

The Carbaborane Group $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$ as a Spectator and Non-spectator Ligand in Di- and Tri-metal Complex Chemistry: X-Ray Crystal Structures of $[\text{PPh}_4][\text{Co}_2\text{W}(\mu\text{-CPh})(\text{CO})_8(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$, $[\text{NEt}_4][\text{FeW}(\mu\text{-CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_5(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$, and $[\text{IrW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PET}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$

Franz-Erich Baumann, Judith A. K. Howard, Rupert J. Musgrove, Paul Sherwood, Miguel A. Ruiz, and F. Gordon A. Stone

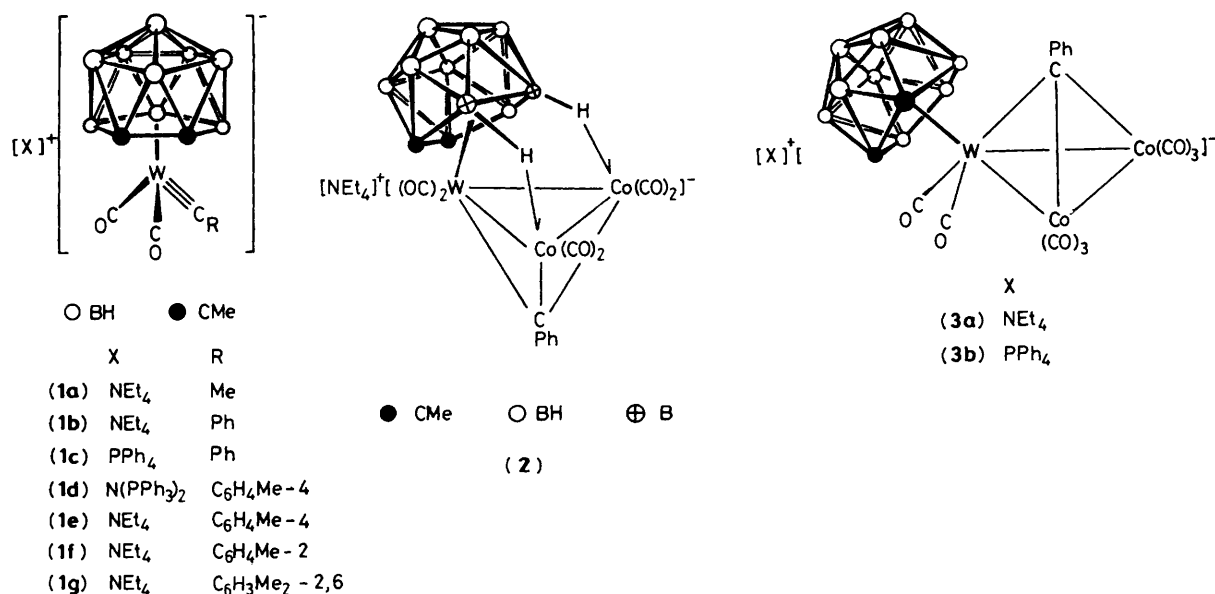
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

Salts containing the anions $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]^-$ ($\text{R} = \text{Ph}, \text{C}_6\text{H}_4\text{Me-2}, \text{C}_6\text{H}_4\text{Me-4}, \text{or } \text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) react with $[\text{Co}_2(\text{CO})_8]$, $[\text{Fe}_3(\text{CO})_{12}]$, or $[\text{IrL}_2(\eta^4\text{-C}_8\text{H}_{12})][\text{PF}_6]$ ($\text{L} = \text{PPh}_3$, $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ or bipyridyl) to yield heteronuclear di- and tri-metal compounds in which the carbaborane ligand adopts a variety of bonding modes.

It has been shown that salts $[\text{X}][\text{W}(\equiv\text{CR})(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (**1**) react with low-valent metal complexes to afford heteronuclear dimetal compounds with bridging alkylidyne groups.^{1,2} In some reactions the $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$ ligand adopts a non-spectator role. We have now found that this behaviour dominates the chemistry of these species, and is

strongly influenced by the different types of metal-metal bond formed, and by the character of the alkylidyne groups. As a consequence, many new di- and tri-metal complexes are accessible with potential for further synthesis.

Treatment of (**1b**) with $[\text{Co}_2(\text{CO})_8]$, in CH_2Cl_2 at room temperature, affords the trimetal compound (**2**) via the



intermediacy of (3a).[†] The latter may be isolated quantitatively by passing CO gas through CH_2Cl_2 solutions of the former.[†] Similar reactions occur between $[\text{Co}_2(\text{CO})_8]$ and (1c)—(1f). The structure of the salt (3b) has been established by X-ray diffraction (Figure 2).[‡] Although related to that of

(4), the product of the reaction of $[\text{Co}_2(\text{CO})_8]$ with $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$,³ the two structures differ in an important respect. In (4) the $\eta\text{-C}_5\text{H}_5$ group lies on the opposite side of the Co_2W triangle to the triply bridging alkylidyne group, whereas in (3b) the isolobal $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$ ligand lies on the same side. Consequently the ready interconversion between (2) and (3a) in the presence and absence of CO necessitates rotation of the $\text{W}(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)$ group about an axis through the tungsten atom and the mid-point of the $\mu_3\text{-CCO}_2$ triangle.

[†] Selected spectroscopic data [n.m.r. chemical shifts in p.p.m., coupling constants in Hz, with measurements in CD_2Cl_2 (^1H , ^{11}B - $\{^1\text{H}\}$, and ^{31}P - $\{^1\text{H}\}$) or $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$ (^{13}C - $\{^1\text{H}\}$). The ^{11}B shifts are positive to high frequency of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (external) and ^{31}P shifts are relative to 85% H_3PO_4 (external)].

Compound (2) (black), ν_{CO} (max) 2019m, 1985s, 1963vs, 1937w, and 1877w cm^{-1} (CH_2Cl_2); n.m.r., ^1H , δ -7.75 [q, 1 H, B(H)Co, $J(\text{BH})$ 90] and -7.30 [q, 1 H, B(H)Co, $J(\text{BH})$ 92]; ^{13}C - $\{^1\text{H}\}$, δ 302.8 ($\mu_3\text{-C}$); ^{11}B , δ 13.9 [B(H)Co, $J(\text{BH})$ 86] and 10.3 [B(H)Co, $J(\text{BH})$ 92]. Compound (3a) (brown), ν_{CO} (max) 2075s, 2036vs, 2018s, 2012(sh), 1878m, and 1816w cm^{-1} (CH_2Cl_2); ^{13}C - $\{^1\text{H}\}$ n.m.r., δ 282.0 ($\mu_3\text{-C}$). Compound (5a) (black), ν_{CO} (max) 2028vs, 1966s, 1954s, 1940(sh), and 1795m cm^{-1} (thf); ^{13}C - $\{^1\text{H}\}$ n.m.r., δ 388.4 [$\mu\text{-C}$, $J(\text{WC})$ 137]. Compound (5b) (brown); ^{13}C - $\{^1\text{H}\}$ n.m.r., δ 387.9 [$\mu\text{-C}$, $J(\text{WC})$ 141]. Compound (6b) (red), ν_{CO} (max) 2030s, 1971(sh), 1963vs, 1950(sh), 1892m, and 1759w cm^{-1} (thf); ^1H , δ 7.58 (s, 1 H, $\mu\text{-CHR}$); ^{13}C - $\{^1\text{H}\}$, δ 116.1 [$\mu\text{-CHR}$, $J(\text{WC})$ 46]. Compound (7b) (red), ^{13}C - $\{^1\text{H}\}$ n.m.r., δ 270.7 ($\mu_3\text{-C}$). Compound (8b) (red brown), n.m.r. (in C_6D_6); ^1H , δ -2.4 [q br, 1 H, B(H)Ir, $J(\text{BH})$ ca. 70]; ^{11}B - $\{^1\text{H}\}$, δ 33.1 [B(H)Ir]; ^{31}P - $\{^1\text{H}\}$, δ 19.7. Compound (9) (orange brown), n.m.r.; isomer (i), ^1H , δ -11.51 [d of d, IrH, $J(\text{PH})$ 18 and 12]; ^{11}B - $\{^1\text{H}\}$, δ 34.7 (B-Ir); ^{31}P - $\{^1\text{H}\}$ (-80°C), δ 38.7 [d, $J(\text{PP})$ 12] and 27.7 (br); ^{13}C - $\{^1\text{H}\}$, δ 271.0 [d, $\mu\text{-C}$, $J(\text{PC})$ 29]; isomer (ii), ^1H , δ -12.08 [d of d, IrH, $J(\text{PH})$ 18 and 12]; ^{11}B - $\{^1\text{H}\}$, δ 29.1 (B-Ir); ^{31}P - $\{^1\text{H}\}$, δ 27.0 [d, $J(\text{PP})$ 7] and 22.2 (br); ^{13}C - $\{^1\text{H}\}$, δ 267.4 [d, $\mu\text{-C}$, $J(\text{PC})$ 30]. Compound (10) (brown), n.m.r.; isomer (i), ^1H , δ -21.3 (s, IrH); ^{11}B - $\{^1\text{H}\}$, δ 23.2 (B-Ir); ^{13}C - $\{^1\text{H}\}$, δ 278.2 [$\mu\text{-C}$, $J(\text{WC})$ 127]; isomer (ii), ^1H , δ -22.6 (s, IrH); ^{11}B - $\{^1\text{H}\}$, δ 29.2 (B-Ir); ^{13}C - $\{^1\text{H}\}$, δ 284.3 ($\mu\text{-C}$).

[‡] Crystal data for (3b): $[\text{C}_{24}\text{H}_{20}\text{P}][\text{C}_{19}\text{H}_{20}\text{B}_9\text{Co}_2\text{O}_8\text{W}] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$, $M = 1157$, monoclinic, space group $P2_1/c$ (No. 14), $a = 19.705(5)$, $b = 13.238(3)$, $c = 22.224(3)$ Å, $\beta = 121.22^\circ$, $U = 4958(2)$ Å³, $Z = 4$, $D_c = 1.55$ g cm^{-3} , $F(000) = 2284$, $\mu(\text{Mo-K}\alpha) = 31.6$ cm^{-1} , $R = 0.074$ ($R_w = 0.067$) for 4677 absorption corrected intensities, Wyckoff ω -scans, $2\theta \leq 50^\circ$, $I \geq 2.0\sigma(I)$, 293 K, Mo-K α ($\lambda = 0.71069$ Å). Data were collected on a Nicolet P3m diffractometer and the structure solved by Patterson and Fourier methods with refinement by blocked-cascade least-squares.

Crystal data for (5a): $[\text{C}_8\text{H}_{20}\text{N}][\text{C}_{18}\text{H}_{24}\text{B}_9\text{FeO}_5\text{W}]$, $M = 787.6$,

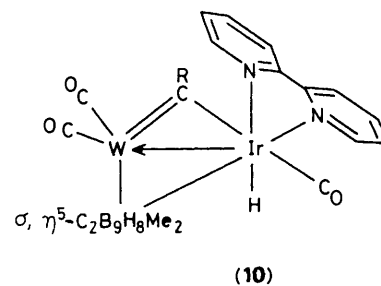
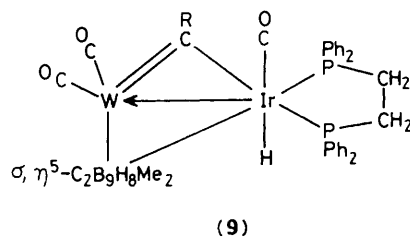
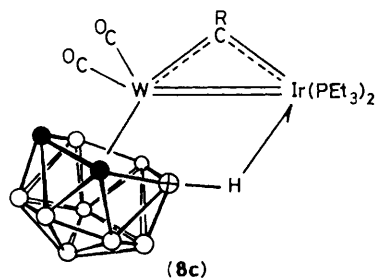
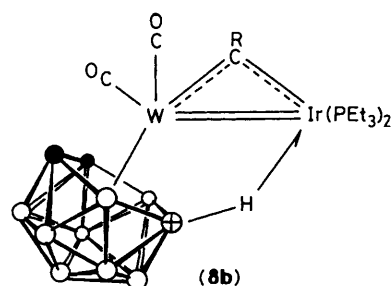
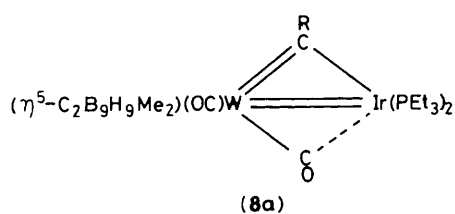
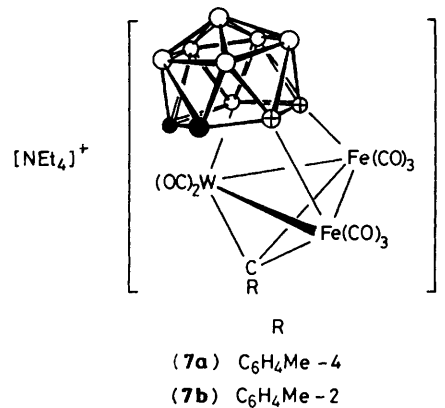
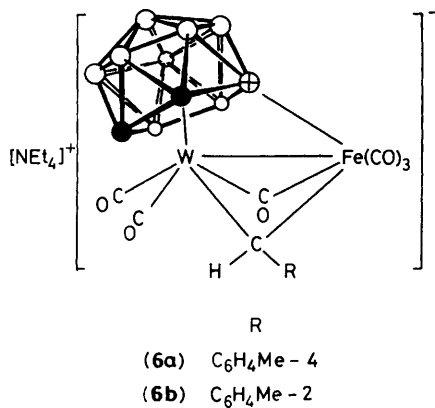
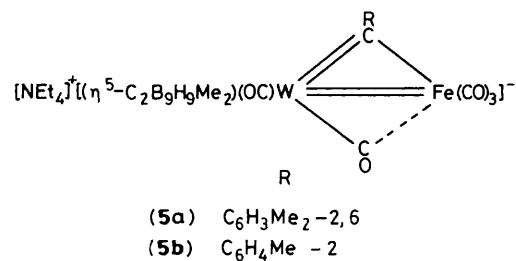
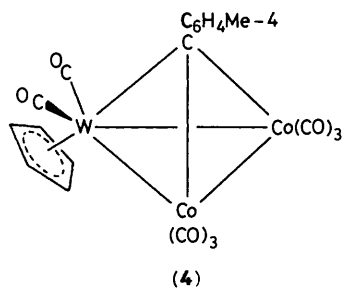
Although (1g) does not afford a stable product with $[\text{Co}_2(\text{CO})_8]$, it reacts with iron carbonyls ($[\text{Fe}_2(\text{CO})_9]$ or $[\text{Fe}_3(\text{CO})_{12}]$) in tetrahydrofuran (thf) to give the 32-valence electron dimetal compound (5a),[†] the structure of which has been established by X-ray diffraction.[‡] This result contrasts with reactions between iron carbonyls and (1e) or (1f). The former yields a mixture of (6a) and (7a),⁴ while the latter gives a mixture of the three species (5b), (6b), and (7b).[†] Moreover, in the presence of CO the μ -alkylidyne complex (5b) is transformed into the μ -alkylidene compound (6b). The absence of products structurally akin to (2), (3), (6), or (7) from reactions employing (1g) may be due to the steric constraints imposed by the $\text{C}_6\text{H}_3\text{Me}_2-2,6$ group.

Treatment of (1d) with $[\text{Ir}(\text{PPh}_3)_2(\eta^4\text{-C}_8\text{H}_{12})][\text{PF}_6]$, followed by addition of PEt_3 , affords the iridium-tungsten compound (8). In solution isomers (8a-c) exist, the proportions of each species being both solvent and temperature

monoclinic, space group Cc (No. 9), $a = 23.498(4)$, $b = 12.109(2)$, $c = 13.044(3)$ Å, $\beta = 115.33(2)^\circ$, $U = 3.355(1)$ Å³, $Z = 4$, $D_c = 1.56$ g cm^{-3} , $F(000) = 1568$, $\mu(\text{Mo-K}\alpha) = 39.7$ cm^{-1} , $R = 0.024$ ($R_w = 0.024$) for 3140 unique absorption corrected intensities [$\omega - 2\theta$ scans, $2\theta \leq 55^\circ$, $I \geq 2.0\sigma(I)$, 293 K].

Crystal data for (8b): $\text{C}_{26}\text{H}_{52}\text{B}_9\text{IrO}_2\text{P}_2\text{W}$, $M = 932.0$, orthorhombic, space group $P2_12_12$ (No. 18), $a = 19.109(7)$, $b = 13.782(3)$, $c = 13.367(5)$ Å, $U = 3520(2)$ Å³ (at 206 K), $Z = 4$, $D_c = 1.76$ g cm^{-3} , $F(000) = 1799$, $\mu(\text{Mo-K}\alpha) = 72.11$ cm^{-1} , $R = 0.037$ ($R_w = 0.037$) for 4128 unique absorption corrected intensities [$2\theta \leq 55^\circ$, $I \geq 2.0\sigma(I)$, 206 K].

Data collection and structure refinements for (5a) and (8b) were as for (3b). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



dependent. The structure of (8b) (Figure 3)[‡] reveals a relatively short Ir–W [2.590(1) Å] distance. The presence of the three-centre two-electron B–H–Ir bond is confirmed by the n.m.r. data,[†] and corresponds to incipient oxidative-addition at the iridium centre. In this context it is interesting that reactions of (1d) with the salts [IrL₂(η⁴-C₈H₁₂)] [PF₆]⁻ (L₂

= Ph₂PCH₂CH₂PPh₂ or bipyridyl) afford the hydrido-complexes (9) and (10), containing μ-σ,η⁵-C₂B₉H₈Me₂ ligands with B–Ir σ bonds. N.m.r. studies reveal that (9) and (10) form as mixtures of isomers. These differ according to whether the B–Ir bond involves the central boron in the η⁵-face of the ligand, or a boron atom adjacent to a CMe group.

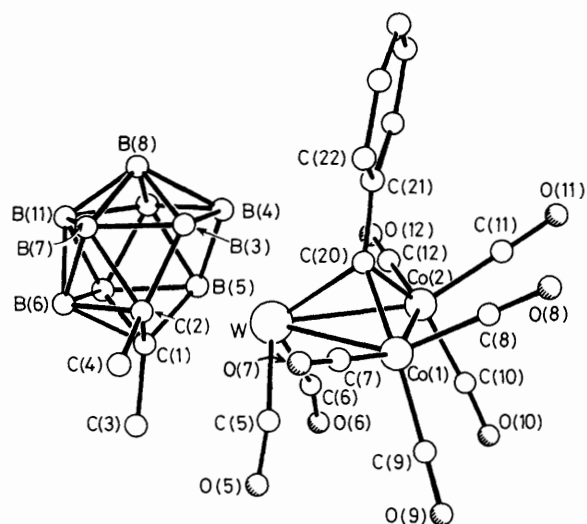


Figure 1. Molecular structure of the anion of $[\text{PPh}_4][\text{Co}_2\text{W}(\mu_3\text{-CPh})(\text{CO})_8(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ (**3b**). Dimensions: W–Co(1) 2.769(2), W–Co(2) 2.767(2), Co(1)–Co(2) 2.502(3), W–C(20) 2.07(1), Co(1)–C(20) 1.93(2), Co(2)–C(20) 1.89(2) Å, W–C(20)–C(21) 133(1), Co(1)–C(20)–C(21) 125(1), Co(2)–C(20)–C(21) 125(1), W–C(5)–O(5) 169(2), W–C(6)–O(6) 165(1)°.

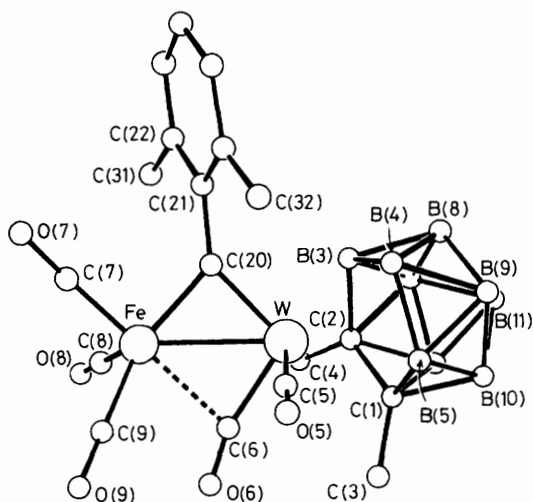


Figure 2. Molecular structure of the anion of $[\text{NEt}_4][\text{FeW}(\mu\text{-CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_5(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (**5a**). Dimensions: W–Fe 2.600(1), W–C(20) 1.976(6), Fe–C(20) 1.891(5), W–C(6) 1.959(7), Fe...C(6) 2.377(7) Å, W–C(20)–C(21) 143.0(3), W–C(6)–O(6) 165.4(6)°.

The results reported herein, as well as those recently reported elsewhere,⁵ demonstrate that the $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$ ligand can play an important role in the synthesis of complexes with heteronuclear metal–metal bonds. Since the various products described can be viewed as polynuclear metal carbaborane clusters, the observed differences in structural

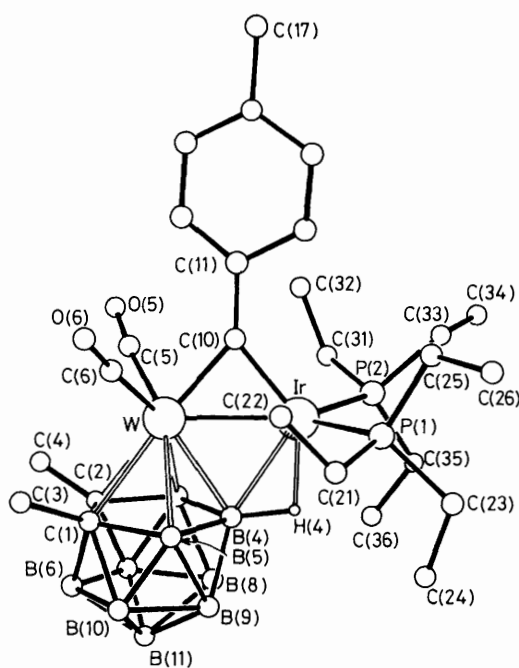


Figure 3. Molecular structure of $[\text{WIr}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\text{-(PEt}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (**8b**). Dimensions: W–Ir 2.590(1), W–C(10) 2.06(1), Ir–C(10) 1.95(1), W–C(1) 2.45(1), W–C(2) 2.44(1), W–B(3) 2.37(1), W–B(4) 2.32(1), W–B(5) 2.42(2), Ir–B(4) 2.34(1), Ir–H(4) 1.8 (located from low-angle difference map, but not refined), B(4)–H(4) 1.2, Ir–P(1) 2.258(3), Ir–P(2) 2.257(3) Å, W–C(10)–C(11) 140.3(7), P(1)–Ir–P(2) 95.7(1)°.

type can be rationalised in terms of the particular electronic requirements of the $\text{C}_2\text{B}_9\text{H}_9\text{Me}_2$ moiety when associated with different d-metal centres. In this respect the carbaborane 'ligand' can display a greater versatility of bonding modes than the cyclopentadienyl group.

We thank the S.E.R.C. for a research studentship (P.S.), the Deutscher Akademischer Austauschdienst for a NATO Fellowship (F.-E.B.) and the U.S.A.F. for partial support.

Received, 7th July 1987; Com. 958

References

- J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 1221; M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *ibid.*, p. 81; M. Green, J. A. K. Howard, A. N. de M. Jelfs, O. Johnson, and F. G. A. Stone, *ibid.*, p. 73; M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, and F. G. A. Stone, *ibid.*, p. 61.
- 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.
- M. J. Chetcuti, P. A. M. Chetcuti, J. C. Jeffery, R. M. Mills, P. Mitprachachon, S. J. Pickering, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 699.
- F.-E. Baumann, J. A. K. Howard, O. Johnson, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, in the press.
- Y. Do, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1987, **109**, 1853.