Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 55.[1] Coupling of Methylene and Alkylidyne Groups at a Trimetal Centre; Crystal Structures of $[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}\mathit{trans}\text{-}CH{=}C(H)R\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]\cdot CH_2Cl_2$ and $[Ru_2W(\mu_3\text{-}CCH_2R)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$ $(R = C_6H_4Me\text{-}4)$ *

David L. Davies, Michael J. Parrott, Paul Sherwood, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The compounds $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$ or Me) react in CH_2Cl_2 at room temperature to give, in low yield, mixtures of the trimetal complexes $[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}\mathit{trans}\text{-}CH{=}C(H)R\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_3]$ (**3a**, $R = C_6H_4Me\text{-}4$; **3b**, R = Me) and $[Ru_2W(\mu_3\text{-}CCH_2R)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$ (**4a**, $R = C_6H_4Me\text{-}4$; **4b**, R = Me). In a similar reaction, $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)(\eta\text{-}C_5H_5)_2]$ afford a mixture of $[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}\mathit{trans}\text{-}CH{=}C(H)R\}(\mu\text{-}CO)(\mu_3\text{-}CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$ (**5**) and $[Ru_2W(\mu_3\text{-}CCH_2R)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$ (**4c**). The unsaturated complex (**5**) in solution reacts reversibly with CO to give $[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}\mathit{trans}\text{-}CH{=}C(H)R\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2\text{-}(\eta\text{-}C_5Me_5)]$ (**3c**). The spectroscopic properties (i.r., and ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r.) of the new compounds are reported and discussed. Compounds (**3c**) and (**4a**) were studied by *X*-ray diffraction. The former, which crystallises with a molecule of CH_2Cl_2, has a structure based on a triangle of metal atoms [Ru–Ru 2.782(1), Ru–W 2.771(1) and 2.952(1) Å]. The ruthenium–ruthenium bond is symmetrically bridged by a CO ligand, and the shorter Ru–W vector is bridged by a *trans*-$CH{=}C(H)C_6H_4Me\text{-}4$ group, which is σ bonded to the tungsten and η^2 co-ordinated to the ruthenium. The latter carries a C_5H_5 ligand as does the other ruthenium atom, which is also ligated by a terminal CO. The tungsten atom is bonded by two CO groups and the η-C_5Me_5 moiety. The structure of (**4a**) proved to be disordered, but it was apparent that the Ru_2W triangle was capped by the $CCH_2C_6H_4Me\text{-}4$ group with the three edges of the metal triangle bridged by CO ligands.

Our interest in polynuclear metal complexes with bridging alkylidyne or alkylidene ligands has been stimulated by a desire to establish rational synthetic routes to cluster compounds, and to explore the reactivity of the bridging organic fragments present in these species.[2] In the latter category of investigation, we have identified new C–C, C–H, C–B, C–P, and C–S bond-forming processes occurring at the heteronuclear di- and trimetal centres.[1,3–5] One such reaction, the coupling of methylene and alkylidyne groups, is of particular interest in the context of stoicheiometric and catalytic processes mediated by transition elements. Previously we have reported[4] reactions of this type with dimetal Ti–W, Pt–W, Fe–W, and Fe–Mo complexes. In this paper we report the first examples of methylene–alkylidyne group coupling within a trimetal system.

As a model for study we have chosen to investigate reactions between the alkylidynetungsten compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)]$ (**1**, $R = C_6H_4Me\text{-}4$ or Me, R′ = H; $R = C_6H_4Me\text{-}4$, R′ = Me) and the diruthenium complex $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)\text{-}(CO)(NCMe)(\eta\text{-}C_5H_5)_2]$ (**2**).[6] The latter species contains a labile acetonitrile ligand, and it was anticipated that this group would be displaced by the C≡W fragments present in (**1**). In the trimetal compounds thus formed a coupling of the methylene and alkylidyne groups might be expected to occur.

Results and Discussion

Samples of the compound $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ in acetonitrile were irradiated with u.v. light in order to generate complex (**2**). After removing the solvent and replacing it by CH_2Cl_2, the portions of (**2**), prepared *in situ*, were treated at room temperature with (**1a**) and (**1b**), respectively. The products were separated by column chromatography on alumina, and in this manner the compounds $[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}\mathit{trans}\text{-}CH{=}C(H)R\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_3]$ (**3a**, $R = C_6H_4Me\text{-}4$; **3b**, R = Me) and $[Ru_2W(\mu_3\text{-}CCH_2R)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$ (**4a**, $R = C_6H_4Me\text{-}4$; **4b**, R = Me) were isolated, albeit in low yield (*ca.* 5—10%). A by-product of these reactions was $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$, which was evidently formed in a process whereby (**2**) readily scavenges CO, and this in part accounts for the poor yields of desired trimetal products.

Compounds (**3a**), (**3b**), (**4a**), and (**4b**) were characterised by microanalysis (Table 1), and by n.m.r. spectroscopy (Table 2). The i.r. spectra of (**3a**) and (**3b**) showed three bands in the CO stretching region, including one peak (*ca.* 1 743 cm^{-1}) corresponding to the presence of a bridging carbonyl ligand. As described later, the molecular structure of (**4a**) was confirmed by an *X*-ray diffraction study.

The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were especially informative. Thus the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**3a**) and (**3b**)

---

* 1,2-μ-Carbonyl-1,3,3-tricarbonyl-1,2-bis(η-cyclopentadienyl)-3-(η-pentamethylcyclopentadienyl)-1,3-μ-[σ:η-2-*p*-tolylvinyl-$C^1(W)C^{1,2}$-(Ru)]-*triangulo*-dirutheniumtungsten–dichloromethane (1/1) and 1,2; 1,3; 2,3-tri-μ-carbonyl-3-carbonyl-1,2,3-tris(η-cyclopentadienyl)-μ_3-(2-*p*-tolylethylidyne)-*triangulo*-dirutheniumtungsten respectively.

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

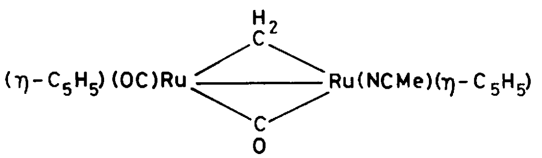
Table 1. Analytical[a] and physical data for the dirutheniumtungsten complexes

	Compound	Colour	ν_{CO}(max.)[b]/cm^{-1}	Analysis (%) C	H
(**3a**)	$[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_3]$	Dark green	1 904s, 1 869m, 1 744m	41.3 (41.5)	3.2 (3.0)
(**3b**)	$[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}CH{=}C(H)Me\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_3]$[c]	Green	1 901s, 1 867m, 1 742m	35.0 (34.8)	2.8 (2.7)
(**3c**)	$[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$[d]	Black	1 898s, 1 857m, 1 734m	42.3 (42.3)	3.8 (3.7)
(**4a**)	$[Ru_2W(\mu_3\text{-}CCH_2C_6H_4Me\text{-}4)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$	Brown	1 954s, 1 877vs, 1 779s	41.5 (41.5)	3.0 (3.0)
(**4b**)	$[Ru_2W(\mu_3\text{-}CEt)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$	Red-brown	1 949s, 1 876vs, 1 775m	35.7 (36.0)	2.8 (2.7)
(**4c**)	$[Ru_2W(\mu_3\text{-}CCH_2C_6H_4Me\text{-}4)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$	Maroon	1 946s, 1 857vs, 1 766s	44.9 (45.0)	4.1 (3.9)
(**5**)	$[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(\mu_3\text{-}CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$	Dark green	1 764m, 1 666s	45.5 (45.1)	4.3 (4.0)

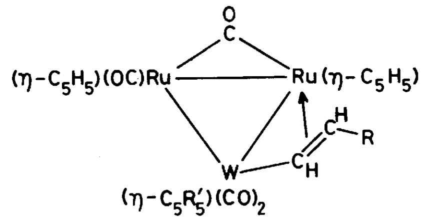
[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. [c] Crystallises with half a molecule of CH_2Cl_2. [d] Crystallises with a molecule of CH_2Cl_2.

$[W(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)]$

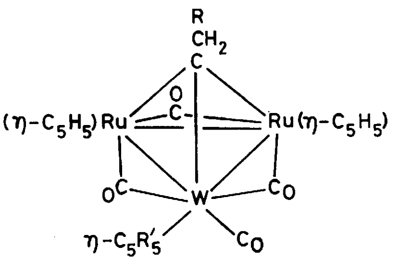
	R	R′
(**1a**)	$C_6H_4Me\text{-}4$	H
(**1b**)	Me	H
(**1c**)	$C_6H_4Me\text{-}4$	Me



(**2**)



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



	R	R′
(**4a**)	$C_6H_4Me\text{-}4$	H
(**4b**)	Me	H
(**4c**)	$C_6H_4Me\text{-}4$	Me

showed (Table 2) four resonances in the carbonyl region. On the basis of the observed chemical shifts[7] and the appearance of $^{183}W-^{13}C$ satellite peaks on two of the resonances, for (**3a**) the following assignment may be made: δ 251.1 $[\overline{Ru(\mu\text{-}CO)Ru}]$, 236.4 and 229.4 (WCO), and 212.9 p.p.m. (RuCO). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**3a**) and (**3b**) also show characteristic signals for the μ-*C*H=*C*(H)R groups. For (**3a**), resonances occur at δ 142.7 [*J*(WC) 96 Hz] and 77.4 p.p.m. This pattern is as expected for the $CH{=}C(H)C_6H_4Me\text{-}4$ group being σ bonded to the tungsten and η co-ordinated to the ruthenium since only one of the resonances for the ligated atoms shows $^{183}W-^{13}C$ satellite peaks. Thus in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of the compound $[FeW\{\mu\text{-}\sigma{:}\eta\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5Me_5)]$, in which the vinyl group bridges the metal–metal bond in a manner similar to that in (**3a**), signals occur at δ 120.4 [μ-*C*H=C(H)R, *J*(WC) 58 Hz] and 101.4 p.p.m. [μ-CH=*C*(H)R].[4b] In contrast, in the spectrum of $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$, in which the vinyl group is σ bonded to the platinum and η bonded to the tungsten, the resonances are at δ 142.4 (μ-*C*R) and 26.7 p.p.m. (CH_2), with no $^{183}W-^{13}C$ coupling being observed on either peak.[8]

In the ^1H n.m.r. spectra of (**3a**) and (**3b**), the *J*(HH) values observed (12 Hz) for the two protons of the vinyl group unambiguously establish a *trans*-CH=C(H)R configuration in these compounds, since generally *J*(*trans*), *J*(*cis*), and *J*(*gem*) are *ca.* 12, 7, and 1—2 Hz respectively.[9] In the ^1H n.m.r. spectrum of $[FeW\{\mu\text{-}\sigma{:}\eta\text{-}trans\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5Me_5)]$ the vinyl group protons show a $^1H-^1H$ coupling of 13 Hz.[4b]

The spectroscopic data for (**4a**) and (**4b**) are also in agreement with the structure proposed with a triangle of Ru_2W atoms capped by a CCH_2R ligand. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of both species show characteristic resonances for the μ_3-C nuclei [**4a**, δ 282.1; **4b**, 286.4 p.p.m.]. Only one CO resonance is observed in each spectrum, indicating site-exchange of these ligands at room temperature on the n.m.r. time-scale. The ^1H spectrum of (**4b**) shows the presence of the CH_2Me group with peaks at δ 1.72 [t, 3 H, *J*(HH) 7] and 4.65 [q, 2 H, *J*(HH) 7 Hz].

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

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(**3a**)	2.26 (s, 3 H, Me-4), 4.50 (s, 5 H, C_5H_5), 4.63 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 12], 5.00 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5), 7.04 (br, 4 H, C_6H_4), 7.32 [d, 1 H, μ-CH, *J*(HH) 12]	[d] 251.1 (μ-CO), 236.4 [CO, *J*(WC) 138], 229.4 [CO, *J*(WC) 164], 212.9 (CO), 142.7 [μ-CH, *J*(WC) 96], 142.3 [C^1 (C_6H_4)], 135.8, 128.9, 126.4 (C_6H_4), 90.6, 87.5, 85.7 (C_5H_5), 21.1 (Me-4)
(**3b**)	1.62 [d, 3 H, Me, *J*(HH) 6], 3.92 [d of q, 1 H, C*H*Me, *J*(HH) 12, 6], 4.67 (s, 5 H, C_5H_5), 4.99 (s, 5 H, C_5H_5), 5.20 (s, 5 H, C_5H_5), [e] 5.30 (0.5 CH_2Cl_2), 6.49 [d, 1 H, μ-CH, *J*(HH) 12]	252.0 (μ-CO), 236.8, 229.7, 213.8 (CO), 147.1 (μ-CH), 90.2, 87.5, 86.0 (C_5H_5), 76.1 [=*C*(H)Me], 27.4 (Me)
(**3c**)	2.09 (s, 15 H, C_5Me_5), 2.27 (s, 3 H, Me-4), 4.42 (s, 5 H, C_5H_5), 4.49 [d, 1 H, μ-CH, *J*(HH) 12], 4.99 (s, 5 H, C_5H_5), [e] 5.29 (CH_2Cl_2), 6.92 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 12], 7.04, 7.10 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8]	[b] 253.0 (μ-CO), 239.0 [CO, *J*(WC) 132], 232.8 [CO, *J*(WC) 169], 213.9 (CO), 146.4 [μ-CH, *J*(WC) 95], 142.7 [C^1 (C_6H_4)], 135.3, 128.6, 126.1 (C_6H_4), 98.4 (*C*$_5$Me$_5$), 90.3, 86.9 (C_5H_5), 78.3 [*C*(H)C_6H_4Me-4], 20.9 (Me-4), 11.0 (C_5*Me*$_5$)
(**4a**)	2.39 (s, 3 H, Me-4), 5.02 (s, 15 H, 3 C_5H_5), 5.95 (s, 2 H, CH_2), 7.22, 7.42 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8]	282.1 (μ_3-C), 237.8 (CO), 143.2 [C^1 (C_6H_4)], 136.2, 130.2, 128.9 (C_6H_4), 92.1 (C_5H_5), 91.3 (2 C_5H_5), 70.4 (CH_2), 21.2 (Me-4)
(**4b**)	1.72 [t, 3 H, Me, *J*(HH) 7], 4.65 [q, 2 H, CH_2, *J*(HH) 7], 4.98 (s, 10 H, 2 C_5H_5), 5.25 (s, 5 H, C_5H_5)	286.4 [μ_3-C, *J*(WC) 96], 237.9 (CO), 91.4 (C_5H_5), 90.7 (2 C_5H_5), 58.9 (CH_2), 14.3 (Me)
(**4c**)	1.89 (s, 15 H, C_5Me_5), 2.39 (s, 3 H, Me-4), 4.91 (s, 10 H, 2 C_5H_5), 5.99 (s, 2 H, CH_2), 7.21, 7.46 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8]	[b] 280.4 [μ_3-C, *J*(WC) 101], 246.9, 238.2, 216.6 (CO), 141.9 [C^1 (C_6H_4)], 135.6, 129.9, 128.5 (C_6H_4), 103.2 (*C*$_5$Me$_5$), 90.9 (C_5H_5), 67.4 (CH_2), 21.1 (Me-4), 10.3 (C_5*Me*$_5$)
(**5**)	1.85 [d, 1 H, C*H*(C_6H_4Me-4), *J*(HH) 12], 2.00 (s, 15 H, C_5Me_5), 2.23 (s, 3 H, Me-4), 4.43 (s, 5 H, C_5H_5), 5.18 (s, 5 H, C_5H_5), 6.94 [d, 1 H, μ-CH, *J*(HH) 12], 6.97, 6.99 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8]	292.0 [CO, *J*(WC) 157], 285.6 [CO, *J*(WC) 152], 239.9 (CO), 146.4 [μ-CH, *J*(WC) 118], 143.2 [C^1 (C_6H_4)], 135.3, 129.2, 125.1 (C_6H_4), 104.3 (*C*$_5$Me$_5$), 93.2, 90.9 (C_5H_5), 75.2 [*C*H(C_6H_4-Me-4)], 21.1 (Me-4), 10.6 (C_5*Me*$_5$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures. [b] Measured in $CDCl_3$. [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] Spectrum measured in $CDCl_3$ and hence resonance due to *C*H(C_6H_4Me-4) obscured. In CD_2Cl_2–CH_2Cl_2, peak is at 77.4 p.p.m. [e] Compound crystallises with CH_2Cl_2, see Table 1.

Table 3. Selected internuclear distances (Å) and angles (°) for the complex [Ru_2W{μ-σ:η-*trans*-CH=C(H)C_6H_4Me-4}(μ-CO)$(CO)_3$(η-C_5H_5)$_2$-(η-C_5Me_5)]·CH_2Cl_2 (**3c**)

W–Ru(1)	2.771(1)	W–Ru(2)	2.952(1)	W–C(1)	2.154(6)	W–C(3)	1.993(6)
W–C(4)	1.957(5)	Ru(1)–Ru(2)	2.782(1)	Ru(1)–C(1)	2.180(5)	Ru(1)–C(2)	2.271(5)
Ru(1)–C(5)	2.024(5)	Ru(2)–C(5)	2.023(6)	Ru(2)–C(6)	1.837(6)	C(1)–C(2)	1.416(8)
C(2)–C(11)	1.471(9)	C(3)–O(3)	1.154(8)	C(4)–O(4)	1.164(6)	C(5)–O(5)	1.179(7)
C(6)–O(6)	1.158(8)	W–C (C_5Me_5) mean	2.355	Ru(1)–C (C_5H_5) mean	2.224	Ru(2)–C (C_5H_5) mean	2.261
Ru(1)–W–Ru(2)	58.1(1)	Ru(1)–W–C(1)	50.7(1)	Ru(2)–W–C(1)	76.0(1)	Ru(1)–W–C(3)	74.3(2)
Ru(2)–W–C(3)	69.8(2)	C(1)–W–C(3)	124.7(2)	Ru(1)–W–C(4)	74.1(2)	Ru(2)–W–C(4)	129.6(2)
C(1)–W–C(4)	86.4(2)	C(3)–W–C(4)	83.6(2)	W–Ru(1)–Ru(2)	64.2(1)	W–Ru(1)–C(1)	49.8(2)
Ru(2)–Ru(1)–C(1)	79.4(1)	W–Ru(1)–C(2)	78.0(1)	Ru(2)–Ru(1)–C(2)	114.9(1)	C(1)–Ru(1)–C(2)	37.0(2)
W–Ru(1)–C(5)	101.2(2)	Ru(2)–Ru(1)–C(5)	46.6(2)	C(1)–Ru(1)–C(5)	81.8(2)	C(2)–Ru(1)–C(5)	98.5(2)
W–Ru(2)–Ru(1)	57.7(1)	W–Ru(2)–C(5)	95.5(1)	Ru(1)–Ru(2)–C(5)	46.6(1)	W–Ru(2)–C(6)	78.8(1)
Ru(1)–Ru(2)–C(6)	103.4(2)	C(5)–Ru(2)–C(6)	86.4(2)	W–C(1)–Ru(1)	79.5(2)	W–C(1)–C(2)	125.8(4)
Ru(1)–C(1)–C(2)	75.0(3)	Ru(1)–C(2)–C(1)	68.0(3)	Ru(1)–C(2)–C(11)	114.6(3)	C(1)–C(2)–C(11)	127.3(5)
W–C(3)–O(3)	170.3(5)	W–C(4)–O(4)	172.6(5)	Ru(1)–C(5)–Ru(2)	86.9(2)	Ru(1)–C(5)–O(5)	136.5(4)
Ru(2)–C(5)–O(5)	136.3(4)	Ru(2)–C(6)–O(6)	170.8(4)				

Likewise, the spectrum of (**4a**) shows a singlet resonance for the CH_2 group at δ 5.95. The ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra (Table 2) of both compounds show resonances corresponding to the presence of C_5H_5 ligands in three environments.

The reaction between compounds (**1c**) and (**2**) was also studied. In CH_2Cl_2 at room temperature no appreciable reaction occurred. However, on refluxing, a dark green complex [Ru_2W{μ-σ:η-CH=C(H)C_6H_4Me-4}(μ-CO)(μ_3-CO)$_2$(η-C_5H_5)$_2$(η-C_5Me_5)] (**5**) was obtained in moderate yield, together with trace amounts of [Ru_2W(μ_3-$CCH_2C_6H_4$Me-4)(μ-CO)$_3$-(CO)(η-C_5H_5)$_2$(η-C_5Me_5)] (**4c**). The data for (**4c**) (Tables 1 and 2) showed that this complex was structurally analogous to (**4a**) and (**4b**). In contrast, the spectroscopic properties of (**5**) were not in accord with a structure similar to those of (**3a**) and (**3b**). Attempts to obtain suitable crystals of (**5**) for an *X*-ray diffraction study were unsuccessful, and hence the proposed structure is based on the spectroscopic data (Tables 1 and 2).

The i.r. spectrum of (**5**) showed bands at 1 764 and 1 666 cm^{-1} in the carbonyl stretching region. The former absorption is as expected for a μ-CO ligand, as found in (**3a**) or (**3b**). The peak at 1 666 cm^{-1} is in the region characteristic for μ_3-CO groups.[10] In agreement, the ^{13}C-{^{1}H} n.m.r. spectrum had characteristic resonances for two triply bridging CO ligands at δ 292.0 [*J*(WC) 157] and 285.6 p.p.m. [*J*(WC) 152 Hz], and an edge-bridging CO ligand at 239.9 p.p.m. The latter did not show ^{183}W–^{13}C coupling and may be assigned to the $\overline{\text{Ru}(\mu\text{-CO})\text{Ru}}$ group. The ^{1}H n.m.r. spectrum of (**5**) (Table 2) had characteristic signals for the two protons of a *trans*-CH=C(H)C_6H_4Me-4 group at δ 1.85 [d, *J*(HH) 12] and 6.94 [d, *J*(HH) 12 Hz].

In support of the formulation of (**5**) as a 46-valence-electron unsaturated species, it reacts rapidly with CO to give the saturated 48-electron complex [Ru_2W{μ-σ:η-CH=C(H)C_6H_4-Me-4}(μ-CO)$(CO)_3$(η-C_5H_5)$_2$(η-C_5Me_5)] (**3c**) in essentially quantitative yield. Data for the latter are given in Tables 1 and 2, confirming that it is structurally similar to (**3a**) and (**3b**). Formation of (**3c**) can be reversed, since (**5**) is reformed on refluxing CH_2Cl_2 solutions of the former. The transformation

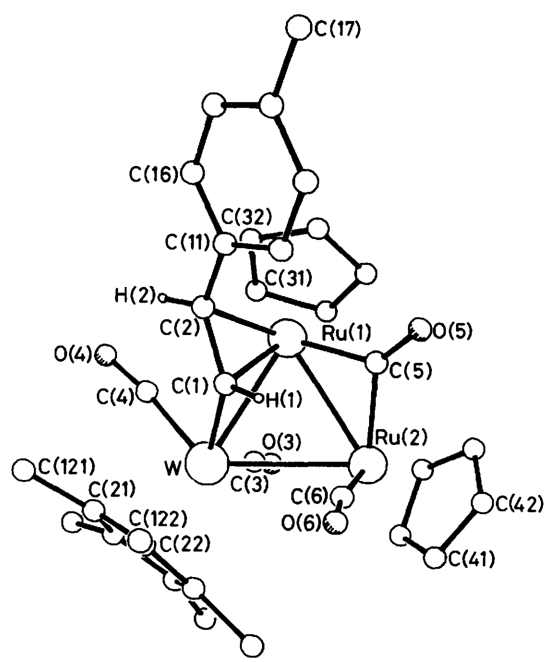


Figure 1. Molecular structure of $[Ru_2W\{\mu\text{-}\sigma:\eta\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$ (**3c**) with the atom-labelling scheme

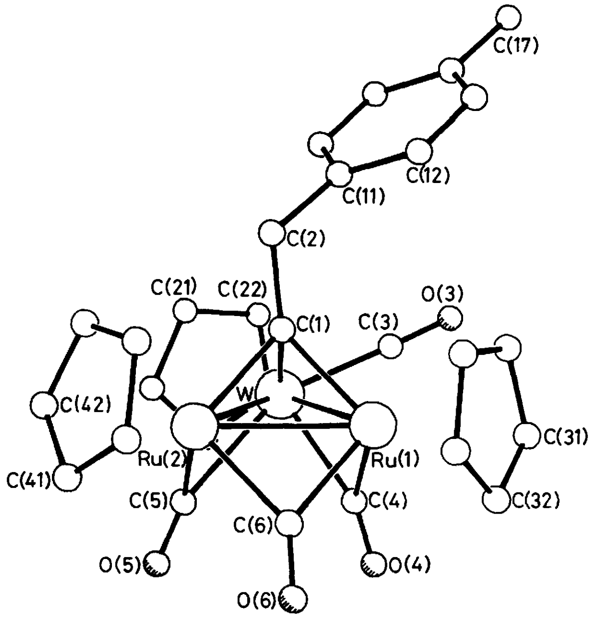
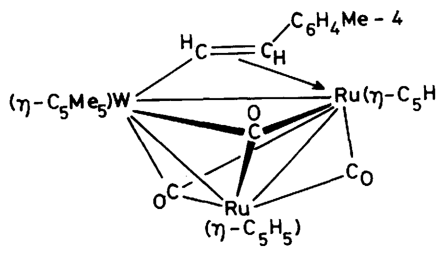


Figure 2. Molecular structure of $[Ru_2W(\mu_3\text{-}CCH_2C_6H_4Me\text{-}4)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$ (**4a**) with the atom-labelling scheme. The structure is disordered (see text) and the diagram shows only the major component at each site

Table 4. Selected internuclear distances[a] (Å) for the complex $[Ru_2W(\mu_3\text{-}CCH_2C_6H_4Me\text{-}4)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$ (**4a**)

W–Ru(1)	2.799	W–Ru(2)	2.903
Ru(1)–Ru(2)	2.679	W–C(1)	2.06
Ru(1)–C(1)	2.07	Ru(2)–C(1)	2.12
C(1)–C(2)	1.53(1)[b]	C(2)–C(11)	1.54(1)
C(3)–O(3)	1.13(2)	C(4)–O(4)	1.13(2)
C(5)–O(5)	1.18(1)	C(6)–O(6)	1.17(2)

[a] Bond lengths involving atoms subject to constraints during refinement are quoted without e.s.d.s. [b] The angle C(1)–C(2)–C(11) is 115(1)°.



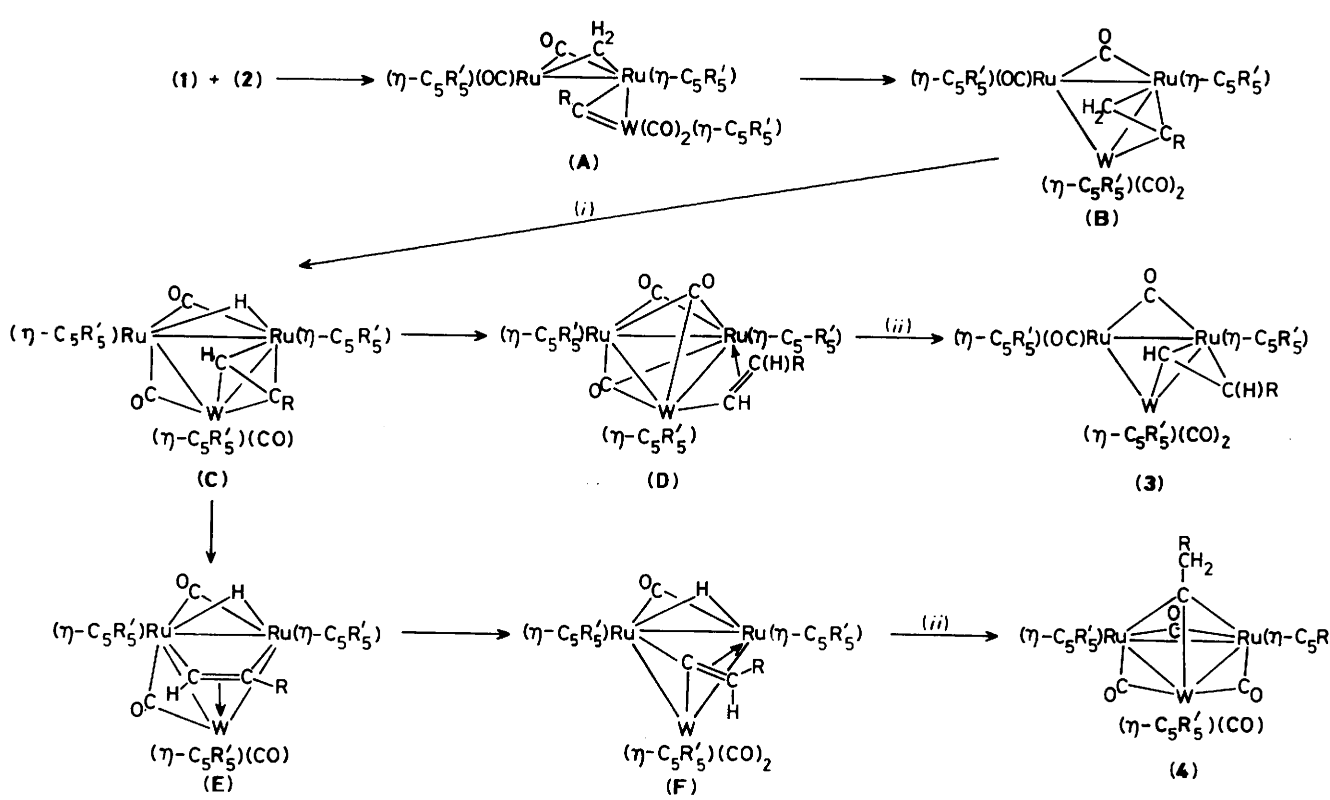
(**5**)

(**5**) + CO $\rightleftharpoons$ (**3c**) provides yet another example of reversible uptake of carbon monoxide by a cluster compound.[11]

It was possible to grow crystals of (**3c**) suitable for an *X*-ray diffraction study. The results are summarised in Table 3. As shown in Figure 1, the structure is based on a triangle of metal atoms. The Ru–Ru bond [2.782(1) Å] is symmetrically bridged by a carbonyl group [Ru(1)–C(5) 2.024(5), Ru(2)–C(5) 2.023(6) Å; Ru(1)–C(5)–O(5) 136.5(4), Ru(2)–C(5)–O(5) 136.3(4)°]. The Ru(2)–W bond [2.952(1) Å] is not bridged, but Ru(1)–W is spanned by the *trans*-$CH{=}C(H)C_6H_4Me$-4 ligand with C(1)–C(2) 1.416(8), C(1)–W 2.154(6), C(1)–Ru(1) 2.180(5), and C(2)–Ru(1) 2.271(5) Å. The tungsten atom is ligated by two CO groups, which show a slight deviation from linearity [W–C(3)–O(3) 170.3(5), W–C(4)–O(4) 172.6(5)°], and also by the C_5Me_5 ligand. Both ruthenium atoms carry C_5H_5 groups and, in addition, Ru(2) is ligated by C(6)O(6), showing some deviation from linearity [Ru(2)–C(6)–O(6) 170.8(4)°].

An *X*-ray diffraction study was also carried out on compound (**4a**), in order to confirm the structure, and by inference establish those of (**4b**) and (**4c**) also. The structure is shown in Figure 2, and selected data are given in Table 4. There was a disorder present in the crystal (see Experimental section) such that in the minor component (33%) the positions of Ru(1) and WC(3)O(3) are interchanged. Atoms Ru(1), W, and C(3) were each refined at two sites, and hence only the major component of each site is shown in Figure 2, together with average positions for all other atoms. Our inability to resolve the disorder and the constraints that were necessary to ensure stable refinement preclude useful discussion of the data in Table 4. The results indicate, however, that the metal triangle is symmetrically capped by the $CCH_2C_6H_4Me$-4 ligand and that each metal–metal vector is symmetrically bridged by a carbonyl group. The tungsten atom carries a terminal CO ligand.

The pathways whereby the compounds (**3**) and (**4**) are formed are of interest. The *trans*-CH=C(H)R groups present in (**3**) imply that in these reactions the W≡C bonds present in (**1**) are cleaved. Moreover, it was observed that the compounds (**3**) could not be converted into (**4**) by heating solutions of the former. This suggests that (**3**) and (**4**) originate from a common intermediate. Possible routes to these species are shown in the Scheme. Previous studies, which amply demonstrate the ligating properties of C≡W groups in (**1**),[12] make formation of the species (**A**) likely in the first step. The transformation of (**A**) into (**B**) *via* coupling of methylene and alkylidyne groups at a dimetal centre has recent precedent.[1,4c] Rearrangement of the vinyl group in (**B**) into the *trans*-CH=C(H)R arrangement found in the complexes (**3**) could proceed *via* intermediates (**C**) and (**D**). In the reaction between (**1c**) and (**2**) intermediate (**D**) is isolated as compound (**5**). Conversion to (**3c**) requires treatment with CO and this perhaps reflects the ability of $\eta\text{-}C_5Me_5$ to stabilise electronically unsaturated cluster complexes. The alkyne-



Scheme. R′ = H or Me, R = C_6H_4Me-4 or Me. (*i*) −CO; (*ii*) +CO

bridged species (**C**) provides a mechanism for isomerism of the vinyl group to yield (**3**), as discussed elsewhere,[1] while at the same time (**C**) could also transform into (**4**) *via* (**E**) and (**F**). The shift of the alkyne ligand from a μ-(η^2-$\perp$) bonding mode in (**C**) into the μ-(η^2-$\|$) form in (**E**) has ample precedent.[13] Indeed, in the compounds $[FeM_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W, R = C_6H_4Me-4), the bonding of the alkyne to the metal triangle is intermediate between that depicted in (**C**) and (**E**).[14] The conversion of (**E**) into (**F**) is modelled on the ready isomerisation of the 1-alkyne ligand in $[Co_2Ru(\mu_3\text{-}HC_2Bu^t)(\mu\text{-}CO)(CO)_8]$ into the vinylidene group in $[Co_2Ru\{\mu_3\text{-}C{=}C(H)Bu^t\}(CO)_9]$, both compounds having been characterised crystallographically.[15] There are several examples in the literature of the transformation of μ-vinylidene ligands into μ_3-alkylidyne *via* addition of metal hydride,[16–19] as postulated for the conversion of (**F**) into (**4**). Moreover, Bruce[20] has demonstrated several of the individual steps invoked in the Scheme in studies on pentanuclear ruthenium compounds.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All separations were carried out on columns *ca.* 3 × 20 cm, packed with Brockman activity II alumina. The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$(R = C_6H_4Me-4 or Me), $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$,[1] and $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$[6] were prepared by methods previously described. Irradiation of the diruthenium compound with u.v. light was carried out with a 500-W medium-pressure Hanovia mercury vapour lamp. The i.r. spectra were measured with Nicolet MX10 or MX5 spectrophotometers, and n.m.r. spectra were recorded with JNM FX 90Q, FX 200, and GX 400 instruments. Analytical and other data for the new compounds are given in Table 1.

Reactions between the Compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) *and* $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(NCMe)(\eta\text{-}C_5H_5)_2]$.—(*i*) A solution of $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ (0.35 g, 0.81 mmol) in MeCN (200 cm^3) was irradiated for 17 h with u.v. light whilst purging the mixture with a stream of nitrogen. Monitoring by i.r. spectroscopy showed that almost complete conversion to (**2**) had occurred. Solvent was removed *in vacuo*, and the residue was redissolved in CH_2Cl_2 (50 cm^3) and treated with (**1a**) (0.325 g, 0.80 mmol) in the same solvent (25 cm^3). The mixture was stirred for 1 h at room temperature. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1 : 1) and chromatographed. Elution with CH_2Cl_2–light petroleum (initially 1 : 3, changing to 2 : 3, and finally to 4 : 1) eluted in succession unreacted (**1a**) (*ca.* 25 mg), $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ (*ca.* 35 mg), and dark green *microcrystals* of $[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}trans\text{-}CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_3]$ (**3a**) (55 mg, 9%). Finally, elution with CH_2Cl_2–tetrahydrofuran (thf) (4:1) gave a red-brown eluate. Removal of solvent *in vacuo* and crystallisation from CH_2Cl_2–light petroleum (−20 °C) gave brown *crystals* of $[Ru_2W(\mu_3\text{-}CCH_2C_6H_4Me\text{-}4)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$ (**4a**) (38 mg, 6%).

(*ii*) A similar reaction between $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ (0.35 g, 0.81 mmol) and (**1b**) (0.266 g, 0.80 mmol), using the same separation procedure, gave traces of both reactants together with green *microcrystals* of $[Ru_2W\{\mu\text{-}\sigma{:}\eta\text{-}trans\text{-}CH{=}C(H)Me\}(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_3]$ (**3b**) (28 mg, 5%) and red-brown *microcrystals* of $[Ru_2W(\mu_3\text{-}CEt)(\mu\text{-}CO)_3(CO)(\eta\text{-}C_5H_5)_3]$ (**4b**) (40 mg, 7%).

Table 5. Atomic positional parameters (fractional co-ordinates) (× 10^4) with estimated standard deviations in parentheses for (**3c**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 306(1)	2 987(1)	1 858(1)	C(23)	−566(6)	3 611(7)	1 237(3)
Ru(1)	2 134(1)	2 009(1)	3 155(1)	C(24)	288(6)	2 776(7)	893(3)
Ru(2)	−655(1)	966(1)	3 183(1)	C(25)	1 664(6)	3 675(7)	613(3)
C(1)	1 486(5)	4 211(5)	2 638(3)	C(121)	2 770(8)	6 470(8)	568(4)
C(2)	2 742(5)	4 651(5)	2 844(3)	C(122)	−269(8)	6 347(8)	1 460(4)
C(3)	1 520(6)	751(7)	2 002(3)	C(123)	−2 165(6)	3 171(9)	1 490(4)
O(3)	1 730(5)	−475(5)	1 984(3)	C(124)	−192(9)	1 258(9)	741(4)
C(4)	3 362(6)	3 343(6)	1 618(3)	C(125)	2 835(7)	3 345(10)	116(4)
O(4)	4 574(4)	3 627(6)	1 399(3)	C(31)	4 053(6)	894(7)	2 930(4)
C(5)	304(5)	1 766(5)	3 866(3)	C(32)	4 342(6)	1 989(7)	3 291(4)
O(5)	−38(4)	1 900(4)	4 444(2)	C(33)	3 435(7)	1 535(7)	3 960(4)
C(6)	−1 430(5)	2 769(7)	3 020(3)	C(34)	2 558(6)	132(7)	4 036(3)
O(6)	−2 076(4)	3 783(5)	2 984(3)	C(35)	2 948(6)	−274(6)	3 391(4)
C(11)	2 877(5)	5 260(5)	3 448(3)	C(41)	−2 552(6)	−588(8)	3 175(4)
C(12)	1 729(5)	5 364(6)	3 955(3)	C(42)	−2 500(7)	−725(8)	3 900(4)
C(13)	1 918(6)	5 916(6)	4 539(3)	C(43)	−1 317(7)	−1 421(7)	4 033(4)
C(14)	3 266(6)	6 356(6)	4 633(3)	C(44)	−647(7)	−1 682(7)	3 397(4)
C(15)	4 398(6)	6 258(6)	4 118(3)	C(45)	−1 436(7)	−1 188(8)	2 868(4)
C(16)	4 213(5)	5 743(6)	3 539(3)	Cl(1)	6 344(3)	−2 530(5)	1 670(2)
C(17)	3 462(8)	6 909(9)	5 254(4)	Cl(2)	5 140(4)	78(4)	990(3)
C(21)	1 635(6)	5 085(7)	824(3)	$C_{sol.}$	4 921(11)	−1 655(12)	1 670(7)
C(22)	267(6)	5 030(7)	1 207(3)				

Reaction between the Compounds [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5Me_5)] *and* [Ru_2(μ-CH_2)(μ-CO)(CO)(NCMe)(η-$C_5H_5)_2$].—A solution of (**2**) in CH_2Cl_2 (75 cm^3) was prepared by u.v. irradiation of [Ru_2(μ-CH_2)(μ-CO)$(CO)_2$(η-$C_5H_5)_2$] (0.33 g, 0.77 mmol). Solid (**1c**) (0.36 g, 0.75 mmol) was added to the solution, and the mixture was refluxed for 1 h during which period the colour of the solution changed from orange-yellow to dark green. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (5 cm^3, 1:1) and chromatographed. Elution with light petroleum, to which portions of CH_2Cl_2 were slowly added, gave traces of unreacted starting materials. Continued elution with CH_2Cl_2 gave a dark green band. Removal of solvent *in vacuo* afforded dark green *microcrystals* of [Ru_2W{μ-σ:η-CH=C(H)C_6H_4Me-4}(μ-CO)$(\mu_3\text{-CO})_2$(η-$C_5H_5)_2$(η-C_5Me_5)] (**5**) (0.213 g, 33%). Finally, elution with CH_2Cl_2—thf (4:1) afforded, after removal of solvent *in vacuo*, maroon *microcrystals* of [$Ru_2W(\mu_3$-$CCH_2C_6H_4$Me-4)(μ-CO$)_3$(CO)(η-$C_5H_5)_2$(η-C_5Me_5)] (**4c**) (5 mg, 1%).

Reaction of [Ru_2W{μ-σ:η-CH=C(H)C_6H_4Me-4}(μ-CO)-$(\mu_3\text{-CO})_2$(η-$C_5H_5)_2$(η-C_5Me_5)] *with* CO.—Carbon monoxide was bubbled through a CH_2Cl_2 (70 cm^3) solution of (**5**) (0.21 g, 0.25 mmol) for 20 min, the colour changing from dark green to black. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed. Elution with CH_2Cl_2–light petroleum (1:1) afforded a black eluate. Removal of solvent *in vacuo* gave black *crystals* of [Ru_2W{μ-σ:η-*trans*-CH=C(H)C_6H_4Me-4}(μ-CO)$(CO)_3$(η-$C_5H_5)_2$(η-C_5Me_5)] (**3c**) (0.18 g, 82%).

Crystal Structure Determinations.—(*i*) Crystals of (**3c**) were grown from CH_2Cl_2–light petroleum, by solvent diffusion, as black parallelepipeds. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.43 × 0.45 × 0.24 mm with well developed faces of the types (1, 0, 0), ($\bar{1}$, 0, 0), (0, 1, 0), (0, $\bar{1}$, 0), (0, 0, 1), (0, 0, $\bar{1}$) on a Nicolet *P*3*m* diffractometer. Of the 5 770 unique data collected (ω–2θ scans, $2\theta \leqslant 50°$), 5 323 had $I \geqslant 2.5\sigma(I)$, and only these were used in structure solution and refinement. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an analytical method.

Crystal data for (**3c**). $C_{33}H_{34}O_4Ru_2W{\cdot}CH_2Cl_2$, $M = 965.55$, triclinic, $a = 9.799(2)$, $b = 9.010(2)$, $c = 19.823(3)$ Å, $\alpha = 73.83(2)$, $\beta = 79.77(1)$, $\gamma = 96.01(2)°$, $U = 1\,632(1)$ Å^3, $Z = 2$, $D_c = 1.96$ g cm^{-3}, $F(000) = 936$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 46.9 cm^{-1}.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. The unit cell was found to contain two molecules of CH_2Cl_2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Atoms H(1) and H(2) were also located by difference-Fourier syntheses, and were refined with fixed isotropic thermal parameters (1.2 × $U_{equiv.}$ of the parent carbon atom). All other hydrogen atoms, except for those in the solvent of crystallisation, were included at calculated positions with fixed isotropic thermal parameters (1.2 × $U_{equiv.}$ of the parent carbon atom) for those attached to aromatic carbon atoms, and with two common refined isotropic thermal parameters for the C_5Me_5 hydrogen atoms and the hydrogens attached to C(17). Refinement by blocked-cascade least-squares methods led to $R = 0.033$ ($R' = 0.035$). A weighting scheme of the form $w = [\sigma^2(F) + 0.000\,68|F|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant 1.1$ or $\leqslant -1.8$ e Å^{-3}, with the largest peaks lying close to the metal atoms.

(*ii*) Crystals of (**4a**) were grown from CH_2Cl_2–light petroleum, by solvent diffusion, as dark brown or black rectangular prisms. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.13 × 0.19 × 0.33 mm. Of the 4 030 unique data collected (ω–2θ scans, $2\theta \leqslant 65°$), 3 459 had $I \geqslant 2.5\sigma(I)$, and only these were used in structure solution and refinement. The data were corrected for Lorentz polarisation and *X*-ray absorption effects, the latter by using an empirical method based on azimuthal scan data.[21]

Crystal data for (**4a**). $C_{28}H_{24}O_4Ru_2W$, $M = 810.49$, orthorhombic, $a = 8.768(1)$, $b = 10.325(3)$, $c = 27.374(4)$ Å, $U = 2\,478(1)$ Å^3, $Z = 4$, $D_c = 2.17$ g cm^{-3}, $F(000) = 1\,544$, space group $P2_12_12_1$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 59.5 cm^{-1}.

Table 6. Atomic positional parameters (fractional co-ordinates) (× 10^4) with estimated standard deviations in parentheses for (**4a**)

Atom	x	y	z
W	1 211(2)	4 740(1)	3 648(1)
Ru(1′)	1 191(7)	4 429(4)	3 791(1)
Ru(1)	−257(2)	6 976(2)	3 984(1)
W′	−140(3)	6 899(2)	3 792(1)
Ru(2)	−135(1)	4 991(1)	4 613(1)
C(1)	−976(10)	5 080(10)	3 887(3)
C(2)	−2 541(12)	4 512(14)	3 759(4)
C(3)	611(23)	5 687(17)	3 033(6)
C(3′)	74(47)	6 375(41)	3 068(14)
O(3)	301(15)	6 158(10)	2 673(3)
C(4)	2 279(15)	6 538(18)	3 789(4)
O(4)	3 381(10)	7 095(9)	3 829(3)
C(5)	2 053(13)	4 698(11)	4 523(5)
O(5)	3 274(9)	4 599(9)	4 697(3)
C(6)	601(13)	6 870(11)	4 670(4)
O(6)	1 131(11)	7 560(9)	4 965(3)
C(11)	−3 028(11)	4 672(13)	3 222(4)
C(12)	−3 846(15)	5 734(12)	3 062(4)
C(13)	−4 297(14)	5 815(12)	2 569(4)
C(14)	−3 946(13)	4 883(13)	2 241(3)
C(15)	−3 122(14)	3 829(14)	2 401(4)
C(16)	−2 664(12)	3 737(15)	2 890(4)
C(17)	−4 410(17)	4 982(14)	1 711(4)
C(21)*	940(8)	2 477(8)	3 493(3)
C(22)	1 403	3 147	3 065
C(23)	2 872	3 678	3 152
C(24)	3 317	3 336	3 634
C(25)	2 123	2 594	3 845
C(31)*	−267(9)	8 805(9)	3 484(3)
C(32)	−94	9 126	3 985
C(33)	−1 423	8 708	4 236
C(34)	−2 417	8 127	3 890
C(35)	−1 702	8 187	3 425
C(41)*	−209(8)	4 390(8)	5 394(3)
C(42)	−432	3 269	5 101
C(43)	−1 821	3 424	4 841
C(44)	−2 457	4 640	4 973
C(45)	−1 460	5 237	5 314

* Pivot atom of a rigid group; remaining atoms in the group have identical standard deviations.

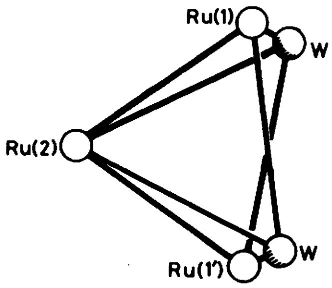


Figure 3. Geometry of the metal core in (**4a**)

The structure was solved by conventional heavy-atom and difference-Fourier methods. Early in the refinement the form of the anisotropic thermal parameters at two of the metal sites [Ru(1) and W] indicated that a disorder was present. The major and minor components at each site were modelled by pairs of atomic positions differing by *ca.* 0.5 Å; these distances were constrained to enable stable refinement and adjusted to minimise electron-density difference features in these regions. In the later stages of refinement, further constraints were applied to give the metal atom triangles of the major and minor components similar dimensions. The final geometry of the metal core is shown in Figure 3, those atoms belonging to the minor component of the disorder being given primed labels. The carbonyl group C(3), O(3) is also severely disordered. The oxygen atoms of the two components occupy the same region of space but C(3′) was refined with an isotropic thermal parameter. The site occupancy of the major component of the disorder refined to 0.67. All remaining non-hydrogen atoms were refined with anisotropic thermal parameters at one site only, the cyclopentadienyl groups being constrained to ideal pentagonal geometries. All hydrogen atoms, except for those attached to C(2), were included at calculated positions with fixed isotropic thermal parameters (1.2 × $U_{\text{equiv.}}$ of the parent carbon atom) for those attached to aromatic carbon atoms, and a common refined isotropic thermal parameter for those attached to C(17). Refinement by blocked-cascade least-squares methods led to $R = 0.048$ ($R' = 0.048$), and a weighting scheme of the form $w = [\sigma^2(F) + 0.000\,4|F|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant 0.96$ or $\leqslant -1.70$ e Å^{-3}. As the space group concerned ($P2_12_12_1$) is chiral an enantiomeric refinement of the type suggested by Rogers[22] was carried out. This verified that the assumed absolute configuration was correct. Scattering factors with corrections for anomalous dispersion were taken from ref. 23. All computations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[21] The atom co-ordinates for (**3c**) and (**4a**) are given in Tables 5 and 6 respectively.

Acknowledgements

We thank the S.E.R.C. for support and for research studentships (to M. J. P. and P. S.), and Dr. J. C. Jeffery for helpful discussion.

References

1 Part 54, E. Delgado, J. Hein, J. C. Jeffery, A. L. Ratermann, F. G. A. Stone, and L. J. Farrugia, *J. Chem. Soc., Dalton Trans.*, preceding paper.

2 F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383; *Pure Appl. Chem.*, 1986, **58**, 529.

3 J. A. K. Howard, J. C. Jeffery, M. Laguna, R. Navarro, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1981, 751; J. C. Jeffery, R. Navarro, H. Razay, and F. G. A. Stone, *ibid.*, p. 2471; K. A. Mead, I. Moore, F. G. A. Stone, and P. Woodward, *ibid.*, 1983, 2083; J. C. Jeffery, H. Razay, F. G. A. Stone, M. J. Went, and P. Woodward, *ibid.*, 1984, 1383; J. C. Jeffery, J. C. V. Laurie, I. Moore, H. Razay, and F. G. A. Stone, *ibid.*, p. 1563; J. C. Jeffery, I. Moore, H. Razay, and F. G. A. Stone, *ibid.*, p. 1581; M. Green, J. A. K. Howard, S. J. Porter, F. G. A. Stone, and D. C. Tyler, *ibid.*, p. 2553; J. C. Jeffery, C. Marsden, and F. G. A. Stone, *ibid.*, 1985, 1315; E. Delgado, A. T. Emo, J. C. Jeffery, and N. D. Simmons, *ibid.*, p. 1323; M. R. Awang, J. C. Jeffery, and F. G. A. Stone, *ibid.*, 1986, 165; J. C. Jeffery, A. G. Orpen, F. G. A. Stone, and M. J. Went, *ibid.*, p. 173; E. Delgado, J. C. Jeffery, and F. G. A. Stone, *ibid.*, p. 2105; L. J. Farrugia, J. C. Jeffery, C. Marsden, P. Sherwood, and F. G. A. Stone, *ibid.*, 1987, 51.

4 (*a*) M. R. Awang, R. D. Barr, M. Green, J. A. K. Howard, T. B. Marder, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2009; (*b*) E. Delgado, J. Hein, J. C. Jeffery, A. L. Ratermann, and F. G. A. Stone, *J. Organomet. Chem.*, 1986, **307**, C23; (*c*) M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1986, 802.

5 M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1985, 1778; M. J. Attfield, J. A. K. Howard, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, in the press.

6 D. L. Davies, S. A. R. Knox, K. A. Mead, M. J. Morris, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1984, 2293; N. M. Doherty, N. J. Forrow, S. A. R. Knox, and M. I. Yates, unpublished work.

7 B. E. Mann and B. F. Taylor, '^{13}C NMR Data for Organometallic Compounds,' Academic Press, London, 1981.

8 J. C. Jeffery, I. Moore, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1571.

9 P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, 1984, **106**, 644; A. F. Dyke, S. A. R. Knox, M. J. Morris, and P. J. Naish, *J. Chem. Soc., Dalton Trans.*, 1983, 1417; C. P. Casey, S. R. Marder, and B. R. Adams, *J. Am. Chem. Soc.*, 1985, **107**, 7700.

10 C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23**, 219.

11 R. D. Adams and I. T. Horváth, *Prog. Inorg. Chem.*, 1985, **33**, 127.

12 J. A. Abad, L. W. Bateman, J. C. Jeffrey, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2075; J. A. Abad, E. Delgado, M. E. Garcia, M. J. Grosse-Ophoff, I. J. Hart, J. C. Jeffery, M. S. Simmons, and F. G. A. Stone, *ibid.*, 1987, 41.

13 A. D. Clauss, J. R. Shapley, C. N. Wilker, and R. Hoffmann, *Organometallics*, 1984, **3**, 619 and refs. therein; Y. Chi and J. R. Shapley, *ibid.*, 1985, **4**, 1900.

14 L. Busetto, J. C. Jeffery, R. M. Mills, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 101; M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, unpublished work.

15 W. Bernhardt and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 141; E. Roland, W. Bernhardt, and H. Vahrenkamp, *Chem. Ber.*, 1985, **118**, 2858.

16 A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614; A. J. Deeming, in 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley-Interscience, Chichester, 1980, ch. 6.

17 P. Brun, G. M. Dawkins, M. Green, R. M. Mills, J-Y. Salaun, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 1357.

18 J. Ros and R. Mathieu, *Organometallics*, 1983, **2**, 771.

19 E. N. Jacobsen and R. G. Bergman, *J. Am. Chem. Soc.*, 1985, **107**, 2023.

20 M. I. Bruce, *Pure Appl. Chem.*, 1986, **58**, 553 and refs. therein.

21 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-ray system, University of Cambridge, 1976; updated Göttingen, 1981.

22 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.

23 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 30*th May* 1986; *Paper* 6/1069