

Preparation of Tetranuclear Heterometallic Clusters by Condensation of Tungsten Acetylides $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CR})(\eta\text{-C}_5\text{H}_5)]$ with Acetylide Clusters $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CR})\text{L}]$ ($\text{L} = \eta\text{-C}_5\text{H}_5$ or $\eta\text{-C}_5\text{Me}_5$, $\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{F-}p$). Crystal Structures of $[\text{W}_2\text{Ru}_2(\text{CO})_9\{\text{CC}(\text{C}_6\text{H}_4\text{F-}p)\text{CC}(\text{C}_6\text{H}_4\text{F-}p)\}(\eta\text{-C}_5\text{H}_5)_2]$ and $[\text{W}_2\text{Ru}_2(\text{CO})_6(\text{C}\equiv\text{CPh})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]^\ddagger$

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Reaction of trinuclear acetylide complexes $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CR})(\eta\text{-C}_5\text{H}_5)]$ with 1.5 molar equivalents $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CR})(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{F-}p$) in refluxing toluene produced two heterometallic cluster complexes $[\text{W}_2\text{Ru}_2(\text{CO})_9(\text{CCRCCR})(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{Ph}$, **2a**; or $\text{C}_6\text{H}_4\text{F-}p$, **2b**) and $[\text{W}_2\text{Ru}_2(\text{CO})_6(\text{C}\equiv\text{CR})_2(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{Ph}$, **3a**; or $\text{C}_6\text{H}_4\text{F-}p$, **3b**). For the analogous reaction of $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{Me}_5)]$ and $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)]$ only the complex $[\text{W}_2\text{Ru}_2(\text{CO})_6(\text{C}\equiv\text{CPh})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$ **3c** was isolated. Crystal data: **2b**, space group *Pbca*, $a = 16.237(3)$, $b = 34.006(2)$, $c = 13.228(3)$ Å, $Z = 8$, final $R = 0.077$, $R' = 0.084$ for 3968 reflections with $I > 2\sigma(I)$; **3c**, space group *P1̄*, $a = 10.202(3)$, $b = 11.703(2)$, $c = 16.600(3)$ Å, $\alpha = 87.97(1)$, $\beta = 103.68(2)$, $\gamma = 102.66(2)^\circ$, $Z = 2$, $R = 0.038$, $R' = 0.030$ for 4714 reflections with $I > 2\sigma(I)$. A plausible reaction pathway which leads to the formation of both complexes **2** and **3** is presented.

The chemistry of heterobimetallic cluster complexes has been the subject of intensive research for many years.¹ The reason is that such complexes containing different transition-metal atoms may show interesting changes in chemical reactivity with respect to those of the homometallic analogues. Seeking to develop a systematic method to synthesise mixed-metal complexes by using the concept of isolobal analogy,² Stone and co-workers³ have used tungsten alkylidyne complexes $[\text{W}(\text{CO})_2(\equiv\text{CR})\text{L}]$ as basic building blocks to prepare mixed-metal clusters containing alkylidyne fragments. Following a similar strategy of using tungsten acetylide complexes $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CR})(\eta\text{-C}_5\text{H}_5)]$ we have successfully prepared several polynuclear cluster derivatives possessing acetylide fragments of various types⁴ and co-ordinated hydrocarbon moieties derived from acetylides.⁵ During our studies we have observed that the acetylide of the trinuclear mixed-metal complexes $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CR})\text{L}]$ undergoes the so-called edge-hopping motion on the W_2Ru triangular face, producing two isomers which differ in the orientation of the acetylide ligand in solution.⁶ In attempts to prepare larger clusters and to examine the difference in reactivity of these two isomers, we have studied the reaction of the acetylide clusters $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CR})\text{L}]$ ($\text{L} = \eta\text{-C}_5\text{H}_5$, $\text{R} = \text{Ph}$, **1a**; or $\text{C}_6\text{H}_4\text{F-}p$, **1b**; $\text{L} = \eta\text{-C}_5\text{Me}_5$, $\text{R} = \text{Ph}$, **1c**) toward acetylide complexes $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CR})(\eta\text{-C}_5\text{H}_5)]$. In this report we describe the crystal structure and spectroscopic characterization of two novel W_2Ru_2 complexes prepared from the reactions mentioned.

Experimental

General Information and Materials.—Infrared spectra were recorded on a Bomen M-100 FT-IR spectrometer, ¹H and ¹³C NMR spectra on a Bruker AM-400 (400.13 MHz) or a Varian Gemini-300 (300 MHz) instrument. Mass spectra were obtained on a JEOL-HX 110 instrument operating in fast-atom bom-

bardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F₂₅₄, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F₂₅₄, E. Merck). The acetylide complexes $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CR})\text{L}]$ ⁷ and the acetylide cluster complexes $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CR})\text{L}]$ ^{6b} were prepared according to literature procedures. Elemental analyses were performed at the NSC Regional Instrument Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)]$ with $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)]$.—A toluene solution (35 cm³) of $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)]$ (196 mg, 0.253 mmol) and $[\text{W}(\text{CO})_3(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)]$ (164 mg, 0.378 mmol) was heated at reflux under nitrogen for 1.5 h. After evaporation of the solvent on a rotary evaporator, the residue was separated by thin-layer chromatography [silica gel, dichloromethane–hexane (1:1)] and recrystallized from a CH_2Cl_2 –heptane solution, giving the orange starting material $[\text{WRu}_2(\text{CO})_8(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)]$ (47 mg, 0.061 mmol, 24%), the black coupling product $[\text{W}_2\text{Ru}_2(\text{CO})_9(\text{CCPhCCPh})(\eta\text{-C}_5\text{H}_5)_2]$ **2a** (75 mg, 0.064 mmol, 25%), and the dark green complex $[\text{W}_2\text{Ru}_2(\text{CO})_6(\text{C}\equiv\text{CPh})_2(\eta\text{-C}_5\text{H}_5)_2]$ **3a** (45 mg, 0.042 mmol, 17%).

Complex 2a. Mass spectrum (FAB, ¹⁰²Ru, ¹⁸⁴W): m/z 1156 (M^+). IR (C_6H_{12}): $\nu(\text{CO})$ 2054vs, 1999vs, 1986m, 1979s, 1967m, 1940w, 1922w and 1894vw cm⁻¹. NMR (CDCl_3 , 294 K): ¹H,

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[‡] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

δ 7.65–7.61 (m, 2H), 7.29–7.16 (m, 7H), 7.07 (t, 1H), 5.68 (s, 5H, C₅H₅) and 4.66 (s, 5H, C₅H₅); ¹³C, δ 281.6 (CPhCCPhC, $J_{\text{CW}} = 178$), 218.1 (WCO, $J_{\text{CW}} = 176$), 215.3 (WCO, $J_{\text{CW}} = 188$), 211.5 (WCO, $J_{\text{CW}} = 168$), 211.4 (RuCO), 210.6 (WCO, $J_{\text{CW}} = 162$), 204.0 (RuCO), 200.3 (RuCO, br), 196.2 (RuCO, br), 194.7 (RuCO, br), 161.7 (CPhCCPhC, $J_{\text{CW}} = 49$), 91.2 (C₅H₅), 90.7 (C₅H₅), 89.8 (CPhCCPhC) and 88.3 (CPhCCPhC, $J_{\text{CW}} = 33$ Hz) (Found: C, 35.30; H, 1.85. Calc. for C₃₅H₂₀O₉Ru₂W₂: C, 36.40; H, 1.75%).

Complex **3a**. Mass spectrum (FAB, ¹⁰²Ru, ¹⁸⁴W): m/z 1072 (M^+). IR (CH₂Cl₂): $\nu(\text{CO})$ 2023s, 1996vs, 1967m and 1944w cm⁻¹. NMR (CDCl₃, 294 K): ¹H, δ 7.70–7.67 (m, 2H), 7.44–7.41 (m, 2H), 7.36–7.16 (m, 6H), 6.02 (s, 5H, C₅H₅) and 5.21 (s, 5H, C₅H₅); ¹³C, δ 306.0 (WCO), 247.3 (WCO), 212.3 (RuCO), 197.1 (RuCO), 195.4 (RuCO) and 192.5 (RuCO) (Found: C, 35.25; H, 2.00. Calc. for C₃₂H₂₀O₆Ru₂W₂: C, 35.90; H, 1.90%).

Reaction of [WRu₂(CO)₈(C≡CC₆H₄F-*p*)(η -C₅H₅)] with [W(CO)₃(C≡CC₆H₄F-*p*)(η -C₅H₅)]—A toluene solution (35 cm³) of [WRu₂(CO)₈(C≡CC₆H₄F-*p*)(η -C₅H₅)] (32 mg, 0.04 mmol) and [W(CO)₃(C≡CC₆H₄F-*p*)(η -C₅H₅)] (21.5 mg, 0.048 mmol) was heated at reflux, during which the colour turned from orange to black in 1 h. After evaporation of the solvent on a rotary evaporator, the residue was separated by thin-layer chromatography [dichloromethane–hexane (1:1)], giving the orange starting material [WRu₂(CO)₈(C≡CC₆H₄F-*p*)(η -C₅H₅)] (10 mg, 0.024 mmol, 32%) the black complex [W₂Ru₂(CO)₆{CC(C₆H₄F-*p*)CC(C₆H₄F-*p*)}(η -C₅H₅)₂] **2b** (9.5 mg, 0.008 mmol, 20%), and the dark green complex [W₂Ru₂(CO)₆{C≡C(C₆H₄F-*p*)}₂(η -C₅H₅)₂] **3b** (7 mg, 0.006 mmol, 15%). Crystals of complex **2b** suitable for X-ray diffraction were obtained by recrystallization from a dichloromethane–methanol mixture at room temperature.

Complex **2b**. Mass spectrum (FAB, ¹⁰²Ru, ¹⁸⁴W): m/z 1192 (M^+). IR (C₆H₁₂): $\nu(\text{CO})$ 2056vs, 2000vs, 1992m, 1979s, 1967m, 1940w and 1920w cm⁻¹. NMR (CDCl₃, 294 K): ¹H, δ 7.62–7.57 (m, 2H), 7.27–7.21 (m, 2H), 6.93–6.85 (m, 4H), 5.69 (s, 5H, C₅H₅) and 4.67 (s, 5H, C₅H₅); ¹³C, δ 217.9 (WCO, $J_{\text{CW}} = 177$), 215.0 (WCO, $J_{\text{CW}} = 189$), 211.1 (RuCO), 211.0 (WCO, $J_{\text{CW}} = 171$), 209.9 (WCO, $J_{\text{CW}} = 164$ Hz), 203.8 (RuCO), 200.0 (RuCO, br), 196.4 (RuCO, br), 194.4 (RuCO, br), 91.2 (C₅H₅) and 90.6 (C₅H₅) (Found: C, 34.50; H, 1.60. Calc. for C₃₅H₁₈F₂O₉Ru₂W₂: C, 35.25; H, 1.50%).

Complex **3b**. Mass spectrum (FAB, ¹⁰²Ru, ¹⁸⁴W): m/z 1108 (M^+). IR (C₆H₁₂): $\nu(\text{CO})$ 2028s, 2004vs, 1975m and 1959w cm⁻¹. ¹H NMR (CDCl₃, 294 K): δ 7.68–7.63 (m, 2H), 7.43–7.39 (m, 2H), 7.05–6.99 (m, 4H), 6.01 (s, 5H, C₅H₅) and 5.21 (s, 5H, C₅H₅) (Found: C, 34.25; H, 1.70. Calc. for C₃₂H₁₈F₂O₆Ru₂W₂: C, 34.75; H, 1.65%).

Reaction of [WRu₂(CO)₈(C≡CPh)(η -C₅Me₅)] with [W(CO)₃(C≡CPh)(η -C₅H₅)]—A toluene solution (35 cm³) of [WRu₂(CO)₈(C≡CPh)(η -C₅Me₅)] (190 mg, 0.225 mmol) and [W(CO)₃(C≡CPh)(η -C₅H₅)] (146 mg, 0.336 mmol) was heated at reflux under nitrogen for 2 h; the colour turned from orange to black. After removal of the solvent *in vacuo*, the residue was separated by thin-layer chromatography [silica gel, dichloromethane–hexane (3:1)], giving the orange starting material [WRu₂(CO)₈(C≡CPh)(η -C₅Me₅)] (11 mg, 0.013 mmol, 6%) and the dark green coupling product [W₂Ru₂(CO)₆(C≡CPh)₂(η -C₅H₅)(η -C₅Me₅)] **3c** (43 mg, 0.038 mmol, 17%). Crystals of complex **3c** suitable for X-ray diffraction were obtained by recrystallization from a dichloromethane–methanol mixture at room temperature.

Complex **3c**. Mass spectrum (FAB, ¹⁰²Ru, ¹⁸⁴W): m/z 1142 (M^+). IR (C₆H₁₂): $\nu(\text{CO})$ 2024s, 1999vs, 1970m and 1952w cm⁻¹. NMR (CDCl₃, 294 K): ¹H, δ 7.66 (m, 2H), 7.39–7.15 (m, 8H), 5.15 (s, 5H, C₅H₅) and 2.31 (s, 15H, C₅Me₅); ¹³C, δ 308.0 (WCO, $J_{\text{CW}} = 131$ and 52), 249.8 (WCO, $J_{\text{CW}} = 174$ Hz), 213.2 (RuCO), 197.5 (RuCO), 196.2 (RuCO), 193.7 (RuCO), 169.8 (CCPh), 164.8 (CCPh), 108.3 (C₅Me₅), 96.2 (C₅H₅) and 12.1

(C₅Me₅) (Found: C, 38.80; H, 2.75. Calc. for C₃₇H₃₀O₆Ru₂W₂: C, 38.90; H, 2.65%).

X-Ray Crystallography.—Diffraction measurements on complexes **2b** and **3c** were carried out on Rigaku AFC-5R and Nonius CAD-4 diffractometers, respectively. Lattice parameters of complex **2b** were determined from 25 randomly selected reflections with 2θ in the range of 79.37–79.93°, whereas the corresponding cell dimensions of complex **3c** were determined from 25 reflections with 2θ in the range of 18.64–25.32°. Intensities were corrected for Lorentz, polarization and absorption effects. All data reduction and structural refinement was performed using the NRCC-SDP-VAX packages. The structures were solved by the heavy-atom method and refined by least-squares cycles; all non-hydrogen atoms were refined with anisotropic thermal parameters. The data collection and refinement parameters for complexes **2b** and **3c** are given in Table 1. Atomic positional parameters for complex **2b** are in Table 2, selected bond angles and lengths in Table 3; the corresponding parameters for complex **3c** are given in Tables 4 and 5, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Cluster Condensation Reaction with [W(CO)₃(C≡CPh)(η -C₅H₅)]—Treatment of the mixed-metal complex [WRu₂(CO)₈(C≡CPh)(η -C₅H₅)] **1a** with 1.5 molar equivalents of [W(CO)₃(C≡CPh)(η -C₅H₅)] in refluxing toluene for 1.5 h yielded a black condensation product [W₂Ru₂(CO)₉(CCPhCCPh)(η -C₅H₅)₂] **2a** (25%) and a dark green derivative [W₂Ru₂(CO)₆(C≡CPh)₂(η -C₅H₅)₂] **3a** (17%), in addition to about 24% unreacted starting material **1a** (Scheme 1). The analogous W₂Ru₂ cluster complexes [W₂Ru₂(CO)₉{CC(C₆H₄F-*p*)CC(C₆H₄F-*p*)}(η -C₅H₅)₂] **2b** and [W₂Ru₂(CO)₆{C≡C(C₆H₄F-*p*)}₂(η -C₅H₅)₂] **3b** were prepared from the reaction between the acetylide complexes [WRu₂(CO)₈(C≡CC₆H₄F-*p*)(η -C₅H₅)] **1b** and [W(CO)₃(C≡CC₆H₄F-*p*)(η -C₅H₅)] under similar conditions. Furthermore, when the acetylide cluster [WRu₂(CO)₈(C≡CPh)(η -C₅Me₅)] was used instead we obtained only [W₂Ru₂(CO)₆(C≡CPh)₂(η -C₅H₅)(η -C₅Me₅)] **3c** in addition to trace amounts of starting material **1c** and several uncharacterized, air-sensitive, cluster derivatives.

The products isolated were separated by preparative thin-layer chromatography and purified by recrystallization. The analysis of the FAB mass spectra suggests that complexes **2** and **3** are tetranuclear W₂Ru₂ derivatives containing two acetylide units and possessing nine and six CO ligands, respectively. Infrared spectroscopy is not very informative but shows the stretching absorptions of terminal CO ligands. Proton NMR data are consistent with the incorporation of two tungsten acetylide units, indicating that the incoming tungsten acetylide [W(CO)₃(C≡CR)(η -C₅H₅)] has attached to the trinuclear W₂Ru template. However, these spectroscopic data are not fully informative about the structure of these complexes. Single-crystal X-ray diffraction studies were therefore carried out on complexes **2b** and **3c** to establish their exact molecular geometry.

Crystal Structure of Complex 2b.—Black, air-stable, plate-shaped crystals were obtained from a layered solution of dichloromethane–hexane at room temperature. The ORTEP diagram of complex **2b** and its atomic numbering scheme are presented in Fig. 1. The important bond lengths and angles are summarized in Table 2. As indicated in Fig. 1, the cluster core consists of a spiked triangular geometry which is consistent with the presence of 64 cluster valence electrons. The triangular base is defined by the Ru(CO)₃, Ru(CO)₂ and W(CO)₂(η -C₅H₅) centres, in which the unique Ru(CO)₂ is further co-ordinated by a second W(CO)₂(η -C₅H₅) unit. The intermetallic bond angles

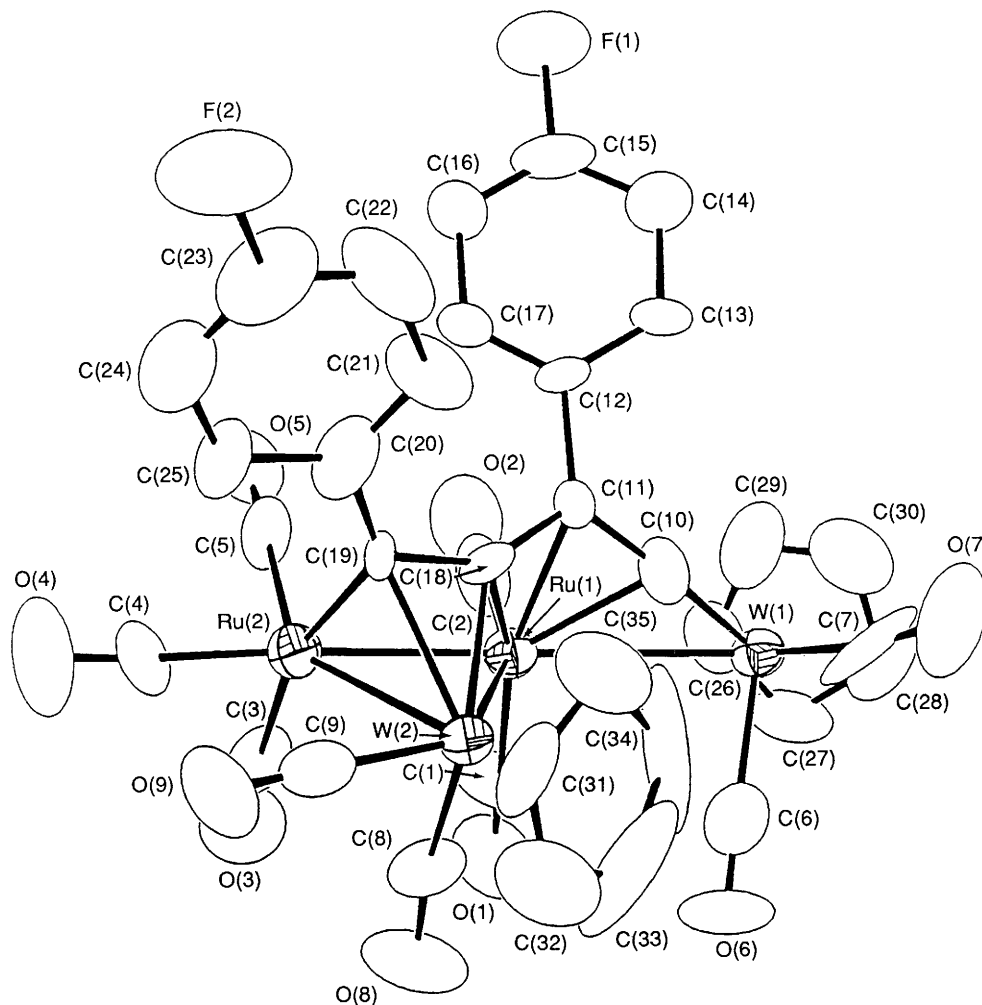
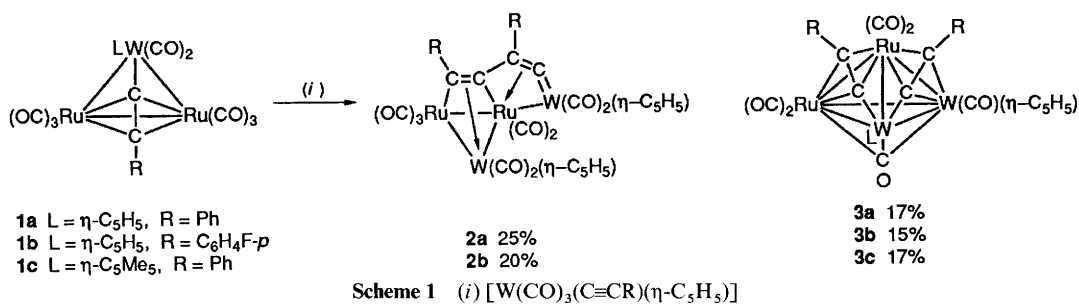


Fig. 1 Molecular structure of [W₂Ru₂(CO)₉{CC(C₆H₄F-*p*)CC(C₆H₄F-*p*)}($\eta\text{-C}_5\text{H}_5$)₂] **2b**

of the metal triangle are close to 60°. The alignment of the metal atoms W(1), Ru(1) and Ru(2) is near linear [165.16(8)°] and the angle between the atoms W(1), Ru(1) and W(2) is much acute [107.09(6)°]. The metal-metal distances of this molecule span a rather large range 2.773(3)–3.042(2) Å, in which the unique Ru–Ru bond is the shortest. Furthermore, all CO ligands are essentially linear with the M–C–O angles in the range 170–179°.

The C₄ hydrocarbon fragment, generated from the head-to-tail coupling of two acetylide moieties, is associated with all four transition-metal atoms. Within this C₄ ligand, the W(1)–C(10) bond distance [1.88(2) Å] is substantially shorter than the other carbon-metal distances [2.17(2)–2.27(2) Å] and the W–C(sp³) distance of a dinuclear acetylide complex [W₂(CO)₄(C≡CPh)(C=CPhH)($\eta\text{-C}_5\text{H}_5$)₂]⁺ [2.19(2) Å],⁸ suggesting that the W(1)–C(10) bond of complex **2b** may retain some double-bond character. The bond distance observed is even shorter than the W–C distances of the doubly bridging alkylidene ligand in the ditungsten complexes [W₂(CO)₃Me(μ-CR)($\eta\text{-C}_5\text{H}_5$)₂] (R =

C₆H₄Me or C₆H₄OMe) (2.01 Å)⁹ and the W=C double bond in W₂Re alkylidene complexes (1.99–2.07 Å).¹⁰ On the other hand, it is comparable with the Mo=C double bond of Mo₂ vinylidene [1.909(5) Å]¹¹ and allenylidene [1.912(3) Å] complexes.¹² Therefore, the C₄ fragment is best visualized as a substituted vinylidene ligand,¹³ in which the vinylidene C₂ linkage is co-ordinated to the W(1) atom *via* a W=C double bond and to the Ru(1) atom *via* a η^2 interaction, and the co-ordinated alkyne substituent C(18)–C(19) is linked to atoms Ru(1) and Ru(2) *via* two σ interactions and to the W(2) atom *via* π bonding (Scheme 1). The planar geometry and bond angles associated with the β -carbon atom C(10) also agree with the structural parameters of a 'side-on' co-ordinated vinylidene.¹³ The W(1)–C(10)–C(11) bond angle of 168(2)° is too large to consider this C₄ fragment as a substituted doubly bridging alkylidene ligand, since the latter assignment would require this bond angle to be close to 120°. Finally, according to simple electron counting, the unsaturated C₄ hydrocarbon fragment

Table 1 Experimental data for the X-ray diffraction studies of complexes **2b** and **3c***

Compound	2b	3c
Formula	C ₃₅ H ₁₈ F ₂ O ₉ Ru ₂ W ₂	C ₃₇ H ₃₀ O ₆ Ru ₂ W ₂ ·CH ₂ Cl ₂
<i>M</i>	1190.37	1140.49
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	16.237(3)	10.202(3)
<i>b</i> /Å	34.006(2)	11.703(2)
<i>c</i> /Å	13.228(3)	16.600(3)
α /°		87.97(1)
β /°		103.68(2)
γ /°		102.66(2)
<i>U</i> /Å ³	7304(2)	1878.6(7)
<i>Z</i>	8	2
<i>D</i> _c /g cm ⁻³	2.165	2.125
<i>F</i> (000)	4430.87	1155.72
Crystal size/mm	0.05 × 0.30 × 0.50	0.10 × 0.30 × 0.50
λ /Å	1.540 56 (Cu-K α)	0.709 30 (Mo-K α)
Scan parameter	1.05 + 0.30 tan θ	0.90 + 0.35 tan θ
2 θ (max.)	120.0°	49.8°
Scan speed/° min ⁻¹	32	16.48/2–16.48/10
<i>h, k, l</i> range	0–18, 0–38, 0–14	–12 to 11, 0–13, –19 to 19
μ /mm ⁻¹	18.77	7.20
Transmission factor (max., min.)	0.0313, 0.4124	0.4581, 0.9991
Standard reflections (three)	12% Decay 10 σ , every 150 reflections	10% Decay every 7200 s
No. of unique data	5191	6605
Data with <i>I</i> > 2 σ (<i>I</i>)	3968	4714
No. of atoms and parameters refined	68, 451	82, 452
Maximum Δ / σ	0.144	0.214
<i>R, R'</i>	0.077; 0.084	0.038; 0.030
g.o.f.	8.23	2.00
Residual electron density (max., min.)/e Å ⁻³	2.83, –2.12	2.04, –1.67

* Features in common: *T* = 297 K; θ –2 θ scan mode, absorption correction by ψ scans; $w = 1/\sigma^2(F_o)$; goodness of fit (g.o.f.) = $[\sum w|F_o - F_c|^2 / (N_o - N_v)]^{1/2}$ where *N*_o = number of observations and *N*_v = number of variables.

Table 2 Atomic coordinates for complex **2b**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ru(1)	0.193 21(10)	0.104 66(6)	0.993 62(15)	C(22)	–0.030 2(19)	0.253 6(9)	0.840 0(22)
Ru(2)	0.165 53(11)	0.114 58(6)	0.788 34(15)	C(23)	–0.044 5(15)	0.255 6(9)	0.741 6(23)
W(1)	0.177 26(6)	0.100 32(3)	1.222 47(8)	C(24)	–0.018 5(18)	0.228 4(8)	0.673 4(20)
W(2)	0.021 41(6)	0.099 20(3)	0.907 51(8)	C(25)	0.015 7(16)	0.196 4(8)	0.711 3(17)
C(1)	0.227 7(17)	0.053 7(7)	0.990 5(23)	C(26)	0.318 8(15)	0.088 9(8)	1.232 1(19)
C(2)	0.301 4(13)	0.121 0(8)	0.997 2(19)	C(27)	0.282 4(15)	0.061 1(7)	1.295 1(20)
C(3)	0.225 2(16)	0.069 0(7)	0.763 1(21)	C(28)	0.245 1(15)	0.084 8(9)	1.370 9(18)
C(4)	0.140 4(16)	0.119 2(9)	0.653 3(19)	C(29)	0.303 0(14)	0.125 4(9)	1.264 8(21)
C(5)	0.257 8(12)	0.146 5(8)	0.783 1(16)	C(30)	0.258 9(16)	0.123 6(9)	1.345 8(24)
C(6)	0.116 2(15)	0.049 6(8)	1.179 5(18)	C(31)	–0.115 3(16)	0.107 9(9)	0.922 9(19)
C(7)	0.082 9(15)	0.112 4(9)	1.287 8(23)	C(32)	–0.100 9(15)	0.069 0(11)	0.943(3)
C(8)	0.073 7(15)	0.049 0(7)	0.882 2(21)	C(33)	–0.055 7(16)	0.063 8(12)	1.024(3)
C(9)	–0.011 5(15)	0.098 3(7)	0.772 7(19)	C(34)	–0.039 4(15)	0.099 2(15)	1.061 9(19)
C(10)	0.143 4(11)	0.136 3(7)	1.122 9(16)	C(35)	–0.082 7(18)	0.131 7(10)	0.997(3)
C(11)	0.134 7(13)	0.162 7(6)	1.038 9(15)	F(1)	0.281 6(13)	0.310 1(5)	1.060 1(14)
C(12)	0.175 7(13)	0.203 5(6)	1.042 2(16)	F(2)	–0.087 2(12)	0.288 3(5)	0.704 8(15)
C(13)	0.178 2(16)	0.221 1(6)	1.133 6(18)	O(1)	0.250 1(14)	0.021 8(6)	0.988 3(15)
C(14)	0.217 7(20)	0.257 6(9)	1.145 7(21)	O(2)	0.367 4(10)	0.135 0(7)	0.998 6(15)
C(15)	0.243 0(19)	0.273 1(7)	1.056 0(21)	O(3)	0.261 9(13)	0.040 3(6)	0.751 7(17)
C(16)	0.242 6(16)	0.256 3(8)	0.965 8(18)	O(4)	0.127 8(12)	0.123 8(8)	0.567 3(14)
C(17)	0.200 9(15)	0.220 1(7)	0.959 8(17)	O(5)	0.315 5(9)	0.165 3(6)	0.777 4(13)
C(18)	0.102 1(13)	0.147 9(6)	0.949 8(16)	O(6)	0.086 5(12)	0.021 2(5)	1.159 3(16)
C(19)	0.080 9(13)	0.155 3(6)	0.850 0(16)	O(7)	0.019 8(11)	0.127 5(7)	1.334 8(14)
C(20)	0.033 5(13)	0.192 8(8)	0.813 5(18)	O(8)	0.088 4(10)	0.013 6(5)	0.872 3(16)
C(21)	0.008 9(17)	0.220 6(7)	0.880 0(20)	O(9)	–0.041 3(11)	0.097 9(6)	0.688 8(13)

provides a total of eight electrons and gives formal electron counts for the W(1), W(2), Ru(1) and Ru(2) atoms of 18, 19, 18 and 17, respectively.

Crystal Structure of Complex 3c.—Dark green, air-stable, plate-shaped crystals were obtained from a layered solution of dichloromethane–methanol at room temperature. The molecular geometry and the atom labelling scheme are shown in Fig. 2.

Selected bond distances and angles are listed in Table 4. The cluster core consists of a distorted W₂Ru₂ tetrahedral arrangement which is associated with 60 outer valence electrons. Each ruthenium atom is co-ordinated by two terminal CO ligands with the M–C–O angles in the range 177(1)–179(1)°. The atom W(1) is co-ordinated by a η -C₅Me₅ ligand and a triply bridging CO ligand with W(1)–C(1)–O(1) 142.2(9)°, whereas W(2) is linked with a η -C₅H₅ and a semibridging CO ligand¹⁴ with

Table 3 Selected bond distances (Å) and angles (°) for complex **2b** with estimated standard deviations (e.s.d.s) in parentheses

Ru(1)–Ru(2)	2.773(3)	Ru(1)–W(1)	3.042(2)
Ru(1)–W(2)	3.019(2)	Ru(2)–W(2)	2.870(2)
Ru(2)–Ru(1)–W(1)	165.16(8)	Ru(2)–Ru(1)–W(2)	59.22(6)
W(1)–Ru(1)–W(2)	107.09(6)	Ru(1)–Ru(2)–W(2)	64.66(6)
Ru(1)–W(2)–Ru(2)	56.12(6)		
C₄ hydrocarbon fragment			
Ru(1)–C(10)	2.18(2)	Ru(1)–C(11)	2.27(2)
Ru(1)–C(18)	2.17(2)	Ru(2)–C(19)	2.12(2)
W(1)–C(10)	1.88(2)	W(2)–C(18)	2.19(2)
W(2)–C(19)	2.27(2)	C(10)–C(11)	1.44(3)
C(11)–C(18)	1.39(3)	C(18)–C(19)	1.39(3)
W(1)–C(10)–C(11)	168(2)	C(10)–C(11)–C(12)	120(2)
W(1)–C(10)–Ru(1)	97(1)	C(10)–C(11)–C(18)	118(2)
Ru(1)–C(10)–C(11)	75(1)	C(12)–C(11)–C(18)	121(2)
C(11)–C(18)–C(19)	147(2)	C(18)–C(19)–C(20)	124(2)
Carbonyl ligands			
Ru(1)–C(1)	1.82(2)	Ru(1)–C(2)	1.84(2)
Ru(2)–C(3)	1.86(2)	Ru(2)–C(4)	1.84(3)
Ru(2)–C(5)	1.85(2)	W(1)–C(6)	2.07(3)
W(1)–C(7)	1.81(3)	W(2)–C(8)	1.94(2)
W(2)–C(9)	1.86(3)		
Ru(1)–C(1)–O(1)	179(3)	Ru(1)–C(2)–O(2)	173(2)
Ru(2)–C(3)–O(3)	177(2)	Ru(2)–C(4)–O(4)	176(2)
Ru(2)–C(5)–O(5)	178(2)	W(1)–C(6)–O(6)	176(2)
W(1)–C(7)–O(7)	170(2)	W(2)–C(8)–O(8)	164(2)
W(2)–C(9)–O(9)	173(2)		

W(2)–C(2)–O(2) 164.4(9)°. The six metal–metal bonds of the molecule span a narrow range: W(1)–W(2) [2.936(1) Å] is the longest, Ru(1)–Ru(2) [2.732(1) Å] the shortest, and the other four heterometallic W–Ru bonds are within the range 2.813(1)–2.873(1) Å. The lengthening of the W(1)–W(2) bond may be due to the unfavourable steric repulsion between the bulky η -C₅H₅ and η -C₅Me₅ ligands of the tungsten centres.

Furthermore, there are two phenyl acetylide ligands which are co-ordinated to the adjacent, edge-sharing, triangular faces of the W₂Ru₂ core. The first one, C(7)–C(8), is co-ordinated to W(1) *via* a σ bond and linked to atoms W(2) and Ru(2) *via* two π interactions. The second acetylide unit, C(15)–C(16), is also co-ordinated to W(1) *via* a σ bond and associated with the opposite Ru(1)–Ru(2) edge by two additional π interactions. Therefore, both acetylide ligands adopt the typical $1\sigma + 2\pi$ bonding mode and donate ten valence electrons in total to the tetrahedral cluster core.¹⁵ The formal electron count for each metal vertex, assuming neutral metal atoms and ligands, amounts to 17 at atoms W(1) and Ru(1) and 19 at W(2) and Ru(2), respectively.

Assignment of the ¹³C NMR Data.—The assignment of the ¹³C NMR data is straightforward on the basis of the structure of complexes **2** and **3**. Furthermore, because the chemical shift of the acetylide carbons is commonly overlapped with the CO resonances in metal clusters,¹⁶ ¹³CO enrichment has been utilized in attempts to identify and differentiate the CO and acetylide signals.

Consistent with the solid-state structure of complex **2b**, the ¹³C NMR spectrum of a ¹³CO-enriched sample shows four WCO and five Ru–CO signals. The CO ligands co-ordinated to the tungsten atoms are assigned on the basis of the presence of the characteristic tungsten satellites. On the other hand, the RuCO signals are grouped according to their fluxional

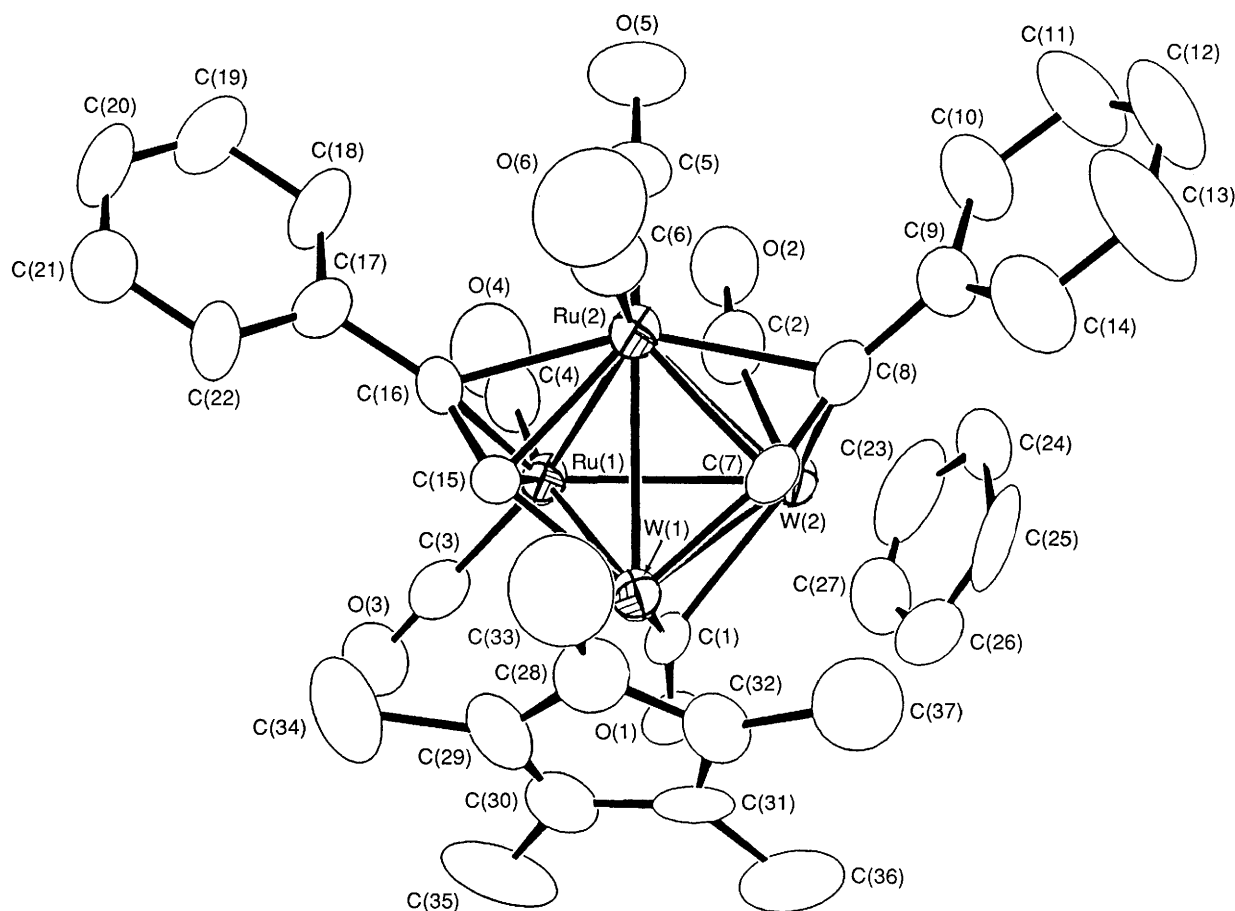
**Fig. 2** Molecular structure of [W₂Ru₂(CO)₆(C≡CPh)₂(η -C₅H₅)(η -C₅Me₅)] **3c**

Table 4 Atomic coordinates for complex **3c**

Atom	x	y	z	Atom	x	y	z
W(1)	0.423 24(5)	0.196 14(4)	0.175 48(3)	C(22)	-0.006 6(11)	-0.086 6(10)	0.234 2(8)
W(2)	0.489 18(5)	0.397 84(4)	0.289 43(3)	C(23)	0.545 2(14)	0.597 3(11)	0.316 1(11)
Ru(1)	0.211 88(9)	0.278 64(8)	0.228 38(6)	C(24)	0.659 2(13)	0.548 8(11)	0.363 4(8)
Ru(2)	0.382 55(9)	0.163 94(8)	0.337 28(6)	C(25)	0.712 5(11)	0.507 4(10)	0.300 6(10)
C(1)	0.375 7(10)	0.357 7(9)	0.153 8(7)	C(26)	0.633 0(13)	0.533 3(11)	0.223 0(8)
C(2)	0.369 8(11)	0.404 7(10)	0.364 9(8)	C(27)	0.535 4(13)	0.583 1(11)	0.236 3(9)
C(3)	0.088 1(10)	0.277 5(10)	0.128 0(7)	C(28)	0.484 3(12)	0.040 9(10)	0.120 5(8)
C(4)	0.095 5(11)	0.345 3(11)	0.278 3(8)	C(29)	0.365 2(11)	0.063 6(11)	0.064 5(7)
C(5)	0.339 5(12)	0.175 5(11)	0.439 0(7)	C(30)	0.387 2(12)	0.175 1(12)	0.031 1(8)
C(6)	0.427 9(13)	0.019 8(11)	0.365 2(8)	C(31)	0.527 8(13)	0.224 2(11)	0.061 7(7)
C(7)	0.553 1(9)	0.230 6(8)	0.281 9(7)	C(32)	0.587 4(11)	0.143 6(11)	0.116 3(7)
C(8)	0.595 7(10)	0.274 0(9)	0.361 2(7)	C(33)	0.501 5(16)	-0.068 3(13)	0.163 8(10)
C(9)	0.707 1(11)	0.279 1(9)	0.436 6(7)	C(34)	0.228 1(14)	-0.029 9(14)	0.043 8(10)
C(10)	0.702 3(12)	0.323 6(12)	0.510 6(8)	C(35)	0.290 2(16)	0.221 1(16)	-0.034 7(9)
C(11)	0.810 9(14)	0.335 3(13)	0.578 0(9)	C(36)	0.604 3(16)	0.339 4(14)	0.033 5(10)
C(12)	0.926 2(14)	0.302 3(15)	0.574 6(10)	C(37)	0.741 0(13)	0.157 2(14)	0.162 1(9)
C(13)	0.933 7(15)	0.258 3(18)	0.504 5(11)	O(1)	0.358 3(7)	0.428 7(7)	0.100 5(5)
C(14)	0.827 0(13)	0.250 1(14)	0.434 3(9)	O(2)	0.323 5(8)	0.428 9(7)	0.419 0(6)
C(15)	0.263 2(10)	0.112 4(8)	0.214 7(6)	O(3)	0.013 5(8)	0.273 1(8)	0.064 0(6)
C(16)	0.169 2(10)	0.101 6(8)	0.261 3(6)	O(4)	0.022 1(9)	0.380 4(9)	0.306 6(7)
C(17)	0.048 5(11)	0.015 7(9)	0.280 1(7)	O(5)	0.310 7(10)	0.185 1(9)	0.502 0(6)
C(18)	-0.005 3(12)	0.041 4(11)	0.342 3(9)	O(6)	0.455 3(11)	-0.069 2(8)	0.382 9(7)
C(19)	-0.121 8(12)	-0.035 7(12)	0.361 5(9)	C(38)	0.118 9(15)	0.590 4(13)	0.115 9(10)
C(20)	-0.173 6(12)	-0.137 3(11)	0.314 9(9)	Cl(1)	-0.054 9(5)	0.550 0(5)	0.110 5(4)
C(21)	-0.119 8(13)	-0.161 8(11)	0.252 6(8)	Cl(2)	0.203 0(5)	0.688 4(4)	0.192 5(4)

Table 5 Selected bond distances (Å) and angles (°) of complex **3c** with e.s.d.s in parentheses

W(1)–W(2)	2.936(1)	Ru(1)–W(1)	2.867(1)
Ru(1)–W(2)	2.813(1)	Ru(1)–W(2)	2.827(1)
Ru(1)–Ru(2)	2.732(1)	Ru(2)–W(2)	2.873(1)
Ru(1)–W(1)–W(2)	58.29(3)	Ru(2)–W(1)–W(2)	59.92(3)
Ru(1)–W(1)–Ru(2)	57.49(3)	W(1)–Ru(2)–W(2)	62.16(3)
W(1)–Ru(2)–Ru(1)	62.24(3)	W(2)–Ru(2)–Ru(1)	60.51(3)
W(1)–W(2)–Ru(1)	59.63(3)	W(1)–W(2)–Ru(2)	57.92(3)
Ru(1)–W(2)–Ru(2)	57.27(3)	W(1)–Ru(1)–W(2)	62.08(3)
W(1)–Ru(1)–Ru(2)	60.27(3)	W(2)–Ru(1)–Ru(1)	62.22(3)
Acetylide fragments			
Ru(1)–C(15)	2.16(1)	Ru(2)–C(15)	2.14(1)
W(1)–C(15)	1.951(9)	Ru(1)–C(16)	2.101(9)
Ru(2)–C(16)	2.221(9)	Ru(2)–C(7)	2.143(9)
W(1)–C(7)	1.94(1)	W(2)–C(7)	2.21(1)
Ru(2)–C(8)	2.22(1)	W(2)–C(8)	2.16(1)
C(15)–C(16)	1.35(1)	C(7)–C(8)	1.36(2)
W(1)–C(15)–C(16)	153.5(8)	W(1)–C(7)–C(8)	154.2(8)
Carbonyl ligands			
Ru(1)–C(1)	2.32(1)	W(1)–C(1)	2.05(1)
W(2)–C(1)	2.29(1)	W(2)–C(2)	1.96(1)
Ru(1)–C(3)	1.84(1)	Ru(1)–C(4)	1.90(1)
Ru(2)–C(5)	1.86(1)	Ru(2)–C(6)	1.86(1)
W(2)–C(2)–O(2)	164.4(9)	Ru(1)–C(3)–O(3)	177(1)
Ru(1)–C(4)–O(4)	177(1)	Ru(2)–C(5)–O(5)	178(1)
Ru(2)–C(6)–O(6)	179(1)	W(1)–C(1)–O(1)	142.2(9)
W(2)–C(1)–O(1)	126.0(8)	Ru(1)–C(1)–O(1)	123.3(7)

behaviour: the first two CO signals at δ 211.1 and 203.8 are attributed to the unique Ru(CO)₂ fragment, because the last three CO signals at δ 200.0, 196.4 and 194.4 are relatively broad, suggesting that the latter is derived from the Ru(CO)₃ unit that undergoes localized, three-fold rotation on the NMR time-scale.

The CO signals of the derivative **2a** are assigned in the same manner. The ¹³C NMR spectrum of a regular sample of **2a** shows four signals of the C₄ fragment at δ 281.6, 161.7, 89.8 and 88.3 in addition to the CO signals within the range δ 218.1–194.7

and the signals due to the phenyl and the η -C₅H₅ resonances in the high-field region. The downfield shift and the presence of a large W–C coupling constant for the signal at δ 281.6 suggests that this signal is due to the α -carbon of the vinylidene fragment.¹⁷ The other three signals are due to the ω -, β - and γ -carbons, as suggested by the observation of the expected one-bond tungsten–carbon coupling for the ω - and γ -carbons.

For the tetrahedral acetylide complexes **3** the ¹³C NMR spectrum of **3c** was taken and served as a model. The spectrum exhibits two WCO signals and four Ru–CO signals, of which the WCO signal at δ 308.0 is assigned to the triply bridging CO ligand, and that at δ 249.8 to the semibridging CO ligand. In addition, the α -carbon of the acetylide ligands appears at δ 169.8 and 164.8, consistent with ¹³C NMR data in the literature.¹⁶ The β -carbon of the acetylides was not determined because of the uncertainty with respect to the assignment of the phenyl signals.

Summary and a Possible Reaction Mechanism.—Reaction of acetylide clusters [WRu₂(CO)₈(C≡CR)L] with mononuclear metal acetylides [W(CO)₃(C≡CR)(η -C₅H₅)] gives tetranuclear cluster derivatives **2** and **3** in moderate yield. We propose that the observed reaction is initiated by elimination of CO from a ruthenium atom of complexes **1** to afford an unsaturated acetylide cluster [WRu₂(CO)₇(C≡CR)L] followed by co-ordination of the tungsten acetylide [W(CO)₃(C≡CR)(η -C₅H₅)] giving an intermediate possessing a spiked triangular Ru₂W₂ core. The isolation and characterization of the analogous Os₂W acetylide complexes [WOs₂(CO)₇(NCMe)(C≡CR)(η -C₅H₅)] by treatment of [WOs₂(CO)₈(C≡CR)(η -C₅H₅)] with Me₃NO in a solution of acetonitrile and dichloromethane¹⁸ serves as a strong indication of the formation of the unsaturated [WRu₂(CO)₇(C≡CR)L]. The product would retain the spiked triangular geometry if the coupling of the acetylide ligands occurs immediately after the co-ordination of [W(CO)₃(C≡CR)(η -C₅H₅)] generating the cluster complexes **2**. However, if the CO loss from the Ru₂W metal triangle proceeds more rapidly than the acetylide coupling, formation of two additional metal–metal bonds is expected, as we obtained the tetrahedral acetylide complexes **3**. More information is required in order to define the exact structure of the proposed intermediate.

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References

- 1 D. A. Roberts and G. L. Geoffroy, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, ch. 40; W. L. Gladfelter and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1980, **18**, 207; M. I. Bruce, in *The Chemistry of Metal Clusters*, eds. D. F. Shriver, H. D. Kaesz and R. D. Adams, VCH, New York, 1990, ch. 8.
- 2 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711; F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89.
- 3 F. G. A. Stone, *ACS Symp. Ser.*, 1983, **211**, 383; S. J. Davies, J. A. K. Howard, R. J. Musgrove and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 624 and refs. therein.
- 4 Y. Chi, G.-H. Lee, S.-M. Peng and B.-J. Liu, *Polyhedron*, 1989, **8**, 2003; Y. Chi, G.-H. Lee, S.-M. Peng and C.-H. Wu, *Organometallics*, 1989, **8**, 1574; Y. Chi, D.-K. Hwang, S.-F. Chen and L.-K. Liu, *J. Chem. Soc., Chem. Commun.*, 1989, 1540; D.-K. Hwang, Y. Chi, S.-M. Peng and G.-H. Lee, *J. Organomet. Chem.*, 1990, **389**, C7.
- 5 Y. Chi, L.-K. Liu, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, 1990, **390**, C50; C.-H. Wu, Y. Chi, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Dalton Trans.*, 1990, 3025.
- 6 (a) E. Rosenberg, J. Wang and R. W. Gellert, *Organometallics*, 1988, **7**, 1093; (b) D.-K. Hwang, Y. Chi, S.-M. Peng and G.-H. Lee, *Organometallics*, 1990, **9**, 2709.
- 7 M. I. Bruce, M. G. Humphrey, J. G. Matison, S. K. Roy and A. G. Swincer, *Aust. J. Chem.*, 1984, **37**, 1955.
- 8 N. E. Kolobova, V. V. Skripkan, T. V. Rozantseva, Y. T. Struchkov, G. G. Alenksandrov and V. G. Andrianov, *J. Organomet. Chem.*, 1981, **218**, 351.
- 9 I. J. Hart, J. A. K. Howard, R. M. Lowry, T. P. Spaniol and F. G. A. Stone, *Polyhedron*, 1989, **8**, 2035.
- 10 G. A. Carriedo, J. C. Jeffery and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1594.
- 11 R. J. Mercer, M. Green and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1986, 567.
- 12 S. F. T. Froom, M. Green, R. J. Mercer, K. R. Nagle and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1986, 1666.
- 13 N. M. Doherty, C. Elschenbroich, H.-J. Kneuper and S. A. R. Knox, *J. Chem. Soc., Chem. Commun.*, 1985, 170.
- 14 F. A. Cotton, *Prog. Inorg. Chem.*, 1976, **21**, 1; R. Colton and J. M. McCormick, *Coord. Chem. Rev.*, 1980, **31**, 1; C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23**, 219.
- 15 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.
- 16 A. J. Carty, A. A. Cherkas and L. H. Randall, *Polyhedron*, 1988, **7**, 1045.
- 17 J. Evans and S. C. McNulty, *J. Chem. Soc., Dalton Trans.*, 1984, 79.
- 18 Y. Chi, G. Huttner and W. Imhof, *J. Organomet. Chem.*, 1990, **384**, 93.

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