Alkylidyne(carbaborane) Complexes of the Group 6 Metals. Part 2.[1] Alkylidene Group Capture on Protonation in the Presence of Chelating Phosphines *

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In CH_2Cl_2 solutions at *ca.* −78 °C the salts $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]$ (R′ = Me or H) upon treatment with $HBF_4\cdot Et_2O$, in the presence of dppm ($Ph_2PCH_2PPh_2$) or dppe ($Ph_2PCH_2CH_2PPh_2$), afford the complexes $[W\{CH(C_6H_4Me\text{-}4)PPh_2(CH_2)_nPPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]$ (*n* = 1 or 2, R′ = Me; *n* = 2, R′ = H). The compound $[W\{CH(Me)PPh_2CH_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ was similarly prepared from $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$, dppe and $HBF_4\cdot Et_2O$. In contrast, treatment of $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ in CH_2Cl_2 at −78 °C with $HBF_4\cdot Et_2O$ and dppe or dmpe ($Me_2PCH_2CH_2PMe_2$) gives the complexes $[W(CO)_2L_2\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ (L_2 = dppe or dmpe). The molecular structure of $[W\{CH(C_6H_4Me\text{-}4)PPh_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ 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 $C_2B_9H_9Me_2$ cage in the usual η^5 manner. The NMR spectra (^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$ and $^{11}B\text{-}\{^1H\}$) of the new compounds are reported and discussed in relation to their structures.

In the previous paper[1] we reported that protonation of the salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4, **1a**; or Me, **1b**) with $HBF_4\cdot Et_2O$ in CH_2Cl_2 at low temperatures (*ca.* −50 to −78 °C) affords the complexes $[W(CO)_4\{\eta^5\text{-}C_2B_9H_8(CH_2R)Me_2\}]$ (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 $[W\{=C(H)R\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$. 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 $HBF_4\cdot Et_2O$ in the presence of PPh_3, when an equilibrium mixture of the complexes $[W(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **2c** and $[W(CO)_3(PPh_3)\{\eta^5\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$ **3** is 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 $HBF_4\cdot Et_2O$, 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 $[W(CO)_2L_2\{\eta^5\text{-}C_2B_9H_8(CH_2R)R'_2\}]$ (L_2 = dppe or dmpe, R = C_6H_4Me-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.[2]

Results and Discussion

For the work described herein it was necessary to prepare the compound $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ **1c**. This reagent was obtained (see Experimental section) by treating $[WBr(\equiv CMe)(CO)_2(NC_5H_4Me\text{-}4)_2]$ **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 $HBF_4\cdot Et_2O$, affords the complexes $[W\{CH(C_6H_4Me\text{-}4)PPh_2(CH_2)_nPPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (*n* = 1, **5a**; or 2, **5b**) in essentially quantitative yield. In similar reactions employing the salts **1c** and **1e**, with dppe and $HBF_4\cdot Et_2O$, the complexes $[W\{CH(R)PPh_2CH_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ (R = C_6H_4Me-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 η^5 co-ordinated on one side by the *nido*-$C_2B_9H_9Me_2$ 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

* *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 $CH(C_6H_4Me\text{-}4)PPh_2CH_2PPh_2$ apparently results from addition of dppm to a transient alkylidene species $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ 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 ^{13}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)[3] for W–C σ bonds, it is appreciably shorter than the W–C separation [2.539(7) Å] in $[WRe(\mu\text{-}CH_2C_6H_4Me\text{-}4)(\mu\text{-dmpm})(CO)_7]$ (dmpm = $Me_2PCH_2PMe_2$).[4] In the latter molecule, while the $CH_2C_6H_4Me$-4 group is σ 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 ^{13}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*-$W(CO)_2$ groups. Examination of the ^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ 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

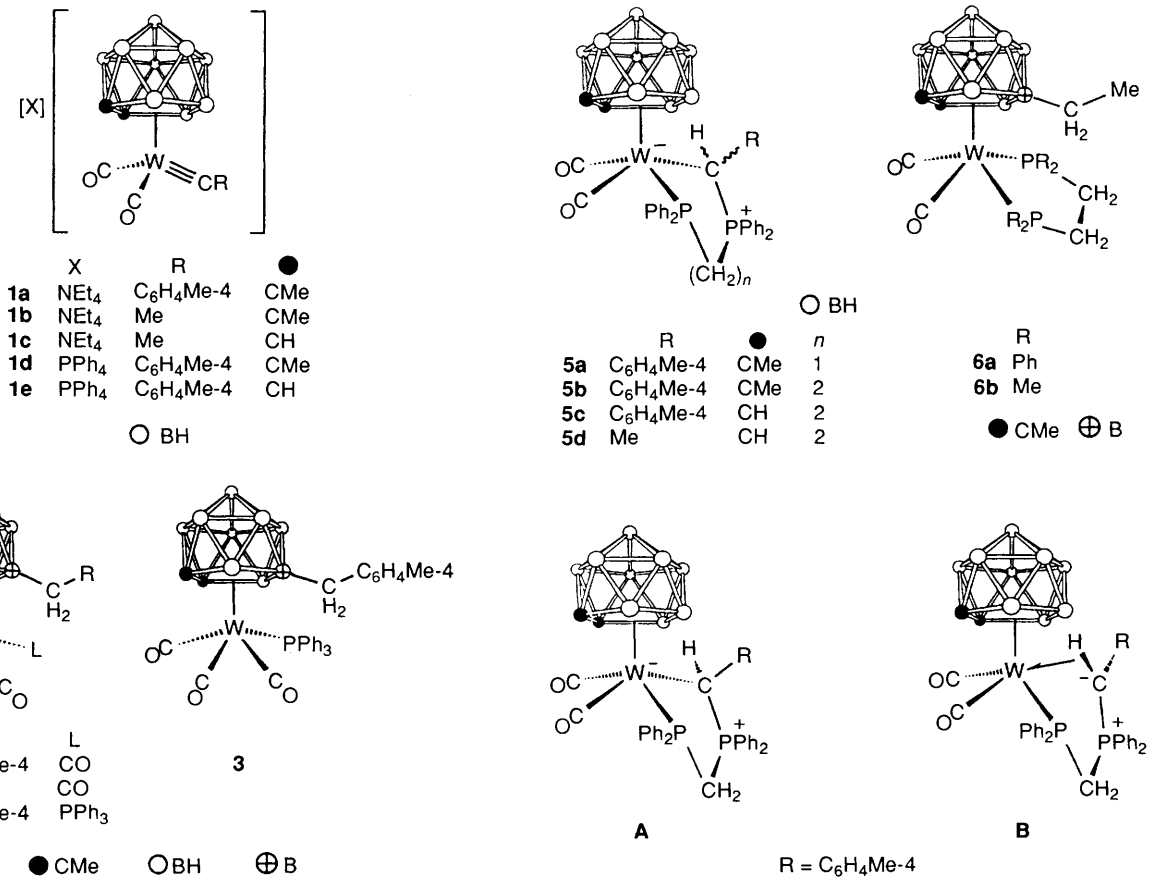

Table 1 Analytical[a] and physical data for the tungsten complexes

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

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] In CH_2Cl_2. [d] N, 2.5 (2.6)%. [e] N, 5.2 (5.3)%.

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

Compound	^1H[b] (δ)	^{13}C[c] (δ)
1c	1.33 [t of t, 12 H, NCH_2*Me*, *J*(HH) 7, *J*(NH) 2], 2.20 (s, 3 H, ≡CMe), 2.39 (s br, 2 H, CH), 3.20 [q, 8 H, NCH_2, *J*(HH) 7]	305.5 [W≡C, *J*(WC) 195], 225.2 [WCO, *J*(WC) 186], 53.2 (NCH_2), 39.1 [C*Me*, *J*(WC) 42], 34.2 (br, CH), 8.0 (NCH_2*Me*)
4	2.34 (s, 3 H, ≡CMe), 2.39 (s, 6 H, Me-4), 7.14, 8.83 [$(AB)_2$, 8 H, NC_5H_4, *J*(AB) 5]	274.9 [W≡C, *J*(WC) 196], 220.5 [WCO, *J*(WC) 171], 152.9 (C^2 of NC_5H_4), 150.6 (C^4 of NC_5H_4), 125.9 (C^3 of NC_5H_4), 35.1 [C*Me*, *J*(WC) 43], 21.0 (Me-4)
5a	[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_2, *J*(PH) 4 and 14, *J*(HH) 14], 4.26 [d of d, 1 H, CH_2, *J*(PH) 6, *J*(HH) 15], 5.03 [d of d of d, 1 H, CH_2, *J*(PH) 7 and 24, *J*(HH) 15], 5.19* [d of d, 1 H, CH_2, *J*(PH) 9, *J*(HH) 14], 6.84–7.85 (m, 24 H, Ph and C_6H_4)	248.4 [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_6H_4), 66.9, 66.6*, 62.4, 62.3* (br, *C*Me), 39.3* [d of d, CH_2, *J*(PC) 18 and 70], 37.6 [d of d, CH_2, *J*(PC) 12 and 66], 32.7, 31.3*, 31.1*, 29.8 (C*Me*), 21.0*, 20.9 (Me-4), 7.9* [d of d, *C*(H)C_6H_4, *J*(PC) 8 and 27], 6.9 [d of d, *C*(H)C_6H_4, *J*(PC) 10 and 20]
5b	[d] 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_2), 3.21*, 3.34 (m, 1 H, CH_2), 3.67 (m, 1 H, CH_2), 3.86* [d of d, 1 H, PCH_2, *J*(PH) 10, *J*(HH) 17], 4.39* (m, 1 H, CH_2), 4.78 [d of d, 1 H, PCH_2, *J*(PH) 16, *J*(HH) 16], 6.60–8.18 (m, 24 H, Ph and C_6H_4)	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_6H_4), 67.5, 64.8*, 62.7, 60.7* (br, *C*Me), 31.9, 31.5, 31.1*, 30.6* (C*Me*), 29.1 [d, CH_2, *J*(PC) 59], 28.2* [d of d, CH_2, *J*(PC) 21 and 21], 24.7 [d of d, CH_2, *J*(PC) 6 and 26], 22.2* [d of d, CH_2, *J*(PC) 4 and 20], 21.0, 20.9* (Me-4), −4.5 [d of d, *C*(H)C_6H_4, *J*(PC) 15 and 18], −8.9* [d of d, *C*(H)C_6H_4, *J*(PC) 11 and 18]
5c	[d,e] 2.02*, 2.18 (s, 3 H, Me-4), 2.60–4.48 (m, 4 H, CH_2), 6.85–7.90 (m, 24 H, Ph and C_6H_4)	[f] 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_6H_4), 46.4, 43.3 (br, cage CH), 28.3 [d, CH_2, *J*(PC) 64], 25.3 [d of d, CH_2, *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]
5d	[d,e] 1.72 [d of d, 3 H, C(H)*Me*, *J*(HH) 7, *J*(PH) 20], 1.94* [d of d, 3 H, C(H)*Me*, *J*(HH) 7, *J*(PH) 23], 2.22, 2.38* (s br, 1 H, cage CH), 2.76–3.81 (m, 4 H, CH_2), 7.04–7.89 (m, 20 H, Ph)	247.6 [d, WCO, *J*(PC) 20], 247.0* [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_2), *J*(PC) 5 and 36], 26.1 [d of d, CH_2, *J*(PC) 13 and 22], 25.7*, 23.6* (m × 2, CH_2), 22.0 [d of d, C(H)*Me*, *J*(PC) 4 and 7], 20.8* [m, C(H)*Me*], −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]
6a	0.01 [q, 2 H, BCH_2, *J*(HH) 7], 0.38 [t, 3 H, CH_2*Me*, *J*(HH) 7], 2.16 (s, 6 H, CMe), [g] 2.40 [m, 4 H, PCH_2, *N* 18], 7.40–7.78 (m, 20 H, Ph)	[g] 231.7 [(AXX'), WCO, *N* 32], 136.5 [(AXX'), C^1 of Ph, *J*(PP') 20, *J*(PC) 58, *J*(P'C) 7], 134.4 (C^4 of Ph), 133.6 [(AXX'), C^1 of Ph, *J*(PP') 20, *J*(PC) 56, *J*(P'C) 9], 132.7 (C^4 of Ph), 131.3, 131.2 [t × 2, C^2 of Ph, *J*(PC) <2], 129.0, 128.9 [t × 2, C^3 of Ph, *J*(PC) <2], 62.1 (*C*Me), 31.9 (C*Me*), [g] 29.2 [(AXX'), PCH_2, *N* 44], 19.4 (vbr, B*C*H_2Me), 16.0 (BCH_2*Me*)
6b	0.40 [q, 2 H, BCH_2, *J*(HH) 7], 0.60 [t, 3 H, CH_2*Me*, *J*(HH) 7], 1.87 [d, 6 H, MeP, *J*(PH) 9], 1.97 [d, 6 H, MeP, *J*(PH) 10], 2.16, 2.25 [t of (AB), 2 H, PCH_2, *J*(AB) 14, $J(PH_A)$ 7, $J(PH_B)$ 6], 2.30 (s, 6 H, CMe)	231.7 [(AXX'), WCO, *J*(PP') 24, *J*(PC) 37, *J*(P'C) 4], 62.1 (*C*Me), 33.0 (C*Me*), 29.7 [(AXX'), PCH_2, *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, B*C*H_2Me), 15.7 (BCH_2*Me*)

[a] Chemical shifts δ, coupling constants in Hz, measurements at room temperature in CD_2Cl_2 unless otherwise stated. Peaks marked with an asterisk are due to minor isomers. [b] Proton resonances for BH groups occur as broad unresolved signals in the range δ *ca.* −2 to +3. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [d] Resonance due to the C(*H*)C_6H_4Me-4 or C(*H*)Me proton not assigned due to uncertainty caused by signals for BH, methyl and methylene protons. [e] Peak(s) due to carbaborane CH protons not assigned. [f] Some peaks due to minor isomer not observed due to insolubility of complex. [g] 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 $^{31}P-\{^1H\}$ 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 $[Rh\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_8R'_2\}L_2]$ (L = CO or PPh_3, R' = H or Me).[5] 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 $^{13}C-\{^1H\}$ 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_2B_9 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 δ 6.9 (**5a**), −4.5 (**5b**), −3.0 (**5c**) and −19.3 (**5d**), and all occurred as doublets of doublets, as expected, due to $^{31}P-^{13}C$ coupling with non-equivalent PPh_2 groups. Although peaks due to the C(H)R protons were not observed in the ^1H NMR spectra, presumably due to the weak signal for a single proton being split by $^{31}P-^1H$ coupling, the presence of these protons was unambiguously established from fully coupled ^{13}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 ± 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→M bonds, as in **B** above, are of the order of 75–100 Hz.[6] It is also noteworthy that **5b** did not react with MeI or $(CF_3)_2CO$, suggesting that the P–C(H)C_6H_4Me-4 bond is not highly polarised as in formulation **B**.

The $^{31}P-\{^1H\}$ and $^{11}B-\{^1H\}$ 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 $^{31}P-\{^1H\}$ NMR spectra each isomer displays two resonances, each a doublet due to $^{31}P-^{31}P$ coupling. However, in each pair of signals one resonance has ^{183}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[a] for the complexes

Compound	^{11}B[b] (δ)	^{31}P[c] (δ)
1c	−9.1 (1 B), −12.2 (2 B), −16.8 (1 B), −17.9 (2 B), −22.6 (2 B), −24.1 (1 B)	
5a	−3.7 (1 B), −6.1 (2 B), −8.3 (3 B), −9.8 (1 B), −11.2 (2 B)	51.28 [d, W–P, *J*(PP) 52, *J*(WP) 250], 36.31 [d, C–P, *J*(PP) 52], 31.03* [d, C–P, *J*(PP) 44], 25.03* [d, W–P, *J*(PP) 44, *J*(WP) 234]
5b	−1.4 to −14.6 (m br, 9 B)	38.58* [d, W–P, *J*(PP) 17, *J*(WP), 228], 28.60* [d, C–P, *J*(PP) 17], 28.35 [d, C–P, *J*(PP) 11], 24.15 [d, W–P, *J*(PP) 11, *J*(WP) 216]
5c	−6.8 (2 B), −8.3 (1 B), −10.1 (2 B), −13.2, −15.2 (1 B × 2), −20.2 (2 B)	36.69* [d, W–P, *J*(PP) 21, *J*(WP) 337], 25.72 [d, C–P, *J*(PP) 8], 20.08 [d, W–P, *J*(PP) 8, *J*(WP) 234], 14.54* [d, C–P, *J*(PP) 21]
5d	−7.7 (1 B), −8.6 (2 B), −14.0, −15.1 (1 B × 2), −17.8, −20.9 (2 B × 2)	29.71* [d, C–P, *J*(PP) 18], 26.10 [d, C–P, *J*(PP) 18], 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_2), −6.1 (1 B), −7.2 (2 B), −10.1 (3 B), −11.2 (2 B)	44.01 [s, *J*(WP) 218]
6b	5.4 (s, 1 B, BCH_2), −7.0 (2 B), −7.8 (1 B), −9.2 (2 B), −10.4 (1 B), −12.1 (2 B)	23.61 [s, *J*(WP) 216]

[a] Chemical shifts δ, coupling constants in Hz, measurements in CD_2Cl_2 at ambient temperature 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 usually result from broad overlapping peaks, and do not necessarily indicate symmetry equivalence. [c] Hydrogen-1 decoupled, chemical shifts to high frequency of 85% H_3PO_4 (external). Peaks for minor isomers indicated by asterisk, see text.

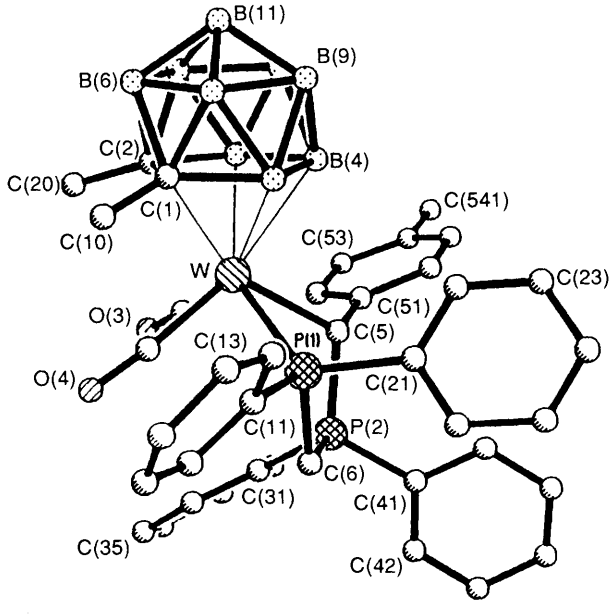

Fig. 1 Molecular structure of [W{CH(C_6H_4Me-4)$PPh_2CH_2PPh_2$}-$(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$] **5a**, showing the atom labelling scheme

tentatively as the ditungsten species $[W_2\{\mu\text{-}C(H)Me\}(CO)_2(dppe)_2(\eta^5\text{-}C_2B_9H_{11})_2]$. The IR spectrum showed two bands (1959s and 1889m cm^{-1}) in accord with the presence of two CO ligands. The ^1H NMR spectrum had a diagnostic resonance for a μ-C(*H*)Me proton at δ 8.94, and in the $^{13}C\text{-}\{^1H\}$ NMR spectrum a peak at δ 168.7 is in the region for the carbon nucleus of a bridging alkylidene ligand.[7] The $^{11}B\text{-}\{^1H\}$ NMR spectrum showed signals corresponding to the presence of two $C_2B_9H_{11}$ cages functioning as spectator ligands. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed resonances for the two dppe ligands in different environments.

Reactions between compound **1b**, $HBF_4{\cdot}Et_2O$ and dppe or dmpe followed a different pathway to those described above, affording the compounds $[W(CO)_2L_2\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ (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_2Cl_2 solution of **1b** at −78 °C was treated with $HBF_4{\cdot}Et_2O$, 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 $[W\{{=}C(H)Me\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, 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 ^1H, $^{13}C\text{-}\{^1H\}$, and $^{11}B\text{-}\{^1H\}$ NMR spectra. Thus in the ^1H NMR spectra there are quartet signals at δ 0.01 (**6a**) and 0.40 (**6b**) and triplet signals at δ 0.38 (**6a**) and 0.60 (**6b**) which may be assigned to the BCH_2Me and BCH_2Me groups, respectively. Correspondingly, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum there are resonances at δ 19.4 (BCH_2Me) and 16.0 (BCH_2Me) for **6a**, and at δ 17.2 (BCH_2Me) and 15.7 (BCH_2Me) for **6b**. In the $^{11}B\text{-}\{^1H\}$ NMR spectra there are diagnostic deshielded resonances for the BEt groups at δ 6.0 (**6a**) and 5.4 (**6b**).

In the compounds **6** the BEt groups involve the boron atom which occupies the β site with respect to the two carbon atoms in the open pentagonal CCB*B*B face of the cage. This may be discerned from the ^1H and $^{13}C\text{-}\{^1H\}$ 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 *C*Me and C*Me* nuclei respectively. This indicates a symmetrical structure which would occur if the W atom, the midpoint of the cage C–C connectivity, and the β–B atom lie in a plane of symmetry, as found in many other structures for this type.[1]

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_3.[1] 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.[8] As discussed previously,[1] 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_2B_9 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.[2]

Isolation of the complexes **5** may be explained if following formation of transient $[W\{{=}C(H)R\}(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]$ (R′ = H or Me) species, and subsequent addition of the chelate phosphine to give a monodentate phosphine complex, *e.g.* $[W\{{=}C(H)C_6H_4Me\text{-}4\}(CO)_2(Ph_2PCH_2PPh_2)(\eta^5\text{-}C_2B_9H_9Me_2)]$, the non co-ordinated PPh_2 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 [W{CH(C_6H_4Me-4)$PPh_2CH_2PPh_2$}(CO)$_2$(η^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)	W–B(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(6)–B(11)	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(10)–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(4)	70.7(4)
P(1)–W–C(5)	72.2(2)	C(3)–W–C(5)	79.4(4)	C(4)–W–C(5)	115.2(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(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)–C(41)	104.7(5)
W–C(3)–O(3)	172.8(9)	W–C(4)–O(4)	173.0(9)	W–C(5)–P(2)	109.5(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.[2]

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_6H_4Me-4 groups. However, whether CH or CMe fragments are present in the C_2B_9 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 β 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 $WPPh_2CH_2CH_2PPh_2$ moiety, perhaps reflecting a less-active B_β–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 η^5-$C_2B_9H_{11}$ cages, PPh_2 phosphines, and C(H)C_6H_4Me-4 groups. Five-membered 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 η^5-$C_2B_9H_9Me_2$, PMe_2 and CH_2Me. 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,[9] and **1e** was obtained by a similar procedure. The tetrafluoroboric acid was an 85% solution of HBF_4·Et_2O in Et_2O as supplied by Aldrich Chemicals. The reagent dmpe was used as a 0.13 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(≡CMe)(CO)$_2$(η^5-$C_2B_9H_{11}$)] **1c**.—A sample of [WBr(≡CMe)(CO)$_4$] (13.1 mmol), prepared *in situ* and dissolved in Et_2O 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_2O (3 × 10 cm^3) at −78 °C to yield yellow *microcrystals* of [WBr(≡CMe)(CO)$_2$-(NC_5H_4Me-4)$_2$] **4** (6.42 g). This compound may be stored under N_2 at −20 °C for several weeks.

Compound **4** (1.0 g, 1.9 mmol) was treated with a solution of $Na_2[C_2B_9H_{11}]$ in thf (tetrahydrofuran) (40 cm^3), generated *in situ* from [$NHMe_3$][$C_2B_9H_{12}$] (0.43 g, 2.3 mmol) and NaH (0.40 g, 9.4 mmol) as described elsewhere.[10] The mixture was stirred for 4 h, then NEt_4Cl·H_2O (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_2Cl_2 (10 cm^3) 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_2Cl_2–Et_2O (3 × 10 cm^3, 1:4) yielded lemon-yellow *microcrystals* of [NEt_4][W(≡CMe)(CO)$_2$(η^5-$C_2B_9H_{11}$)] **1c** (0.80 g).

Although the salt **1b** has been previously reported,[11] having been obtained from [WBr(≡CMe)(CO)$_4$], it is obtained in better yield (*ca.* 82%) from **4** and [$NHMe_3$][$C_2B_9H_{10}Me_2$] (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^3) 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_4·Et_2O (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^3. The remainder was chromatographed (2 × 12 cm column) in CH_2Cl_2 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^3, 1:4) gave yellow *microcrystals* of [W{CH(C_6H_4Me-4)$PPh_2CH_2PPh_2$}(CO)$_2$(η^5-$C_2B_9H_9Me_2$)] **5a** (0.17 g).

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2544(1)	1858(1)	1005(1)	C(16)	5741(12)	115(6)	1326(5)
P(1)	4528(2)	1608(2)	1605(1)	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(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_4·Et_2O (40 μl, 0.20 mmol), gave $[W\{CH(C_6H_4Me\text{-}4)PPh_2CH_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **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_2Cl_2 was treated with HBF_4·Et_2O (40 μl, 0.20 mmol). After column chromatography and crystallisation from CH_2Cl_2–hexane (10 cm^3, 3:2), pale orange *microcrystals* of $[W\{CH(C_6H_4Me\text{-}4)PPh_2CH_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ **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_2Cl_2 (20 cm^3) at −78 °C with HBF_4·Et_2O (70 μl, 0.39 mmol) followed by chromatography (2 × 15 cm column) separated four fractions. The first eluate, yellow in colour, and eluted with CH_2Cl_2–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 $[W_2\{\mu\text{-}C(H)Me\}(CO)_2(dppe)_2(\eta^5\text{-}C_2B_9H_{11})_2]$ (0.16 g) (Found: C, 46.0; H, 4.9. $C_{60}H_{74}B_{18}O_2P_4W_2$·$CH_2Cl_2$ requires C, 45.8; H, 4.8%); ν_{max}(CO) at 1959s and 1889m cm^{-1} (in CH_2Cl_2). NMR (CD_2Cl_2): ^1H, δ 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, μ-C(*H*)Me, *J*(PH) 26 and 2 Hz]; $^{13}C\text{-}\{^1H\}$, 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_2P); $^{31}P\text{-}\{^1H\}$, δ 54.9 [*J*(WP) 200] and 41.8 [*J*(WP) 202 Hz]. Further elution of the column with CH_2Cl_2–hexane (3:2) gave an orange-yellow eluate. Removal of the solvent *in vacuo* yielded yellow *microcrystals* of $[W\{CH(Me)PPh_2CH_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_{11})]$ **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^3) at −78 °C was treated with dppe (0.12 g, 0.29 mmol) and HBF_4·Et_2O (50 μl, 0.29 mmol). After removal of solvent *in vacuo*, CH_2Cl_2–hexane (3 cm^3, 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 $[W(CO)_2(dppe)\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ **6a** (0.22 g).

(*vi*) A CH_2Cl_2 (20 cm^3) solution of the salt **1b** (0.16 g, 0.29 mmol) at −78 °C was treated with HBF_4·Et_2O (50 μl, 0.29 mmol). A rapid colour change was observed from yellow to red. Within 30 s, dmpe (2.2 cm^3, 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^3) 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 $[W(CO)_2(dmpe)\{\eta^5\text{-}C_2B_9H_8(Et)Me_2\}]$ **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_2Cl_2 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 × 0.25 × 0.50 mm) and mounted in a sealed glass capillary under N_2. Diffracted intensities were collected on a Siemens R3m/V four-circle diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å) using Wyckoff-ω scans in the range $5 \leqslant 2\theta \leqslant 50°$. Of 7029 unique intensities, 4602 had $F \geqslant 5\sigma(F)$. 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 $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), a = 10.629(5), b = 16.153(7), c = 23.18(1) Å, β = 93.76(3)°, U = 3971(3) $Å^3$, Z = 4, D_c = 1.49 g cm^{-3}, F(000) = 1776, μ(Mo-Kα) = 30.8 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. In addition, the terminal hydrogen atoms of the carbaborane cage were located in a low-angle ($2\theta < 30°$) 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 ($U_{iso} = 0.08$ 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^{-3}. These are attributed to inadequately corrected absorption errors (2.2 and 1.6 e Å^{-3}) 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.[12] 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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References

1 Part 1, S. A. Brew, D. D. Devore, P. D. Jenkins, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, preceding paper.
2 H. Fischer, E. O. Fischer, C. G. Kreiter and H. Werner, *Chem. Ber.*, 1974, **107**, 2459; H. Werner and H. Rascher, *Inorg. Chim. Acta*, 1968, **2**, 181; E. O. Fischer, *Adv. Organomet. Chem.*, 1976, **14**, 1.
3 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
4 J. C. Jeffery, A. G. Orpen, F. G. A. Stone and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1986, 173.
5 M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1990, 2625.
6 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.
7 W. A. Herrmann, *J. Organomet. Chem.*, 1983, **250**, 319; *Adv. Organomet. Chem.*, 1982, **20**, 160.
8 M. J. Attfield, J. A. K. Howard, A. N. de M. Jelfs, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2219.
9 F.-E. Baumann, J. A. K. Howard, A. P. James, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2661.
10 R. A. Wiesbock and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642.
11 M. Green, J. A. K. Howard, A. P. James, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 61.
12 G. M. Sheldrick, SHELXTL PLUS programs used with the Siemens R3m/V X-ray system.

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