# Preparation of Tetranuclear Heterometallic Clusters by Condensation of Tungsten Acetylides $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ with Acetylide Clusters $[WRu_2(CO)_8(C{\equiv}CR)L]$ (L = $\eta$-$C_5H_5$ or $\eta$-$C_5Me_5$, R = Ph or $C_6H_4F$-*p*). Crystal Structures of $[W_2Ru_2(CO)_9\{CC(C_6H_4F\text{-}p)CC(C_6H_4F\text{-}p)\}(\eta\text{-}C_5H_5)_2]$ and $[W_2Ru_2(CO)_6(C{\equiv}CPh)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$‡

**Der-Kweng Hwang,[a] Po-Jin Lin,[a] Yun Chi,*,[a] Shie-Ming Peng†,[b] and Gene-Hsiang Lee[b]**

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, Republic of China*

[b] *Department of Chemistry, National Taiwan University, Taipei 10764, Taiwan, Republic of China*

Reaction of trinuclear acetylide complexes $[WRu_2(CO)_8(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ with 1.5 molar equivalents $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ (R = Ph or $C_6H_4F$-*p*) in refluxing toluene produced two heterometallic cluster complexes $[W_2Ru_2(CO)_9(CCRCCR)(\eta\text{-}C_5H_5)_2]$ (R = Ph, **2a**; or $C_6H_4F$-*p*, **2b**) and $[W_2Ru_2(CO)_6(C{\equiv}CR)_2(\eta\text{-}C_5H_5)_2]$ (R = Ph, **3a**; or $C_6H_4F$-*p*, **3b**). For the analogous reaction of $[WRu_2(CO)_8(C{\equiv}CPh)(\eta\text{-}C_5Me_5)]$ and $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ only the complex $[W_2Ru_2(CO)_6(C{\equiv}CPh)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ **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 $P\bar{1}$, *a* = 10.202(3), *b* = 11.703(2), *c* = 16.600(3) Å, α = 87.97(1), β = 103.68(2), γ = 102.66(2)°, *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-workers[3] have used tungsten alkylidyne complexes $[W(CO)_2({\equiv}CR)L]$ as basic building blocks to prepare mixed-metal clusters containing alkylidyne fragments. Following a similar strategy of using tungsten acetylide complexes $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ we have successfully prepared several polynuclear cluster derivatives possessing acetylide fragments of various types[4] and co-ordinated hydrocarbon moieties derived from acetylides.[5] During our studies we have observed that the acetylide of the trinuclear mixed-metal complexes $[WRu_2(CO)_8(C{\equiv}CR)L]$ 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 $[WRu_2(CO)_8(C{\equiv}CR)L]$ (L = $\eta$-$C_5H_5$, R = Ph, **1a**; or $C_6H_4F$-*p*, **1b**; L = $\eta$-$C_5Me_5$, R = Ph, **1c**) toward acetylide complexes $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$. 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 $^{13}C$ 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 bombardment (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 $F_{254}$, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 $F_{254}$, E. Merck). The acetylide complexes $[W(CO)_3(C{\equiv}CR)L]$[7] and the acetylide cluster complexes $[WRu_2(CO)_8(C{\equiv}CR)L]$[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* $[WRu_2(CO)_8(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ *with* $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$.—A toluene solution (35 $cm^3$) of $[WRu_2(CO)_8(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (196 mg, 0.253 mmol) and $[W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (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 $[WRu_2(CO)_8(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (47 mg, 0.061 mmol, 24%), the black coupling product $[W_2Ru_2(CO)_9(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ **2a** (75 mg, 0.064 mmol, 25%), and the dark green complex $[W_2Ru_2(CO)_6(C{\equiv}CPh)_2(\eta\text{-}C_5H_5)_2]$ **3a** (45 mg, 0.042 mmol, 17%).

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

---

† To whom correspondence on the crystallographic work should be addressed.

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

δ 7.65–7.61 (m, 2 H), 7.29–7.16 (m, 7 H), 7.07 (t, 1 H), 5.68 (s, 5 H, $C_5H_5$) and 4.66 (s, 5 H, $C_5H_5$); $^{13}C$, δ 281.6 (CPhCCPh*C*, $J_{CW}$ = 178), 218.1 (WCO, $J_{CW}$ = 176), 215.3 (WCO, $J_{CW}$ = 188), 211.5 (WCO, $J_{CW}$ = 168), 211.4 (RuCO), 210.6 (WCO, $J_{CW}$ = 162), 204.0 (RuCO), 200.3 (RuCO, br), 196.2 (RuCO, br), 194.7 (RuCO, br), 161.7 (CPh*C*CPhC, $J_{CW}$ = 49), 91.2 ($C_5H_5$), 90.7 ($C_5H_5$), 89.8 (CPhC*C*PhC) and 88.3 (CPh*C*CPhC, $J_{CW}$ = 33 Hz) (Found: C, 35.30; H, 1.85. Calc. for $C_{35}H_{20}O_9Ru_2W_2$: C, 36.40; H, 1.75%).

Complex **3a**. Mass spectrum (FAB, $^{102}Ru$, $^{184}W$): *m/z* 1072 ($M^+$). IR ($CH_2Cl_2$): ν(CO) 2023s, 1996vs, 1967m and 1944w $cm^{-1}$. NMR ($CDCl_3$, 294 K): $^1H$, δ 7.70–7.67 (m, 2 H), 7.44–7.41 (m, 2 H), 7.36–7.16 (m, 6 H), 6.02 (s, 5 H, $C_5H_5$) and 5.21 (s, 5 H, $C_5H_5$); $^{13}C$, 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 $C_{32}H_{20}O_6Ru_2W_2$: C, 35.90; H, 1.90%).

*Reaction of* $[WRu_2(CO)_8(C\equiv CC_6H_4F\text{-}p)(\eta\text{-}C_5H_5)]$ *with* $[W(CO)_3(C\equiv CC_6H_4F\text{-}p)(\eta\text{-}C_5H_5)]$.—A toluene solution (35 $cm^3$) of $[WRu_2(CO)_8(C\equiv CC_6H_4F\text{-}p)(\eta\text{-}C_5H_5)]$ (32 mg, 0.04 mmol) and $[W(CO)_3(C\equiv CC_6H_4F\text{-}p)(\eta\text{-}C_5H_5)]$ (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 $[WRu_2(CO)_8(C\equiv CC_6H_4F\text{-}p)(\eta\text{-}C_5H_5)]$ (10 mg, 0.024 mmol, 32%) the black complex $[W_2Ru_2(CO)_9\{CC(C_6H_4F\text{-}p)CC(C_6H_4F\text{-}p)\}(\eta\text{-}C_5H_5)_2]$ **2b** (9.5 mg, 0.008 mmol, 20%), and the dark green complex $[W_2Ru_2(CO)_6\{C\equiv C(C_6H_4F\text{-}p)\}_2(\eta\text{-}C_5H_5)_2]$ **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, $^{102}Ru$, $^{184}W$): *m/z* 1192 ($M^+$). IR ($C_6H_{12}$): ν(CO) 2056vs, 2000vs, 1992m, 1979s, 1967m, 1940w and 1920w $cm^{-1}$. NMR ($CDCl_3$, 294 K): $^1H$, δ 7.62–7.57 (m, 2 H), 7.27–7.21 (m, 2 H), 6.93–6.85 (m, 4 H), 5.69 (s, 5 H, $C_5H_5$) and 4.67 (s, 5 H, $C_5H_5$); $^{13}C$, δ 217.9 (WCO, $J_{CW}$ = 177), 215.0 (WCO, $J_{CW}$ = 189), 211.1 (RuCO), 211.0 (WCO, $J_{CW}$ = 171), 209.9 (WCO, $J_{CW}$ = 164 Hz), 203.8 (RuCO), 200.0 (RuCO, br), 196.4 (RuCO, br), 194.4 (RuCO, br), 91.2 ($C_5H_5$) and 90.6 ($C_5H_5$) (Found: C, 34.50; H, 1.60. Calc. for $C_{35}H_{18}F_2O_9Ru_2W_2$: C, 35.25; H, 1.50%).

Complex **3b**. Mass spectrum (FAB, $^{102}Ru$, $^{184}W$): *m/z* 1108 ($M^+$). IR ($C_6H_{12}$): ν(CO) 2028s, 2004vs, 1975m and 1959w $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 294 K): δ 7.68–7.63 (m, 2 H), 7.43–7.39 (m, 2 H), 7.05–6.99 (m, 4 H), 6.01 (s, 5 H, $C_5H_5$) and 5.21 (s, 5 H, $C_5H_5$) (Found: C, 34.25; H, 1.70. Calc. for $C_{32}H_{18}F_2O_6Ru_2W_2$: C, 34.75; H, 1.65%).

*Reaction of* $[WRu_2(CO)_8(C\equiv CPh)(\eta\text{-}C_5Me_5)]$ *with* $[W(CO)_3(C\equiv CPh)(\eta\text{-}C_5H_5)]$.—A toluene solution (35 $cm^3$) of $[WRu_2(CO)_8(C\equiv CPh)(\eta\text{-}C_5Me_5)]$ (190 mg, 0.225 mmol) and $[W(CO)_3(C\equiv CPh)(\eta\text{-}C_5H_5)]$ (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 $[WRu_2(CO)_8(C\equiv CPh)(\eta\text{-}C_5Me_5)]$ (11 mg, 0.013 mmol, 6%) and the dark green coupling product $[W_2Ru_2(CO)_6(C\equiv CPh)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ **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, $^{102}Ru$, $^{184}W$): *m/z* 1142 ($M^+$). IR ($C_6H_{12}$): ν(CO) 2024s, 1999vs, 1970m and 1952w $cm^{-1}$. NMR ($CDCl_3$, 294 K): $^1H$, δ 7.66 (m, 2 H), 7.39–7.15 (m, 8 H), 5.15 (s, 5 H, $C_5H_5$) and 2.31 (s, 15 H, $C_5Me_5$); $^{13}C$, δ 308.0 (WCO, $J_{CW}$ = 131 and 52), 249.8 (WCO, $J_{CW}$ = 174 Hz), 213.2 (RuCO), 197.5 (RuCO), 196.2 (RuCO), 193.7 (RuCO), 169.8 (*C*CPh), 164.8 (*C*CPh), 108.3 ($C_5Me_5$), 96.2 ($C_5H_5$) and 12.1 ($C_5Me_5$) (Found: C, 38.80; H, 2.75. Calc. for $C_{37}H_{30}O_6Ru_2W_2$: 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.

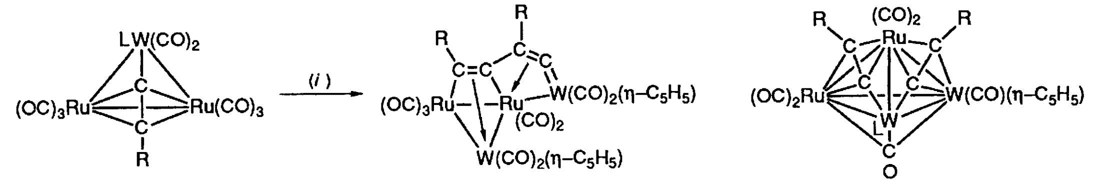
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

*Cluster Condensation Reaction with* $[W(CO)_3(C\equiv CPh)(\eta\text{-}C_5H_5)]$.—Treatment of the mixed-metal complex $[WRu_2(CO)_8(C\equiv CPh)(\eta\text{-}C_5H_5)]$ **1a** with 1.5 molar equivalents of $[W(CO)_3(C\equiv CPh)(\eta\text{-}C_5H_5)]$ in refluxing toluene for 1.5 h yielded a black condensation product $[W_2Ru_2(CO)_9(CCPhCCPh)(\eta\text{-}C_5H_5)_2]$ **2a** (25%) and a dark green derivative $[W_2Ru_2(CO)_6(C\equiv CPh)_2(\eta\text{-}C_5H_5)_2]$ **3a** (17%), in addition to about 24% unreacted starting material **1a** (Scheme 1). The analogous $W_2Ru_2$ cluster complexes $[W_2Ru_2(CO)_9\{CC(C_6H_4F\text{-}p)CC(C_6H_4F\text{-}p)\}(\eta\text{-}C_5H_5)_2]$ **2b** and $[W_2Ru_2(CO)_6\{C\equiv C(C_6H_4F)\}_2(\eta\text{-}C_5H_5)_2]$ **3b** were prepared from the reaction between the acetylide complexes $[WRu_2(CO)_8(C\equiv CC_6H_4F\text{-}p)(\eta\text{-}C_5H_5)]$ **1b** and $[W(CO)_3(C\equiv CC_6H_4F\text{-}p)(\eta\text{-}C_5H_5)]$ under similar conditions. Furthermore, when the acetylide cluster $[WRu_2(CO)_8(C\equiv CPh)(\eta\text{-}C_5Me_5)]$ was used instead we obtained only $[W_2Ru_2(CO)_6(C\equiv CPh)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ **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 $W_2Ru_2$ 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 $[W(CO)_3(C\equiv CR)(\eta\text{-}C_5H_5)]$ has attached to the trinuclear $W_2Ru$ 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 $W(CO)_2(\eta\text{-}C_5H_5)$ centres, in which the unique $Ru(CO)_2$ is further co-ordinated by a second $W(CO)_2(\eta\text{-}C_5H_5)$ unit. The intermetallic bond angles



**1a** L = η-C$_5$H$_5$, R = Ph
**1b** L = η-C$_5$H$_5$, R = C$_6$H$_4$F-*p*
**1c** L = η-C$_5$Me$_5$, R = Ph

**2a** 25%
**2b** 20%

**3a** 17%
**3b** 15%
**3c** 17%

**Scheme 1** (*i*) [W(CO)$_3$(C≡CR)(η-C$_5$H$_5$)]

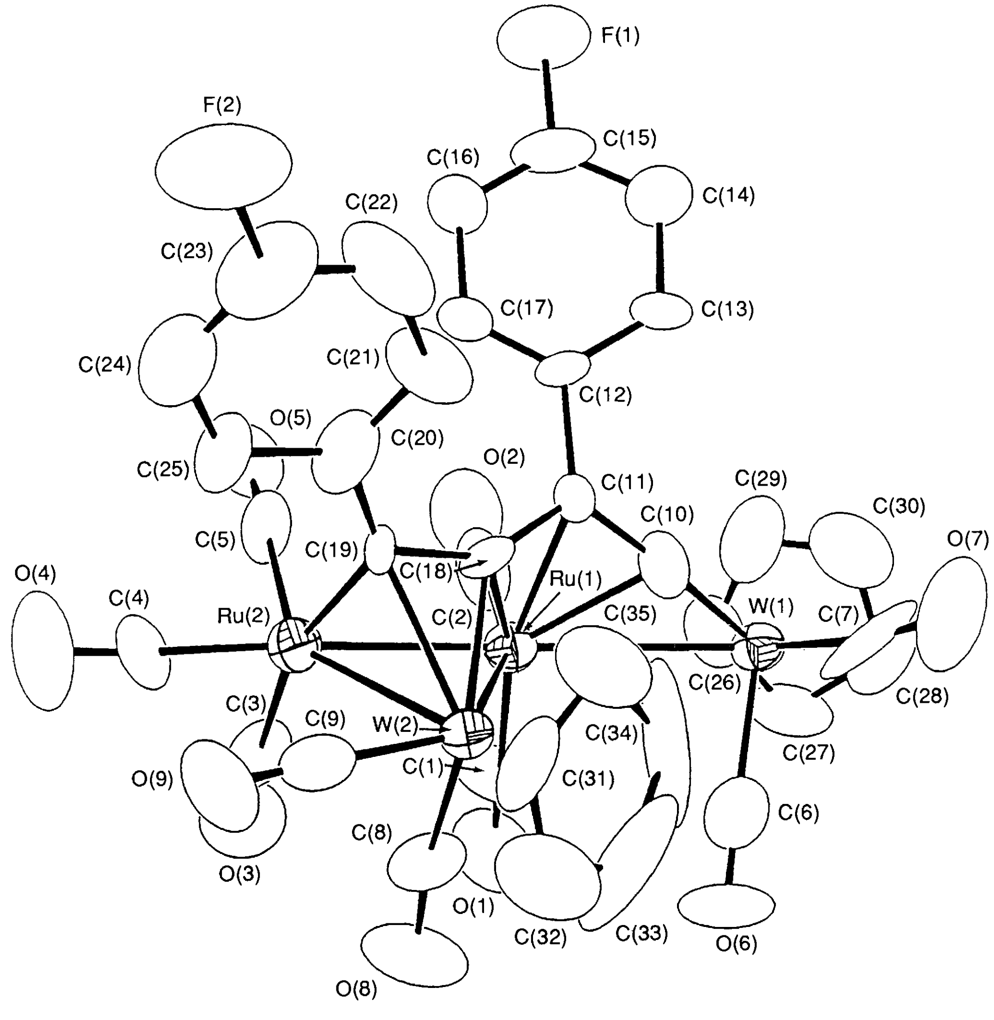


**Fig. 1** Molecular structure of [W$_2$Ru$_2$(CO)$_9${CC(C$_6$H$_4$F-*p*)CC(C$_6$H$_4$F-*p*)}(η-C$_5$H$_5$)$_2$] **2b**

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 C$_4$ hydrocarbon fragment, generated from the head-to-tail coupling of two acetylide moieties, is associated with all four transition-metal atoms. Within this C$_4$ 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(sp$^3$) distance of a dinuclear acetylide complex [W$_2$(CO)$_4$(C≡CPh)(C=CPhH)(η-C$_5$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 alkylidyne ligand in the ditungsten complexes [W$_2$(CO)$_3$Me(μ-CR)(η-C$_5$H$_5$)$_2$] (R = C$_6$H$_4$Me or C$_6$H$_4$OMe) (2.01 Å)[9] and the W=C double bond in W$_2$Re alkylidyne complexes (1.99–2.07 Å).[10] On the other hand, it is comparable with the Mo=C double bond of Mo$_2$ vinylidene [1.909(5) Å][11] and allenylidene [1.912(3) Å] complexes.[12] Therefore, the C$_4$ fragment is best visualized as a substituted vinylidene ligand,[13] in which the vinylidene C$_2$ 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 C$_4$ fragment as a substituted doubly bridging alkylidyne ligand, since the latter assignment would require this bond angle to be close to 120°. Finally, according to simple electron counting, the unsaturated C$_4$ hydrocarbon fragment

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

| Compound | **2b** | **3c** |
|---|---|---|
| Formula | $C_{35}H_{18}F_2O_9Ru_2W_2$ | $C_{37}H_{30}O_6Ru_2W_2{\cdot}CH_2Cl_2$ |
| $M$ | 1190.37 | 1140.49 |
| Crystal system | Orthorhombic | Triclinic |
| Space group | *Pbca* | $P\bar{1}$ |
| $a$/Å | 16.237(3) | 10.202(3) |
| $b$/Å | 34.006(2) | 11.703(2) |
| $c$/Å | 13.228(3) | 16.600(3) |
| $\alpha$/° |  | 87.97(1) |
| $\beta$/° |  | 103.68(2) |
| $\gamma$/° |  | 102.66(2) |
| $U$/Å$^3$ | 7304(2) | 1878.6(7) |
| $Z$ | 8 | 2 |
| $D_c$/g cm$^{-3}$ | 2.165 | 2.125 |
| $F$(000) | 4430.87 | 1155.72 |
| Crystal size/mm | 0.05 × 0.30 × 0.50 | 0.10 × 0.30 × 0.50 |
| $\lambda$/Å | 1.540 56 (Cu-K$\alpha$) | 0.709 30 (Mo-K$\alpha$) |
| Scan parameter | $1.05 + 0.30 \tan\theta$ | $0.90 + 0.35 \tan\theta$ |
| $2\theta$ (max.) | 120.0° | 49.8° |
| Scan speed/° min$^{-1}$ | 32 | 16.48/2–16.48/10 |
| $h,k,l$ range | 0–18, 0–38, 0–14 | −12 to 11, 0–13, −19 to 19 |
| $\mu$/mm$^{-1}$ | 18.77 | 7.20 |
| Transmission factor (max., min.) | 0.0313, 0.4124 | 0.4581, 0.9991 |
| Standard reflections (three) | 12% Decay 10 $\sigma$, every 150 reflections | 10% Decay every 7200 s |
| No. of unique data | 5191 | 6605 |
| Data with $I > 2\sigma(I)$ | 3968 | 4714 |
| No. of atoms and parameters refined | 68, 451 | 82, 452 |
| Maximum $\Delta/\sigma$ | 0.144 | 0.214 |
| $R$, $R'$ | 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; $\theta$–$2\theta$ scan mode, absorption correction by $\psi$ scans; $w = 1/\sigma^2(F_o)$; goodness of fit (g.o.f.) = $[\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{\frac{1}{2}}$ where $N_o$ = number of observations and $N_v$ = number of variables.

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

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru(1) | 0.193 21(10) | 0.104 66(6) | 0.993 62(15) |
| Ru(2) | 0.165 53(11) | 0.114 58(6) | 0.788 34(15) |
| W(1) | 0.177 26(6) | 0.100 32(3) | 1.222 47(8) |
| W(2) | 0.021 41(6) | 0.099 20(3) | 0.907 51(8) |
| C(1) | 0.227 7(17) | 0.053 7(7) | 0.990 5(23) |
| C(2) | 0.301 4(13) | 0.121 0(8) | 0.997 2(19) |
| C(3) | 0.225 2(16) | 0.069 0(7) | 0.763 1(21) |
| C(4) | 0.140 4(16) | 0.119 2(9) | 0.653 3(19) |
| C(5) | 0.257 8(12) | 0.146 5(8) | 0.783 1(16) |
| C(6) | 0.116 2(15) | 0.049 6(8) | 1.179 5(18) |
| C(7) | 0.082 9(15) | 0.112 4(9) | 1.287 8(23) |
| C(8) | 0.073 7(15) | 0.049 0(7) | 0.882 2(21) |
| C(9) | −0.011 5(15) | 0.098 3(7) | 0.772 7(19) |
| C(10) | 0.143 4(11) | 0.136 3(7) | 1.122 9(16) |
| C(11) | 0.134 7(13) | 0.162 7(6) | 1.038 9(15) |
| C(12) | 0.175 7(13) | 0.203 5(6) | 1.042 2(16) |
| C(13) | 0.178 2(16) | 0.221 1(6) | 1.133 6(18) |
| C(14) | 0.217 7(20) | 0.257 6(9) | 1.145 7(21) |
| C(15) | 0.243 0(19) | 0.273 1(7) | 1.056 0(21) |
| C(16) | 0.242 6(16) | 0.256 3(8) | 0.965 8(18) |
| C(17) | 0.200 9(15) | 0.220 1(7) | 0.959 8(17) |
| C(18) | 0.102 1(13) | 0.147 9(6) | 0.949 8(16) |
| C(19) | 0.080 9(13) | 0.155 3(6) | 0.850 0(16) |
| C(20) | 0.033 5(13) | 0.192 8(8) | 0.813 5(18) |
| C(21) | 0.008 9(17) | 0.220 6(7) | 0.880 0(20) |
| C(22) | −0.030 2(19) | 0.253 6(9) | 0.840 0(22) |
| C(23) | −0.044 5(15) | 0.255 6(9) | 0.741 6(23) |
| C(24) | −0.018 5(18) | 0.228 4(8) | 0.673 4(20) |
| C(25) | 0.015 7(16) | 0.196 4(8) | 0.711 3(17) |
| C(26) | 0.318 8(15) | 0.088 9(8) | 1.232 1(19) |
| C(27) | 0.282 4(15) | 0.061 1(7) | 1.295 1(20) |
| C(28) | 0.245 1(15) | 0.084 8(9) | 1.370 9(18) |
| C(29) | 0.303 0(14) | 0.125 4(9) | 1.264 8(21) |
| C(30) | 0.258 9(16) | 0.123 6(9) | 1.345 8(24) |
| C(31) | −0.115 3(16) | 0.107 9(9) | 0.922 9(19) |
| C(32) | −0.100 9(15) | 0.069 0(11) | 0.943(3) |
| C(33) | −0.055 7(16) | 0.063 8(12) | 1.024(3) |
| C(34) | −0.039 4(15) | 0.099 2(15) | 1.061 9(19) |
| C(35) | −0.082 7(18) | 0.131 7(10) | 0.997(3) |
| F(1) | 0.281 6(13) | 0.310 1(5) | 1.060 1(14) |
| F(2) | −0.087 2(12) | 0.288 3(5) | 0.704 8(15) |
| O(1) | 0.250 1(14) | 0.021 8(6) | 0.988 3(15) |
| O(2) | 0.367 4(10) | 0.135 0(7) | 0.998 6(15) |
| O(3) | 0.261 9(13) | 0.040 3(6) | 0.751 7(17) |
| O(4) | 0.127 8(12) | 0.123 8(8) | 0.567 3(14) |
| O(5) | 0.315 5(9) | 0.165 3(6) | 0.777 4(13) |
| O(6) | 0.086 5(12) | 0.021 2(5) | 1.159 3(16) |
| O(7) | 0.019 8(11) | 0.127 5(7) | 1.334 8(14) |
| O(8) | 0.088 4(10) | 0.013 6(5) | 0.872 3(16) |
| 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 $W_2Ru_2$ 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 $\eta$-$C_5Me_5$ ligand and a triply bridging CO ligand with W(1)–C(1)–O(1) 142.2(9)°, whereas W(2) is linked with a $\eta$-$C_5H_5$ and a semibridging CO ligand[14] 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) | | |
| $C_4$ 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-$C_5H_5$ and η-$C_5Me_5$ 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 $W_2Ru_2$ 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 1σ + 2π 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* $^{13}C$ *NMR Data.*—The assignment of the $^{13}C$ 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] $^{13}CO$ 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 $^{13}C$ NMR spectrum of a $^{13}CO$-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

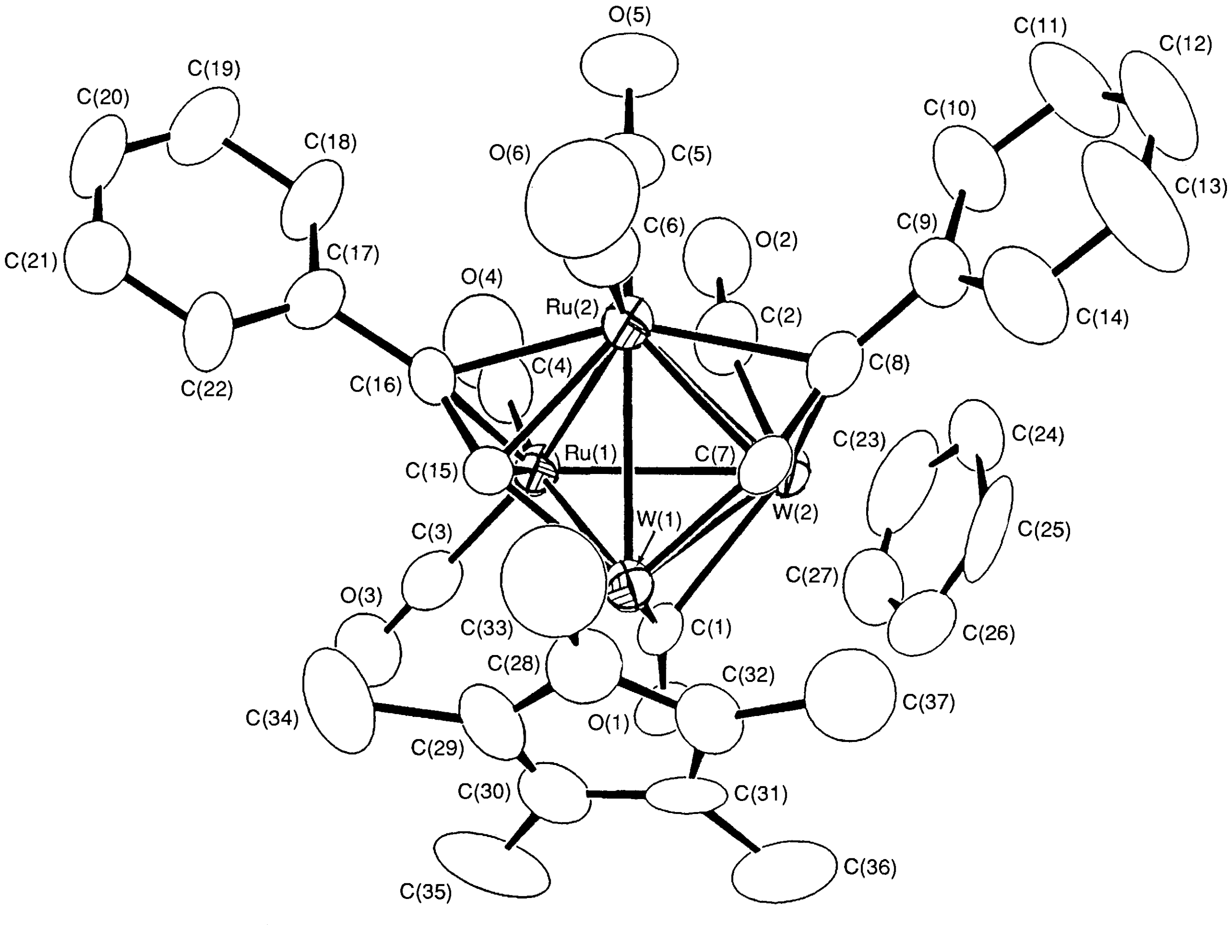


**Fig. 2** Molecular structure of $[W_2Ru_2(CO)_6(C{\equiv}CPh)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ **3c**

**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 $^{13}C$ NMR spectrum of a regular sample of **2a** shows four signals of the $C_4$ 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-$C_5H_5$ 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 $^{13}C$ 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 $^{13}C$ 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 $[WRu_2(CO)_8(C{\equiv}CR)L]$ with mononuclear metal acetylides $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ 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 $[WRu_2(CO)_7(C{\equiv}CR)L]$ followed by co-ordination of the tungsten acetylide $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ giving an intermediate possessing a spiked triangular $Ru_2W_2$ core. The isolation and characterization of the analogous $Os_2W$ acetylide complexes $[WOs_2(CO)_7(NCMe)(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ by treatment of $[WOs_2(CO)_8(C{\equiv}CR)(\eta\text{-}C_5H_5)]$ with $Me_3NO$ in a solution of acetonitrile and dichloromethane[18] serves as a strong indication of the formation of the unsaturated $[WRu_2(CO)_7(C{\equiv}CR)L]$. The product would retain the spiked triangular geometry if the coupling of the acetylide ligands occurs immediately after the co-ordination of $[W(CO)_3(C{\equiv}CR)(\eta\text{-}C_5H_5)]$, generating the cluster complexes **2**. However, if the CO loss from the $Ru_2W$ 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.

## Acknowledgements

We are grateful to the National Science Council of the Republic of China for financial support (Grant no. NSC80-0208-M007-60).

## 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. Matisons, 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.

*Received 27th December* 1990; *Paper* 0/05794K