Alkylidyne(carbaborane) Complexes of the Group 6 Metals. Part 5.[1] Protonation Studies on $[NEt_4][W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$†

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Dichloromethane solutions of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4OMe-2) at −78 °C on treatment with $HBF_4{\cdot}Et_2O$ in the presence of the substrates L = CO, PPh_3, $PHPh_2$, $CNBu^t$ and PhC_2Ph afford the complexes $[W(CO)_2L_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ (L = CO, $PHPh_2$ or $CNBu^t$), $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ and $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ respectively. The corresponding protonation reaction employing dppm ($Ph_2PCH_2PPh_2$) as the substrate yields $[W(CO)_2(dppm)\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ as the major product, together with small quantities of $[W\{CH(R)PPh_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$. The structure of $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ has been established by X-ray diffraction. The tungsten atom is η^5 co-ordinated by the *nido*-icosahedral fragment $C_2B_9H_8(CH_2R)Me_2$. In the latter the exopolyhedral CH_2R group is bonded to the boron atom which is in the β position with respect to the two carbon atoms in the open pentagonal CCB*B*B face of the cage ligating the tungsten. The latter also carries three terminally bound CO groups and the PPh_3 ligand. Addition of aqueous HI to CH_2Cl_2 solutions of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ affords the salt $[NEt_4][WI(CO)_3\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$. In the latter there is a 2,1,8 arrangement for the non-boron vertices of the WC_2B_9 icosahedron, in contrast with the *closo*-3,1,2-WC_2B_9 structures of the other products. The NMR data (^1H, $^{13}C\text{-}\{^1H\}$, $^{11}B\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$) for the new compounds are reported and discussed in relation to the molecular structures.

The isolobally mapped alkylidynetungsten compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Y][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ [Y = NEt_4, PPh_4, $N(PPh_3)_2$, *etc.*; R = aryl or alkyl] afford a variety of structurally different complexes upon protonation. The nature of these products depends on the acid used for protonation, the R group attached to the ligated carbon of the alkylidyne ligand, and upon whether the tungsten atom carries a C_5H_5 or a $C_2B_9H_9Me_2$ ligand.[1,2] The effect of different R groups is illustrated by protonation studies on the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 **1a** or C_6H_4OMe-2 **1b**). Treatment of **1a** with $HBF_4{\cdot}Et_2O$ affords the μ-alkyne-ditungsten complex $[W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$ **2**.[2a] There is good evidence that this product forms *via* the intermediacy of $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **3a**. However, this alkylidenetungsten complex cannot be isolated.[2a,3] In contrast, treatment of **1b** with $HBF_4{\cdot}Et_2O$ gives $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **3b**, which is sufficiently stable to be characterised spectroscopically. Moreover, the alkylidene group in **3b** can be captured by addition of PPh_3 to yield the ylide complex $[W\{\sigma,\eta^2\text{-}CH(PPh_3)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **4**.[2b]

Substituting *nido*-η^5-$C_2B_9H_9Me_2$ cage ligands for η-C_5H_5 groups in alkylidynetungsten chemistry produces very different reactivity patterns. Thus treatment of $[NEt_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5a** with $HBF_4{\cdot}Et_2O$ gives $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **6a**, a product which very likely forms *via* the intermediacy of the complex $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$. Insertion of the alkylidene group in the latter into a cage B–H bond, with addition at the tungsten centre of CO molecules from the solution, affords the final product **6a**.[2c] The non-spectator role of the η^5-$C_2B_9H_9Me_2$ ligand thus permits a reaction pathway not possible with the alkylidene complex **3a**. Consequently, the latter reacts with its precursor **1a**, present in the reaction mixtures, to yield the ditungsten salt **2**.

In this paper we extend the scope of these studies by employing the species $[NEt_4][W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5b**. These new experiments allow comparisons to be made with previous protonation reactions involving the reagents **1b** and **5a**.

Results and Discussion

Treatment of a CO-saturated CH_2Cl_2 solution of compound **5b** at −78 °C with $HBF_4{\cdot}Et_2O$ affords the complex $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **6b**, an analogue of **6a**.[2c] The same product is formed in the absence of CO, but in lower yield. Compound **6b** was characterised by the data given in Tables 1–3. The NMR spectra of **6a** and **6b** are very similar, in accord with their closely related structures. Thus the ^1H NMR spectra show broad resonances at δ 2.28 (**6a**) and 2.30 (**6b**) for the two protons of the BCH_2 group, and in the $^{11}B\text{-}\{^1H\}$ NMR spectra this moiety gives rise to signals at δ 9.4 (**6a**) and 8.6 (**6b**). As with **5a**, the protonation of **5b** proceeds very rapidly at −78 °C and no intermediate alkylidenetungsten complex $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_n(\eta^5\text{-}C_2B_9H_9Me_2)]$ (*n* = 2 or 3) was identified. Indeed, it would be surprising if such intermediates could be isolated as they would readily add CO at the tungsten centre to provide a filled valence shell for the metal. However, in the synthesis of **6b**, addition of $HBF_4{\cdot}Et_2O$ to **5b** resulted in an immediate colour change of the CH_2Cl_2 solutions from orange-red to green, but the latter colour rapidly disappeared as the reaction proceeded. The transient green species could well be an alkylidenetungsten complex akin to **3b**, with the η-C_5H_5 group replaced by η^5-$C_2B_9H_9Me_2$ and neutral rather than cationic.

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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[b]		Colour	Yield (%)	ν_{max}(CO)[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
6b	$[\mathrm{W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}}]$	Yellow	58	2093vs, 2022s (sh), 1998vs (br)	33.4 (33.3)	4.2 (4.0)
6d	$[\mathrm{W(CO)_2(PHPh_2)_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}}]$	Yellow	55	1939s, 1853vs	51.2 (51.1)	5.4 (5.1)
6e	$[\mathrm{W(CO)_2(CNBu^t)_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}}]$[d]	Pale yellow	27	[e] 1975vs, 1913vs	[f] 42.4 (42.0)	6.6 (6.0)
7a	$[\mathrm{W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}}]$	Yellow	58	2024vs, 1950s, 1924vs	48.6 (48.9)	4.6 (4.7)
8a	$[\mathrm{W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}}]$	Yellow	50	2070vs	57.4 (58.0)	5.5 (5.1)
9	$[\mathrm{W(CO)_2(dppm)\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}}]$	Yellow	78	1959vs, 1874vs	51.1 (51.8)	5.2 (5.0)
12b	$[\mathrm{NEt_4}][\mathrm{WI(CO)_3\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}}]$[g]	Dark red	40	2008vs, 1914vs (br)	[h] 34.9 (34.3)	6.3 (5.4)

[a] Calculated values are given in parentheses. [b] R = $\mathrm{C_6H_4OMe}$-2. [c] Measured in $\mathrm{CH_2Cl_2}$. All complexes display a broad B–H absorption at *ca.* 2550 cm^{-1}. [d] Formed as a mixture of isomers , see text. [e] ν_{max}(NC) 2169s and 2137s cm^{-1}. [f] N, 3.9 (4.1%). [g] Complex has a 2,1,8-$\mathrm{WC_2B_9}$ arrangement for the icosahedral fragment rather than the 3,1,2-$\mathrm{WC_2B_9}$ structure present in all the other compounds reported (see text). [h] N, 1.6 (1.7%).

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

Compound	^{1}H[b] (δ)	^{13}C[c] (δ)
6b	2.30 (s, br, 2 H, $\mathrm{BCH_2}$), 2.44 (s, 6 H, CMe), 3.73 (s, 3 H, OMe), 6.68–7.04 (m, 4 H, $\mathrm{C_6H_4}$)	209.4 [CO, *J*(WC) 115], 156.9, 135.0, 129.4, 125.3, 119.8, 109.2 ($\mathrm{C_6H_4}$), 69.3 (*C*Me), 54.6 (OMe), 33.3 (C*Me*), 28.3 (vbr, $\mathrm{BCH_2}$)
6d	2.20 [d, 6 H, CMe, *J*(PH) 3], 2.34 (s, br, 2 H, $\mathrm{BCH_2}$), 3.67 (s, 3 H, OMe), 6.63–7.01 (m, 4 H, $\mathrm{C_6H_4}$), 7.27 [d, 2 H, PH, *J*(PH) 386], 7.33–7.82 (m, 20 H, Ph)	231.1 [t, CO, *J*(PC) 23], 228.2 [t, CO, *J*(PC) 32], 157.0, 136.5, 134.5, 132.5, 130.9 [d, *J*(PC) 12], 130.7, 128.7, 124.5, 119.3, 109.8 ($\mathrm{C_6H_4}$ and Ph), 62.5 (*C*Me), 55.1 (OMe), 29.1 (C*Me*), 25.0 (vbr, $\mathrm{BCH_2}$)
6e[d]	[e] 1.60 (s, 18 H, $\mathrm{Bu^t}$), 1.62* (s, 18 H, $\mathrm{Bu^t}$), 2.25 (s, 6 H, CMe), 2.30* (s, 6 H, CMe), 2.20–2.40 (m, 2 H, $\mathrm{BCH_2}$), 3.71 (s, 3 H, OMe), 3.72* (s, 3 H, OMe), 6.58–6.97 (m, 4 H, $\mathrm{C_6H_4}$)	228.6, 221.8* (CO), 157.1, 157.0* ($\mathrm{C_6H_4}$), 148.2, 141.5* (CN), 137.1, 137.0*, 130.2*, 130.0, 124.4, 124.3*, 119.4, 109.7*, 109.5 ($\mathrm{C_6H_4}$), 64.6 (*C*Me), 59.7 (*C*$\mathrm{Me_3}$), 59.2* (*C*Me), 55.1* (OMe), 55.0* (*C*$\mathrm{Me_3}$), 54.9 (OMe), 32.6, 32.5* (C*Me*), 30.7, 30.6* (C*$\mathrm{Me_3}$*), 26.8 (vbr, $\mathrm{BCH_2}$)
7a	1.94 (s, 2 H, $\mathrm{BCH_2}$), 1.98 (s, 6 H, CMe), 3.76 (s, 3 H, OMe), 6.68–6.96 (m, 4 H, $\mathrm{C_6H_4}$), 7.51–7.68 (m, br, 15 H, Ph)	222.1 [d, 2 × CO, *J*(PC) 30], 221.5 [d, CO, *J*(PC) 9], 156.7, 136.2, 133.9, 133.8, 131.7, 130.4, 128.8, 124.6, 119.2, 109.3 ($\mathrm{C_6H_4}$ and Ph), 66.4 (*C*Me), 54.5 (OMe), 31.0 (C*Me*), 26.8 (vbr, $\mathrm{BCH_2}$)
8a[f]	[e] 1.31 (s, 3 H, CMe), 1.78, 2.04 [AB, 2 H, $\mathrm{BCH_2}$, *J*(HH) 13], 2.42 (s, 3 H, CMe), 3.31 (s, 3 H, OMe), 6.59–8.37 (m, 24 H, $\mathrm{C_6H_4}$, Ph)	210.4 (CO), 185.7, 177.5, 172.5 (*C*Ph), 156.4–108.5 (Ph, $\mathrm{C_6H_4}$), 68.7, 65.1 (*C*Me), 54.1 (OMe), 30.2, 27.1 (C*Me*), 27.0 (vbr, $\mathrm{BCH_2}$)
9	1.27 (s, br, 2 H, $\mathrm{BCH_2}$), 2.25 (s, br, 6 H, CMe), 3.61 (s, 3 H, OMe), 4.95 [d of t, 1 H, $\mathrm{PCH_2P}$, *J*(PH) 11, *J*(HH) 14], 5.26 [d of t, 1 H, $\mathrm{PCH_2P}$, *J*(PH) 9, *J*(HH) 14], 6.55–6.94 (m, 4 H, $\mathrm{C_6H_4}$), 7.34–7.73 (m, 20 H, Ph)	[g] 232.9 (AXX′, CO, *N* 32), 157.0, 136.9, 133.4, 131.7, 131.1, 130.7, 128.7, 124.4, 119.2, 109.7 ($\mathrm{C_6H_4}$ and Ph), 63.4 (*C*Me), 55.0 (OMe), 48.8 [t, $\mathrm{PCH_2P}$, *J*(PC) 28], 33.1 (C*Me*), 28.5 (vbr, $\mathrm{BCH_2}$)
12b	1.31 [t, br, 12 H, $\mathrm{CH_2}$*Me*, *J*(HH) 7], 1.57 (s, 3 H, CMe), 1.92 (s, 3 H, CMe), 2.31, 2.45 [AB, br, 2 H, $\mathrm{BCH_2}$, *J*(HH) 10], 3.18 [q, 8 H, C*$\mathrm{H_2}$*Me, *J*(HH) 7], 3.70 (s, 3 H, OMe), 6.69–6.95 (m, 4 H, $\mathrm{C_6H_4}$)	[h] 230.9, 222.0, 221.4 (CO), 157.5, 138.2, 130.5, 124.6, 119.8, 110.2 ($\mathrm{C_6H_4}$), 63.4 (*C*Me), 61.9 (br, *C*Me), 55.3 (OMe), 53.1 (*C*$\mathrm{H_2}$Me), 32.8, 29.6 (C*Me*), 26.5 (vbr, $\mathrm{BCH_2}$), 7.9 ($\mathrm{CH_2}$*Me*)

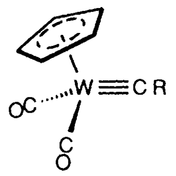
[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. [b] Measured in $\mathrm{CD_2Cl_2}$ unless otherwise stated. Protons of BH groups display broad unresolved signals in the range δ *ca.* −2 to +3. [c] Hydrogen-1 decoupled chemical shifts, measured in $\mathrm{CDCl_3}$ unless otherwise stated, are positive to high frequency of $\mathrm{SiMe_4}$. [d] Peaks due to the minor isomer are marked with an asterisk. However, some signals are obscured by those of major isomer. [e] Measured in $\mathrm{CDCl_3}$. [f] Measured at −40 °C. [g] $N = |J(\mathrm{PC}) + J(\mathrm{P'C})|$. [h] Measured in $\mathrm{CD_2Cl_2}$–$\mathrm{CH_2Cl_2}$.

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

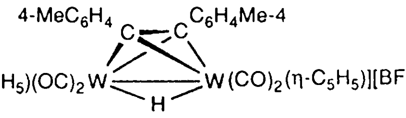
Compound	^{11}B[b] (δ)	^{31}P[c] (δ)
6b	8.6 (1 B, $\mathrm{BCH_2}$), −1.0 (1 B, BH), −2.8 (2 B, BH), −8.0 (5 B, BH)	
6d	7.4 (1 B, $\mathrm{BCH_2}$), −6.5 (3 B, BH), −9.0 (2 B, BH), −10.9 (3 B, BH)	15.2 [*J*(WP) 186]
6e	[d] 6.8 (1 B, $\mathrm{BCH_2}$), −6.0 (3 B, BH), −8.2 (2 B, BH), −11.2 (3 B, BH)	
7a	7.2 (1 B, $\mathrm{BCH_2}$), −4.0 (1 B, BH), −5.1 (2 B, BH), −8.7 (2 B, BH), −10.1 (3 B, BH)	11.1 [*J*(WP) 161]
8a	[d] 9.88 (1 B, $\mathrm{BCH_2}$), −5.5 to −12.1 (br, 8 B, BH)	
9	7.0 (1 B, $\mathrm{BCH_2}$), −6.3 (5 B, BH), −10.1 (3 B, BH)	−33.2 [*J*(WP) 186]
10a[e]		52.2 [d, *J*(PP) 50, *J*(WP) 213], 40.1 [d, *J*(PP) 50]
12b	3.7 (1 B, $\mathrm{BCH_2}$), −4.0 (2 B, BH), −5.3 (1 B, BH), −8.4 (1 B, BH), −10.4 (1 B, BH), −11.1 (1 B, BH), −13.1 (1 B, BH), −16.3 (1 B, BH)	

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, measurements in $\mathrm{CD_2Cl_2}$–$\mathrm{CH_2Cl_2}$ at ambient temperatures unless otherwise stated. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $\mathrm{BF_3\cdot Et_2O}$ (external). Signals ascribed to more than one boron nucleus may result from overlapping peaks, and do not necessarily indicate symmetry equivalence. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% $\mathrm{H_3PO_4}$ (external). [d] Measured in $\mathrm{CDCl_3}$. [e] Compound formed as a mixture with **9**, see text.

Addition of $\mathrm{HBF_4\cdot Et_2O}$ to a $\mathrm{CH_2Cl_2}$ solution containing complex **5b** and $\mathrm{PPh_3}$ at −78 °C affords $[\mathrm{W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}}]$ **7a**. As described below, the structure of this product was established by an X-ray diffraction study. However, before discussing the crystallographic data, it is interesting to contrast the formation of the stable complex **7a** with the earlier results obtained by protonating **5a** in the presence of $\mathrm{PPh_3}$.[2c] This reaction affords compound **7b**, an



	R
1a	$C_6H_4Me\text{-}4$
1b	$C_6H_4OMe\text{-}2$



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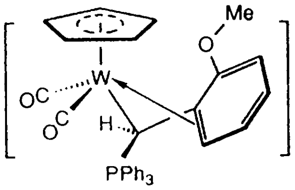
$[(\eta\text{-}C_5H_5)(OC)_2W{=}C(H)R][BF_4]$

	R
3a	$C_6H_4Me\text{-}4$
3b	$C_6H_4OMe\text{-}2$



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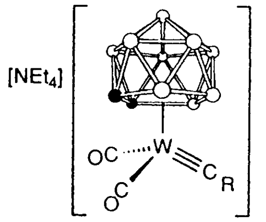
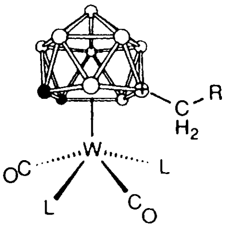
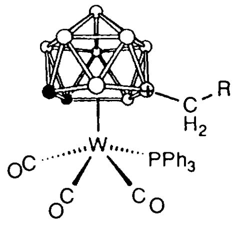


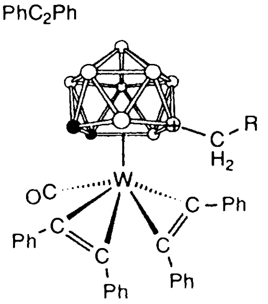
	R
5a	$C_6H_4Me\text{-}4$
5b	$C_6H_4OMe\text{-}2$



	R	L
6a	$C_6H_4Me\text{-}4$	CO
6b	$C_6H_4OMe\text{-}2$	CO
6c	$C_6H_4Me\text{-}4$	PPh_3
6d	$C_6H_4OMe\text{-}2$	$PHPh_2$
6e	$C_6H_4OMe\text{-}2$	$CNBu^t$
6f	$C_6H_4Me\text{-}4$	$CNBu^t$
6g	$C_6H_4Me\text{-}4$	PhC_2Ph
6h	$C_6H_4OMe\text{-}2$	PhC_2Ph



	R
7a	$C_6H_4OMe\text{-}2$
7b	$C_6H_4Me\text{-}4$



	R
8a	$C_6H_4OMe\text{-}2$
8b	$C_6H_4Me\text{-}4$

● CMe ○ BH ⊕ B

analogue of **7a**, but the former species is somewhat unstable, and its solution disproportionates to yield crystals of the bis(triphenylphosphine)tungsten complex **6c**. We observed no similar decomposition on the part of solutions of **7a**. The reason for the difference in stability of **7a** and **7b** is not clear at the present time.

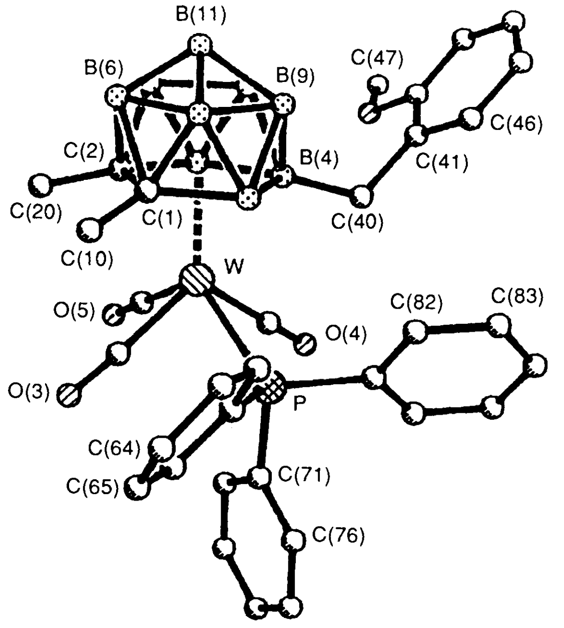


Fig. 1 Molecular structure of the compound $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **7a**, showing the crystallographic labelling scheme

The significant data from the X-ray diffraction study on compound **7a** are given in Table 4, and the structure of the molecule is shown in Fig. 1. The tungsten atom is η^5 co-ordinated by the *nido*-icosahedral fragment $C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2$. In the latter the $CH_2C_6H_4OMe\text{-}2$ group is attached to the boron atom which is in the β position with respect to the two carbon atoms in the open pentagonal $\overline{CCB\mathit{B}B}$ face of the cage. This structural feature is common to all of the many species that have now been synthesised containing $C_2B_9H_8(CH_2R)Me_2$ (R = alkyl or aryl) groups.[2c,e,f,4] The tungsten atom is also ligated by three terminally bound CO molecules (W–C–O av. 177.5°) and the PPh_3 group. The various structural parameters for **7a** are very similar to those obtained from the X-ray diffraction study of **6c**.[2c] Thus for **7a** the B(4)–C(40) separation [1.630(6) Å] is comparable with the corresponding $B\text{-}CH_2C_6H_4Me\text{-}4$ distance [1.65(2) Å] in compound **6c**. The W–P bond lengths in **7a** [2.572(1) Å] and in **6c** [2.571(5) Å] are essentially identical.

The NMR data for compound **7a** (Tables 2 and 3) are in accord with the structure established by X-ray diffraction. Moreover, as expected, they are very similar to those for **7b**.[2c] Thus **7a** shows diagnostic NMR resonances for the BCH_2 group [^1H, δ 1.94; $^{13}C\text{-}\{^1H\}$, δ 26.8; $^{11}B\text{-}\{^1H\}$, δ 7.2], as does **7b** [^1H, δ 1.79; $^{13}C\text{-}\{^1H\}$, δ 31.5; $^{11}B\text{-}\{^1H\}$, δ 7.2]. In the $^{31}P\text{-}\{^1H\}$ NMR spectra of the two complexes resonances occur at δ 11.1 (**7a**) and 10.69 (**7b**), with $^{183}W\text{-}^{31}P$ couplings of 161 and 165 Hz, respectively.

Protonation of the salt **5b** in the presence of $PHPh_2$ was next investigated. This reaction afforded the complex $[W(CO)_2(PHPh_2)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **6d**. Data given in Tables 1–3 fully characterise this product. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum (Table 2) there are two resonances for non-equivalent CO groups and both signals are triplets, due to $^{31}P\text{-}^{13}C$ coupling with chemically equivalent $PHPh_2$ ligands. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum (Table 3) there is a singlet at δ 15.2 [J(WP) 186 Hz]. These data can be explained if the two $PHPh_2$ groups are transoid to one another in a structure similar to **7a**, with one phosphine ligand lying below B(3) and the other below B(5) (Fig. 1). In this arrangement one carbonyl ligand is *cis* to the BCH_2 fragment and the other transoid to it. This

Table 4 Selected internuclear distances (Å) and angles (°) for $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **7a**, with estimated standard deviations in parentheses

W–P	2.572(1)	W–C(1)	2.408(4)	W–C(2)	2.390(4)	W–B(3)	2.358(4)
W–B(4)	2.443(4)	W–B(5)	2.380(3)	W–C(3)	1.999(4)	W–C(4)	1.990(4)
W–C(5)	1.999(4)	P–C(61)	1.846(5)	P–C(71)	1.837(3)	P–C(81)	1.850(4)
C(1)–C(10)	1.529(8)	C(1)–C(2)	1.664(6)	C(1)–B(5)	1.729(6)	C(2)–C(20)	1.526(5)
C(2)–B(3)	1.722(7)	B(3)–B(4)	1.814(5)	B(4)–B(5)	1.824(7)	B(4)–B(8)	1.789(6)
B(4)–B(9)	1.794(5)	B(4)–C(40)	1.630(6)	C(3)–O(3)	1.157(5)	C(4)–O(4)	1.147(6)
C(5)–O(5)	1.135(5)	C(40)–C(41)	1.505(5)	C(42)–O(40)	1.375(5)	O(40)–C(47)	1.410(9)

P–W–C(3)	73.2(1)	P–W–C(4)	74.5(1)	P–W–C(5)	119.8(1)
C(1)–W–C(2)	40.6(1)	C(1)–W–B(3)	71.3(2)	C(1)–W–B(4)	73.1(1)
B(3)–W–B(4)	44.4(1)	C(1)–W–B(5)	42.3(1)	C(3)–W–C(4)	111.0(1)
C(3)–W–C(5)	73.3(2)	C(4)–W–C(5)	73.0(2)	W–P–C(61)	114.7(1)
W–P–C(71)	114.2(1)	C(61)–P–C(71)	101.6(2)	W–P–C(81)	114.8(1)
C(61)–P–C(81)	108.8(2)	C(71)–P–C(81)	101.0(2)	W–C(1)–C(10)	110.2(2)
W–C(1)–C(2)	69.1(2)	C(10)–C(1)–C(2)	121.3(3)	W–C(1)–B(5)	68.0(2)
C(10)–C(1)–B(5)	124.8(4)	C(2)–C(1)–B(5)	109.4(3)	W–C(2)–C(20)	110.1(2)
W–C(2)–B(3)	67.8(2)	C(1)–C(2)–B(3)	110.3(3)	W–B(3)–C(2)	69.7(2)
W–B(3)–B(4)	70.3(2)	C(2)–B(3)–B(4)	108.8(3)	W–B(4)–B(3)	65.4(2)
W–B(4)–B(5)	66.0(2)	W–B(4)–C(40)	114.0(2)	B(3)–B(4)–C(40)	126.2(4)
B(5)–B(4)–C(40)	127.3(3)	B(8)–B(4)–C(40)	116.2(3)	B(9)–B(4)–C(40)	116.7(3)
W–B(5)–C(1)	69.7(2)	W–B(5)–B(4)	69.6(2)	C(1)–B(5)–B(4)	108.8(3)
W–C(3)–O(3)	177.2(3)	W–C(4)–O(4)	176.5(4)	W–C(5)–O(5)	178.8(4)
B(4)–C(40)–C(41)	116.4(3)	P–C(61)–C(62)	123.8(4)	P–C(61)–C(66)	118.0(3)

interpretation assumes that the $W(CO)_2(PHPh_2)_2$ moiety does not rotate with respect to the cage.

It is interesting that protonation of complex **5b** in the presence of $PHPh_2$ yields a bis(phosphine)tungsten species whereas the corresponding reaction involving PPh_3, even with the latter in excess, yields a monophosphinetungsten complex. We assume that this is due to the lower steric requirements of the $PHPh_2$ group which facilitates addition of two molecules of this reagent to the above-mentioned electronically unsaturated intermediate $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$.

Treatment of CH_2Cl_2 solutions containing a mixture of complex **5b** and $CNBu^t$ in 1:2 mol ratio with $HBF_4 \cdot Et_2O$ gives $[W(CO)_2(CNBu^t)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **6e**. Examination of the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of this product revealed that it is formed as an inseparable mixture of two isomers in ratio *ca.* 2:1, based on peak intensities in the ^1H spectrum. The isomers of **6e** are assumed to correspond to cisoid and transoid arrangements of the $CNBu^t$ ligands in the $W(CO)_2(CNBu^t)_2$ fragment, and in the structural formula shown only the transoid structure is depicted. The analogous compound **6f** has been previously prepared by protonating the reagent **5a** with $HBF_4 \cdot Et_2O$ in the presence of $CNBu^t$.[2c] Complex **6f** also exists in solution as an equilibrating mixture of the isomers. Isolation of **6e** and **6f** reveals that the rod-like ligand $CNBu^t$ can effectively replace two CO ligands in the compounds **6a** and **6b** whereas the more bulky PPh_3 formally replaces only one CO to yield the complexes **7**. Examination of space-filling models of **7a**, using data obtained from the X-ray study, reveals that the ligands are very crowded at the metal centre.

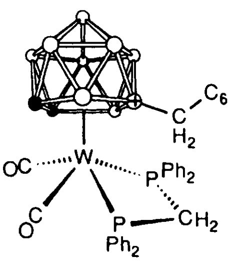
Addition of $HBF_4 \cdot Et_2O$ to a CH_2Cl_2 solution containing complex **5b** and PhC≡CPh in 1:2 mol ratio affords $[W(CO)(PhC_2Ph)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **8a**, data for which are given in Tables 1–3. This product is an analogue of compound **8b** obtained from **5a**, PhC≡CPh, and $HBF_4 \cdot Et_2O$.[2c] Formation of **8b** occurs *via* the intermediacy of a bis(alkyne)tungsten species **6g** which releases a CO molecule at low temperatures. In the synthesis of **8a** a transient intermediate, possibly **6h**, was detected by IR spectroscopy, displaying two CO stretching bands at 1988 and 2048 cm^{-1}. It is noteworthy that **6g** has CO absorptions at 1985 and 2045 cm^{-1}.

In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of complex **8a** (Table 2) the resonances for the ligated carbon atoms of the alkyne occur in the chemical shift range expected when alkynes are formally donating three electrons to a metal centre.[5] A similar feature is observed in the spectrum of **8b**, but this molecule exhibits dynamic behaviour corresponding to rotation of the $Ph\mathit{C}_2Ph$ groups, and only one broad resonance was observed at δ 178.2 in the room-temperature $^{13}C\text{-}\{^1H\}$ NMR spectrum. With **8a** it was possible to measure the spectrum at −40 °C when the asymmetry in the molecule is revealed by the observation of *C*Ph signals at δ 185.7, 177.5 and 172.5, and resonances for the non-equivalent cage CMe groups at δ 68.7, 65.1 (*C*Me) and 30.2, 27.1 (C*Me*). It is possible that the observation of three *C*Ph peaks, rather than the four expected, is due to a coincidence of two of the signals. Like all the compounds reported herein, the $^{13}C\text{-}\{^1H\}$ NMR signal for the BCH_2 group is very broad, occurring at δ 27.0. The broadness of these signals may be ascribed to the quadrupolar effect of the adjacent boron atom.

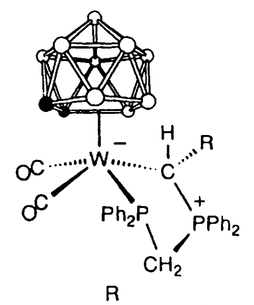
If the reagent **5b** is protonated with $HBF_4 \cdot Et_2O$ in the presence of dppm ($Ph_2PCH_2PPh_2$) the complex $[W(CO)_2(dppm)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **9** is obtained, together with small amounts of a minor product isolated in quantities too small to allow full characterisation. However, it seems very probable that this minor species is $[W\{CH(C_6H_4OMe\text{-}2)PPh_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **10a**, an analogue of the well characterised compound **10b**, previously isolated by treating mixtures of **5a** and dppm with $HBF_4 \cdot Et_2O$.[2e] The structure of **10b** has been established by X-ray diffraction. It displays in its IR spectrum CO bands at 1919 and 1828 cm^{-1}, and in its $^{31}P\text{-}\{^1H\}$ NMR spectrum there are resonances at δ 51.3 [d, *J*(PP) 52, *J*(WP) 250] and 36.3 [d, *J*(PP) 52 Hz]. The corresponding data for **10a** are: ν_{max}(CO) at 1920 and 1830 cm^{-1}; $^{31}P\text{-}\{^1H\}$, δ 52.2 [d, *J*(PP) 50, *J*(WP) 213] and 40.1 [d, *J*(PP) 50 Hz].

Compound **10b** is the major product formed from **5a**, dppm and $HBF_4 \cdot Et_2O$, whereas **10a** is the minor product obtained from mixtures of **5b** and dppm, and the acid. Interestingly, complex **10a** is closely mapped with $[W\{CH(C_6H_4OMe\text{-}2)PPh_2CH_2PPh_2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **11**. The latter has been obtained by adding $HBF_4 \cdot Et_2O$ to a CH_2Cl_2 solution of **1b** and dppm.[2h]

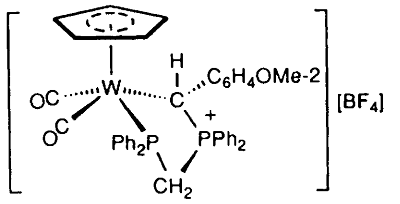
The structures of the species **10** and **11** implicate, following protonation, the initial formation of an alkylidene complex, the W=C(H)R group of which is then captured by addition of a tertiary phosphine to the ligated carbon. Such reactions are well



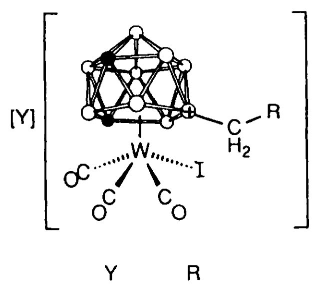
9



	R
10a	C_6H_4OMe-2
10b	C_6H_4Me-4



11



	Y	R
12a	PPh_4	C_6H_4Me-4
12b	NEt_4	C_6H_4OMe-2

● CMe ○ BH ⊕ B

established in alkylidenemetal complex chemistry.[6] However, when the tungsten atom carries an η^5-$C_2B_9H_9Me_2$ ligand, addition of phosphine to the intermediate alkylidene species is in competition with insertion of the latter into a cage B–H bond. Formation of the complexes **7** and **9** shows that the latter process is more rapid than the former in the reactions affording these products. This is in contrast with the formation of the compounds **10**.

Complex **9** is structurally related to the compounds $[W(CO)_2L_2\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ $[L_2 = Me_2P(CH_2)_2PMe_2$ or $Ph_2P(CH_2)_2PPh_2]$, prepared by treating CH_2Cl_2 solutions of $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ at −78 °C with $HBF_4 \cdot Et_2O$ in the presence of the chelating phosphines.[2e] In these reactions also, migration of the C(H)Me group from tungsten to the cage is more favourable than its capture by phosphine. As mentioned earlier, it was observed that during the synthesis of the compound **6b**, immediately following addition of $HBF_4 \cdot Et_2O$ to the orange-red solutions containing **5b**, a green colour developed. Similar behaviour occurred during the preparation of **6d**, **6e**, **7a**, **8a** and **9**. We suggest that the transient green colour is due to the alkylidenetungsten complex $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, which is very reactive due to the electronic unsaturation at the tungsten centre.

The spectroscopic data for complex **9** are in complete accord with its formulation. The presence of the $BCH_2C_6H_4OMe$-2 group is clearly revealed by diagnostic peaks in the ^1H, ^{13}C-$\{^1H\}$, and ^{11}B-$\{^1H\}$ NMR spectra (Tables 2 and 3). The ^{31}P-$\{^1H\}$ NMR spectrum displays a single resonance at δ −33.2, the magnitude of the observed ^{183}W–^{31}P coupling (186 Hz) being in accord with the phosphorus nuclei being bound to the tungsten. The appearance of a singlet signal indicates the presence of equivalent phosphorus atoms. Moreover, the ^1H and ^{13}C-$\{^1H\}$ NMR spectra reveal that the cage CMe groups are also equivalent. In the latter spectrum these fragments give rise to resonances at δ 63.4 (*C*Me) and 33.1 (C*Me*). These data imply that the molecule has a plane of symmetry through the W atom, the BCH_2 group, and the midpoint of the cage C–C connectivity, with the PPh_2 groups lying on either side of this plane. The aforementioned compounds $[W(CO)_2L_2\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ have NMR spectra (^1H, ^{13}C-$\{^1H\}$, ^{11}B-$\{^1H\}$ and ^{31}P-$\{^1H\}$) very similar to those of **9**, except for differences due to the presence of a PCH_2P fragment in the latter and $P(CH_2)_2P$ fragments in the former.[2e]

It was mentioned in the introduction that the nature of the products obtained by protonating the salts $[Y][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ depended on the acid used. Thus whereas **5a**, and $HBF_4 \cdot Et_2O$ afford the neutral compound **6a**, treatment of $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with aqueous HI yields the salt $[PPh_4][WI(CO)_3\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **12a**.[2f,7] Moreover, in the latter there is no connectivity between the carbon atoms of the cage, which adopts with the tungsten atom a *closo*-2,1,8-WC_2B_9 icosahedral structure. This is in contrast with **6a**, and the other complexes described above, all of which have a *closo*-3,1,2-WC_2B_9 arrangement for the 12-atom core. During the work described herein the reagent **5b** was treated with aqueous HI. The product isolated was $[NEt_4][WI(CO)_3\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **12b**, analogous to **12a** with a 2,1,8 arrangement for the non-boron vertices of the WC_2B_9 icosahedron. The salt **12b** was fully characterised by the data listed in Tables 1–3. An interesting and useful diagnostic tool for distinguishing between 3,1,2- and 2,1,8-WC_2B_9 polytopal isomers is based on their ^{13}C-$\{^1H\}$ NMR spectra.[1,2f] For the 3,1,2-WC_2B_9 species the resonances for the cage carbons are sharp signals, with either one or two peaks appearing, depending on the overall molecular symmetry. For the 2,1,8-WC_2B_9 isomers the carbons are non-equivalent, and there are two resonances, but crucially one signal is broad. The latter may be assigned to the carbon lying in the second pentagonal CB_4 ring lying above the W atom, the broadening of the signal being due to the connectivity with five ^{11}B nuclei. Compound **12b** is no exception. In the ^{13}C-$\{^1H\}$ NMR spectrum the two cage *C*Me signals occur at δ 63.4 and 61.9, with the former peak sharp and the latter broad.

Like all the new compounds reported herein, in the ^{11}B-$\{^1H\}$ NMR spectrum of **12b** there is a diagnostic resonance (δ 3.7) for the BCH_2 fragment. These signals remain as singlets in fully coupled ^{11}B spectra, indicating that they are not due to BH groups.

It is evident from the results described in this paper that the products obtained by protonating the salt **5b** in the presence of donor molecules are in general structurally similar to the compounds obtained from **5a** in similar reactions. However, some differences in reactivity patterns and relative product stability were observed in reactions of the reagents **5** with PPh_3, PhC≡CPh, and dppm.

Experimental

The instrumentation used for the spectroscopic measurements, and the experimental techniques employed have been described in previous Parts of this series.[1,2b–f] Chromatography columns used were *ca.* 20 cm long and 3 cm in diameter, unless otherwise stated, and were packed with alumina (Aldrich, Brockmann Activity III). The tetrafluoroboric acid was an 85% solution of $HBF_4 \cdot Et_2O$ in Et_2O, as supplied by Aldrich Chemicals.

The reagent **5b** was prepared from $[W(\equiv CC_6H_4OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$ (py = pyridine),[2b] $Na_2[C_2B_9H_9Me_2]$

and $[NEt_4]Cl$ as follows. A solution of $Na_2[C_2B_9H_9Me_2]$ was obtained by refluxing in thf (tetrahydrofuran) (10 cm^3) $[NHMe_3][C_2B_9H_{10}Me_2]$ (0.60 g, 2.7 mmol)[8] with NaH (0.55 g, 13.8 mmol, from a 60% dispersion in mineral oil). This solution was decanted, and added to a thf (20 cm^3) solution of $[W(\equiv CC_6H_4OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$ (1.60 g, 2.50 mmol). After stirring the mixture for *ca.* 4 h, $[NEt_4]Cl{\cdot}H_2O$ (0.70 g, 3.80 mmol) was added, and the stirring was continued for 30 min. The mixture was then filtered through a short Celite plug (2 × 5 cm), after which solvent was removed *in vacuo* from the resulting solution. The residue was dissolved in CH_2Cl_2 (20 cm^3) and chromatographed at −20 °C. Elution with CH_2Cl_2–Et_2O (3:1) afforded an orange eluate. Solvent was removed *in vacuo*, and the residue was crystallised from CH_2Cl_2–Et_2O (20 cm^3, 1:4) to give salmon-pink *microcrystals* of $[NEt_4][W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5b** (1.34 g, 81%), after washing the product with Et_2O (10 cm^3) and drying *in vacuo* (Found: C, 40.6; H, 6.8; N, 2.4. $C_{22}H_{42}B_9NO_3W$ requires C, 40.7; H, 6.5; N, 2.2%), $\nu_{max}(CO)$ at 1962vs and 1879vs cm^{-1} in CH_2Cl_2. NMR (in CD_2Cl_2): ^1H, δ 1.23 [t, br, 12 H, $CH_2\mathit{Me}$, $J(HH)$ 7], 2.08 (s, 6 H, CMe), 3.10 [q, 8 H, $C\mathit{H}_2Me$, $J(HH)$ 7], 3.88 (s, 3 H, OMe) and 6.79–7.47 (m, 4 H, C_6H_4); $^{13}C\text{-}\{^1H\}$, δ 292.9 [C≡W, $J(WC)$ 204], 227.8 [CO, $J(WC)$ 185], 158.7, 140.6, 131.0, 129.2, 120.6, 111.9 (C_6H_4), 62.0 (br, *C*Me), 56.3 (OMe), 53.0 (*C*H_2Me), 29.9 (C*Me*) and 7.7 (CH_2*Me*).

Table 5 Crystallographic data for compound **7a**[a]

Crystal dimensions/mm	0.15 × 0.60 × 0.40
Formula	$C_{33}H_{38}B_9O_4PW$
M	810.8
Crystal colour, shape	Yellow cubes
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.947(3)
b/Å	11.522(2)
c/Å	15.764(4)
α/°	68.74(2)
β/°	69.94(2)
γ/°	89.03(2)
U/Å³	1727(1)
Z	2
D_c/g cm^{-3}	1.56
μ(Mo-Kα)/cm^{-1}	35.0
F(000)	804
T/K	293
No. of unique reflections	6453
No. of observed reflections [$F_o \geqslant 5F_o$]	5587
R(*R*′)[b]	0.022 (0.024)
Final difference map features (maximum, minimum)/e Å^{-3}	0.49, −0.73

[a] Data collected on a Siemens R3m/V four-circle diffractometer operating in the Wyckoff ω-scan mode in the range $5 \leqslant 2\theta \leqslant 50°$; graphite monochromated Mo-Kα X-radiation, $\bar{\lambda}$ = 0.710 69 Å. Refinement was by full-matrix least squares with a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ with g = 0.0008; $\sigma^2(F_o)$ is the variance in F_o due to counting statistics and g was chosen so as to minimise variation in $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

Protonation Studies using $HBF_4{\cdot}Et_2O$.—(*i*) A CH_2Cl_2 (15 cm^3) solution of compound **5b** (0.20 g, 0.31 mmol) at −78 °C was saturated with CO gas for *ca.* 5 min. The introduction of CO was continued during addition of $HBF_4{\cdot}Et_2O$ (40 μl, 0.30 mmol). The mixture instantly changed colour from orange-red to green, and as it was warmed slowly to room temperature under the CO atmosphere the colour further changed to brown. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2–hexane (10 cm^3, 1:1), and the resulting solution was chromatographed at −20 °C. Elution with the same solvent mixture gave a pale yellow eluate. Solvent was removed *in vacuo*, and the residue was crystallised from CH_2Cl_2–hexane (5 cm^3, 1:4) to give yellow *microcrystals* of $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **6b** (0.104 g).

(*ii*) A CH_2Cl_2 (10 cm^3) solution of complex **5b** (0.10 g, 0.15 mmol) and $PHPh_2$ (0.26 mmol, 2.0 cm^3 of a 0.13 mol dm^{-3} solution in CH_2Cl_2) at −78 °C was treated with $HBF_4{\cdot}Et_2O$ (20 μl, 0.15 mmol). The solution turned green, and upon warming slowly to room temperature became brown. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–hexane (10 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture afforded a pale yellow eluate. Removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–hexane (5 cm^3, 1:4) gave yellow *microcrystals* of $[W(CO)_2(PHPh_2)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4OMe\text{-}2)Me_2\}]$ **6d** (0.076 g).

(*iii*) In a similar experiment a CH_2Cl_2 (10 cm^3) solution containing complex **5b** (0.10 g, 0.15 mmol) and $CNBu^t$ (20 μl, 0.18 mmol) at −78 °C was treated with $HBF_4{\cdot}Et_2O$ (20 μl, 0.15

Table 6 Atom positional parameters (fractional coordinates, × 10^4) with estimated standard deviations in parentheses for complex **7a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2259(1)	2252(1)	1652(1)	P	1292(1)	4034(1)	2185(1)
C(1)	2793(3)	813(3)	2986(3)	C(10)	3762(4)	1488(4)	3210(3)
C(2)	3280(3)	378(3)	2036(3)	C(20)	4715(4)	627(4)	1361(3)
B(3)	1979(4)	202(3)	1697(3)	B(4)	508(4)	495(3)	2533(3)
B(5)	1134(4)	943(3)	3318(3)	B(6)	3098(5)	−736(4)	3186(3)
B(7)	2595(5)	−1124(4)	2370(3)	B(8)	886(4)	−1075(4)	2718(3)
B(9)	360(4)	−594(4)	3724(3)	B(10)	1749(5)	−363(4)	3991(3)
B(11)	1584(5)	−1621(4)	3629(3)	C(3)	3771(4)	3490(3)	1322(3)
O(3)	4679(3)	4173(3)	1122(3)	C(4)	1160(4)	2996(3)	859(3)
O(4)	553(3)	3389(3)	376(2)	C(5)	3376(4)	2634(4)	257(3)
O(5)	3992(3)	2848(3)	−539(2)	C(40)	−854(3)	820(3)	2343(3)
C(41)	−1967(3)	−230(3)	2862(3)	C(42)	−2147(4)	−1052(3)	2435(3)
C(43)	−3149(4)	−2054(4)	2948(4)	C(44)	−3977(5)	−2226(5)	3857(4)
C(45)	−3858(5)	−1412(5)	4301(4)	C(46)	−2849(4)	−428(5)	3790(3)
O(40)	−1295(3)	−805(3)	1499(2)	C(47)	−1598(6)	−1450(5)	975(4)
C(61)	1898(4)	4330(3)	3055(3)	C(62)	1389(5)	3668(4)	4048(3)
C(63)	1934(6)	3888(5)	4658(4)	C(64)	2977(6)	4798(5)	4279(4)
C(65)	3505(5)	5453(5)	3302(4)	C(66)	2982(4)	5225(4)	2679(3)
C(71)	1696(3)	5586(3)	1188(3)	C(72)	2337(3)	5774(3)	221(3)
C(73)	2528(4)	6969(3)	−503(3)	C(74)	2085(4)	7969(3)	−248(3)
C(75)	1467(4)	7794(3)	714(3)	C(76)	1259(4)	6605(3)	1436(3)
C(81)	−520(3)	3892(3)	2663(3)	C(82)	−1269(4)	3132(4)	3604(3)
C(83)	−2639(4)	3035(5)	3924(3)	C(84)	−3247(4)	3706(5)	3303(4)
C(85)	−2497(5)	4432(5)	2355(4)	C(86)	−1137(4)	4531(4)	2037(3)

mmol) to give pale yellow *microcrystals* of [W(CO)$_2$(CNBu^t)$_2${η^5-C$_2$B$_9$H$_8$(CH$_2$C$_6$H$_4$OMe-2)Me$_2$}] **6e** (0.029 g).

(*iv*) The compound [W(CO)$_3$(PPh$_3$){η^5-C$_2$B$_9$H$_8$(CH$_2$C$_6$H$_4$OMe-2)Me$_2$}] **7a** (0.072 g) was similarly obtained by addition of HBF$_4$·Et$_2$O (20 μl, 0.15 mmol) to a CH$_2$Cl$_2$ (10 cm^3) solution containing **5b** (0.10 g, 0.15 mmol) and PPh$_3$ (0.050 g, 0.19 mmol) at -78 °C.

(*v*) Similarly, the reagents **5b** (0.10 g, 0.15 mmol) and PhC≡CPh (0.055 g, 0.31 mmol) in CH$_2$Cl$_2$ (10 cm^3) at -78 °C were treated with HBF$_4$·Et$_2$O (20 μl, 0.15 mmol). The IR spectrum of the product mixture showed ν_{max}(CO) bands at 1988 and 2048 cm^{-1} attributed to compound **6h** (see Discussion). After column chromatography, as in (*ii*) above, the crude product was crystallised from CH$_2$Cl$_2$–hexane (5 cm^3, 1:4) at -50 °C, and then washed with cold hexane (3 cm^3, -10 °C) to give yellow *microcrystals* of [W(CO)(PhC≡CPh)$_2${η^5-C$_2$B$_9$H$_8$(CH$_2$C$_6$H$_4$OMe-2)Me$_2$}] **8a** (0.065 g).

(*vi*) Following a similar procedure to that used for the synthesis of **6d**, a mixture of the reagents **5b** (0.10 g, 0.15 mmol) and dppm (0.060 g, 0.16 mmol) in CH$_2$Cl$_2$ at room temperature gave, after addition of HBF$_4$·Et$_2$O (20 μl, 0.15 mmol), yellow *microcrystals* of [W(CO)$_2$(dppm){η^5-C$_2$B$_9$H$_8$(CH$_2$C$_6$H$_4$OMe-2)Me$_2$}] **9** (0.109 g). The synthesis of **9** was accompanied by the formation of a minor product formulated as [$\overline{\text{W}\{\text{CH(C}_6\text{H}_4\text{OMe-2)PPh}_2\text{CH}_2\text{P}}Ph_2$}(CO)$_2$(η^5-C$_2B_9H_9Me_2$)] **10a** (see Discussion).

Protonation with Aqueous HI.—A CH$_2$Cl$_2$ (10 cm^3) solution of compound **5b** (0.10 g, 0.15 mmol) was treated at room temperature with HI (57% aqueous solution, 0.10 cm^3, 0.70 mmol). The mixture initially turned green, and then became brown. After stirring for 30 min, solvent was removed *in vacuo*, the residue was dissolved in CH$_2$Cl$_2$ (5 cm^3), and the solution obtained was chromatographed at -30 °C on a short column (4 cm in length). Elution with CH$_2$Cl$_2$–Et$_2$O (3:1) removed a trace of a purple eluate which was discarded. The second fraction, orange-red, was collected and solvent was removed *in vacuo*. The residue was crystallised from CH$_2$Cl$_2$–hexane (5 cm^3, 1:4), and the oily product was washed with Et$_2$O (10 cm^3) and dried *in vacuo* to afford dark red *microcrystals* of [NEt$_4$][WI(CO)$_3${η^5-C$_2$B$_9$H$_8$(CH$_2$C$_6$H$_4$OMe-2)Me$_2$}] **12b** (0.049 g).

Crystal Structure Determination and Refinement.—Crystals of compound **7a** were obtained from CH$_2$Cl$_2$–hexane (1:5) as yellow cubes. Data are given in Table 5. The structure was solved by conventional heavy-atom methods, and successive Fourier difference syntheses were used to locate all the non-hydrogen atoms, as well as the hydrogens bonded to cage boron atoms. Other hydrogen atoms were included in calculated positions (C–H 0.96 Å), and all hydrogen atoms were given fixed isotropic thermal parameters (U_{iso} = 0.08 Å^2). Non-hydrogen atoms were refined anisotropically. All computations were performed on a DEC μ-Vax II computer using the SHELXTL PLUS system of programs.[9] Scattering factors with corrections for anomalous dispersion are inlaid in the programs. Atom coordinates are given in Table 6.

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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