Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 60.[1] Di- and Tri-metal Compounds prepared from the Metal Alkylidyne Complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5Me_5)]$ (R = Me or C_6H_4Me-4) and $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$ [M = Mo, R = C_6H_4Me-4; M = W, R = Me; $HB(pz)_3$ = Hydrotris(pyrazol-1-yl)borate]

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The metal alkylidyne complexes $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$, and $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ [M = Cr or Mo, $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate] have been prepared. These species, and the previously reported compounds $[W(\equiv CR)(CO)_2L]$ [R = Me, L = $HB(pz)_3$; R = C_6H_4Me-4, L = $\eta\text{-}C_5Me_5$], have been used to synthesise several di- and tri-metal complexes, including $[MCo_2(\mu_3\text{-}CR)(CO)_8L]$ (M = Cr, R = C_6H_4Me-4, L = $\eta\text{-}C_5H_5$; M = W, R = Me, L = $\eta\text{-}C_5Me_5$), $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n\{HB(pz)_3\}]$ (*n* = 5 or 6), $[RhW(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]$, $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_3]$, $[Mo_2W(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)_2\{HB(pz)_3\}]$, and $[MW_2(\mu\text{-}CR)_2(\mu\text{-}CO)_2(CO)_4L_2]$ [M = Mo, R = Me, L = $HB(pz)_3$; M = Mo or W, R = C_6H_4Me-4, L = $\eta\text{-}C_5Me_5$]. Spectroscopic data for the new compounds and some reactions are reported and discussed.

Earlier we have described how the alkylidyne–tungsten and –molybdenum compounds $[M(\equiv CR)(CO)_2L]$ [M = W, L = $\eta\text{-}C_5H_5$, R = C_6H_4Me-4 (**1a**)[2] or Me (**1b**);[3,4] M = Mo, L = $\eta\text{-}C_5H_5$, R = C_6H_4Me-4 (**1c**)[5,6] or Me (**1d**);[7] M = W, L = $\eta\text{-}C_5Me_5$, R = C_6H_4Me-4 (**1f**)[4,8] or Me (**1g**);[4] M = W, L = $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate, R = C_6H_4-Me-4 (**1j**)[1,9,10] or Me (**1k**)[9]] may be used to prepare complexes with bonds between these metals and other transition elements. Herein we describe the syntheses of the new metal alkylidyne compounds $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ [L = $\eta\text{-}C_5H_5$ (**1e**) or $HB(pz)_3$ (**1h**)], $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1g**), and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (**1i**), as well as some reactions in which these species are used to prepare complexes with heteronuclear metal–metal bonds. Additional studies with (**1k**) are also reported.

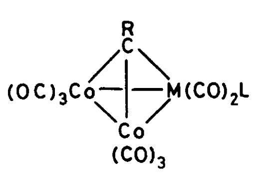
Results and Discussion

Treatment of $[Cr(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$, prepared *in situ* from $[Cr\{=C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$, with $Na(C_5H_5)$ in Et_2O affords the red complex $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (**1e**). Similarly, $[W(\equiv CMe)Br(CO)_4]$ and $K(C_5Me_5)$ yield the compound $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1g**). The two compounds $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ [M = Cr (**1h**) or Mo (**1i**)] were obtained by treating the complexes $[M(\equiv CC_6H_4\text{-}Me\text{-}4)Br(CO)_4]$ with $K[HB(pz)_3]$ in CH_2Cl_2. The new metal alkylidyne compounds were characterised by the data given in Tables 1 and 2. Compounds (**1e**), (**1g**), (**1h**), and (**1i**) display two CO stretching bands in their i.r. spectra. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra show resonances for the ligating carbon nuclei of the alkylidyne groups in the range δ 293—327 p.p.m. Signals in this region are also observed in the spectra of the related compounds (**1a**)—(**1d**), (**1f**), (**1j**), and (**1k**).

The chromium compound (**1e**) was somewhat unstable, in contrast with its tungsten [(**1a**)] and molybdenum [(**1c**)] analogues. Consequently (**1e**) proved not to be a useful reagent for preparing polynuclear metal compounds. Thus, with $[Fe_2(CO)_9]$, compound (**1e**) gave a mixture of unidentified

$[M(\equiv CR)(CO)_2L]$

	M	R	L
(**1a**)	W	C_6H_4Me - 4	$\eta\text{-}C_5H_5$
(**1b**)	W	Me	$\eta\text{-}C_5H_5$
(**1c**)	Mo	C_6H_4Me - 4	$\eta\text{-}C_5H_5$
(**1d**)	Mo	Me	$\eta\text{-}C_5H_5$
(**1e**)	Cr	C_6H_4Me - 4	$\eta\text{-}C_5H_5$
(**1f**)	W	C_6H_4Me - 4	$\eta\text{-}C_5Me_5$
(**1g**)	W	Me	$\eta\text{-}C_5Me_5$
(**1h**)	Cr	C_6H_4Me - 4	$HB(pz)_3$
(**1i**)	Mo	C_6H_4Me - 4	$HB(pz)_3$
(**1j**)	W	C_6H_4Me - 4	$HB(pz)_3$
(**1k**)	W	Me	$HB(pz)_3$



	M	R	L
(**2a**)	Cr	C_6H_4Me - 4	$\eta\text{-}C_5H_5$
(**2b**)	Mo	C_6H_4Me - 4	$\eta\text{-}C_5H_5$
(**2c**)	W	C_6H_4Me - 4	$\eta\text{-}C_5H_5$
(**2d**)	W	Me	$\eta\text{-}C_5H_5$
(**2e**)	W	Me	$\eta\text{-}C_5Me_5$
(**2f**)	W	C_6H_4Me - 4	$\eta\text{-}C_5Me_5$
(**2g**)	W	Me	$HB(pz)_3$
(**2h**)	W	C_6H_4Me - 4	$HB(pz)_3$

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

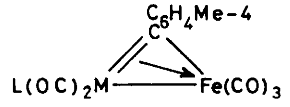
Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$	Analysis (%) C	H	N
(1e) $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]^c$	Red	25	1 997s, 1 935s	64.7 (65.2)	4.5 (4.3)	
(1g) $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$	Yellow	43	^{d}1 979s, 1 900s	41.4 (41.8)	4.6 (4.5)	
(1h) $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$	Purple-brown	52	1 997s, 1 913s	53.7 (53.8)	4.1 (4.0)	19.8 (19.8)
(1i) $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$	Orange	47	1 998s, 1 921s	48.8 (48.7)	4.1 (3.6)	17.4 (17.9)
(2a) $[CrCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$	Green	51	2 085m, 2 045s, 2 035s, 2 012w, 2 002w, 1 916m, 1 875w	44.8 (44.9)	2.4 (2.3)	
(2e) $[WCo_2(\mu_3\text{-}CMe)(CO)_8(\eta\text{-}C_5Me_5)]$	Green	95	2 077m, 2 064s, 2 055m, 2 034m, 2 022vs, 1 998vs, 1 983vs, 1 966w, 1 932w, 1 866w	34.7 (34.9)	2.6 (2.6)	
(3a) $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$	Purple	61	2 050s, 1 999s, 1 968s, 1 921vs, 1 876m	43.4 (43.4)	3.0 (2.8)	13.5 (13.8)
(4a) $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{HB(pz)_3\}]$	Red	90	2 050s, 2 014m, 1 992vs, 1 968vs, 1 922m, 1 876m	43.1 (43.4)	2.7 (2.7)	13.3 (13.2)
(5a) $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)\{HB(pz)_3\}]$	Purple	75	^{e}1 985s, 1 916s, 1 823w	43.5 (43.9)	4.2 (4.0)	12.5 (12.8)
(6a) $[FeMo\{\mu\text{-}\eta\text{-}SC(C_6H_4Me\text{-}4)\}(CO)_5\{HB(pz)_3\}]$	Red	58	^{e}2 058s, 1 985s, 1 859s	41.3 (41.3)	2.8 (2.7)	12.9 (13.1)
(9a) $[RhW(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]$	Red-brown	77	^{e}1 974m; 1 911s, 1 821m	44.3 (44.6)	3.9 (3.9)	
(10a) $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_3]$	Dark green	51	^{e}1 831s, 1 761m, 1 734 (sh)	46.2 (46.4)	5.4 (5.3)	
(11a) $[Mo_2W(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)_2\{HB(pz)_3\}]$	Brown	90	^{e}2 014w, 1 978m, 1 958vs, 1 913s, 1 884m	35.3 (35.5)	3.1 (2.7)	8.9 (9.6)
(12a) $[MoW_2(\mu\text{-}CMe)_2(\mu\text{-}CO)_2(CO)_4\{HB(pz)_3\}_2]$	Red-brown	40	^{e}2 001w, 1 987m, 1 963s, 1 942m, 1 861m, 1 712w	29.3 (30.3)	2.6 (2.4)	14.3 (15.1)
(12b) $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Purple	48	^{e}1 987w, 1 956s, 1 936m (sh), 1 925m (sh), 1 831m, 1 686w br	46.9 (45.9)	4.4 (4.0)	
(12c) $[W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Purple	31	^{e}1 990m, 1 960s, 1 929s, 1 859m, 1 830w	42.2 (42.1)	3.6 (3.9)	
(13a) $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5Me_5)]$	Green	14	^{f}2 066m, 1 989m, 1 965m, 1 940s, 1 921m, 1 892w	37.5 (37.4)	2.5 (2.7)	

[a] Calculated values are given in parentheses. [b] Measured in light petroleum unless otherwise stated. [c] Parent ion in mass spectrum at m/z = 276. [d] In Et_2O. [e] In CH_2Cl_2. [f] In tetrahydrofuran.

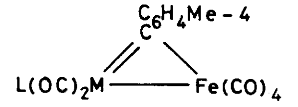
complexes in low yield. In contrast, **(1a)** and **(1c)** afford with $[Fe_2(CO)_9]$ well defined iron–tungsten[11] and iron–molybdenum[5] species which have an extensive chemistry.[12,13] However, it was observed that compound **(1e)** reacts with $[Co_2(CO)_8]$ in light petroleum to give the green trimetal complex $[CrCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ **(2a)**. We have previously shown that $[Co_2(CO)_8]$ reacts readily with alkylidyne–tungsten and -molybdenum species to give trimetal compounds **(2b)**—**(2d)**, and **(2f)**—**(2h)**.[6,8,9,14] In the work reported herein, the complex $[WCo_2(\mu_3\text{-}CMe)(CO)_8(\eta\text{-}C_5Me_5)]$ **(2e)** was prepared in essentially quantitative yield (Table 1) from the reaction between **(1g)** and $[Co_2(CO)_8]$.

Both **(2a)** and **(2e)** have spectroscopic properties similar to those reported for the other compounds of type **(2)**. Thus the number of observed bands in the carbonyl stretching region of their i.r. spectra (Table 1) suggests the presence of rotational isomers, a phenomenon discussed elsewhere.[8,9,14] The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of **(2e)** shows a characteristic resonance for the triply bridging alkylidyne carbon nucleus at δ 279.1 p.p.m. (Table 2). The corresponding signal in the spectrum of **(2a)**, at 306.7 p.p.m., is significantly more deshielded, as found with other chromium-containing alkylidyne complexes.[6]

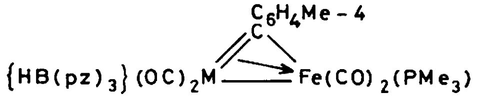
Complex **(1i)** reacts with $[Fe_2(CO)_9]$ in Et_2O to give a mixture of the 32-valence-electron unsaturated purple species $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ **(3a)**, and the saturated red compound $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{HB(pz)_3\}]$ **(4a)**; both characterised by the data given in Tables 1 and 2. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of **(3a)** differs from that of **(4a)** in that the resonance for the ligated carbon nucleus of the bridging



	M	L
(3a)	Mo	$HB(pz)_3$
(3b)	W	$HB(pz)_3$
(3c)	Mo	$\eta\text{-}C_5H_5$
(3d)	W	$\eta\text{-}C_5H_5$
(3e)	W	$\eta\text{-}C_5Me_5$



	M	L
(4a)	Mo	$HB(pz)_3$
(4b)	W	$HB(pz)_3$
(4c)	Mo	$\eta\text{-}C_5H_5$
(4d)	W	$\eta\text{-}C_5H_5$
(4e)	W	$\eta\text{-}C_5Me_5$



	M
(5a)	Mo
(5b)	W

Table 2. Hydrogen-1 and ^{13}C n.m.r. data[a] for the complexes

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(**1e**)	2.33 (s, 3 H, Me-4), 5.10 (s, 5 H, $\mathrm{C_5H_5}$), 7.15, 7.35 [$\mathrm{(AB)_2}$, 4 H, $\mathrm{C_6H_4}$, *J*(AB) 8]	[d]326.7 (C≡Cr), 238.5 (CO), 145.2 [C^1 ($\mathrm{C_6H_4}$)], 140.6, 129.8, 128.9 ($\mathrm{C_6H_4}$), 89.7 ($\mathrm{C_5H_5}$), 22.0 (Me-4)
(**1g**)	1.80 (s, 3 H, Me), 2.17 (s, 15 H, $\mathrm{C_5Me_5}$)	[e]313.3 [C≡W, *J*(WC) 208], 225.5 [CO, *J*(WC) 193], 104.1 ($\mathit{C}_5\mathrm{Me}_5$), 39.4 (Me), 11.2 ($\mathrm{C_5}\mathit{Me}_5$)
(**1h**)	2.37 (s, 3 H, Me-4), 6.16 (s, 3 H, $\mathrm{C_3H_3N_2}$), 7.07—7.57 (m, 4 H, $\mathrm{C_6H_4}$), 7.62 (s, 3 H, $\mathrm{C_3H_3N_2}$), 7.80 (s, 1 H, $\mathrm{C_3H_3N_2}$), 7.88 (s, 2 H, $\mathrm{C_3H_3N_2}$)	310.0 (C≡Cr), 231.6 (CO), 145.4 [C^1 ($\mathrm{C_6H_4}$)], 143.9—105.6 ($\mathrm{C_6H_4}$ and $\mathrm{C_3H_3N_2}$), 22.0 (Me-4)
(**1i**)	2.32 (s, 3 H, Me-4), 6.17 (m, 3 H, H^4), 7.08, 7.41 [$\mathrm{(AB)_2}$, 4 H, $\mathrm{C_6H_4}$, *J*(AB) 8], 7.63 (m, 4 H, $\mathrm{C_3H_3N_2}$), 7.89 [d, 2 H, $\mathrm{C_3H_3N_2}$, *J*(HH) 2]	293.1 (C≡Mo), 224.9 (CO), 143.4 [C^1 ($\mathrm{C_6H_4}$)], 142.6—104.6 ($\mathrm{C_6H_4}$ and $\mathrm{C_3H_3N_2}$), 20.8 (Me-4)
(**2a**)	2.36 (s, 3 H, Me-4), 4.69 (s, 5 H, $\mathrm{C_5H_5}$), 7.11 (m, 4 H, $\mathrm{C_6H_4}$)	[f]306.7 (μ_3-C), 248.8, 201.7 (CO), 161.3 [C^1 ($\mathrm{C_6H_4}$)], 137.0, 128.7, 127.8 ($\mathrm{C_6H_4}$), 94.5 ($\mathrm{C_5H_5}$), 21.3 (Me-4)
(**2e**)	[g]2.17 (s, 15 H, $\mathrm{C_5Me_5}$), 3.67 (s, 3 H, μ_3-CMe)	[h]279.1 (μ_3-C), 260.2 (WCO), 205.7 (CoCO), 101.8 ($\mathit{C}_5\mathrm{Me}_5$), 44.3 ($\mu_3$-C*Me*), 11.3 ($\mathrm{C_5}\mathit{Me}_5$)
(**3a**)	2.33 (s, 3 H, Me-4), 5.98 (s, 2 H, $\mathrm{C_3H_3N_2}$), 6.24 (s, 2 H, $\mathrm{C_3H_3N_2}$), 6.42 (s, 1 H, $\mathrm{C_3H_3N_2}$), 7.20 (m, 4 H, $\mathrm{C_6H_4}$), 7.63 (s, 1 H, $\mathrm{C_3H_3N_2}$), 7.80 (s, 2 H, $\mathrm{C_3H_3N_2}$), 8.62 (s, 1 H, $\mathrm{C_3H_3N_2}$)	422.8 (μ-C), 230.8, 226.3 (MoCO), 213.5 (FeCO), 151.3 [C^1 ($\mathrm{C_6H_4}$)], 147.3—105.7 ($\mathrm{C_6H_4}$ and $\mathrm{C_3H_3N_2}$), 21.8 (Me-4)
(**4a**)[i]		315.3 (μ-C), 227.4 (MoCO), 214.0 (FeCO), 152.5 [C^1 ($\mathrm{C_6H_4}$)], 144.6—106.4 ($\mathrm{C_6H_4}$ and $\mathrm{C_3H_3N_2}$), 21.5 (Me-4)
(**5a**)[i]		422.3 [μ-C, *J*(PC) 6], 233.5 (MoCO), 220.6 [d, FeCO, *J*(PC) 21], 156.2 [C^1 ($\mathrm{C_6H_4}$)], 146.7—105.4 ($\mathrm{C_6H_4}$ and $\mathrm{C_3H_3N_2}$), 21.5 (Me-4), 20.1 [d, MeP, *J*(PC) 28]
(**6a**)	2.40 (s, 3 H, Me-4), 6.09, 6.25, 6.35 (m × 3, 3 H, $\mathrm{C_3H_3N_2}$), 7.10—7.50 (m, 4 H, $\mathrm{C_6H_4}$), 7.60—7.90 (m, 6 H, $\mathrm{C_3H_3N_2}$)	232.5, 227.3 (MoCO), 210.4, 208.4 (FeCO), 144.7—106.6 ($\mathrm{C_6H_4}$ and $\mathrm{C_3H_3N_2}$), 106.0 (μ-$\mathit{C}\mathrm{C_6H_4Me}$-4), 21.3 (Me-4)
(**9a**)	1.70 [d, 3 H, μ-CMe, *J*(RhH) 1], 2.02 (s, 15 H, $\mathrm{C_5Me_5}$), 5.94 (m, 3 H, $\mathrm{C_9H_7}$), 7.14 (m, 4 H, $\mathrm{C_9H_7}$)	[f]317.6 [d, μ-C, *J*(RhC) 27, *J*(WC) 79], 232.8 [WCO, *J*(WC) 96], 230.1 [WCO, *J*(WC) 88], 191.1 [d, RhCO, *J*(RhC) 90], 125.6—115.8 ($\mathrm{C_9H_7}$), 103.3 ($\mathit{C}_5\mathrm{Me}_5$), 103.1, 83.9, 80.5 ($\mathrm{C_9H_7}$), 44.0 (μ-C*Me*), 10.7 ($\mathrm{C_5}\mathit{Me}_5$)
(**10a**)	1.66 (s, 30 H, $\mathrm{C_5Me_5}$), 1.96 (s, 15 H, $\mathrm{C_5Me_5}$), 4.03 (s, 3 H, μ_3-CMe)	[j]302.7, 302.6 [t × 2, μ_3-C, *J*(RhC) 36], 237.4 [WCO, *J*(WC) 88], 228.8, 228.7 [t × 2, μ-CO, *J*(RhC) 45], 102.0 [br, (η-$\mathit{C}_5\mathrm{Me}_5$)Rh], 101.8 [(η-$\mathit{C}_5\mathrm{Me}_5$)W], 43.4 [$\mu_3$-C*Me*, *J*(RhC) 6], 10.8, 9.1 ($\mathrm{C_5}\mathit{Me}_5$)
(**11a**)	2.41 (s, 3 H, μ_3-CMe), 5.30, 5.66 (s × 2, 10 H, $\mathrm{C_5H_5}$), 6.23 (m, 3 H, $\mathrm{C_3H_3N_2}$), 7.26 (m, 4 H, $\mathrm{C_3H_3N_2}$), 7.65 (m, 2 H, $\mathrm{C_3H_3N_2}$)	223.5 [WCO, *J*(WC) 162], 206.8 [WCO, *J*(WC) 170], 201.7 (MoCO), 145.1—106.5 ($\mathrm{C_3H_3N_2}$), 92.4 ($\mathrm{C_5H_5}$), 31.0 (μ_3-C*Me*)
(**12a**)	3.07 (s, 6 H, μ-CMe), 6.28 (m, 6 H, $\mathrm{C_3H_3N_2}$), 7.80 (m, 8, H, $\mathrm{C_3H_3N_2}$), 7.97 (br, 4 H, $\mathrm{C_3H_3N_2}$)	336.7 [μ-C, *J*(WC) 151], 231.3 (MoCO), 229.0 [WCO, *J*(WC) 180], 223.4 [WCO, *J*(WC) 175], 145.2—106.1 ($\mathrm{C_3H_3N_2}$), 41.3 (μ-C*Me*)
(**12b**)	1.90 (s, 15 H, $\mathrm{C_5Me_5}$), 2.34 (s, 3 H, Me-4), 6.76, 7.13 [$\mathrm{(AB)_2}$, $\mathrm{C_6H_4}$, *J*(AB) 8]	356.4 (μ-C), 236.4, 233.1, 223.0 (CO), 159.9—121.3 ($\mathrm{C_6H_4}$), 105.6 ($\mathit{C}_5\mathrm{Me}_5$), 21.4 (Me-4), 10.5 ($\mathrm{C_5}\mathit{Me}_5$)
(**12c**)	1.86 (s, 30 H, $\mathrm{C_5Me_5}$), 2.41 (s, 6 H, Me-4), 6.60, 7.15 [$\mathrm{(AB)_2}$, 8 H, $\mathrm{C_6H_4}$, *J*(AB) 8]	372.9 [μ-C, *J*(WC) 140], 233.4 [CO, *J*(WC) 171], 230.8 [CO, *J*(WC) 165], 220.8 [CO, *J*(WC) 186], 162.0—120.3 ($\mathrm{C_6H_4}$), 105.4 ($\mathit{C}_5\mathrm{Me}_5$), 21.2 (Me-4), 10.4 ($\mathrm{C_5}\mathit{Me}_5$)
(**13a**)	2.08 (s, 15 H, $\mathrm{C_5Me_5}$), 2.34 (s, 3 H, Me-4), 6.50, 7.15 [$\mathrm{(AB)_2}$, 4 H, $\mathrm{C_6H_4}$, *J*(AB) 8]	[f]309.1 [μ-C, *J*(WC) 147], 218.9 [CO, *J*(WC) 181], 202.1 [CO, *J*(WC) 136], 199.0 [CO, *J*(WC) 122], 162.9—122.6 ($\mathrm{C_6H_4}$), 105.6 ($\mathit{C}_5\mathrm{Me}_5$), 21.5 (Me-4), 10.8 ($\mathrm{C_5}\mathit{Me}_5$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperature unless otherwise stated. [b] Measured in $\mathrm{CDCl_3}$ unless otherwise stated. [c] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of $\mathrm{SiMe_4}$. Measurements in $\mathrm{CD_2Cl_2}$–$\mathrm{CH_2Cl_2}$, unless otherwise stated. [d] Measured at −30 °C. [e] In $\mathrm{CDCl_3}$. [f] Measured at −40 °C. [g] In $\mathrm{CD_2Cl_2}$. [h] Measured at −50 °C. [i] Hydrogen-1 spectra showed broad signals. [j] Two isomers, see text.

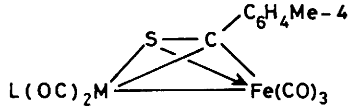
tolylmethylidyne group in the former is significantly more deshielded (by *ca.* 108 p.p.m.) than that in the latter. We have previously noted and discussed this property.[10] Thus the ^{13}C-{^{1}H} resonances for the contact-carbon nuclei of (**3d**) and (**4d**) occur at δ 392.5 and 331.3 p.p.m., respectively. A better comparison is that of (**3b**) with (**4b**), the tungsten analogues of (**3a**) and (**4a**). In the spectrum of the unsaturated iron–tungsten compound (**3b**) the μ-C resonance is at 408.8 p.p.m. If solutions of the latter are treated with CO gas this alkylidyne carbon signal disappears and is replaced by one at 290.9 p.p.m. The latter is believed to be due to the μ-C resonance of (**4b**), which apparently has only a transient existence, readily reverting to (**3b**). This behaviour is in contrast with the relative stabilities of the molybdenum species (**3a**) and (**4a**). Although the former is kinetically the more stable, it is possible to isolate the latter in crystalline form. However, as described in the Experimental section, solutions of (**4a**) in $\mathrm{CH_2Cl_2}$ under nitrogen afford (**3a**) after a few hours.

The synthesis of (**3a**) and (**4a**) extends the range of known compounds of this class. In addition to (**3b**) and (**4b**), mentioned above, the species (**3e**), (**4e**), and (**4c**) have been well characterised.[5,8] The relative stabilities of (**3e**) and (**4e**) are delicately balanced, as they are for (**3a**) and (**4a**). However, (**3c**) has not been unambiguously identified in studies on the chemistry of (**4c**). With (**3d**) and (**4d**), both of which are unstable, the equilibrium lies predominantly in favour of the latter, the former decomposing in solution above *ca.* −20 °C.[10]

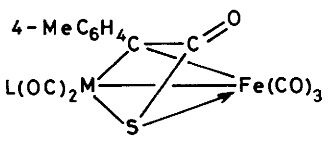
Treatment of (**3a**) with $\mathrm{PMe_3}$ in light petroleum affords the purple unsaturated complex [FeMo(μ-$\mathrm{CC_6H_4Me}$-4)$\mathrm{(CO)_4}$-$\mathrm{(PMe_3)}$\{$\mathrm{HB(pz)_3}$\}] (**5a**), data for which are given in Tables 1 and 2. The tungsten analogue (**5b**) has been previously prepared.[10] As expected, the two complexes have very similar spectroscopic properties with the exception that the ^{1}H n.m.r. spectrum of (**5a**) showed broad unresolved peaks, probably due to a paramagnetic impurity. The ^{13}C-{^{1}H} n.m.r. spectrum was informative. The μ-C resonance at δ 422.3 p.p.m. was a doublet

[J(PC) 6 Hz]. The corresponding signal in (**5b**) is at 404.4 p.p.m.[10] In the CO region of the $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum of (**5a**) there are two resonances (Table 2) of relative intensity 1 : 1 at δ 233.5 (MoCO) and 220.6 p.p.m. (FeCO). The latter is a doublet [J(PC) 21 Hz], indicating that the PMe_3 group is bonded to the iron centre. Since there is only one resonance for the carbonyl groups attached to iron, site-exchange of these ligands must occur, presumably *via* a pivoting mechanism for the $Fe(CO)_2(PMe_3)$ fragment.

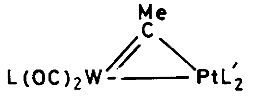
Compound (**3a**) reacts with sulphur to give the red complex $[FeMo\{\mu\text{-}\eta\text{-}SC(C_6H_4Me\text{-}4)\}(CO)_5\{HB(pz)_3\}]$ (**6a**). Related compounds (**6b**) and (**6c**) have been prepared previously from reactions between sulphur and (**4c**) and (**3e**), respectively.[8,13] The molecular structure of (**6b**) has been established by *X*-ray diffraction. The synthesis of (**6a**) was sometimes accompanied by formation of trace amounts of a yellow product. The latter is believed to be (**7a**), since its i.r. spectrum in the carbonyl region is very similar to that of (**7b**),[13] which is also yellow in colour. Compound (**7b**) is formed simultaneously with (**6b**) in the reaction between sulphur and (**4c**). Although the presumed (**7a**) was observed to decompose into (**6a**), in contrast (**7b**) does not release CO and form (**6b**).



	M	L
(**6a**)	Mo	$HB(pz)_3$
(**6b**)	Mo	$\eta\text{-}C_5H_5$
(**6c**)	W	$\eta\text{-}C_5Me_5$



	M	L
(**7a**)	Mo	$HB(pz)_3$
(**7b**)	Mo	$\eta\text{-}C_5H_5$

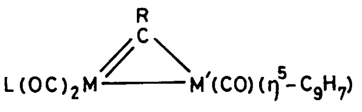


	L	L′
(**8a**)	$\eta\text{-}C_5H_5$	PMe_3
(**8b**)	$\eta\text{-}C_5Me_5$	PMe_3
(**8c**)	$HB(pz)_3$	PMe_3
(**8d**)	$HB(pz)_3$	$P(OMe)_3$
(**8e**)	$\eta\text{-}C_5Me_5$	$P(OMe)_3$

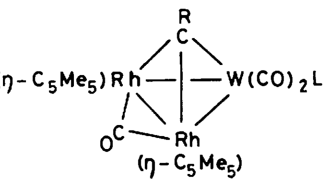
Compound (**8a**) is a very stable complex, prepared by treating (**1b**) with $[Pt(C_2H_4)(PMe_3)_2]$.[3c] It was of interest to determine therefore whether the new tungsten ethylidyne complex (**1g**) would form an analogous complex (**8b**) on treatment with $[Pt(C_2H_4)(PMe_3)_2]$. Surprisingly, (**8b**) could not be isolated from mixtures of the reactants, although there was n.m.r. evidence that it was formed in solution. Thus a $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectrum [chemical shifts to high frequency of 85% H_3PO_4 (external) taken as positive] of the crude reaction mixture showed characteristic signals for a *cis*-$Pt(PMe_3)_2$ group [δ −13.2, d, J(PP) 17, J(PtP) 4 053; −22.8 p.p.m., d, J(PP) 17, J(PtP) 2 541 Hz]. The $^{195}Pt\text{-}\{^{1}H\}$ spectrum displayed a resonance at δ 338 p.p.m. [to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz], appearing as a doublet of doublets [J(PPt) 2 541 and 4 053 Hz]. The corresponding $^{31}P\text{-}\{^{1}H\}$ and $^{195}Pt\text{-}\{^{1}H\}$ data for (**8a**) are remarkably similar [$^{31}P\text{-}\{^{1}H\}$, δ −13.2 and −23.3 p.p.m., J(PP) 15, J(PtP) 2 527 and 4 104; $^{195}Pt\text{-}\{^{1}H\}$, δ 391 p.p.m., J(PPt) 2 527 and 4 104 Hz]. Thus there is good evidence for the presence of (**8b**) in solutions containing equivalent amounts of (**1g**) and $[Pt(C_2H_4)(PMe_3)_2]$. Attempts to isolate (**8b**) as a solid from the mixtures led only to identification of its disproportionation product, the trimetal compound $[PtW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$.[4]

In the preceding paper[1] we described an unsuccessful attempt to prepare (**8c**) by treating (**1k**) with $[Pt(C_2H_4)(PMe_3)_2]$. The product of this reaction was the trimetal compound $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$. Hence both (**1g**) and (**1k**) behave somewhat similarly towards the platinum reagent. Since in the previous work treatment of (**1k**) with $[Pt(C_2H_4)\{P(OMe)_3\}_2]$ afforded the complex (**8d**), albeit an unstable species, an attempt was made to prepare the compound $[PtW(\mu\text{-}CMe)(CO)_2\{P(OMe)_3\}_2(\eta\text{-}C_5Me_5)]$ (**8e**) from (**1g**) and $[Pt(C_2H_4)\{P(OMe)_3\}_2]$. However, this was unsuccessful, only the trimetal species $[PtW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ being identified[4] spectroscopically as a product.

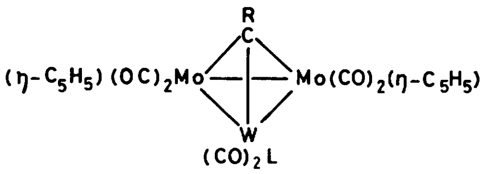
The tungsten ethylidyne compound (**1g**) reacts with $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ to give the dimetal complex $[RhW(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]$ (**9a**). Several related compounds, *viz.* (**9b**)—(**9i**), have been prepared previously.[3a,6,7,9,15] The spectroscopic data for (**9a**) (Tables 1 and 2) and for (**9d**)[7] are very similar. Both complexes show three CO stretching bands in their i.r. spectra [(**9a**), 1 974, 1 911, and 1 821; (**9d**), 1 995, 1 919, and 1 834 cm^{-1}], the absorption at lowest



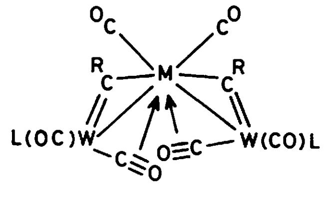
	M	M′	R	L
(**9a**)	W	Rh	Me	$\eta\text{-}C_5Me_5$
(**9b**)	W	Rh	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5Me_5$
(**9c**)	W	Ir	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5Me_5$
(**9d**)	W	Rh	Me	$\eta\text{-}C_5H_5$
(**9e**)	W	Rh	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(**9f**)	W	Ir	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(**9g**)	W	Rh	$C_6H_4Me\text{-}4$	$HB(pz)_3$
(**9h**)	Mo	Rh	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(**9i**)	Mo	Ir	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$



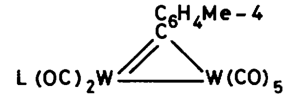
	R	L
(**10a**)	Me	$\eta\text{-}C_5Me_5$
(**10b**)	Me	$\eta\text{-}C_5H_5$
(**10c**)	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$



	R	L
(11a)	Me	$HB(pz)_3$
(11b)	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$



	M	R	L
(12a)	Mo	Me	$HB(pz)_3$
(12b)	Mo	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5Me_5$
(12c)	W	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5Me_5$
(12d)	Mo	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(12e)	W	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$



	L
(13a)	$\eta\text{-}C_5Me_5$
(13d)	$\eta\text{-}C_5H_5$

$[L(OC)_3W{-}W(\equiv CC_6H_4Me\text{-}4)(CO)_4]$

	L
(13b)	$\eta\text{-}C_5Me_5$
(13c)	$\eta\text{-}C_5H_5$

frequency corresponding to the presence of a semi-bridging carbonyl ligand.[16] The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**9a**) shows a characteristic resonance for the μ-*C*Me group at δ 317.6 p.p.m., occurring as a doublet with *J*(RhC) 27 Hz. The corresponding data for (**9d**) are δ 323.4 p.p.m., with *J*(RhC) 27 Hz.

Treatment of (**1g**) with $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ affords the trimetal compound $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_3]$ (**10a**), a species related to previously reported (**10b**) and (**10c**).[3a,15] The i.r. spectrum of (**10a**) in the CO region shows three bands at 1 831, 1 761, and 1 734 cm^{-1}, the latter appearing as a shoulder on the broad peak at 1 761 cm^{-1}. In the i.r. spectrum of (**10b**) the CO bands are at 1 860, 1 795, and 1 778 cm^{-1}, and an *X*-ray diffraction study revealed that in addition to the presence of the μ-CO ligand across the Rh–Rh bond, the remaining two carbonyl groups each semi-bridge a Rh–W bond. This accounts for the relatively low frequencies of all three bands in each species.

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**10a**) (Table 2) was revealing in indicating the presence in solution of two isomers which probably arise *via* different orientations of the $W(\eta\text{-}C_5Me_5)$ group, with the latter located either towards or away from the capping CMe ligand. The WCO (237.4 p.p.m.) and RhC_5Me_5 (102.0 p.p.m.) signals are somewhat broadened, while the μ_3-*C*Me and μ-CO ligands each give rise to two resonances of almost equal intensity. These appear as overlapping triplets due to $^{103}Rh\text{-}^{13}C$ coupling. For the μ_3-*C*Me groups the peaks are at δ 302.7 and 302.6 p.p.m., with *J*(RhC) 36 Hz, and for the μ-CO ligands at δ 228.8 and 228.7 p.p.m., with *J*(RhC) 45 Hz. In each isomer there would be a plane of symmetry through the tungsten, the μ_3-C atom, and the mid-point of the rhodium–rhodium vector. Similar isomerism would be possible with (**10b**), but the less bulky $W(\eta\text{-}C_5H_5)$ group evidently results in rapid interconversion between isomers on the n.m.r. time-scale, since the μ_3-C and μ-CO groups give rise to a single n.m.r. signal at δ 299.7 [*J*(RhC) 30] and 229.2 p.p.m. [*J*(RhC) 46 Hz], respectively.[3a]

Reactions between compound (**1k**) and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ or $[Mo(CO)_3(NCMe)_3]$ afford the trimetal complexes $[Mo_2W(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)_2\{HB(pz)_3\}]$ (**11a**) and $[MoW_2(\mu\text{-}CMe)_2(\mu\text{-}CO)_2(CO)_4\{HB(pz)_3\}_2]$ (**12a**), respectively. Data for these species are summarised in Tables 1 and 2.

Compound (**11a**) is structurally similar to the previously prepared complex (**11b**),[17] obtained from $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and (**1a**). The absence of a μ_3-*C*Me resonance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**11a**) is due to a weak sample resulting from poor solubility, but peaks due to the μ_3-C*Me* group are seen in both the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Table 2).

The two compounds $[MW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ [M = Mo (**12b**) or W (**12c**)] were prepared from reactions between (**1f**) and $[Mo(CO)_3(NCMe)_3]$ and $[W(CO)_4(cod)]$ (cod = cyclo-octa-1,5-diene), respectively. The spectroscopic properties of the three related compounds (**12a**)—(**12c**) are similar to those of the previously described[18] species (**12d**) and (**12e**). The molecular structure of (**12d**) has been established by *X*-ray diffraction.

The reaction between (**1f**) and $[W(CO)_4(cod)]$ also afforded a green dimetal complex (**13**). The structure of this second product is uncertain, but it seems likely that it should be formulated as $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5Me_5)]$ (**13a**), with a tolylmethylidyne group bridging the metal–metal bond. An alternative structure (**13b**) in which the alkylidyne ligand is terminally bonded to one tungsten centre cannot be entirely ruled out as a consequence of earlier results involving the reaction of (**12e**) with CO.[18] The very unstable ditungsten compound produced in this reaction was formulated as (**13c**) rather than (**13d**), because its i.r. spectrum in the carbonyl region was very similar to that of $[W_2(\equiv CPh)(CO)_7(\eta\text{-}C_5H_5)]$, a complex with a terminal alkylidyne ligand which had been prepared by treating $[W(\equiv CPh)Br(CO)_4]$ with $Na[W(CO)_3(\eta\text{-}C_5H_5)]$.[19] However, the i.r. spectrum of the green compound (**13**) in the carbonyl region is not similar to the product formulated as (**13c**)[18] nor to that of $[W_2(\equiv CPh)(CO)_7(\eta\text{-}C_5H_5)]$.[19] The last two compounds show four terminal CO stretching bands in their i.r. spectra rather than the six shown by (**13a**) (Table 1).

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**13a**) (Table 2) shows a characteristic resonance for the ligated carbon of the alkylidyne group at δ 309.1 p.p.m. [*J*(WC) 147 Hz]. Three CO resonances are observed at 218.9, 202.1, and 199.0 p.p.m.

Experimental

Experiments were carried out under an atmosphere of dry oxygen-free nitrogen, using Schlenk-tube techniques. Light petroleum refers to that fraction of b.p. 40—60 °C. The salt $K[HB(pz)_3]$[20] and the compounds $[Cr\{=C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$,[21] $[M(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ (M = Mo or W),[22] $[M(\equiv CR)(CO)_2L]$ [M = W, R = C_6H_4Me-4, L = η-C_5Me_5;[8] R = Me, L = $HB(pz)_3$[9]], $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[10] $[Mo(CO)_3(NCMe)_3]$,[23] $[W(CO)_4(cod)]$,[24] $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[25] and $[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]$[26] were prepared as described elsewhere. Chromatography was carried out on alumina (Brockman activity II) or Florisil (Aldrich, 100—200 mesh) columns (*ca.* 3 × 20 cm). Analytical and other data for the new complexes are given in Table 1. The instrumentation used has been described earlier.[3]

Synthesis of the Mononuclear Metal Alkylidyne Compounds.—(*i*) The compound $[Cr\{=C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ (3.2 g, 10 mmol) in light petroleum (120 cm^3) at −20 °C was treated with BBr_3 (3 portions of 0.3 cm^3). A yellow precipitate, presumed to be $[Cr(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$, formed immediately. The mixture was stirred at −20 °C for 1.5 h by which time all the carbene complex was consumed (verified by i.r.). Solvent was decanted and the bromo(carbyne)chromium complex washed with light petroleum (3 × 50 cm^3, −30 °C) and dried *in vacuo* (30 min at −20 °C). This material was treated with Et_2O (100 cm^3) at −30 °C followed by $Na(C_5H_5)$ (0.5 g). The mixture turned green. After 2 h, with stirring at −30 °C, a second portion of $Na(C_5H_5)$ (0.5 g) was added (total 11.2 mmol). The reactants were then stirred at −30 °C overnight. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3, −30 °C) and chromatographed on alumina at −20 °C, eluting with light petroleum–CH_2Cl_2 (4 : 1). Removal of solvent gave crude $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.80 g). Further purification was carried out by dissolving in CH_2Cl_2 (5 cm^3) and rechromatographing on Florisil at −20 °C, eluting with light petroleum—CH_2Cl_2 (4 : 1) thereby affording brick-red *microcrystals* of $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (**1e**) (0.70 g) after removal of solvent.

(*ii*) Solid $K(C_5Me_5)$ (6.8 g, 39 mmol) was added to $[W(\equiv CMe)Br(CO)_4]$ (10.5 g, 26 mmol) in Et_2O (100 cm^3) at −15 °C, and the mixture stirred for 4 h. The dark brown suspension was filtered through an alumina pad (*ca.* 4 × 8 cm) at −30 °C, and then the alumina further eluted with *ca.* 100 cm^3 of Et_2O at −30 °C. Solvent was removed *in vacuo*, affording a brown solid. The latter was extracted with light petroleum (*ca.* 3 × 100 cm^3), and the extracts chromatographed on alumina at 10 °C. Elution with light petroleum gave a yellow solution from which yellow *crystals* of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1g**) (4.5 g) were obtained, after removal of solvent *in vacuo*.

(*iii*) A rapidly stirred light petroleum (120 cm^3) solution of $[Cr\{=C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ (3.2 g, 10 mmol) at −20 °C was treated with BBr_3 (3 × 0.30 cm^3) to generate $[Cr(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ *in situ*. After 1.5 h, solvent was decanted and the residue washed with light petroleum (3 × 50 cm^3, −30 °C). After drying *in vacuo* (0.5 h), the residue was treated with CH_2Cl_2 (50 cm^3, −30 °C) and solid $K[HB(pz)_3]$ (3.0 g, 12 mmol) added. The mixture was stirred for 5 h at −20 °C, and then the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on alumina at −10 °C, eluting with light petroleum–CH_2Cl_2 (4 : 1). Removal of solvent *in vacuo* afforded purple-brown *microcrystals* of $[Cr(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (**1h**) (2.2 g).

(*iv*) The compounds $K[HB(pz)_3]$ (1.20 g, 4.76 mmol) and $[Mo(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ (1.83 g, 4.7 mmol) were stirred together in CH_2Cl_2 (100 cm^3) for 6 h. Solvent was removed *in vacuo*, and the residue was dissolved in light petroleum–CH_2Cl_2 (5 : 1) and the resulting solution chromatographed on alumina. Elution with light petroleum–CH_2Cl_2 (6 : 1) removed an orange band. This eluate was concentrated to *ca.* 10 cm^3, and cooled to −20 °C affording orange *crystals* of $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (**1i**) (1.03 g).

Synthesis of $[CrCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$.—A mixture of $[Co_2(CO)_8]$ (0.24 g, 0.72 mmol) and (**1e**) (0.20 g, 0.72 mmol) in light petroleum (20 cm^3) was stirred for 1 h. Solvent was removed *in vacuo*, and the residue dissolved in light petroleum (*ca.* 5 cm^3) and chromatographed on Florisil. Elution with light petroleum removed an orange band containing $[Co_2(CO)_8]$. Further elution gave a green solution which after removal of solvent *in vacuo* afforded green *microcrystals* of $[CrCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (**2a**) (0.21 g).

Reaction of $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ *with* $[Fe_2(CO)_9]$.—A mixture of (**1i**) (0.20 g, 0.47 mmol) and $[Fe_2(CO)_9]$ (0.17 g, 0.47 mmol) in Et_2O (100 cm^3) was stirred at room temperature for 5 h. Solvent was removed *in vacuo*. The residue was dissolved in light petroleum–CH_2Cl_2 (*ca.* 5 cm^3, 4 : 1) and chromatographed at −20 °C on Florisil, eluting with light petroleum. A trace quantity of green $[Fe_3(CO)_{12}]$, identified by i.r., was removed in the first eluate. This was followed by a purple band from which $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ (**3a**) (0.074 g) was recovered. The eluting solution was changed to light petroleum–CH_2Cl_2 (4:1) to remove a red-purple band shown by i.r. to be a mixture of (**3a**) and $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{HB(pz)_3\}]$ (**4a**). Solvent was removed *in vacuo*, and the residue obtained dissolved in CH_2Cl_2 (*ca.* 50 cm^3) and stirred under nitrogen for 12 h. This procedure quantitatively converts (**4a**) into (**3a**). Removal of solvent gave a purple residue of the latter compound. This was combined with the sample of (**3a**) isolated initially, and crystallised from light petroleum at −20 °C to yield purple *crystals* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ (**3a**) (0.16 g).

Alternatively, (**3a**) may be isolated by chromatographing the initial product mixture on Florisil at room temperature, eluting with light petroleum–CH_2Cl_2 (3:1). After removal of solvent *in vacuo*, the mixture of (**3a**) and (**4a**) thus obtained was dissolved in CH_2Cl_2 (50 cm^3) and stirred under nitrogen for 12 h to produce a solution containing only (**3a**).

Compound (**4a**) may be prepared by treating a light petroleum (15 cm^3) solution of (**3a**) (0.12 g, 0.19 mmol) with a stream of CO for 5 min. Red *crystals* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\{HB(pz)_3\}]$ (**4a**) (0.11 g), which are only slightly soluble in light petroleum, appear. Compound (**4a**) is readily soluble in CH_2Cl_2, but in this solvent release of CO and formation of (**3a**) easily occurs.

Reactions of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$.—(*i*) Compound (**3a**) (0.12 g, 0.19 mmol) in light petroleum (*ca.* 15 cm^3) at −60 °C was treated with PMe_3 (0.4 cm^3 of a 0.50 mol dm^{-3} solution in light petroleum), and the mixture stirred for 30 min. Solvent was removed *in vacuo* at *ca.* −20 °C. The brown residue was dissolved in light petroleum–CH_2Cl_2 (5 cm^3, 4:1), and chromatographed on Florisil. Elution with light petroleum removed a small quantity of (**1i**). Further elution with light petroleum–CH_2Cl_2 (1:1) afforded a purple solution. Removal of solvent *in vacuo* gave a purple residue. The latter was crystallised at −20 °C from CH_2Cl_2 (*ca.* 2 cm^3) to which light petroleum (*ca.* 10 cm^3) was added. This procedure gave dark purple *needles* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)\{HB(pz)_3\}]$ (**5a**) (0.09 g).

(*ii*) A sample of (**3a**) (0.12 g, 0.20 mmol) was treated with sulphur (*ca.* 20 mg) in Et_2O (20 cm^3) at room temperature, and the mixture stirred (15 h). Solvent was removed *in vacuo*, and the residue dissolved in light petroleum (20 cm^3). The solution was then chromatographed on Florisil. Elution with light petroleum removed a trace of (**1i**). Elution with light petroleum–CH_2Cl_2 (3:1) gave initially a red eluate, followed by a purple band. The latter was identified (i.r.) as unreacted (**3a**). The red solution was concentrated to give at −20 °C red *crystals* of $[FeMo\{\mu\text{-}\eta\text{-}SC(C_6H_4Me\text{-}4)\}(CO)_5\{HB(pz)_3\}]$ (**6a**) (0.07 g).

In some syntheses traces of a yellow microcrystalline compound were observed. This species was formed in greater quantity in reactions between (**4a**) and sulphur but could not be identified. However, the i.r. spectrum in the carbonyl region was similar to (**7b**), suggesting that the yellow material was (**7a**).

Reactions of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$.—(*i*) Solid $[Co_2(CO)_8]$ (0.12 g, 0.29 mmol) was added to a light petroleum (10 cm^3) solution of (**1g**) (0.10 g, 0.20 mmol) and the mixture stirred for 10 min. Carbon monoxide was evolved, and the solution turned dark green in colour. After cooling to *ca.* −78 °C for *ca.* 10 h, the supernatant liquid was decanted, and the residue washed with light petroleum (2 × 5 cm^3, −78 °C), and dried *in vacuo* to give dark green *microcrystals* of $[WCo_2(\mu_3\text{-}CMe)(CO)_8(\eta\text{-}C_5Me_5)]$ (**2e**) (0.21 g).

(*ii*) Carbon monoxide was bubbled (10 min) through a light petroleum (50 cm^3) solution of $[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.10 g, 0.36 mmol) to generate $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ *in situ*. Solid (**1g**) (0.15 g, 0.37 mmol) was added, and the mixture stirred for 3 h. Concentration of the solution *in vacuo* to *ca.* 10 cm^3 and cooling to *ca.* −78 °C precipitated a red-brown compound. Removal of the supernatant liquid with a syringe, washing the residue with cold (*ca.* −78 °C) light petroleum (2 × 5 cm^3), and drying *in vacuo* afforded red-brown *microcrystals* of $[RhW(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]$ (**9a**) (0.18 g).

(*iii*) A mixture of (**1g**) (0.08 g, 20 mmol) and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.10 g, 0.19 mmol) was refluxed in thf (10 cm^3) for 10 h. Solvent was removed *in vacuo*, and a light petroleum (*ca.* 5 cm^3) slurry of the residue was transferred to the top of an alumina column. Elution with light petroleum–CH_2Cl_2 (1:1) removed trace amounts of blue $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and an unidentified yellow material. Elution with light petroleum–CH_2Cl_2 (1:9) gave a green solution. Removal of solvent *in vacuo* afforded dark green *microcrystals* of $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_3]$ (**10a**) (0.09 g).

Synthesis of Molybdenum–Tungsten Complexes.—(*i*) The compounds $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.16 g, 0.42 mmol) and (**1k**) (0.20 g, 0.42 mmol) in toluene (10 cm^3) were heated at 100 °C for 24 h in a Schlenk-tube fitted with a high-pressure stopcock. On cooling to room temperature, brown microcrystals appeared which were filtered off, washed with light petroleum (3 × 10 cm^3), and dried *in vacuo*, yielding *microcrystals* of $[Mo_2W(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)_2\{HB(pz)_3\}]$ (**11a**) (0.35 g).

(*ii*) A mixture of $[Mo(CO)_3(NCMe)_3]$ (0.25 g, 0.80 mmol) and (**1k**) (0.80 g, 1.6 mmol) in hexane (50 cm^3) was refluxed for 2 h. After cooling to room temperature, solvent was reduced to *ca.* 15 cm^3 *in vacuo* and decanted off. The residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on an alumina column (3 × 10 cm). Elution with CH_2Cl_2–Et_2O (1:4) gave a red-brown solution. Removal of solvent *in vacuo* and washing the residue with light petroleum (3 × 5 cm^3) gave, after drying *in vacuo*, red-brown *microcrystals* of $[MoW_2(\mu\text{-}CMe)_2(\mu\text{-}CO)_2(CO)_4\{HB(pz)_3\}_2]$ (**12a**) (0.29 g).

(*iii*) A mixture of $[Mo(CO)_3(NCMe)_3]$ (0.19 g, 0.62 mmol) and (**1f**) (0.30 g, 0.62 mmol) was refluxed in light petroleum (35 cm^3) for 4 h. After cooling to room temperature, solvent was removed *in vacuo* and the residue dissolved in light petroleum–CH_2Cl_2 (10 cm^3, 2:3) and chromatographed on Florisil. Elution with the same solvent mixture afforded a purple eluate. Removal of solvent *in vacuo*, and crystallisation from light petroleum–CH_2Cl_2 (3:1) gave $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (**12b**) (0.17 g).

(*iv*) A mixture of (**1f**) (0.52 g, 1.08 mmol) and $[W(CO)_4(cod)]$ (0.47 g, 1.08 mmol) in thf (40 cm^3) was stirred at room temperature for 3 d. Solvent was removed *in vacuo*, and the residue dissolved in light petroleum–CH_2Cl_2 (10 cm^3, 1:1) and chromatographed on Florisil at −10 °C. Elution with light petroleum removed a green band from which $[W_2(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_7(\eta\text{-}C_5Me_5)]$ (**13a**) (0.12 g) was obtained as green *crystals* from light petroleum at *ca.* −78 °C. Elution with light petroleum–CH_2Cl_2 (1:2) removed a purple eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from light petroleum–CH_2Cl_2 (2:1) at *ca.* −20 °C gave purple *crystals* of $[W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (**12c**) (0.18 g).

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