Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands.* Part 49.[1] Synthesis of Mixed-metal Complexes with Bonds between Cr, Mo or W and Co, Rh, Ir or Re; Crystal Structure of [CrReRh$_2$(μ_3CC$_6$H$_4$Me-4)(μ-CO)(CO)$_9$(η-C$_9$H$_7$)$_2$]†

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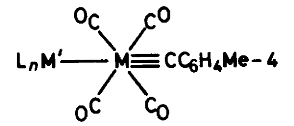
Treatment of the compounds [ReM($\equiv$CR)(CO)$_9$] (M = Cr or W, R = C$_6$H$_4$Me-4) with one equivalent of [Rh(CO)$_2$(η-C$_9$H$_7$)] in light petroleum or tetrahydrofuran (thf) affords the trimetal complexes [MReRh(μ-CR)(CO)$_{10}$(η-C$_9$H$_7$)]. The latter, in refluxing thf, release CO and yield the trimetallatetrahedrane clusters [MReRh(μ_3-CR)(CO)$_9$(η-C$_9$H$_7$)]. Reactions between [Rh(CO)$_2$(η-C$_9$H$_7$)] and [MReRh(μ-CR)(CO)$_{10}$(η-C$_9$H$_7$)] give the compounds [MReRh$_2$(μ_3-CR)(μ-CO)(CO)$_9$(η-C$_9$H$_7$)$_2$]. The molecular structure of the tetranuclear metal cluster containing chromium has been established by *X*-ray diffraction. A CrRh$_2$ triangle of metal atoms [Cr–Rh 2.713(1) and 2.720(2), Rh–Rh 2.659(1) Å] is essentially symmetrically capped by the *p*-tolylmethylidyne ligand [μ_3-C–Cr 1.910(7), mean μ_3-C–Rh 2.044 Å]. The Rh–Rh bond is symmetrically bridged by a CO ligand, and each rhodium carries a η-C$_9$H$_7$ group. The chromium atom, in addition to being part of the μ_3-CCrRh$_2$ fragment, is ligated by an Re(CO)$_5$ moiety and four CO groups, two of which weakly semibridge the Cr–Rh bonds. The cobalt–tungsten complexes [CoW($\equiv$CR)(CO)$_8$] (R = Me or C$_6$H$_4$Me-4) with [Rh(CO)$_2$(η-C$_9$H$_7$)] in light petroleum yield the cobaltdirhodium compounds [CoRh$_2$(μ_3-CR)(μ-CO)(CO)$_3$(η-C$_9$H$_7$)$_2$]. Structurally related [CoRh$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_3$(η-C$_5$Me$_5$)$_2$] has been obtained from [CoW($\equiv$CC$_6$H$_4$Me-4)(CO)$_8$] and [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$]. Similar syntheses using [MoW($\equiv$CR)(CO)$_7$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4) with [Co$_2$(CO)$_8$] or [Rh(CO)$_2$(η-C$_9$H$_7$)] afford [MoCo$_2$(μ_3-CR)(CO)$_8$(η-C$_5$H$_5$)], and a mixture of the di- and tri-metal compounds [MoRh(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] and [MoRh$_2$(μ_3-CR)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η-C$_9$H$_7$)$_2$], respectively. Related *p*-tolylmethylidyne bridged complexes [MoM(μ-CR)(CO)$_2$(L)(η-C$_5$H$_5$)(η-C$_9$H$_7$)] (M = Rh, L = PMe$_3$; M = Ir, L = CO), [WM(μ-CR)(CO)$_3$(η-C$_5$Me$_5$)(η-C$_9$H$_7$)] (M = Rh or Ir), [WRh$_2$(μ_3-CR)(μ-CO)$_2$(CO)$_2$(η-C$_5$Me$_5$)(η-C$_9$H$_7$)$_2$], and [WRhIr(μ_3-CR)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η-C$_9$H$_7$)$_2$] have also been synthesised. Spectroscopic data for the new compounds are reported, and are discussed in relation to the structures proposed.

We have recently employed the dimetal compounds [ReM($\equiv$CC$_6$H$_4$Me-4)(CO)$_9$] (**1a**, M = Cr; **1b**, M = Mo; **1c**, M = W) and [CoW($\equiv$CC$_6$H$_4$Me-4)(CO)$_8$] (**1d**) as precursors to a variety of cluster compounds containing heteronuclear metal–metal bonds.[2] The M$\equiv$C bonds present in the species (**1a**)—(**1d**) are reactive sites towards low-valent metal fragments, and reactions readily occur with [Co$_2$(CO)$_8$], [Ni(cod)$_2$] (cod = cyclo-octa-1,5-diene), [Pt(C$_2$H$_4$)$_3$], [Pt(C$_2$H$_4$)(PMe$_3$)$_2$], [Pt(C$_2$H$_4$)$_2$\{P(cyclo-C$_6$H$_{11}$)$_3$\}], or [Fe$_2$(CO)$_9$]. In this manner new tri-, tetra-, and penta-nuclear metal compounds have been obtained. In this paper we report further reactions of (**1a**), (**1c**), and (**1d**), as well as some studies with [MoW($\equiv$CC$_6$H$_4$Me-4)(CO)$_7$(η-C$_5$H$_5$)] (**1e**). We also report some syntheses of heteronuclear di- and tri-metal compounds from [Mo($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] and [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$Me$_5$)].



	M	M′L$_n$
(**1a**)	Cr	Re(CO)$_5$
(**1b**)	Mo	Re(CO)$_5$
(**1c**)	W	Re(CO)$_5$
(**1d**)	W	Co(CO)$_4$
(**1e**)	W	Mo(CO)$_3$(η-C$_5$H$_5$)

Results and Discussion

Treatment of the compounds (**1a**) or (**1c**) with one equivalent of [Rh(CO)$_2$(η-C$_9$H$_7$)] in dichloromethane or light petroleum affords the trimetal complexes [MReRh(μ-CC$_6$H$_4$Me-4)(CO)$_{10}$(η-C$_9$H$_7$)] (**2a**, M = Cr; **2b**, M = W), respectively. These species were identified by microanalysis and by their spectroscopic properties (Tables 1 and 2). In particular, the ^{13}C-\{^{1}H\} n.m.r. spectra showed characteristic resonances for the ligated carbon nuclei of the μ-*C*C$_6$H$_4$Me-4 groups[3] which appear as doublets due to ^{103}Rh-^{13}C coupling [(**2a**), 355.9 p.p.m., *J*(RhC) 31 Hz; (**2b**), 318.8 p.p.m., *J*(RhC) 28, *J*(WC) 138 Hz]. The compounds (**2**) are related to the previously reported trimetal complexes [MRePt(μ-CC$_6$H$_4$Me-4)(CO)$_9$(PMe$_3$)$_2$] (M = Cr or W)[2b] and [MReFe(μ-CC$_6$H$_4$Me-4)(CO)$_{13}$] (M = Mo or W),[2c] since the groups Rh(CO)(η-C$_9$H$_7$), Pt(PMe$_3$)$_2$,

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*This series has previously been entitled 'Chemistry of Di- and Trimetal Complexes with Bridging Carbene or Carbyne Ligands.'

† 1,2-μ-Carbonyl-3,3,3,3-tetracarbonyl-1,2-bis(η-indenyl)-3-(pentacarbonylrhenio)-μ_3-*p*-tolylmethylidyne-*triangulo*-dirhodiumchromium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 1. Analytical[a] and physical data for the di-, tri-, and tetra-nuclear metal compounds

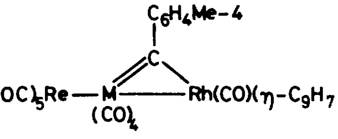
	Compound[b]	Colour	Yield (%)	$\nu(CO)^c/cm^{-1}$	Analyses(%)	
					C	H
(2a)	$[CrReRh(\mu\text{-}CR)(CO)_{10}(\eta\text{-}C_9H_7)]$	Orange	32	2 104m, 2 023m, 2 006s, 1 977m, 1 954w, 1 913w	38.4(38.6)	1.4(1.7)
(2b)	$[WReRh(\mu\text{-}CR)(CO)_{10}(\eta\text{-}C_9H_7)]$	Orange	43	2 099m, 2 033m, 2 005s, 1 980s, 1 957m, 1 937w	33.5(33.4)	1.2(1.5)
(3a)	$[CrReRh(\mu_3\text{-}CR)(CO)_9(\eta\text{-}C_9H_7)]$	Brown	77	2 076s, 2 031s, 2 019s, 1 996m, 1 986m, 1 955m, 1 938w br, 1 872w br	38.7(38.5)	2.0(1.7)
(3b)	$[WReRh(\mu_3\text{-}CR)(CO)_9(\eta\text{-}C_9H_7)]$	Brown	73	2 075s, 2 041s, 2 012s, 1 994s, 1 984(sh), 1 948s, 1 944(sh), 1 910w br	33.4(33.1)	1.3(1.5)
(4a)	$[CrReRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]^d$	Green	20	2 104m, 2 008s, 1 986m, 1 968m, 1 908w br, 1 831w	39.1(38.9)	1.7(2.0)
(4b)	$[WReRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]$	Green	33	2 099m, 2 010m, 2 000s, 1 975m, 1 930w br, 1 833w br	33.4(33.1)	1.3(1.5)
(6a)	$[CoRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_9H_7)_2]$	Green	80	[e]2 037s, 1 992(sh), 1 805m br	50.6(50.7)	2.8(3.0)
(6b)	$[CoRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(PPh_3)(\eta\text{-}C_9H_7)_2]$	Green	65	[e] 1 994s, 1 949s, 1 780m br	59.6(59.8)	3.8(3.8)
(6c)	$[CoRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_9H_7)_2]$	Green	62	[e] 2 038vs, 1 988s, 1 803m	44.9(45.4)	2.6(2.7)
(7)	$[CoRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)_2]$	Brown	19	2 026vs, 1 982s, 1 965s, 1 785m	50.9(51.2)	5.2(5.0)
(8)	$[MoCo_2(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$	Green	90	2 083m, 2 073w, 2 043s, 2 033vs, 2 020m, 2 006s, 1 997w, 1 937w, 1 890w	41.6(41.6)	2.0(2.0)
(9)	$[MoRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$	Green	41	1 983s, 1 933s, 1 788m	52.8(52.1)	3.5(3.3)
(10a)	$[MoRh(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$	Red	20	2 015w, 1 991m, 1 938vs, 1 872m br	53.4(53.0)	3.6(3.4)
(10b)	$[MoRh(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$	Black	92	[e] 1 883vs, 1 786m br	53.7(53.1)	4.4(4.1)
(10c)	$[MoIr(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$	Brown	80	1 976s, 1 931vs, 1 874m -	46.0(45.8)	3.1(2.9)
(11a)	$[WRh(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5Me_5)(\eta\text{-}C_9H_7)]$	Red	80	[e] 1 975m, 1 909s, 1 828m	52.2(49.7)	5.1(4.0)
(11b)	$[WIr(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5Me_5)(\eta\text{-}C_9H_7)]$	Brown	65	1 964s, 1 912vs, 1 846m	44.8(44.3)	3.7(3.6)
(12)	$[WRhIr(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$	Purple	10	[e] 1 982vs, 1 920vs, 1 751m	42.2(42.5)	2.9(2.7)
(13)	$[WRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)(\eta\text{-}C_9H_7)_2]$	Green	26	[e] 1 975m, 1 913s, 1 767m	49.4(49.7)	4.0(3.8)

[a] Calculated values are given in parentheses. [b] $R = C_6H_4Me\text{-}4$. [c] Measured in light petroleum, unless otherwise stated. [d] Crystallises with a molecule of CH_2Cl_2. [e] Measured in CH_2Cl_2.

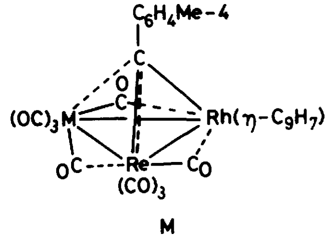
and $Fe(CO)_4$ present in these various species are all isolobal[4] with CH_2. Thus formally the products result from co-ordination of the rhodium, platinum, and iron metal–ligand fragments with the $M{\equiv}C$ bonds in **(1a)**—**(1c)**.[5]

When the compounds **(2)** are refluxed in tetrahydrofuran (thf) solution carbon monoxide is released, and the trimetallatetrahedrane clusters $[MReRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9(\eta\text{-}C_9H_7)]$ (**3a**, M = Cr; **3b**, M = W) are formed. Data for **(3)** are summarised in Tables 1 and 2. Synthesis of the compounds **(3)** in this manner is similar to the formation of the complexes $[MReFe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{12}]$ (M = Mo or W) *via* CO release from $[MReFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{13}]$.[2c]

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the compounds **(3)** (Table 2) are informative. Resonances for the μ_3-C groups are seen as doublets: that for **(3a)** occurring at δ 316.1 [J(RhC) 46 Hz], and that for **(3b)** at 301.6 p.p.m. [J(RhC) 46, J(WC) 46 Hz]. These chemical shifts may imply that the *p*-tolylmethylidyne ligands are asymmetrically bridging the metal triangles. Generally trimetal compounds with $\mu_3\text{-}CC_6H_4Me\text{-}4$ groups show signals in the range 250—300 p.p.m.[6,7] However, in the complexes $[ReW_2(\mu\text{-}Br)(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2]$,[8] $[AuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$,[9] and $[FeWPt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$[10] the μ_3-C groups resonate at 305.2, 303.3, and 323.1 p.p.m., respectively. These compounds have been studied by *X*-ray diffraction, and for each species it has been found that the μ_3-C groups asymmetrically bridge the metal triangles in such a manner that they are essentially equidistant from two metal centres, while being significantly further from the third. In contrast, in the compounds $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$,[11] $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$,[7] and $[CuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$,[12] wherein the μ_3-C groups symmetrically bridge the metal triangles, the chemical shifts for the alkylidyne carbon nuclei are appreciably less deshielded; occurring at 282.6, 287.3, and 266.5 p.p.m., respectively.



M
(2a) Cr
(2b) W



M
(3a) Cr
(3b) W

In the carbonyl region of their $^{13}C\text{-}\{^1H\}$ n.m.r. spectra, the complexes **(3)** show six signals (Table 2). Definitive assignments are possible on the basis of chemical shifts and peak intensities. Thus for **(3b)** a doublet signal at 219.2 p.p.m. [J(RhC) 19 Hz] may be ascribed to a CO ligand asymmetrically bridging a bond between rhodium and either rhenium or tungsten. The relatively small $^{103}Rh\text{–}^{13}C$ coupling of 19 Hz contrasts with that found (47 Hz) for the CO ligand which symmetrically bridges the Rh–Rh bond in $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}$

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the di-, tri, and tetra-nuclear metal compounds

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
(2a)	2.37 (s, 3 H, Me-4), 5.42, 5.58, 6.10 (3 × m, 3 H, C_9H_7), 5.8—7.3 (m, 8 H, C_6H_4, C_9H_7)	355.9 [d, μ-C, *J*(RhC) 31], 233.1 (4 CrCO), 194.7 (4 ReCO), 188.1 [d, 1 RhCO, *J*(RhC) 92], 182.9 (1 ReCO), 155.0 [$C^1(C_6H_4)$], 146.0—84.4 (C_6H_4, C_9H_7), 21.8 (Me-4)
(2b)	2.28 (s, 3 H, Me-4), 5.53, 5.63, 6.20 (3 × m, 3 H, C_9H_7), 7.0—7.3 (m, 8 H, C_6H_4, C_9H_7)	318.8 [d, μ-C, *J*(RhC) 28, *J*(WC) 138], 211.2 [4 WCO, *J*(WC) 122], 195.2 (4 ReCO), 188.1 [d, 1 RhCO, *J*(RhC) 89], 176.8 (1 ReCO), 156.9 [$C^1(C_6H_4)$], 140.0—101.5 (C_6H_4, C_9H_7), 21.9 (Me-4)
(3a)	2.46 (s, 3 H, Me-4), 4.53 [d of d, 1 H, H^2, C_9H_7, *J*(HH) 5 and 3], 5.84 (m, 2 H, H^1 and H^3, C_9H_7), 7.0—7.5 (m, 8 H, C_6H_4, C_9H_7)	316.1 [d, μ_3-C, *J*(RhC) 46], 222.9 (1 CrCO), 221.3 (4 CrCO), 211.2 [d, μ-CO, *J*(RhC) 9], 192.5, 191.2, 185.5 (ReCO), 159.4 [$C^1(C_6H_4)$], 138.9—82.7 (C_6H_4, C_9H_7), 21.2 (Me-4)
(3b)	2.43 (s, 3 H, Me-4), 4.45 [d of d, 1 H, H^2, C_9H_7, *J*(HH) 5 and 3], 5.85 (m, 2 H, H^1 and H^3, C_9H_7), 6.9—7.4 (m, 8 H, C_6H_4, C_9H_7)	301.6 [d, μ_3-C, *J*(RhC) 46, *J*(WC) 46], 219.2 [d, μ-CO, *J*(RhC) 19], 197.4 [1 WCO, *J*(WC) 127], 195.7 [4 WCO, *J*(WC) 119], 195.2, 194.0, 188.1 (ReCO), 160.6 [$C^1(C_6H_4)$], 138.5—80.6 (C_6H_4, C_9H_7), 21.2 (Me-4)
(4a)	2.32 (s, 3 H, Me-4), 5.32, 5.41, 6.25 (3 × m, 6 H, C_9H_7), 6.1—7.2 (m, 12 H, C_6H_4, C_9H_7)	333.3 [t, μ_3-C, *J*(RhC) 31], 242.7 (br, 2 CrCO), 231.5 (br, 2 CrCO), 219.8 [t, μ-CO, *J*(RhC) 50], 194.1 (4 ReCO), 182.4 (1 ReCO), 156.0 [$C^1(C_6H_4)$], 136.2—86.4 (C_6H_4, C_9H_7), 21.2 (Me-4)
(4b)	2.29 (s, 3 H, Me-4), 5.27, 5.43, 6.27 (3 × m, 6 H, C_9H_7), 6.0—7.1 (m, 12 H, C_6H_4, C_9H_7)	299.8 [t, μ_3-C, *J*(RhC) 30], 218.5 [t, μ-CO, *J*(RhC) 51], 193.9 (br, CO), 157.1 [$C^1(C_6H_4)$], 135.9—84.4 (C_6H_4, C_9H_7), 21.2 (Me-4)
(6a)	2.35 (s, 3 H, Me-4), 5.14, 5.69, 5.84 (3 × m, 6 H, C_9H_7), 6.3—7.0 (m, 12 H, C_6H_4, C_9H_7)	[d,e] 257.2 (br, μ-CO), 200.2 (CoCO), 155.0 [$C^1(C_6H_4)$], 137.2—83.4 (C_6H_4, C_9H_7), 21.5 (Me-4)
(6b)	2.31 (s, 3 H, Me-4), 4.75, 5.30, 5.82 (3 × m, 6 H, C_9H_7), 5.9—7.7 (m, 27 H, C_6H_4, Ph, C_9H_7)	[d] 308.6 [d of t, μ_3-C, *J*(PC) 21, *J*(RhC) 32], 230.6 [t, μ-CO, *J*(RhC) 50], 203.7 (br, CoCO), 153.8—83.9 (C_6H_4, Ph, C_9H_7), 21.4 (Me-4)
(6c)	2.23 [t, 3 H, Me, *J*(RhH) 2], 5.47 (m, 2 H, C_9H_7), 5.96 (m, 4 H, C_9H_7), 6.9—7.3 (m, 8 H, C_9H_7)	[f] 324.9 [t, μ_3-C, *J*(RhC) 32], 228.8 [t, μ-CO, *J*(RhC) 52], 200.7 (CoCO), 126.2—83.9 (C_9H_7), 42.3 (Me)
(7)	1.60 (s, 30 H, C_5Me_5), 2.38 (s, 3 H, Me-4), 7.15 (m, 4 H, C_6H_4)	[d] 296.2 [t, μ_3-C, *J*(RhC) 38], 240.2 [t, μ-CO, *J*(RhC) 46], 202.9 (CoCO), 154.9 [$C^1(C_6H_4)$], 136.2, 128.3, 128.1 (C_6H_4), 100.9 (C_5Me_5), 21.5 (Me-4), 9.2 ($C_5\mathit{Me}_5$)
(8)	[g] 2.35 (s, 3 H, Me-4), 5.29 (s, 5 H, C_5H_5), 7.03, 7.19 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[h] 270.7 (μ_3-C), 223.6 (MoCO), 204.1 (CoCO), 155.7 [$C^1(C_6H_4)$], 137.1, 128.6, 128.4 (C_6H_4), 90.2 (C_5H_5), 21.4 (Me-4)
(9)	2.27 (s, 3 H, Me-4), 5.06 (s, 5 H, C_5H_5), 5.80—5.86 (m br, 6 H, C_9H_7), 6.9—7.4 (m, 12 H, C_6H_4, C_9H_7)	302.8 (μ_3-C), 231.6 (MoCO), 227.0 [t, μ-CO, *J*(RhC) 50], 155.7 [$C^1(C_6H_4)$], 134.5—98.0 (C_6H_4, C_9H_7), 89.8 (C_5H_5), 85.3—80.8 (C_9H_7), 21.1 (Me-4)
(10a)	[g] 2.28 (s, 3 H, Me-4), 5.35 (s, 5 H, C_5H_5), 5.80 (m br, 3 H, C_9H_7), 6.9—7.4 (m, 8 H, C_6H_4, C_9H_7)	337.3 [d, μ-C, *J*(RhC) 30], 235.0, 233.8 (MoCO), 189.5 [d, RhCO, *J*(RhC) 89], 152.0 [$C^1(C_6H_4)$], 139.2—102.7 (C_6H_4, C_9H_7), 93.4 (C_5H_5), 92.4—81.1 (C_9H_7), 21.7 (Me-4)
(10b)	[g] 1.05 [d of d, 9 H, PMe, *J*(PH) 10, *J*(RhH) 1], 2.18 (s, 3 H, Me-4), 5.29 (m, 1 H, C_9H_7), 5.49 (s, 5 H, C_5H_5), 6.00 (m br, 2 H, C_9H_7), 6.4—7.5 (m, 8 H, C_6H_4, C_9H_7)	348.8 [d, μ-C, *J*(RhC) 28], 246.6, 245.0 (MoCO), 150.9 [$C^1(C_6H_4)$], 138.1—104.1 (C_6H_4, C_9H_7), 93.3 (C_5H_5), 80.5—76.9 (C_9H_7), 21.6 (Me-4), 18.9 [d, MeP, *J*(PC) 28]
(10c)	[f] 2.21 (s, 3 H, Me-4), 5.29 (s, 5 H, C_5H_5), 5.81 (m, 3 H, C_9H_7), 6.8—7.3 (m, 8 H, C_6H_4, C_9H_7)	325.3 (μ-C), 234.6, 231.8 (MoCO), 170.8 (IrCO), 152.8 [$C^1(C_6H_4)$], 139.2—95.8 (C_6H_4, C_9H_7), 93.6 (C_5H_5), 77.8—77.7 (C_9H_7), 21.9 (Me-4)
(11a)	[f] 1.90 (s, 15 H, C_5Me_5), 2.23 (s, 3 H, Me-4), 5.5—7.2 (m, 11 H, C_6H_4, C_9H_7)	[d] 307.9 [d, μ-C, *J*(RhC) 28, *J*(WC) 158], 232.9 (WCO), 228.3 [WCO, *J*(WC) 171], 190.4 [d, RhCO, *J*(RhC) 89], 154.7 [$C^1(C_6H_4)$], 136.8—103.0 (C_6H_4, C_9H_7), 102.4 (C_5Me_5), 83.4—82.2 (C_9H_7), 21.8 (Me-4), 9.6 ($C_5\mathit{Me}_5$)
(11b)	[f] 1.89 (s, 15 H, C_5Me_5), 2.19 (s, 3 H, Me-4), 5.51, 5.74, 5.88 (3 × m, 3 H, C_9H_7), 6.9—7.2 (m, 8 H, C_6H_4, C_9H_7)	296.7 [μ-C, *J*(WC) 141], 233.6 [WCO, *J*(WC) 202], 224.7 [WCO, *J*(WC) 165], 171.3 (IrCO), 156.0 [$C^1(C_6H_4)$], 135.6—114.1 (C_6H_4, C_9H_7), 104.0 (C_5Me_5), 95.9—79.5 (C_9H_7), 21.7 (Me-4), 10.7 ($C_5\mathit{Me}_5$)
(12)	[f] 2.29 (s, 3 H, Me-4), 5.07 (s, 5 H, C_5H_5), 5.2—7.3 (m, 18 H, C_6H_4, C_9H_7)	262.8 [d, μ_3-C, *J*(RhC) 27], 217.9, 215.6 (WCO), 212.5 [d, μ-CO, *J*(RhC) 42], 156.1 [$C^1(C_6H_4)$], 134.3—96.4 (C_6H_4, C_9H_7), 87.3 (C_5H_5), 84.9—75.4 (C_9H_7), 21.0 (Me-4)
(13)	2.18 (br, 18 H, Me-4, C_5Me_5), 5.1—7.2 (m, 18 H, C_6H_4, C_9H_7)	279.6 (br, μ_3-C), 229.6 [μ-CO, *J*(RhC) 119], 219.4 [WCO, *J*(WC) 165], 155.2 [$C^1(C_6H_4)$], 133.2—114.7 (C_6H_4, C_9H_7), 100.8 (C_5Me_5), 98.4—77.1 (C_9H_7), 21.1 (Me-4), 11.6 ($C_5\mathit{Me}_5$)

[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, to high frequency of $SiMe_4$, measured in CD_2Cl_2–CH_2Cl_2. [d] Measured at −50 °C. [e] Resonance for μ_3-C nucleus not observed; poor signal-to-noise ratio. [f] Measured at −40 °C. [g] Measured in $CDCl_3$. [h] Measured at −70 °C.

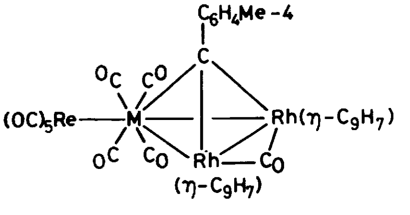
$C_9H_7)_2\{HB(pz)_3\}]$ [$HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate].[13] Resonances in the spectrum of **(3b)** at δ 197.4 and 195.7 p.p.m. (relative intensity 1:4) show ^{183}W–^{13}C satellite peaks, and these signals may therefore be assigned to the $W(CO)_5$ fragment. Three peaks observed at δ 195.2, 194.0, and 188.1 p.p.m. are typical for an $Re(CO)_3$ group. In the $^{13}C-\{^1H\}$ n.m.r. spectrum of $[ReW_2(\mu\text{-}Br)(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2]$ which also contains a $Re(CO)_3$ fragment, signals for the latter occur at 196.5, 194.8, and 188.8 p.p.m.[8] The structures proposed for the complexes **(3)**, on the basis of the n.m.r. data, are similar to those of the compounds $[MReFe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{12}]$ (M = Cr, Mo, or W).[2c] That the latter species and **(3)** should have similar molecular structures is likely since they differ only by replacing the $Fe(CO)_3$ fragment in one by the isolobal $Rh(\eta\text{-}C_9H_7)$ moiety in the other.

In an attempt to add a further $Rh(\eta\text{-}C_9H_7)$ fragment to the compounds **(2)** the latter were treated with $[Rh(CO)_2(\eta\text{-}C_9H_7)]$. In this manner the tetranuclear metal complexes $[MReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]$ (**4a**, M =

Table 3. Selected internuclear distances (Å) and angles (°) for $[CrReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]\cdot CH_2Cl_2$ **(4a)**

Re–Cr	3.052(1)	Re–C(1)	1.96(1)	Re–C(2)	2.04(1)	Re–C(3)	1.99(1)
Re–C(4)	1.99(1)	Re–C(5)	2.021(1)	Rh(1)–Rh(2)	2.659(1)	Rh(1)–Cr	2.713(1)
Rh(1) ••• C(9)	2.440(8)	Rh(1)–C(10)	2.00(1)	Rh(1)–C(20)	2.040(7)	Rh(1)–C(31)	2.428(8)
Rh(1)–C(32)	2.23(1)	Rh(1)–C(33)	2.214(9)	Rh(1)–C(34)	2.242(8)	Rh(1)–C(35)	2.437(7)
Rh(2)–Cr	2.720(2)	Rh(2) ••• C(8)	2.519(8)	Rh(2)–C(10)	1.984(9)	Rh(2)–C(20)	2.047(9)
Rh(2)–C(41)	2.425(9)	Rh(2)–C(42)	2.179(9)	Rh(2)–C(43)	2.22(1)	Rh(2)–C(44)	2.25(1)
Rh(2)–C(45)	2.450(8)	Cr–C(6)	1.89(1)	Cr–C(7)	1.921(8)	Cr–C(8)	1.911(9)
Cr–C(9)	1.895(9)	Cr–C(20)	1.910(7)	C(1)–O(1)	1.14(1)	C(2)–O(2)	1.14(1)
C(3)–O(3)	1.13(1)	C(4)–O(4)	1.13(1)	C(5)–O(5)	1.11(1)	C(6)–O(6)	1.15(1)
C(7)–O(7)	1.12(1)	C(8)–O(8)	1.15(1)	C(9)–O(9)	1.17(1)	C(10)–O(10)	1.16(1)
C(20)–C(21)	1.47(9)	C(11)–Cl(1)	1.73(2)	C(11)–Cl(2)	1.78(2)		
Rh(2)–Rh(1)–Cr	60.8(1)	Rh(2)–Rh(1)–C(10)	47.9(2)	Rh(2)–Rh(1)–C(20)	49.5(2)	Cr–Rh(1)–C(20)	44.6(2)
Rh(1)–Rh(2)–Cr	60.6(1)	Rh(1)–Rh(2)–C(10)	48.4(3)	Rh(1)–Rh(2)–C(20)	49.3(2)	Cr–Rh(2)–C(2)	44.5(2)
Re–Cr–Rh(1)	144.0(1)	Re–Cr–Rh(2)	145.2(1)	Rh(1)–Cr–Rh(2)	58.6(1)	Re–Cr–C(20)	160.0(3)
Rh(1)–Cr–C(20)	48.6(2)	Rh(2)–Cr–C(20)	48.7(3)	Cr–C(6)–O(6)	176.0(8)	Cr–C(7)–O(7)	176.0(8)
Cr–C(8)–O(8)	170.1(8)	Cr–C(9)–O(9)	167.2(2)	Rh(1)–C(10)–Rh(2)	83.7(4)	Rh(1)–C(10)–O(10)	137.5(7)
Rh(2)–C(10)–O(10)	138.8(8)	Rh(1)–C(20)–Rh(2)	81.2(3)	Rh(1)–C(20)–Cr	86.7(3)	Rh(2)–C(20)–Cr	86.8(3)
Rh(1)–C(20)–C(21)	120.2(5)	Rh(2)–C(20)–C(21)	121.0(6)	Cr–C(20)–C(21)	142.2(7)	Cl(1)–C(11)–Cl(2)	105(1)

range Re–C–O 177(1)–179(1)



	M
(4a)	Cr
(4b)	W

Cr; **4b**, M = W) were obtained, and data for these are given in Tables 1 and 2. The molecular structure of **(4a)** was established by a single-crystal *X*-ray diffraction study (Figure and Table 3).

In **(4a)**, a $CrRh_2$ triangle of metal atoms [Cr–Rh(1) 2.713(1), Cr–Rh(2) 2.720(2), and Rh(1)–Rh(2) 2.659(1) Å] is essentially symmetrically capped by the μ_3-C group [C(20)–Cr 1.910(7), C(20)–Rh(1) 2.040(7), and C(20)–Rh(2) 2.047(9) Å]. The Rh(1)–Rh(2) bond is symmetrically spanned by the C(10)O(10) ligand [Rh(1)–C(10) 2.00(1), Rh(2)–C(10) 1.984(9) Å; Rh(1)–C(10)–O(10) 137.5(7), Rh(2)–C(10)–O(10) 138.8(8)°]. The chromium atom carries a pendant $Re(CO)_5$ group [Cr–Re 3.052(1) Å] and has four CO ligands, two of which are terminal and two of which weakly semibridge the Cr–Rh bonds [Cr–C(9)–O(9) 167.2(2), Cr–C(8)–O(8) 170.1(8)°]. The five CO groups on the rhenium are essentially linear and orthogonal to one another, and the radial ligands are staggered with respect to the corresponding CO groups on the chromium. The molecule has a plane of symmetry defined by the plane of the tolyl ring and the atoms C(20), C(10), Cr, and Re. The resulting structure is thus closely related to that of the complex $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$.[2a] However, the two molecules differ in one important respect. In the latter the plane of the tolyl group lies parallel to the Co–Co axis whereas in **(4a)** the plane of the ring is essentially perpendicular (84°) to the Rh(1)–Rh(2) vector. This difference results from the presence of a μ-CO ligand in **(4a)** which favours the conformer with the aryl ring in the molecular symmetry plane.[2c]

Having established the structure of **(4a)**, the spectroscopic data for both complexes **(4)** are readily interpreted. The presence of the Rh(μ-CO)Rh group is revealed by i.r. bands in the bridging carbonyl region [**(4a)**, 1 831; **(4b)**, 1 833 cm^{-1}], and by characteristic signals in the ^{13}C-$\{^1H\}$ n.m.r. spectra [**(4a)**, δ 219.8, t, *J*(RhC) 50; **(4b)**, δ 218.5 p.p.m., t, *J*(RhC) 51 Hz]. It will be noted that the symmetrically bridging μ-CO ligands lead to significantly larger ^{103}Rh–^{13}C coupling than that observed for the weakly bridging CO groups in **(3)**. Moreover, the *J*(RhC) values found for **(4)** are close to that observed for the μ-CO ligand in $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\{HB(pz)_3\}]$, discussed above.

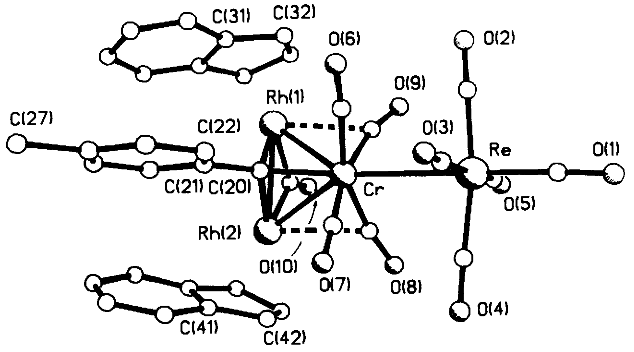
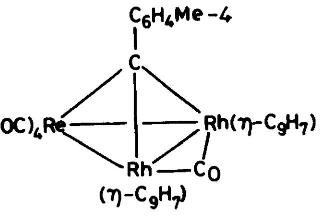


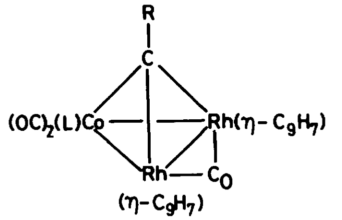
Figure. The molecular structure of $[CrReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]\cdot CH_2Cl_2$ **(4a)** showing the atom-labelling scheme

Signals for the μ_3-C nuclei in **(4)** are observed at δ 333.3 **(4a)** and 299.8 p.p.m. **(4b)**, and both resonances are triplets due to coupling with two rhodium nuclei in equivalent sites. The resonance for **(4b)** is just within the range expected for a μ_3-C group (see earlier discussion) but that for **(4a)** might imply, in the absence of the *X*-ray results to the contrary, that the *p*-tolylmethylidyne ligand was asymmetrically bonded to the $CrRh_2$ triangle. However, we believe that the greater deshielding observed with **(4a)** compared with **(4b)** is the result of a paramagnetic shift due to the chromium atom. A similar trend is observed with the ^{13}C-$\{^1H\}$ n.m.r. spectra of the structurally related complexes $[MReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ [δ(μ_3-C), 294.2 (M = Cr); 260 p.p.m. (M = W)], the chromium-containing species giving the more deshielded signal.

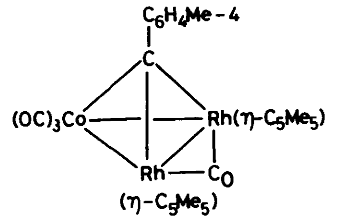
The ^{13}C-$\{^1H\}$ n.m.r. spectrum of **(4b)** in the CO region shows, in addition to the μ-CO peak mentioned above, only one broad resonance. It is thus evident that at room temperature site exchange of carbonyls occurs on the rhenium and tungsten centres, and also between these metals. In contrast, the spectrum



(5)



	L	R
(6a)	CO	C_6H_4Me-4
(6b)	PPh_3	C_6H_4Me-4
(6c)	CO	Me



(7)

of (4a) shows resonances for the terminal carbonyl signals at δ 242.7 (2 CrCO), 231.5 (2 CrCO), 194.1 (4 ReCO), and 182.4 p.p.m. (1 ReCO), as well as the μ-CO peak at δ 219.8. This band pattern is in accord with the results of the *X*-ray diffraction study, but clearly the equivalence of the four radial carbonyl ligands on rhenium suggests that rotation of the $Re(CO)_5$ group about the Re–Cr axis is occurring in solution. The difference in ^{13}C-$\{^1H\}$ n.m.r. properties of (4a) and (4b) in the CO region of the spectrum is likely to be the result of the Cr–Re and Cr–Rh distances in the former being shorter than the W–Re and W–Rh separations in the latter. This would lead to a more compact structure for (4a) resulting in the $Cr(CO)_4$ and $Re(CO)_4$ groups having higher barriers for rotation or for exchange between the metal centres.

Surprisingly, refluxing the compounds (4) in toluene failed to produce the complex $[ReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_4(\eta\text{-}C_9H_7)_2]$ (5) *via* loss of chromium or tungsten carbonyl fragments. The compounds $[MReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (M = Cr, Mo, or W), structurally similar to (4), on heating are readily converted to $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$,[2a] a species akin to (5). Nevertheless, the latter species was not isolated in the present work.

Treatment of (1d) with two equivalents of $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ in light petroleum at room temperature affords the green cobaltdirhodium complex $[CoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_9H_7)_2]$ (6a), characterised by the data given in Tables 1 and 2. With triphenylphosphine, (6a) affords $[CoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(PPh_3)(\eta\text{-}C_9H_7)_2]$ (6b). A ^{31}P-$\{^1H\}$ n.m.r. spectrum of the latter (in CD_2Cl_2) revealed a very broad signal at 34.0 p.p.m. (relative to 85% H_3PO_4, external), as expected for a $Co(PPh_3)$ group. Reaction between $[CoW(\equiv CMe)(CO)_8]$ and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ in light petroleum at room temperature gave the dark green ethylidynecobaltdirhodium compound $[CoRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_9H_7)_2]$ (6c). The synthesis of (6a) and (6c) was accompanied by the formation of $[W(CO)_6]$. Hence the preparation of the cobaltdirhodium compounds in this manner mimics the synthesis of $[CoFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9]$ from (1d) and $[Fe_2(CO)_9]$, a process which also affords $[W(CO)_6]$.[2c]

The compounds (1d) and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ react in thf at room temperature to give $[CoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)_2]$ (7). Tungsten hexacarbonyl is also formed, as well as $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9]$, and significant amounts of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$. Evidently the reaction pathway to (7) is very complex, and includes fragmentation of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. Cleavage of the dirhodium compound has been observed previously in reaction with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ which affords a mixture of the di-and tri-metal compounds $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$.[7]

In the ^{13}C-$\{^1H\}$ n.m.r. spectrum of (7) the μ_3-C resonance occurs at 296.2 p.p.m. [t, *J*(RhC) 38 Hz], whereas for the structurally related $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ the corresponding signal is at 271.8 p.p.m. [t, *J*(RhC) 34 Hz]. The latter is well within the chemical shift range for μ_3-C ligands whereas for (7) it is at the extreme end of this range, becoming comparable with those observed for alkylidyne-carbon nuclei bridging two rather than three metal centres. Since there is no reason to suspect that the *p*-tolylmethylidyne group in (7) is asymmetrically bridging the $CoRh_2$ triangle, the difference in the observed chemical shifts between the two compounds must be due to the effect of a $Co(CO)_3$ group *versus* the isolobal $W(CO)_2(\eta\text{-}C_5H_5)$ fragment. It is not surprising that different metal–ligand fragments in structurally similar complexes cause differences in the ^{13}C n.m.r. chemical shifts of ligated μ_3-C groups. Indeed we referred earlier to the increase in deshielding observed for the μ_3-C resonance in the species $[MReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (M = Cr or W) when the $W(CO)_4$ group is replaced by $Cr(CO)_4$.

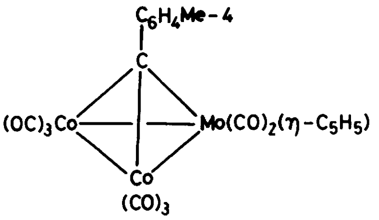
As with (7) the compounds (6) contain a $Co(CO)_3$ group. Although the μ_3-C resonance in the ^{13}C-$\{^1H\}$ n.m.r. spectrum of (6a) was not observed, the signals for the alkylidyne carbon nuclei in the spectra of (6b) (308.6 p.p.m.) and (6c) (324.9 p.p.m.) are, like that of (7), relatively deshielded for complexes containing triply-bridging carbyne groups. Interestingly, when two $Co(CO)_3$ fragments are present in a trimetal complex, as in $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ [$\delta(\mu_3$-C) 257 p.p.m.],[6] the resonance for the alkylidyne-carbon nucleus falls within the normal range of δ 250—300 p.p.m.

The data for (6a) and (6c) exemplify another factor affecting alkylidyne-carbon chemical shifts, namely complexes containing μ_3-*C*Me groups have resonances which are more deshielded than those with μ_3-*C*C_6H_4Me-4 ligands. This feature is further illustrated by the data for the pairs of compounds: (*i*) $[WRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ [$\delta(\mu_3$-C), 299.7 (R = Me);[14] 271.8 p.p.m. (R = C_6H_4Me-4)[7]], (*ii*) $[WRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_9H_7)_2\{HB(pz)_3\}]$ [$\delta(\mu_3$-C), 329.9 (R = Me); 278.2 p.p.m. (R = C_6H_4Me-4)][13], and (*iii*) $[WCo_2(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ [$\delta(\mu_3$-C), 264.4 (R = Me);[15] 257 p.p.m. (R = C_6H_4Me-4)[6]].

Finally, as discussed above, the observed μ_3-C chemical shifts in the ^{13}C-$\{^1H\}$ n.m.r. spectra of complexes containing a trimetallatetrahedrane core are also a function of any asymmetry in the carbon–metal bonding. Additional evidence for this correlation is provided by comparing the ^{13}C-$\{^1H\}$ n.m.r. and structural data for the complex $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ [μ_3-C–Co 1.95(1), μ_3-C–W 2.10(1) Å; $\delta(\mu_3$-C) 257 p.p.m.][6] with that for $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ [μ_3-C–Co 1.90(2), μ_3-C–Re 2.19(1) Å; $\delta(\mu_3$-C) 297.9 p.p.m.].[2a] In the dicobaltrhenium compound the μ_3-C ligand is distinctly more asymmetrically attached to the metal triangle and this feature correlates with the observed greater deshielding of the μ_3-C resonance as compared with the dicobalttungsten complex. However, caution is merited in interpreting these data since replacing a $W(CO)_2(\eta\text{-}C_5H_5)$ group by the $Re(CO)_4$ moiety might enhance deshielding, as is apparently found with $Co(CO)_3$ and $Cr(CO)_4$ groups.

Tungsten hexacarbonyl is also eliminated in the reaction between (**1e**) and [Co$_2$(CO)$_8$] which affords the dicobaltmolybdenum compound [MoCo$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_8$(η-C$_5$H$_5$)] (**8**). The tungsten analogue of the latter has been prepared from [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] and [Co$_2$(CO)$_8$].[6] The spectroscopic properties of (**8**) (Tables 1 and 2) are in accord with the proposed structure. The observation of several CO stretching bands in the i.r. spectrum indicates the presence of rotational isomers in solution, as found with the tungsten analogue.[6] These isomers probably correspond to different orientations of the Mo(CO)$_2$(η-C$_5$H$_5$) fragment with respect to the μ_3-CCo$_2$ triangle. However, interconversion between these species is evidently rapid on the n.m.r. time-scale since even at -70 °C the ^{13}C-{^{1}H} n.m.r. spectrum of (**8**) shows only one broad resonance for the two CO ligands on the molybdenum (Table 2), indicating that rotation of the Mo(CO)$_2$(η-C$_5$H$_5$) fragment is a low energy process.

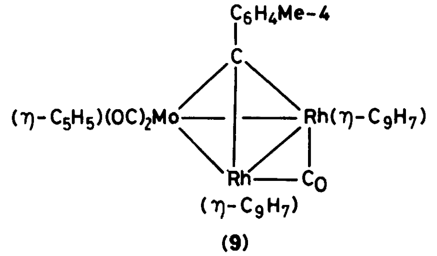
Reaction between (**1e**) and [Rh(CO)$_2$(η-C$_9$H$_7$)] in thf affords [W(CO)$_6$] and a mixture of the compounds [MoRh$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η-C$_9$H$_7$)$_2$] (**9**) and [MoRh(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] (**10a**), data for which are given in Tables 1 and 2. Synthesis of (**9**) in this manner is analogous to the formation of (**6a**) from (**1d**) and [Rh(CO)$_2$(η-C$_9$H$_7$)], and contrasts with the reaction of the latter with (**1a**) or (**1c**), which initially affords the compounds (**2**), and subsequently (**4**) with excess of [Rh(CO)$_2$(η-C$_9$H$_7$)]. Evidently (**1d**) and (**1e**) add a second Rh(C$_9$H$_7$) fragment with release of [W(CO)$_6$] more readily than (**1a**) or (**1c**). Moreover, as mentioned above, the compounds (**4**) on heating failed to give (**5**). A similar effect is seen with [Co$_2$(CO)$_8$] as the reagent. With (**1d**) and (**1e**) dicobalt octacarbonyl affords the trimetal compounds [Co$_3$(μ_3-CC$_6$H$_4$Me-4)(CO)$_9$][2c] and (**8**) directly, whereas (**1a**), (**1b**), or (**1c**) yield initially tetranuclear metal complexes [MReCo$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_{15}$], which only on subsequent heating in toluene give the trimetal compound [ReCo$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_{10}$].[2a]



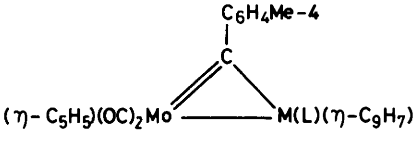
(**8**)

In the reaction of (**1e**) with [Rh(CO)$_2$(η-C$_9$H$_7$)] formation of (**10a**) simultaneously with (**9**) may imply release of a tungsten carbonyl fragment from a transient trimetal compound [MoWRh(μ-CC$_6$H$_4$Me-4)(CO)$_8$(η-C$_5$H$_5$)(η-C$_9$H$_7$)]. The latter would be structurally similar to (**2**) but with the Re(CO)$_5$ group replaced by a Mo(CO)$_3$(η-C$_5$H$_5$) moiety. However, it is also possible that (**10a**) forms by elimination of an Rh(η-C$_9$H$_7$) fragment from (**9**), as observed for iron carbonyl groups in certain reactions of [WFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)].[1,16]

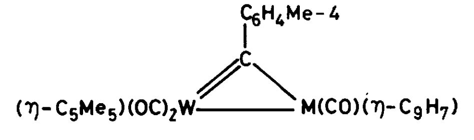
Prior to the characterisation of (**10a**), only one other dimetal compound containing an alkylidyne ligand bridging a bond between molybdenum and another transition element has been reported, *viz.* [MoRh(acac)(μ-CMe)(CO)$_3$(η-C$_5$H$_5$)] (acac = acetylacetonate).[3] In order to extend the range of such compounds, and to show that previously reported syntheses employing [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] apply also to its molybdenum analogue, reactions were carried out between [Mo($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] and [Rh(CO)(PMe$_3$)(η-C$_9$H$_7$)] and [Ir(CO)$_2$(η-C$_9$H$_7$)], respectively. In this manner the compounds [MoRh(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)(η-C$_5$H$_5$)(η-C$_9$H$_7$)] (**10b**) and [MoIr(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] (**10c**) (Tables 1 and 2) were prepared. The ^{13}C-{^{1}H} n.m.r. spectra of both compounds showed characteristic resonances for alkylidyne-carbon nuclei bridging two metal centres,[3] with the signal for (**10b**) a doublet, as expected {(**10b**), δ 348.8 [J(RhC) 28 Hz]; (**10c**), δ 325.3 p.p.m.}. In the i.r. spectrum



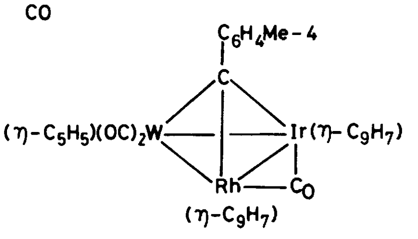
(**9**)



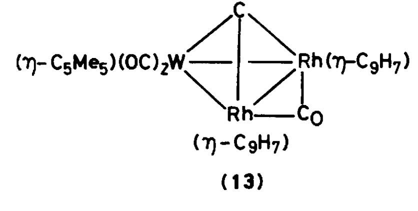
	M	L
(**10a**)	Rh	CO
(**10b**)	Rh	PMe$_3$
(**10c**)	Ir	CO



	M
(**11a**)	Rh
(**11b**)	Ir



(**12**)



(**13**)

of (**10a**), (**10b**), and (**10c**) bands at 1 872, 1 786, and 1 874 cm^{-1}, respectively, suggest that one of the CO ligands in each species semibridges the metal–metal bond. The presence of a semibridging CO group has been confirmed by *X*-ray diffraction in $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ [$\nu_{max.}$(CO) at 1 945 and 1 783 cm^{-1}],[17] the tungsten analogue of (**10b**). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**10b**) has a doublet resonance for the $Rh(PMe_3)$ group at δ 2.86 p.p.m. [*J*(RhP) 208 Hz]. The corresponding signal in the spectrum of $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ is at δ 5.04 p.p.m., with $^{103}Rh\text{-}^{31}P$ coupling also of 208 Hz.

The dimetal complexes $[WM(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5Me_5)(\eta\text{-}C_9H_7)]$ [(**11a**), M = Rh; (**11b**), M = Ir] were prepared from reactions between the compounds $[M(CO)_2(\eta\text{-}C_9H_7)]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$. Data for (**11a**) and (**11b**) are given in Tables 1 and 2, and they provide the first examples of μ-alkylidyne dimetal compounds with $W(\eta\text{-}C_5Me_5)$ groups. The $W(\eta\text{-}C_5H_5)$ analogues have previously been reported, having been prepared by similar reactions using $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.[3]

The cluster compound $[WRhIr(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ (**12**) was prepared by heating $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ with $[Ir(CO)_2(\eta\text{-}C_9H_7)]$ in toluene at 70 °C. A by-product of the reaction was $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$.[7] Compound (**12**) is a member of a growing class of complex wherein a *p*-tolylmethylidyne ligand triply bridges three different transition elements.[18] In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**12**) (Table 2) the μ_3-C resonance is a doublet at δ 262.8 p.p.m. [*J*(RhC) 27 Hz], while the Rh(μ-CO)Ir group reveals itself by a doublet signal at 212.5 p.p.m. [*J*(RhC) 42 Hz]. In the i.r. spectrum of (**12**) there is a bridging CO band at 1 751 cm^{-1}.

At room temperature, in light petroleum, the compounds $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ react to give (**11a**) as the main product. In refluxing thf the reagent $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ affords a mixture of (**11a**) and $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ (**13**), characterised by the data in Tables 1 and 2. A similar synthesis of the $\eta\text{-}C_5H_5$ analogue of (**13**) has been reported.[7]

The compounds reported herein significantly extend the range of known di-, tri-, and tetra-nuclear metal complexes with bridging *p*-tolylmethylidyne ligands. Most previous work has employed the compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ as a precursor to such species.[18,19] The results described in this paper further demonstrate the utility of (**1a**)—(**1d**) as starting materials,[2] and introduce the use of compounds (**1e**), $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ as reagents in this field.

Experimental

The experimental techniques used and the instrumentation employed have been described in previous parts of this series.[2] Light petroleum refers to that fraction of b.p. 40—60 °C. The compounds (**1**) were prepared by the methods used to obtain their phenylmethylidyne analogues.[20] The compounds $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$,[21] $[Rh(CO)(PMe_3)(\eta\text{-}C_9H_7)]$,[17] $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[22] and $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$[3] were prepared by published methods. The reagents $[M(CO)_2(\eta\text{-}C_9H_7)]$ (M = Rh or Ir) were generally prepared *in situ* by passing CO through light petroleum solutions of $[M(C_2H_4)_2(\eta\text{-}C_9H_7)]$.[23]

The new compound $[CoW(\equiv CMe)(CO)_8]$, required for the synthesis of (**6c**), was prepared as follows. A sample of $[WBr(\equiv CMe)(CO)_4]$[24] (6.65 g, 16.5 mmol) was dissolved in cold (*ca.* −30 °C) Et_2O (150 cm^3) and stirred at this temperature for 36 h with a slight excess of $Na[Co(CO)_4]$ (4.0 g, 21 mmol). The excess $Na[Co(CO)_4]$ and NaBr formed were allowed to settle. The diethyl ether solution was then decanted and filtered through a Kieselgel plug at −35 °C. Solvent was removed from the solution *in vacuo*, and the residue was dissolved in the minimum amount of light petroleum (*ca.* 400 cm^3) at 0 °C. This solution was cooled to −78 °C and the solvent decanted to yield yellow *microcrystals* of $[CoW(\equiv CMe)(CO)_8]$ (4.91 g, 60%) (Found: C, 24.4; H, 0.5. $C_{10}H_3CoO_8W$ requires C, 24.3; H, 0.6%), $\nu_{max.}$(CO) at 2 050m, 2 034s, and 1 954w cm^{-1} (in light petroleum). N.m.r. (−20 °C): ^1H (CH_2Cl_2), δ 2.27 (s, Me); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 299.4 [*C*Me, *J*(WC) 184], 204.6 (CoCO), 198.9 [WCO, *J*(WC) 128 Hz], and 39.1 p.p.m. (Me).

The complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ was prepared by treating $[WBr(\equiv CC_6H_4Me\text{-}4)(CO)_4]$ with $K(C_5Me_5)$.[25] Analytical and other data for the new compounds are given in Tables 1 and 2.

Synthesis of the Compounds $[MReRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{10}(\eta\text{-}C_9H_7)]$ (M = Cr *or* W).—The compounds $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) and (**1a**) (0.59 g, 1.0 mmol) were dissolved in CH_2Cl_2 (3 cm^3) at −20 °C for 3 d. A colour change from yellow to red was observed. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2–light petroleum (*ca.* 25 cm^3, 1:10), and the solution chromatographed on an alumina column (3 × 20 cm). Elution with the same solvent mixture gave a bright orange band. The eluate was collected, solvent was removed *in vacuo*, and the residue was crystallised from light petroleum giving orange *crystals* of $[CrReRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{10}(\eta\text{-}C_9H_7)]$ (**2a**) (0.27 g).

A light petroleum (20 cm^3) solution of $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) and (**1c**) (0.73 g, 1.0 mmol) was stirred at room temperature for 3 d, after which solvent was removed *in vacuo*. The residue was dissolved in light petroleum (*ca.* 15 cm^3) and the solution chromatographed on alumina. Elution with the same solvent gave an orange eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from light petroleum gave bright orange *crystals* of $[WReRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{10}(\eta\text{-}C_9H_7)]$ (**2b**) (0.42 g).

Synthesis of the Compounds $[MReRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9(\eta\text{-}C_9H_7)]$ (M = Cr *or* W).—Complex (**2a**) (0.20 g, 0.24 mmol) was refluxed in thf (20 cm^3) for 30 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:10) and chromatographed on alumina. Elution with the same solvent mixture gave a brown eluate. Removal of solvent *in vacuo*, and crystallisation from light petroleum gave brown *crystals* of $[CrReRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9(\eta\text{-}C_9H_7)]$ (**3a**) (0.15 g).

Similarly, refluxing (**2b**) (0.55 g, 0.57 mmol) in thf (20 cm^3) for 1 h gave dark brown *crystals* of $[WReRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9(\eta\text{-}C_9H_7)]$ (**3b**) (0.39 g).

Synthesis of the Complexes $[MReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]$ (M = Cr *or* W).—A light petroleum (20 cm^3) solution of (**2a**) (0.20 g, 0.24 mmol) and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.07 g, 0.24 mmol) was refluxed for 24 h. Solvent was removed *in vacuo*, and the residue dissolved in the minimum volume of CH_2Cl_2–light petroleum (*ca.* 5 cm^3, 1:5) and chromatographed on alumina. Elution with the same solvent mixture yielded initially a small amount of (**3a**), followed by a green band. Removal of solvent *in vacuo* from this eluate, and crystallisation from light petroleum gave green *crystals* of $[CrReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]\cdot CH_2Cl_2$ (**4a**) (0.05 g).

A thf (20 cm^3) solution of (**2b**) (0.15 g, 0.15 mmol) and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ (0.04 g, 0.15 mmol) was refluxed for 30 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (*ca.* 5 cm^3, 1:5) and chromatographed on alumina. Elution with the same solvent mixture afforded initially a trace of brown (**3b**), followed by a green eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from light petroleum gave dark green *crystals* of $[WReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]$ (**4b**) (0.06 g).

Synthesis of the Cobalt-containing Complexes.—(*i*) A light petroleum (30 cm^3) solution of $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.55 g, 2 mmol) was treated with CO gas (15 min) in order to generate $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ *in situ*. Solid (**1d**) (0.60 g, 1.05 mmol) was added, and the mixture stirred for 12 h, giving a dark green precipitate. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (15 cm^3, 1:2) and chromatographed on alumina. Elution with the same solvent mixture afforded initially $[W(CO)_6]$ (identified by i.r.), followed by a trace of red $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9]$, also identified spectroscopically. The final green fraction was evaporated *in vacuo*, and crystallised from CH_2Cl_2–light petroleum (1:10) to give dark green *microcrystals* of $[CoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_9H_7)_2]$ (**6a**) (0.57 g).

(*ii*) A thf (10 cm^3) solution of (**6a**) (0.14 g, 0.20 mmol) and PPh_3 (0.08 g, 0.03 mmol) was stirred at room temperature for 48 h. Solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (6 cm^3, 1:2) and the solution chromatographed on Florisil. Elution with the same solvent mixture gave initially a dark green and subsequently a light green solution. The former contained unreacted (**6a**) (0.035 g). The latter, after removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–light petroleum (1:10), gave green *microcrystals* of $[CoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(PPh_3)(\eta\text{-}C_9H_7)_2]$ (**6b**) (0.09 g).

(*iii*) The compound $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.41 g, 1.5 mmol) in light petroleum was treated with a stream of CO gas to give $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ *in situ*. Solid $[CoW(\equiv CMe)(CO)_8]$ (0.25 g, 0.50 mmol) was added, and the mixture was stirred for 3 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:2) and chromatographed on Kieselgel. Elution with the same solvent mixture gave solutions containing $[W(CO)_6]$ and $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (i.r. identified), followed by a green eluate. Removal of solvent *in vacuo* from the latter, and crystallisation of the residue from Et_2O at −78 °C gave dark green *crystals* of $[CoRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_9H_7)_2]$ (**6c**) (0.20 g).

(*iv*) A mixture of (**1d**) (0.22 g, 0.38 mmol) and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.40 g, 0.75 mmol) in thf (10 cm^3) was stirred for 24 h. Solvent was removed *in vacuo*, and the black residue dissolved in CH_2Cl_2–light petroleum (20 cm^3, 1:3) and chromatographed on alumina. Elution with light petroleum gave initially $[W(CO)_6]$ and $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9]$, followed by $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.11 g), all identified by i.r. Further elution of the column with CH_2Cl_2–light petroleum (1:4) led to the isolation of brown *microcrystals* of $[CoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)_2]$ (**7**) (0.06 g).

(*v*) The compound (**1e**) (0.32 g, 0.50 mmol) in light petroleum (20 cm^3) was treated with $[Co_2(CO)_8]$ (0.17 g, 0.50 mmol), and the mixture refluxed for 1 h. Formation of $[W(CO)_6]$ was observed by monitoring the reaction by i.r. spectroscopy. After removal of solvent *in vacuo*, the residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 1:4), and the solution chromatographed on alumina. Elution with the same solvent mixture gave, after removal of solvent *in vacuo*, green *microcrystals* of $[MoCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (**8**) (0.27 g).

Synthesis of the Complexes $[MoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ *and* $[MoRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$.—A light petroleum (20 cm^3) solution of $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ was generated from $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.13 g, 0.50 mmol) and CO. After removal of solvent *in vacuo*, the residue was treated with (**1e**) (0.32 g, 0.50 mmol) in thf (10 cm^3). The mixture was refluxed (1 h), and formation of $[W(CO)_6]$ was observed by i.r. Removal of solvent *in vacuo* afforded a residue, which was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed on alumina. Elution with the same solvent mixture gave, after removal of solvent *in vacuo*, red *microcrystals* of $[MoRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (**10a**) (0.06 g) and green *microcrystals* of $[MoRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ (**9**) (0.16 g). Compound (**10a**) was also prepared by treating $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ with $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in light petroleum at room temperature for 8 h.

Synthesis of Dimetal Complexes.—(*i*) The compound $[Rh(CO)(PMe_3)(\eta\text{-}C_9H_7)]$ (0.16 g, 0.50 mmol) in Et_2O (10 cm^3) was treated with $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.16 g, 0.50 mmol), and the reactants were stirred at room temperature for 2 d. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:4) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (2:3) gave a red brown solution which yielded, after removal of solvent *in vacuo*, black *microcrystals* of $[MoRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (**10b**) (0.28 g).

(*ii*) Carbon monoxide was bubbled through a light petroleum (20 cm^3) solution of $[Ir(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.13 g, 0.35 mmol) for 20 min in order to generate $[Ir(CO)_2(\eta\text{-}C_9H_7)]$ *in situ*. Solid $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.11 g, 0.35 mmol) was added to the mixture, which was then stirred at room temperature for 2 h. The mixture was then chromatographed on alumina. Elution with Et_2O–light petroleum (1:9) removed traces of the reactants. A brown eluate was then obtained using the same solvents in 1:1 ratio. Removal of solvent *in vacuo* gave brown *microcrystals* of $[MoIr(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (**10c**) (0.18 g).

(*iii*) Red *crystals* of $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5Me_5)(\eta\text{-}C_9H_7)]$ (**11a**) (0.29 g) were similarly prepared from $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.15 g, 0.50 mmol), carbon monoxide, and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.24 g, 0.50 mmol). A trace of complex (**13**) was also formed in the reaction.

(*iv*) Similarly, $[Ir(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.21 g, 0.60 mmol) was treated with CO in light petroleum (50 cm^3). The compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.27 g, 0.60 mmol) was added, and the mixture was stirred at room temperature (4 h). Chromatography with Et_2O–light petroleum (1:4) gave, after removal of solvent, brown *microcrystals* of $[WIr(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5Me_5)(\eta\text{-}C_9H_7)]$ (**11b**) (0.30 g).

Synthesis of the Complex $[WRhIr(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$.—The compounds $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (0.16 g, 0.25 mmol) and $[Ir(CO)_2(\eta\text{-}C_9H_7)]$ (0.09 g, 0.25 mmol) in toluene (5 cm^3) were heated at 70 °C (15 h) in a Schlenk tube fitted with a high-pressure stopcock. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (8 cm^3, 1:1) and the resulting solution chromatographed on alumina. Elution with the same solvent mixture removed $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ and $[Ir(CO)_2(\eta\text{-}C_9H_7)]$ (i.r. identified) in minor amounts. Elution with CH_2Cl_2–light petroleum (2:1) gave initially the known[7] complex $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ (0.04 g, 32%), identified by i.r., and secondly a purple eluate from which purple-red *micro-*

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

Atom	*x*	*y*	*z*
Re	247(1)	−3 204(1)	2 161(1)
Rh(1)	3 945(1)	474(1)	2 125(1)
Rh(2)	1 535(1)	1 082(1)	2 033(1)
Cr	1 668(1)	−806(1)	2 435(1)
C(1)	−674(10)	−4 738(9)	1 982(7)
O(1)	−1 233(7)	−5 622(6)	1 883(6)
C(2)	2 147(10)	−3 524(8)	2 189(7)
O(2)	3 249(7)	−3 665(7)	2 196(6)
C(3)	285(10)	−2 815(9)	3 485(6)
O(3)	322(8)	−2 602(8)	4 233(5)
C(4)	−1 493(9)	−2 658(8)	2 109(6)
O(4)	−2 490(7)	−2 354(7)	2 074(5)
C(5)	315(10)	−3 511(8)	833(7)
O(5)	366(9)	−3 660(7)	107(4)
C(6)	2 748(9)	−1 163(7)	3 269(5)
O(6)	3 469(7)	−1 334(6)	3 774(5)
C(7)	262(8)	−522(7)	3 237(5)
O(7)	−527(7)	−293(6)	3 718(4)
C(8)	375(9)	−943(7)	1 471(5)
O(8)	−449(7)	−1 183(5)	885(4)
C(9)	2 760(9)	−1 468(7)	1 534(6)
O(9)	3 248(7)	−2 055(6)	951(5)
C(10)	2 806(8)	592(7)	1 109(6)
O(10)	2 861(6)	422(6)	345(4)
C(20)	2 513(7)	715(7)	3 028(5)
C(21)	2 877(7)	1 546(7)	3 922(5)
C(22)	2 693(9)	1 253(8)	4 697(5)
C(23)	3 050(10)	2 043(8)	5 539(6)
C(24)	3 591(8)	3 131(7)	5 638(6)
C(25)	3 792(8)	3 435(8)	4 883(5)
C(26)	3 451(8)	2 652(7)	4 042(5)
C(27)	3 980(11)	4 033(9)	6 556(6)
C(31)	6 089(8)	907(8)	3 050(6)
C(32)	5 760(8)	−204(9)	2 405(6)
C(33)	5 801(8)	−75(8)	1 542(6)
C(34)	5 938(8)	1 048(8)	1 632(6)
C(35)	6 189(7)	1 690(8)	2 584(6)
C(36)	6 537(8)	2 831(8)	3 053(6)
C(37)	6 763(9)	3 162(9)	3 958(7)
C(38)	6 639(9)	2 393(9)	4 432(6)
C(39)	6 314(8)	1 317(8)	3 995(6)
C(41)	198(8)	2 449(7)	2 794(5)
C(42)	−526(8)	1 432(8)	2 200(6)
C(43)	−248(9)	1 335(8)	1 300(6)
C(44)	847(9)	2 245(7)	1 378(5)
C(45)	1 094(8)	2 969(6)	2 296(6)
C(46)	1 929(10)	3 972(7)	2 690(7)
C(47)	1 850(11)	4 531(9)	3 602(7)
C(48)	977(11)	4 009(11)	4 080(7)
C(49)	179(10)	2 990(10)	3 718(7)
Cl(1)	3 085(5)	4 206(5)	146(4)
Cl(2)	5 062(8)	3 621(8)	1 102(5)
C(11)	4 120(21)	3 230(16)	42(12)

crystals of [WRhIr(μ_3-CC_6H_4Me-4)(μ-CO)$(CO)_2$(η-C_5H_5)(η-$C_9H_7)_2$] (**12**) (0.025 g) were recovered after removal of solvent.

Synthesis of the Complex [WRh_2(μ_3-CC_6H_4Me-4)(μ-CO)$(CO)_2$(η-C_5Me_5)(η-$C_9H_7)_2$].—A mixture of [W($\equiv$$CC_6H_4$-Me-4)$(CO)_2$($\eta$-$C_5Me_5$)] (0.52 g, 1.1 mmol) and [Rh$(C_2H_4)_2$-(η-C_9H_7)] (0.30 g, 1.1 mmol) was refluxed in thf (30 cm^3) for 8 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1 : 4), and chromatographed on alumina at −20 °C. Elution with CH_2Cl_2–light petroleum (1 : 2) led to the isolation of red *crystals* (from light petroleum at −78 °C) of [WRh(μ-CC_6H_4Me-4)$(CO)_3$(η-C_5Me_5)(η-C_9H_7)] (**11a**) (0.11 g), after removal of solvent. Further elution of the column gave green *microcrystals* of [WRh_2(μ_3-CC_6H_4Me-4)-(μ-CO)$(CO)_2$(η-C_5Me_5)(η-$C_9H_7)_2$] (**13**) (0.28 g).

Crystal Structure Determination of [$CrReRh_2$(μ_3-CC_6H_4-Me-4)(μ-CO)$(CO)_9$(η-$C_9H_7)_2$]·CH_2Cl_2 (**4a**).—Crystals of (**4a**) grow as dark green prisms. Diffracted intensities were recorded at 298 K from a crystal of dimensions *ca.* 0.45 × 0.30 × 0.20 mm. Of the 4 323 reflections ($2\theta \leqslant 45°$), measured on a Nicolet *P*3*m* four-circle diffractometer (θ–2θ scans), 3 854 had $F \geqslant 5\sigma(F)$, and only these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz polarisation and *X*-ray absorption effects. The latter by an empirical method based upon azimuthal scan data.[26]

Crystal data for (**4a**). $C_{36}H_{21}CrO_{10}ReRh_2\cdot CH_2Cl_2$, M = 1 142.5, triclinic, a = 9.942(4), b = 12.860(6), c = 15.833(8) Å, α = 108.28(4), β = 91.70(4), γ = 99.95(4)°, U = 1 886(2) Å^3, Z = 2, D_c = 2.01 g cm^{-3}, $F(000)$ = 1 096, space group $P\bar{1}$, μ(Mo-K_α) = 45.6 cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference Fourier methods. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters *ca.* 1.2 times $U_{equiv.}$ of their parent carbon atoms. All remaining atoms were given anisotropic thermal parameters. Refinement by blocked-cascade least squares, with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,5|F|^2]$, converged at R = 0.035 (R' = 0.038). The final electron-density difference synthesis showed no peaks $\geqslant$0.9 e Å^{-3}. Scattering factors with corrections for the effects of anomalous dispersion were from ref. 27. All calculations were carried out on a Data General Eclipse computer with the SHELXTL system of programs.[26] Atomic co-ordinates for (**4a**) are listed in Table 4.

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