Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 72.[1] Di- and Tri-metal Compounds prepared from the Alkylidyne Tungsten Complexes $[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}][R = C_6H_4Me\text{-}4$ or Me, $H_2B(pz)_2$ = dihydrobis(pyrazol-1-yl)borate]

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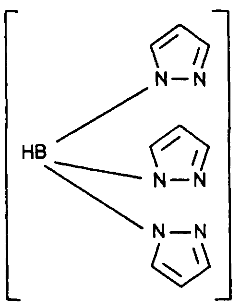
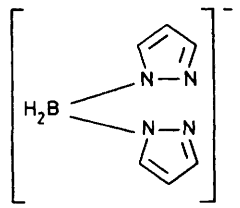
The alkylidynetungsten compounds $[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}]$ [R = C_6H_4Me-4 or Me, $H_2B(pz)_2$ = dihydrobis(pyrazol-1-yl)borate] have been prepared, and used to prepare several complexes containing bonds between tungsten and other transition elements. Thus the compounds $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9\{H_2B(pz)_2\}]$, $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta^5\text{-}C_9H_7)_2\{H_2B(pz)_2\}]$ (η^5-C_9H_7 = indenyl), $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{H_2B(pz)_2\}]$, $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(cod)\{H_2B(pz)_2\}]$ (cod = cyclo-octa-1,5-diene), and $[MW_2(\mu\text{-}CR)_2(CO)_6\{H_2B(pz)_2\}_2]$ (M = Ni or Pt, R = C_6H_4Me-4; M = Pt, R = Me) have been synthesised by treating the appropriate alkylidynetungsten compound with $[Co_2(CO)_8]$, $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$, $[Fe_2(CO)_9]$, or $[M(cod)_2]$ (M = Ni or Pt), respectively. The unsaturated dimetal compound $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{H_2B(pz)_2\}]$ reacts with dppm ($Ph_2PCH_2PPh_2$), RC≡CR (R = Me or Ph), and CH_2N_2 to afford the complexes $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_3\{H_2B(pz)_2\}]$, $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(R)C(R)\}(CO)_6\{H_2B(pz)_2\}]$, and $[FeW\{\mu\text{-}trans\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_6\{H_2B(pz)_2\}]$, respectively. N.m.r. data (^1H, ^{13}C-$\{^1H\}$, ^{31}P-$\{^1H\}$, or ^{195}Pt-$\{^1H\}$) for the new compounds are reported and discussed in relation to the structures proposed.

The uninegative tridentate hydrotris(pyrazol-1-yl)borate anion (**1**) has become a useful ligand for the transition elements.[2] In its co-ordination chemistry (**1**) displays similarities with the two cyclopentadienyl groups $C_5H_5^-$ or $C_5Me_5^-$, particularly the latter.[3,4] In contrast, the dihydrobis(pyrazol-1-yl)borate anion (**2**) is bidentate, and forms complexes akin to those of the acetylacetonato ligand.[2]

We have recently used the potassium salt of (**1**) to prepare the alkylidynetungsten complexes $[W(\equiv CR)(CO)_2\{HB(pz)_3\}]$ [R = C_6H_4Me-4 (**3a**) or Me (**3b**); $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate], and have used these species as precursors for the synthesis of compounds wherein tungsten forms bonds with other transition metals.[5] The W≡C groups present in (**3a**) and (**3b**) combine with co-ordinatively unsaturated metal–ligand fragments to form metal–metal bonds bridged by the alkylidyne fragments. In this respect, (**3a**) and (**3b**) display many similarities with the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)]$ (R = C_6H_4Me-4 or Me; R′ = H or Me).[5d,6,7] However, some differences have been observed in the properties or even the formulations of the products obtained containing the $HB(pz)_3$ ligand, compared with those in which η-$C_5R'_5$ groups are present. These results[5] have prompted us to prepare the new alkylidynetungsten compounds $[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}]$ [R = C_6H_4Me-4 (**3c**) or Me (**3d**)], and to investigate their use as precursors for the synthesis of complexes with metal–metal bonds. The presence in the compounds (**3c**) and (**3d**) of a ligand (**2**) which is less sterically demanding than (**1**), and also having an additional CO group ligating the tungsten atom, might be expected to lead to somewhat different chemistry fom that observed with (**3a**) and (**3b**).



(**1**)



(**2**)

$[W(\equiv CR)(CO)_nL]$

	R	L	*n*
(**3a**)	C_6H_4Me-4	$HB(pz)_3$	2
(**3b**)	Me	$HB(pz)_3$	2
(**3c**)	C_6H_4Me-4	$H_2B(pz)_2$	3
(**3d**)	Me	$H_2B(pz)_2$	3

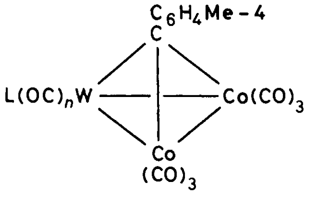
Results and Discussion

Addition of the salt $K[H_2B(pz)_2]$ to thf (tetrahydrofuran) solutions of the compounds $[W(\equiv CR)Br(CO)_4]$ affords the complexes $[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}]$ [R = C_6H_4Me-4 (**3c**) or Me (**3d**)], data for which are given in Tables 1 and 2. Both complexes show two strong carbonyl stretching bands in their i.r. spectra. In the ^{13}C-$\{^1H\}$ n.m.r. spectra there are resonances for the ligated carbon nuclei of the alkylidyne groups at δ 284.5 (**3c**) and 293.9 p.p.m. (**3d**), and these signals may be compared with those in the spectra of (**3a**) and (**3b**) at δ 284.8 and 295.2 p.p.m., respectively.[5a] The ethylidynetungsten complex (**3d**) was found to be thermally relatively unstable. Even in the solid state and stored in a refrigerator it slowly decomposed. Consequently, apart from three reactions described below, its chemistry was not investigated. In contrast, (**3c**) was much more robust and

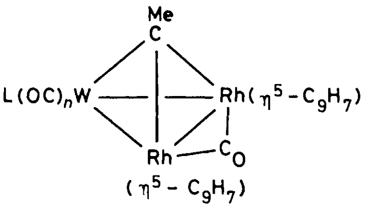
Table 1. Analytical[a] and physical data for the complexes

Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$	Analysis (%) C	H	N
(**3c**) $[W(\equiv CC_6H_4Me\text{-}4)(CO)_3\{H_2B(pz)_2\}]$	Orange	50	1 980vs, 1 888vs	40.2 (39.4)	3.0 (2.9)	11.9 (10.9)
(**3d**) $[W(\equiv CMe)(CO)_3\{H_2B(pz)_2\}]$	Yellow	40	1 976vs, 1 881s	30.2 (29.9)	2.1 (2.5)	12.5 (12.7)
(**4a**) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9\{H_2B(pz)_2\}]$	Green-brown	85	2 078m, 2 037s, 2 024m, 2 007s, 1 993s, 1 964m, 1 904m, 1 842m	34.8 (34.3)	2.5 (1.9)	7.0 (7.0)
(**5a**) $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta^5\text{-}C_9H_7)_2\{H_2B(pz)_2\}]$	Black	66	1 871s(br), 1 792m	40.8 (39.8)	2.5 (2.8)	5.9 (6.2)
(**6a**) $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{H_2B(pz)_2\}]$	Purple	95	2 048vs, 1 987vs, 1 963s, 1 924m, 1 903m, 1 862m	36.1 (36.5)	2.8 (2.3)	8.0 (8.5)
(**7a**) $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_3\{H_2B(pz)_2\}]$	Brown	89	1 953vs, 1 900s, 1 856m, 1 709w	52.3 (52.4)	3.5 (3.8)	6.0 (5.7)
(**8a**) $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}(CO)_6\{H_2B(pz)_2\}]$	Green	90	2 038s, 1 974vs, 1 934m, 1 889m, 1 818m	40.8 (40.5)	3.5 (3.0)	8.2 (7.9)
(**8b**) $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}(CO)_6\{H_2B(pz)_2\}]$	Brown	70	2 051s, 2 019w, 1 978vs, 1 888s, 1 829m	48.7 (48.8)	3.2 (3.0)	6.8 (6.7)
(**9a**) $[FeW\{\mu\text{-}trans\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_6\{H_2B(pz)_2\}]$	Yellow	60	2 051m, 2 036m, 2 006s, 1 977vs, 1 943m, 1 909s, 1 649w	36.8 (37.8)	2.8 (2.5)	7.6 (8.0)
(**12**) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(cod)\{H_2B(pz)_2\}]$	Dark red	73	1 948vs(br), 1 744m(br)	36.8 (36.6)	3.3 (3.3)	7.3 (6.8)
(**13a**) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)_2\{H_2B(pz)_2\}]$	Red-brown	80	1 937s, 1 889s, 1 732m	30.9 (31.9)	3.5 (3.8)	6.4 (6.5)
(**14a**) $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6\{H_2B(pz)_2\}_2]$	Dark red	80	1 951s, 1 923vs, 1 740m	33.4 (33.2)	2.4 (2.5)	9.6 (9.1)
(**14b**) $[PtW_2(\mu\text{-}CMe)_2(CO)_6\{H_2B(pz)_2\}_2]$	Red	84	1 955s, 1 930s, 1 792m	25.3 (24.5)	2.8 (2.1)	11.0 (10.4)
(**14c**) $[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6\{H_2B(pz)_2\}_2]$	Dark red	73	1 970s, 1 946s, 1 787m	36.8 (37.3)	2.7 (2.8)	10.8 (10.2)
(**15a**) $[W(S_2CMe)(CO)_3\{H_2B(pz)_2\}]$	Red	21	1 937vs, 1 847s	26.6 (26.1)	2.7 (2.2)	12.0 (11.1)
(**16a**) $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(PPh_3)\{H_2B(pz)_2\}]$	Brown	50	1 991s, 1 905vs	54.5 (54.3)	4.1 (4.0)	7.1 (7.5)
(**16b**) $[W\{{=}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)\{HB(pz)_3\}]$	Violet	90	1 879vs, 1 723w(br)	42.4 (41.8)	4.3 (4.1)	13.0 (13.3)
(**16c**) $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(PMe_3)\{H_2B(pz)_2\}]$	Orange	70	1 989s, 1 899vs	40.4 (40.3)	4.3 (4.3)	10.2 (9.9)

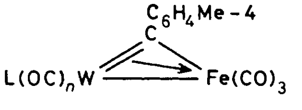
[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2.



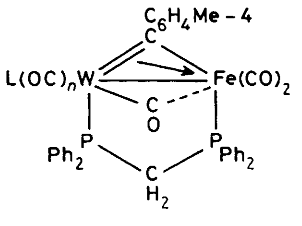
	L	n
(**4a**)	$H_2B(pz)_2$	3
(**4b**)	$HB(pz)_3$	2



	L	n
(**5a**)	$H_2B(pz)_2$	3
(**5b**)	$HB(pz)_3$	2



	L	n
(**6a**)	$H_2B(pz)_2$	3
(**6b**)	$HB(pz)_3$	2



	L	n
(**7a**)	$H_2B(pz)_2$	1
(**7b**)	$HB(pz)_3$	0

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	^{1}H[b,c]	^{13}C[d]
(3c)	2.32 (s, 3 H, Me-4), 6.30 (m, 2 H, $C_3H_3N_2$), 7.09, 7.40 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.64 (m, 3 H, $C_3H_3N_2$), 7.90 (m, 1 H, $C_3H_3N_2$)	284.5 [C≡W, *J*(WC) 189], 224.6 [CO, *J*(WC) 167], 145.3 [$C^1(C_6H_4)$], 144.3, 136.0, 129.3, 129.0 (C_6H_4 and $C_3H_3N_2$), 106.2 ($C_3H_3N_2$), 21.8 (Me-4)
(3d)	2.41 [s, 3 H, Me, *J*(WH) 7], 6.23 (m, 2 H, $C_3H_3N_2$), 7.26 (s, 3 H, $C_3H_3N_2$), 7.63—7.95 (m, 1 H, $C_3H_3N_2$)	293.9 [C≡W, *J*(WC) 189], 222.3 [CO, *J*(WC) 168], 144.4, 135.1, 105.5 ($C_3H_3N_2$), 37.9 (Me)
(4a)	2.21 (s, 3 H, Me-4), 6.03 (m, 2 H, $C_3H_3N_2$), 7.04—7.61 (m, 7 H, C_6H_4 and $C_3H_3N_2$), 7.89 (m, 1 H, $C_3H_3N_2$)	274.1 (μ_3-C), 224.2 (br, WCO), 201.3 (br, CoCO), 148.7—127.9 ($C_3H_3N_2$ and C_6H_4), 106.5 ($C_3H_3N_2$), 21.3 (Me-4)
(5a)	1.05 [t, μ_3-CMe, *J*(RhH) 3], 5.66—6.27 (m, 8 H, C_9H_7 and $C_3H_3N_2$), 6.79—6.88 (m, 8 H, C_9H_7), 7.30 (m, 3 H, $C_3H_3N_2$), 7.81 (m, 1 H, $C_3H_3N_2$)	327.3 [t, μ_3-C, *J*(RhC) *ca.* 40, *J*(WC) 168], 230.5 [WCO, *J*(WC) 162], 217.8 [t, μ-CO, *J*(RhC) *ca.* 100], 140.5, 133.1 ($C_3H_3N_2$), 123.7—112.2 (C_9H_7), 104.5 ($C_3H_3N_2$), 103.4—85.3 (C_9H_7), 38.5 (Me)
(6a)	2.30 (s, 3 H, Me-4), 6.03—6.43 (m, 2 H, $C_3H_3N_2$), 7.20 (m, 7 H, C_6H_4 and $C_3H_3N_2$), 7.79 (m, 1 H, $C_3H_3N_2$)	407.7 [μ-C, *J*(WC) 140], 225.8 [WCO, *J*(WC) 162], 213.9 (FeCO), 147.2 [$C^1(C_6H_4)$], 134.7, 131.2, 128.3, 106.8 (C_6H_4 and $C_3H_3N_2$), 20.5 (Me-4)
(7a)	2.22 (s, 3 H, Me-4), 2.97 (m, 2 H, CH_2), 6.02 (m, 2 H, $C_3H_3N_2$), 6.73—8.01 (m, 28 H, C_6H_4, Ph, and $C_3H_3N_2$)	382.3 (μ-C), 268.1 (μ-CO), 224.2 [WCO, *J*(WC) 165], 220.4 (FeCO), 146.4—105.3 (C_6H_4, Ph, and $C_3H_3N_2$), 59.1 (m, CH_2), 21.3 (Me-4)
(8a)	1.27 (s, 3 H, CMe), 1.50 (s, 3 H, CMe), 2.10 (s, 3 H, Me-4), 6.39 (m, 2 H, $C_3H_3N_2$), 7.26—7.71 (m, 8 H, C_6H_4 and $C_3H_3N_2$)	223.3 [WCO, *J*(WC) 167], 214.4 (FeCO), 147.6—104.5 (C_6H_4, *C*C_6H_4Me-4, and $C_3H_3N_2$), 71.4, 69.5 (*C*Me), 22.4 (Me-4), 16.3, 15.8 (C*Me*)
(8b)	2.29 (s, 3 H, Me-4), 6.21 (m, 2 H, $C_3H_3N_2$), 7.32—7.99 (m, 18 H, C_6H_4, Ph and $C_3H_3N_2$)	224.5 [WCO, *J*(WC) 162], 212.9 (FeCO), 147.2—106.2 (C_6H_4, Ph, *C*C_6H_4Me-4, and $C_3H_3N_2$), 89.6 (*C*Ph), 21.8 (Me-4)
(9a)	2.31 (s, 3 H, Me-4), 3.47 [d, 1 H, CH=C(*H*)C_6H_4Me-4, *J*(HH) 12], 6.24 (m, 2 H, $C_3H_3N_2$), 7.26—8.00 (m, 8 H, C_6H_4 and $C_3H_3N_2$), 8.35 [d, 1 H, C*H*=C(H)C_6H_4Me-4, *J*(HH) 12]	277.8 (μ-CO), 222.3 [WCO, *J*(WC) 140], 213.0 (FeCO), 147.4—101.5 (C_6H_4, *C*H=*C*H, and $C_3H_3N_2$), 21.0 (Me-4)
(12)	2.27 (s, 3 H, Me-4), 2.30 (vbr, 8 H, CH_2), 4.57—5.32 [m, 4 H, CH(cod)], 5.91 (m, 2 H, $C_3H_3N_2$), 6.54, 6.96 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.49 (m, 3 H, $C_3H_3N_2$), 7.87 (m, 1 H, $C_3H_3N_2$)	329.0 [μ-C, *J*(PtC) 797, *J*(WC) 153], 232.4 [CO, *J*(WC) 98], 229.4 [CO, *J*(WC) 160], 224.6 [CO, *J*(WC) 160], 143.1, 142.7, 134.7, 128.5, 127.7, 107.1 (C_6H_4 and $C_3H_3N_2$), 104.4, 94.6 (cod), 20.1 (Me-4)
(13a)	1.19 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 33], 1.60 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 23], 2.20 (s, 3 H, Me-4), 6.15 (m, 2 H, $C_3H_3N_2$), 6.48, 6.81 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.58 (m, 2 H, $C_3H_3N_2$), 7.86 (m, 1 H, $C_3H_3N_2$)	331.4 [d, μ-C, *J*(PC) 54, *J*(PtC) 701], 233.8 [CO, *J*(WC) 161], 144.3 [$C^1(C_6H_4)$], 139.2, 133.9, 127.8, 126.5 (C_6H_4 and $C_3H_3N_2$), 105.1 ($C_3H_3N_2$), 20.4 (Me-4), 18.1 [d, MeP, *J*(PC) 27], 17.0 [d, MeP, *J*(PC) 24]
(14a)	2.29 (s, 6 H, Me-4), 6.25 (m, 4 H, $C_3H_3N_2$), 6.92, 6.99 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 7.65 (m, 6 H, $C_3H_3N_2$), 7.98 (m, 2 H, $C_3H_3N_2$)	299.4 [μ-C, *J*(PtC) 715, *J*(WC) 147], 232.0 [CO, *J*(WC) 75], 229.1 [CO, *J*(WC) 154], 225.0 [CO, *J*(WC) 156], 144.5 [$C^1(C_6H_4)$], 136.2, 135.6, 129.1, 125.7 (C_6H_4 and $C_3H_3N_2$), 106.6 ($C_3H_3N_2$), 21.6 (Me-4)
(14b)	2.95 (s, 3 H, μ-CMe), 6.20 (m, 4 H, $C_3H_3N_2$), 7.67 (m, 6 H, $C_3H_3N_2$), 7.87 (m, 2 H, $C_3H_3N_2$)	307.5 [μ-C, *J*(PtC) 693, *J*(WC) 146], 227.6 [CO, *J*(WC) 160], 142.7, 133.9, 104.6 ($C_3H_3N_2$), 38.6 (Me)
(14c)	2.14 (s, 6 H, Me-4), 6.15 (m, 4 H, $C_3H_3N_2$), 6.97, 7.19 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 7.48 (m, 6 H, $C_3H_3N_2$), 7.82 (m, 2 H, $C_3H_3N_2$)	300.1 [μ-C, *J*(WC) 158], 233.6 [CO, *J*(WC) 158], 224.1 [CO, *J*(WC) 161], 154.5 [$C^1(C_6H_4)$], 142.4, 133.6, 127.7, 122.5 (C_6H_4 and $C_3H_3N_2$), 104.2 ($C_3H_3N_2$), 20.5 (Me-4)
(15a)	2.63 (s, 3 H, Me), 6.26 (m, 2 H, $C_3H_3N_2$), 7.26 (m, 3 H, $C_3H_3N_2$), 8.21 (m, 1 H, $C_3H_3N_2$)	226.6 (*C*SMe), 224.3 (CO), 145.3, 135.2, 105.9 ($C_3H_3N_2$), 42.6 (Me)
(16a)	2.31 (s, 3 H, Me-4), 6.30 (m, 2 H, $C_3H_3N_2$), 7.26 (m, br, 23 H, C_6H_4, Ph, $C_3H_3N_2$)	285.4 [d, C≡W, *J*(PC) 28], 232.1, 226.5 [CO, *J*(WC) 161], 146.5—126.4 (C_6H_4, Ph, $C_3H_3N_2$), 105.4 ($C_3H_3N_2$), 22.1 (Me-4)
(16b)	1.31 [d, 9 H, MeP, *J*(PH) 8], 2.25 (s, 3 H, Me-4), 6.32 (m, 3 H, $C_3H_3N_2$), 7.01 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.44 (m, 4 H, $C_3H_3N_2$), 7.90 (m, 2 H, $C_3H_3N_2$)	230.8 [*C*(C_6H_4Me-4), *J*(WC) 161], 216.5 (C=O), 205.4 (CO), 146.7—127.3 (C_6H_4 and $C_3H_3N_2$), 106.1 ($C_3H_3N_2$), 21.6 (Me-4), 17.8 [d, MeP, *J*(PC) 29]
(16c)	1.54 [d, 9 H, MeP, *J*(PH) 13], 2.33 (s, 3 H, Me-4), 6.30 (m, 2 H, $C_3H_3N_2$), 7.11—7.30 (m, 4 H, C_6H_4), 7.58 (m, 3 H, $C_3H_3N_2$), 7.73 (m, 1 H, $C_3H_3N_2$)	298.3 [d, C≡W, *J*(PC) 29], 228.9 [CO, *J*(WC) 161], 224.5 [CO, *J*(WC) 161], 147.4—126.5 (C_6H_4 and $C_3H_3N_2$), 106.1 ($C_3H_3N_2$), 22.1 (Me-4), 17.4 [d, MeP, *J*(PC) 30]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures. [b] Measured in $CDCl_3$. [c] Proton resonances for BH_2 groups not observed. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 p.p.m.), with measurements in CD_2Cl_2–CH_2Cl_2.

could be used as a precursor to several compounds containing metal–metal bonds.

At room temperature in toluene, (**3c**) and $[Co_2(CO)_8]$ gave the trimetal compound $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9\{H_2B(pz)_2\}]$ (**4a**) in high yield. This product is closely related to the complex $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{HB(pz)_3\}]$ (**4b**) obtained previously from (**3a**) and $[Co_2(CO)_8]$.[5a] Both compounds belong to a large class of species containing a μ_3-CCo_2W core structure.[1,7,8] The ^{13}C-{^{1}H} n.m.r. spectrum of (**4a**) (Table 2) shows a characteristic resonance for the triply bridging carbon nucleus at δ 274.1 p.p.m. In the spectrum of (**4b**) the corresponding peak is at δ 265.7 p.p.m. The i.r. spectrum of (**4a**) reveals eight CO stretching bands, suggesting the presence of stereoisomers in solution, as found with the other compounds of this structural type.[7,8]

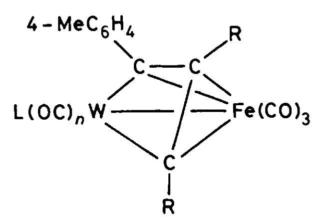
Compound (**3d**) reacts with either of the two rhodium complexes $[RhL_2(\eta^5\text{-}C_9H_7)]$ (L = CO or C_2H_4, C_9H_7 = indenyl) to afford the trimetal species $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta^5\text{-}C_9H_7)_2\{H_2B(pz)_2\}]$ (**5a**). The analogue $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2\{HB(pz)_3\}]$ (**5b**) has been prepared from (**3b**) and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$.[5a] The i.r. spectrum of (**5a**) shows a band for the bridging carbonyl group at 1 792 cm^{-1}, and there is a similar peak in the spectrum of (**5b**) at 1 799 cm^{-1}. The two compounds (**5**) have similar ^{13}C-{^{1}H} n.m.r. spectra with characteristic resonances for the μ_3-C [δ 327.3 (**5a**) and 329.9 p.p.m. (**5b**)] and μ-CO [δ 217.8 (**5a**) and 220.4 p.p.m. (**5b**)] groups. These signals occur as triplets, due to ^{103}Rh–^{13}C coupling.

The reaction between (**3c**) and [$Fe_2(CO)_9$] yields the dimetal compound [FeW(μ-CC_6H_4Me-4)$(CO)_6${$H_2B(pz)_2$}] (**6a**). It has been previously found that (**3a**) and [$Fe_2(CO)_9$] afford the related complex [FeW(μ-CC_6H_4Me-4)$(CO)_5${$HB(pz)_3$}] (**6b**), the structure of which has been established by *X*-ray diffraction.[5b] Both compounds (**6**) are electronically unsaturated 32-valence-electron dimetal species, and other iron–tungsten members of this type of complex include the anions [FeW(μ-CR)$(CO)_5$(η^5-$C_2B_9H_9Me_2$)]$^-$ (R = C_6H_4Me-2 or $C_6H_3Me_2$-2,6),[9] and the neutral compounds [FeW(μ-CC_6H_4-Me-4)$(CO)_5$(η-$C_5R'_5$)] (R′ = H[5b] or Me[7b]). The compound [FeW(μ-CC_6H_4Me-4)$(CO)_5$(η-C_5H_5)], however, is unstable, decomposing above −20 °C, while its analogue containing the η-C_5Me_5 group in the presence of CO exists in equilibrium with the electronically saturated complex [FeW(μ-CC_6H_4Me-4)-$(CO)_6$(η-C_5Me_5)]. There is evidence from spectroscopic data that in solution (**6b**) will add a CO molecule, but no product of formulation [FeW(μ-CC_6H_4Me-4)$(CO)_6${$HB(pz)_3$}] can be isolated.[5b] Moreover, we obtained no evidence for addition of CO to (**6a**). It is thus apparent that the groups (**1**) and (**2**) when substituents on tungsten in the molecules (**3a**) and (**3c**) promote the ability of these species to bond a 14-electron $Fe(CO)_3$ fragment. This suggests that the W≡C groups in (**3a**) and (**3c**) can function formally as four-electron donors in the compounds (**6**), as discussed previously.[5b] The ligands (**1**) and (**2**) are strong σ-electron donors, and this may result in an enhancement of the donor ability of the W≡C groups allowing them to function as four- rather than two-electron donors. However, steric effects may also have a role in determining whether $Fe(CO)_3$ or $Fe(CO)_4$ adducts are formed.

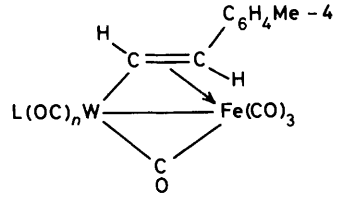
It is a characteristic feature of the ^{13}C-{^{1}H} n.m.r. spectra of the 32-valence-electron iron–tungsten compounds, mentioned above, that the resonances for the bridging alkylidyne carbon nuclei are *ca.* 80 p.p.m. more deshielded than those of the 34-valence-electron complexes. Indeed this property can be used for diagnostic purposes. Thus in the ^{13}C-{^{1}H} n.m.r. spectrum of compound (**6a**) (Table 2) the peak for the μ-C group occurs at δ 407.7 p.p.m., to be compared with the correspondingly deshielded signal in the spectrum of (**6b**) at 408.8 p.p.m.[5b] It is also a feature of these unsaturated dimetal compounds that they are purple in colour.

We have previously reported[5b] several reactions of (**6b**), and in order to establish whether or not similar products are obtained from (**6a**) and the same reagents the following studies have been carried out. Treatment of (**6a**) with dppm ($Ph_2PCH_2PPh_2$) affords [FeW(μ-CC_6H_4Me-4)(μ-CO)(μ-dppm)-$(CO)_3${$H_2B(pz)_2$}] (**7a**), an analogue of [FeW(μ-CC_6H_4Me-4)(μ-CO)(μ-dppm)$(CO)_2${$HB(pz)_3$}] (**7b**) prepared from (**6b**) and dppm. The spectroscopic properties of (**7a**) reveal that it is structurally similar to (**7b**). Thus the i.r. spectrum of the former shows a CO band at 1 709 cm^{-1}, corresponding to a strongly semi-bridging or bridging carbonyl group, while the latter has a similar band in its spectrum at 1 718 cm^{-1}. In the ^{13}C-{^{1}H} n.m.r. spectrum of (**7a**) the resonance for the μ-C nucleus occurs at δ 382.3 p.p.m., while in the spectrum of (**7b**) the signal is at 377.2 p.p.m.[5b] The ^{31}P-{^{1}H} n.m.r. spectrum of (**7a**) has peaks at δ 24.5 [d, *J*(PP) 78, *J*(WP) 327] and 59.3 p.p.m. [d, *J*(PP) 78 Hz]. A very similar pattern of signals is observed in the ^{31}P-{^{1}H} n.m.r. spectrum of (**7b**): δ 23.6 [d, *J*(PP) 71, *J*(WP) 325] and 52.5 p.p.m. [d, *J*(PP) 71 Hz]. The observation of ^{183}W–^{31}P satellite peaks associated with the resonances at δ 24.5 (**7a**) and 23.6 p.p.m. (**7b**) indicates that these signals are due to the phosphorus atoms ligating the tungsten centres in these molecules.

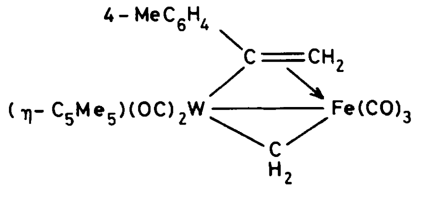
Compound (**6a**) reacts at room temperature with the alkynes RC≡CR (R = Me or Ph) to give the complexes [FeW{μ-



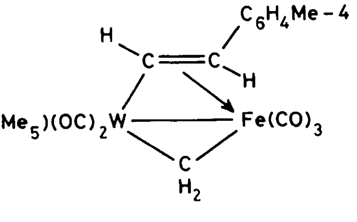
	R	L	n
(**8a**)	Me	$H_2B(pz)_2$	3
(**8b**)	Ph	$H_2B(pz)_2$	3
(**8c**)	Me	$HB(pz)_3$	2
(**8d**)	Ph	$HB(pz)_3$	2



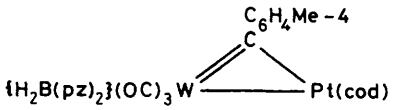
	L	n
(**9a**)	$H_2B(pz)_2$	3
(**9b**)	η-C_5Me_5	2



(**10**)



(**11**)



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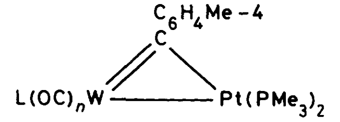
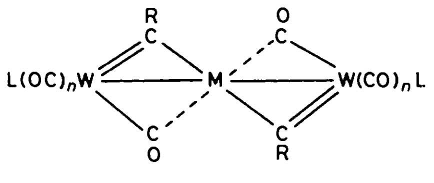
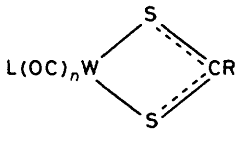


	L	*n*
(13a)	$H_2B(pz)_2$	3
(13b)	$HB(pz)_3$	2



	M	R	L	*n*
(14a)	Pt	C_6H_4Me-4	$H_2B(pz)_2$	2
(14b)	Pt	Me	$H_2B(pz)_2$	2
(14c)	Ni	C_6H_4Me-4	$H_2B(pz)_2$	2
(14d)	Pt	C_6H_4Me-4	$HB(pz)_3$	1
(14e)	Pt	Me	$HB(pz)_3$	1



	R	L	*n*
(15a)	Me	$H_2B(pz)_2$	3
(15b)	C_6H_4Me-4	$\eta-C_5H_5$	2

$C(C_6H_4Me-4)C(R)C(R)\}(CO)_6\{H_2B(pz)_2\}]$ [R = Me (**8a**) or Ph (**8b**)]. Similar products have been prepared from reactions between (**6b**) and the two alkynes.[10] Data for compounds (**8a**) and (**8b**) are given in Tables 1 and 2, and are in accord with the structures proposed. The formation of (**8a**) and (**8b**) results from a coupling of the *p*-tolylmethylidyne group with the alkyne at the dimetal centre. Several similar reactions at di- or tri-metal centres have been observed previously.[11]

The reaction between (**6a**) and CH_2N_2 was also studied, and found to give the bridged-vinyl complex $[FeW\{\mu\text{-}trans\text{-}CH{=}C(H)C_6H_4Me-4\}(\mu-CO)(CO)_6\{H_2B(pz)_2\}]$ (**9a**), data for which are listed in Tables 1 and 2. The corresponding reaction between (**6b**) and CH_2N_2 gave in low yield a very complex mixture of products which could not be separated and characterised. However, the compound $[FeW\{\mu\text{-}trans\text{-}CH{=}C(H)C_6H_4Me-4\}(\mu-CO)(CO)_5(\eta-C_5Me_5)]$ (**9b**), possessing the same two ligands bridging an Fe–W bond, is one of three products of the reaction between CH_2N_2 and the unsaturated dimetal compound $[FeW(\mu-CC_6H_4Me-4)(CO)_5(\eta-C_5Me_5)]$, the others being $[FeW\{\mu-C(C_6H_4Me-4){=}CH_2\}(\mu-CH_2)(CO)_5(\eta-C_5Me_5)]$ (**10**) and $[FeW\{\mu\text{-}trans\text{-}CH{=}C(H)\text{-}C_6H_4Me-4\}(\mu-CH_2)(CO)_5(\eta-C_5Me_5)]$ (**11**).[7b] Interestingly, with $[FeW(\mu-CC_6H_4Me-4)(CO)_5(\eta-C_5Me_5)]$ and an excess of CH_2N_2 the major product is (**10**), whereas (**9a**) was the only product isolated in the corresponding reaction of (**6a**).

The presence of the *trans*-$CH{=}C(H)C_6H_4Me-4$ group in (**9a**) is revealed by the ^1H n.m.r. spectrum (Table 2). Resonances corresponding in intensity to one proton are seen as doublets [*J*(HH) 12 Hz] at δ 3.47 and 8.35. The *J*(HH) value corresponds to that expected for a *trans*-CH=CH arrangement.[12] The corresponding signals in the ^1H n.m.r. spectrum of (**9b**) are at δ 3.85 and 8.14, with *J*(HH) 13 Hz.[7b]

Reactions of (**3c**) with zerovalent platinum complexes were next investigated. Treatment of (**3c**) in light petroleum with 1 equivalent of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene), in the presence of ethylene to labilise the cod groups, gave the compound $[PtW(\mu-CC_6H_4Me-4)(CO)_3(cod)\{H_2B(pz)_2\}]$ (**12**). Addition of 2 equivalents of PMe_3 to the latter afforded the complex $[PtW(\mu-CC_6H_4Me-4)(CO)_3(PMe_3)_2\{H_2B(pz)_2\}]$ (**13a**), a species which may also be prepared from the reaction between (**3c**) and $[Pt(C_2H_4)(PMe_3)_2]$. Similarly, the cod ligand present in (**12**) may also be displaced by adding 1 equivalent of (**3c**), thereby yielding the trimetal complex $[PtW_2(\mu-CC_6H_4Me-4)_2(CO)_6\{H_2B(pz)_2\}_2]$ (**14a**). The latter may be obtained directly from $[Pt(cod)_2]$ by addition of 2 equivalents of (**3c**) to ethylene-saturated light petroleum solutions of the platinum reagent. The compound $[PtW_2(\mu-CMe)_2(CO)_6\{H_2B(pz)_2\}_2]$ (**14b**) was similarly prepared from (**3d**) and $[Pt(cod)_2]$, using a 2:1 ratio of reactants. Treatment of $[Ni(cod)_2]$ with 2 equivalents of (**3c**) also yielded a trimetal compound $[NiW_2(\mu-CC_6H_4Me-4)_2(CO)_6\{H_2B(pz)_2\}_2]$ (**14c**).

The various compounds (**12**), (**13**), and (**14a**)—(**14c**) were characterised by microanalysis and spectroscopic data (Tables 1 and 2). Formation of (**12**) was of interest, because in previous work involving reactions between $[Pt(cod)_2]$ and the various alkylidynetungsten compounds $[W(\equiv CR)(CO)_2(\eta-C_5R'_5)]$ (R = alkyl or aryl, R′ = H or Me)[13] or $[W(\equiv CR)(CO)_2\{HB(pz)_3\}]$ (**3a** or **3b**)[5c] the products have always been trimetal species of structural type (**14**), even when the reactants were employed in 1:1 ratio, or when an excess of $[Pt(cod)_2]$ was used. Formation of the compounds (**14a**)—(**14c**) was not unexpected when 2 equivalents of the appropriate reagent (**3c**) or (**3d**) were used with $[M(cod)_2]$ (M = Pt or Ni) in view of the large number of complexes of this type now known,[13] including the species (**14d**) and (**14e**), obtained from (**3a**) and (**3b**), respectively.[5c] The $^{13}C-\{^1H\}$ and $^{195}Pt-\{^1H\}$ n.m.r. data for related compounds are very similar leaving little doubt of their structural identity. Thus for (**14b**), the $^{13}C-\{^1H\}$ n.m.r. resonance for the μ-C nuclei is seen at δ 307.5 p.p.m., with typical $^{195}Pt-^{13}C$ and $^{183}W-^{13}C$ couplings of 693 and 146 Hz, respectively. The corresponding data for **(14e)** are δ 310.3 p.p.m. [*J*(PtC) 700, *J*(WC) 153 Hz]. Moreover, the ^{195}Pt-{^{1}H} n.m.r. spectrum of **(14b)** has a single resonance at δ 1 461 p.p.m. with *J*(WPt) 117 Hz, which may be compared with a signal in the spectrum of **(14e)** at δ 1 468 p.p.m., with *J*(WPt) also 117 Hz. The structure of **(14e)** has been established by an *X*-ray diffraction study.[5c]

Interestingly, the ^{195}Pt-{^{1}H} n.m.r. spectrum of compound **(12)** showed weak signals due to the presence of **(14a)**, while that of **(13a)** revealed that **(14a)** predominated in solution under the conditions of measurement. These observations reveal a tendency for **(12)** and **(13a)** to disproportionate in solution. Indeed the propensity of species of type **(13)** to decompose to the more stable trimetal compounds of type **(14)** has been discussed earlier.[5c] The ^{31}P-{^{1}H} n.m.r. spectrum of **(13a)** was structurally informative showing resonances for a *cis*-$\mathrm{Pt(PMe_3)_2}$ group at δ −15.1 [d, *J*(PP) 12, *J*(PtP) 3 833] and −19.9 p.p.m. [d, *J*(PP) 12, *J*(PtP) 2 851 Hz]. The corresponding data for the structurally related complex **(13b)** are δ −12.1 [d, *J*(PP) 10, *J*(PtP) 3 793] and −20.9 [d, *J*(PP) 10, *J*(PtP) 2 849 Hz].[5a]

During the course of the work described herein, the reaction of **(3d)** with sulphur was investigated and found to give $\mathrm{[W(S_2CMe)(CO)_3\{H_2B(pz)_2\}]}$ **(15a)**, the C≡W bond in **(3d)** having been cleaved to form a dithiocarboxylate ligand. The corresponding reaction of **(3b)** with sulphur has not been studied, but $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]}$ undergoes a similar reaction to yield $\mathrm{[W(S_2CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]}$ **(15b)**.[14] The ^{13}C-{^{1}H} n.m.r. spectrum of **(15a)** (Table 2) shows the absence of a resonance due to a W≡C nucleus. The peaks at δ 224.3 and 226.6 were of relative intensity 3:1 and are therefore assigned to the CO and CS groups, respectively.

Reactions of the compounds $\mathrm{[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]}$ (R = alkyl or aryl) with tertiary phosphines have been extensively studied.[8b,15] With 1 equivalent of the phosphine, the ketenyl complexes $\mathrm{[\overline{W\{=C(R)C}(O)\}(CO)(PR'_3)(\eta\text{-}C_5H_5)]}$ (R′ = alkyl or aryl) are formed. With $\mathrm{PMe_3}$ and $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]}$ the compound $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta\text{-}C_5H_5)]}$ is also produced in a side reaction.[15] In view of these results it was of interest to establish whether the alkylidynetungsten compounds **(3)** react with tertiary phosphines in a similar manner. No reaction was observed between **(3a)** and $\mathrm{PPh_3}$, perhaps because of the combined steric demands of the ligand **(1)** and the substrate phosphine. In contrast, compound **(3c)**, containing the less sterically demanding ligand **(2)**, reacts with $\mathrm{PPh_3}$ to afford $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(PPh_3)\{H_2B(pz)_2\}]}$ **(16a)**. A CO group in **(3c)** is replaced by $\mathrm{PPh_3}$ but a ketenyl complex analogous to those obtained from the compound $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]}$ is not formed.

Although **(3a)** was inert to $\mathrm{PPh_3}$ (cone angle 145°), it reacts with $\mathrm{PMe_3}$ (cone angle 118°) to give an η^2-ketenyl complex $\mathrm{[\overline{W\{=C(C_6H_4Me\text{-}4)C}(O)\}(CO)(PMe_3)\{HB(pz)_3\}]}$ **(16b)**. In contrast, **(3d)** reacts with $\mathrm{PMe_3}$ to give the phosphine complex $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(PMe_3)\{H_2B(pz)_2\}]}$ **(16c)** rather than a ketenyl derivative. It may well be that in this reaction, and also in the synthesis of **(16a)**, an η^2-ketenyl complex is initially formed, which subsequently releases carbon monoxide from the $\mathrm{\overline{W=C(C_6H_4Me\text{-}4)C}(O)}$ group.[15] Whatever the pathway by which these reactions proceed it appears that the nature of the final product is dependent on whether the tungsten is ligated by a $\mathrm{H_2B(pz)_2}$ or a $\mathrm{HB(pz)_3}$ group, and since in the former situation an additional carbonyl group is bonded to the tungsten this feature also may be crucial in determining the nature of the products formed.

The results described in this paper show that the alkylidynetungsten complexes containing the ligand **(2)** can be used to prepare a variety of compounds containing heteronuclear metal–metal bonds. This is especially valid for **(3c)** which is thermally more stable than **(3d)**. The nature of the products obtained from **(3c)** and **(3d)** is in general similar to those previously prepared from **(3a)** or **(3b)** and the low-valent metal compounds. However, some differences are seen as in the isolation of **(12)**. Moreover, species containing the ligand **(2)** appear to be more reactive than those containing **(1)**. This is well illustrated in the reactions of the complexes **(6)** with alkynes. Compounds **(8a)** and **(8b)** are formed in reactions at room temperature, whereas in the preparation of **(8c)** and **(8d)** reflux conditions are required.

Experimental

The experimental techniques used, and the instrumentation employed in spectroscopic measurements, have been given earlier.[5] The compounds $\mathrm{[W(\equiv CR)Br(CO)_4]}$[16] and $\mathrm{K[H_2B(pz)_2]}$[17] were prepared by methods described previously. Light petroleum refers to that fraction of b.p. 40—60 °C. Alumina used in chromatography was B.D.H. aluminium oxide (Brockman activity II), and Florisil used for the same purpose was Aldrich (100—200 mesh). Proton-decoupled ^{31}P and ^{195}Pt n.m.r. measurements were made on $\mathrm{CDCl_3}$ solutions, unless otherwise stated, and chemical shifts are to high frequency of 85% $\mathrm{H_3PO_4}$ (external) and $\Xi(^{195}\mathrm{Pt})$ = 21.4 MHz, respectively. Analytical and other data for the new complexes are given in Tables 1 and 2.

Preparation of the Compounds.—$\mathrm{[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}]}$ (R = $\mathrm{C_6H_4Me}$-4 or Me). (*i*) Solid $\mathrm{K[H_2B(pz)_2]}$ (1.30 g, 7.0 mmol) was added to a thf (50 cm^3) solution of $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]}$ (2.50 g, 6.20 mmol) at −20 °C, and the mixture was stirred for 15 h. Solvent was removed *in vacuo*, and the brown residue was dissolved in $\mathrm{CH_2Cl_2}$ (10 cm^3) and placed on top of a Florisil packed chromatography column (4 × 15 cm). Elution with $\mathrm{CH_2Cl_2}$–light petroleum (1:1) removed an orange eluate. Removal of solvent *in vacuo* from the latter afforded orange *microcrystals* of $\mathrm{[W(\equiv CC_6H_4Me\text{-}4)(CO)_3\{H_2B(pz)_2\}]}$ **(3c)** (1.60 g).

(*ii*) Similarly, a mixture of $\mathrm{[W(\equiv CMe)Br(CO)_4]}$ (5.0 g, 12.4 mmol) and $\mathrm{K[H_2B(pz)_2]}$ (2.40 g, 12.9 mmol) in thf (60 cm^3) at −20 °C was stirred for 5 h. Removal of solvent *in vacuo*, dissolving the residue in $\mathrm{CH_2Cl_2}$ (10 cm^3), and chromatography on Florisil at −20 °C, eluting with $\mathrm{CH_2Cl_2}$–light petroleum (2:1), gave a yellow eluate. Removal of solvent *in vacuo* from the latter yielded yellow *microcrystals* of $\mathrm{[W(\equiv CMe)(CO)_3\{H_2B(pz)_2\}]}$ **(3d)** (2.20 g). This complex is thermally unstable, turning green and finally black, even when stored under nitrogen at *ca.* −10 °C.

Tungsten–cobalt and -rhodium compounds. (*i*) Solid $\mathrm{[Co_2(CO)_8]}$ (0.10 g, 0.29 mmol) was added to a toluene (5 cm^3) solution of **(3c)** (0.12 g, 0.29 mmol), and the mixture was stirred at room temperature for 3 h. Solvent was removed *in vacuo*, and the residue was dissolved in $\mathrm{CH_2Cl_2}$ (5 cm^3) and chromatographed on an alumina column (3 × 10 cm). Elution with $\mathrm{CH_2Cl_2}$–light petroleum (1:3), followed by removal of solvent *in vacuo*, gave green-brown *microcrystals* of $\mathrm{[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9\{H_2B(pz)_2\}]}$ **(4a)** (0.20 g).

(*ii*) Solid compound **(3d)** (0.06 g, 0.20 mmol) was added to a toluene (20 cm^3) solution of $\mathrm{[Rh(CO)_2(\eta^5\text{-}C_9H_7)]}$ {0.10 g, 0.20 mmol; prepared *in situ* by treating $\mathrm{[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]}$ with CO gas}. The mixture was refluxed (1 h) under nitrogen. Solvent was removed *in vacuo*. The black residue was dissolved in $\mathrm{CH_2Cl_2}$ (5 cm^3) and chromatographed on an alumina column (4 × 15 cm), eluting with $\mathrm{CH_2Cl_2}$–light petroleum (1:4). Removal of solvent *in vacuo* yielded black *microcystals* of $\mathrm{[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta^5\text{-}C_9H_7)_2\{H_2B(pz)_2\}]}$ **(5a)** (0.11 g). This product may also be obtained in *ca.* 60% yield by refluxing $\mathrm{[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]}$ with **(3d)** in toluene.

Iron–tungsten compounds. (*i*) A Et_2O (50 cm^3) solution of compound **(3c)** (0.25 g, 0.50 mmol) was treated with $[Fe_2(CO)_9]$ (0.22 g, 1.0 mmol), and the mixture was stirred for 1 h at room temperature. Solvent was removed *in vacuo*, and the purple residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on a Florisil column (4 × 15 cm). Elution with CH_2Cl_2–light petroleum (1:5) gave a purple eluate, from which solvent was removed *in vacuo* affording *microcrystals* of $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{H_2B(pz)_2\}]$ **(6a)** (0.25 g).

(*ii*) A CH_2Cl_2 (10 cm^3) solution of compound **(6a)** (0.05 g, 0.08 mmol) was treated with dppm (0.02 g, 0.08 mmol), and the mixture was stirred for 4 h. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (1:2) followed by removal of solvent from the brown eluate gave a brown solid, which on addition of CH_2Cl_2–light petroleum (1:6) and cooling to −20 °C gave *microcrystals* of $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_3\{H_2B(pz)_2\}]$ **(7a)** (0.07 g). Phosphorus-31 n.m.r. (in CD_2Cl_2): δ 24.5 [d, WP, *J*(PP) 78, *J*(WP) 327] and 59.3 p.p.m. [d, FeP, *J*(PP) 78 Hz].

(*iii*) A light petroleum (20 cm^3) solution of compound **(6a)** (0.05 g, 0.08 mmol) and $MeC{\equiv}CMe$ (7.66 mmol) was stirred at room temperature for 6 h. A green precipitate was removed by filtration and crystallised from CH_2Cl_2–light petroleum (*ca.* 15 cm^3, 1:2) to give *crystals* of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}(CO)_6\{H_2B(pz)_2\}]$ **(8a)** (0.05 g).

A mixture of **(6a)** (0.15 g, 0.24 mmol) and $PhC{\equiv}CPh$ (0.05 g, 0.30 mmol) in Et_2O (50 cm^3) was stirred at room temperature for 15 h. After removal of solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on an alumina column (3 × 15 cm). Elution with CH_2Cl_2–light petroleum (1:3) removed a brown band which, after removal of solvent *in vacuo*, gave brown *microcrystals* of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}(CO)_6\{H_2B(pz)_2\}]$ **(8b)** (0.14 g).

(*iv*) An Et_2O (10 cm^3) solution of compound **(6a)** (0.10 g, 0.16 mmol) was treated with a large excess of CH_2N_2. After stirring the mixture for 1 h, solvent was removed *in vacuo*, and the yellow residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on alumina, using CH_2Cl_2–light petroleum (1:3) as eluant. A yellow fraction was collected which after removal of solvent *in vacuo* gave yellow *microcrystals* of $[FeW\{\mu\text{-}trans\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_6\{H_2B(pz)_2\}]$ **(9a)** (0.07 g).

Platinum–tungsten complexes. (*i*) A light petroleum (25 cm^3) solution of compound **(3c)** (0.20 g, 0.39 mmol) was added to a solution of $[Pt(cod)_2]$ (0.39 mmol) in the same solvent (50 cm^3), saturated with ethylene, and the mixture was stirred for 20 min at 0 °C. Solvent was removed *in vacuo*, and the dark red residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on alumina at *ca.* 10 °C. Elution with CH_2Cl_2–light petroleum (1:1) gave a red-brown eluate, which after removal of solvent *in vacuo* gave dark red *microcrystals* of $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(cod)\{H_2B(pz)_2\}]$ **(12)** (0.23 g). Platinum-195 n.m.r.: δ 619 p.p.m.

(*ii*) A light petroleum (100 cm^3) solution of compound **(3c)** (0.20 g, 0.39 mmol) was added with stirring to a light petroleum (10 cm^3) solution of $[Pt(C_2H_4)(PMe_3)_2]$ (0.39 mmol) at 0 °C. The platinum complex was prepared *in situ* by treating an ethylene-saturated light petroleum (10 cm^3) solution of $[Pt(cod)_2]$ with 2 equivalents (0.77 mmol, 8 μl) of PMe_3. The reactants were stirred for 1 h at 0 °C. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on alumina at *ca.* 10 °C. Elution with CH_2Cl_2–light petroleum (1:4) gave a brown fraction. Removal of solvent *in vacuo* at *ca.* −20 °C afforded red-brown *microcrystals* of $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)_2\{H_2B(pz)_2\}]$ **(13a)** (0.21 g). Crystals may be obtained from Et_2O–light petroleum (10 cm^3, 1:1) at *ca.* −20 °C. Phosphorus-31 n.m.r.: δ −15.1 [d, *J*(PP) 12, *J*(PtP) 3 833] and −19.9 [d, *J*(PP) 12, *J*(PtP) 2 851 Hz].

Compound **(13a)** may also be prepared by adding 2 equivalents of PMe_3 to **(12)** in CH_2Cl_2 solution at 0 °C.

(*iii*) A CH_2Cl_2 (10 cm^3) solution of compound **(12)** (0.06 g, 0.12 mmol) was treated with **(3c)** (0.10 g, 0.12 mmol), and the mixture was stirred for 30 min at room temperature. The solution was reduced in volume to *ca.* 5 cm^3, and then chromatographed on an alumina column (4 × 15 cm). Elution with CH_2Cl_2–light petroleum (1:4) gave a dark red fraction from which solvent was removed *in vacuo* to yield dark red *microcrystals* of $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6\{H_2B(pz)_2\}_2]$ **(14a)** (0.12 g).

Alternatively, **(3c)** (0.11 g, 0.21 mmol) in light petroleum (15 cm^3) was added to $[Pt(cod)_2]$ (0.04 g, 0.10 mmol) in the same solvent (10 cm^3) saturated with ethylene at 0 °C. The mixture was stirred for *ca.* 30 min at 0 °C. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2, and the solution chromatographed on alumina as described above to give **(14a)** (0.09 g, 63%). Platinum-195 n.m.r.: δ 1 454 p.p.m. [*J*(WPt) 117 Hz].

(*iv*) Similarly, 2 equivalents of compound **(3d)** (0.10 g, 0.22 mmol), suspended in light petroleum (60 cm^3), were added to 1 equivalent of an ethylene-saturated light petroleum (20 cm^3) solution of $[Pt(cod)_2]$ (0.04 g, 0.10 mmol). After stirring for 30 min, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (1:1) afforded a red fraction, which after removal of solvent *in vacuo* afforded red *microcrystals* of $[PtW_2(\mu\text{-}CMe)_2(CO)_6\{H_2B(pz)_2\}_2]$ **(14b)** (0.10 g). The product may be crystallised from Et_2O–light petroleum (20 cm^3, 1:1) at *ca.* −20 °C. Platinum-195 n.m.r.: δ 1 461 p.p.m. [*J*(WPt) 117 Hz].

$[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6\{H_2B(pz)_2\}_2]$. Solid $[Ni(cod)_2]$ (0.05 g, 0.24 mmol) was added to a thf (20 cm^3) solution of **(3c)** (0.25 g, 0.48 mmol), and the mixture was stirred for 2 h. Solvent was removed *in vacuo*, and the dark red residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (1:4) gave a red eluate, from which was obtained, after removal of solvent *in vacuo*, red *microcrystals* of $[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6\{H_2B(pz)_2\}_2]$ **(14c)** (0.19 g), recrystallised from Et_2O–light petroleum (15 cm^3, 1:2) at *ca.* −20 °C.

Reaction of $[W({\equiv}CMe)(CO)_3\{H_2B(pz)_2\}]$ *with Sulphur.*—Sulphur (0.03 g, 0.10 mmol) was added to a suspension of compound **(3d)** (0.10 g, 0.23 mmol) in thf (15 cm^3), and the mixture was refluxed for 90 min under nitrogen. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on an alumina column (4 × 15 cm). Elution with CH_2Cl_2—light petroleum (1:1) gave an orange fraction which, following removal of solvent *in vacuo*, gave deep red *microcrystals* of $[W(S_2CMe)(CO)_3\{H_2B(pz)_2\}]$ **(15a)** (0.03 g).

Reactions of Alkylidynetungsten Compounds with Tertiary Phosphines.—(*i*) A CH_2Cl_2 (15 cm^3) solution of compound **(3c)** (0.15 g, 0.29 mmol) was treated with PPh_3, and the mixture stirred for *ca.* 18 h. Solvent was removed *in vacuo*, and the brown residue was washed with Et_2O–light petroleum (3 × 5 cm^3, 1:2), dissolved in CH_2Cl_2 (5 cm^3), and chromatographed on an alumina column (2.5 × 15 cm). After eluting with CH_2Cl_2–light petroleum (2:1), and removal of solvent *in vacuo* from the brown eluate, *microcrystals* of $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)\{H_2B(pz)_2\}]$ **(16a)** (0.11 g) were obtained. Phosphorus-31 n.m.r.: δ −16.4 p.p.m. [*J*(WP) 286 Hz].

(*ii*) A CH_2Cl_2 (10 cm^3) solution of compound **(3a)** (0.12 g, 0.24 mmol) was treated with PMe_3 (25 μl, 0.24 mmol), and the mixture was stirred at room temperature for 24 h. After reduction in volume to *ca.* 5 cm^3, the solution was chromatographed on alumina, eluting with CH_2Cl_2–light petroleum (1:5). Removal of solvent *in vacuo* from a violet eluate afforded *microcrystals* of $[\overline{\mathrm{W}\{=\mathrm{C}(\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}4)\mathrm{C}}(\mathrm{O})\}\text{-}(\mathrm{CO})(\mathrm{PMe}_3)\{\mathrm{HB}(\mathrm{pz})_3\}]$ (**16b**) (0.13 g). Phosphorus-31 n.m.r.: δ −12.9 p.p.m. [*J*(WP) 342 Hz].

(*iii*) Similarly, compound (**3c**) (0.14 g, 0.26 mmol) in CH_2Cl_2 (15 cm^3) with PMe_3 (30 μl, 0.26 mmol) gave, after chromatography on a Florisil column and crystallisation from CH_2Cl_2–Et_2O (20 cm^3, 1:5) at *ca.* −20 °C, *microcrystals* of $[\mathrm{W}(\equiv\mathrm{CC}_6\mathrm{H}_4\mathrm{Me}\text{-}4)(\mathrm{CO})_2(\mathrm{PMe}_3)\{\mathrm{H}_2\mathrm{B}(\mathrm{pz})_2\}]$ (**16c**) (0.10 g). Phosphorus-31 n.m.r.: δ −12.6 p.p.m. [*J*(WP) 340 Hz].

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