# Alkylidyne(carbaborane) Complexes of the Group 6 Metals. Part 2.<sup>1</sup> Alkylidene Group Capture on Protonation in the Presence of Chelating Phosphines \*

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In CH<sub>2</sub>Cl<sub>2</sub> solutions at *ca*. –78 °C the salts [PPh<sub>4</sub>] [W(=CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R'<sub>2</sub>)] (R' = Me or H) upon treatment with HBF<sub>4</sub>·Et<sub>2</sub>O, in the presence of dppm (Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) or dppe (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), afford the complexes [W{CH(C<sub>6</sub>H<sub>4</sub>Me-4)PPh<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>}(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R'<sub>2</sub>)] (n = 1 or 2, R' = Me; n = 2, R' = H). The compound [W{CH(Me)PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R'<sub>2</sub>)] (n = 1 or 2, R' = Me; n = 2, R' = H). The compound [W{CH(Me)PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>1</sub>)] was similarly prepared from [NEt<sub>4</sub>][W(=CMe)(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>1</sub>)], dppe and HBF<sub>4</sub>·Et<sub>2</sub>O. In contrast, treatment of [NEt<sub>4</sub>][W(=CMe)(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] in CH<sub>2</sub>Cl<sub>2</sub> at -78 °C with HBF<sub>4</sub>·Et<sub>2</sub>O and dppe or dmpe (Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>) gives the complexes [W(CO)<sub>2</sub>L<sub>3</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>(Et)Me<sub>2</sub>]] (L<sub>2</sub> = dppe or dmpe). The molecular structure of [W{CH(C<sub>6</sub>H<sub>4</sub>Me-4)PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] has been established by a single-crystal X-ray diffraction study. Within the five-membered WCPCP ring the bond distances are W-C 2.342(9), C-P 1.802(9), P-C 1.81(1) and P-W 2.482(3) Å. The ligated carbon and phosphorus atoms of the ring, and the two essentially linearly bound CO ligands, form a pyramidal arrangement with the tungsten atom, the other side of which is co-ordinated by the *nido*-icosahedral C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub> cage in the usual  $\eta^{5}$  manner. The NMR spectra (<sup>1</sup>H, <sup>13</sup>C-{<sup>1</sup>H}, <sup>31</sup>P-{<sup>1</sup>H} and <sup>11</sup>B-{<sup>1</sup>H}) of the new compounds are reported and discussed in relation to their structures.

In the previous paper <sup>1</sup> we reported that protonation of the salts  $[NEt_4][W(\equiv CR)(CO)_2(\eta^5 - C_2B_9H_9Me_2)](R = C_6H_4Me-4, 1a; or Me, 1b)$  with HBF<sub>4</sub>·Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> at low temperatures (*ca.* -50 to -78 °C) affords the complexes  $[W(CO)_4\{\eta^5 - C_2B_9H_8 - (CH_2R)Me_2\}](R = C_6H_4Me-4, 2a; or Me, 2b)$ . It is very probable that these compounds are formed *via* the intermediacy of an electronically unsaturated tungsten–alkylidene species  $[W{=C(H)R}(CO)_2(\eta^5 - C_2B_9H_9Me_2)]$ . Addition to the latter of CO molecules present in the solutions would afford the products 2a and 2b in which the alkylidene groups have inserted into a cage B–H bond.

Migration of the alkylidyne group also takes place if the reagent 1a is protonated with HBF<sub>4</sub>·Et<sub>2</sub>O in the presence of PPh<sub>3</sub>, when an equilibrium mixture of the complexes  $\begin{bmatrix} W(CO)_2(PPh_3)_2 \{\eta^5 - C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\} \end{bmatrix} \begin{array}{l} 2c \text{ and} \\ \begin{bmatrix} W(CO)_3(PPh_3) \{\eta^5 - C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\} \end{bmatrix} \begin{array}{l} 3 \text{ is} \\ \end{bmatrix}$ formed. Although solutions containing these two species slowly decompose, it was possible to obtain crystals of 3 for analysis by X-ray diffraction, thereby establishing the molecular structure. Formation of compounds 2c and 3 also very probably proceeds via the intermediacy of complexes containing  $W=C(H)C_6H_4Me$ -4 groups, the addition of  $PPh_3$  ligands to the tungsten centre promoting migration of the alkylidene group to the carbaborane cage. In order to gain a better understanding of these processes we have studied reactions between salts of type 1 and HBF<sub>4</sub>·Et<sub>2</sub>O, in the presence of the chelating ligands dppe  $(Ph_2PCH_2CH_2PPh_2)$ , dppm  $(Ph_2PCH_2PPh_2)$  or dmpe  $(Me_2PCH_2CH_2PMe_2)$ . Although it seemed probable that species of the type  $[W(CO)_2L_2\{\eta^5-C_2B_9H_8(CH_2R)R'_2\}]$ (L<sub>2</sub> = dppe or dmpe, R = C<sub>6</sub>H<sub>4</sub>Me-4 or Me, R' = Me or H) might form, it was also possible that the reactions might follow a

different pathway with the phosphines intercepting an initially generated W=C(H)R group. It is noteworthy that reactions between monodentate tertiary phosphines and alkylidene complexes of Group 6 metals can be complicated, yielding under certain conditions ylide compounds, resulting from addition of the phosphine to the ligated carbons of the alkylidene ligands.<sup>2</sup>

#### **Results and Discussion**

For the work described herein it was necessary to prepare the compound  $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5-C_2B_9H_{11})]$  1c. This reagent was obtained (see Experimental section) by treating  $[WBr(\equiv CMe)(CO)_2(NC_5H_4Me-4)_2]$  4 with  $Na_2[C_2B_9H_{11}]$ , followed by addition of  $NEt_4Cl$ . Data characterising complexes 1c and 4, also a new compound, are given in Tables 1–3.

The reagent 1d in  $CH_2Cl_2$  at -78 °C upon treatment with dppm or dppe, followed by addition of HBF<sub>4</sub>·Et<sub>2</sub>O, affords the complexes [W{CH(C<sub>6</sub>H<sub>4</sub>Me-4)PPh<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>}-(CO)<sub>2</sub>( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] (n = 1, 5a; or 2, 5b) in essentially quantitative yield. In similar reactions employing the salts 1c and 1e, with dppe and HBF<sub>4</sub>·Et<sub>2</sub>O, the complexes [W{CH(R)PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}(CO)<sub>2</sub>( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (R = C<sub>6</sub>H<sub>4</sub>Me-4, 5c; or Me, 5d) were obtained. The compounds 5 were characterised by the data given in Tables 1–3. However, discussion of the spectroscopic properties is deferred until the results of a single-crystal diffraction study on complex 5a are given.

The structure of compound **5a** is shown in Fig. 1, and selected internuclear distances and angles are listed in Table 4. As expected the tungsten atom is  $\eta^5$  co-ordinated on one side by the *nido*-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub> cage. On the other side, arranged in a pyramidal manner, are two CO ligands (av. W–C–O 172.9°), and a phosphorus and a carbon atom. These two atoms form

<sup>\*</sup> Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1992, Issue 1, pp. xx-xxv.

part of a five-membered WCPCP ring [W-C(5) 2.342(9), C(5)-P(2) 1.802(9), P(2)-C(6) 1.81(1), C(6)-P(1) 1.85(1) and P(1)-W 2.482(3) Å], which is bent away from the carbaborane cage [W-C(5)-P(2) 109.5(4), W-P(1)-C(6) 105.4(3)°].

The ylide fragment CH(C<sub>6</sub>H<sub>4</sub>Me-4)PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> apparently results from addition of dppm to a transient alkylidene species [W{=C(H)C<sub>6</sub>H<sub>4</sub>Me-4}(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] formed on protonation of 1d. The five-membered ring may be formulated in two ways A or B. However, we favour representation A for the ground state, based on the observed W-C(5) bond distance, and the chemical and <sup>13</sup>C NMR properties discussed below. Although the W-C(5) distance [2.342(9) Å] is somewhat longer than that generally found (2.238 Å)<sup>3</sup> for W-C  $\sigma$  bonds, it is appreciably shorter than the W-C separation [2.539(7) Å] in [WRe( $\mu$ -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)( $\mu$ -dmpm)(CO)<sub>7</sub>] (dmpm = Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub>).<sup>4</sup> In the latter

molecule, while the  $CH_2C_6H_4Me$ -4 group is  $\sigma$  bonded to the Re atom, it also forms an agostic C-H-->W bond, as invoked for **B** above. The hydrogen atom attached to C(5) in the molecule **5a** was not detected by the X-ray diffraction study, but was clearly revealed by the <sup>13</sup>C NMR data, to be discussed.

Having established the structure of complex **5a** it is possible to interpret the spectral data readily, and also those of **5b–5d**. Similar spectroscopic properties indicate that all four products have similar structures. Each of the complexes **5** displays two CO stretching bands in its IR spectrum (Table 1), their relative intensities being in accord with the presence of the *cis*-W(CO)<sub>2</sub> groups. Examination of the <sup>1</sup>H, <sup>13</sup>C-{<sup>1</sup>H}, and <sup>31</sup>P-{<sup>1</sup>H} NMR spectra of the four compounds **5** (Tables 2 and 3) revealed in each spectrum peaks indicating the existence of an equilibrium mixture of two isomers. The isomers may be separated by careful column chromatography, but in solution re-equilibrate in less





Compound <sup>b</sup>		Viald	$v_{max}^{c}/cm^{-1}$		Analysis (%)	
		(%)	со	BH	C	Н
1c $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5-C_2B_9H_{11})]$ 4 $[WBr(\equiv CMe)(CO)_2(NC_5H_4Me-4)_2]$	Yellow Yellow	80 92	1964s, 1875vs 1982s, 1890vs	2515w (br)	<sup>d</sup> 32.0 (31.8) <sup>e</sup> 35.7 (36.1)	6.20 (6.45) 3.25 (3.20)
5a $[W{CH(R)PPh_2CH_2PPh_2}(CO)_2(\eta^5-C_2B_9H_9Me_2)]$	Yellow	93	1919s, 1828m (br)	2550w (br)	53.3 (52.7)	5.75 (5.10)
<b>5b</b> $[W{CH(R)PPh_2CH_2CH_2PPh_2}(CO)_2(\eta^5-C_2B_9H_9Me_2)]$	Yellow	89	1914s, 1825m (br)	2545w (br)	52.6 (53.2)	5.55 (5.25)
<b>5c</b> $\left[W^{(CH(R)PPh_2CH_2CH_2Ph_2)(CO)_2(\eta^5-C_2B_9H_{11})}\right]$	Pale orange	77	1920s, 1826m	2557w (br)	51.5 (52.2)	5.55 (4.95)
5d $\left[W\left\{CH(Me)PPh_2CH_2CH_2PPh_2\right\}(CO)_2(\eta^5-C_2B_9H_{11})\right]$	Yellow	41	1931s, 1833m (br)	2534w (br)	47.9 (48.1)	5.45 (4.90)
6a $[W(CO)_{2}(dppe)\{\eta^{5}-C_{2}B_{9}H_{8}(Et)Me_{2}\}]$	Orange	90	1956s, 1863m	2553w (br)	48.9 (49.4)	5.25 (5.25)
<b>6b</b> $[W(CO)_2(dmpe)\{\eta^5 - C_2B_9H_8(Et)Me_2\}]$	Yellow	65	1940s, 1859m	2553w (br)	29.1 (29.1)	6.60 (6.10)

Table 2 Hydrogen-1 and carbon-13 NMR data<sup>a</sup> for the complexes

·H·(0)	<sup>13</sup> C <sup>1</sup> (8)
1.33 [t of t, 12 H, NCH <sub>2</sub> $Me$ , $J$ (HH) 7, $J$ (NH) 2], 2.20 (s, 3 H, $\equiv$ CMe), 2.39 (s br, 2 H, CH), 3.20 [q, 8 H, NCH <sub>3</sub> , $J$ (HH) 7]	305.5 [W≡C, $J$ (WC) 195], 225.2 [WCO, $J$ (WC) 186], 53.2 (NCH <sub>2</sub> ), 39.1 [CMe $J$ (WC) 42], 34.2 (br, CH), 8.0 (NCH <sub>2</sub> Me)
2.34 (s, 3 H, $\equiv$ CMe), 2.39 (s, 6 H, Me-4), 7.14, 8.83 (AB), 8 H, NC-H, $J(AB)$ 5]	274.9 [W=C, J(WC) 196], 220.5 [WCO, J(WC) 171], 152.9 (C <sup>2</sup> of NC <sub>5</sub> H <sub>4</sub> ) 150.6 (C <sup>4</sup> of NC <sub>5</sub> H <sub>4</sub> ), 125.9 (C <sup>3</sup> of NC <sub>5</sub> H <sub>4</sub> ), 35.1 [CMe, J(WC) 43], 21.0 (Me-4)
${}^{d}$ 1.53*, 1.63, 1.72*, 2.04 (s × 2, 6 H, CMe), 2.19*, 2.20 (s, 3 H, Me-4), 3.97* [d of d of d, 1 H, CH <sub>2</sub> , J(PH) 4 and 14, J(HH) 14], 4.26 [d of d, 1 H, CH <sub>2</sub> , J(PH) 6, J(HH) 15], 5.03 [d of d of d, 1 H, CH <sub>2</sub> , J(PH) 7 and 24, J(HH) 15], 5.19* [d of d, 1 H, CH <sub>2</sub> , J(PH) 9, J(HH) 14], 6.84–7.85 (m, 24 H, Ph and C <sub>6</sub> H <sub>4</sub> )	248.4 [d, WCO, $J(PC)$ 33], 247.7* [d, WCO, $J(PC)$ 20], 244.9 (br, WCO) 240.2* [d, WCO, $J(PC)$ 33], 247.7* [d, WCO, $J(PC)$ 20], 244.9 (br, WCO) 240.2* [d, WCO, $J(PC)$ 7], 139.1–123.6 (m, Ph and C <sub>6</sub> H <sub>4</sub> ), 66.9, 66.6*, 62.4 62.3* (br, CMe), 39.3* [d of d, CH <sub>2</sub> , $J(PC)$ 18 and 70], 37.6 [d of d, CH <sub>2</sub> , $J(PC)$ 12 and 66], 32.7, 31.3*, 31.1*, 29.8 (CMe), 21.0*, 20.9 (Me-4), 7.9* [d of d C(H)C <sub>6</sub> H <sub>4</sub> , $J(PC)$ 8 and 27], 6.9 [d of d, $C(H)C_6H_4$ , $J(PC)$ 10 and 20]
<sup>d</sup> 1.90 <sup>*</sup> , 1.94, 2.16, 2.17, 2.22 <sup>*</sup> , 2.23 <sup>*</sup> (s $\times$ 3, 9 H, CMe and Me-4), 2.60–2.85 (m, 1 H, CH <sub>2</sub> ), 3.21 <sup>*</sup> , 3.34 (m, 1 H, CH <sub>2</sub> ), 3.67 (m, 1 H, CH <sub>2</sub> ), 3.86 <sup>*</sup> [d of d, 1 H, PCH <sub>2</sub> , J(PH) 10, J(HH) 17], 4.39 <sup>*</sup> (m, 1 H, CH <sub>2</sub> ), 4.78 [d of d, 1 H, PCH <sub>2</sub> , J(PH) 16, J(HH) 16], 6.60–8.18 (m, 24 H, Ph and C <sub>6</sub> H <sub>4</sub> )	249.6 [d, WCO, $J(PC)$ 26], 249.3* [d, WCO, $J(PC)$ 31], 247.9 [d, WCO, $J(PC)$ 6], 241.2* [d, WCO, $J(PC)$ 7], 144.7–122.7 (m, Ph and C <sub>6</sub> H <sub>4</sub> ), 67.5, 64.8*, 62.7 60.7* (br, CMe), 31.9, 31.5, 31.1*, 30.6* (CMe), 29.1 [d, CH <sub>2</sub> , $J(PC)$ 59], 28.2* [d of d, CH <sub>2</sub> , $J(PC)$ 21 and 21], 24.7 [d of d, CH <sub>2</sub> , $J(PC)$ 6 and 26], 22.2* [d of d, CH <sub>2</sub> , $J(PC)$ 4 and 20], 21.0, 20.9* (Me-4), -4.5 [d of d, C(H)C <sub>6</sub> H <sub>4</sub> , $J(PC)$ 15 and 18], -8.9* [d of d, C(H)C <sub>6</sub> H <sub>4</sub> , $J(PC)$ 11 and 18]
<sup><i>d.e.</i></sup> 2.02 <sup>*</sup> , 2.18 (s, 3 H, Me-4), 2.60–4.48 (m, 4 H, CH <sub>2</sub> ), 6.85–7.90 (m, 24 H, Ph and $C_6H_4$ )	<sup>f</sup> 248.9 [d, WCO, $J(PC)$ 21], 245.0 [d, WCO, $J(PC)$ 6], 240.2* (br, WCO) 137.9–121.7 (m, Ph and C <sub>6</sub> H <sub>4</sub> ), 46.4, 43.3 (br, cage CH), 28.3 [d, CH <sub>2</sub> , $J(PC)$ 64], 25.3 [d of d, CH <sub>2</sub> , $J(PC)$ 6 and 28], 21.5*, 20.9 (Me-4), $-3.0$ [d of d $C(H)C_6H_4$ , $J(PC)$ 13 and 22]
<sup><i>d.e</i></sup> 1.72 [d of d, 3 H, C(H) <i>Me</i> , <i>J</i> (HH) 7, <i>J</i> (PH) 20], 1.94* [d of d, 3 H, C(H) <i>Me</i> , <i>J</i> (HH) 7, <i>J</i> (PH) 23], 2.22, 2.38* (s br, 1 H, cage CH), 2.76–3.81 (m, 4 H, CH <sub>2</sub> ), 7.04–7.89 (m, 20 H, Ph)	247.6 [d, WCO, $J(PC)$ 20], $2\overline{47.0*}$ [d, WCO, $J(PC)$ 26], 241.8 [d, WCO, $J(PC)$ 6], 241.0* (br, WCO), 138.0–121.1 (m, Ph), 42.4, 39.2*, 38.2, 35.9* (br, cage CH), 28.8 [d of d, CH <sub>2</sub> ), $J(PC)$ 5 and 36], 26.1 [d of d, CH <sub>2</sub> , $J(PC)$ 13 and 22] 25.7*, 23.6* (m × 2, CH <sub>2</sub> ), 22.0 [d of d, C(H) <i>Me</i> , $J(PC)$ 4 and 7], 20.8* [m C(H) <i>Me</i> ], -19.3 [d of d, $C(H)Me$ , $J(PC)$ 18 and 22], -25.7* [d of d, $C(H)Me$ J(PC) 7 and 17]
0.01 [q, 2 H, BCH <sub>2</sub> , <i>J</i> (HH) 7], 0.38 [t, 3 H, CH <sub>2</sub> <i>Me</i> , <i>J</i> (HH) 7], 2.16 (s, 6 H, CMe), <sup>9</sup> 2.40 [m, 4 H, PCH <sub>2</sub> , <i>N</i> 18], 7.40–7.78 (m, 20 H, Ph)	<sup>9</sup> 231.7 [(AXX'), WCO, N 32], 136.5 [(AXX'), C <sup>1</sup> of Ph, J(PP') 20, J(PC) 58 J(P'C) 7], 134.4 (C <sup>4</sup> of Ph), 133.6 [(AXX'), C <sup>1</sup> of Ph, J(PP') 20, J(PC) 56 J(P'C) 9], 132.7 (C <sup>4</sup> of Ph), 131.3, 131.2 [t × 2, C <sup>2</sup> of Ph, J(PC) <2], 129.0 128.9 [t × 2, C <sup>3</sup> of Ph, J(PC) <2], 62.1 (CMe), 31.9 (CMe), <sup>9</sup> 29.2 [(AXX'), PCH, N 44] 19.4 (vhr. BCH, Me) 16.0 (BCH, Me)
0.40 [q, 2 H, BCH <sub>2</sub> , <i>J</i> (HH) 7], 0.60 [t, 3 H, CH <sub>2</sub> <i>Me</i> , <i>J</i> (HH) 7], 1.87 [d, 6 H, MeP, <i>J</i> (PH) 9], 1.97 [d, 6 H, MeP, <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 2 H, PCH <sub>2</sub> , <i>J</i> (AB) 14, <i>J</i> (PH <sub>A</sub> ) 7, <i>J</i> (PH <sub>B</sub> ) 6], 2.30	231.7 [(AXX'), WCO, J(PP') 24, J(PC) 37, J(P'C) 4], 62.1 (CMe), 33.0 (CMe) 29.7 [(AXX'), PCH <sub>2</sub> , J(PP') 24, J(PC) 34, J(P'C) 8], 20.6 [(AXX'), MeP J(PP') 24, J(PC) 43, J(P'C) 5], 18.4 [(AXX'), MeP, J(PP') 24, J(PC) 35, J(P'C) 2], 17.2 (vbr, BCH <sub>2</sub> Me), 15.7 (BCH <sub>2</sub> Me)
	1.33 [t of t, 12 H, NCH <sub>2</sub> <i>Me</i> , <i>J</i> (HH) 7, <i>J</i> (NH) 2], 2.20 (s, 3 H, $\equiv$ CMe), 2.39 (s br, 2 H, CH), 3.20 [q, 8 H, NCH <sub>2</sub> , <i>J</i> (HH) 7] 2.34 (s, 3 H, $\equiv$ CMe), 2.39 (s, 6 H, Me-4), 7.14, 8.83 [(AB) <sub>2</sub> , 8 H, NC <sub>5</sub> H <sub>4</sub> , <i>J</i> (AB) 5] <sup>d</sup> 1.53*, 1.63, 1.72*, 2.04 (s × 2, 6 H, CMe), 2.19*, 2.20 (s, 3 H, Me-4), 3.97* [d of d of d, 1 H, CH <sub>2</sub> , <i>J</i> (PH) 4 and 14, <i>J</i> (HH) 14], 4.26 [d of d, 1 H, CH <sub>2</sub> , <i>J</i> (PH) 6, <i>J</i> (HH) 15], 5.03 [d of d of d, 1 H, CH <sub>2</sub> , <i>J</i> (PH) 7 and 24, <i>J</i> (HH) 15], 5.19* [d of d, 1 H, CH <sub>2</sub> , <i>J</i> (PH) 9, <i>J</i> (HH) 14], 6.84–7.85 (m, 24 H, Ph and C <sub>6</sub> H <sub>4</sub> ) <sup>d</sup> 1.90*, 1.94, 2.16, 2.17, 2.22*, 2.23* (s × 3, 9 H, CMe and Me-4), 2.60–2.85 (m, 1 H, CH <sub>2</sub> ), 3.21*, 3.34 (m, 1 H, CH <sub>2</sub> ), 3.67 (m, 1 H, CH <sub>2</sub> ), 3.86* [d of d, 1 H, PCH <sub>2</sub> , <i>J</i> (PH) 10, <i>J</i> (HH) 17], 4.39* (m, 1 H, CH <sub>2</sub> ), 4.78 [d of d, 1 H, PCH <sub>2</sub> , <i>J</i> (PH) 16, <i>J</i> (HH) 16], 6.60–8.18 (m, 24 H, Ph and C <sub>6</sub> H <sub>4</sub> ) <sup>d.e.</sup> 2.02*, 2.18 (s, 3 H, Me-4), 2.60–4.48 (m, 4 H, CH <sub>2</sub> ), 6.85–7.90 (m, 24 H, Ph and C <sub>6</sub> H <sub>4</sub> ) <sup>d.e.</sup> 1.72 [d of d, 3 H, C(H) <i>Me</i> , <i>J</i> (HH) 7, <i>J</i> (PH) 20], 1.94* [d of d, 3 H, C(H) <i>Me</i> , <i>J</i> (HH) 7, <i>J</i> (PH) 23], 2.22, 2.38* (s br, 1 H, cage CH), 2.76–3.81 (m, 4 H, CH <sub>2</sub> ), 7.04–7.89 (m, 20 H, Ph) 0.01 [q, 2 H, BCH <sub>2</sub> , <i>J</i> (HH) 7], 0.38 [t, 3 H, CH <sub>2</sub> <i>Me</i> , <i>J</i> (HH) 7], 2.16 (s, 6 H, CMe), <sup>g</sup> 2.40 [m, 4 H, PCH <sub>2</sub> , <i>N</i> 18], 7.40–7.78 (m, 20 H, Ph) 0.40 [q, 2 H, BCH <sub>2</sub> , <i>J</i> (HH) 7], 0.60 [t, 3 H, CH <sub>2</sub> <i>Me</i> , <i>J</i> (HH) 7], 1.87 [d, 6 H, MeP, <i>J</i> (PH) 9], 1.97 [d, 6 H, MeP, <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 2 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 2 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 2 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 2 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 2 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 3 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 3 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 3 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.25 [t of (AB), 3 H, PCH <sub>2</sub> , <i>J</i> (AB) 14 <i>J</i> (PH) 10], 2.16, 2.

<sup>a</sup> Chemical shifts  $\delta$ , coupling constants in Hz, measurements at room temperature in CD<sub>2</sub>Cl<sub>2</sub> unless otherwise stated. Peaks marked with an asterisk are due to minor isomers.<sup>b</sup> Proton resonances for BH groups occur as broad unresolved signals in the range  $\delta ca$ . – 2 to + 3.<sup>c</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe<sub>4</sub>.<sup>d</sup> Resonance due to the C(H)C<sub>6</sub>H<sub>4</sub>Me-4 or C(H)Me proton not assigned due to uncertainty caused by signals for BH, methyl and methylene protons.<sup>e</sup> Peak(s) due to carbaborane CH protons not assigned. <sup>f</sup> Some peaks due to minor isomer not observed due to insolubility of complex.<sup>g</sup> Insufficient resolution prevents full analysis of coupling constants; N = |J(AX) + J(AX')|.

than 30 min and cannot be individually characterised. Based on relative peak intensities in the <sup>31</sup>P-{<sup>1</sup>H} NMR spectra for **5a**, **5b** and **5c** the equilibrium isomer ratio is *ca*. 2:1, and for **5d** *ca*. 8:3. The isomerisation is believed to involve different orientations of the C(H)R groups with respect to the remainder of the molecule, a phenomenon observed previously for these fragments in the rhodium compounds [Rh{ $\sigma,\eta^5$ -CH(C<sub>6</sub>H<sub>4</sub>Me-4)C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>R'<sub>2</sub>}-L<sub>2</sub>] (L = CO or PPh<sub>3</sub>, R' = H or Me).<sup>5</sup> Interconversion of the isomers of compounds **5** requires rotation of the W-C(H)R bonds, perhaps *via* the intermediacy of structures of the type **B** above.

In the <sup>13</sup>C-{<sup>1</sup>H} NMR spectra of the complexes **5a**, **5b** and **5d** each isomer displays (Table 2) two CO resonances and two signals for the carbon atoms of the C<sub>2</sub>B<sub>9</sub> cage, in agreement with the asymmetry of the molecules. Complex **5c** was relatively insoluble and therefore the spectrum was of lower quality, hence only three CO and two CH resonances were observed. Signals due to the C(H)R nuclei were clearly observed. For the major isomers these resonances were at  $\delta$  6.9 (**5a**), -4.5 (**5b**), -3.0 (**5c**) and -19.3 (**5d**), and all occurred as doublets of doublets, as expected, due to <sup>31</sup>P-<sup>13</sup>C coupling with non-equivalent PPh<sub>2</sub> groups. Although peaks due to the C(H)R protons were not observed in the <sup>1</sup>H NMR spectra, presumably due to the weak signal for a single proton being split by <sup>31</sup>P-<sup>1</sup>H coupling, the presence of these protons was unambiguously established

from fully coupled <sup>13</sup>C spectra. Under these conditions of measurement the aforementioned signals for the C(H)R nuclei of **5b–5d** occurred as doublets of doublets of doublets, with J(HC) 120  $\pm$  5 Hz. The magnitude of these couplings is typical for two-centre two-electron C-H bonds, as in **A** above. Couplings in species with three-centre C-H $\rightarrow$ M bonds, as in **B** above, are of the order of 75–100 Hz.<sup>6</sup> It is also noteworthy that **5b** did not react with MeI or (CF<sub>3</sub>)<sub>2</sub>CO, suggesting that the P-C(H)C<sub>6</sub>H<sub>4</sub>Me-4 bond is not highly polarised as in formulation **B**.

The <sup>31</sup>P-{<sup>1</sup>H} and <sup>11</sup>B-{<sup>1</sup>H} NMR spectra (Table 3) of the species 5 are as expected. The latter spectra all show broad unresolved bands due to nine boron nuclei, and none of these resonances is deshielded, as occurs when a cage boron atom forms an *exo*-polyhedral bond. In the <sup>31</sup>P-{<sup>1</sup>H} NMR spectra each isomer displays two resonances, each a doublet due to <sup>31</sup>P-<sup>31</sup>P coupling. However, in each pair of signals one resonance has <sup>183</sup>W satellite peaks [J(WP) ca. 207-337 Hz], and these resonances may be assigned to the phosphorus atoms co-ordinated to tungsten.

During the synthesis of compound **5d** another major product was formed but could not be identified. Single crystals of this green solid could not be obtained for analysis by X-ray diffraction. However, microanalytical and spectroscopic data (see Experimental section) lead us to formulate this product

Table 3 Boron-11 and phosphorus-31 NMR data<sup>a</sup> for the complexes

Compound	${}^{11}\mathbf{B}^{b}(\delta)$	$^{31}\mathbf{P}^{c}(\delta)$
1-		
IC	-9.1 (1 B), $-12.2$ (2 B), 16 8 (1 P) 170 (2 P)	
	-10.8 (1 B), $-17.9$ (2 B), -22.6 (2 B) $-24.1$ (1 B)	
50	-37(1  B) -61(2  B)	51.28 Fd W_P I(PP) 52
Ja	-3.7 (1 B), $-0.1$ (2 B), -8.3 (3 B) $-9.8$ (1 B)	$U(WP) 2501 36 31 [d C_P]$
	-112(2  B)	I(PP) 521 31 03* [d, C-P
	11.2 (2 D)	$I(PP) 441 25 03* [d, W_P]$
		I(PP) AA I(WP) 23A
5h	-14  to  -146  (m br  9  B)	$3858*[d W_P I(PP) 17$
50		I(WP) 2281 28 60* [d
		$C_{-P}$ I(PP) 171 28 35 [d]
		C-P $I(PP)$ 11] 24.15 [d
		W-P $J(PP)$ 11 $J(WP)$
		216]
5c	-6.8 (2 B). $-8.3$ (1 B).	36.69* [d. W-P. J(PP) 21.
	-10.1 (2 B), $-13.2$ , $-15.2$	J(WP) 337], 25.72 [d, C–P.
	$(1 \text{ B} \times 2), -20.2 (2 \text{ B})$	J(PP) 87. 20.08 [d. W-P.
		J(PP) = 8, J(WP) = 2341,
		14.54* [d, C-P, J(PP) 21]
5d	-7.7 (1 B), $-8.6$ (2 B),	29.71* [d, C-P, J(PP) 18],
	$-14.0, -15.1 (1 B \times 2),$	26.10 [d, C-P, J(PP) 18],
	$-17.8, -20.9 (2 B \times 2)$	16.57 [d, W-P, J(PP) 18,
		J(WP) 263], 9.19* [d, W-P,
		J(PP) 18, J(WP) 207]
6a	6.0 (s, 1 B, BCH <sub>2</sub> ), $-6.1$	44.01 [s, J(WP) 218]
	$(1 \ B), -7.2 \ (2 \ B), -10.1$	
	(3 B), -11.2 (2 B)	
6b	5.4 (s, 1 B, BCH <sub>2</sub> ), $-7.0$	23.61 [s, J(WP) 216]
	(2 B), -7.8 (1 B), -9.2	
	(2 B), -10.4 (1 B), -12.1	
	(2 B)	

<sup>a</sup> Chemical shifts  $\delta$ , coupling constants in Hz, measurements in CD<sub>2</sub>Cl<sub>2</sub> at ambient temperature unless otherwise stated. <sup>b</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of BF<sub>3</sub>-Et<sub>2</sub>O (external). Signals ascribed to more than one boron nucleus usually result from broad overlapping peaks, and do not necessarily indicate symmetry equivalence. <sup>c</sup> Hydrogen-1 decoupled, chemical shifts to high frequency of 85% H<sub>3</sub>PO<sub>4</sub> (external). Peaks for minor isomers indicated by asterisk, see text.



Fig. 1 Molecular structure of  $[W{CH(C_6H_4Me-4)PPh_2CH_2PPh_2}-(CO)_2(\eta^5-C_2B_9H_9Me_2)]$  5a, showing the atom labelling scheme

tentatively as the ditungsten species  $[W_2{\mu-C(H)Me}(CO)_2-(dppe)_2(\eta^5-C_2B_9H_{11})_2]$ . The IR spectrum showed two bands (1959s and 1889m cm<sup>-1</sup>) in accord with the presence of two CO

ligands. The <sup>1</sup>H NMR spectrum had a diagnostic resonance for a  $\mu$ -C(H)Me proton at  $\delta$  8.94, and in the <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum a peak at  $\delta$  168.7 is in the region for the carbon nucleus of a bridging alkylidene ligand.<sup>7</sup> The <sup>11</sup>B-{<sup>1</sup>H} NMR spectrum showed signals corresponding to the presence of two C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> cages functioning as spectator ligands. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum showed resonances for the two dppe ligands in different environments.

Reactions between compound 1b, HBF<sub>4</sub>·Et<sub>2</sub>O and dppe or dmpe followed a different pathway to those described above, affording the compounds  $[W(CO)_2L_2\{\eta^5-C_2B_9H_8(Et)Me_2\}]$  $(L_2 = dppe, 6a; or dmpe, 6b)$ . The synthesis of compound 6b however, required a slightly different procedure from the other syntheses described (see Experimental section), due to the high nucleophilicity of dmpe, which is protonated faster than the anion of salt 1b. To avoid this problem, a CH<sub>2</sub>Cl<sub>2</sub> solution of 1b at -78 °C was treated with HBF<sub>4</sub>·Et<sub>2</sub>O, resulting in an immediate colour change from yellow to red. The dmpe was then swiftly added to this mixture which gradually became yellow again as complex 6b was formed. Spectroscopic identification of the red compound, which was perhaps  $[W{=C(H)Me}(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ , was unfortunately not possible due to its very rapid conversion at temperatures above -78 °C into compound 2b.1 This alternative procedure could also be used to synthesise compound 6a and the complexes 5 with no detectable effect on yield.

Data characterising the products **6** are given in Tables 1–3. The presence of the cage BEt groups is clearly revealed from the <sup>1</sup>H, <sup>13</sup>C-{<sup>1</sup>H}, and <sup>11</sup>B-{<sup>1</sup>H} NMR spectra. Thus in the <sup>1</sup>H NMR spectra there are quartet signals at  $\delta$  0.01 (**6a**) and 0.40 (**6b**) and triplet signals at  $\delta$  0.38 (**6a**) and 0.60 (**6b**) which may be assigned to the BCH<sub>2</sub>Me and BCH<sub>2</sub>Me groups, respectively. Correspondingly, in the <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum there are resonances at  $\delta$  19.4 (BCH<sub>2</sub>Me) and 16.0 (BCH<sub>2</sub>Me) for **6a**, and at  $\delta$  17.2 (BCH<sub>2</sub>Me) and 15.7 (BCH<sub>2</sub>Me) for **6b**. In the <sup>11</sup>B-{<sup>1</sup>H} NMR spectra there are diagnostic deshielded resonances for the BEt groups at  $\delta$  6.0 (**6a**) and 5.4 (**6b**).

In the compounds 6 the BEt groups involve the boron atom which occupies the  $\beta$  site with respect to the two carbon atoms in the open pentagonal CCBBB face of the cage. This may be discerned from the <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR spectra (Table 2). In the former only a single cage CMe resonance is observed, and in the latter the CMe groups give rise to two peaks, for the CMe and CMe nuclei respectively. This indicates a symmetrical structure which would occur if the W atom, the midpoint of the cage C-C connectivity, and the  $\beta$ -B atom lie in a plane of symmetry, as found in many other structures for this type.<sup>1</sup>

Formation of the complexes 6 parallels the synthesis of the complexes 2c and 3 when the protonation of reagent 1a is carried out in the presence of PPh<sub>3</sub>.<sup>1</sup> In the formation of compounds 2, 3 and 5 the alkylidyne groups in the reagents 1 migrate to the cage by inserting into a B–H bond, a feature first observed in the synthesis of several tungsten–platinum species.<sup>8</sup> As discussed previously,<sup>1</sup> it is likely that these processes proceed via the initial formation of an alkylidenetungsten species containing the W=C(H)R fragment. Addition of phosphine or other Lewis bases to the electronically unsaturated metal centre could promote alkylidene insertion into the BH bond of a boron atom adjacent to the tungsten in the icosahedral WC<sub>2</sub>B<sub>9</sub> fragment. Such displacement of an alkylidene ligand from a metal centre by tertiary phosphines is effectively a new variation of a well known aspect of Group 6 metal–alkylidene chemistry.<sup>2</sup>

Isolation of the complexes 5 may be explained if following formation of transient  $[W{=C(H)R}(CO)_2(\eta^5-C_2B_9H_9R'_2)]$ (R' = H or Me) species, and subsequent addition of the chelate phosphine to give a monodentate phosphine complex, *e.g.*  $[W{=C(H)C_6H_4Me-4}(CO)_2(Ph_2PCH_2PPh_2)(\eta^5-C_2B_9H_9-Me_2)]$ , the non co-ordinated PPh<sub>2</sub> group attacks the ligated carbon of the alkylidene group before insertion of the latter into a B-H group can occur. As mentioned earlier, formation of ylide

**Table 4** Selected internuclear distances (Å) and angles (°) for  $[\dot{W}_{CH(C_6H_4Me-4)PPh_2CH_2PPh_2(CO)_2(\eta^5-C_2B_9H_9Me_2)]$  **5a** 

W-P(1)	2.482(3)	W-C(3)	1.98(1)	W-C(4)	1.95(1)	W-C(5)	2.342(9)	
W-C(1)	2.41(1)	W-C(2)	2.38(1)	W-B(3)	2.36(1)	WB(4)	2.43(1)	
W-B(5)	2.41(1)	P(1) - C(6)	1.85(1)	P(1) - C(11)	1.83(1)	P(1)-C(21)	1.851(9)	
P(2) - C(5)	1.802(9)	P(2) - C(6)	1.81(1)	P(2)-C(31)	1.82(1)	P(2)-C(41)	1.80(1)	
C(3) - O(3)	1.16(1)	C(4) - O(4)	1.17(1)	C(5)-C(51)	1.52(1)	C(1)-C(10)	1.50(2)	
C(1) - C(2)	1.65(1)	C(1) - B(5)	1.76(2)	C(1)-B(6)	1.74(2)	C(1) - B(10)	1.71(2)	
C(2) - C(20)	1.55(1)	C(2) - B(3)	1.70(2)	C(2)-B(6)	1.75(2)	C(2) - B(7)	1.71(2)	
B(3)-B(4)	1.74(2)	B(3) - B(7)	1.80(2)	B(3)-B(8)	1.79(2)	B(4) - B(5)	1.82(2)	
B(4) - B(8)	1.79(2)	B(4) - B(9)	1.78(2)	B(5)-B(9)	1.80(2)	B(5) - B(10)	1.77(2)	
B(6)-B(7)	1.74(2)	B(6)-B(10)	1.77(2)	<b>B(6)–B(11)</b>	1.75(2)	B(7)-B(8)	1.74(2)	
B(7) - B(11)	1.76(2)	B(8) - B(9)	1.76(2)	B(8) - B(11)	1.77(2)	B(9) - B(10)	1.77(2)	
B(9) - B(11)	1.75(2)	<b>B</b> (10)– <b>B</b> (11)	1.79(2)					
P(1)-W	-C(3)	121.8(3)	P(1)-W-C(4)	77.2(3)	C(3)-W-C	C(4) 70.7	′(4)	
P(1)-W	-C(5)	72.2(2)	C(3)-W-C(5)	79.4(4)	C(4)-W-C	C(5) = 115.2	2(4)	
W - P(1)	⊢C(6)	105.4(3)	W - P(1) - C(11)	118.7(3)	C(6) - P(1)	-C(11) 105.1	(5)	
W-P(1)	-C(21)	122.5(3)	C(6)-P(1)-C(21)	100.2(4)	C(11)-P(1	)-C(21) 102.3	6(4)	
C(5)-P(	(2)-C(6)	106.0(5)	C(5)-P(2)-C(31)	116.1(4)	C(6) - P(2)	-C(31) 109.1	(5)	
C(5)-P(	2)-C(41)	114.7(5)	C(6)-P(2)-C(41)	105.7(5)	C(31)-P(2	2)-C(41) 104.7	(5)	
W-C(3)	-O(3)	172.8(9)	W-C(4)-O(4)	173.0(9)	W-C(5)-I	P(2) 109.5	5(4)	
W-C(5)	-C(51)	120.6(6)	P(2)-C(5)-C(51)	115.7(7)	P(1)-C(6)	-P(2) 106.9	(5)	
W-C(1)	-C(10)	110.0(7)	W-C(2)-C(20)	110.2(7)				
								_

structures by attack of Lewis bases on alkylidene ligands is well established.<sup>2</sup>

However, synthesis of the complexes 6 indicates that a balance exists between the two reaction pathways, which may be rationalised in two ways. The first argument is along kinetic lines, and suggests that insertion of the alkylidene moiety into an adjacent B-H bond is more rapid for C(H)Me than for  $C(H)C_6H_4Me-4$  groups. Formation of ylide structures is therefore favoured starting from those reagents 1 containing W=CC<sub>6</sub>H<sub>4</sub>Me-4 groups. However, whether CH or CMe fragments are present in the C<sub>2</sub>B<sub>9</sub> cages also influences the nature of the product. Thus formation of the complexes 5d and **6b** reflects the activation of a BH bond in the  $\beta$  site by cage CMe fragments. Hence insertion of a C(H)Me group, obtained by protonating the CMe moiety in 1b, proceeds readily to give 6b, but the alternative pathway can be enforced by starting from the reagent 1c which contains a  $C_2B_9H_{11}$  cage, protonation leading to the ylide product 5d. This indicates capture of the W=C(H)Me group by the phosphorus atom of a pendant WPPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> moiety, perhaps reflecting a less-active B<sub>B</sub>-H site.

Alternatively, a thermodynamically based argument may apply. Thus in ylide complexes of type 5 the negative charge on tungsten may be stabilised by complexes having  $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> cages, PPh<sub>2</sub> phosphines, and C(H)C<sub>6</sub>H<sub>4</sub>Me-4 groups. Fivemembered metallacycles formed from dppm might also be favoured. Conversely, complexes of type 6 would be expected to arise in the presence of the more electron-releasing groups  $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>, PMe<sub>2</sub> and CH<sub>2</sub>Me. The chelate effect favouring five-membered rings will in this case arise when using the bis(phosphino)ethane complexes dppe and dmpe. The data so far obtained unfortunately do not provide any evidence to support either argument over the other, and so both must be considered with equal weight.

### Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C. Experiments were carried out using Schlenk-tube techniques under dry oxygen-free nitrogen and all solvents were rigorously dried before use. Alumina (Aldrich, Brockmann activity III) was used for chromatography employing water-jacketed columns of given dimensions at *ca.* 10 °C unless otherwise stated. The salt **1d** was prepared as previously described,<sup>9</sup> and **1e** was obtained by a similar procedure. The tetrafluoroboric acid was an 85% solution of HBF<sub>4</sub>·Et<sub>2</sub>O in Et<sub>2</sub>O as supplied by Aldrich

Chemicals. The reagent dmpe was used as a  $0.13 \text{ mol dm}^{-3}$  solution in hexane. The NMR spectra were recorded with JEOL JNM GX270 and GX400 spectrometers and the IR spectra with a Perkin-Elmer FT1600 spectrometer.

Preparation of the Reagent  $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5 - C_2B_9H_{11})]$  1c.—A sample of  $[WBr(\equiv CMe)(CO)_4]$  (13.1 mmol), prepared *in situ* and dissolved in Et<sub>2</sub>O at -20 °C, was treated with 2 equivalents of 4-methylpyridine also cooled to -20 °C. The mixture was slowly warmed to *ca*. 10 °C over *ca*. 2 h, during which period CO evolution was observed. Solvent was removed *in vacuo* and the residue was washed with Et<sub>2</sub>O (3 × 10 cm<sup>3</sup>) at -78 °C to yield yellow *microcrystals* of  $[WBr(\equiv CMe)(CO)_2-(NC_5H_4Me-4)_2]$  4 (6.42 g). This compound may be stored under N<sub>2</sub> at -20 °C for several weeks.

Compound 4 (1.0 g, 1.9 mmol) was treated with a solution of Na<sub>2</sub>[C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] in thf (tetrahydrofuran) (40 cm<sup>3</sup>), generated *in* situ from [NHMe<sub>3</sub>][C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] (0.43 g, 2.3 mmol) and NaH (0.40 g, 9.4 mmol) as described elsewhere.<sup>10</sup> The mixture was stirred for 4 h, then NEt<sub>4</sub>Cl·H<sub>2</sub>O (0.69 g, 3.8 mmol) was added and stirring continued for 1 h. The mixture was filtered through a Celite plug (3 × 3 cm), the solvent was removed *in* vacuo, and the residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) for chromatography on alumina (3 × 10 cm) at -20 °C, eluting with the same solvent. Removal of the solvent *in* vacuo and recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O (3 × 10 cm<sup>3</sup>, 1:4) yielded lemon-yellow microcrystals of [NEt<sub>4</sub>][W(=CMe)(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] **1c** (0.80 g).

Although the salt **1b** has been previously reported,<sup>11</sup> having been obtained from [WBr( $\equiv$ CMe)(CO)<sub>4</sub>], it is obtained in better yield (*ca.* 82%) from **4** and [NHMe<sub>3</sub>][C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me<sub>2</sub>] (0.50 g, 2.3 mmol), as described above for **1c**.

Synthesis of the Complexes.—(i) The salt 1d (0.17 g, 0.20 mmol) was dissolved in  $CH_2Cl_2$  (20 cm<sup>3</sup>) and cooled to -78 °C. One equivalent of dppm (0.078 g, 0.20 mmol) was added and allowed to dissolve, and the solution was treated with HBF<sub>4</sub>·Et<sub>2</sub>O (40 µl, 0.20 mmol). The mixture was allowed to warm to room temperature over *ca.* 1 h before reduction of solvent volume *in vacuo* to *ca.* 3 cm<sup>3</sup>. The remainder was chromatographed (2 × 12 cm column) in CH<sub>2</sub>Cl<sub>2</sub> to isolate a single yellow fraction from which solvent was again removed *in vacuo*. Recrystallisation of the resulting oil from  $CH_2Cl_2$ -hexane (5 cm<sup>3</sup>, 1:4) gave yellow *microcrystals* of  $[W{CH(C_6H_4Me-4)PPh_2CH_2PPh_2}(CO)_2(\eta^5-C_2B_9H_9Me_2)]$  5a (0.17 g).

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Table 5	Atomic positional	parameters (fractional coordinates	$\times 10^4$ ) for compound 5a	, with estimated standard devi	ations in parentheses
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Atom	x	у	Z	Atom	x	у	Ζ
W	2544(1)	1858(1)	1005(1)	C(16)	5741(12)	115(6)	1326(5)
<b>P(1)</b>	4528(2)	1608(2)	1605(1)	$\mathbf{C}(21)$	4841(9)	2075(5)	2329(4)
P(2)	5139(2)	3069(2)	920(1)	C(22)	3933(11)	2492(7)	2608(5)
C(3)	2550(9)	2264(7)	201(4)	C(23)	4216(14)	2894(8)	3123(6)
O(3)	2487(8)	2426(5)	-288(3)	C(24)	5446(14)	2871(9)	3375(6)
C(4)	3426(10)	1065(7)	544(5)	C(25)	6345(14)	2418(9)	3118(5)
O(4)	3856(8)	598(6)	223(4)	C(26)	6055(11)	2045(7)	2583(5)
C(5)	3559(8)	3134(6)	1154(4)	C(31)	5285(10)	3085(7)	144(4)
C(6)	5784(10)	2108(6)	1210(5)	C(32)	5072(14)	3829(9)	-138(5)
C(1)	1196(9)	732(7)	1254(5)	C(33)	5188(16)	3851(12)	-731(6)
C(10)	1775(12)	- 77(7)	1100(6)	C(34)	5573(17)	3183(14)	-1020(6)
C(2)	487(9)	1334(6)	760(4)	C(35)	5755(16)	2449(12)	- 753(6)
C(20)	354(11)	1091(8)	112(5)	C(36)	5610(13)	2393(8)	- 157(5)
B(3)	446(11)	2330(8)	997(5)	C(41)	6191(10)	3868(6)	1199(4)
B(4)	1118(11)	2362(8)	1703(5)	C(42)	7246(11)	4085(9)	941(6)
B(5)	1676(13)	1318(8)	1861(5)	C(43)	8084(15)	4656(11)	1169(6)
B(6)	-434(13)	665(9)	1151(6)	C(44)	7852(14)	5049(10)	1666(7)
B(7)	-924(11)	1673(8)	991(6)	C(45)	6854(15)	4819(11)	1952(7)
<b>B</b> (8)	-564(13)	2307(9)	1586(6)	C(46)	5980(12)	4230(9)	1721(5)
B(9)	216(12)	1688(8)	2119(5)	C(51)	2866(9)	3939(6)	1012(4)
B(10)	341(12)	667(9)	1851(6)	C(52)	2375(12)	4163(7)	477(6)
B(11)	-1043(12)	1274(9)	1691(6)	C(53)	1722(12)	4916(7)	388(6)
C(11)	5061(9)	539(6)	1723(4)	C(54)	1560(12)	5445(8)	841(7)
C(12)	4706(11)	126(7)	2202(5)	C(55)	1956(14)	5219(8)	1362(6)
C(13)	4962(13)	- 698(8)	2285(6)	C(56)	2650(12)	4475(7)	1462(5)
C(14)	5641(14)	-1114(8)	1906(7)	C(541)	863(14)	6253(8)	734(8)
C(15)	6032(14)	- 703(8)	1421(7)	. ,		. ,	(-)

(*ii*) A similar procedure using dppe (0.081 g, 0.20 mmol) instead of dppm, with compound 1d and HBF<sub>4</sub>·Et<sub>2</sub>O (40  $\mu$ l, 0.20 mmol), gave [W{CH(C<sub>6</sub>H<sub>4</sub>Me-4)PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}-(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>Me<sub>2</sub>)] **5b** (0.16 g) as yellow *microcrystals*.

(*iii*) Using the same method, a mixture of the salt **1e** (0.17 g, 0.20 mmol) and dppe (0.081 g, 0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was treated with HBF<sub>4</sub>·Et<sub>2</sub>O (40 µl, 0.20 mmol). After column chromatography and crystallisation from CH<sub>2</sub>Cl<sub>2</sub>-hexane (10 cm<sup>3</sup>, 3:2), pale orange *microcrystals* of  $[W{CH(C_6H_4Me-4)PPh_2CH_2CH_2PPh_2}(CO)_2(\eta^5-C_2B_9-H_{11})]$  **5c** (0.13 g) were obtained.

(iv) Treatment of compound 1c (0.20 g, 0.39 mmol) and dppe (0.15 g, 0.39 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) at  $-78 \degree \text{C}$  with HBF<sub>4</sub>·Et<sub>2</sub>O (70 µl, 0.39 mmol) followed by chromatography  $(2 \times 15 \text{ cm column})$  separated four fractions. The first eluate, yellow in colour, and eluted with CH2Cl2-hexane (1:1) afforded after removal of solvent in vacuo only a trace of material. The second fraction, after removal of solvent in vacuo, gave lime-green microcrystals of a product formulated tentatively as  $[W_2{\mu-C(H)Me}(CO)_2(dppe)_2(\eta^5-C_2B_9H_{11})_2]$  (0.16 g) (Found: C, 46.0; H, 4.9. C<sub>60</sub>H<sub>74</sub>B<sub>18</sub>O<sub>2</sub>P<sub>4</sub>W<sub>2</sub>•CH<sub>2</sub>Cl<sub>2</sub> requires C, 45.8; H, 4.8%);  $v_{max}(CO)$  at 1959s and 1889m cm<sup>-1</sup> (in CH<sub>2</sub>Cl<sub>2</sub>). NMR (CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H,  $\delta$  1.60 (s br, 4 H, CH of  $C_2B_9H_{11}$ ), 2.37, 2.70, 2.86, 3.54 (m × 4, 8 H,  $CH_2P$ ), 7.25–7.56 (m, 40 H, Ph) and 8.94 [d of d, 1 H,  $\mu$ -C(H)Me, J(PH) 26 and 2 Hz]; <sup>13</sup>C-{<sup>1</sup>H}, δ 231.3 [d, CO, J(PC) 12], 231.1 [d, CO, J(PC) 15], 168.7 [s br, μ-C(H)Me], 135.0–128.5 (Ph), 43.6 (s br, CH of  $C_2B_9H_{11}$ ), 29.8 and 29.0 (m × 2, CH<sub>2</sub>P); <sup>31</sup>P-{<sup>1</sup>H},  $\delta$  54.9 [J(WP) 200] and 41.8 [J(WP) 202 Hz]. Further elution of the column with CH<sub>2</sub>Cl<sub>2</sub>-hexane (3:2) gave an orange-yellow eluate. Removal of the solvent in vacuo yielded yellow microcrystals of  $[\dot{W}{CH(Me)PPh_2CH_2CH_2\dot{P}Ph_2}(CO)_2(\eta^5 C_2B_9H_{11}$ ] 5d (0.13 g). The fourth eluate was another trace yellow product, which was not identified.

(v) The compound **1b** (0.16 g, 0.29 mmol) in  $CH_2Cl_2$  (20 cm<sup>3</sup>) at -78 °C was treated with dppe (0.12 g, 0.29 mmol) and HBF<sub>4</sub>·Et<sub>2</sub>O (50 µl, 0.29 mmol). After removal of solvent *in* vacuo,  $CH_2Cl_2$ -hexane (3 cm<sup>3</sup>, 1:1) was added to the residue and the resulting mixture chromatographed (2 × 12 cm column) using the same solvent mixture. A single dark yellow band was collected and solvent removed from it *in vacuo* to yield orange *microcrystals* of  $[W(CO)_2(dppe)\{\eta^5-C_2B_9H_8(Et)-Me_2\}]$  6a (0.22 g).

(vi) A  $CH_2CI_2$  (20 cm<sup>3</sup>) solution of the salt **1b** (0.16 g, 0.29 mmol) at -78 °C was treated with HBF<sub>4</sub>·Et<sub>2</sub>O (50 µl, 0.29 mmol). A rapid colour change was observed from yellow to red. Within 30 s, dmpe (2.2 cm<sup>3</sup>, 0.29 mmol) was added and the temperature allowed to rise to ambient over *ca*. 1 h, during which time the colour changed gradually back to yellow. Solvent was removed *in vacuo* and alumina (*ca*. 3 g) added, followed by  $CH_2Cl_2$  (3 cm<sup>3</sup>) which was then similarly removed. The resulting powder was transferred to the top of a chromatography column (2 × 15 cm). Elution with  $CH_2Cl_2$ -hexane (2:3) separated a yellow product which was isolated after removal of solvent *in vacuo*, as bright yellow *microcrystals* of  $[W(CO)_2(dmpe)\{\eta^5-C_2B_9H_8(Et)Me_2\}]$  **6b** (0.11 g). Several very minor fractions were not isolated.

Crystal Structure Determination .-- Crystals of compound 5a were grown by diffusion of hexane into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution over several days. Solvent was removed via a syringe and the crystals dried under a stream of nitrogen. The crystals occupied two different habits (rhombs and parallelepipeds) which could be separated under a microscope. Only the rhombs were good-quality crystals, so one was selected (ca.  $0.25 \times 0.25 \times 0.50$  mm) and mounted in a sealed glass capillary under N<sub>2</sub>. Diffracted intensities were collected on a Siemens R3m/V four-circle diffractometer (293 K, Mo-Ka X-radiation, graphite monochromator,  $\bar{\lambda} = 0.710$  69 Å) using Wyckoff- $\omega$  scans in the range  $5 \le 2\theta \le 50^\circ$ . Of 7029 unique intensities, 4602 had  $F \ge 5\sigma(F)$ . 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.12

Crystal data.  $C_{39}H_{45}B_9O_2P_2W$ , M = 888.9, monoclinic, space group  $P_{2_1/n}$  (non-standard setting of  $P_{2_1/c}$ , no. 14), a = 10.629(5), b = 16.153(7), c = 23.18(1) Å,  $\beta = 93.76(3)^\circ$ , U = 3971(3) Å<sup>3</sup>, Z = 4,  $D_c = 1.49$  g cm<sup>-3</sup>, F(000) = 1776,  $\mu$ (Mo-K $\alpha$ ) = 30.8 cm<sup>-1</sup>.

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. In addition, the terminal hydrogen atoms of the carbaborane cage were located in a low-angle ( $2\theta < 30^{\circ}$ ) difference map, and their positions refined. Aromatic, methyl and methylene hydrogen atoms were included in calculated positions (C-H 0.96 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms were assigned fixed isotropic thermal parameters ( $U_{iso} = 0.08 \text{ Å}^2$ ). No attempt was made to locate or calculate the position of the hydrogen atom bound to C(5). Refinement by full-matrix least squares converged at R = 0.049 (R' = 0.048) with a weighting scheme of the form  $w^{-1} = [\sigma^2(F) + 0.0009|F|^2]$  giving a satisfactory analysis of variance. The final electron-density difference synthesis showed two peaks > 0.79 or < -0.94 e Å<sup>-3</sup>. These are attributed to inadequately corrected absorption errors (2.2 and 1.6 e Å<sup>-3</sup>) due to their proximity to the tungsten atom (*ca.* 1 Å).

A study of the one of the parallelepipeds, mentioned above, identified it as being monoclinic, space group *Pbca*. Analysis of the X-ray diffraction data showed only slight structural differences from the  $P2_1/n$  structure described above; the orientation of the phenyl ring numbered C(11)–C(16), and the orientation of the carbaborane cage, which was displaced by one fifth of a rotation clockwise, as viewed down the B(11)–W axis. There was no significant difference in the orientation of the tolyl ring, and we do not believe these differences to be those responsible for the observation of isomers in the solution NMR spectra.

All calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.<sup>12</sup> Scattering factors with corrections for anomalous dispersion are inlaid in the programs. Atom coordinates are listed in Table 5.

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

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