 779	C(84A)	11 841	1 740	4 969
C(35A)	4 660	1 278	5 796	C(85A)	11 333	1 239	5 114
C(36A)	5 526	1 551	5 623	Cl(1)	5 795(12)	3 300(5)	1 504(4)
C(37A)	3 685(13)	409(7)	6 008(6)	Cl(2)	5 701(12)	3 845(4)	2 408(5)
C(5A)	9 609(9)	1 846(5)	3 739(4)	C(100)	6 199(27)	3 370(14)	2 090(14)
C(51A)	9 538(7)	2 136(3)	3 255(2)				

before removal of solvent *in vacuo* and chromatography (2 × 12 cm column). Elution with CH_2Cl_2–hexane (1:4) afforded a single green band which was collected and stripped of solvent *in vacuo*. Recrystallisation of the resulting powder from CH_2Cl_2–hexane (6 cm^3, 1:10) yielded dark green *microcrystals* of $[MoW(\mu-CC_6H_4Me-4)(CO)_2(PMe_3)(\eta-C_5H_5)\{\eta^5-2,8-C_2B_9H_8-10-(CH_2C_6H_4Me-4)-2,8-Me_2\}]$ **8e** (0.060 g).

(*viii*) Dichloromethane (15 cm^3) was cooled to 0 °C and added to a sample of compound **9a** (0.10 g, 0.11 mmol), followed immediately by excess of PMe_3 (40 μl, 0.39 mmol) thus minimising the formation of **8a**. A rapid reaction occurred, accompanied by evolution of gas, which was complete within 10 min. Solvent volume was reduced *in vacuo* to *ca.* 2 cm^3 and hexane (8 cm^3) added. The mixture was cooled to −78 °C and the supernatant removed *via* a syringe to yield purple *microcrystals* of $[W_2(\mu-CC_6H_4Me-4)(CO)_3(PMe_3)(\eta-C_5H_5)\{\eta^5-2,8-C_2B_9H_8-10-(CH_2C_6H_4Me-4)-2,8-Me_2\}]$ **9b** (0.10 g).

Polytopal Rearrangements of the Carbaborane Cages.—(*i*) A mixture of compounds **4b** (X = NMe_3Ph) (0.20 g, 0.25 mmol) and $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ (0.085 g, 0.26 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and treated with $AgBF_4$ (0.049 g, 0.25 mmol). The reaction mixture darkened and evolution of gas was observed. After 30 min solvent was removed *in vacuo* and the residue treated with CH_2Cl_2–hexane (3 cm^3, 1:4) for transfer to a chromatography column (2 × 15 cm) *via* a syringe. Elution at −20 °C with the same solvent mixture afforded a single green fraction which was collected, stripped of solvent *in vacuo*, and recrystallised from CH_2Cl_2–hexane (10 cm^3, 1:10) at −78 °C to yield dark green *microcrystals* of the known compound **6b** (0.18 g, 90%).[3]

(*ii*) An identical procedure starting from compounds **4a** (X = NEt_4) (0.20 g, 0.28 mmol) and $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ (0.10 g, 0.30 mmol), dissolved in CH_2Cl_2 (20 cm^3) and treated with $AgBF_4$ (0.060 g, 0.29 mmol), afforded only dark green *microcrystals* of compound **6a** (0.18 g, 87%).

Crystal Structure Determination.—Crystals of compound **9b** were grown as deep purple prisms by diffusion of hexane into a concentrated CH_2Cl_2 solution over several days. Solvent was removed *via* a syringe and the crystals dried under a stream of nitrogen. The selected crystal had dimensions 0.5 × 0.2 × 0.3 mm, and was mounted in a sealed glass capillary under N_2. Diffracted intensities were collected on a Siemens R3m/V four-circle diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å) using Wyckoff ω scans in the range $5 \leqslant 2\theta \leqslant 45°$. Of 9986 unique intensities, 7113 had $F \geqslant 4\sigma(F)$. Only these were used for structure solution and refinement, after all the data had been corrected for Lorentz, polarisation and X-ray absorption effects, the latter by an empirical method based upon azimuthal scan data.[13]

Crystal data. $C_{62}H_{88}B_{18}O_6P_2W_4\cdot CH_2Cl_2$, M = 2006.2, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$ no. 14), a = 12.149(4), b = 23.448(6), c = 27.282(8) Å, β = 102.04(2)°, U = 7603(4) $Å^3$, Z = 4, D_c = 1.75 g cm^{-3}, $F(000)$ = 3864, μ(Mo-Kα) = 63.2 cm^{-1}.

Structure solution and refinement. The structure was solved by conventional heavy-atom methods, and Fourier difference syntheses were used to locate all non-hydrogen atoms. The asymmetric unit was found to contain two similar but crystallographically independent molecules of the complex (the second has been denoted by the suffix A in Tables 4 and 5), and a molecule of dichloromethane. The principal differences between the molecules were the orientations of the tolyl ring and phosphine-methyl groups with respect to the metal atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters and the aromatic ring systems were treated as rigid groups [C–C 1.395 (C_6H_5) and 1.420 Å (C_5H_5)]. Hydrogen atoms were included in calculated positions (C–H 0.96, B–H 1.1 Å[14]), with fixed isotropic thermal parameters (U_{iso} 0.08 $Å^2$). Refinements by full-matrix least squares were performed on a μ-Vax computer with the SHELXTL system of programs.[13] Scattering factors with corrections for anomalous dispersion are inlaid in the programs. Atom coordinates are given in Table 5. Refinement converged at R = 0.040 (R' = 0.037) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,4|F|^2]$. The final electron-density difference synthesis showed no peaks > 1.07 or < -0.76 e $Å^{-3}$.

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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