

Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 43.¹ Carbon–Tungsten Triple Bonds as Formal Four-electron Donors; Synthesis and Reactions of the Compounds $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\text{L}]$ $\{\text{L} = \text{HB}(\text{pz})_3$ [Tris(pyrazol-1-yl)borate] or $\eta\text{-C}_5\text{H}_5\}$ and X-Ray Crystal Structures of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$ and $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)(\text{CO})_2\{\text{HB}(\text{pz})_3\}]^*$

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The compounds $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ [$\text{HB}(\text{pz})_3 = \text{tris}(\text{pyrazol-1-yl})\text{borate}$] and $[\text{Fe}_2(\text{CO})_9]$ react in diethyl ether to give the *p*-tolylmethylidyne-bridged iron–tungsten complex $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$. The structure of this unsaturated (32 valence electron) compound has been established by X-ray diffraction. The parameters for the $\text{Fe}(\mu\text{-C})\text{W}$ ring [$\text{Fe}\text{-W}$ 2.612(2), $\mu\text{-C}\text{-Fe}$ 1.826(6), $\mu\text{-C}\text{-W}$ 2.025(7) Å] suggest partial multiple bonding in the metal–metal and $\mu\text{-C}\text{-Fe}$ bonds, as expected if the $\{\text{HB}(\text{pz})_3\}(\text{OC})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{Me-4}$ fragment were acting formally as a four-electron donor to the tricarbonyliron group. An analogous but less stable iron–tungsten complex $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ has been obtained from the reaction between $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ and the bis(cyclo-octene)iron complex $[\text{Fe}(\text{CO})_3(\eta\text{-C}_8\text{H}_{14})_2]$. Both 32 valence electron compounds $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\text{L}]$ [$\text{L} = \eta\text{-C}_5\text{H}_5$ or $\text{HB}(\text{pz})_3$] react reversibly with CO affording the electronically-saturated 34 valence electron complexes $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6\text{L}]$. The equilibrium is in favour of the $\text{Fe}(\text{CO})_4$ -containing species when $\text{L} = \eta\text{-C}_5\text{H}_5$, and the $\text{Fe}(\text{CO})_3$ species when $\text{L} = \text{HB}(\text{pz})_3$. The resonances for the ligated alkylidyne carbon atoms in the $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectra of the compounds $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\text{L}]$ are considerably more deshielded than those in the spectra of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6\text{L}]$, and this is considered to reflect the variable electron-pair donor properties (four or two electrons, respectively) of the $\text{L}(\text{OC})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{Me-4}$ fragments in these complexes. The unsaturated compounds react readily with monodentate or bidentate tertiary phosphines, and several types of product are described, some being formally electronically saturated (34 electron iron–tungsten species) while others are not. Initial attack of the phosphine groups occurs at the iron centre, but the compounds $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ and $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{dppm})\{\text{HB}(\text{pz})_3\}]$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) release CO and form $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ and $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\mu\text{-dppm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$, respectively, in which both metal centres are co-ordinated by a PMe_3 ligand or by the $\mu\text{-dppm}$ group. An X-ray diffraction study on $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\mu\text{-dmpm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ ($\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$) established that in this molecule the $\text{Fe}\text{-W}$ bond [2.605(1) Å] is bridged by the dmpm group and by the alkylidyne ligand [$\mu\text{-C}\text{-Fe}$ 1.911(3), $\mu\text{-C}\text{-W}$ 1.951(4)], and is strongly semi-bridged by a CO ligand on tungsten [$\text{W}\text{-C}\text{-O}$ 162.1(4) $^\circ$]. The iron atom carries two terminally bound CO groups and the tungsten is ligated by the $\text{HB}(\text{pz})_3^-$ anion. Alkylation ($\text{SO}_3\text{CF}_3\text{Me}$) of the compounds $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ and $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\mu\text{-L-L})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ ($\text{L-L} = \text{dppm}$ or dmpm) affords the salts $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\mu\text{-COMe})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ [SO_3CF_3] and $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-COMe})(\mu\text{-L-L})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ [SO_3CF_3], respectively. Spectroscopic data [i.r. and n.m.r. (^1H , $^{13}\text{C}\text{-}\{^1\text{H}\}$, and $^{31}\text{P}\text{-}\{^1\text{H}\}$)] for all the new compounds are reported and discussed.

We have recently prepared the alkylidyne tungsten complexes $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{RB}(\text{pz})_3\}]$ ($\text{R} = \text{H}$ or pz ; $\text{pz} = \text{pyrazol-1-yl}$) (1) and have used these species to prepare

* 1,1,1,2,2-Pentacarbonyl- μ -*p*-tolylmethylidyne-2-[tris(pyrazol-1-yl)borato]jirontungsten (*Fe-W*) and μ -bis(dimethylphosphino)methane- μ -carbonyl-1,1-dicarbonyl- μ -*p*-tolylmethylidyne-2-[tris(pyrazol-1-yl)borato]jirontungsten (*Fe-W*) respectively.

Supplementary data available (No. SUP 56523, 7 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

heteronuclear cluster compounds containing bonds between tungsten and iron, cobalt, rhodium, or platinum.² Herein we describe the synthesis, structure, and some reactions of an unsaturated (32 valence electron) dimetal compound $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$ (2a), the discovery of which prompted isolation of its cyclopentadienyl analogue (2b). A preliminary account of some of the results presented in this paper has been given.³

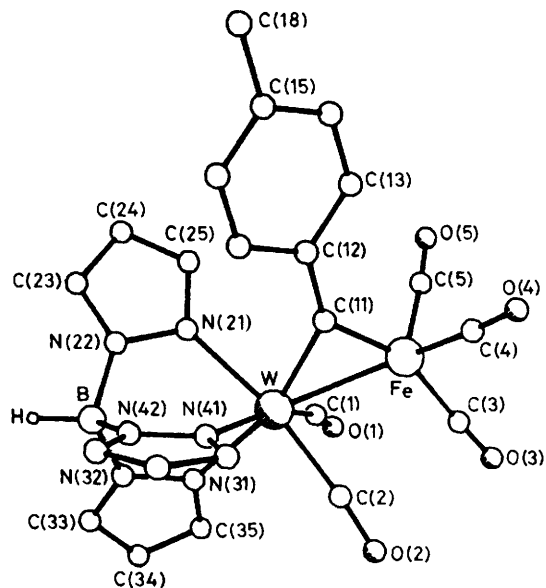
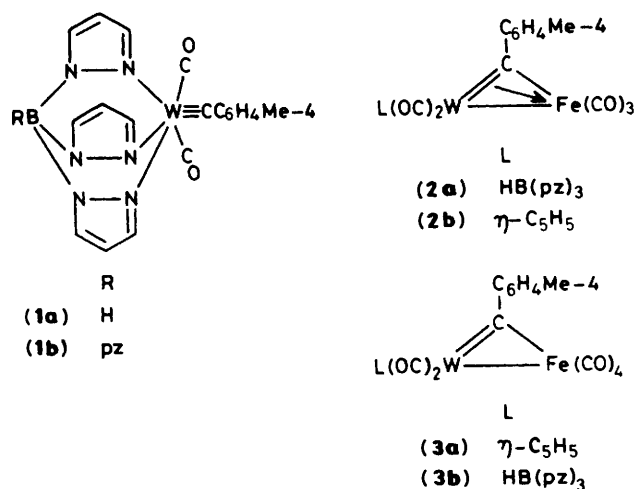
Results and Discussion

Treatment of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ (1a) with $[\text{Fe}_2(\text{CO})_9]$ in diethyl ether at room temperature afforded the

Table 1. Analytical^a and physical data for the iron-tungsten complexes

Compound ^b	Colour	Yield (%)	$\nu_{\max}(\text{CO})^c/\text{cm}^{-1}$	Analysis (%)		
				C	H	N
(2a) $[\text{FeW}(\mu\text{-CR})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$	Purple	84	^d 2 048s, 1 988s, 1 954s, 1 925m, 1 863m	37.9 (37.9)	2.3 (2.4)	12.2 (12.1)
(2b) $[\text{FeW}(\mu\text{-CR})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$	Purple	65	^d 2 054s, 1 992s, 1 973s, 1 943m, 1 888m	37.5 (39.5)	1.9 (2.2)	
(4a) $[\text{FeW}(\mu\text{-CR})(\text{CO})_4(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$	Purple	81	1 989s, 1 921s, 1 850m	54.1 (53.7)	3.2 (3.5)	
(4b) $[\text{FeW}(\mu\text{-CR})(\text{CO})_4(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]$	Purple	70	1 983s, 1 917s, 1 834m	40.6 (42.5)	3.7 (3.8)	
(4c) $[\text{FeW}(\mu\text{-CR})(\text{CO})_4(\text{PMe}_3)\{\text{HB}(\text{pz})_3\}]$	Purple	90	1 979s, 1 909s, 1 807m	38.7 (39.1)	3.2 (3.5)	11.0 (11.4)
(4d) $[\text{FeW}(\mu\text{-CR})(\text{CO})_4(\text{PEt}_3)\{\text{HB}(\text{pz})_3\}]$	Purple	81	1 977s, 1 907m, 1 895 (sh), 1 812m	41.5 (41.2)	4.2 (4.1)	9.9 (10.6)
(5b) $[\text{FeW}(\mu\text{-CR})(\text{CO})_5(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]^e$	Brown	70	^d 2 022s, 1 964s, 1 944m, 1 904s, 1 864m			
(6) $[\text{FeW}(\mu\text{-CR})(\text{CO})_4(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$	Green	64	1 956s, 1 890s, 1 863s, 1 780w	40.9 (41.1)	4.3 (4.5)	
(7) $[\text{FeW}(\mu\text{-CR})(\mu\text{-CO})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$	Green	67	1 943s, 1 885s, 1 707w	39.9 (41.0)	4.4 (4.7)	
(9) $[\text{FeW}(\mu\text{-CR})(\text{CO})_4(\text{dppm})\{\text{HB}(\text{pz})_3\}]$	Purple	95	1 983s, 1 902s, 1 820m	52.1 (52.5)	4.7 (3.7)	6.8 (7.9)
(10a) $[\text{FeW}(\mu\text{-CR})(\mu\text{-CO})(\mu\text{-dppm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$	Brown	86	1 954vs, 1 901s, 1 718m	52.0 (52.7)	3.7 (3.8)	8.1 (8.2)
(10b) $[\text{FeW}(\mu\text{-CR})(\mu\text{-CO})(\mu\text{-dmpm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$	Green	83	1 952s, 1 896s, 1 688m	38.4 (38.7)	4.0 (4.0)	10.5 (10.8)
(11) $[\text{FeW}(\mu\text{-CR})(\mu\text{-COMe})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{SO}_3\text{CF}_3]$	Blue	73	2 006s, 1 964m	35.0 (35.7)	4.0 (4.1)	
(12a) $[\text{FeW}(\mu\text{-CR})(\mu\text{-COMe})(\mu\text{-dppm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}][\text{SO}_3\text{CF}_3]$	Green	80	2 017s, 1 974s	46.7 (47.5)	3.6 (3.3)	6.4 (7.1)
(12b) $[\text{FeW}(\mu\text{-CR})(\mu\text{-COMe})(\mu\text{-dmpm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}][\text{SO}_3\text{CF}_3]$	Green	89	2 011s, 1 970s	33.3 (34.1)	3.6 (3.6)	8.1 (8.8)

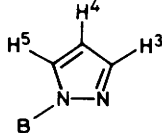
^a Calculated values are given in parentheses. ^b R = C₆H₄Me-4. ^c In CH₂Cl₂ unless otherwise stated. ^d In hexane. ^e Labile species, formed in equilibrium with (4b), see text.

**Figure 1.** The molecular structure of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$ (2a) showing the atom-numbering scheme

purple crystalline complex (2a). The i.r. spectrum showed five bands in the carbonyl stretching region (Table 1), one of which (1 863 cm^{-1}) was characteristic of a semi-bridging ligand. The n.m.r. data are summarised in Table 2, but discussion is deferred until the results of an X-ray diffraction study are described. The formulation of (2a) as a tricarbonyliron complex was an unexpected result, necessitating unambiguous establishment of the molecular structure. Previously we had observed⁴ formation

of the electronically-saturated 34-electron complex $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ (3a) as the initial product of the reaction of $[\text{Fe}_2(\text{CO})_9]$ with $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$

Table 2. Hydrogen-1 and carbon-13 n.m.r. data^a for the iron-tungsten complexes

Complex	$\delta(^1\text{H})^b$		$\delta(^{13}\text{C})^c$
(2a)	2.30 (s, 3 H, Me-4), 5.30 (m, 2 H, H ⁴), 6.42 (m, 3 H, C ₆ H ₄ and H ⁵), 7.26 (m, 5 H, C ₆ H ₄ and H ³ or H ⁵), 7.82 (m, 3 H, H ³ or H ⁵)		408.8 [μ -C, <i>J</i> (WC) 134], 226.0 [WCO, <i>J</i> (WC) 154], 214.5 (FeCO), 152.2 [C ¹ (C ₆ H ₄)], 147.9—106.2 (C ₃ H ₃ N ₂ and C ₆ H ₄), 21.3 (Me-4)
(2b) ^d	2.49 (s, 3 H, Me-4), 5.76 (s, 5 H, C ₅ H ₅), 7.28 (m, 4 H, C ₆ H ₄)		392.5 [μ -C, <i>J</i> (WC) 153], 221.4 [WCO, <i>J</i> (WC) 153], 214.6 (FeCO), 158.6 [C ¹ (C ₆ H ₄)], 138.2, 127.8, 123.9 (C ₆ H ₄), 93.6 (C ₅ H ₅), 20.7 (Me-4)
(4a) ^d	^e 2.39 (s, 3 H, Me-4), 5.50 (s, 5 H, C ₅ H ₅), 6.66 (m, 4 H, C ₆ H ₄), 7.01—7.53 (m, 15 H, Ph)		388.4 (μ -C), 222.8 (FeCO), 222.3 [WCO, <i>J</i> (WC) 175], 163.9 [C ¹ (C ₆ H ₄)], 133.4—118.3 (C ₆ H ₄ and Ph), 93.1 (C ₅ H ₅), 20.6 (Me-4)
(4b) ^d	1.04 [d, 9 H, MeP, <i>J</i> (PH) 10], 2.43 (s, 3 H, Me-4), 5.60 (s, 5 H, C ₅ H ₅), 7.16 (m, 4 H, C ₆ H ₄)		388.1 [μ -C, <i>J</i> (WC) 150], 223.6 [WCO, <i>J</i> (WC) 178], 221.6 [d, FeCO, <i>J</i> (PC) 21], 163.1 [C ¹ (C ₆ H ₄)], 134.7, 127.5, 119.8 (C ₆ H ₄), 92.6 (C ₅ H ₅), 20.6 (Me-4), 18.8 [d, MeP, <i>J</i> (PC) 31]
(4c)	1.19 [d, 9 H, MeP, <i>J</i> (PH) 11], 2.23 (s, 3 H, Me-4), 5.98 (m, 2 H, H ⁴), 6.37 (m, 1 H, H ⁴), 6.57 (m, 3 H, H ³ or H ⁵), 6.98, 7.06 [(AB) ₂ , 4 H, C ₆ H ₄ , <i>J</i> (AB) 8], 8.04 (m, 3 H, H ³ or H ⁵)		404.4 [μ -C, <i>J</i> (WC) 128], 229.4 [WCO, <i>J</i> (WC) 156], 221.4 [d, FeCO, <i>J</i> (PC) 21], 157.4 [C ¹ (C ₆ H ₄)], 147.6—105.8 (C ₃ H ₃ N ₂ and C ₆ H ₄), 21.3 (Me-4), 19.9 [d, MeP, <i>J</i> (PC) 30]
(4d)	^e 0.93 [d of t, 9 H, MeCH ₂ P, <i>J</i> (PH) 16, <i>J</i> (HH) 8], 1.48 (m, 6 H, MeCH ₂ P), 2.24 (s, 3 H, Me-4), 5.94 (m, 2 H, H ⁴), 6.32 (m, 1 H, H ⁴), 6.60 (m, 2 H, C ₆ H ₄), 6.98 (m, 4 H, C ₆ H ₄ and H ³ or H ⁵), 7.67 (m, 3 H, H ³ or H ⁵), 8.53 (m, 1 H, H ³ or H ⁵)		402.8 (μ -C), 229.1 (WCO), 227.7 [d, FeCO, <i>J</i> (PC) 21], 159.1 [C ¹ (C ₆ H ₄)], 147.1—105.4 (C ₃ H ₃ N ₂ and C ₆ H ₄), 20.9 (Me-4), 20.4 [d, MeCH ₂ P, <i>J</i> (PC) 22], 7.1 (MeCH ₂ P)
(5b) ^{d,f}			354.4 [d, μ -C, <i>J</i> (PC) 18, <i>J</i> (WC) 144], 234.4 [WCO, <i>J</i> (WC) 205], 225.7 [WCO, <i>J</i> (WC) 184], 217.4 [d, FeCO, <i>J</i> (PC) 33], 214.0 [d, FeCO, <i>J</i> (PC) 31], 208.2 [d, FeCO, <i>J</i> (PC) 61], 160.8 [C ¹ (C ₆ H ₄)], 136.1, 128.1, 124.6 (C ₆ H ₄), 92.1 (C ₅ H ₅), 20.9 (Me-4), 15.2 [d, MeP, <i>J</i> (PC) 28]
(6) ^d	1.17 (m, 18 H, MeP), 2.22 (s, 3 H, Me-4), 5.24 (s, 5 H, C ₅ H ₅), 7.11, 7.38 [(AB) ₂ , 4 H, C ₆ H ₄ , <i>J</i> (AB) 8]		365.7 [t, μ -C, <i>J</i> (PC) 17], 238.9, 237.1 (WCO), 221.2 [t, FeCO, <i>J</i> (PC) 32], 219.7 [t, FeCO, <i>J</i> (PC) 28], 160.3 [C ¹ (C ₆ H ₄)], 134.9, 128.2, 126.9 (C ₆ H ₄), 91.5 (C ₅ H ₅), 20.9 (Me-4), 18.0 (m, MeP)
(7) ^d	1.08 [d, 18 H, MeP, <i>J</i> (PH) 10], 2.45 (s, 3 H, Me-4), 5.18 (s, 5 H, C ₅ H ₅), 7.03, 7.19 [(AB) ₂ , 4 H, C ₆ H ₄ , <i>J</i> (AB) 8]		354.7 (μ -C), 269.6 (μ -CO), 227.4 [d, FeCO, <i>J</i> (PC) 28], 224.3 [d, FeCO, <i>J</i> (PC) 18], 161.3 [C ¹ (C ₆ H ₄)], 133.0, 127.2, 123.1 (C ₆ H ₄), 90.1 (C ₅ H ₅), 25.6 [d, MeP, <i>J</i> (PC) 34], 21.6 [d, MeP, <i>J</i> (PC) 31], 20.6 (Me-4)
(9)	2.16 (s, 3 H, Me-4), 2.96 (m, 2 H, CH ₂), 5.75 (m, 3 H, H ⁴), 6.57—8.11 (m, 30 H, H ³ , H ⁵ , C ₆ H ₄ and Ph)		^g 403.8 (μ -C), 228.8 (WCO), 222.5 [d, FeCO, <i>J</i> (PC) 22], 157.4 [C ¹ (C ₆ H ₄)], 147.3—105.1 (C ₃ H ₃ N ₂ , C ₆ H ₄ , and Ph), 21.5 (Me-4)
(10a)	2.24 (s, 3 H, Me-4), 2.99 (m, 2 H, CH ₂), 5.83 (m, 3 H, H ⁴), 6.61—7.73 (m, 30 H, H ³ , H ⁵ , C ₆ H ₄ , and Ph)		^g 377.2 (μ -C), 266.1 (μ -CO), 228.2 (FeCO), 222.4 [d, FeCO, <i>J</i> (PC) 15], 146.4—105.3 (C ₃ H ₃ N ₂ , C ₆ H ₄ , and Ph), 21.0 (Me-4)
(10b)	0.93 [d, 3 H, MeP, <i>J</i> (PH) 9], 1.12 [d, 3 H, MeP, <i>J</i> (PH) 10], 1.22 [d, 3 H, MeP, <i>J</i> (PH) 9], 1.80 [d, 3 H, MeP, <i>J</i> (PH) 10], 2.38 (s, 3 H, Me-4), 2.45 (m, 1 H, CH ₂), 2.91 (m, 1 H, CH ₂), 5.13—6.17 (m \times 3, 3 H, H ⁴), 6.46—7.03 (m, 6 H, C ₆ H ₄ and H ³ or H ⁵), 7.50 (m, 1 H, H ³ or H ⁵), 7.71 (m, 1 H, H ³ or H ⁵), 7.84 (m, 2 H, H ³ or H ⁵)		362.5 (μ -C), 271.0 (μ -CO), 226.9 [d, FeCO, <i>J</i> (PC) 16], 224.2 [d, FeCO, <i>J</i> (PC) 21], 159.8 [C ¹ (C ₆ H ₄)], 146.5—104.3 (C ₃ H ₃ N ₂ and C ₆ H ₄), 58.7 [d of d, CH ₂ , <i>J</i> (PC) 22, 22], 21.5 [d, MeP, <i>J</i> (PC) 28], 20.4 (Me-4), 18.3 [d, MeP, <i>J</i> (PC) 16], 17.9 [d, MeP, <i>J</i> (PC) 15], 15.0 [d, MeP, <i>J</i> (PC) 21]
(11) ^d	1.09 [d, 9 H, MeP, <i>J</i> (PH) 11], 1.32 [d, 9 H, MeP, <i>J</i> (PH) 10], 2.50 (s, 3 H, Me-4), 4.84 (s, 3 H, MeO), 5.73 (s, 5 H, C ₅ H ₅), 7.03, 7.33 [(AB) ₂ , 4 H, C ₆ H ₄ , <i>J</i> (AB) 8]		338.7, 336.4 (μ -C), 221.8 [d, FeCO, <i>J</i> (PC) 19], 215.5 [d, FeCO, <i>J</i> (PC) 31], 156.4 [C ¹ (C ₆ H ₄)], 136.1, 128.0, 123.3 (C ₆ H ₄), 94.3 (C ₅ H ₅), 70.5 (MeO), 25.1 [d, MeP, <i>J</i> (PC) 40], 20.9 [d, MeP, <i>J</i> (PC) 34], 20.6 (Me-4)
(12a)	^g 2.33 (s, 3 H, Me-4), 4.70 (s, 3 H, MeO), 5.58—6.50 (m \times 6, 6 H, H ⁴ and H ³ or H ⁵), 6.73—7.93 (m, 27 H, C ₆ H ₄ , Ph, and H ³ or H ⁵)		^g 347.0, 336.4 (μ -C), 220.4 [d, FeCO, <i>J</i> (PC) 23], 155.2 [C ¹ (C ₆ H ₄)], 148.9—105.9 (C ₃ H ₃ N ₂ , C ₆ H ₄ , and Ph), 68.6 (MeO), 20.8 (Me-4)
(12b)	^g 1.45 [d, 3 H, MeP, <i>J</i> (PH) 10], 1.75—1.88 (m, 6 H, MeP), 2.16 [d, 3 H, MeP, <i>J</i> (PH) 10], 2.45 (s, 3 H, Me-4), 4.70 (s, 3 H, MeO), 5.07 (s, 1 H, H ⁴), 5.81 (s, 1 H, H ⁴), 6.20 (s, 1 H, H ⁴), 6.51, 7.18 [(AB) ₂ , 4 H, C ₆ H ₄ , <i>J</i> (AB) 7], 7.88 (s, 3 H, H ³ or H ⁵), 8.00—8.60 (m \times 3, 3 H, H ³ or H ⁵)		^g 341.3, 329.5 (μ -C), 222.6 [d, FeCO, <i>J</i> (PC) 12], 217.1 [d, FeCO, <i>J</i> (PC) 25], 155.7 [C ¹ (C ₆ H ₄)], 146.5—105.8 (C ₃ H ₃ N ₂ and C ₆ H ₄), 67.8 (MeO), 20.5 (Me-4), 16.5 (m, MeP)

^a Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at room temperature unless otherwise stated. ^b Measured in CD₂Cl₂ unless otherwise stated. ^c Hydrogen-1 decoupled, to high frequency of SiMe₄, and measured in CD₂Cl₂—CH₂Cl₂. ^d Carbon-13 spectrum measured at -40 °C. ^e Measured in CDCl₃. ^f Labile species formed in equilibrium with (4b) (see text). ^g Peaks due to PCH₂P not assigned.

Table 3. Selected internuclear distances* (Å) and angles (°) for [FeW(μ-CC₆H₄Me-4)(CO)₅{HB(pz)₃}] (**2a**)

Fe-W	2.612(2)	W-C(11)	2.025(7)	Fe-C(11)	1.826(6)	C(11)-C(12)	1.445(9)
W-C(1)	2.006(6)	C(1)-O(1)	1.144(7)	W-C(2)	1.988(7)	C(2)-O(2)	1.149(9)
Fe-C(3)	1.858(8)	C(3)-O(3)	1.125(10)	Fe-C(4)	1.783(8)	C(4)-O(4)	1.142(10)
Fe-C(5)	1.769(8)	C(5)-O(5)	1.141(9)	W-N(21)	2.217(5)	B-N(22)	1.547(9)
W-N(31)	2.217(6)	B-N(32)	1.528(9)	W-N(41)	2.202(5)	B-N(24)	1.553(8)
B-H	1.08(8)						
W-Fe-C(11)	50.6(2)	Fe-W-C(11)	44.2(2)	W-C(11)-Fe	85.3(3)	W-C(11)-C(12)	139.4(4)
Fe-C(11)-C(12)	135.1(5)	W-C(1)-O(1)	169.6(6)	W-C(2)-O(2)	174.3(6)	Fe-C(3)-O(3)	178.3(7)
Fe-C(4)-O(4)	176.2(8)	Fe-C(5)-O(5)	175.5(6)	C(3)-Fe-C(4)	98.9(4)	C(3)-Fe-C(5)	95.2(3)
C(4)-Fe-C(5)	94.4(3)	C(11)-W-C(1)	104.8(2)	C(11)-W-N(21)	83.9(2)	C(11)-W-C(2)	105.8(3)
C(11)-W-N(41)	93.1(2)	C(11)-W-N(31)	162.6(2)	C(1)-W-C(2)	81.5(2)	C(2)-W-N(41)	92.4(2)
N(41)-W-N(21)	82.8(2)	N(21)-W-C(1)	100.2(2)	N(31)-W-C(1)	83.5(2)	N(31)-W-C(2)	90.4(2)
N(31)-W-N(41)	79.6(2)	N(31)-W-N(21)	79.5(2)	W-N(21)-N(22)	122.2(4)	W-N(31)-N(32)	122.3(4)
W-N(41)-N(42)	123.2(3)	B-N(22)-N(21)	119.9(5)	B-N(32)-N(31)	120.3(5)	B-N(42)-N(41)	119.5(4)
H-B-N(22)	108(4)	H-B-N(32)	110(4)	H-B-N(42)	115(4)		

* For C₃H₃N₂ groups, mean C-N 1.338(8), mean C-C 1.382(10), and mean N-N 1.365(7) Å.

C₅H₅]. Compound (**3a**), however, is very labile, and in particular affords the trimetal compounds [Fe₂W(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₈(η-C₅H₅)] and [FeW₂{μ-C₂(C₆H₄Me-4)₂}(CO)₆(η-C₅H₅)₂] in the presence of excess of [Fe₂(CO)₉] or [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)], respectively.

The structure of (**2a**) is shown in Figure 1, and selected internuclear distances and angles are listed in Table 3. The results fully confirm the presence of the Fe(CO)₃ group. The three carbonyl groups are terminally bound to the iron and are essentially orthogonal to each other. The ligand C(3)O(3), transoid to the bridging alkyldiyne group, lies furthest [1.858(8) Å] from the iron atom [Fe-C(4) 1.783(8), Fe-C(5) 1.769(8) Å]. This is a common feature of groups in such an environment, and is due to the *trans* influence of the μ-CC₆H₄Me-4 fragment. The dimensions of the C(11)FeW ring are of interest. The Fe-W separation [2.612(2) Å] is appreciably shorter than that found [2.720(1) Å] in the dimetal species [FeW{μ-C(C₆H₄Me-4)-C(Me)C(Me)}(CO)₅(η-C₅H₅)].⁵ The latter compound is presumed to contain an iron-tungsten single bond. The C(11)-W distance [2.025(7) Å], apart from a single exception, is longer than those found by X-ray diffraction in several compounds containing the dimetal ring system $\overline{M(\mu-CC_6H_4Me-4)W}$ (M = Co, Rh, Ti, or Pt).⁶ The exception is the complex [CrW(μ-CC₆H₄Me-4)(CO)₄(η-C₅H₅)(η-C₆Me₆)] [μ-C-W 2.025(6) Å], a species which may well have atypical ring-bonding characteristics, discussed further below. The C(11)-Fe separation [1.826(6) Å] suggests multiple bond character. Thus in the mononuclear iron complex [Fe(CCl₂)(H₂O)(tpp)] (tpp = 5,10,15,20-tetraphenylporphyrinate) the C=Fe distance is 1.83(3) Å,⁷ close to that in (**2a**), while in the saturated di-ironcyclopropane ring compound [Fe₂(μ-CHMe)(μ-CO)(CO)₂(η-C₅H₅)₂] the μ-C-Fe separation is 1.986(3) Å.⁸

The tungsten atom in (**2a**) is in a distorted octahedral environment ligated by the tridentate HB(pz)₃ group, two CO ligands, and the mid-point of the C(11)-Fe vector. The HB(pz)₃⁻ anion displays the usual geometry.² The C(2)O(2) group adopts an essentially linear bonding mode to the tungsten atom [W-C(2)-O(2) 174.3(6)°] but C(1)O(1) semi-bridges the Fe-W bond [W-C(1)-O(1) 169.6(6)°] thus accounting for the observation of a band in the i.r. spectrum at 1 863 cm⁻¹.

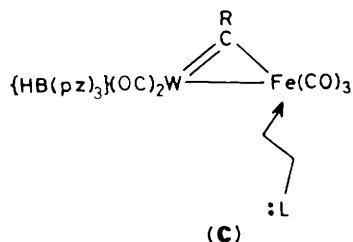
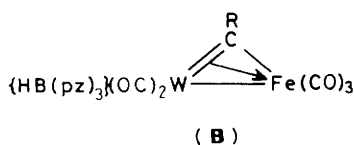
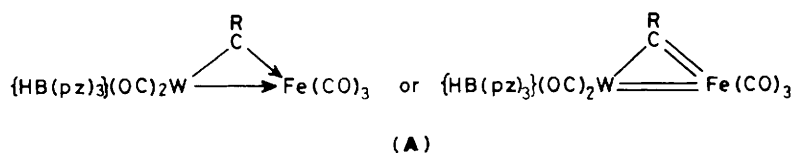
The ¹³C-{¹H} n.m.r. spectrum of (**2a**) showed two resonances for CO ligands. The signal at δ 214.5 p.p.m. is assigned to the Fe(CO)₃ group and that observed at δ 226.0, with ¹⁸³W satellite peaks [*J*(WC) 154 Hz], to the W(CO)₂ system. Evidently, at room temperature, CO site-exchange occurs *via* dynamic processes which do not exchange the ligands between the two metal centres. The most interesting feature of the ¹³C-{¹H}

n.m.r. spectrum was the observation of a highly deshielded μ-C signal at δ 408.8 p.p.m. [*J*(WC) 134 Hz]. In dimetal complexes containing the ring systems $\overline{W(\mu-CR)M}$ (M = Ti, Zr, Mn, Re, Fe, Ru, Co, Rh, Ir, or Pt) resonances for the ligated alkyldiyne carbon nuclei generally occur in the range *ca.* δ 300–390 p.p.m., with the great majority being found between 300 and 350 p.p.m.^{6,9} Moreover, X-ray crystallographic studies on several of these species reveal μ-C-W separations corresponding to the presence of a C=W bond within the $\overline{W(\mu-CR)M}$ ring. This is in accord with the (η-C₅H₅)(OC)₂W≡CR (R = C₆H₄Me-4 or Me) group acting formally as a two-electron donor to the metal centre M. An exception in the pattern of ¹³C-{¹H} n.m.r. chemical shifts is shown by the compound [CrW(μ-CC₆H₄Me-4)(CO)₄(η-C₅H₅)(η-C₆Me₆)], mentioned above and discussed further below, which has a resonance for μ-C at 430.9 p.p.m.

The relatively deshielded chemical shift observed for the μ-C group in the spectrum of compound (**2a**) is of interest in the context of ¹³C-{¹H} n.m.r. data for mononuclear metal alkyne compounds, the alkyne ligands of which can function formally as two-, three-, or four-electron donors.¹⁰⁻¹² There exists an empirical correlation between ¹³C-{¹H} n.m.r. shifts and the variable electron donor property of the alkyne.¹¹ Species in which the alkyne formally donates four electrons to a metal centre have ligated-carbon resonances *ca.* 80 p.p.m. more deshielded than those in which the ligand donates two electrons. It is, therefore, significant that the resonance for the μ-C nucleus in (**2a**) occurs *ca.* 77 p.p.m. downfield of the corresponding signal in the spectrum of (**3a**) (δ 331.3 p.p.m.).

The dimensions of the Fe(μ-C)W ring system in (**2a**), and the deshielded μ-C chemical shift in the ¹³C-{¹H} n.m.r. spectrum, lead to the proposal that in this molecule the alkyldiyne tungsten fragment, isolobal with an alkyne,¹³ functions as a four-electron donor to the iron centre, as in (A) below. However, the reactivity of (**2a**) towards electron-pair donor molecules leads us to represent the ring system as (B), in order to reflect the ease with which the C≡W fragment reverts to a two-electron functionality as in (C).

It should be mentioned in passing that since the compound [CrW(μ-CC₆H₄Me-4)(CO)₄(η-C₅H₅)(η-C₆Me₆)] is a 34-electron species it is unnecessary to invoke the idea that in this complex a C≡W fragment functions formally as a four-electron donor to the chromium centre. Indeed, the structure of this molecule,⁶ which features two CO ligands on chromium, one of which strongly semi-bridges the Cr-W bond, implies that the tungsten atom is the electron-rich metal centre rather than the chromium.¹⁴ The very deshielded μ-C resonance in the ¹³C-



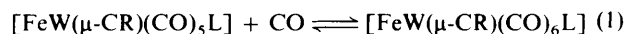
$\{^1\text{H}\}$ n.m.r. spectrum is thus difficult to explain, but the relatively short $\mu\text{-C}-\text{Cr}$ distance [1.928(6) Å], corresponding to a $\text{C}=\text{Cr}$ bond, may suggest an explanation. It has recently been demonstrated that the electronically saturated fragment $\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{Me}_6)$ can donate an electron pair to another metal centre in the stable compound $[(\eta\text{-C}_6\text{Me}_6)(\text{OC})_3\text{-Cr}\rightarrow\text{Rh}(\text{CO})(\eta\text{-C}_5\text{Me}_5)]$.¹⁵ In this compound two of the CO ligands on chromium semi-bridge the $\text{Cr}-\text{Rh}$ bond. This is as expected¹⁴ since the rhodium atom would be the electron-rich centre, as apparently is tungsten in $[\text{CrW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{Me}_6)]$.⁶ Thus in the latter species, a fragment $\text{Cr}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)$ might formally donate three electrons to the $\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ group, two *via* a $\text{Cr}\rightarrow\text{W}$ bond and one *via* the bridging alkylidyne ligand. Moreover, the $\mu\text{-CC}_6\text{H}_4\text{Me-4}$ ligand in the chromium-tungsten compound more symmetrically bridges the metal-metal bond than this ligand does in related heteronuclear dimetal structures,⁶ indicating greater electron delocalisation in the three-membered $\text{Cr}(\mu\text{-C})\text{W}$ ring. These effects may be responsible for the remarkably deshielded signal at δ 430.9 p.p.m. in the $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum, a shift comparable with those observed in certain mononuclear (alkylidene)chromium complexes.¹⁶

The isolation of (2a), and the earlier discovery of (3a), raised the possibility of preparing a compound $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2b) in which an $\text{Fe}(\text{CO})_3$ group was captured by a molecule of $[\text{W}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$. To prepare (2b) a source of ' $\text{Fe}(\text{CO})_3$ ' was required, and a reagent meeting this requirement is the species $[\text{Fe}(\text{CO})_3(\eta\text{-C}_8\text{H}_{14})_2]$ (C_8H_{14} = cyclo-octene).¹⁷ The latter with $[\text{W}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$, in hexane at -20°C , gave the purple complex (2b). The i.r. spectrum of the latter in the carbonyl stretching region is very similar to that of (2a) (Table 1). Moreover, the $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum of (2b) showed a deshielded $\mu\text{-C}$ resonance at δ 392.5 p.p.m. [$J(\text{WC})$ 153 Hz], *ca.* 61 p.p.m. downfield of the corresponding signal in the 34-electron complex (3a). Signals in the $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum of (2b) (Table 2) at δ 221.4 [$J(\text{WC})$ 153 Hz] and 214.6 p.p.m. are assigned to the $\text{W}(\text{CO})_2$ and $\text{Fe}(\text{CO})_3$ groups, respectively.

Complex (2b) is much less stable than (2a), decomposing in solution above -20°C . Compound (3a) was an observed decomposition product of (2b). In contrast, compound (2a) is stable in the solid state and it is also stable in organic solvents under nitrogen, even after several hours. Compound (3a) is formed on treatment of (2b) with CO, in dichloromethane at -20°C , but this reaction may be partially reversed by pumping

solid samples of (3a), as detected by examination of the i.r. spectra of mixtures.

The ability of the $\text{C}\equiv\text{W}$ groups in (2a) and (2b) to switch from a four- to a two-electron bonding mode at the iron centres is a dominant feature of their chemistry. Solutions of (2a) in dichloromethane under CO (1 atm, 10^5 Pa) change in colour from purple to red, the latter being attributed to the presence of the species (3b). The $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum of solutions of (2a), measured at -40°C under a CO atmosphere (10^5 Pa), showed characteristic resonances for (2a) [δ 408.8 ($\mu\text{-C}$), 226.0 (WCO), and 214.5 p.p.m. (FeCO)] and a new set of signals assignable to (3b) [δ 290.9 ($\mu\text{-C}$), 221.9 (WCO), and 213.6 p.p.m. (FeCO)]. The $\mu\text{-C}$ peak for (3b) occurs at the lower end of the range for dimetal complexes with ring systems $\text{W}(\mu\text{-CR})\text{W}$ (see above). When solutions containing (3b) are flushed with nitrogen the colour reverts to purple, and the i.r. spectrum shows only the CO bands of compound (2a). The equilibrium for the reaction [equation (1); $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{L} = \text{HB}(\text{pz})_3$



or $\eta\text{-C}_5\text{H}_5$) evidently lies in favour of the pentacarbonyl iron-tungsten complex when $\text{L} = \text{HB}(\text{pz})_3$ and in favour of the hexacarbonyl derivative when $\text{L} = \eta\text{-C}_5\text{H}_5$. These results explain why treatment of (1a) with $[\text{Fe}_2(\text{CO})_9]$, a source of $\text{Fe}(\text{CO})_4$ groups, produces (2a), since compound (3b), if formed, would release a CO group. In contrast, treatment of $[\text{W}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{Fe}_2(\text{CO})_9]$ yields (3a), the thermodynamically more stable species in the above equilibrium. The enhanced stability of (2a) *versus* (2b) can be attributed to the relatively greater donor properties of the ligand $\text{HB}(\text{pz})_3$ compared with $\eta\text{-C}_5\text{H}_5$. The σ -donor properties of the former group would increase electron donation by the $\text{W}\equiv\text{C}$ system.

Treatment of compound (2b) with either one equivalent or excess of PPh_3 afforded a purple complex $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ (4a) (Table 1). The $\mu\text{-C}$ resonance in the $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum occurs at δ 388.4 p.p.m., with CO signals at δ 222.8 (FeCO) and 222.3 p.p.m. [WCO , $J(\text{WC})$ 175 Hz]. The $^{31}\text{P}-\{^1\text{H}\}$ spectrum had a resonance at 82.4 p.p.m. (Table 4) and this signal showed no $^{183}\text{W}-^{31}\text{P}$ coupling, and hence the PPh_3 group is attached to the iron. Compound (4a) reacted with excess of CO (10^5 Pa) to give (3a). Surprisingly, the PPh_3 group was displaced rather than the complex $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ (5a) being produced. The reaction was followed by i.r. and removal of CO by pumping the solutions containing displaced PPh_3 resulted in regeneration of (4a).

Addition of one equivalent of PMe_3 to compound (2b) in light petroleum at -20°C , with further cooling to -50°C , gave a brown precipitate of the complex $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]$ (5b), together with small amounts of the 32-electron complex (4b). When (5b) is refluxed in diethyl ether it is converted into the purple complex (4b). This process is reversed with CO at 10^5 Pa. These reactions again illustrate the delicate balance between 32 and 34 valence electron configurations for the dimetal compounds. Failure to isolate (5a) in the reaction of (4a) with CO is probably due to the steric bulk of PPh_3 compared with PMe_3 . The spectroscopic data for (4b) and (5b) (Tables 1, 2, and 4) are in accord with the structures proposed. The absence of $^{183}\text{W}-^{31}\text{P}$ satellite peaks on the ^{31}P -

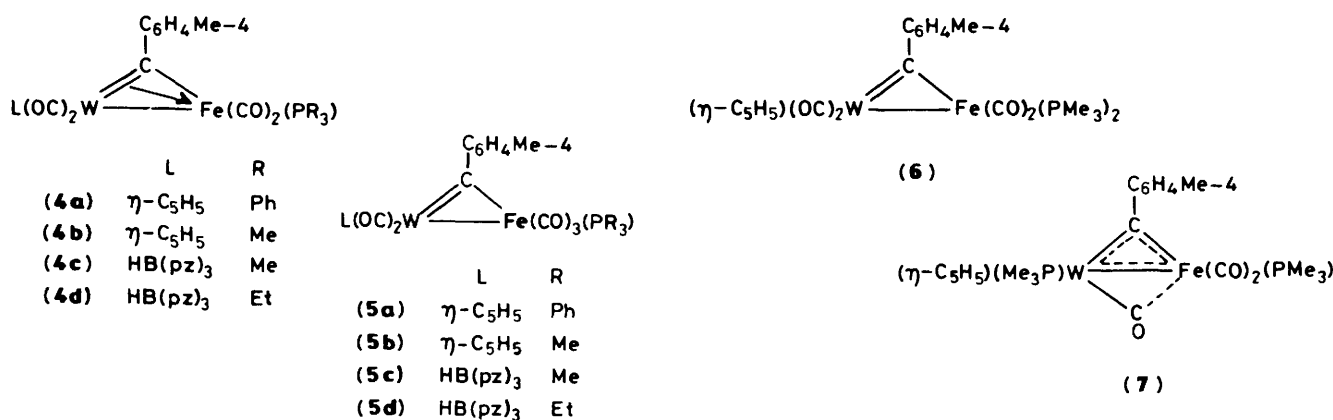


Table 4. Phosphorus-31 n.m.r. data^a for the iron-tungsten complexes

Compound	δ(³¹ P) ^b
(4a) ^c	82.4 (FeP)
(4b)	44.4 (FeP)
(4c)	40.8 (FeP)
(4d) ^c	69.5 (FeP)
(5b)	14.2 (FeP)
(6) ^d	18.7 (FeP)
(7)	39.5 (FeP)
	-17.5 [WP, J(WP) 417]
(9)	70.8 [d, FeP, J(PP) 42]
	-27.7 [d, P, J(PP) 42]
(10a)	52.5 [d, FeP, J(PP) 71]
	23.6 [d, WP, J(PP) 71, J(WP) 325]
(10b)	43.0 [d, FeP, J(PP) 44]
	-13.8 [d, WP, J(PP) 44, J(WP) 327]
(11)	46.0 [d, FeP, J(PP) 4]
	-13.8 [d, WP, J(PP) 4, J(WP) 414]
(12a)	65.7 [d, FeP, J(PP) 61]
	17.0 [d, WP, J(PP) 61, J(WP) 304]
(12b)	56.4 [d, FeP, J(PP) 47, J(WP) 17]
	-11.7 [d, WP, J(PP) 47, J(WP) 298]

^a Hydrogen-1 decoupled, chemical shifts in p.p.m., coupling constants in Hz. ^b Chemical shifts to high frequency of 85% H₃PO₄ (external), and measured at room temperature in CD₂Cl₂ unless otherwise stated. ^c Measured in CDCl₃. ^d Measured at -40 °C.

¹H n.m.r. resonances of (4b) and (5b) establish the presence of Fe(PMe₃) rather than W(PMe₃) groups in these species. The signal for the μ-C group in the ¹³C-¹H n.m.r. spectrum of (4b) is at δ 388.1 p.p.m. [*J*(WC) 150 Hz], and is more deshielded than the μ-C resonance {δ 354.4 [d, *J*(PC) 18, *J*(WC) 144 Hz]} for (5b), following the trend for alkylidyne carbon signals in (2b) and (3a), discussed above.

Treatment of (4b) with a further equivalent of PMe₃ in diethyl ether at room temperature gives the bis(trimethylphosphine)-iron-tungsten complex [FeW(μ-CC₆H₄Me-4)(CO)₄(PMe₃)₂(η-C₅H₅)] (6), characterised by the data given in Tables 1, 2, and 4. The ¹³C-¹H and ³¹P-¹H n.m.r. data were obtained at -40 °C to obtain limiting spectra. Room temperature measurements showed that dynamic processes occurred. The process of lowest energy leads to equivalence of the PMe₃ ligands on iron and of the CO ligands on tungsten, and a higher energy process involves site-exchange of CO ligands on iron. The observation of the μ-C resonance (δ 365.7 p.p.m.) in the limiting spectrum (Table 2) as a triplet [*J*(PC) 17 Hz] implies that the PMe₃ ligands are transoid on the iron atom.

When compound (6) is refluxed in dichloromethane, carbon monoxide is released and the complex [FeW(μ-CC₆H₄Me-4)-

(μ-CO)(CO)₂(PMe₃)₂(η-C₅H₅)] (7) is produced. This compound is characterised by the data given in Tables 1, 2, and 4. In particular, the ³¹P-¹H n.m.r. spectrum had two resonances at δ 39.5 and -17.5 p.p.m., with the latter showing strong ¹⁸³W-³¹P coupling [*J*(WP) 417 Hz], establishing that a PMe₃ ligand on iron in (6) had migrated to tungsten in (7). A band in the i.r. spectrum of (7) (Table 1) at 1707 cm⁻¹ indicates that the molecule has a bridging or very strongly semi-bridging CO group, and this ligand reveals itself in the ¹³C-¹H n.m.r. spectrum as a resonance at δ 269.6 p.p.m. (Table 2). The two CO ligands bonded to iron give rise to doublet signals at 227.4 [*J*(PC) 28 Hz] and 224.3 p.p.m. [*J*(PC) 18 Hz]. The μ-C resonance is at 354.7 p.p.m., but is less deshielded than in the precursor (6). Thus, although (7) is a 32-electron species it does not appear to involve a C≡W moiety acting as a formal four-electron donor. Probably the bridging CO group helps to delocalise the electron density in the Fe(μ-CO)(μ-CC₆H₄Me-4)W ring system.

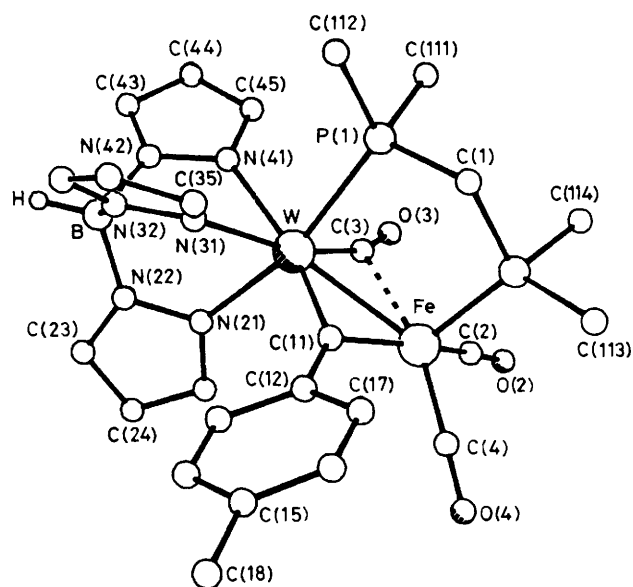
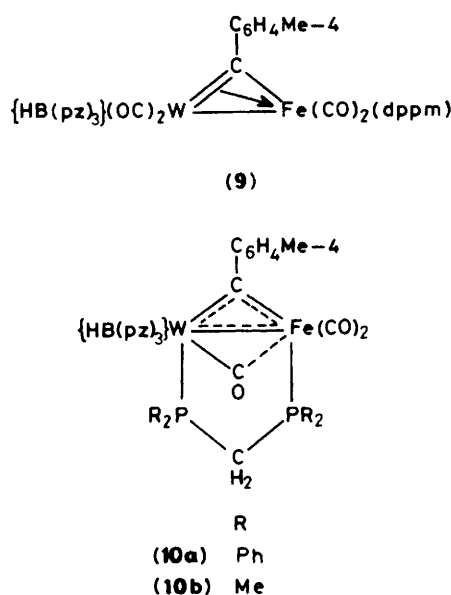
Treatment of the tris(pyrazol-1-yl)borato iron-tungsten complex (2a) with one equivalent of PMe₃ or PEt₃ in dichloromethane affords the purple monophosphine substituted complexes [FeW(μ-CC₆H₄Me-4)(CO)₄(PR₃){HB(pz)₃}] (4c, R = Me; 4d, R = Et), respectively. In their ¹³C-¹H n.m.r. spectra (Table 2) both compounds show low-field resonances for the μ-C nuclei [(4c), δ 404.4; (4d), 402.8 p.p.m.] in accord with Fe(μ-C)W ring bonding similar to that proposed for (2a). Interestingly, although the formation of (4c) and (4d) occurred rapidly from (2a), during the reactions a colour change from purple to red-brown to purple was observed, perhaps indicating the transient formation of the 34-valence electron intermediates [FeW(μ-CC₆H₄Me-4)(CO)₅(PR₃){HB(pz)₃}] (5c, R = Me; 5d, R = Et), which were not isolated. Treatment of (4c) with excess of PMe₃ in dichloromethane at room temperature gave a mixture of products including (1a) and [W(≡CC₆H₄Me-4)(CO)(PMe₃){HB(pz)₃}] (8).

Reactions between compound (2a) and the chelating phosphines R₂PCH₂PR₂ (R = Ph, dppm; R = Me, dmpm) were also investigated. Treatment of (2a) with dppm in diethyl ether afforded the purple complex [FeW(μ-CC₆H₄Me-4)(CO)₄(dppm){HB(pz)₃}] (9). The CO stretching region of the i.r. spectrum (Table 1) was similar to those of (4c) and (4d). The ³¹P-¹H n.m.r. spectrum confirmed that only one of the phosphorus atoms was ligated to the iron [δ 70.8 p.p.m., *J*(PP) 42 Hz], the other phosphorus atom [δ -27.7 p.p.m., *J*(PP) 42 Hz] being unco-ordinated. In the compound [PtW{μ-C(O)Me}C₆H₄Me-4}(μ-dppm)(CO)₄(dppm)] the non-ligated PPh₂ group resonates at -27.6 p.p.m.¹⁸ In the free ligand, the ³¹P-¹H resonance is at -22.0 p.p.m. In the ¹³C-¹H n.m.r. spectrum of (9) the μ-C resonance occurs at δ 403.8 p.p.m., indicative of the C≡W moiety functioning as a four-electron donor.

Table 5. Selected internuclear distances* (Å) and angles (°) for [FeW(μ-CC₆H₄Me-4)(μ-CO)(μ-dmpm)(CO)₂{HB(pz)₃}] (**10b**)

Fe-W	2.605(1)	Fe-C(11)	1.911(3)	W-C(11)	1.951(4)	C(11)-C(12)	1.456(5)
Fe-C(3)	2.423(5)	W-C(3)	1.951(4)	C(3)-O(3)	1.191(5)	Fe-C(2)	1.787(4)
C(2)-O(2)	1.152(5)	Fe-C(4)	1.767(5)	C(4)-O(4)	1.150(6)	Fe-P(2)	2.167(1)
P(2)-C(1)	1.850(4)	P(1)-C(1)	1.827(5)	W-P(1)	2.489(2)	W-N(21)	2.210(3)
W-N(31)	2.247(3)	W-N(41)	2.279(4)	B-H	1.116(46)	B-N(42)	1.541(5)
B-N(22)	1.541(5)	B-N(32)	1.534(5)				
W-Fe-C(11)	48.2(1)	Fe-W-C(11)	46.9(1)	Fe-C(11)-W	84.8(1)	W-C(11)-C(12)	141.6(2)
Fe-C(11)-C(12)	133.3(3)	W-C(3)-Fe	72.2(1)	W-C(3)-O(3)	162.1(4)	Fe-C(3)-O(3)	125.2(3)
Fe-C(2)-O(2)	176.8(5)	Fe-C(4)-O(4)	177.9(5)	C(2)-Fe-C(4)	96.8(2)	P(2)-Fe-C(2)	93.3(1)
P(2)-Fe-C(4)	99.0(1)	Fe-P(2)-C(1)	110.1(1)	P(2)-C(1)-P(1)	111.4(2)	C(1)-P(1)-W	110.2(1)
C(3)-W-P(1)	86.7(1)	C(3)-W-N(41)	84.3(2)	C(3)-W-N(21)	98.2(1)	C(3)-W-C(11)	108.9(2)
C(3)-W-N(31)	163.9(2)	P(1)-W-N(41)	89.2(1)	N(41)-W-N(21)	78.0(1)	N(21)-W-C(11)	95.7(1)
C(11)-W-P(1)	95.4(1)	N(31)-W-P(1)	89.5(1)	N(31)-W-N(41)	80.1(1)	N(31)-W-N(21)	82.1(1)
N(31)-W-C(11)	86.9(1)	W-N(21)-N(22)	122.5(2)	W-N(31)-N(32)	123.0(2)	W-N(41)-N(42)	121.8(2)
B-N(22)-N(21)	120.5(2)	B-N(32)-N(31)	119.5(3)	B-N(42)-N(41)	119.8(3)	H-B-N(22)	107(2)
H-B-N(32)	114(2)	H-B-N(42)	110(2)				

* For C₃H₃N₂ groups, mean C-N 1.344(5), mean C-C 1.378(6), and mean N-N 1.369(4) Å.

**Figure 2.** The molecular structure of [FeW(μ-CC₆H₄Me-4)(μ-CO)(μ-dmpm)(CO)₂{HB(pz)₃}] (**10b**)

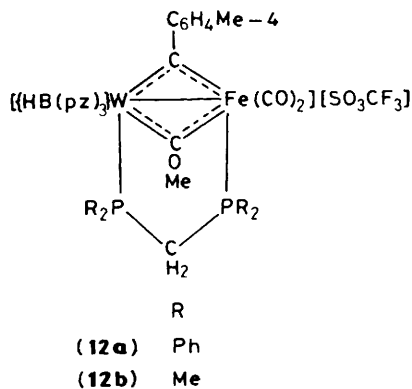
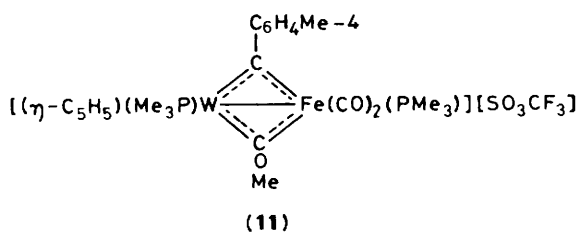
If compound (**9**) is stirred for several hours with dichloromethane as solvent it loses CO and affords [FeW(μ-CC₆H₄Me-4)(μ-CO)(μ-dppm)(CO)₂{HB(pz)₃}] (**10a**) in which the dppm ligand bridges the two metal centres. In the ³¹P-¹H} n.m.r. spectrum there are doublet resonances at 52.5 [FeP, *J*(PP) 71 Hz] and 23.6 p.p.m. [WP, *J*(PP) 71, *J*(WP) 325 Hz]. The i.r. spectrum shows a CO stretch at 1 718 cm⁻¹ suggesting that a bridging or strongly semi-bridging CO group is present, and this is confirmed by the ¹³C-¹H} n.m.r. spectrum which shows a resonance at 266.1 p.p.m.¹⁶ The μ-C resonance (377.2 p.p.m.) is at relatively high field but this may be due to extensive electron delocalisation within the Fe(μ-CO)(μ-CC₆H₄Me-4)W ring, as proposed for structurally related (7).

Reaction between (**2a**) and dmpm affords [FeW(μ-CC₆H₄Me-4)(μ-CO)(μ-dmpm)(CO)₂{HB(pz)₃}] (**10b**); a precursor analogous to (**9**) not being isolated. Data for (**10b**) are summarised in Tables 1, 2, and 4, but an X-ray diffraction study was carried out to establish the structure in the solid state. The results are summarised in Table 5, and the molecule is shown in Figure 2.

The Fe-W separation [2.605(1) Å] is short as in (**2a**) [2.612(2) Å]. This may indicate some multiple bond character

but the effect may in part be due to the steric requirements of the bridging ligands. The μ-C(11) atom bridges the Fe-W bond [Fe-C(11) 1.911(3), W-C(11) 1.951(4) Å] but is more symmetrically disposed than is μ-C in (**2a**) [Fe-C(11) 1.826(6), W-C(11) 2.025(7) Å]. In (**10b**) the W-C(11) separation is comparable with that found in several compounds containing dimetallacyclopropene rings with some multiple C-W bonding.⁶ The Fe-C(11) distance, while longer than that in (**2a**) is somewhat shorter than that expected for an iron-carbon σ bond (see earlier discussion).

The dmpm ligand bridges the metal-metal bond as expected, and the P(2)-Fe [2.167(1) Å] and P(1)-W [2.489(2) Å] distances may be compared with those in [Fe₂(μ-CO)(μ-dppm)(CO)₆] [P-Fe 2.253(3) Å]¹⁹ and in [PtW{μ-C(OMe)-C₆H₄Me-4}(μ-dppm)(CO)₅] [P-W 2.544(7) Å].¹⁸ The iron atom carries two terminally bound carbonyl groups, but C(3)O(3) attached to tungsten semi-bridges the metal-metal bond [W-C(3)-O(3) 162.1(4)°]. The C(3)O(3) group must be responsible for the CO stretching band in the i.r. at 1 688 cm⁻¹, although this frequency is very low for a semi-bridging ligand.



Presumably the presence of the strongly σ -donating groups $\text{HB}(\text{pz})_3$ and dmpm on the tungsten contribute significantly to lowering the CO stretch.

The tungsten atom is in a distorted octahedral environment defined by N(21), N(31), N(41), P(1), C(3) and the mid-point of the Fe-C(11) vector. The N-W distances vary, reflecting the different *trans* influences of the groups present $\{\text{W-N}(21) 2.210(3)$ [*trans* to P(1)], $\text{W-N}(31) 2.247(3)$ [*trans* to C(3)], and $\text{W-N}(41) 2.279(4)$ Å [*trans* to C(11)-Fe] $\}$.

The low stretching frequencies observed for the semi-bridging CO ligands in the i.r. spectra of the compounds (7) and (10) suggested that these species might be readily methylated at the μ -CO oxygen atoms. Using $\text{CF}_3\text{SO}_3\text{Me}$ in dichloromethane as the reagent, the compounds $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-COMe})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{SO}_3\text{CF}_3]$ (11) and $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-COMe})(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)(\text{CO})_2\{\text{HB}(\text{pz})_3\}][\text{SO}_3\text{CF}_3]$ (12a, R = Ph; 12b, R = Me), were prepared, and data for these salts are given in Tables 1, 2, and 4. For each salt, only two CO stretching bands are observed in the i.r. spectra, and the bands assignable to the μ -CO ligands in the precursors are absent in these products. The presence of two bridging alkyldiene ligands in each cation is established by the appearance of two μ -C resonances in each $^{13}\text{C}\{^1\text{H}\}$ spectrum [(11), δ 338.7 and 336.4; (12a), δ 347.0 and 336.4; (12b), δ 341.3 and 329.5 p.p.m.]. The ^1H n.m.r. spectra of all three salts (Table 2) showed signals attributable to an OMe group. The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. data (Table 4) were also in accord with the proposed formulations.

Experimental

Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere. Light petroleum refers to that fraction of b.p. 40–60 °C. All chromatography was carried out on 2 × 20 cm columns using alumina (Brockman activity II) or Florisil (Aldrich, 100–200 mesh) as specified. The compounds $[\text{W}(\equiv\text{CR})(\text{CO})_2\text{L}]$ [R = $\text{C}_6\text{H}_4\text{Me-4}$, L = $\text{HB}(\text{pz})_3$ or $\eta\text{-C}_5\text{H}_5$]²⁰ and $[\text{Fe}(\text{CO})_3(\eta\text{-C}_8\text{H}_{14})_2]$ ¹⁷ were prepared by methods described elsewhere. The i.r. spectra were measured with Nicolet MX-10 and MX-5 spectrophotometers and n.m.r. spectra were recorded with JNM FX

90Q and FX 200 instruments. Analytical and other data for the new compounds are given in Table 1.

Synthesis of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$.—The compounds (1a) (0.56 g, 1.0 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (0.72 g, 2.0 mmol) were stirred in diethyl ether (20 cm³) for 5 h. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 -light petroleum (30 cm³, 1:4), and chromatographed on Florisil. Elution with the same solvent mixture removed trace amounts of $[\text{Fe}_3(\text{CO})_{12}]$. Further elution with CH_2Cl_2 -light petroleum (1:1) afforded a purple eluate. Solvent was removed *in vacuo* giving purple microcrystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$ (2a) (0.58 g).

Synthesis of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$.—The compound $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (0.82 g, 2.0 mmol) was added to a hexane (80 cm³) solution of $[\text{Fe}(\text{CO})_3(\eta\text{-C}_8\text{H}_{14})_2]$ (0.73 g, 2.0 mmol) at -30 °C, and the mixture was stirred at -20 °C for 8 h. Solvent was removed *in vacuo* at -20 °C, and the purple residue was dissolved in Et_2O -light petroleum (50 cm³, 1:4) at -20 °C, and chromatographed on Florisil at -20 °C. Elution with the same solvent mixture gave a trace of brown (3a). Further elution, followed by removal of solvent *in vacuo*, gave purple microcrystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2b) (0.72 g).

Reactions of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2b).—(a) *With carbon monoxide.* A CH_2Cl_2 (5 cm³) solution of (2b) (0.08 g, 0.14 mmol) was placed in a Schlenk tube fitted with a high-pressure stopcock. The reaction vessel was attached to a vacuum line, cooled to -196 °C and evacuated, and CO gas (ca. 0.14 mmol) was introduced. The stopcock was closed and the reactants were warmed to room temperature; the colour changing from purple to brown. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 -light petroleum (10 cm³, 1:4) and chromatographed at -20 °C on Florisil. Elution with the same solvent mixture, followed by removal of solvent *in vacuo*, afforded the compound $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ (3a), identified spectroscopically.

(b) *With PMe_3 .* A light petroleum (10 cm³) solution of (2b) (0.20 g, 0.36 mmol) was treated with PMe_3 (0.36 mmol) at -20 °C, and the solution was cooled further to -50 °C. Solvent was removed with a syringe leaving a brown residue of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]$ (5b) (0.15 g) containing some of the complex (4b) (see below).

Treatment of (2b) (0.84 g, 1.53 mmol) in diethyl ether (30 cm³) with PMe_3 (1.53 mmol), and subsequently refluxing for 5 h gave a purple solution. Volatiles were removed *in vacuo*, and the residue dissolved in Et_2O (10 cm³) and filtered through an alumina pad (2 × 4 cm). Removal of solvent *in vacuo* gave purple microcrystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]$ (4b) (0.64 g). This complex may also be prepared by refluxing diethyl ether solutions of (5b) for ca. 5 h.

(c) *With PPh_3 .* Excess PPh_3 (0.20 g, 0.76 mmol) was added to a CH_2Cl_2 (10 cm³) solution of (2b) (0.12 g, 0.22 mmol) at -20 °C. The mixture was warmed to room temperature and stirred (15 min). Solvent was removed *in vacuo*, and the residue washed with Et_2O (2 × 10 cm³). The product was dissolved in CH_2Cl_2 -light petroleum (20 cm³, 1:1) and chromatographed on Florisil. Elution with the same solvent mixture and removal of solvent *in vacuo* afforded purple microcrystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ (4a) (0.14 g).

Reactions of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PR}_3)(\eta\text{-C}_5\text{H}_5)]$ (R = Me or Ph).—(a) *With CO.* A CH_2Cl_2 (10 cm³) solution of (4a) (0.14 g, 0.18 mmol) contained in a Schlenk tube cooled to -196 °C and evacuated, was treated with carbon monoxide (ca. 0.18 mmol). The stopcock connecting the reaction vessel to the

vacuum line was closed and the mixture was warmed to room temperature. No reaction occurred. However, when further CO was admitted (10^5 Pa), the solution changed in colour from purple to brown, and an i.r. spectrum of the solution revealed only bands due to (3a) in the carbonyl stretching region. However, removal of solvent from the mixture resulted in quantitative regeneration of (4a).

In a similar experiment, a sample of (4b) was treated with CO (10^5 Pa). The i.r. spectrum of the resulting solution indicated complete conversion to (5b). Removal of solvent and examination of the i.r. spectrum (CH_2Cl_2) of the residue indicated that it was a mixture of (4b) and (5b).

(b) *With* PMe_3 . An Et_2O (20 cm^3) solution of (4b) (0.13 g, 0.21 mmol) was treated with PMe_3 (0.21 mmol). Partial removal of solvent *in vacuo* produced a dark green precipitate. The remaining solvent was removed with a syringe and the residue was washed with Et_2O ($2 \times 10\text{ cm}^3$) and dried *in vacuo*, yielding dark green microcrystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ (6) (0.09 g).

A CH_2Cl_2 (20 cm^3) solution of (6) (0.08 g, 0.12 mmol) was refluxed for 3 h. Solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 -light petroleum (10 cm^3 , 1:1) and chromatographed on alumina. Elution with the same solvent mixture afforded, after removal of solvent *in vacuo*, green microcrystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ (7) (0.05 g).

Reactions of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$ (2a).—(a) *With* PMe_3 or PEt_3 . A CH_2Cl_2 (10 cm^3) solution of (2a) (0.35 g, 0.50 mmol) was treated with PMe_3 (0.50 mmol) with stirring for 30 min. Solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 -light petroleum (20 cm^3 , 1:4), and then chromatographed on alumina. Elution with CH_2Cl_2 -light petroleum (1:1) afforded a purple eluate. Removal of solvent *in vacuo* gave purple crystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PMe}_3)\{\text{HB}(\text{pz})_3\}]$ (4c) (0.33 g).

In a similar synthesis, excess of PEt_3 (0.2 cm^3) and (2a) (0.35 g, 0.50 mmol) in CH_2Cl_2 (10 cm^3) gave purple crystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{PEt}_3)\{\text{HB}(\text{pz})_3\}]$ (4d) (0.32 g).

Treatment of (4c) (0.28 g, 0.40 mmol) in CH_2Cl_2 (10 cm^3) with PMe_3 (0.40 mmol) at room temperature gave an orange mixture. Solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 -light petroleum (20 cm^3 , 1:4) and chromatographed on alumina. Elution with the same solvent mixture gave an orange solution which yielded, after removal of solvent, orange microcrystals of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ (1a) (0.12 g). Elution with CH_2Cl_2 -light petroleum (2:3) afforded, after removal of solvent and crystallization from hexane (5 cm^3) at -20°C , red microcrystals of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PMe}_3)\{\text{HB}(\text{pz})_3\}]$ (8) (0.05 g, 21%) [*Found*: C, 41.7; H, 4.5; N, 14.7. $\text{C}_{21}\text{H}_{26}\text{BN}_6\text{OPW}$ requires C, 41.7; H, 4.3; N, 13.9%, $\nu_{\text{max}}(\text{CO})$ at 1866 cm^{-1} (in Et_2O). N.m.r.: ^1H (in CD_2Cl_2), δ 1.52 [d, 9 H, MeP, $J(\text{PH})$ 8], 2.22 (s, 3 H, Me-4), 6.14–6.29 (m, 3 H, $\text{C}_3\text{H}_3\text{N}_2$), 6.99, 7.14 [(AB)₂, 4 H, C_6H_4 , $J(\text{AB})$ 8], and 7.60–8.04 (m, 6 H, $\text{C}_3\text{H}_3\text{N}_2$); ^{13}C - $\{^1\text{H}\}$ (in CD_2Cl_2 - CH_2Cl_2), δ 272.0 [d, $\text{C}\equiv\text{W}$, $J(\text{PC})$ 12], 248.6 (CO), 149.0 [$\text{C}(\text{C}_6\text{H}_4)$], 144.7–105.1 ($\text{C}_3\text{H}_3\text{N}_2$ and C_6H_4), 21.1 (Me-4), and 20.3 p.p.m. [d, MeP, $J(\text{PC})$ 31]; ^3P - $\{^1\text{H}\}$ (in CD_2Cl_2), δ -10.6 p.p.m. [$J(\text{WP})$ 359 Hz].

(b) *With* *dppm* or *dmpm*. Compound (2a) (0.35 g, 0.50 mmol) and *dppm* (0.19 g, 0.50 mmol) in Et_2O (10 cm^3) were stirred together for 10 min, thereby affording a purple precipitate. Solvent was removed with a syringe and the product washed with Et_2O ($2 \times 10\text{ cm}^3$) giving purple microcrystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{dppm})\{\text{HB}(\text{pz})_3\}]$ (9) (0.50 g).

Compound (9) (0.50 g, 0.48 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and stirred for 12 h. Solvent was removed *in vacuo* and the brown residue dissolved in CH_2Cl_2 -light petroleum (20

cm^3 , 1:1) and chromatographed. Elution with CH_2Cl_2 gave a brown eluate. Evaporation of solvent *in vacuo* gave a residue which was crystallised from CH_2Cl_2 -light petroleum (5 cm^3 , 1:2) at -20°C yielding brown crystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\mu\text{-dppm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ (10a) (0.45 g).

The ligand *dmpm* (1.0 cm^3 of a 0.50 mol dm^{-3} solution in tetrahydrofuran) was added to a CH_2Cl_2 (10 cm^3) solution of (2a) (0.35 g, 0.50 mmol) and the mixture stirred for 3 h. Solvent was removed *in vacuo* and the green residue dissolved in CH_2Cl_2 -light petroleum (20 cm^3 , 1:1) and chromatographed on alumina. A green eluate was collected, solvent evaporated, and the residue crystallised from CH_2Cl_2 -light petroleum (*ca.* 5 cm^3 , 1:2) at -20°C affording green crystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\mu\text{-dmpm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}]$ (10b) (0.34 g).

Methylation Reactions.—Excess $\text{CF}_3\text{SO}_3\text{Me}$ (0.20 cm^3) was added to a CH_2Cl_2 (10 cm^3) solution of (10a) (0.51 g, 0.50 mmol), and the mixture was stirred (12 h). Solvent was removed *in vacuo*, and the green residue washed with Et_2O ($2 \times 5\text{ cm}^3$). Crystallisation from CH_2Cl_2 -light petroleum (*ca.* 10 cm^3 , 1:2) at -20°C gave green crystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-COMe})(\mu\text{-dppm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}][\text{SO}_3\text{CF}_3]$ (12a) (0.48 g).

Similarly, (10b) (0.41 g, 0.50 mmol) and $\text{CF}_3\text{SO}_3\text{Me}$ (0.20 cm^3) in CH_2Cl_2 (10 cm^3) after 3 h gave green crystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-COMe})(\mu\text{-dmpm})(\text{CO})_2\{\text{HB}(\text{pz})_3\}][\text{SO}_3\text{CF}_3]$ (12b) (0.43 g).

Reaction between (7) (0.05 g, 0.08 mmol) and excess $\text{CF}_3\text{SO}_3\text{Me}$ (0.20 cm^3) in CH_2Cl_2 (5 cm^3) for 30 min gave a blue solution. Removal of solvent *in vacuo* and crystallisation from CH_2Cl_2 -light petroleum (*ca.* 5 cm^3 , 1:2) gave blue crystals of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-COMe})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{SO}_3\text{CF}_3]$ (11) (0.046 g).

Crystal Structure Determination of Complex (2a).—A suitable crystal of (2a) (*ca.* $0.15 \times 0.30 \times 0.60\text{ mm}$) was grown from diethyl ether-light petroleum (1:4). Diffracted intensities were collected on a Nicolet *P3m* diffractometer at 190 K using the θ - 2θ scan mode ($2.9 \leq 2\theta \leq 58^\circ$).

Crystal data. $\text{C}_{22}\text{H}_{17}\text{BFeN}_6\text{O}_5\text{W}$, $M = 695.9$, monoclinic, $a = 8.959(7)$, $b = 22.610(17)$, $c = 12.415(8)\text{ \AA}$, $\beta = 103.85(6)^\circ$, $U = 2.442(3)\text{ \AA}^3$, $Z = 4$, $D_c = 1.90\text{ g cm}^{-3}$, $F(000) = 1344$, space group $P2_1/n$ (no. 14), Mo- K_α X-radiation (graphite monochromator), $\lambda = 0.71069\text{ \AA}$, $\mu(\text{Mo-}K_\alpha) 54.5\text{ cm}^{-1}$.

Data were corrected for Lorentz and polarisation effects and an empirical correction was applied for X-ray absorption based on an ellipsoidal model with azimuthal scan data.²¹ Of 5677 unique reflections, 4563 had $I \geq 4\sigma(I)$, and only these were used for the structure solution and refinement. The structure was solved by conventional heavy-atom and electron-density difference methods and was refined by blocked-cascade full-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atom on boron was located and refined with a fixed isotropic thermal parameter ($U_{\text{iso}} = 0.03\text{ \AA}^2$). All other hydrogen atoms were incorporated at calculated positions (C-H 0.960 \AA) with isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of the attached carbon atom. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.0004|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $> 3.2\text{ e \AA}^{-3}$ and these were located near the metal atoms. At convergence $R = 0.045$ ($R' = 0.047$). Scattering factors were from ref. 22. All computations were carried out on an 'Eclipse' Data General computer with the SHELXTL system of programs.²¹ Table 6 lists the atomic coordinates.

Crystal Structure Determination of Complex (10b).—Black crystals of (10b) were grown from dichloromethane-light

Table 6. Atomic positional (fractional co-ordinates) parameters ($\times 10^4$), with estimated standard deviations in parentheses, for compound (**2a**)

Atom	x	y	z	Atom	x	y	z
W	2 100(1)	1 013(1)	1 379(1)	C(33)	3 888(7)	-661(3)	557(6)
Fe	551(1)	2 000(1)	1 231(1)	C(34)	3 341(7)	-480(3)	-531(6)
C(11)	1 428(7)	1 565(3)	2 458(5)	C(35)	2 692(7)	66(3)	-450(5)
C(12)	1 461(7)	1 600(3)	3 626(5)	N(41)	4 389(5)	872(2)	2 489(4)
C(13)	387(7)	1 931(3)	4 049(5)	N(42)	4 902(5)	335(2)	2 907(4)
C(14)	418(8)	1 941(3)	5 170(6)	C(43)	6 309(7)	387(3)	3 590(5)
C(15)	1 533(8)	1 630(3)	5 936(5)	C(44)	6 737(7)	972(3)	3 627(6)
C(16)	2 604(8)	1 307(3)	5 543(5)	C(45)	5 498(7)	1 261(3)	2 918(5)
C(17)	2 547(7)	1 281(3)	4 420(6)	C(1)	309(7)	985(3)	54(5)
C(18)	1 584(11)	1 653(4)	7 146(6)	O(1)	-559(5)	929(2)	-781(4)
B	3 930(8)	-225(3)	2 494(6)	C(2)	2 942(7)	1 529(3)	371(5)
N(21)	1 428(5)	309(2)	2 414(4)	O(2)	3 486(6)	1 786(2)	-238(4)
N(22)	2 383(5)	-153(2)	2 828(4)	C(3)	137(10)	2 245(4)	-240(7)
C(23)	1 729(7)	-489(3)	3 482(5)	O(3)	-130(9)	2 405(3)	-1 123(5)
C(24)	348(8)	-246(3)	3 520(6)	C(4)	939(9)	2 704(3)	1 886(7)
C(25)	201(7)	251(3)	2 847(5)	O(4)	1 198(8)	3 140(3)	2 361(6)
N(31)	2 850(5)	216(2)	611(4)	C(5)	-1 395(8)	1 987(3)	1 309(5)
N(32)	3 601(5)	-243(2)	1 228(4)	O(5)	-2 639(6)	1 940(3)	1 374(5)

Table 7. Atomic positional (fractional co-ordinates) parameters ($\times 10^4$), with estimated standard deviations in parentheses, for compound (**10b**)

Atom	x	y	z	Atom	x	y	z
W	2 122(1)	2 598(1)	3 555(1)	C(35)	1 909(4)	3 254(2)	-409(4)
Fe	3 730(1)	1 647(1)	4 681(1)	N(41)	313(3)	3 078(2)	3 844(4)
P(1)	577(1)	1 607(1)	1 625(1)	N(42)	220(3)	3 804(2)	3 582(4)
C(111)	-715(5)	1 071(3)	2 502(7)	C(43)	-887(4)	3 946(3)	3 982(5)
C(112)	-469(4)	1 822(3)	-527(6)	C(44)	-1 523(4)	3 325(3)	4 532(5)
P(2)	2 763(1)	682(1)	3 060(1)	C(45)	-753(4)	2 793(2)	4 434(5)
C(113)	3 743(5)	136(2)	2 125(6)	B	1 356(4)	4 317(2)	3 061(5)
C(114)	1 771(6)	-29(3)	4 050(7)	C(2)	3 685(5)	1 187(2)	6 690(5)
C(1)	1 520(4)	935(2)	1 082(5)	O(2)	3 699(5)	871(2)	7 970(4)
C(11)	3 731(3)	2 396(2)	2 971(4)	C(3)	1 855(4)	2 000(2)	5 542(4)
C(12)	4 660(3)	2 675(2)	1 938(4)	O(3)	1 373(4)	1 711(2)	6 643(4)
C(13)	5 093(4)	3 433(2)	1 876(5)	C(4)	5 413(4)	1 586(2)	4 780(6)
C(14)	6 000(4)	3 713(2)	938(5)	O(4)	6 520(4)	1 555(2)	4 897(7)
C(15)	6 501(4)	3 250(2)	-24(5)	H(111A)	-1 462(49)	1 291(25)	2 424(60)
C(16)	6 045(4)	2 506(2)	-35(5)	H(111B)	-1 088(45)	670(23)	1 802(58)
C(17)	5 155(4)	2 221(2)	943(5)	H(111C)	-428(44)	976(24)	3 692(57)
C(18)	7 507(5)	3 547(3)	-1 029(6)	H(112A)	-1 170(45)	1 474(24)	-1 038(57)
N(21)	3 073(3)	3 630(2)	5 027(4)	H(112B)	136(45)	1 980(23)	-1 251(57)
N(22)	2 647(3)	4 287(2)	4 538(4)	H(112C)	-809(45)	2 243(24)	-266(57)
C(23)	3 451(4)	4 820(2)	5 626(5)	H(113A)	4 173(46)	-61(24)	2 960(58)
C(24)	4 409(4)	4 517(2)	6 843(5)	H(113B)	4 307(45)	365(24)	1 647(56)
C(25)	4 135(4)	3 771(2)	6 418(5)	H(113C)	3 093(45)	-309(23)	1 479(57)
N(31)	1 856(3)	3 352(2)	1 252(4)	H(114A)	1 079(46)	-404(25)	3 123(60)
N(32)	1 522(3)	4 034(2)	1 327(4)	H(114B)	2 303(45)	-220(23)	4 716(56)
C(33)	1 363(4)	4 339(2)	-265(5)	H(114C)	1 367(47)	213(25)	4 829(61)
C(34)	1 596(4)	3 856(2)	-1 412(5)				

petroleum (1:4), and that chosen for study had dimensions $0.25 \times 0.10 \times 0.10$ mm (faces indexed $\langle 001 \rangle$, $\langle \bar{1}10 \rangle$, $\langle 110 \rangle$, and $\langle 0\bar{1}0 \rangle$). Data were collected ($2.9 \leq 2\theta \leq 50^\circ$) as described above but at 293 K. Of the 5 158 unique reflections, 4 757 with $I \geq 4\sigma(I)$ were used for structure refinement after corrections for Lorentz and polarisation effects. A numerical correction was applied for X-ray absorption.

Crystal data. $C_{25}H_{31}BF_3N_6O_3P_2W$, $M = 776.0$, triclinic, $a = 10.495(6)$, $b = 18.532(10)$, $c = 7.875(3)$ Å, $\alpha = 88.71(4)$, $\beta = 105.31(4)$, $\gamma = 98.94(5)^\circ$, $U = 1 459(1)$ Å³, $Z = 2$, $D_c = 1.77$ g cm⁻³, $F(000) = 764$, space group $P\bar{1}$ (no. 2), $\mu(\text{Mo-}K_\alpha) = 46.82$ cm⁻¹.

The structure solution and refinement were similar to that described above for (**2a**), except that all hydrogen atoms were located and refined with fixed isotropic thermal parameters. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.000 15|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density

difference synthesis showed no peaks > 0.8 e Å⁻³. Refinement led to $R = 0.022$ ($R' = 0.023$). Scattering factors, corrections for anomalous dispersion,²² and all calculations²¹ were as for (**2a**). The atomic positional parameters for (**10b**) are given in Table 7.

Acknowledgements

We thank the S.E.R.C. for support and Shell Research Ltd. for a CASE award (to A. P. J.).

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Received 26th September 1985; Paper 5/1679