Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 41.[1] Synthesis of Alkylidynetungsten Complexes with (Pyrazol-1-yl)borato Ligands; Crystal Structures of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{B(pz)_4\}]$, $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\{HB(pz)_3\}]\cdot CH_2Cl_2$ and $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}MeC_2Me)(CO)_4(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ *

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Reactions between the poly(pyrazol-1-yl)borato-salts $K[R'B(pz)_3]$ (pz = $C_3H_3N_2$; **1a**, R' = $C_3H_3N_2$; **1b**, R' = H) and the bromo(alkylidyne)tungsten complexes $[W(\equiv CR)Br(CO)_4]$ afford the compounds $[W(\equiv CR)(CO)_2\{R'B(pz)_3\}]$ (**2a**, R = C_6H_4Me-4, R' = $C_3H_3N_2$; **2b**, R = C_6H_4Me-4, R' = H; **2c**, R = Me, R' = H). The structure of (**2a**) has been established by *X*-ray diffraction. The tungsten atom is in an essentially octahedral environment ligated by two CO groups, the alkylidyne fragment CC_6H_4Me-4 [C≡W 1.821(7) Å], and the $[B(pz)_4]^-$ anion functioning as a tridentate ligand. Interestingly, the three N–W distances in the latter are not equal, that *trans* to the alkylidyne carbon being significantly longer [2.284(6) Å] than those *trans* to the CO ligands [2.219(6) and 2.186(5) Å]. The compounds (**2**) have been used to prepare the cluster complexes $[Co_2W(\mu_3\text{-}CR)(CO)_8\{R'B(pz)_3\}]$ [**3a**, R = C_6H_4Me-4, R' = $C_3H_3N_2$; **3b**, R = C_6H_4Me-4, R' = H; **3c**, R = Me, R' = H), $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ (**4**), $[Rh_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\{HB(pz)_3\}]$ (**5a**, R = C_6H_4Me-4; **5b**, R = Me), $[FeRhW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ (**6a**, R = C_6H_4Me-4; **6b**, R = Me), and $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(L)(PMe_3)\{HB(pz)_3\}]$ (**8a**, L = PMe_3; **8b**, L = CO). The structure of (**5a**) was determined by *X*-ray diffraction. The almost isosceles metal-atom triangle [Rh–Rh 2.646(2), Rh–W mean 2.848 Å] is capped by the tolylmethylidyne group [μ_3-C–Rh mean 2.072, μ_3-C–W 2.010(6) Å]. The Rh–Rh bond is symmetrically bridged by a CO ligand, and the two carbonyl groups on tungsten semibridge the two Rh–W bonds [W–C–O 168.0(6) and 164.5(6)°]. The indenyl group attached to each rhodium shows slippage to an η^3-bonding mode. The tridentate tris(pyrazol-1-yl)borato ligand is co-ordinated to the tungsten with the N–W separation [2.245(5) Å] *transoid* to the alkylidyne carbon being somewhat longer than the other two N–W distances [mean 2.222 Å]. The trimetal compounds (**6**) react with but-2-yne to give the alkylidyne- and alkyne-bridged complexes $[FeRhW(\mu_3\text{-}CR)(\mu\text{-}MeC_2Me)(CO)_4(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ (**7a**, R = C_6H_4Me-4; **7b**, R = Me); the structure of (**7a**) being established by *X*-ray diffraction. The metal atoms form a triangle [Fe–Rh 2.577(2), Fe–W 2.756(2), Rh–W 2.677(2) Å] the face of which is bridged asymmetrically by the μ_3-CC_6H_4Me-4 ligand [μ_3-C–Fe 1.926(3), μ_3-C–Rh 2.202(4), μ_3-C–W 2.042(4) Å]. The Rh–W edge is bridged transversely on the opposite face of the triangle by the MeC≡CMe ligand. The iron atom carries three terminal carbonyl groups, while the remaining CO attached to the tungsten semibridges the Fe–W bond [W–C–O 165.3(4)°]. The $[HB(pz)_3]^-$ ligand is bonded to the tungsten with three essentially equal N–W distances, while the indenyl group on the rhodium shows the customary slippage towards η^3 bonding. The spectroscopic properties (i.r. and n.m.r.) of the new compounds are reported and discussed.

We have previously shown that the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) combine with a variety of low-valent metal–ligand fragments to afford complexes with bonds between tungsten and other transition elements (Ti, Zr, V, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au).[1-3] These syntheses provide a versatile route to species containing heteronuclear metal–metal bonds bridged by alkylidyne ligands. In order to extend this area of chemistry, we have used the potassium (pyrazol-1-yl)borato salts (**1**) to prepare the alkylidyne tungsten complexes (**2**) with the object of using the latter as precursors to new cluster compounds.

The ligating properties of the (pyrazol-1-yl)borato anions are well established,[4] and these species are useful reagents in organometallic chemistry.[5-8] However, the possibility that these anions might play a useful role in metal–alkylidyne chemistry has not been exploited, apart from the discovery of a stable mercaptocarbyne complex $[W(\equiv CSMe)(CO)_2\{HB(pz)_3\}]$[9] and the recent synthesis of halogenomethylidyne–molybdenum and –tungsten complexes, and some derivatives of these species in which the metal atoms are ligated by hydrotris- or tetrakis-(3,5-dimethylpyrazol-1-yl)borato-anions.[10] A preliminary account of our work in this area has been given.[11]

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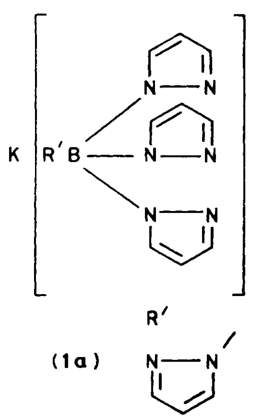
* Dicarbonyl[tetrakis(pyrazol-1-yl)borato-$N^2,N^{2'},N^{2''}$]-*p*-tolylmethylidynetungsten, 1,2-μ-carbonyl-3,3-dicarbonyl-3-[hydrotris(pyrazol-1-yl)borato-$N^2,N^{2'},N^{2''}$]-1,2-bis(η^3-indenyl)-μ_3-*p*-tolylmethylidyne-*triangulo*-dirhodiumtungsten—dichloromethane (1/1), and 1,3-μ-but-2-yne-2,2,2,3-tetracarbonyl-3-[hydrotris(pyrazol-1-yl)borato-$N^2,N^{2'},N^{2''}$]-1-η^3-indenyl-μ_3-*p*-tolylmethylidyne-*triangulo*-rhodiumirontungsten respectively.

Supplementary data available (No. SUP 56370, 16 pp.): H-atom co-ordinates, thermal parameters, complete bond parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Results and Discussion

Addition of the salt (**1a**) to a solution of $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ in tetrahydrofuran (thf) afforded the orange crystalline complex (**2a**). A similar reaction employing the salt (**1b**) gave compound (**2b**), while complex (**2c**) was prepared from (**1b**) and $[W(\equiv CMe)Br(CO)_4]$. The new compounds (**2**) were characterised by microanalysis and by their spectroscopic data (Tables 1 and 2). The presence of the C≡W group in the three complexes was clearly established by the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra, which showed deshielded resonances for the alkylidyne carbon nuclei at δ 286.4 (**2a**), 284.8 (**2b**), and 295.2 p.p.m. (**2c**), with ^{183}W satellite peaks. The chemical shifts of these signals are somewhat less deshielded than those observed in the spectra of the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4, δ 300.1; R = Me, δ 311.4 p.p.m.).[12,13]



(**1a**)

(**1b**) H

$[(RC\equiv)W(CO)_2\{R'B(pz)_3\}]$

	R	R′
(**2a**)	C_6H_4Me-4	$C_3H_3N_2$
(**2b**)	C_6H_4Me-4	H
(**2c**)	Me	H

Since it was our intention to explore the chemistry of the compounds (**2**) in detail, it was decided to establish the structure of one of these species by *X*-ray diffraction. Of particular interest would be the C≡W separation. Suitable crystals of (**2a**) were available for study, and the crystallographic results are summarised in Table 3 with the molecule shown in Figure 1.

The tungsten atom is in an essentially octahedral environment. The C(3)–W separation [1.821(7) Å] corresponds closely to that previously found in $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ [1.82(2) Å].[12] Evidently, replacement of the cyclopentadienyl ligand in the latter by a $B(pz)_4$ group in (**2a**) has little effect on the C≡W distance. The W–C(3)–C(4) angle [164.0(6)°], however, is significantly more bent than that in $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ [176(2)°], being comparable with that found[14] for $[W(\equiv CPh)I(CO)_4]$ [162(4)°]. The C(3)–C(4) separation [1.451(9) Å] in (**2a**) is within the range (1.28—1.47 Å) observed for such distances in several alkylidyne tungsten complexes.[15] The angle between the two carbonyl groups in (**2a**) is 88.1(3)°, and the two ligands are essentially linearly bound to the metal. Again this is similar to the situation found for $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.

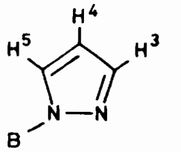
The $[B(pz)_4]^-$ anion consists of four $C_3H_3N_2$ rings tetrahedrally arranged around the boron atom, and three of the rings are co-ordinated to the tungsten atom *via* N(11), N(21), and N(31). The N–W–N angles are similar. However, the N–W distances vary, with N(11) which is *trans* to the carbyne carbon C(3), being further away [2.284(6) Å] than N(21) [2.219(6) Å] or N(31) [2.186(5) Å], which are *trans* to the CO ligands. This feature probably reflects the greater *trans* influence of ≡CR *versus* CO. The non-chelating $C_3H_3N_2$ ring has a shorter B–N distance [1.511(8) Å] than those involving the ligating system (mean 1.547 Å). The dihedral angles between the rings N(11)—C(15) and N(31)—C(35), and between N(21)—C(25) and N(31)—C(35), are 46.5 and 57.5°, respectively.

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

			Yield		Analysis (%)		
	Compound	Colour	(%)	$\nu_{max.}(CO)^b/cm^{-1}$	C	H	N
(**2a**)	$[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{B(pz)_4\}]$	Orange	76	[c]1 986s, 1 903s	[d]42.4(42.4)	3.1(3.1)	18.1(18.0)
(**2b**)	$[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$	Orange	72	[c]1 986s, 1 903s	40.4(41.0)	2.9(3.0)	14.7(15.1)
(**2c**)	$[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$	Yellow	55	1 983s, 1 899s	32.2(32.5)	3.1(2.7)	
(**3a**)	$[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{B(pz)_4\}]$	Green	92	2 078m, 2 036s, 2024m, 2 014m, 1 995m, 1 967m, 1 856m	37.1(37.1)	2.5(2.1)	11.6(12.3)
(**3b**)	$[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{HB(pz)_3\}]$	Green	95	2 077m, 2 036s, 2 023m, 2 013m, 1 995m, 1 967m, 1 856m	35.4(35.6)	1.8(2.0)	9.7(10.0)
(**3c**)	$[Co_2W(\mu_3\text{-}CMe)(CO)_8\{HB(pz)_3\}]$	Green	82	2 076m, 2 033s, 2 018m, 2 011m, 1 988w, 1 977w, 1 955m, 1 861m	29.8(28.9)	1.8(1.7)	11.0(11.1)
(**4**)	$[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$	Orange-brown	16	[c]1 979m, 1 921s, 1 830m	43.8(43.4)	3.5(3.0)	8.7(10.5)
(**5a**)	$[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\text{-}\{HB(pz)_3\}]$	Black	30	[c]1 874s, 1 799m	[d]43.1(43.5)	3.1(3.0)	6.7(7.6)
(**5b**)	$[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\{HB(pz)_3\}]$	Black	73	[c]1 873s, 1 799m	[e]41.7(42.4)	3.4(3.6)	8.5(8.3)
(**6a**)	$[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_9H_7)\text{-}\{HB(pz)_3\}]$	Black	78	2 050vs, 2 006s, 1 978s, 1 913s, 1 844m, 1 823m	39.8(40.8)	2.8(2.5)	8.3(8.9)
(**6b**)	$[FeRhW(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$	Black	83	[c]2 046s, 1 994s, 1 974s, 1 901s, 1 823m, 1 800(sh)	35.8(36.0)	2.2(2.3)	9.6(9.7)
(**7a**)	$[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}MeC_2Me)(CO)_4(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$	Dark green	58	2 011vs, 1 946m, 1 932vs, 1 855m	42.6(43.4)	3.4(3.2)	8.7(8.9)
(**7b**)	$[FeRhW(\mu_3\text{-}CMe)(\mu\text{-}MeC_2Me)(CO)_4(\eta\text{-}C_9H_7)\text{-}\{HB(pz)_3\}]$	Dark green	55	[c]2 001vs, 1 934s, 1 918s, 1 819m	38.8(38.9)	3.0(3.2)	9.5(9.7)
(**8a**)	$[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2\{HB(pz)_3\}]$	Red	65	1 914s, 1 764s	33.4(33.8)	4.1(3.8)	9.0(9.1)
(**8b**)	$[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)\{HB(pz)_3\}]$	Pink	15	2 018s, 1 937s, 1 823m	33.1(32.3)	3.6(3.1)	8.6(9.8)

[a] Calculated values are given in parentheses. [b] In hexane, unless otherwise stated. [c] In CH_2Cl_2. [d] Contains a CH_2Cl_2 molecule of crystallisation. [e] Contains a Et_2O molecule of crystallisation.

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



Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(2a)	2.21 (s, 3 H, Me-4), 6.15 (m, 3 H, H^4), 6.53 (m, 1 H, H^4), 7.04, 7.31 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.51 (s, 2 H, H^3 or H^5), 7.72 (m, 1 H, H^3 or H^5), 7.87 (m, 3 H, H^3 or H^5), 8.03 (s, 2 H, H^3 or H^5)	286.4 [$C\equiv$W, J(WC) 190], 224.7 [CO, J(WC) 170], 148.4, 146.5, 145.3, 142.6, 139.3, 136.5, 135.9 [$C^1(C_6H_4)$ and $C_3H_3N_2$], 129.6, 129.3 (C_6H_4), 107.8, 106.7 ($C_3H_3N_2$), 22.0 (Me-4)
(2b)	2.33 (s, 3 H, Me-4), 6.27 (m, 3 H, H^4), 7.15, 7.41 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.75 (br s, 4 H, H^3 or H^5), 8.05 (br s, 2 H, H^3 or H^5)	284.8 [$C\equiv$W, J(WC) 189], 224.9 [CO, J(WC) 167], 148.4, 145.6, 144.6, 139.1, 136.2 [$C^1(C_6H_4)$ and $C_3H_3N_2$], 129.6, 129.2 (C_6H_4), 106.5 ($C_3H_3N_2$), 22.1 (Me-4)
(2c)	2.43 (s, 3 H, Me), 6.28 (m, 3 H, H^4), 7.73 (m, 4 H, H^3 or H^5), 7.99 (br s, 2 H, H^3 or H^5)	295.2 [$C\equiv$W, J(WC) 189], 223.3 [CO, J(WC) 169], 145.0, 144.1, 135.6, 105.9 ($C_3H_3N_2$), 37.9 (Me)
(3a)[d]	2.41 (s, 3 H, Me-4), 6.25 (m, 3 H, H^4), 6.64 (m, 1 H, H^4), 7.12—8.03 (m, 12 H, C_6H_4, H^3 and H^5)	267.3 (μ_3-C), 226.8 (WCO), 201.1 (CoCO), 159.2 [$C^1(C_6H_4)$], 148.5, 146.4, 137.6, 136.9 ($C_3H_3N_2$), 129.9, 128.1 (C_6H_4), 107.5, 106.5 ($C_3H_3N_2$), 21.2 (Me-4)
(3b)	2.39 (s, 3 H, Me-4), 6.25 (br s, 3 H, H^4), 7.15, 7.35 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.76 (m, 4 H, H^3 or H^5), 7.99 (m, 2 H, H^3 or H^5)	265.7 (μ_3-C), 226.5 (WCO), 200.8 (CoCO), 158.8 [$C^1(C_6H_4)$], 146.8, 144.1, 136.9, 136.1 ($C_3H_3N_2$), 129.5, 127.5 (C_6H_4), 106.6, 106.5 ($C_3H_3N_2$), 21.5 (Me-4)
(3c)[e]	4.10 (s, 3 H, Me), 6.28 [t, 3 H, H^4, J(HH) 2], 7.75—7.77 (m, 6 H, H^3 and H^5)	263.4 [μ_3-C, J(WC) 83], 228.5 [WCO, J(WC) 152], 219.9 [WCO, J(WC) 154], 202.8, 201.3, 199.2, 194.0 (CoCO), 146.8, 143.4, 135.7, 106.1 ($C_3H_3N_2$), 46.4 (Me)
(4)[d]	2.26 (s, 3 H, Me-4), 5.62 (m, 1 H, C_9H_7), 6.10 (m, 5 H, C_9H_7 and H^4), 6.63, 6.94 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.06—7.24 (m, 4 H, C_9H_7), 7.61—7.65 (m, 6 H, H^3 and H^5)	296.6 [d, μ-C, J(RhC) 24], 231.2, 230.7 (WCO), 193.1 [d, RhCO, J(RhC) 92], 156.8 [$C^1(C_6H_4)$], 143.7, 142.6, 135.1 ($C_3H_3N_2$), 134.5—118.4 (C_9H_7, C_6H_4), 105.2, 103.3 ($C_3H_3N_2$), 83.3 (C_9H_7), 20.8 (Me-4)
(5a)	2.04 (s, 3 H, Me-4), 4.35 [d, 2 H, C_9H_7, J(HH) 8], 5.56 (m, 4 H, C_9H_7), 6.11 [t, 3 H, H^4, J(HH) 2], 6.23—6.50 (m, 10 H, C_6H_4 and C_9H_7), 7.03—7.92 (m, 8 H, C_6H_4, H^3 and H^5)	278.2 [t, μ_3-C, J(RhC) 33], 233.4 [WCO, J(WC) 156], 217.5 [t, RhCO, J(RhC) 47], 153.7 [$C^1(C_6H_4)$], 143.6, 135.3 ($C_3H_3N_2$), 128.8—117.2 (C_9H_7 and C_6H_4), 106.7, 105.5, 105.2 ($C_3H_3N_2$, C_9H_7), 88.6, 85.3 (C_9H_7), 20.4 (Me-4)
(5b)	1.03 [t, 3 H, Me, J(RhH) 2], 5.68—6.27 (m × 3, 9 H, C_9H_7 and H^4), 6.83—6.99 (m, 8 H, C_9H_7), 7.15 [d, 2 H, H^3 or H^5, J(HH) 2], 7.62 (m, 3 H, H^3 or H^5), 7.79 [d, 1 H, H^3 or H^5, J(HH) 2]	329.9 [t, μ_3-C, J(RhC) 24], 233.0 [WCO, J(WC) 156], 220.4 [t, RhCO, J(RhC) 52], 143.4, 142.5, 135.2 ($C_3H_3N_2$), 125.5—113.8 (C_9H_7), 106.1, 105.2 ($C_3H_3N_2$), 102.4, 87.7, 86.9 (C_9H_7), 39.5 (Me)
(6a)	2.05 (s, 3 H, Me-4), 4.90—6.20 (m × 6, 6 H, C_9H_7, $C_3H_3N_2$), 6.30—7.90 (m × 10, 14 H, C_9H_7, C_6H_4 and $C_3H_3N_2$)	333.1 [d, μ_3-C, J(RhC) 27, J(WC) 104], 232.9 [WCO, J(WC) 144], 230.8 [WCO, J(WC) 150], 229.3 [d, μ-CO, J(RhC) 42], 217.3 (br s, FeCO), 158.1 [$C^1(C_6H_4)$], 145.5—135.4 ($C_3H_3N_2$), 129.5—107.3 (C_9H_7, C_6H_4), 106.1, 105.9 ($C_3H_3N_2$), 90.3 [d, C_9H_7, J(RhC) 5], 88.5 [d, C_9H_7, J(RhC) 7], 20.3 (Me-4)
(6b)	2.62 (s, 3 H, Me), 5.81—6.41 (m × 5, 6 H, C_9H_7 and H^4), 6.95—7.57 (m × 5, 10 H, C_9H_7, H^3 and H^5)	343.3 [d, μ_3-C, J(RhC) 28], 233.3 (WCO), 230.6 [d, μ-CO, J(RhC) 45], 228.6 (WCO), 212.4 (FeCO), 145.9—135.2 ($C_3H_3N_2$), 127.3—117.0 (C_9H_7), 105.9, 105.8, 105.6 ($C_3H_3N_2$), 103.3 [d, C_9H_7, J(RhC) 1], 90.6 [d, C_9H_7, J(RhC) 2], 87.7 [d, C_9H_7, J (RhC) 1], 44.3 (Me)
(7a)[f]	1.71* (s, 3 H, MeC), 1.87 (s, 3 H, MeC), 2.05* (s, 3 H, Me-4), 2.31 (s, 3 H, Me-4), 2.65* [d, 3 H, MeC, J(RhH) 2], 3.05 [d, 3 H, MeC, J(RhH) 1], 5.11—5.71 (m × 3, 3 H, C_9H_7), 5.79—6.21 (m, 3 H, H^4), 6.99—7.57 (m, 14 H, C_6H_4, C_9H_7, H^3 and H^5)	291.2 [d, μ_3-C, J(RhC) 25], 254.7, 246.9* (WCO), 215.7, 214.6* (FeCO), 144.8—117.5 (C_9H_7, C_6H_4, $C_3H_3N_2$), 106.4—105.2 ($C_3H_3N_2$), 95.7, 94.3* (C_9H_7), 92.3 [d, *C*Me, J(RhC) 17], 84.2*, 82.1, 80.3, 78.3* (C_9H_7), 41.1 (C*Me*), 20.9, 20.5* (Me-4), 15.7*, 15.3 (C*Me*)
(7b)	1.74 (s, 3 H, MeC), 2.57 (s, 3 H, MeC), 3.00 (s, 3 H, MeC), 5.81—6.53 (m × 3, 6 H, C_9H_7 and H^4), 7.23—7.79 (m × 5, 10 H, C_9H_7, H^3 and H^5)	290.6 [d, μ_3-C, J(RhC) 25], 249.1 [WCO, J(WC) 132], 216.2 (FeCO), 143.9—134.3 ($C_3H_3N_2$), 124.9—117.1 (C_9H_7), 106.3, 105.6, 105.0 ($C_3H_3N_2$), 95.0 (C_9H_7), 94.1 [d, *C*Me, J(RhC) 30], 81.4, 78.0 (C_9H_7), 40.3 (μ_3-C*Me*), 14.9, 13.9 (MeC_2Me)
(8a)	1.25 [d, 9 H, PMe_3, J(PH) 9, J(PtH) 35], 1.67 [d, 9 H, PMe_3, J(PH) 8, J(PtH) 20], 2.26 (s, 3 H, Me-4), 6.28 (m, 1 H, H^4), 6.44 (m, 2 H, H^4), 6.54, 6.82 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.42—7.95 (m, 6 H, H^3 and H^5)	332.0 [d, μ-C, J(PC) 54, J(PtC) 644], 234.4 [WCO, J(WC) 162], 161.5 [$C^1(C_6H_4)$, J(PC) 5, J(PtC) 35], 146.0 (C_6H_4), 144.8, 143.5, 134.8, 134.7 ($C_3H_3N_2$), 127.2, 119.8, 119.6 (C_6H_4), 105.8, 104.6 ($C_3H_3N_2$), 20.8 (Me-4), 18.5 [d, PMe_3, J(PC) 27], 17.5 [d, PMe_3, J(PC) 26]
(8b)[d]	1.32 [d, 9 H, PMe_3, J(PH) 10, J(PtH) 33], 2.33 (s, 3 H, Me-4), 5.98 (m, 2 H, H^4), 6.24 (m, 1 H, H^4), 6.36, 6.95 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.42 (m, 2 H, H^3 or H^5), 7.57 (m, 2 H, H^3 or H^5), 7.62 (m, 1 H, H^3 or H^5), 7.91 (m, 1 H, H^3 or H^5)	322.4 [μ-C, J(PtC) 657], 231.7 [WCO, J(WC) 140], 197.9 [PtCO, J(PtC) 1 422], 158.8 [$C^1(C_6H_4)$], 145.4, 143.1, 135.0 134.8 ($C_3H_3N_2$), 126.9, 119.2 (C_6H_4), 105.8, 104.7 ($C_3H_3N_2$), 20.5 (Me-4), 15.7 [d, PMe_3, J(PC) 28, J(PtC) 40]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures unless otherwise stated. [b] Measured in CD_2Cl_2, unless otherwise stated. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2—CH_2Cl_2. [d] Hydrogen-1 spectrum in $CDCl_3$. [e] Carbon-13 spectrum measured at −50 °C. [f] Peaks due to minor isomer marked with an asterisk (see text).

Table 3. Selected internuclear distances (Å) and angles (°) for $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{B(pz)_4\}]$ (**2a**)

W–C(3)	1.821(7)	C(3)–C(4)	1.451(9)	W–C(1)	1.965(7)	C(1)–O(1)	1.164(8)
W–C(2)	1.977(7)	C(2)–O(2)	1.155(9)	W–N(11)	2.284(6)	W–N(21)	2.219(6)
W–N(31)	2.186(5)	N(11)–N(12)	1.363(7)	N(21)–N(22)	1.367(7)	N(31)–N(32)	1.370(7)
N(12)–B	1.551(9)	N(22)–B	1.543(9)	N(32)–B	1.549(9)	B–N(41)	1.511(8)
N(41)–N(42)	1.377(8)	C(15)–N(11)	1.340(9)	C(15)–C(14)	1.396(11)	C(14)–C(13)	1.349(10)
C(13)–N(12)	1.360(9)	N(21)–C(25)	1.348(9)	C(25)–C(24)	1.399(10)	C(24)–C(23)	1.370(10)
C(23)–N(22)	1.354(9)	N(31)–C(35)	1.357(9)	C(35)–C(34)	1.392(9)	C(34)–C(33)	1.364(10)
C(33)–N(32)	1.354(9)	N(41)–N(45)	1.370(9)	C(45)–C(44)	1.361(10)	C(44)–C(43)	1.368(11)
C(43)–N(42)	1.330(9)						
W–C(3)–C(4)	164.0(6)	W–C(1)–O(1)	176.4(6)	W–C(2)–O(2)	177.5(6)	C(1)–W–C(2)	88.1(3)
C(1)–W–N(31)	172.2(2)	C(2)–W–N(21)	170.7(3)	C(3)–W–N(11)	170.8(3)	N(11)–W–N(31)	80.5(2)
N(21)–W–N(31)	80.2(2)	N(21)–W–N(11)	80.5(2)	N(22)–B–N(32)	107.3(6)	N(12)–B–N(22)	107.6(5)
N(32)–B–N(41)	107.8(5)	N(32)–B–N(12)	109.7(5)	N(41)–B–N(22)	113.5(5)	N(12)–B–N(41)	110.4(5)

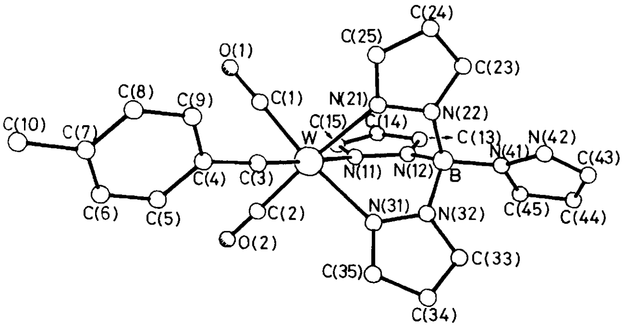
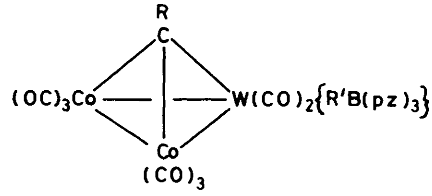
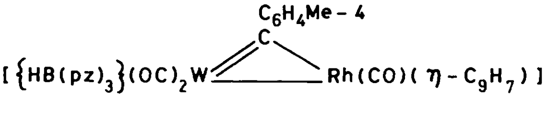


Figure 1. Molecular structure of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{B(pz)_4\}]$ (**2a**) showing the atom-labelling scheme

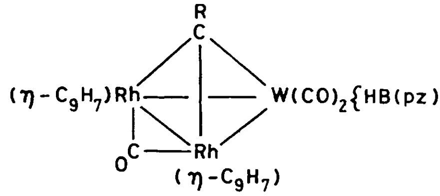


	R	R'
(3a)	$C_6H_4Me\text{-}4$	$C_3H_3N_2$
(3b)	$C_6H_4Me\text{-}4$	H
(3c)	Me	H



$[\{HB(pz)_3\}(OC)_2W(\mu\text{-}CC_6H_4Me\text{-}4)Rh(CO)(\eta\text{-}C_9H_7)]$

(4)



	R
(5a)	$C_6H_4Me\text{-}4$
(5b)	Me

Having fully characterised the alkylidyne tungsten complexes (**2**) they were used to prepare a variety of compounds with heteronuclear metal–metal bonds *via* reactions similar to those previously employed with the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$ or Me).[1–3] Thus the dicobalttungsten complexes (**3**) were obtained in high yield from reactions between $[Co_2(CO)_8]$ and either (**2a**), (**2b**), or (**2c**) at room temperature. The new compounds were characterised in the usual manner (Tables 1 and 2), and in their $^{13}C\text{-}\{^1H\}$ n.m.r. spectra all three complexes show a typical resonance for a $\mu_3\text{-}CR$ group [(**3a**), δ 267.3; (**3b**), 265.7; (**3c**), 263.4 p.p.m.]. As previously reported,[16] octacarbonyldicobalt and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ react to give $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ quantitatively. The latter has a resonance in its $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum for the μ_3-C nucleus at δ 257 p.p.m.

The i.r. spectra of the complexes (**3**) in the CO stretching region (Table 1) show seven [(**3a**) and (**3b**)] or eight (**3c**) absorptions. Likewise the i.r. spectrum of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ has more than the expected number of CO stretching bands for the presence in solution of a single species. As discussed previously,[16,17] we believe that these dicobalttungsten complexes exhibit rotational isomerism.

Compound (**2b**) reacts with $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ in toluene at 60 °C to give a mixture of the complexes (**4**) and (**5a**); the mixture being separated by chromatography. Compound (**5a**) could also be prepared by heating (**2b**) with $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ at 100 °C. In a similar reaction, (**2c**) gave compound (**5b**). The complexes $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_9H_7)(\eta\text{-}C_5H_5)]$ ($R = Me$ or $C_6H_4Me\text{-}4$), analogous to (**4**), have been prepared from room temperature reactions between $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$.[3a] Moreover, the compound $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2(\eta\text{-}C_5H_5)]$ analogous to (**5a**) and (**5b**) has been obtained by treating the dimetal complex $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_9H_7)(\eta\text{-}C_5H_5)]$ with $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ in toluene at 60 °C.[18] Apparently the compounds (**2b**) and (**2c**) are somewhat less reactive towards the low-valent rhodium species than the complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = Me$ or $C_6H_4Me\text{-}4$).

Compounds (**4**), (**5a**), and (**5b**) were characterised by microanalysis, and by their spectroscopic properties (Tables 1 and 2). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4**) showed a doublet signal for the $\mu\text{-}CC_6H_4Me\text{-}4$ group at 296.6 p.p.m. [*J*(RhC) 24 Hz], and three CO resonances at δ 231.2, 230.7, and 193.1 p.p.m. The latter was a doublet signal, and can thus be assigned to the

Table 4. Selected internuclear distances (Å) and angles (°) for [$Rh_2W(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_2(\eta-C_9H_7)_2\{HB(pz)_3\}$] **(5a)**

Rh(1)–Rh(2)	2.646(2)					C(1)–O(1)	1.159(11)
Rh(1)–W	2.853(2)	Rh(2)–W	2.843(2)			C(2)–O(2)	1.168(9)
Rh(1)–C(31)	2.067(8)	Rh(2)–C(31)	2.077(8)	W–C(31)	2.010(6)	C(3)–O(3)	1.173(10)
Rh(1)–C(3)	1.958(9)	Rh(2)–C(3)	1.976(10)	W–C(1)	1.989(9)	N(41)–N(42)	1.345(9)
Rh(1)–C(1)	2.533(6)	Rh(2)–C(2)	2.476(6)	W–C(2)	1.969(8)	N(51)–N(52)	1.361(9)
Rh(1)–C(11)	2.453(8)	Rh(2)–C(21)	2.458(10)	W–N(41)	2.245(5)	N(61)–N(62)	1.364(9)
Rh(1)–C(12)	2.240(10)	Rh(2)–C(22)	2.254(10)	W–N(51)	2.211(7)	N(42)–B	1.549(11)
Rh(1)–C(13)	2.219(11)	Rh(2)–C(23)	2.224(11)	W–N(61)	2.232(8)	N(52)–B	1.560(14)
Rh(1)–C(14)	2.249(12)	Rh(2)–C(24)	2.248(12)			N(62)–B	1.525(14)
Rh(1)–C(15)	2.451(10)	Rh(2)–C(25)	2.488(11)			B–H	1.056(10)
Rh(2)–Rh(1)–W	62.1(0)	W–Rh(2)–Rh(1)	62.1(0)	Rh(2)–W–Rh(1)	55.4(0)	W–C(1)–O(1)	168.0(6)
C(12)–Rh(1)–W	164.3(2)	C(22)–Rh(2)–W	159.5(2)	N(41)–W–C(31)	165.8(3)	W–C(2)–O(2)	164.5(6)
C(13)–Rh(1)–C(31)	162.6(4)	C(23)–Rh(2)–C(31)	158.9(4)	N(61)–W–C(1)	165.6(2)	Rh(2)–C(3)–O(3)	136.7(9)
C(14)–Rh(1)–Rh(2)	174.8(2)	C(24)–Rh(2)–Rh(1)	173.3(2)	N(51)–W–C(2)	160.3(2)	Rh(1)–C(3)–O(3)	138.8(9)
Rh(2)–C(31)–W	88.1(2)			N(51)–W–C(1)	92.7(3)	N(42)–B–N(52)	105.4(8)
W–C(31)–Rh(1)	88.8(3)			C(1)–W–C(2)	85.4(4)	N(52)–B–N(62)	107.6(6)
Rh(1)–C(31)–Rh(2)	79.4(3)			C(2)–W–N(61)	95.7(3)	N(62)–B–N(42)	109.0(8)
				N(61)–W–N(51)	81.4(3)	H–B–N(42)	117.1(6)
				C(31)–W–Rh(1)	46.4(2)	H–B–N(52)	102.6(9)
				C(31)–W–Rh(2)	46.9(2)	H–B–N(62)	114.1(9)

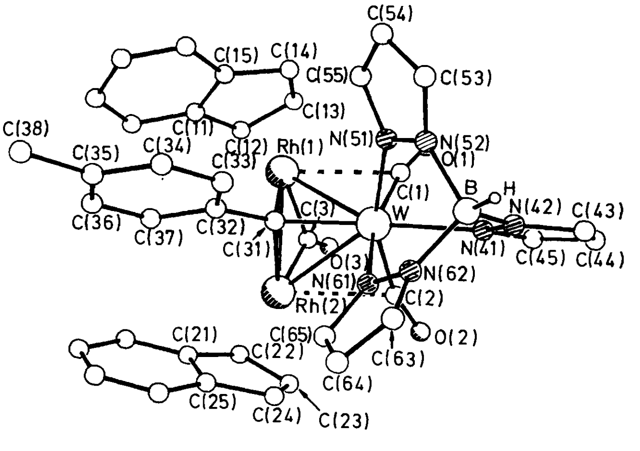


Figure 2. Molecular structure of [$Rh_2W(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_2(\eta-C_9H_7)_2\{HB(pz)_3\}$]·$CH_2Cl_2$ **(5a)** showing the atom-labelling scheme

RhCO group [*J*(RhC) 92 Hz]. The structurally similar compound [$RhW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_9H_7)(\eta-C_5H_5)$] has a $^{13}C-\{^1H\}$ n.m.r. spectrum with peaks at δ 312.4 [*J*(RhC) 30 Hz], 226.2, 222.6, and 188.7 p.p.m. [*J*(RhC) 88 Hz].[3a] In the $^{13}C-\{^1H\}$ n.m.r. spectra of **(5a)** and **(5b)** characteristic resonances for the capping μ_3-C nuclei are observed as triplets at δ 278.2 [*J*(RhC) 33] and 329.9 p.p.m. [*J*(RhC) 24 Hz], respectively. The μ_3-C signal for **(5a)** is of similar chemical shift to the corresponding peak in the spectrum of [$Rh_2W(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_2(\eta-C_9H_7)_2(\eta-C_5H_5)$] [δ 286.0 p.p.m., *J*(RhC) 32 Hz],[18] that for **(5b)** is more deshielded. It is noteworthy that the μ_3-C resonance in **(5b)** is *ca.* 52 p.p.m. more deshielded than that in **(5a)**, and it is possible that this reflects different degrees of asymmetric bridging of the Rh_2W triangles by the ligands μ_3-CMe and $\mu_3-CC_6H_4Me-4$. A similar trend of μ_3-C chemical shifts is observed for the compounds [$Rh_2W(\mu_3-CR)(\mu-CO)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2$] (R = Me, δ 299.7; R = C_6H_4Me-4, δ 271.8 p.p.m.) with the ethylidyne complex showing the more deshielded signal (*ca.* 28 p.p.m.).[3e]

In order to place the structures of these various μ_3-CRh_2W complexes on a firm basis, an *X*-ray diffraction study was carried out on **(5a)**. The results are summarised in Table 4, and the molecule is shown in Figure 2. It possesses a pseudo non-crystallographic mirror plane passing through the atoms C(31), C(3), W and B, and the tolyl and C(45)—N(41) rings. The tolyl group lies approximately perpendicular (98.4°) to the Rh_2W triangular plane. The μ_3-C(31) atom is situated almost symmetrically between Rh(1) and Rh(2) [2.067(8) and 2.077(8) Å, respectively] and is slightly closer to the tungsten atom [2.010(6) Å]. The bridging carbonyl group C(3)–O(3) is essentially symmetrically related to the two rhodium atoms [1.976(10) and 1.958(9) Å]. The two carbonyl ligands on the tungsten atom semibridge the W–Rh(1) and W–Rh(2) edges of the triangle [W–C(1)–O(1) 168.0(6), W–C(2)–O(2) 164.5(6)°]. In accord with the presence of semibridging and bridging carbonyl ligands, the i.r. spectrum of **(5a)** (Table 1) shows bands at 1 874 and 1 799 cm^{-1}, respectively.

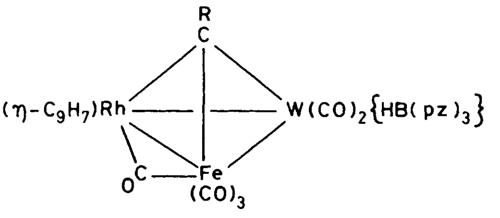
The metal triangle in **(5a)** is almost isosceles [Rh–W 2.853(2) and 2.843(2); Rh–Rh 2.646(2) Å] with the metal–metal separations being perceptibly longer than those in [$Rh_2W(\mu_3-CC_6H_4Me-4)(acac)_2(\mu-CO)(CO)_2(\eta-C_5H_5)$] [acac = acetylacetonate(1–): Rh–W 2.809(2) and 2.764(2); Rh–Rh 2.613(2) Å].[16] Interestingly, the plane defined by C(1), C(2), N(51), and N(61) lies almost parallel to that defined by Rh(1), Rh(2), C(3), and O(3). The N–W distances vary less than in **(2a)**, with N(41)–W *trans* to μ_3-C(31) being insignificantly different from N(51)–W or N(61)–W (Table 4). The three B–N distances show little variation, and are similar to the corresponding separations in **(2a)**. The dihedral angles between the $C_3H_3N_2$ rings are 55.6° for C(45)—N(41) and C(65)—N(61), and 61.2° for C(45)—N(41) and C(55)—N(51).

The indenyl ligands on both rhodium atoms show the familiar tendency of slippage towards an η^3-bonding mode.[18,19] Thus for the C(11)—C(15) ring the data are Rh(1)–C(12) 2.240(10), Rh(1)–C(13) 2.219(11), and Rh(1)–C(14) 2.249(12) Å; whereas Rh(1)–C(11) 2.453(8), and Rh(1)–C(15) 2.451(10) Å. A similar feature is shown in the attachment of the C(21)—C(25) ring to Rh(2). For both rings, the central atom of the 'allyl-like' group [C(13) or C(23)] is closer to each rhodium than the other two carbon atoms [C(12) and C(14), and C(22) and C(24), respectively].

Earlier we prepared the trimetal complex [$FeRhW(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_5(\eta-C_9H_7)(\eta-C_5H_5)$] by treating [$RhW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_9H_7)(\eta-C_5H_5)$] with [$Fe_2(CO)_9$].[18] It was of interest to determine whether an analogous complex **(6a)** could be obtained. Treatment of the iron–tungsten complex [$FeW(\mu-CC_6H_4Me-4)(CO)_5\{HB(pz)_3\}$][11] with [$Rh(CO)_2(\eta$-

Table 5. Selected internuclear distances (Å) and angles (°) for [FeRhW(μ_3-CC$_6$H$_4$Me-4)(μ-MeC$_2$Me)(CO)$_4$(η-C$_9$H$_7$){HB(pz)$_3$}] (**7a**)

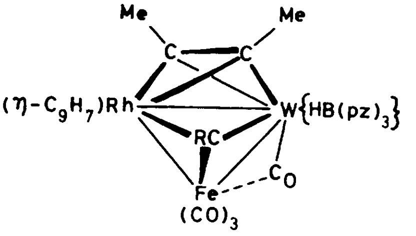
W–Fe	2.756(2)	Rh–W	2.677(2)	Fe–Rh	2.577(2)	C(51)–C(61)	1.346(5)
W–C(11)	2.042(4)	Rh–C(11)	2.202(4)	Fe–C(11)	1.926(3)	C(5)–C(51)	1.495(6)
W–C(51)	2.153(4)	Rh–C(51)	2.136(4)	Fe–C(2)	1.766(4)	C(6)–C(61)	1.484(5)
W–C(61)	2.086(4)	Rh–C(61)	2.157(4)	Fe–C(3)	1.813(5)	N(41)–N(42)	1.357(5)
W–N(41)	2.226(4)	Rh–C(21)	2.436(4)	Fe–C(4)	1.785(4)	N(51)–N(52)	1.354(4)
W–N(51)	2.216(3)	Rh–C(22)	2.233(5)	Fe$\cdots$C(1)	2.523	N(61)–N(62)	1.372(5)
W–N(61)	2.224(3)	Rh–C(23)	2.215(5)	C(2)–O(2)	1.156(6)	B–N(42)	1.536(6)
W–C(1)	1.998(4)	Rh–C(24)	2.223(5)	C(3)–O(3)	1.134(6)	B–N(52)	1.536(5)
C(1)–O(1)	1.166(5)	Rh–C(25)	2.434(4)	C(4)–O(4)	1.142(5)	B–N(62)	1.536(5)
						B–H	0.99(6)
Fe–W–Rh	56.6(0)	Fe–Rh–W	63.2(0)	W–Fe–Rh	60.2(0)		
C(11)–W–N(41)	162.8(1)	C(51)–Rh–C(61)	36.5(1)	Rh–Fe–C(2)	167.4(1)	H–B–N(42)	114(3)
C(11)–W–N(51)	84.8(1)	C(51)–C(61)–C(6)	137.2(4)	Rh–Fe–C(3)	91.2(1)	H–B–N(52)	103(3)
C(11)–W–N(61)	92.8(1)	C(5)–C(51)–C(61)	134.0(4)	Rh–Fe–C(4)	96.5(1)	H–B–N(62)	116(4)
C(51)–W–C(61)	36.9(1)	W–C(1)–O(1)	165.3(4)	W–Fe–C(2)	107.9(1)	N(41)–W–N(51)	80.3(1)
C(51)–W–N(61)	156.6(1)	W–C(11)–C(12)	135.0(2)	W–Fe–C(3)	113.4(1)	N(41)–W–N(61)	76.6(1)
C(61)–W–N(61)	155.6(1)	Rh–C(11)–C(12)	126.8(2)	W–Fe–C(4)	142.7(1)	N(51)–W–N(61)	81.8(1)
C(1)–W–N(51)	165.6(1)	Fe–C(11)–C(12)	130.5(2)	C(11)–Fe–C(2)	113.4(2)	W–N(41)–N(42)	123.4(2)
Fe–W–N(41)	150.3(1)	W–C(11)–Fe	87.9(1)	C(11)–Fe–C(3)	146.9(2)	B–N(42)–N(41)	119.4(3)
Rh–W–N(61)	146.4(1)	W–C(11)–Rh	78.1(1)	C(11)–Fe–C(4)	95.6(2)	W–N(51)–N(52)	124.5(2)
Fe–W–N(51)	129.0(1)	Fe–C(11)–Rh	76.9(1)	Fe–C(2)–O(2)	178.1(4)	B–N(52)–N(51)	118.9(3)
				Fe–C(3)–O(3)	174.4(5)	W–N(61)–N(62)	121.8(2)
				Fe–C(4)–O(4)	174.8(4)	B–N(62)–N(61)	121.1(3)



R

(**6a**) C$_6$H$_4$Me-4

(**6b**) Me



R

(**7a**) C$_6$H$_4$Me-4

(**7b**) Me

C$_9$H$_7$)] in diethyl ether at room temperature afforded a black crystalline complex identified by microanalysis and its spectroscopic properties as (**6a**) (Tables 1 and 2). Similarly, reaction between [FeW(μ-CMe)(CO)$_5${HB(pz)$_3$}] and [Rh(CO)$_2$(η-C$_9$H$_7$)] gave the analogous ethylidyne complex (**6b**). The i.r. spectra of both products showed six bands in the CO stretching frequency region, and the absorptions at 1 823 cm^{-1} (**6a**) and 1 800 cm^{-1} (**6b**) may be attributed to the μ-CO group. The structure of the compound [FeRhW(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_5$(η-C$_9$H$_7$)(η-C$_5$H$_5$)] has been firmly established by *X*-ray diffraction,[18] and the i.r. spectrum shows a band for the carbonyl group bridging the Fe–Rh bond at 1 825 cm^{-1}. The ^{13}C-{^{1}H} n.m.r. spectra of (**6a**) and (**6b**) show characteristic doublet signals for the μ_3-C nuclei at δ 333.1 [*J*(RhC) 27] and 343.3 p.p.m. [*J*(RhC) 28 Hz], respectively. Each spectrum shows four CO resonances (Table 2) which may be assigned to the two non-equivalent carbonyl ligands bound to the tungsten, the μ-CO group, and the Fe(CO)$_3$ fragment. The observation of a single peak for the latter is in accord with the occurrence of site exchange of CO ligands within the Fe(CO)$_3$ moiety at room temperature. In each spectrum, the resonance for the μ-CO group is a well resolved doublet due to ^{103}Rh–^{13}C coupling. Interestingly, the ^{13}C-{^{1}H} n.m.r. spectrum of [FeRhW(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_5$(η-C$_9$H$_7$)(η-C$_5$H$_5$)], measured at room temperature, shows only one CO resonance, indicating exchange of these ligands between the various sites. Evidently, the complexes (**6**) have a higher energy barrier for dynamic behaviour.

During the course of our work we have investigated reactions between the compounds (**6**) and but-2-yne in toluene solution at *ca.* 100 °C. Data for the dark green products are given in Tables 1 and 2. In order to establish firmly the structures of these complexes an *X*-ray diffraction study was carried out on (**7a**). The results are summarised in Table 5, and the molecule is shown in Figure 3.

The structure consists of a triangle of metal atoms with a face of the triangle capped by an alkylidyne carbon atom C(11), and the Rh–W edge transversely bridged by a MeC≡CMe ligand. The overall geometry is thus similar to that previously established[20] for the trinuclear metal complex [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-Me$_3$SiC$_2$SiMe$_3$)(CO)$_7$(η-C$_5$H$_5$)]. Moreover, just as in the latter molecule, a CO ligand semibridges the Fe–Fe edge of the triangle, so in (**7a**) there is a semibridging CO group [W–C(1)–O(1) 165.3(4)°, Fe$\cdots$C(1) 2.523 Å]. The three carbonyl ligands on the iron atom are effectively linear (Fe–C–O 174—178°) with C(3)O(3), which lies transoid to μ_3-C(11), being further from iron [1.813(5) *versus* 1.785(4) and 1.766(4) Å].

As often observed, the plane defined by the tolyl group lies effectively perpendicular to the metal triangle, but C(11)

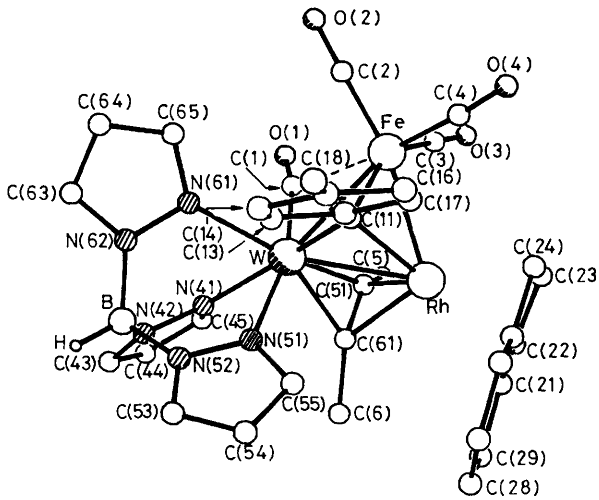
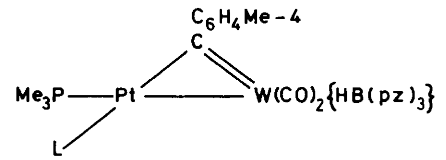


Figure 3. Molecular structure of [FeRhW(μ_3-CC$_6$H$_4$Me-4)(μ-MeC$_2$Me)(CO)$_4$(η-C$_9$H$_7$){HB(pz)$_3$}] (**7a**) showing the atom-labelling scheme

asymmetrically bridges the latter [Fe–C(11) 1.926(3), Rh–C(11) 2.202(4), and W–C(11) 2.042(4) Å]. The noticeably short Fe–C(11) distance may be compared with the shorter of the two Fe–μ_3-C separations [1.941(11) Å] in [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-Me$_3$SiC$_2$SiMe$_3$)(CO)$_7$(η-C$_5$H$_5$)], in which the tolylmethylidyne group also bridges the metal triangle. The Fe–W distance [2.756(2) Å] in (**7a**) may also be compared with that [2.773(2) Å] in [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-Me$_3$SiC$_2$SiMe$_3$)(CO)$_7$(η-C$_5$H$_5$)]. The Rh–W distance in (**7a**) [2.677(2) Å] is considerably shorter than that in (**5a**) [2.853(2) Å], an effect due to the almost symmetrically bridging μ-MeC$_2$Me ligand. In the latter the methyl groups are bent away from the metal triangle [C(51)–C(61)–C(6) 137.2(4), and C(5)–C(51)–C(61) 134.0(4)°], and the C(51)–C(61) distance [1.346(5) Å] shows the characteristic lengthening of a co-ordinated alkyne, being in the range [1.27(4)—1.44(1) Å] previously observed[20–23] in trimetal compounds with μ-(η^2-$\perp$) alkyne ligands.

The separations in (**7a**) between the rhodium atom and the indenyl ligand show the η^3 slippage discussed above for compound (**5a**). The tridentate [HB(pz)$_3$]$^-$ ligand in (**7a**) does not show any significant differences among the N–W distances, nor does the geometry within the rings vary very much. The dihedral angles between the rings C(45)—N(41) and C(65)—N(61), and between the rings C(45)—N(41) and C(55)—N(51) are 52.7 and 59.1°, respectively.

Having established the structure of (**7a**), it is possible to discuss the spectroscopic data obtained for this complex, and that for (**7b**) also (Tables 1 and 2). The bands in the i.r. spectra at 1 855 (**7a**) and 1 819 cm^{-1} (**7b**) may be attributed to the CO ligand semibridging the Fe–W bond. The ^{13}C-{^{1}H} n.m.r. spectrum of (**7b**) was as expected with resonances at δ 290.6, 249.1, and 216.2 p.p.m. characteristic for the μ_3-C, WCO, and Fe(CO)$_3$ groups, respectively. The appearance of only one signal for the tricarbonyliron group is in accord with the customary low-energy site exchange of CO ligands within the Fe(CO)$_3$ fragment on the n.m.r. time-scale. Peaks due to Me groups were observed at 40.3, 14.9, and 13.9 p.p.m. for the μ_3-C*Me*, and two μ-C*Me* fragments, respectively. A doublet resonance at 94.1 p.p.m. [*J*(RhC) 30 Hz] is clearly due to one of the ligated carbon nuclei of but-2-yne. However, the second signal for this ligand was not seen, being probably masked by resonances due to the C$_9$H$_7$ or C$_3$H$_3$N$_2$ rings.



L
(**8a**) PMe$_3$
(**8b**) CO

Surprisingly, the ^{13}C-{^{1}H} n.m.r. spectrum of (**7a**) revealed the presence in solution of a minor isomer. Although only one μ_3-C resonance was observed [δ 291.2 p.p.m., doublet with *J*(RhC) 25 Hz], there were two pairs of CO signals at δ 254.7 (WCO) and 215.7 p.p.m. (FeCO), and at δ 246.9 (WCO) and 214.6 p.p.m. (FeCO), the latter pair of bands being of weak intensity. Peaks due to the minor isomer are marked with an asterisk in Table 2, and are seen in both the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra. The ^{1}H spectrum in particular shows two Me-4 group resonances, and four peaks for the Me groups on the but-2-yne ligand. The nature of the minor isomer is not established by the data available, but may result from the C$_6$H$_4$Me-4 group adopting two different orientations, consequent upon restricted rotation about C(11)–C(12) (Figure 3); imposed by steric crowding, due to the bulky HB(pz)$_3$ and C$_9$H$_7$ ligands. That the isomerism is somehow associated with the tolyl group is supported by the observation of only one form of (**7b**) in solution. Moreover, in the i.r. spectra of both (**7a**) and (**7b**) only four CO stretching bands are observed.

The platinum–tungsten compounds (**8**) were also prepared as part of the work reported herein. Both species (**8a**) and (**8b**) were formed in the reaction between [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] and (**2b**) in light petroleum at room temperature, with (**8a**) as the major product (Table 1). Compound (**8a**) is an analogue of several complexes [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)] (R = alkyl or aryl), previously reported.[2,24,25] In the ^{13}C-{^{1}H} n.m.r. spectrum of (**8a**) (Table 2) the resonance seen as a doublet at δ 332.0 p.p.m. [*J*(PC) 54 Hz], with ^{195}Pt–^{13}C satellite peaks [*J*(PtC) 644 Hz], is characteristic for a species containing the $\overline{\text{Pt}(\mu\text{-C})\text{W}}$ core structure. The presence of the *cis*-Pt(PMe$_3$)$_2$ group is confirmed by the ^{31}P-{^{1}H} n.m.r. spectrum which shows two resonances (both doublets) at δ –12.1 p.p.m. [*J*(PP) 10, *J*(PtP) 3 793 Hz] and –20.9 p.p.m. [*J*(PP) 10, *J*(PtP) 2 849 Hz].

Compound (**8b**), formed simultaneously with (**8a**), is assigned the structure shown in which a PMe$_3$ group of the latter, *trans* to the μ-CC$_6$H$_4$Me-4 ligand, has been substituted by CO. Compounds [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(PR$_3$)(η-C$_5$H$_5$)] (R = alkyl or aryl) have been prepared previously by treating the complexes [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)] in toluene with CO at 10^5 Pa.[26] The tricarbonyl complexes are characterised by three CO stretching bands in their i.r. spectra and by a ^{31}P-{^{1}H} n.m.r. spectrum showing a single singlet resonance. In accord with this, the i.r. spectrum of (**8b**) shows three CO bands, and the ^{31}P-{^{1}H} n.m.r. spectrum has one signal at δ –14.9 p.p.m., with ^{195}Pt–^{31}P coupling [*J*(PtP) 3 290 Hz]. Evidently (**8b**) forms due to a PMe$_3$ ligand in (**8a**) being especially labile in the presence of CO; the source of the latter being (**2b**). The ^{13}C-{^{1}H} n.m.r. spectrum of (**8b**) shows the expected resonance for the μ-C nucleus at 322.4 p.p.m. [*J*(PtC) 657 Hz].

The work described in this paper shows that cluster complexes can be readily prepared containing (pyrazol-1-yl)borato ligands and bridging alkylidyne groups. The structures of the various products are similar to those previously obtained employing the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ as precursors. Qualitatively the latter appear to be somewhat more reactive towards low-valent metal species than the compounds (**2**). However, further work is required to delineate differences in chemical behaviour.

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. The instrumentation used to obtained spectroscopic data has been described in previous papers in this series. The $^{31}P\text{-}\{^1H\}$ chemical shifts for compounds (**8**) reported in the text are measured to high frequency of 85% H_3PO_4 (external). The salts $K[R'B(pz)_3]$ (**1a**, $R' = C_3H_3N_2$; **1b**, $R' = H$)[27] and the compound $[Rh(\eta\text{-}C_2H_4)_2(\eta\text{-}C_9H_7)]$[19] were prepared as described elsewhere. The complex $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ was prepared *in situ* by treating solutions of $[Rh(\eta\text{-}C_2H_4)_2(\eta\text{-}C_9H_7)]$ with CO. All chromatography was carried out on 2 × 20 cm alumina columns (Brockman activity II). Analytical and other data for the new complexes are given in Table 1.

Synthesis of the Alkylidyne–Tungsten Compounds $[W(\equiv CR)(CO)_2\{R'B(pz)_3\}]$ ($R = C_6H_4Me\text{-}4$, $R' = C_3H_3N_2$ *or* H; R = Me, R′ = H).—The salt (**1a**) (0.32 g, 1.0 mmol) was added to $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ (0.48 g, 1.0 mmol) in thf (10 cm^3) at −40 °C. The temperature of the mixture was raised to *ca.* −5 °C, with stirring for 2 d. Reaction is slow because of the insolubility of the salt (**1a**). Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane (10 cm^3) and added to de-gassed alumina (*ca.* 4 g). After removal of dichloromethane *in vacuo*, the alumina residue, on which product had been adsorbed, was transferred to the top of a chromatography column. Elution with dichloromethane–light petroleum (1:4) gave an orange eluate. Solvent was slowly removed *in vacuo* until crystals appeared. Cooling to −78 °C afforded additional product. Solvent was decanted off to give orange *crystals* of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{B(pz)_4\}]$ (**2a**) (0.47 g), which were dried *in vacuo*.

Similarly, (**1b**) (0.25 g, 1.0 mmol) was added to $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ (0.48 g, 1.0 mmol) in thf (−40 °C), and the mixture then stirred for 1 h at *ca.* −20 °C. Solvent was removed *in vacuo*, the residue dissolved in dichloromethane (10 cm^3), adsorbed on de-gassed alumina, and treated as above. Elution of the chromatography column with dichloromethane–light petroleum (1:4) gave an orange solution. The latter was reduced in volume until crystallisation commenced, and then cooled to −78 °C. Solvent was decanted off, and orange *crystals* of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (**2b**) (0.40 g) recovered, and dried *in vacuo*.

Treatment of $[W(\equiv CMe)Br(CO)_4]$ (0.40 g, 1.0 mmol) with (**1b**) (0.25 g, 1.0 mmol) in diethyl ether (10 cm^3) at −20 °C for 12 h afforded a yellow solution. After warming to room temperature, solvent was removed *in vacuo*, and the residue treated as described above. Chromatography, using dichloromethane–light petroleum (1:4), gave a yellow solution. Removal of solvent *in vacuo* and crystallisation from diethyl ether–light petroleum (1:1) at −20 °C gave yellow *crystals* of $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ (**2c**) (0.26 g).

Synthesis of the Dicobalttungsten Complexes $[Co_2W(\mu_3\text{-}CR)(CO)_8\{R'B(pz)_3\}]$ ($R = C_6H_4Me\text{-}4$, $R' = C_3H_3N_2$; $R = C_6H_4Me\text{-}4$ *or* Me, R′ = H).—Compound (**2a**) (0.31 g, 0.50 mmol) and $[Co_2(CO)_8]$ (0.17 g, 0.50 mmol) were stirred together in toluene (10 cm^3) for 30 min, during which time CO evolution was observed, and the solution turned green. Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane (10 cm^3). This solution was adsorbed onto alumina (*ca.* 4 g) and after removal of the dichloromethane by pumping, the alumina was added to the top of a chromatography column. The product eluted as a green band with dichloromethane–light petroleum (1:4). Solvent was partially removed *in vacuo*, and the solution cooled to −20 °C affording green-black *crystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{B(pz)_4\}]$ (**3a**) (0.42 g), which were dried *in vacuo*.

In a similar synthesis, (**2b**) (0.56 g, 1.0 mmol) and $[Co_2(CO)_8]$ (0.34 g, 1.0 mmol) on stirring in diethyl ether (10 cm^3) for 1 h gave green-black *crystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{HB(pz)_3\}]$ (**3b**) (0.80 g). Correspondingly, (**2c**) (0.24 g, 0.50 mmol) and $[Co_2(CO)_8]$ (0.17 g, 0.50 mmol) after 30 min in diethyl ether (10 cm^3) afforded dark green *microcrystals* of $[Co_2W(\mu_3\text{-}CMe)(CO)_8\{HB(pz)_3\}]$ (**3c**) (0.31 g).

Reactions between $[W(\equiv CR)(CO)_2\{HB(pz)_3\}]$ ($R = C_6H_4Me\text{-}4$ *or* Me) *and* $[RhL_2(\eta\text{-}C_9H_7)]$ ($L = C_2H_4$ *or* CO).—Compound (**2b**) (0.56 g, 1.0 mmol) and $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) were heated (60 °C) in toluene (10 cm^3) for 1 h. Solvent was removed *in vacuo* and the residue dissolved in dichloromethane (10 cm^3). This solution was added to *ca.* 4 g of de-gassed alumina which was then pumped dry. The residue was transferred to a chromatography column. Elution with dichloromethane–light petroleum (1:4) led to the recovery of (**2b**) (0.19 g, 35%). Further elution with dichloromethane–light petroleum (1:1) gave an orange-brown solution. Removal of solvent *in vacuo* gave *microcrystalline* $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ (**4**) (0.13 g). Elution of the column with dichloromethane, removal of solvent *in vacuo*, and crystallisation from dichloromethane–light petroleum (1:1) at −20 °C gave black *crystals* of $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\{HB(pz)_3\}]\cdot CH_2Cl_2$ (**5a**) (0.31 g).

Compound (**5a**) (0.46 g, 90%) may also be prepared by heating (**2b**) (0.28 g, 0.50 mmol) with $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) in toluene (10 cm^3) at 100 °C for 4 h. Indeed, this method also afforded the related complex (**5b**). Thus (**2c**) (0.24 g, 0.50 mmol) and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) in toluene (10 cm^3), after heating at 100 °C for 10 h, gave black *crystals* of $[Rh_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\{HB(pz)_3\}]$ (**5b**) (0.34 g): recovered after chromatography of the product, eluting with dichloromethane, and crystallising at −20 °C from dichloromethane–diethyl ether (1:2).

Reactions between $[FeW(\mu\text{-}CR)(CO)_5\{HB(pz)_3\}]$ ($R = C_6H_4Me\text{-}4$ *or* Me) *and* $[Rh(CO)_2(\eta\text{-}C_9H_7)]$.—(*a*) The compounds $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ (0.35 g, 0.50 mmol) and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.14 g, 0.50 mmol) were stirred together (2 h) in diethyl ether (20 cm^3). Solvent was removed *in vacuo*, the residue dissolved in dichloromethane (10 cm^3) and adsorbed on alumina (*ca.* 4 g). The latter was transferred to the top of a chromatography column, and the product eluted with dichloromethane. After removal of solvent *in vacuo*, and crystallisation from dichloromethane–light petroleum (1:1) at −20 °C, black *crystals* of $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ (**6a**) (0.37 g) were obtained.

(*b*) Similarly, $[FeW(\mu\text{-}CMe)(CO)_5\{HB(pz)_3\}]$ (0.31 g, 0.50 mmol) and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.14 g, 0.50 mmol) in diethyl ether (20 cm^3) were stirred for 2 h. Black *crystals* of $[FeRhW(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ (**6b**) (0.36 g) were isolated, as described for (**6a**).

Reactions of $[FeRhW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_9H_7)\{HB(pz)_3\}]$ ($R = C_6H_4Me\text{-}4$ *or* Me) *with But-2-yne.*—(*a*) A toluene (15 cm^3) solution of compound (**6a**) (0.47 g, 0.50 mmol) was placed in a Schlenk tube fitted with a high pressure stopcock. Excess but-2-yne (1 cm^3) was condensed into the

Table 6. Crystal data and experimental parameters *

	(2a)	**(5a)**	**(7a)**
Compound	$C_{22}H_{19}BN_8O_2W$	$C_{38}H_{31}BN_6O_3Rh_2W{\cdot}CH_2Cl_2$	$C_{34}H_{30}BFeN_6O_4RhW$
M	622.2	1 105.1	940.1
Crystal system	Monoclinic	Triclinic	Monoclinic
Crystal habit	Irregular	Hexagonal prism	Rhombs
Colour	Orange	Black	Black
Space group	$P2_1/n$	$P\bar{1}$	Cc
a/Å	8.738(5)	10.526(5)	14.907(8)
b/Å	23.827(14)	11.497(4)	13.915(9)
c/Å	10.896(6)	18.116(11)	15.989(12)
α/°		108.99(4)	
β/°	97.27(4)	89.83(4)	96.32(5)
γ/°		110.83(3)	
U/Å^3	2 250(2)	1 922(2)	3 296(4)
Z	4	2	4
D_c/g cm^{-3}	1.84	1.91	1.89
F(000)	1 208	1 068	1 832
T/K	190	293	190
μ(Mo-K_α)/cm^{-1}	52.8	40.7	45.3
Crystal size (mm)	0.2 × 0.45 × 0.3	0.19 × 0.18 × 0.08	0.4 × 0.4 × 0.4
2θ min.: max.	3:55	3:50	3:65
Data recorded	4 842	6 902	6 413
Data unique	4 748	6 517	6 147
Data used	3 381	5 691	5 865
$I \geqslant n\sigma(I)$	$n = 3.0$	$n = 3.5$	$n = 5.0$
Absorption correction	Empirical	Numerical	Numerical
Faces/indices		<1 1 1> <1 0 1> <0 1 0>	<0 1 0> <1 1 0> <1 0 0> <1 1 1>
Weighting scheme: g $w^{-1} = [\sigma^2(F) + g\|F\|^2]$	0.000 4	0.000 8	0.000 3
$R(R')$	0.036(0.035)	0.049(0.053)	0.021(0.022)

* Nicolet $P3m$ automated diffractometer, operating in an ω–2θ scan mode, with Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å. Refinement was by blocked-cascade least squares.

reaction vessel and the mixture heated for 2 h at 100 °C. Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane (10 cm^3). This solution was adsorbed on degassed alumina (*ca.* 4 g). After pumping *in vacuo* the latter was transferred to the top of a chromatography column. Elution with dichloromethane—light petroleum (1:4) afforded a yellow-brown solution, an i.r. spectrum of which showed that it contained a very small amount of the compound [FeW{μ-C(C_6H_4Me-4)C(Me)C(Me)}(CO)$_5${HB(pz)$_3$}].[28] Further elution with dichloromethane—light petroleum (1:1) afforded a green solution. Solvent was reduced in volume *in vacuo* and cooled to −20 °C to give green *crystals* of [FeRhW(μ_3-CC_6H_4Me-4)(μ-MeC_2Me)(CO)$_4$(η-C_9H_7){HB(pz)$_3$}] (**7a**) (0.27 g).

(*b*) The compounds (**6b**) (0.43 g, 0.50 mmol) and but-2-yne (1 cm^3) in toluene (15 cm^3) were heated at 100 °C for 3 h. Green *crystals* of [FeRhW(μ_3-CMe)(μ-MeC_2Me)(CO)$_4$(η-C_9H_7){HB(pz)$_3$}] (**7b**) (0.24 g) were obtained by the procedure described for (**7a**).

Reaction between [W(≡CC_6H_4Me-4)(CO)$_2${HB(pz)$_3$}] *and* [Pt(C_2H_4)(PMe$_3$)$_2$].—An ethylene-saturated light petroleum (15 cm^3) solution of [Pt(C_2H_4)(PMe$_3$)$_2$] {1 mmol, prepared *in situ* from [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene)} was added to a light petroleum (10 cm^3) solution of (**2b**) (0.56 g, 1.0 mmol). The mixture was stirred for 2 h, during which period a precipitate formed. Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane (10 cm^3) and adsorbed on alumina (*ca.* 4 g), which was transferred to the top of a chromatography column. Elution with dichloromethane–light petroleum (3:7) afforded, after removal of solvent *in vacuo*, pink *microcrystals* of [PtW(μ-CC_6H_4Me-4)(CO)$_3$(PMe$_3$){HB(pz)$_3$}] (**8b**) (0.13 g). Further elution with dichloromethane–light petroleum (1:1) afforded a brown eluate, which after removal of solvent, and crystallisation from diethyl ether–light petroleum at −20 °C,

Table 7. Atomic positional parameters (fractional co-ordinates)(× 10^4) for complex (**2a**), with estimated standard deviations in parentheses

Atom	x	y	z
W	1 666(1)	1 079(1)	1 848(1)
B	4 847(8)	1 095(3)	3 967(6)
N(11)	3 748(7)	494(3)	2 175(5)
N(12)	4 965(6)	602(2)	3 055(5)
C(13)	6 175(8)	274(3)	2 834(7)
C(14)	5 740(9)	−45(3)	1 828(7)
C(15)	4 204(8)	95(3)	1 435(6)
N(21)	3 516(7)	1 710(3)	2 308(5)
N(22)	4 743(6)	1 643(2)	3 206(5)
C(23)	5 753(8)	2 070(3)	3 145(7)
C(24)	5 157(9)	2 434(3)	2 235(7)
C(25)	3 755(9)	2 196(3)	1 726(6)
N(31)	1 915(6)	1 032(3)	3 867(5)
N(32)	3 335(6)	1 043(3)	4 562(5)
C(33)	3 136(8)	1 031(3)	5 774(6)
C(34)	1 600(8)	1 007(4)	5 885(6)
C(35)	858(8)	1 012(4)	4 677(6)
N(41)	6 180(6)	1 086(3)	4 996(5)
C(45)	6 786(8)	631(3)	5 657(7)
C(44)	7 624(9)	823(4)	6 711(7)
C(43)	7 491(8)	1 395(3)	6 656(7)
N(42)	6 602(7)	1 568(3)	5 646(5)
C(1)	1 750(7)	1 117(3)	56(6)
O(1)	1 735(7)	1 159(2)	−1 009(5)
C(2)	273(8)	427(3)	1 539(7)
O(2)	−585(7)	59(2)	1 351(6)
C(3)	−83(8)	1 479(3)	1 363(6)
C(4)	−1 502(8)	1 691(3)	687(6)
C(5)	−2 800(8)	1 346(3)	442(7)
C(6)	−4 092(8)	1 530(3)	−309(7)
C(7)	−4 154(9)	2 066(3)	−803(6)
C(8)	−2 886(9)	2 417(3)	−530(7)
C(9)	−1 574(8)	2 231(3)	198(7)
C(10)	−5 559(10)	2 266(4)	−1 641(9)

Table 8. Atomic positional parameters (fractional co-ordinates)(× 10^4) for complex (**5a**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	4 160(1)	1 272(1)	3 326(1)	C(37)	1 449(8)	−2 611(8)	1 529(5)
Rh(1)	3 602(1)	691(1)	1 677(1)	C(38)	−2 259(12)	−4 725(13)	1 610(9)
Rh(2)	4 941(1)	−569(1)	2 133(1)	C(1)	4 765(8)	2 729(7)	2 885(4)
C(11)	2 205(9)	−168(9)	397(5)	O(1)	5 208(8)	3 717(6)	2 763(4)
C(12)	3 562(10)	813(9)	469(5)	C(2)	6 074(7)	1 395(8)	3 328(4)
C(13)	3 616(10)	2 011(9)	1 013(5)	O(2)	7 257(6)	1 728(6)	3 475(4)
C(14)	2 376(10)	1 776(9)	1 392(5)	C(3)	5 525(8)	875(8)	1 693(5)
C(15)	1 484(8)	429(9)	967(5)	O(3)	6 553(6)	1 534(7)	1 539(4)
C(16)	99(9)	−333(10)	1 015(5)	B	2 951(10)	1 808(10)	5 101(5)
C(17)	−485(10)	−1 585(11)	510(6)	N(41)	5 003(6)	2 869(6)	4 508(3)
C(18)	234(11)	−2 163(10)	−44(5)	N(42)	4 364(7)	2 906(7)	5 155(3)
C(19)	1 547(10)	−1 496(10)	−108(5)	C(43)	5 101(10)	3 968(8)	5 780(5)
C(21)	5 103(10)	−2 651(9)	1 274(5)	C(44)	6 264(10)	4 655(8)	5 522(5)
C(22)	6 299(9)	−1 489(9)	1 398(6)	C(45)	6 164(9)	3 947(7)	4 731(5)
C(23)	6 833(9)	−989(9)	2 206(6)	N(51)	2 321(6)	1 684(6)	3 713(3)
C(24)	5 879(9)	−1 703(9)	2 605(5)	N(52)	2 001(7)	1 853(7)	4 460(4)
C(25)	4 839(9)	−2 818(9)	2 017(5)	C(53)	824(9)	2 064(9)	4 521(6)
C(26)	3 764(10)	−3 927(9)	2 039(7)	C(54)	356(9)	2 023(10)	3 808(6)
C(27)	2 956(12)	−4 838(10)	1 376(6)	C(55)	1 323(8)	1 784(8)	3 311(5)
C(28)	3 203(12)	−4 715(10)	640(7)	N(61)	3 583(6)	59(6)	4 105(4)
C(29)	4 255(11)	−3 627(10)	587(5)	N(62)	3 087(6)	460(6)	4 800(4)
C(31)	3 093(7)	−390(7)	2 423(4)	C(63)	2 766(9)	−497(9)	5 114(5)
C(32)	1 770(7)	−1 524(7)	2 226(4)	C(64)	3 004(10)	−1 539(9)	4 655(5)
C(33)	758(8)	−1 537(8)	2 733(5)	C(65)	3 536(9)	−1 154(8)	4 003(5)
C(34)	−524(10)	−2 562(9)	2 543(6)	Cl(1)	−87(6)	3 600(5)	2 366(3)
C(35)	−840(9)	−3 626(9)	1 824(6)	Cl(2)	−315(7)	5 238(5)	3 919(4)
C(36)	166(10)	−3 634(8)	1 357(5)	C(111)	−718	4 396	2 971
				C(211)	594	5 091	3 139

Table 9. Atomic positional parameters (fractional co-ordinates)(× 10^4) for complex (**7a**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	5 000	7 765(1)	5 000	C(44)	7 299(3)	9 488(4)	4 282(3)
Rh	3 930(1)	8 060(1)	6 215(1)	C(45)	6 407(3)	9 365(3)	4 412(3)
Fe	3 159(1)	7 485(1)	4 780(1)	N(51)	6 041(2)	6 991(2)	5 840(2)
C(11)	4 123(2)	6 798(2)	5 423(2)	N(52)	6 827(2)	6 657(2)	5 602(2)
C(12)	4 183(2)	5 786(2)	5 695(2)	C(53)	7 300(3)	6 193(3)	6 245(3)
C(13)	4 859(3)	5 180(3)	5 432(2)	C(54)	6 811(3)	6 232(3)	6 929(2)
C(14)	4 902(3)	4 208(3)	5 637(3)	C(55)	6 032(2)	6 731(3)	6 646(2)
C(15)	4 279(3)	3 794(3)	6 113(3)	N(61)	5 441(2)	6 739(2)	4 060(2)
C(16)	3 611(3)	4 376(3)	6 385(3)	N(62)	6 327(2)	6 471(2)	4 064(2)
C(17)	3 571(3)	5 347(3)	6 180(2)	C(63)	6 411(3)	5 893(3)	3 404(3)
C(18)	4 327(5)	2 737(3)	6 319(4)	C(64)	5 573(3)	5 759(4)	2 964(3)
C(21)	4 150(3)	8 293(3)	7 733(2)	C(65)	4 994(3)	6 299(3)	3 396(3)
C(22)	3 625(3)	9 024(3)	7 264(3)	C(1)	4 285(3)	8 417(3)	4 033(2)
C(23)	2 806(3)	8 594(4)	6 885(3)	O(1)	4 043(3)	8 893(3)	3 451(2)
C(24)	2 888(3)	7 583(4)	7 018(3)	C(2)	2 872(3)	7 012(3)	3 761(3)
C(25)	3 700(3)	7 399(4)	7 585(2)	O(2)	2 661(3)	6 712(4)	3 094(2)
C(26)	4 078(3)	6 551(4)	7 953(2)	C(3)	2 521(3)	8 594(3)	4 642(3)
C(27)	4 875(3)	6 618(4)	8 484(3)	O(3)	2 077(3)	9 257(3)	4 600(3)
C(28)	5 303(4)	7 500(6)	8 641(3)	C(4)	2 268(3)	6 835(3)	5 183(3)
C(29)	4 972(4)	8 332(4)	8 274(3)	O(4)	1 656(2)	6 446(3)	5 391(2)
B	7 063(3)	6 884(3)	4 712(3)	C(51)	4 504(3)	9 100(3)	5 449(2)
N(41)	6 237(2)	8 449(2)	4 608(2)	C(61)	5 177(2)	8 747(3)	5 990(2)
N(42)	7 033(2)	7 980(3)	4 596(2)	C(5)	4 201(3)	10 093(3)	5 195(3)
C(43)	7 676(3)	8 590(3)	4 399(3)	C(6)	5 907(3)	9 134(3)	6 604(3)

gave red *microcrystals* of [PtW(μ-CC_6H_4Me-4)$(CO)_2$$(PMe_3)_2$$\{HB(pz)_3\}$] (**8a**) (0.59 g).

Crystal Structure Determinations.—The crystal and other experimental data for compounds (**2a**), (**5a**), and (**7a**) are summarised in Table 6. Crystals of (**2a**) and (**7a**) were investigated at 190 K using a dry nitrogen gas flow system. Diffracted intensities for (**5a**) were collected at room temperature. The lattice of this complex contained a disordered molecule of CH_2Cl_2. All data were corrected for Lorentz, polarisation, and *X*-ray absorption effects. The structures were solved by Patterson and Fourier methods, by which all non-hydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were incorporated at calculated positions (C–H 0.96 Å, riding model) for (**2a**) and (**5a**), whereas all hydrogen atoms in (**7a**) and that on boron in (**5a**) were located, and refined with fixed isotropic thermal parameters. Significant residual electron density in the difference-Fourier syntheses at convergence was found only near the metal atoms [(**2a**), 1.3; (**5a**), 3.0; (**7a**), 1.1 e Å^{-3}]. All computations were carried out within the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[29] Scattering factors were from ref. 30. Atom coordinates are in Tables 7—9.

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