Alkylidyne(carbaborane) Complexes of the Group 6 Metals. Part 1. Proton-induced Alkylidyne Ligand Migration *

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Treatment of carbon monoxide-saturated solutions of the salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ ($R = C_6H_4Me\text{-}4$ or Me) at *ca.* −78 °C with $HBF_4{\cdot}Et_2O$ affords the complexes $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$. If these protonation reactions are carried out in the presence of $PhC\equiv CPh$, the alkynetungsten complexes $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ are formed *via* the intermediacy of dicarbonyl species $[W(CO)_2(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$. The latter ($R = C_6H_4Me\text{-}4$) with PMe_3 yields the compound $[W(CO)(PMe_3)(PhC_2Ph)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$. Treatment of $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with $HBF_4{\cdot}Et_2O$ in the presence of $CNBu^t$ yields $[W(CO)_2(CNBu^t)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$, whereas if PPh_3 is used instead of $CNBu^t$ a tricarbonyl species $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ is isolated. However, the latter disproportionates in solution to afford the bis(triphenylphosphine) complex $[W(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$, crystals of which have been analysed by X-ray crystallography. The tungsten atom is η^5 co-ordinated by the $C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2$ ligand and is ligated by two CO and two PPh_3 groups, having transoid arrangements. The $CH_2C_6H_4Me\text{-}4$ substituent on the cage is bonded to the boron atom which is in the β site with respect to the two carbons in the open pentagonal $\overline{\mathrm{CCB}B\mathrm{B}}$ face of the *nido*-icosahedral C_2B_9 fragment. This geometry accounts for the NMR data (^1H, $^{13}C\text{-}\{^1H\}$ and $^{11}B\text{-}\{^1H\}$) for all the new complexes reported containing the $C_2B_9H_8(CH_2R)Me_2$ cage system.

Synthesis of salts of the anionic complexes $[M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]^-$ (M = Mo or W; R = alkyl, alkynyl or aryl; R′ = H or Me) and $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]^-$ (M = Mo or W) has added a new dimension to alkylidynemetal chemistry. Numerous metal–ligand fragments co-ordinate to the C≡M bonds of these reagents to afford di-, tri or poly-nuclear metal compounds.[1] Moreover, in many of the products the carbaborane cage adopts a non-spectator role. Either exopolyhedral B–H→M or B–M (metal) bonds are formed with adjacent metal centres, or complexes are produced in which the alkylidyne ligand has inserted into a B–H group.

So far we have largely neglected studies of reactions of the anionic alkylidyne(carbaborane)-molybdenum or -tungsten species with substrates other than metal–ligand fragments, yet these complexes would be expected to display reactivity patterns under some conditions very different from those of their isolobal cyclopentadienyl analogues $[M(\equiv CR)(CO)_2(\eta^5\text{-}C_5R'_5)]$ (M = Mo or W, R′ = H or Me). In the carbaborane-metal complexes the alkylidyne group is a peripheral ligand lying on the surface of an icosahedral MC_2B_9 or a docosahedral MC_2B_{10} fragment. Hence addition of certain reagents to the C≡M bonds might be expected to be followed by insertion or migratory reagents on the surface of the cages, or by polytopal rearrangements of the vertex atoms of the polyhedra. Such pathways are not available for the compounds $[M(\equiv CR)(CO)_2(\eta^5\text{-}C_5R'_5)]$. In this paper we describe results obtained by protonating with $HBF_4{\cdot}Et_2O$ the salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **1a** ($R = C_6H_4Me\text{-}4$) and **1b** (R = Me), affording products in which the CR groups migrate from the tungsten to the C_2B_9 fragment.

We have previously reported[2] that treatment of **1c** with $HBF_4{\cdot}Et_2O$ affords the ditungsten compound $[N(PPh_3)_2][W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta^5\text{-}C_2B_9H_{11})_2]$ **2a**, in which the two carbaborane ligands adopt spectator roles. Formation of **2a** is analogous to the synthesis of the salt $[W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta^5\text{-}C_5H_5)_2][BF_4]$ **3**, obtained by protonating $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$.[3] Hence $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5H_5)]$ and **1c** behave similarly towards $HBF_4{\cdot}Et_2O$, in contrast with **1a** or **1b** as will be described below.

Earlier we also described[2] the protonation of compound **1d** with $HBF_4{\cdot}Et_2O$ or HI. The oily product obtained was poorly characterised but was erroneously thought to be a mononuclear tungsten species $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_{10}Me_2)]$. Recent re-examination of these reactions, however, has revealed that the products obtained from protonation of salts of type **1** depend critically on the choice of acid, and on the substitution of CMe for CH fragments in the cage, but not on the nature of the cation. Thus protonation of **1a** with HX (X = Cl or I) leads to a polytopal rearrangement of the CMe groups,[4] whereas protonation of **1e** with $HBF_4{\cdot}Et_2O$ gives the NEt_4^+ salt **2b**, with spectroscopic properties similar to those of **2a**, confirming our earlier result. Protonations with $HBF_4{\cdot}Et_2O$ of the dimethyl-cage-substituted salts **1a** and **1b** are described below.

Results and Discussion

Treatment of CO-saturated CH_2Cl_2 solutions of compounds **1a** or **1b** at −78 °C with 1 equivalent of $HBF_4{\cdot}Et_2O$ gives the neutral compounds $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ **4a** ($R = C_6H_4Me\text{-}4$) or **4b** (R = Me). If these reactions are carried out in the absence of CO the same products are formed, but in lower yield. Complexes **4a** and **4b** were characterised by the data given in Tables 1–3.

The presence of the CH_2R substituents on the C_2B_9 cage in the compounds **4** was clearly revealed by comparison of the ^1H, $^{13}C\text{-}\{^1H\}$, and $^{11}B\text{-}\{^1H\}$ NMR data with those of several other species which are known to contain this structural feature. Thus examination of the $^{11}B\text{-}\{^1H\}$ NMR spectra (Table 3) of **4a** and

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

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

Compound	Colour	Yield (%)	ν_{max}[b]/cm^{-1} CO	ν_{max}[b]/cm^{-1} BH	Analysis (%) C	Analysis (%) H
4a $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$	Tan	79	[c] 2092s, 2025m, 1996s (br)	[c] 2576w (br)	34.0 (34.3)	4.3 (4.1)
4b $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$	Yellow	81	2092s, 2018m (sh), 1996s (br)	2523w (br)	25.3 (24.8)	4.2 (4.0)
4c $[W(CO)_2(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$[d]	Brown		2045s, 1985m	2565w (br)		
4e $[W(CO)_2(CNBu^t)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$	Yellow	92	1975s, 1913vs, [e] 2170m, [e] 2138m	2556w (br)	42.9 (43.0)	6.8 (6.2)
5a $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$	Yellow	86	2067vs	2566w (br)	58.7 (59.1)	5.2 (5.2)
5b $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$	Yellow	69	2068vs	2563w (br)	56.1 (55.6)	5.2 (5.2)
6 $[W(CO)(PMe_3)(PhC_2Ph)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$	Purple	70	1941s	2570w (br)	49.2 (49.3)	6.0 (5.8)
7 $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$	Yellow	62	2023s, 1923s (br)	2528w (br)	48.7 (49.9)	4.7 (4.8)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2 unless otherwise stated. [c] Measured in Et_2O. [d] Unstable (see text) hence only spectroscopic data available. [e] $\nu_{max}(NC)$.

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

Compound	^1H[b] (δ)	^{13}C[c] (δ)
4a	2.26 (s, 3 H, Me-4), 2.28 (s, br, 2 H, BCH_2), 2.44 (s, 6 H, CMe), 6.90, 6.98 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	209.1 [CO, *J*(WC) 115], 143.1 [$C^1(C_6H_4)$], 134.4, 129.1, 128.8 (C_6H_4), 70.3 (br, *C*Me), 33.7 (C*Me*), 32.3 (vbr, BCH_2), 21.1 (Me-4)
4b	0.75 [t, 3 H, BCH_2*Me*, *J*(HH) 7], 0.91 [q, 2 H, BCH_2, *J*(HH) 7], 2.47 (s, 6 H, CMe)	209.9 [CO, *J*(WC) 114], 70.6 (br, *C*Me), 33.7 (C*Me*), 17.7 [q, vbr, BCH_2, *J*(BC) 60], 14.9 (BCH_2*Me*)
4c[d]	[e] 1.26 (s, 6 H, CMe), 2.14 (s, 3 H, Me-4), 6.54, 6.72 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.23–7.55 (m, 20 H, Ph)	
4e	[e,f] 1.57, 1.58* (s, 18 H, Bu^t), 2.23, 2.24* (s, 3 H, Me-4), 2.25, 2.31* (s, 6 H, CMe), 6.79, 6.85*, 6.90, 6.91* [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[f] 229.1, 221.6* [CO, *J*(WC) 125], 148.4*, 146.7 [t, br, *C*NBu^t, *J*(NC) 15], 144.9, 144.7* [$C^1(C_6H_4)$], 132.6, 132.5* [$C^4(C_6H_4)$], 129.33*, 129.25 [$C^2(C_6H_4)$], 128.0 [$C^3(C_6H_4)$], 65.3*, 65.2 (s, br, *C*Me), 60.0*, 59.7 (s, br, CN*C*Me_3), 32.5*, 32.4 (C*Me*), 30.7, 30.6* (CNCMe_3), 30.4 (vbr, BCH_2), 20.8 (Me-4)
5a	[e,g] 1.58 (s, br, 6 H, CMe), 2.18 (s, 3 H, Me-4), 6.62, 6.84 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.04–7.57 (m, 20 H, Ph)	212.1 [CO, *J*(WC) 107], 178.2 (br, PhC_2Ph), 143.8 [$C^1(C_6H_4)$], 135.0–127.2 (m, Ph and C_6H_4), 56.7 (*C*Me), 33.0 (br, BCH_2), 21.0 (Me-4), 18.7 (C*Me*)
5b	[h] 0.34 [d of q, 1 H, BCH_2, *J*(HH) 5 and 7], 0.44 (d of d, 3 H, CH_2*Me*, *J*(HH) 7 and 7], 0.72 [d of q, 1 H, BCH_2, *J*(HH) 5 and 7], 1.33, 2.40 (s × 2, 6 H, CMe), 6.93–8.32 (m, 20 H, Ph)	[i] 211.9 (CO), 176.8 (br, PhC_2Ph), 134.9–127.7 (Ph), 68.8 (br, *C*Me), 29.2 (br, C*Me*), 17.2 (br, BCH_2), 14.4 (CH_2*Me*)
6	1.47 (s, 3 H, CMe), 1.55 [d, 9 H, MeP, *J*(PH) 10], 1.96 [d, 1 H, BCH_2, *J*(HH) 14], 2.05 (s, 3 H, Me-4), 2.25 (s, 3 H, CMe), 2.62 [d, 1 H, BCH_2, *J*(HH) 14], 6.86, 6.95 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7], 7.24–7.48 (m, 10 H, Ph)	[g] 229.1 [d, CO, *J*(PC) 7], 209 (vbr, PhC_2Ph), 144.4 [$C^1(C_6H_4)$], 139.5–127.1 (m, Ph and C_6H_4), 61.1 (br, *C*Me), 32.5 (C*Me*), 32.0 (vbr, BCH_2), 28.7 (C*Me*), 21.1 [d, MeP, *J*(PC) 36], 21.0 (Me-4)
7	1.79 (s, 2 H, BCH_2), 1.99 (s, 6 H, CMe), 2.20 (s, 3 H, Me-4), 6.63, 6.88 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.28–7.71 (m, 15 H, Ph)	222.4 [d, 2 CO, *J*(PC) 29], 221.4 [d, CO, *J*(PC) 9], 144.4 [$C^1(C_6H_4)$], 137.6–128.7 (m, Ph and C_6H_4), 67.0 (*C*Me), 31.5 (br, BCH_2), 31.3 (C*Me*), 20.9 (Me-4)

[a] Chemical shifts δ in ppm, coupling constants in Hz. Measurements at room temperature in CD_2Cl_2 unless otherwise stated. [b] Proton resonances for terminal B–H groups occur as broad unresolved resonances in the range δ *ca.* −2 to +3. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [d] Complex unstable, $^{13}C\text{-}\{^1H\}$ NMR spectrum not measured. [e] Peaks due to BCH_2 not observed. [f] Peaks due to minor isomer indicated by asterisk, see text. [g] Measured in $CDCl_3$. [h] Spectrum recorded at −60 °C. [i] Spectrum recorded at room temperature due to insolubility of complex at −60 °C.

4b revealed deshielded resonances corresponding to one boron nucleus at δ 9.4 and 10.1, respectively, and these signals remain as singlets in fully coupled ^{11}B spectra, indicating that the boron atoms are not bonded directly to hydrogen atoms. We have recently reported[5] that treatment of **1a** with $HBF_4 \cdot Et_2O$ in the presence of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ gives the ditungsten complex $[W_2(\mu\text{-}CMe)(CO)_3\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}(\eta\text{-}C_5H_5)]$. In the $^{11}B\text{-}\{^1H\}$ NMR spectrum of this species the resonance for the BCH_2 group is also deshielded at δ 5.5. In the spectra of several other compounds containing $BCH_2C_6H_4Me\text{-}4$ groups the $^{11}B\text{-}\{^1H\}$ resonances for these fragments occur with similar chemical shifts to those of the compounds **4**, *e.g.* $[Mo(CO)_3L\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}(\eta\text{-}C_5H_5)]$ [L = PMe_3 (δ 9.7) or CO (δ 13.4)][6] and $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (C_9H_7 = indenyl, δ 4.6).[7]

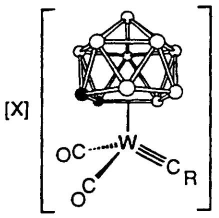
In the $^{13}C\text{-}\{^1H\}$ NMR spectra (Table 2) of the complexes **4** broad peaks at δ 32.3 (**4a**) and 17.7 (**4b**) may be ascribed to the BCH_2 nuclei. Similar signals are observed in the spectra of $[W_2(\mu\text{-}CMe)(CO)_3\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}(\eta\text{-}C_5H_5)]$ (δ 42.0),[5] $[MoW(\mu\text{-}PPh_2)(CO)_3(\eta^5\text{-}C_9H_7)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (δ 38.5),[7] $[WPt(CO)_2(PEt_3)_2\{\eta^6\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (δ 36.8)[8] and $[NEt_4][Rh(CO)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (δ 34.0).[9] Diagnostic signals for the BCH_2 protons are seen in the ^1H NMR spectra of compounds **4a** and **4b** at δ 2.28 and 0.91, respectively. These resonances may be compared with the corresponding peaks in the spectra of $[Mo(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (δ 2.18)[6] and $[WPt(CO)_2(PEt_3)_2\{\eta^6\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ (δ 1.53).[8]

Based on earlier studies[3] with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, protonation of the salts **1a** and **1b** probably proceeds

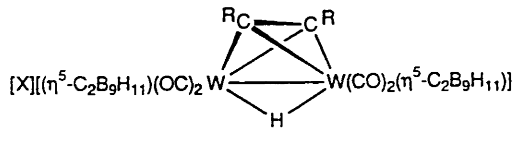
Table 3 Boron-11 and phosphorus-31 NMR data[a] for the complexes

Compound	$^{11}B^{b}$ (δ)
4a	9.4 (s, 1 B, BCH_2), 0.0 (1 B), −1.9 (2 B), −8.0 (5 B)
4b	10.1 (s, 1 B, BCH_2), −0.1 (1 B), −2.5, −7.9, −8.4 (2 B × 3), −9.1 (1 B)
4c	9.7 (s, 1 B, BCH_2), −2.3 to −13.2 (m, br, 8 B)
4e	7.1 (s, 1 B, BCH_2), −5.8, −6.2, −6.8, −8.3 (1 B × 4), −9.3 (2 B), −10.7, −11.9 (1 B × 2)
5a	9.8 (s, 1 B, BCH_2), −4.6 to −12.1 (m, br, 8 B)
5b	11.3 (s, 1 B, BCH_2), −4.3 to −13.4 (m, br, 8 B)
6[c]	6.9 (s, 1 B, BCH_2), −3.5, −5.2 (1 B × 2), −7.3 (3 B), −10.5 (2 B), −16.3 (1 B)
7[c]	7.2 (s, 1 B, BCH_2), −3.8 (1 B), −5.3 (2 B), −8.7 (3 B), −10.0 (2 B)

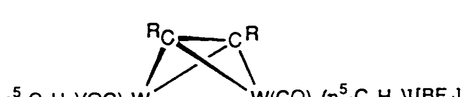
[a] Chemical shifts in ppm, coupling constants in Hz. Measurements in CD_2Cl_2 at ambient temperatures unless otherwise stated. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). Signals ascribed to more than one boron nucleus may result from broad overlapping peaks, and do not necessarily indicate symmetry equivalence. [c] Hydrogen-1 decoupled, ^{31}P chemical shifts to high frequency of 85% H_3PO_4 (external): **6**, −11.88 [s, *J*(WP) 388]; **7**, 10.69 [s, *J*(WP) 165]; **4d**, 15.54 [s, *J*(WP) 172 Hz].



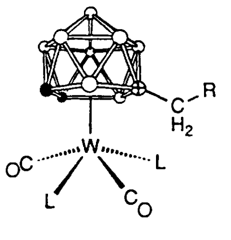
	X	R	●
1a	NEt_4	C_6H_4Me-4	CMe
1b	NEt_4	Me	CMe
1c	$N(PPh_3)_2$	C_6H_4Me-4	CH
1d	$N(PPh_3)_2$	C_6H_4Me-4	CMe
1e	NEt_4	C_6H_4Me-4	CH



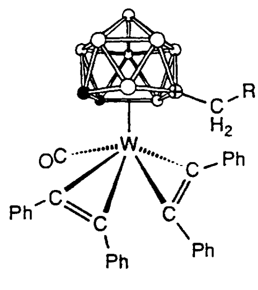
	X	R
2a	$N(PPh_3)_2$	C_6H_4Me-4
2b	NEt_4	C_6H_4Me-4



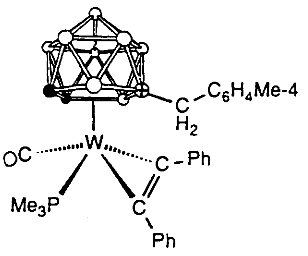
3 R = C_6H_4Me-4



	R	L
4a	C_6H_4Me-4	CO
4b	Me	CO
4c	C_6H_4Me-4	PhC_2Ph
4d	C_6H_4Me-4	PPh_3
4e	C_6H_4Me-4	$CNBu^t$



	R
5a	C_6H_4Me-4
5b	Me



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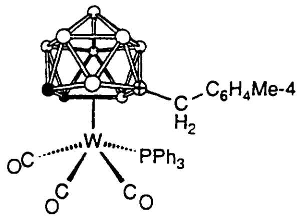

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● CMe ○ BH ⊕ B

via the initial formation of an alkylidenetungsten complex [W{=C(H)R}$(CO)_2(\eta^5$-$C_2B_9H_9Me_2)$] in which the metal centre is electronically unsaturated. Addition of CO molecules, which are present in the solutions, to the tungsten atom could promote insertion of the alkylidene group into an adjacent B–H bond. It is assumed that the boron atom is β rather than α to the carbon atoms of the CCB*B*B ring in the open face of the *nido*-icosahedral C_2B_9 cage. This is supported by an X-ray diffraction study on a structurally related complex, described below, similar X-ray studies on several compounds containing $WC_2B_9H_8(CH_2C_6H_4Me$-4$)Me_2$ fragments,[5,7,8] and by the ^1H and ^{13}C-{^1H} NMR spectra of the complexes **4**. The NMR data (Table 2) confirm that the molecules are symmetrical, in accord with the CH_2R substituents being attached to the β boron of the CCB*B*B ring. Thus in the ^1H NMR spectra the cage CMe groups display a single resonance, and in the ^{13}C-{^1H} NMR spectra these groups show two signals for the *C*Me and C*Me* nuclei. The equivalence of the CMe fragments is in accord with the BCH_2 moiety lying in a plane of symmetry through the W atom, the β–B atom, and the midpoint of the C–C connectivity of the cage.

Geoffroy and co-workers[10] have shown that when the complex [W(≡CC_6H_4Me-4)$(CO)_2(\eta$-$C_5H_5)$] is protonated in the presence of PhC≡CPh a stable vinylcarbene complex [W{=C(Ph)C(Ph)=C(H)C_6H_4Me-4}$(CO)_2(\eta$-$C_5H_5)$][BF_4] is formed. In view of this result it was of interest to protonate the salts **1a** and **1b** with $HBF_4{\cdot}Et_2O$ in the presence of PhC≡CPh.

If compound **1a** in CH_2Cl_2 at −50 °C is treated with PhC≡CPh followed by 1 equivalent of $HBF_4{\cdot}Et_2O$ and the mixture is worked up in such a manner that the temperature is never allowed to rise above −30 °C it is possible to isolate as a brown oil a labile complex [W$(CO)_2(PhC_2Ph)_2${η^5-$C_2B_9H_8(CH_2C_6H_4Me$-4$)Me_2$}] **4c**. The latter shows in its IR spectrum ν_{max}(CO) at 2045 and 1985 cm^{-1}. The ^{11}B-{^1H} NMR spectrum has a diagnostic resonance for the BCH_2 group at δ 9.7. The instability of the complex prevented measurement of the ^{13}C-{^1H} NMR spectrum, and in the ^1H spectrum the signal due to the BCH_2 moiety, likely to be broad, was not observed. However, the resonances which were seen are in accord with the proposed formulation for **4c**.

If the salt **1a** is treated successively with $PhC\equiv CPh$ and $HBF_4 \cdot Et_2O$ and the mixture allowed to warm to room temperature a stable yellow complex $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **5a** [$\nu_{max}(CO)$ 2067 cm^{-1}] is obtained. This product was fully characterised by the data given in Tables 1–3. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum a resonance at δ 33.0 may be attributed to the BCH_2 group, and a broad signal at δ 178.2 to the ligated carbon atoms of the alkyne. The chemical shift is in accord with each alkyne formally donating three electrons to the tungsten centre,[11] and the broadness of the signal indicates a degree of dynamic behaviour involving rotation of the alkyne groups, but poor solubility prevented the recording of useful low-temperature NMR spectra. The $^{11}B\text{-}\{^1H\}$ NMR spectrum shows a diagnostic resonance for the BCH_2 group at δ 9.8. Compound **5a** is also isolated if the temperature of a solution of **4c** is allowed to rise above *ca.* −20 °C. That this conversion occurs cleanly in the absence of free $PhC\equiv CPh$ is further confirmation of the structure assigned to **4c**.

If a solution of compound **4c**, formed at low temperature, is treated with PMe_3 the monoalkyne tungsten complex $[W(CO)(PMe_3)(PhC_2Ph)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **6** is obtained, one CO molecule and one $PhC\equiv CPh$ being displaced in the reaction. Data for the purple complex **6** are in excellent agreement with the formulation. One CO band (1941 cm^{-1}) is seen in the IR spectrum. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a singlet resonance at δ −11.88, with strong $^{183}W\text{-}^{31}P$ coupling (388 Hz). The ^1H and $^{13}C\text{-}\{^1H\}$ NMR data (Table 2) are also in agreement with the structure proposed. The molecule lacks a plane of symmetry and so resonances for non-equivalent cage CMe groups are seen in both spectra. In the $^{13}C\text{-}\{^1H\}$ spectrum a broad peak for the $Ph\mathit{C}_2Ph$ nuclei is observed at δ 209, in the range expected for a four-electron-donor alkyne ligand.[11] A diagnostic signal for the BCH_2 group occurs at δ 6.9 in the $^{11}B\text{-}\{^1H\}$ spectrum.

Treatment of a mixture of the salt **1b** and $PhC\equiv CPh$ with $HBF_4 \cdot Et_2O$ affords the complex $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ **5b**, analogous to **5a**. During the formation of **5b** there was IR evidence for a transient species [$\nu_{max}(CO)$ 2047 and 1986 cm^{-1}] similar to the dicarbonyl complex **4c**, but it could not be isolated. Data for compound **5b** are given in Tables 1–3, fully characterising this product. One notable difference between compounds **5a** and **5b** is that the latter exhibits a greater degree of fluxionality such that all peaks in the NMR spectra measured at room temperature are considerably broadened. On cooling to −60 °C a limiting spectrum is observed as the ^1H NMR resonances are resolved. The data reveal that the molecule adopts a conformation which no longer contains a plane of symmetry. Thus two signals are observed for the CMe groups of the carbaborane cage at δ 1.33 and 2.40, and the BCH_2 protons are not equivalent, appearing at δ 0.34 and 0.72. It is therefore inferred that when static, on the NMR time-scale, the alkyne ligands are twisted with respect to one another to remove the molecular symmetry. Unfortunately, compound **5b** was too insoluble for an informative low-temperature $^{13}C\text{-}\{^1H\}$ NMR spectrum to be recorded, however the room-temperature spectrum clearly shows that rotation of the alkyne ligands restores the symmetry plane, leading to single resonances for the ligated carbon atoms of the alkyne (δ 176.8), the *C*Me (δ 68.8) and the C*Me* (δ 29.2) nuclei.

Protonation of the reagent **1a** in the presence of $CNBu^t$ afforded the complex $[W(CO)_2(CNBu^t)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$, displaying two CO (1975 and 1913 cm^{-1}) and two NC (2170 and 2138 cm^{-1}) absorptions in its IR spectrum. Examination of the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of this product revealed the presence of two isomers in the ratio 2:1, which could not be separated by column chromatography. It is likely that these two isomers differ by having transoid- and cisoid-$W(CO)_2(CNBu^t)_2$ groups. The former arrangement **4e**, expected to be the major component for steric reasons, is depicted in the structural formula. In each species it is possible to have a mirror plane through the W atom, the $B_\beta C$ group, and the midpoint of the connectivity between the CMe groups, thereby giving rise to the observation in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra (Table 2) of equivalent CMe groups.

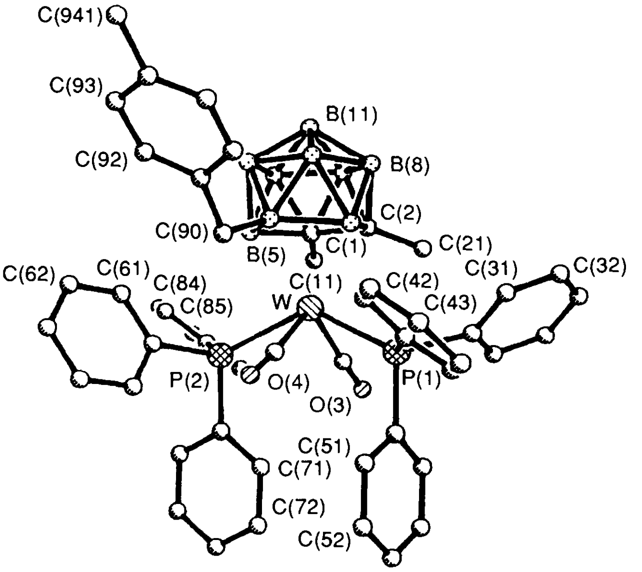

Fig. 1 Molecular structure of $[W(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **4d**, showing the crystallographic atom labelling scheme

In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of $[W(CO)_2(CNBu^t)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ resonances are seen for the ligated carbons of the $CNBu^t$ ligands at δ 148.4 (minor isomer) and 146.7 [*J*(NC) 15 Hz] (major isomer). These chemical shifts are in the range expected for ligated $CNBu^t$ groups,[12] the resonances for which are often difficult to observe due to quadrupolar decoupling by the ^{14}N nucleus. Hence, the triplet signal expected and observed for the major isomer may appear as a broad singlet in unfavourable cases.

Addition of $HBF_4 \cdot Et_2O$ to a mixture of compound **1a** and PPh_3 at *ca.* −50 °C yielded, after column chromatography, the monophosphine complex $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **7**. Although the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra indicated that this synthesis gave only one product, the more discerning $^{31}P\text{-}\{^1H\}$ spectrum (Table 3) revealed not only a resonance for **7** at δ 10.69, but also a weak signal at δ 15.54 for another species **4d**, discussed below. The ^1H, $^{13}C\text{-}\{^1H\}$ and $^{11}B\text{-}\{^1H\}$ NMR data were all as expected for the formulation of **7** shown. In particular, the BCH_2 group is revealed in the $^{11}B\text{-}\{^1H\}$ spectrum with a resonance at δ 7.2, in the $^{13}C\text{-}\{^1H\}$ spectrum with a signal at δ 31.5, and in the ^1H spectrum with a peak at δ 1.79.

An interesting result was obtained in attempting to grow crystals of complex **7** for an X-ray diffraction study. During the time required to grow suitable crystals (< 48 h) decomposition of the solutions was observed. The X-ray diffraction study on a single crystal identified the molecule $[W(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **4d**, containing two PPh_3 ligands, which was evidently formed by a disproportionation of complex **7**. This disproportionation is apparently reversible, since crystals of **4d** reform compound **7** within *ca.* 10 min when dissolved in CD_2Cl_2, with unidentified decomposition products again in evidence.

Selected structural parameters for **4d** are listed in Table 4, and the molecule is shown in Fig. 1. The presence of the $CH_2C_6H_4Me\text{-}4$ group attached to B(4), the boron atom in the β site relative to the two carbons in the $\overline{CCB\beta B}$ ring, is immediately conspicuous. Moreover, the CO and PPh_3 groups in the $W(CO)_2(PPh_3)_2$ fragment [W–P(1) 2.572(5), W–P(2)

Table 4 Selected internuclear distances (Å) and angles (°) for $[W(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **4d**

W–P(1)	2.572(5)	W–P(2)	2.571(5)	W–C(1)	2.52(2)	W–C(2)	2.51(1)
W–B(3)	2.36(2)	W–B(4)	2.47(2)	W–B(5)	2.40(2)	W–C(3)	1.95(1)
C(3)–O(3)	1.19(2)	W–C(4)	1.99(2)	C(4)–O(4)	1.15(2)	C(1)–C(11)	1.50(3)
C(2)–C(21)	1.54(2)	B(4)–C(90)	1.65(2)	C(1)–C(2)	1.64(3)	C(2)–B(3)	1.72(3)
B(3)–B(4)	1.84(3)	B(4)–B(5)	1.84(4)	B(4)–B(6)	1.79(3)	B(4)–B(7)	1.78(3)
B(5)–B(6)	1.79(2)	B(5)–B(10)	1.79(3)	B(3)–B(7)	1.80(2)	B(3)–B(8)	1.78(3)
C(2)–B(8)	1.67(2)	C(2)–B(9)	1.76(3)	C(1)–B(9)	1.74(3)	C(1)–B(10)	1.70(2)
B(10)–B(9)	1.67(3)	B(9)–B(8)	1.76(4)	B(8)–B(7)	1.73(2)	B(7)–B(6)	1.77(3)
B(11)–B(6)	1.77(3)	B(11)–B(7)	1.74(3)	B(11)–B(8)	1.76(3)	B(11)–B(9)	1.71(3)
B(11)–B(10)	1.75(3)	P–C (av.)	1.85				

P(1)–W–P(2)	128.0(1)	C(3)–W–C(4)	106.3(6)	P(1)–W–C(3)	76.4(5)
P(1)–W–C(4)	71.6(5)	P(2)–W–C(3)	78.8(5)	P(2)–W–C(4)	72.7(6)
W–C(3)–O(3)	175(1)	W–C(4)–O(4)	175.0(9)	W–C(1)–C(11)	110.4(9)
W–C(2)–C(21)	111.0(8)	W–B(4)–C(90)	109.6(9)	B(4)–C(90)–C(91)	115(1)

2.571(5) Å; P(1)–W–P(2) 128.0(1), C(3)–W–C(4) 106.3(6)°] adopt transoid arrangements. The W–C–O groups deviate little from linearity. The various internuclear distances in the WC_2B_9 cage are similar to those observed in the several related structures[5,7,8] mentioned in this paper, and call for no comment.

From the results reported herein it is evident that protonation of the complex **1a** or **1b** with $HBF_4{\cdot}Et_2O$ follows a different pathway to the protonation of either the salts **1c** or **1e** or $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$. The latter affords the ditungsten complex **3**, resulting from combination of an alkylidenetungsten intermediate $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)]^+$ with a molecule of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, followed by rearrangement of a μ-$C(C_6H_4Me\text{-}4){=}C(H)C_6H_4Me\text{-}4$ fragment to give the μ-H and μ-$C_2(C_6H_4Me\text{-}4)_2$ ligands present in **3**.[3,10] Compounds **1c** and **1e** behave similarly, affording the ditungsten compounds **2**. In contrast, compounds **1a** and **1b** afford products **4a** and **4b** respectively, evidently formed by insertion of an alkylidene C(H)R into a B–H bond. This process is apparently very favourable, since in the presence of PhC≡CPh alkynetungsten complexes are formed, rather than C–C bond formation leading to a vinylcarbene tungsten complex.[10]

Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free atmosphere. All solvents were rigorously dried before use. Alumina (Aldrich, Brockmann activity III), silica (Fluka, Kieselgel 70–230 mesh) and Florisil (Aldrich, 100–200 mesh) were used for column chromatography employing water-jacketed columns of given dimensions at *ca.* 10 °C unless otherwise stated. The salts **1a** and **1b** were prepared as previously reported.[1a,13] Tetrafluoroboric acid was an 85% solution of $HBF_4{\cdot}Et_2O$ in Et_2O as supplied by Aldrich. The NMR spectra were recorded with JEOL JNM GX270 and GX400 spectrometers, the IR spectra with a Perkin-Elmer FT1600 spectrometer.

Synthesis of the Tungsten Complexes.—(*i*) Compound **1a** (0.20 g, 0.33 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and cooled to −78 °C. The solution was saturated with CO gas and $HBF_4{\cdot}Et_2O$ (60 μl, 0.35 mmol) added. A slow stream of CO gas was bubbled through the mixture as it warmed to room temperature (*ca.* 30 min). Solvent was removed *in vacuo*, and the residue was dissolved in Et_2O (*ca.* 5 cm^3) before chromatography on Florisil at −40 °C (3 × 15 cm). Elution with the same solvent afforded a yellow fraction which, after removal of solvent *in vacuo*, afforded tan *microcrystals* of $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **4a** (0.14 g).

(*ii*) Similarly, treatment of compound **1b** (0.16 g, 0.29 mmol) with $HBF_4{\cdot}Et_2O$ (50 μl, 0.29 mmol) yielded yellow *microcrystals* of $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ **4b** (0.11 g).

(*iii*) The reagent **1a** (0.20 g, 0.33 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and cooled to *ca.* −50 °C. Diphenylacetylene (0.12 g, 0.67 mmol) was added and allowed to dissolve, followed by $HBF_4{\cdot}Et_2O$ (60 μl, 0.35 mmol). There was an immediate colour change from orange to brown and an IR spectrum showed only the presence of $[W(CO)_2(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **4c**. This species could be isolated as a brown oil by reduction of solvent volume to *ca.* 5 cm^3 and chromatography in CH_2Cl_2 on Kieselgel (−60 °C, 2 × 10 cm), followed by removal of solvent *in vacuo*, taking care never to allow the temperature to rise above −30 °C, particularly under reduced pressure.

(*iv*) In a similar synthesis to (*iii*) above, compound **1a** (0.20 g, 0.33 mmol) and $CNBu^t$ (80 μl, 0.71 mmol) in place of PhC≡CPh were treated at *ca.* −50 °C with $HBF_4{\cdot}Et_2O$ (60 μl, 0.35 mmol). The solution was allowed to warm to room temperature over *ca.* 1 h and the solvent was removed *in vacuo*. Dissolving the residue in CH_2Cl_2–hexane (3 cm^3, 2:3) followed by chromatography on an alumina column (2 × 17 cm) and elution with the same solvent mixture yielded yellow *microcrystals* of $[W(CO)_2(CNBu^t)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **4e** (0.20 g).

(*v*) Compound **1a** (0.20 g, 0.33 mmol) in CH_2Cl_2 (20 cm^3) was cooled to *ca.* −50 °C and treated with PhC≡CPh (0.12 g, 0.67 mmol) followed by $HBF_4{\cdot}Et_2O$ (60 μl, 0.35 mmol) as described in (*iii*) above. The reaction mixture was then allowed to warm to room temperature, which resulted in the mixture becoming more yellow in colour. Reduction of solvent volume to *ca.* 3 cm^3 *in vacuo* followed by chromatography on alumina (2 × 15 cm, 10 °C) in CH_2Cl_2 yielded, after removal of solvent *in vacuo*, yellow *microcrystals* of $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **5a** (0.24 g).

(*vi*) The salt **1b** (0.16 g, 0.29 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and cooled to *ca.* −50 °C. Diphenylacetylene (0.10 g, 0.56 mmol) was added and allowed to dissolve, followed by $HBF_4{\cdot}Et_2O$ (50 μl, 0.29 mmol), as in (*iii*) above. An immediate colour change from yellow to brown was observed, and an IR spectrum showed $\nu_{max}(CO)$ bands at 2047 and 1986 cm^{-1}, indicating the formation of a product analogous to **4c**. However, as the solution began to warm up the two CO bands disappeared, and were rapidly replaced by a band at 2068 cm^{-1} precluding isolation of the intermediate species. Once the mixture had reached room temperature (*ca.* 30 min), solvent was reduced *in vacuo* to *ca.* 3 cm^3 and chromatographed on alumina (2 × 10 cm) in CH_2Cl_2 to yield $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ **5b** (0.15 g) as yellow *microcrystals*.

(*vii*) Addition of PMe_3 (40 μl, 0.39 mmol) to the cold (−50 °C) reaction mixture containing compound **4c**, described in (*iii*) above, produced a rapid reaction. Allowing the solution to warm to room temperature, followed by removal of the solvent *in vacuo* and redissolving the residue in CH_2Cl_2–light petroleum (2 cm^3, 1:4) yielded, after chromatography on alumina (2 × 20 cm) in the same solvent mixture, two fractions. The first was purple, and was reduced in volume *in vacuo* to *ca.* 5

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

Atom	*x*	*y*	*z*
W	8 143(1)	395(1)	1 996(1)
P(1)	9 793(3)	378(2)	2 501(2)
P(2)	7 274(3)	1 252(2)	2 318(3)
C(1)	7 103(10)	−507(7)	1 784(9)
C(11)	7 008(11)	−591(7)	2 616(9)
C(2)	7 955(10)	−785(7)	1 731(8)
C(21)	8 628(10)	−1 153(7)	2 559(8)
B(3)	8 140(11)	−361(10)	964(10)
B(4)	7 244(12)	209(9)	363(11)
B(5)	6 647(12)	111(8)	1 007(11)
B(6)	6 266(12)	−256(8)	−70(10)
B(7)	7 202(13)	−562(8)	−91(11)
B(8)	7 666(13)	−1 138(9)	742(12)
B(9)	6 978(14)	−1 227(9)	1 231(13)
B(10)	6 195(13)	−676(9)	796(12)
B(11)	6 521(13)	−1 076(9)	101(12)
C(3)	8 688(9)	353(7)	3 305(9)
O(3)	8 981(7)	290(5)	4 094(6)
C(4)	8 475(10)	1 234(8)	1 705(9)
O(4)	8 612(8)	1 716(5)	1 477(7)
C(30)	10 387	−381	2 954
C(31)	10 579(7)	−754(5)	2 388(5)
C(32)	10 951	−1 356	2 669
C(33)	11 131	−1 584	3 516
C(34)	10 940	−1 211	4 082
C(35)	10 568	−609	3 801
C(40)	10 156	560	1 664
C(41)	9 568(5)	667(5)	756(6)
C(42)	9 878	842	165
C(43)	10 776	911	481
C(44)	11 364	804	1 389
C(45)	11 054	629	1 981
C(50)	10 444	1 004	3 353
C(51)	10 548(7)	1 594(5)	3 038(5)
C(52)	11 032	2 072	3 647
C(53)	11 411	1 960	4 572
C(54)	11 307	1 370	4 888
C(55)	10 824	892	4 278
C(60)	6 664	1 806	1 376
C(61)	5 879(7)	1 643(4)	618(7)
C(62)	5 481	2 069	−99
C(63)	5 868	2 659	−59
C(64)	6 653	2 822	699
C(65)	7 051	2 396	1 417
C(70)	7 901	1 825	3 229
C(71)	8 808(7)	1 899(5)	3 628(7)
C(72)	9 232	2 344	4 316
C(73)	8 749	2 715	4 605
C(74)	7 842	2 642	4 205
C(75)	7 418	2 197	3 518
C(80)	6 534	973	2 733
C(81)	6 946(5)	782(5)	3 634(6)
C(82)	6 446	578	4 029
C(83)	5 534	566	3 525
C(84)	5 122	757	2 624
C(85)	5 622	961	2 228
C(90)	7 200(11)	868(7)	−192(9)
C(91)	6 785(13)	786(9)	−1 216(12)
C(92)	5 914(14)	936(8)	−1 738(12)
C(93)	5 500(15)	932(11)	−2 698(15)
C(94)	5 990(21)	754(13)	−3 090(15)
C(941)	5 546(19)	722(12)	−4 131(12)
C(95)	6 836(20)	581(11)	−2 600(14)
C(96)	7 239(15)	596(9)	−1 662(12)

cm^3 before cooling to −78 °C. Removal of the supernatant *via* a syringe gave purple *microcrystals* of $[W(CO)(PMe_3)(PhC_2Ph)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **6** (0.17 g). The second band was a minor yellow product which was not identified.

(*viii*) Following a similar synthesis to (*iv*), using compound **1a** (0.20 g, 0.33 mmol), and PPh_3 (0.10 g, 4.42 mmol) in place of PhC≡CPh, protonation with $HBF_4 \cdot Et_2O$ (60 μl, 0.35 mmol) at *ca.* −50 °C gave a brown reaction mixture which was allowed to warm to room temperature over *ca.* 1 h. Solvent was then removed *in vacuo* and the residue dissolved in CH_2Cl_2–hexane (3 cm^3, 2:3) for chromatography on an alumina column (2 × 17 cm). Elution with the same solvent mixture gave a yellow eluate from which solvent was removed to yield yellow *microcrystals* of $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **7** (0.16 g). By slow recrystallisation of **7** from CH_2Cl_2–hexane, X-ray-quality crystals of $[W(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **4d** were obtained, as described below.

Crystal Structure Determination.—Crystals of compound **4d** were grown as yellow prisms by diffusion of hexane into a concentrated CH_2Cl_2 solution of compound **7** over *ca.* 48 h at −20 °C. During this time decomposition was evident in the remaining solution, which became pale green. Solvent was removed *via* a syringe and the crystals were dried under a stream of nitrogen.

The selected crystal had dimensions *ca.* 0.20 × 0.25 × 0.30 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 θ–2θ scans in the range $3 \leqslant 2\theta \leqslant 50°$. Of 9435 unique intensities, 3556 had $F \geqslant 6\sigma(F)$. 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.[14]

Crystal data. $C_{50}H_{53}B_9O_2P_2W$, $M = 1029.0$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.398(9)$, $b = 21.000(9)$, $c = 16.908(9)$ Å, $\beta = 118.68(3)°$, $U = 5420(4)$ Å^3, $Z = 4$, $D_c = 1.25$ g cm^{-3}, $F(000) = 2072$, μ(Mo-Kα) = 22.7 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. All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the carbon atoms of the PPh_3 groups, which were refined as rigid isotropic rings. Hydrogen atoms were included in calculated positions (C–H 0.96, B–H 1.1 Å[15]), with fixed isotropic thermal parameters [C–H, $U_{iso} = 0.08$; B–H, $U_{iso} = 1.2\ U_{iso}(B)$ Å^2]. Calculations by full-matrix least squares were performed on a μ-Vax computer with the SHELXTL system of programs.[14] Scattering factors with corrections for anomalous dispersion are inlaid in the programs. Atom coordinates are given in Table 5. Refinement converged at $R = 0.056$ ($R' = 0.050$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0004|F|^2]$. The final electron-density difference synthesis showed no peaks >0.97 or < -1.45 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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