Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 80.[1] Mixed-metal Tungsten and Ruthenium Compounds

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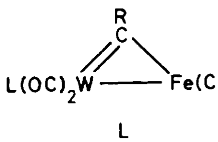
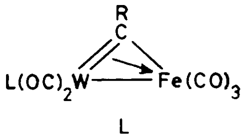
Treatment of the compounds $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ $\{L = \eta\text{-}C_5H_5$ or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]$\}$ with a three-fold excess of $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ in light petroleum affords as the only products the tetranuclear metal cluster complexes $[WRu_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}L]$. In contrast, a similar reaction ($L = \eta\text{-}C_5H_5$) employing a W:Ru mol ratio of 2:1 gives in high yield the trinuclear metal complex $[W_2Ru\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$, which in refluxing cyclohexane releases CO and affords the electronically unsaturated species $[W_2Ru(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)_2]$. With hydrogen and with diazomethane the latter compound affords the complexes $[W_2RuH(\mu\text{-}H)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[W_2Ru(\mu\text{-}CH_2)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2]$, respectively, whereas alkynes yield the species $[W_2Ru(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}R^1C_2R^2)(CO)_3(\eta\text{-}C_5H_5)_2]$ ($R^1 = R^2 =$ Me or Ph; $R^1 = H$, $R^2 = Ph$). Reactions of $[W_2Ru(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)_2]$ with the alkylidyne–tungsten complexes $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ ($L = \eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$) afford the tetranuclear metal compounds $[W_3Ru(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_2L]$. The n.m.r. data for the new compounds are reported and discussed in relation to their structures.

In this paper we describe several tri- and tetra-nuclear metal compounds containing bonds between tungsten and ruthenium. By employing the alkylidyne–tungsten compounds $[W(\equiv CR)(CO)_2L]$ $\{R = C_6H_4Me\text{-}4$, $L = \eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]; $R =$ Me or Ph, $L = \eta\text{-}C_5H_5\}$ as reagents, we have earlier prepared a variety of complexes with bonds between tungsten and iron, ruthenium, or osmium.[2] However, as described below, the majority of the ruthenium-containing species which have been identified are structurally different from those having tungsten–iron bonds, and in part these differences prompted the work described herein.

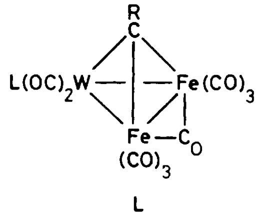
Previous studies with iron carbonyl reagents have yielded several di- and tri-metal compounds. Thus treatment of the complexes $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ ($L = \eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$) with $[Fe_2(CO)_9]$ affords the dimetal compounds $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6L]$ (**1**).[2a,f] However, $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ with $[Fe_2(CO)_9]$ yields the unsaturated 32-valence electron compound $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ (**2a**).[2e] The related species $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5L]$ [$L = \eta\text{-}C_5H_5$ (**2b**) or $\eta\text{-}C_5Me_5$ (**2c**)] have also been obtained. Complex (**2b**) has been prepared by treating $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $[Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2]$ (C_8H_{14} = cyclo-octene).[2e] Compound (**2c**) is formed simultaneously with (**1b**) in the reaction of $[Fe_2(CO)_9]$ with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$, since in the presence of CO the compounds (**1b**) and (**2c**) exist together in equilibrium.[2f] Compound (**1a**) is unstable, and (**2b**) has only a fleeting existence at low temperatures, with both species decomposing to give the trimetal complexes $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**3a**) and $[W_2Fe\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**4**). However, (**3a**) is best obtained by treating $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with an excess of $[Fe_2(CO)_9]$, while (**4**) is formed when an excess of the alkylidyne–tungsten compound is used in the reaction with the iron carbonyl.[2a] These syntheses proceed *via* the intermediacy of the dimetal compounds (**1a**) and (**2b**). Compound (**3b**) is readily prepared from the reaction between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Fe_2(CO)_9]$ when employing an excess of the latter reagent.[2f]



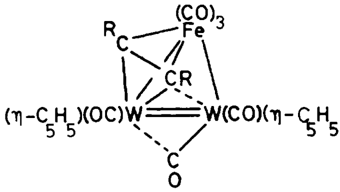
(1a) $\eta\text{-}C_5H_5$
(1b) $\eta\text{-}C_5Me_5$



(2a) $HB(pz)_3$
(2b) $\eta\text{-}C_5H_5$
(2c) $\eta\text{-}C_5Me_5$



(3a) $\eta\text{-}C_5H_5$
(3b) $\eta\text{-}C_5Me_5$



(4)

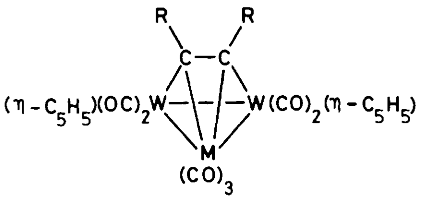
$R = C_6H_4Me\text{-}4$

The reaction between $[Ru_3(CO)_{12}]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in toluene at 80 °C affords $[W_2Ru\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**5a**), but only in low yield (*ca.* 10%).[2b] This contrasts with the high yields obtained in the synthesis of most of the tungsten–iron compounds mentioned above. Complex (**5a**), like its osmium analogue $[W_2Os\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**5b**), obtained from reactions between $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$[2b] or $[Os_3(\mu\text{-}H)_2(CO)_{10}]$[3] and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, exists as a mixture of two isomers (**A**) and (**B**), with the μ_3-alkyne adopting the $\mu_3\text{-}(\eta^2\text{-}\|)$ bonding mode. Interestingly, an iron analogue of (**5a**) or (**5b**) has not been isolated, although *via* a

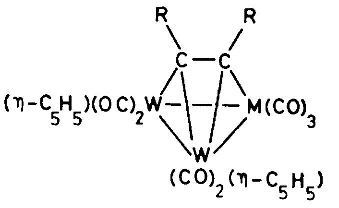
Table 1. Analytical[a] and physical data for the tungsten–ruthenium complexes

	Compound[b]	Colour	Yield (%)	$\nu_{max.}(CO)$[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(9a)	$[WRu_3(\mu_3\text{-}CR)(CO)_{11}\{HB(pz)_3\}]$	Dark purple	68	2 077m, 2 041vs, 2 035s, 2 008m, 1 997w, 1 983w, 1 861vw(br), 1 819vw(br)	[d]30.2 (30.3)	1.6 (1.5)
(9b)	$[WRu_3(\mu_3\text{-}CR)(CO)_{11}(\eta\text{-}C_5H_5)]$	Dark purple	59	2 076m, 2 040vs, 2 033s, 2 010m, 1 980w, 1 968w, 1 956w, 1 835vw(br)	30.0 (29.9)	1.4 (1.3)
(10a)	$[W_2Ru(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_5(\eta\text{-}C_5H_5)_2]$	Black	85	[e]2 044s, 1 985m, 1 958m	39.3 (39.4)	2.9 (2.6)
(11b)	$[W_2RuH(\mu\text{-}H)(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(\eta\text{-}C_5H_5)_2]$	Brown	34	2 052vs, 2 024w, 1 990s, 1 968s, 1 887w(br)	38.7 (38.0)	3.1 (2.8)
(12)	$[W_2Ru(\mu\text{-}CH_2)(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(\eta\text{-}C_5H_5)_2]$	Black	41	2 049s, 1 996m, 1 972m, 1 850vw(br)	39.6 (40.0)	2.9 (2.8)
(13a)	$[W_2Ru(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu_3\text{-}C_2Ph_2)(CO)_3(\eta\text{-}C_5H_5)_2]$	Red	39	2 048s, 1 994m, 1 980m	48.4 (48.4)	3.6 (3.2)
(13b)	$[W_2Ru(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu_3\text{-}C_2Me_2)(CO)_3(\eta\text{-}C_5H_5)_2]$	Orange	79	2 038s, 1 981m, 1 973m	42.5 (42.0)	3.4 (3.1)
(13c)	$[W_2Ru(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu_3\text{-}PhC_2H)(CO)_3(\eta\text{-}C_5H_5)_2]$	Orange	40	2 048s, 1 995m, 1 977m	45.5 (44.8)	3.6 (3.1)
(14c)	$[W_3Ru(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$	Black	40	1 981s, 1 926vs, 1 749m, 1 369m	43.4 (43.0)	3.7 (3.5)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] Measured in light petroleum unless otherwise stated. [d] N, 7.5 (7.6%). [e] In cyclohexane.

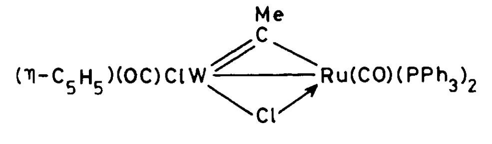


(A)



(B)

	M	R
(5a)	Ru	C_6H_4Me-4
(5b)	Os	C_6H_4Me-4
(5c)	Ru	Me



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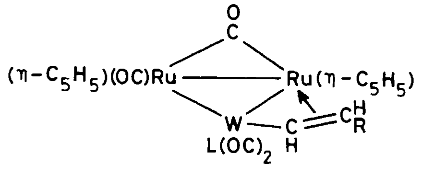


	L	R
(7a)	η-C_5H_5	Me
(7b)	η-C_5H_5	C_6H_4Me-4
(7c)	η-C_5Me_5	C_6H_4Me-4

process involving coupling of alkylidyne fragments at a trimetal centre, the compound $[W_2Fe(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$, structurally similar to (**5**), has been obtained.[4]

No ruthenium analogues of the species (**1**) and (**2**) have as yet been characterised. However, the dimetal compound $[WRu(\mu\text{-}Cl)(\mu\text{-}CMe)Cl(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ (**6**) has been isolated as a product of the reaction between $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and $[RuCl_2(PPh_3)_3]$.[2c] In another attempt to obtain a dimetal tungsten–ruthenium species with a bridging alkylidyne ligand, the complexes $[Ru(CO)_n(PPh_3)_{5-n}]$ (n = 2 or 3) were treated with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$. The product, however, was the trimetal compound $[W_2Ru(\mu_3\text{-}MeC_2Me)(CO)_6(PPh_3)(\eta\text{-}C_5H_5)_2]$, which on addition of $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) to remove PPh_3, affords $[W_2Ru(\mu_3\text{-}MeC_2Me)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**5c**).[2c]

In an investigation concerned with the coupling of alkylidyne and methylene groups at a trimetal centre, the reaction between $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2L]$ (L = η-C_5H_5, R = Me or C_6H_4Me-4; L = η-C_5Me_5, R = C_6H_4Me-4) has been studied.[2g] The products are the tungsten–diruthenium compounds $[WRu_2\{\mu\text{-}\sigma\text{:}\eta\text{-}trans\text{-}CH{=}C(H)R\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2L]$ [L = η-C_5H_5, R = Me (**7a**) or C_6H_4Me-4 (**7b**); L = η-C_5Me_5, R = C_6H_4Me-4 (**7c**)] and $[WRu_2(\mu_3\text{-}CCH_2R)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_2L]$ [L = η-C_5H_5, R = Me (**8a**) or C_6H_4Me-4 (**8b**); L = η-C_5Me_5, R = C_6H_4Me-4 (**8c**)].

In extending the range of compounds with W–Ru bonds we have employed the readily available reagent $[Ru(CO)_4(\eta\text{-}C_2H_4)]$[5] as a source of the fragment $Ru(CO)_4$, isolobal with methylene, and the results are described herein.

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

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
(9a)[d]	2.07 (s, 3 H, Me-4), 6.22—7.79 (C_6H_4 and $C_3H_3N_2$)	329.6 (μ_3-C), 247.3 [WCO, *J*(WC) 127], 197.6, 194.8 (RuCO), 162.8 [$C^1(C_6H_4)$], 146.8—106.9 (C_6H_4 and $C_3H_3N_2$), 21.1 (Me-4)
(9b)[d]	2.30 (s, 3 H, Me-4), 5.51 (s, 5 H, C_5H_5), 7.11—7.36 (m, 4 H, C_6H_4)	301.3 [μ_3-C, *J*(WC) 86], 199.8, 193.5 (CO), 164.7 [$C^1(C_6H_4)$], 137.8, 131.2, 128.4 (C_6H_4), 90.1 (C_5H_5), 21.4 (Me-4)
(10a)[d]	2.23 (s, 3 H, Me-4), 2.54 (s, 3 H, Me-4), 5.31 (s, 10 H, C_5H_5), 6.73—7.44 (m, 8 H, C_6H_4)	381.7 [μ-C, *J*(WC) 136], 261.9 [μ_3-C, *J*(WC) 96], 241.6 [WCO, *J*(WC) 167], 197.8 (RuCO), 165.9, 162.8 [$C^1(C_6H_4)$], 133.9, 133.6 [$C^4(C_6H_4)$], 128.5—119.4 (C_6H_4), 94.9 (C_5H_5), 20.0, 19.7 (Me-4)
(11b)[e]	−11.25 [d, 1 H, μ-H, *J*(HH) 7, *J*(WH) 17], −0.51 [d, 1 H, WH, *J*(HH) 7, *J*(WH) 110, 10], 2.03 (s, 3 H, Me-4), 2.40 (s, 3 H, Me-4), 4.68 (s, 5 H, C_5H_5), 5.23 (s, 5 H, C_5H_5), 6.64—7.46 (m, 8 H, C_6H_4)	372.5 [μ-C, *J*(WC) 134], 259.6 (μ_3-C), 217.4 (WCO), 196.0, 195.3, 194.3 (RuCO), 165.0, 162.8 [$C^1(C_6H_4)$], 133.5, 133.3 [$C^4(C_6H_4)$], 129.3—119.4 (C_6H_4), 96.2, 91.4 (C_5H_5), 21.0, 20.6 (Me-4)
(12)	2.29 (s, 3 H, Me-4), 2.50 (s, 3 H, Me-4), 3.48 [d, 1 H, CH_2, *J*(HH) 10], 5.14 (s, 5 H, C_5H_5), 5.49 (s, 5 H, C_5H_5), 5.63 [d, 1 H, CH_2, *J*(HH) 10], 6.54—7.25 (m, 8 H, C_6H_4)	365.9 [μ-C, *J*(WC) 137], 259.3 [μ_3-C, *J*(WC) 103], 238.1 [WCO, *J*(WC) 178], 198.3, 195.5, 190.0 (RuCO), 166.7, 163.2 [$C^1(C_6H_4)$], 132.8, 132.4 [$C^4(C_6H_4)$], 128.2—118.9 (C_6H_4), 107.9 [μ-CH_2, *J*(WC) 99], 96.9, 95.6 (C_5H_5), 20.8, 20.5 (Me-4)
(13a)	2.33 (s, 3 H, Me-4), 2.51 (s, 3 H, Me-4), 5.34 (s, 10 H, C_5H_5), 6.55—7.24 (m, 18 H, C_6H_4 and Ph)	334.0 [μ-C, *J*(WC) 146], 282.0 [μ_3-C, *J*(WC) 113], 199.6, 193.3 (RuCO), 163.5—120.7 (C_6H_4 and Ph), 140.9 [μ_3-C_2Ph_2, *J*(WC) 93], 100.8 (C_5H_5), 20.7, 20.6 (Me-4)
(13b)	2.29 (s, 3 H, Me-4), 2.40 (s, 6 H, C_2Me_2), 2.49 (s, 3 H, Me-4), 5.64 (s, 10 H, C_5H_5), 6.43—7.15 (m, 8 H, C_6H_4)	331.4 [μ-C, *J*(WC) 146], 277.2 [μ_3-C, *J*(WC) 111], 197.4 (RuCO), 163.8 [$C^1(C_6H_4)$], 135.3 [μ_3-C_2Me_2, *J*(WC) 98], 132.3—121.0 (C_6H_4), 99.4 (C_5H_5), 29.5 ($C_2\mathit{Me}_2$), 20.7, 20.6 (Me-4)
(13c)	2.32 (s, 3 H, Me-4), 2.47 (s, 3 H, Me-4), 5.39 (s, 5 H, C_5H_5), 5.72 (s, 5 H, C_5H_5), 6.43—7.13 (m, 13 H, C_6H_4 and Ph), 8.40 (s, 1 H, ≡CH)	[f] 337.6 [μ-C, *J* (WC) 146], 282.5 [μ-C, *J* (WC) 111], 202.1 196.7, 194.4 (RuCO), 164.4—122.2 (C_6H_4 and Ph), 137.3 [μ_3-Ph*C*≡CH, *J*(WC) 92], 113.5 [μ_3-PhC≡*C*H, *J*(WC) 100], 100.8, 99.2 (C_5H_5), 20.9, 20.7 (Me-4)
(14c)	1.90 (s, 15 H, C_5Me_5), 2.26 (s, 3 H, Me-4), 2.47 (s, 3 H, Me-4), 2.57 (s, 3 H, Me-4), 5.05 (s, 5 H, C_5H_5), 5.72 (s, 5 H, C_5H_5), 6.19—7.35 (m, 12 H, C_6H_4)	347.0, 346.6 (μ-C), 291.1 (μ_3-C), 289.4 (μ_3-η-CO), 276.9 [μ-CO, *J*(WC) 154], 219.1 (WCO), 205.5 (RuCO), 166.2—121.6 (C_6H_4), 104.9 (C_5Me_5), 102.6, 101.1 (C_5H_5), 21.3, 21.0, 20.6 (Me-4), 9.8 ($C_5\mathit{Me}_5$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at room temperature unless otherwise stated. [b] Measured in $CDCl_3$ 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, unless otherwise stated. [d] Measured in CD_2Cl_2. [e] Measured in C_6D_6. [f] Measured at −80 °C in CD_2Cl_2.

Results and Discussion

Treatment of [$Ru(CO)_4(\eta$-$C_2H_4)$] in light petroleum with [$W(\equiv CC_6H_4Me$-$4)(CO)_2\{HB(pz)_3\}$] in a 3:1 mol ratio affords the tetranuclear metal complex [$WRu_3(\mu_3$-CC_6H_4Me-$4)(CO)_{11}\{HB(pz)_3\}$] (**9a**) as the only product. A similar reaction occurs between [$Ru(CO)_4(\eta$-$C_2H_4)$] and [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$] yielding [$WRu_3(\mu_3$-CC_6H_4Me-$4)(CO)_{11}(\eta$-$C_5H_5)$] (**9b**). However, in this synthesis [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$] must be added dropwise to the ruthenium reagent otherwise a different product is obtained, as described below. Data characterising complexes (**9a**) and (**9b**) are given in Tables 1 and 2, and these products are structurally similar to the previously obtained tungsten–osmium compound [$WOs_3(\mu_3$-CC_6H_4Me-$4)(CO)_{11}(\eta$-$C_5H_5)$] (**9c**) prepared in low yield (16%) by treating [$Os_3(CO)_{10}(\eta^2$-$C_8H_{14})_2$] with [$W(\equiv CC_6H_4$-Me-$4)(CO)_2(\eta$-$C_5H_5)$].[2b]

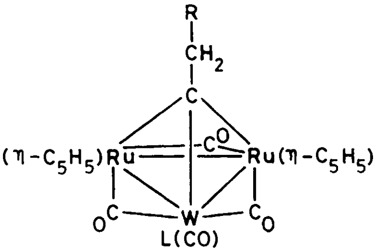
The ^{13}C-{^{1}H} n.m.r. spectra of compounds (**9a**) and (**9b**) show resonances for the μ_3-C nuclei at δ 329.6 and 301.3 p.p.m. respectively, while that for (**9c**) occurs at δ 264.7 p.p.m.[2b] The significantly more deshielded signals observed for (**9a**) and (**9b**) in contrast with (**9c**) suggests that in (**9a**) and (**9b**) the *p*-tolylmethylidyne group asymmetrically bridges the WRu_2 triangle.[6]

If the reaction between [$Ru(CO)_4(\eta$-$C_2H_4)$] and [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$] is carried out with the former reagent added to the latter using a 1:2 mol ratio the product is the trinuclear metal compound [$W_2Ru\{\mu_3$-$C_2(C_6H_4Me$-$4)_2\}(CO)_7(\eta$-$C_5H_5)_2$] (**5a**) isolated in 80% yield. As mentioned earlier, when (**5a**) is prepared by heating [$Ru_3(CO)_{12}$] with [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$] in toluene at 80 °C the yield is only *ca.* 10%. Compound (**5a**) was also obtained in the present work in *ca.* 60% yield by irradiating with visible light mixtures of [$Ru_3(CO)_{12}$] and [$W(\equiv CC_6H_4Me$-$4)(CO)_2(\eta$-$C_5H_5)$] in light petroleum. Evidently under these conditions the metal–metal bonds in [$Ru_3(CO)_{12}$] are readily broken so that addition of the *p*-tolylmethylidyne–tungsten group can readily occur.

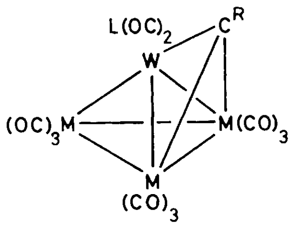
The ready availability of (**5a**) has allowed aspects of its chemistry to be explored. When refluxed in cyclohexane (b.p. 82 °C), with the solution purged with a stream of nitrogen, (**5a**) is smoothly converted into the air-sensitive 46-valence electron complex [$W_2Ru(\mu$-CC_6H_4Me-$4)(\mu_3$-CC_6H_4Me-$4)(CO)_5(\eta$-$C_5H_5)_2$] (**10a**), data for which are given in Tables 1 and 2. A similar scission of the alkyne ligand occurs when (**5b**) is refluxed in methylcyclohexane (b.p. 101 °C) with the solution flushed with argon; a process affording the tungsten–osmium compound [$W_2Os(\mu$-CC_6H_4Me-$4)(\mu_3$-CC_6H_4Me-$4)(CO)_5(\eta$-$C_5H_5)_2$] (**10b**).[7]

The n.m.r. data for (**10a**) are in accord with the structure shown. In the ^{13}C-{^{1}H} spectrum the resonance for the μ-C group occurs at δ 381.7, while that for the μ_3-C nucleus is seen at 261.9 p.p.m.[8] The corresponding signals in the spectrum of (**10b**) occur at δ 384.1 and 244.5 p.p.m.[7] As expected, the ^{1}H and the ^{13}C-{^{1}H} n.m.r. spectra of (**10a**) show two resonances for the chemically non-equivalent Me-4 groups. However, the spectra show only one peak for the η-C_5H_5 ligands, implying that (**10a**) has a mirror plane.

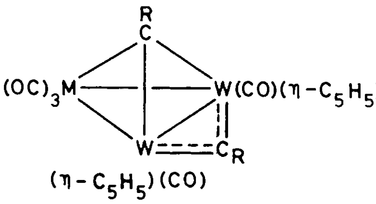
Both (**10a**) and (**10b**) readily react with CO regenerating the μ_3-alkyne complexes (**5a**) and (**5b**), respectively. This result



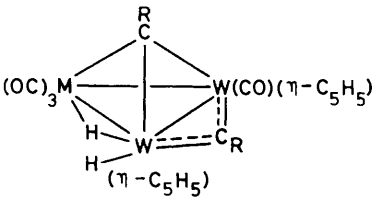
	L	R
(8a)	η-C_5H_5	Me
(8b)	η-C_5H_5	C_6H_4Me-4
(8c)	η-C_5Me_5	C_6H_4Me-4



	M	L
(9a)	Ru	HB(pz)$_3$
(9b)	Ru	η-C_5H_5
(9c)	Os	η-C_5H_5



	M
(10a)	Ru
(10b)	Os



	M
(11a)	Os
(11b)	Ru

R = C_6H_4Me-4

prompted us to study reactions of (**10a**) with other molecules which react readily with unsaturated cluster compounds. Chi and Shapley[7] have reported that (**10b**) reacts with hydrogen (1 atm, 101 °C) to afford the 46-valence electron complex $[W_2OsH)(\mu\text{-H})(\mu\text{-CC}_6H_4Me\text{-}4)(\mu_3\text{-CC}_6H_4Me\text{-}4)(CO)_4(\eta\text{-C}_5H_5)_2]$ (**11a**). A similar reaction occurs between (**10a**) and hydrogen in refluxing cyclohexane to yield $[W_2RuH(\mu\text{-H})(\mu\text{-CC}_6H_4Me\text{-}4)(\mu_3\text{-CC}_6H_4Me\text{-}4)(CO)_4(\eta\text{-C}_5H_5)_2]$ (**11b**). The spectroscopic data for (**11a**) and (**11b**) (Tables 1 and 2) are very similar. In particular, the ^1H n.m.r. spectrum of (**11b**) shows resonances at δ −11.25 and −0.51 for the bridging and terminal hydrido ligands, respectively, with *J*(HH) 7 Hz. The corresponding signals in the ^1H n.m.r. spectrum of (**11a**) are seen at δ −13.15 and −1.87 with *J*(HH) 7 Hz.[7] The terminal hydrido ligand in the compounds (**11**) is coupled in the ^1H spectrum to the two tungsten atoms [(**11a**), *J*(WH) 100 and 11 Hz; (**11b**), *J*(WH) 110 and 10 Hz].

Since compound (**11b**) does not have a plane of symmetry both the ^1H and the ^{13}C-{^1H} n.m.r. spectra show two resonances for each of the groups Me-4 and η-C_5H_5 (Table 2). The signals for the μ-C and μ_3-C nuclei in the ^{13}C-{^1H} spectrum occur at δ 372.5 and 259.6 p.p.m., respectively. The $Ru(CO)_3$ moiety shows three resonances, in contrast with the spectrum of (**10a**) where only one peak for this group occurs, indicating site-exchange of the carbonyl groups at the ruthenium centre in the latter species.

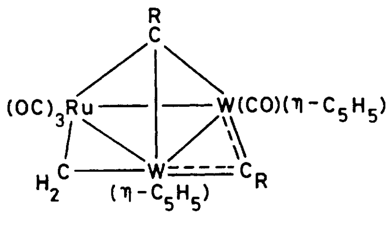
Compound (**10a**) reacts with diazomethane in Et_2O, yielding a product formulated as $[W_2Ru(\mu\text{-CH}_2)(\mu\text{-CC}_6H_4Me\text{-}4)(\mu_3\text{-CC}_6H_4Me\text{-}4)(CO)_4(\eta\text{-C}_5H_5)_2]$ (**12**). The n.m.r. spectra of this complex (Table 2) revealed that no C–C bond formation had occurred between the methylene group and *p*-tolylmethylidyne fragments. This is in marked contrast with the ready formation of μ-vinyl groups as a consequence of coupling of CH_2 and μ-CR fragments in the reaction of (**1b**) with CH_2N_2,[2f] and in the synthesis of the compounds (**7**).[2g]

The ^{13}C-{^1H} n.m.r. spectrum of (**12**) shows the characteristic signals for the μ-C (365.9 p.p.m.) and μ_3-C (259.3 p.p.m.) groups, a resonance for the WCO group, and three peaks for the $Ru(CO)_3$ moiety (Table 2). The resonance for the μ-CH_2 ligand occurs at δ 107.9 p.p.m. [*J*(WC) 99 Hz]. In the ^{13}C-{^1H} spectrum of the complex $[MoFe(\mu\text{-CH}_2)\{\mu\text{-}\sigma:\eta\text{-C}(C_6H_4Me\text{-}4)\text{=}CH_2\}(CO)_5(\eta\text{-C}_5H_5)]$, the signal for the μ-$CH_2$ group is at δ 107.4 p.p.m.,[9] while in the spectra of $[WFe(\mu\text{-CH}_2)\{\mu\text{-}\sigma:\eta\text{-C}(C_6H_4Me\text{-}4)\text{=}CH_2\}(CO)_5(\eta\text{-C}_5Me_5)]$ and $[WFe(\mu\text{-CH}_2)\{\mu\text{-}\sigma:\eta\text{-CH=C(H)C}_6H_4Me\text{-}4\}(CO)_5(\eta\text{-C}_5Me_5)]$ the μ-CH_2 resonances are at δ 89.9 and 88.2 p.p.m., respectively, with *J*(WC) 58 and 61 Hz.[2f]

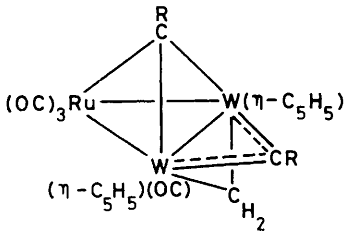
Although the ^1H and ^{13}C-{^1H} n.m.r. spectra of (**12**) identify the various groups present, there are two possible molecular structures, (**12a**) and (**12b**), which fit the data. Unfortunately, it was not possible to grow crystals for an *X*-ray diffraction study. In (**12b**) the methylene group spans the W–W bond while in (**12a**) it bridges the W–Ru bond. Structure (**12a**) is favoured, since that of (**12b**) suggests that coupling of the CH_2 and CC_6H_4Me-4 groups so as to generate a vinyl group would occur, on account of their proximity, but as mentioned this feature is not observed.

We have also studied reactions of (**10a**) with the alkynes PhC≡CPh, MeC≡CMe, and PhC≡CH. Similar products of formulation $[W_2Ru(\mu\text{-CC}_6H_4Me\text{-}4)(\mu_3\text{-CC}_6H_4Me\text{-}4)(\mu_3\text{-R}^1\text{-C}_2R^2)(CO)_3(\eta\text{-C}_5H_5)_2]$ [$R^1 = R^2$ = Ph (**13a**) or Me (**13b**); R^1 = Ph, R^2 = H (**13c**)] were obtained from each of the alkynes, and data for these products are given in Tables 1 and 2.

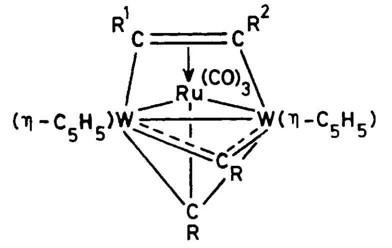
It is evident from the ^{13}C-{^1H} n.m.r. data for the complexes (**13**) that these species each retain the μ-CC_6H_4Me-4 and μ_3-



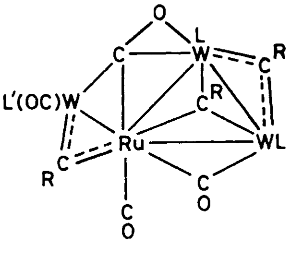
(12a)



(12b)



	R^1	R^2
(13a)	Ph	Ph
(13b)	Me	Me
(13c)	Ph	H



	R	L	L'
(14a)	C_6H_4Me-4	η-C_5H_5	η-C_5H_5
(14b)	Ph	η-C_5H_5	η-C_5H_5
(14c)	C_6H_4Me-4	η-C_5H_5	η-C_5Me_5

CC_6H_4Me-4 fragments present in the precursor (**10a**), since characteristic resonances for these alkylidyne groups occur in each spectrum [μ-C, δ 334.0 (**13a**), 331.4 (**13b**), 337.6 p.p.m. (**13c**); μ_3-C, δ 282.0 (**13a**), 277.2 (**13b**), and 282.5 p.p.m. (**13c**)]. Coupling between the alkylidyne groups and the alkynes has therefore not occurred. This is a somewhat surprising result in view of the many alkylidyne–alkyne coupling reactions observed in reactions of the compounds (**1**)—(**3**) with alkynes.[10]

Examination of the n.m.r. data for (**13a**) and (**13b**) reveals that in these molecules there must be a mirror plane, *i.e.* the alkyne adopts the μ_3-(η^2-$\parallel$) bonding mode with the axis of the ligating carbon atoms lying parallel to the W–W bond. Thus in the ^1H and ^{13}C-{^1H} n.m.r. spectra of (**13a**) and (**13b**) (Table 2) there is only one resonance for the C_5H_5 ligands, and in the ^1H spectrum of (**13b**) there is only one signal for the μ_3-C_2Me_2 group, a feature also apparent in the ^{13}C-{^1H} spectrum. Moreover, in the latter there is a single peak for the ligating carbon atoms of the C_2Me_2 ligand. The ^{13}C-{^1H} n.m.r. spectra of (**13a**) and (**13b**) are also revealing in showing the absence of any resonance due to a WCO group. The $Ru(CO)_3$ moiety in the spectrum of (**13a**) gives rise to two peaks at δ 199.6 and 193.3 p.p.m. of relative intensity 1 : 2. Only one such signal is observed in the spectrum of (**13b**) (δ 197.4 p.p.m.) probably due to dynamic behaviour. A mass spectrum of (**13b**), however, showed that this species contained three carbonyl groups.

The n.m.r. spectra of (**13c**) are more complex, since this species lacks a mirror plane. The ^{13}C-{^1H} n.m.r. spectrum (at −80 °C) showed resonances for two η-C_5H_5 ligands (δ 100.8 and 99.2 p.p.m.), and two peaks for the ligating carbon atoms of the alkyne (δ 137.3 and 113.5 p.p.m.). Both μ_3-C_2 signals showed ^{183}W satellite peaks in support of the assignment. Three resonances occur for the $Ru(CO)_3$ moiety (δ 202.1, 196.7, and 194.4 p.p.m.), but there was no peak assignable to a carbonyl group ligating tungsten. In a spectrum measured at room temperature only one resonance was observed for the $Ru(CO)_3$ fragment, indicating site-exchange of the CO ligands under these conditions.

Because of the isolobal relationship between alkynes and the species [W(≡CC_6H_4Me-4)$(CO)_2$L] (L = η-C_5H_5 or η-C_5Me_5), we have also studied reactions of the latter with compound (**10a**). In refluxing heptane, (**10a**) and [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] afford the tetranuclear metal compound [W_3Ru(μ-CO)(μ_3-η-CO)(μ-CC_6H_4Me-4)$_2$(μ_3-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)$_3$] (**14a**). This product has been previously obtained[11] by treating the mononuclear ruthenium compounds [Ru(η^6-C_8H_{10})(cod)] (C_8H_{10} = cyclo-octa-1,3,5-triene, cod = cyclo-octa-1,5-diene) or [Ru(η^6-$C_{10}H_8$)(cod)] ($C_{10}H_8$ = napthalene) with [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)]. Moreover, the structure of the phenylmethylidyne analogue (**14b**) has been established by *X*-ray diffraction.[11]

The preparation of (**14a**) from (**10a**) and [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] is a more rational synthesis than that described earlier, and the compound was isolated in better yield, since in the earlier work (**5a**) was obtained as a side product. Evidently the electronically unsaturated compound (**10a**) should combine with a variety of metal–ligand fragments to afford cluster compounds. Thus (**10a**) with [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5Me_5)], when refluxed together in heptane, affords [W_3Ru(μ-CO)(μ_3-η-CO)(μ-CC_6H_4Me-4)$_2$(μ_3-CC_6H_4Me-4)-$(CO)_2$(η-C_5H_5)$_2$(η-C_5Me_5)] (**14c**), data for which are given in Tables 1 and 2.

The i.r. spectrum of (**14**) in the carbonyl stretching region shows four bands at 1 981, 1 926, 1 749, and 1 369 cm^{-1}. These absorptions may be compared with those in the spectrum of (**14a**) at 1 972, 1 936, 1 734, and 1 380 cm^{-1}. The two bands in each spectrum at lowest frequency may be assigned to the μ-CO and μ_3-η-CO groups, respectively. However, the assignment[12] for the μ_3-η-CO ligand must be regarded as tentative because of the appearance of C–C bands in this region due to the organic groups.

In the ^{13}C-{^1H} n.m.r. spectrum of (**14c**) resonances for the edge-bridging $\mu\text{-}CC_6H_4Me\text{-}4$ nuclei are seen at δ 347.0 and 346.6 p.p.m., while that for the $\mu_3\text{-}CC_6H_4Me\text{-}4$ nucleus occurs at δ 291.1 p.p.m. The corresponding peaks in the spectrum of (**14a**) are observed at δ 350.1 and 348.0 p.p.m., and at 292.8 p.p.m. The data for the two compounds are also very similar in the carbonyl region of the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, in accord with their similar structures: $\mu_3\text{-}\eta\text{-}CO$, δ 290.4 (**14a**), 289.4 (**14c**); μ-CO, δ 275.8 (**14a**), 276.9 (**14c**); WCO, δ 215.3 (**14a**), 219.1 (**14c**); and RuCO, δ 205.5 (**14a**), 205.5 p.p.m. (**14c**).

The results described in this paper extend the range of known compounds with Ru–W bonds. Conversion of (**5a**) into (**10a**), and the reaction of the latter with hydrogen to yield (**11b**), occur under milder conditions than the corresponding reactions involving the osmium-containing species (**5b**) and (**10b**). Formation of the tetranuclear metal compounds (**9a**) and (**9b**), from the reactions between $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ [L = $HB(pz)_3$ or $\eta\text{-}C_5H_5$], rather than dimetal products, reflects the ease with which carbonyl ruthenium fragments combine to form Ru–Ru bonds.

Experimental

All experiments were carried out using Schlenk-tube techniques under an atmosphere of dry oxygen-free nitrogen, with all solvents dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction of b.p. 40—60 °C. Chromatography columns (*ca.* 3 × 20 cm) were packed with alumina (Brockman activity II). Infrared spectra were measured with Nicolet MX5 and MX10 spectrophotometers, and n.m.r. spectra with JEOL JNM GX400, GX270, and FX90Q instruments. The compounds $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ [L = $\eta\text{-}C_5H_5$,[13] $\eta\text{-}C_5Me_5$,[2f] or $HB(pz)_3$[2e]] were prepared by published methods. The reagent $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ was prepared as follows. A suspension of finely divided $[Ru_3(CO)_{12}]$ in light petroleum at 10 °C was irradiated with visible light (two 100-W bulbs) while C_2H_4 was passed in slow stream through the mixture. Conversion to $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ is complete when the yellow-orange colour due to $[Ru_3(CO)_{12}]$ has disappeared (*ca.* 2—6 h), and the i.r. spectrum of the resulting colourless solution shows $\nu_{max.}$(CO) bands at 2 104w, 2 023s, and 1 998s cm^{-1}. Diazomethane was generated using Aldrich Chemical Co. Diazald kits. Analytical and other data for the new compounds are given in Table 1.

Reactions of $[Ru(CO)_4(\eta\text{-}C_2H_4)]$.—(*i*) A light petroleum (150 cm^3) solution of $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ (0.94 mmol of Ru) was treated at room temperature dropwise (30 min) with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.17 g, 0.31 mmol) in the same solvent (100 cm^3). The resulting mixture was stirred, and after 18 h all the reactants had been consumed (monitored by i.r.), and a dark purple solid had formed. Solvent was decanted, and the residue was washed with light petroleum (3 × 10 cm^3), and crystallised from CH_2Cl_2–n-hexane (1:2) to afford large purple-black *crystals* of $[WRu_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}\{HB(pz)_3\}]$ (**9a**) (0.23 g).

(*ii*) (*a*) Similarly, $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.13 g, 0.32 mmol) in light petroleum (100 cm^3) was added dropwise to $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ (0.94 mmol of Ru) in the same solvent (150 cm^3), giving a black solution. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (20 cm^3, 1:1) and chromatographed. Eluting with the same solvent mixture removed a trace of $[Ru_3(CO)_{12}]$ (identified by i.r.), followed by a purple fraction. Removal of solvent *in vacuo* from the latter, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:4) gave dark purple *crystals* of $[WRu_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{11}(\eta\text{-}C_5H_5)]$ (**9b**) (0.18 g).

(*ii*) (*b*) A light petroleum (150 cm^3) solution of $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ (0.94 mmol in Ru) was added dropwise (*ca.* 1 h) to a rapidly stirred solution of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.80 g, 1.96 mmol) in Et_2O (100 cm^3). After 18 h, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (30 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture removed in succession unreacted $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, $[Ru_3(CO)_{12}]$, and a red fraction. Removal of solvent *in vacuo* from the latter and crystallisation from CH_2Cl_2–light petroleum (1:4) afforded red *crystals* of $[W_2Ru\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**5a**) (0.75 g, 80%), identified spectroscopically.[2b]

Reaction between $[Ru_3(CO)_{12}]$ *and* $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.—A mixture of $[Ru_3(CO)_{12}]$ (0.03 g, 0.047 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.12 g, 0.29 mmol) in light petroleum (100 cm^3) at *ca.* 10 °C was irradiated with visible light for 48 h. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (30 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture separated in sequence unreacted $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Ru_3(CO)_{12}]$, and a red fraction. Removal of solvent *in vacuo* from the latter afforded red *crystals* of (**5a**) (0.085 g, 60%), identified spectroscopically.

Thermolysis of $[W_2Ru\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$.—A cyclohexane (80 cm^3) solution of (**5a**) (0.20 g, 0.20 mmol) was refluxed for 25 min while purging the mixture with a stream of nitrogen. The colour of the solution changed from red to black, and monitoring by i.r. showed that all of (**5a**) had been consumed. Solvent was removed *in vacuo*, and the residue was dissolved in Et_2O (50 cm^3) and passed through an alumina pad (3 × 3 cm). The solution was concentrated to *ca.* 1 cm^3. Slow addition of n-hexane (10 cm^3) with cooling (*ca.* −30 °C) overnight gave black *microcrystals* of $[W_2Ru(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)_2]$ (**10a**) (0.16 g).

Reactions of $[W_2Ru(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)_2]$ (**10a**).—(*i*) *With hydrogen.* A stream of H_2 was passed through a refluxing cyclohexane (100 cm^3) solution of (**10a**) (0.35 mmol, prepared *in situ* as described above). The reaction mixture was placed on a chromatography column. Elution with Et_2O–light petroleum (1:9) yielded one major yellow-brown fraction. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:5), gave brown *microcrystals* of $[W_2RuH(\mu\text{-}H)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**11b**) (0.11 g).

(*ii*) *With diazomethane.* An Et_2O (30 cm^3) solution of (**10a**) (0.39 mmol) at 0 °C was treated with an excess of CH_2N_2. The mixture was warmed to room temperature and stirred for 2 h; after which time monitoring by i.r. revealed that all of (**10a**) had been consumed. Solvent was removed *in vacuo*, and the residue was dissolved in the minimum amount (*ca.* 10 cm^3) of CH_2Cl_2–light petroleum (1:5), and chromatographed. Elution with the same solvent mixture removed in sequence a mustard yellow fraction, a trace of an unidentified purple fraction, and a red eluate [identified by i.r. as (**5a**) (0.05 g)]. Removal of solvent *in vacuo* from the yellow eluate, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:4), yielded black *crystals* of $[W_2Ru(\mu\text{-}CH_2)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**12**) (0.15 g).

(*iii*) *With diphenylacetylene.* A mixture of (**10a**) (0.21 mmol) and PhC≡CPh (0.045 g, 0.25 mmol) was refluxed in cyclohexane (80 cm^3) for 3.5 h, after which period monitoring by i.r. showed that the reaction was complete. The cooled solution was added to a chromatography column, which was eluted initially with light petroleum, to remove unreacted PhC≡CPh. Subsequent elution with CH_2Cl_2–light petroleum (1:5) gave an orange fraction. Removal of solvent *in vacuo*, and crystallisation from light petroleum, yielded dark red *crystals* of [W_2Ru(μ-

CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)(μ_3-C_2Ph_2)$(CO)_3$(η-C_5H_5)$_2$] (**13a**) (0.09 g).

(*iv*) *With but*-2-*yne.* A mixture of (**10a**) (0.20 mmol) and MeC≡CMe (0.5 cm^3, excess) was refluxed in cyclohexane (80 cm^3), the Schlenk tube being attached to a reflux condenser to retain the alkyne in the reaction mixture. After 10 h, when i.r. monitoring revealed that the reaction was complete, the solution was cooled to room temperature and chromatographed. The chromatography column was eluted with CH_2Cl_2–light petroleum (1:4) affording one major orange fraction, followed by traces of (**5a**) and (**10a**). Removal of solvent *in vacuo* from the orange eluate, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:3), gave orange *microcrystals* of [W_2Ru(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)(μ_3-C_2Me_2)$(CO)_3$(η-C_5H_5)$_2$] (**13b**) (0.15 g).

(*v*) *With phenylacetylene.* A mixture of (**10a**) (0.30 mmol) and PhC≡CH (0.50 g, 4.9 mmol) in cyclohexane (80 cm^3) was refluxed for 10 min after which time the reaction was complete. After cooling the solution, it was added to a chromatography column which was eluted with CH_2Cl_2–light petroleum (1:4). There was one major orange band followed by trace amounts of several other fractions. Recovery of the orange eluate, removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:4) afforded orange *microcrystals* of [W_2Ru(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)(μ_3-PhC_2H)$(CO)_3$(η-C_5H_5)$_2$] (**13c**) (0.12 g).

(*vi*) *With* [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5Me_5)]. A mixture of (**10a**) (0.18 mmol) and [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5Me_5)] (0.085 g, 0.18 mmol) was refluxed in heptane (80 cm^3) for 20 min. The mixture was cooled to room temperature and filtered through a Celite pad (2 × 1 cm). The resulting filtrate was reduced in volume *in vacuo* to *ca.* 30 cm^3. Cooling to −20 °C gave black *crystals* of [W_3Ru(μ-CO)(μ_3-η-CO)(μ-CC_6H_4Me-4)$_2$(μ_3-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)$_2$(η-C_5Me_5)] (**14c**) (0.095 g).

(*vii*) *With* [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)]. Similarly, in refluxing heptane (30 cm^3) a mixture of [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] (0.03 g, 0.072 mmol) and (**10a**) (0.063 mmol) gave, after cooling and removal of solvent *in vacuo*, a residue which was dissolved in Et_2O–light petroleum (20 cm^3, 1:4) and chromatographed. Elution with the same solvent mixture afforded in sequence a trace of unreacted [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] and a green fraction. Removal of solvent *in vacuo*, and crystallisation of the residue from Et_2O–hexane yielded green *microcrystals* of [W_3Ru(μ-CO)(μ_3-η-CO)(μ-CC_6H_4Me-4)$_2$(μ_3-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)$_3$] (**14a**) (0.04 g, 44%), identified spectroscopically.[11]

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