Reactions of the Mixed-metal Clusters Prepared from Tungsten Acetylide Complexes; X-Ray Structural Analyses of Two Novel Butterfly Clusters with 60 Valence Electrons

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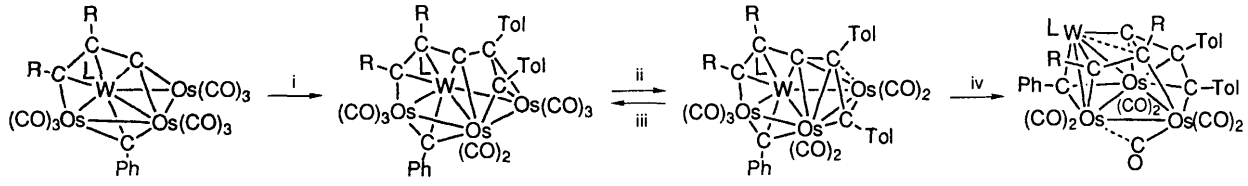
Reaction of $WL(CO)_3C{\equiv}CPh$ and $Os_3(CO)_{10}(C_2R_2)$ produced $WOs_3L(CO)_9(\mu_3\text{-}CPh)(CCRCR)$, L = Cp, R = Tol (*p*-$MeC_6H_4$) **1a**; L = C_5Me_5, R = Me, **1b**; treatment of complexes **1** with ditolylacetylene yielded planar clusters $WOs_3L(CO)_8(\mu_3\text{-}CPh)$[C(Tol)C(Tol)CCRCR], L = Cp, R = Tol, **2a**; L = C_5Me_5, R = Me, **2b**; complex **2b** underwent reversible loss of CO to produce an unsaturated cluster $WOs_3C_5Me_5(CO)_7(\mu_3\text{-}CPh)$[CMeCMeCC(Tol)C(Tol)] **3b**; thermolysis of **3b** in refluxing xylene induced the rearrangement of the cluster core, giving another unsaturated complex **4b** with identical molecular formula; complexes **1a**, **3b** and **4b** have been examined by X-ray diffraction studies.

We have recently devised syntheses of several polynuclear cluster complexes from reactions of group 6 mononuclear metal acetylide and hydride complexes with group 8 cluster complexes, such as $Os_3(CO)_{10}(NCMe)_2$, $Ru_3(CO)_{12}$, $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ and $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}COMe)$, and examined the crystal structures and reactivities of the new heterometallic clusters prepared.[1] We report here the preparation of Os_3W clusters $WOs_3L(CO)_9(\mu_3\text{-}CPh)(CCRCR)$, L = Cp, R = Tol(*p*-$MeC_6H_4$), **1a**; L = C_5Me_5, R = Me, **1b** *via*

† For crystallographic enquiries.



1 a R = Tol, L = Cp
b R = Me, L = C_5Me_5

2 a R = Tol, L = Cp
b R = Me, L = C_5Me_5

3b R = Me, L = C_5Me_5

4b R = Me, L = C_5Me_5

Scheme 1 i, excess C_2Tol_2; ii, −CO, 140 °C, 20 min; iii, +CO, 110 °C, 5 min; iv, 140 °C, 65 min

cleavage of the acetylide C–C triple-bond and some results of the subsequent reactivity studies. The reaction of **1b** with ditolylacetylene coupled the alkyne to the coordinated C_3 hydrocarbon, giving one saturated cluster compound with a multi-site bound C_5 ligand. On heating this compound loses a CO ligand, yielding two novel, 60-electron, coordinatively unsaturated cluster compounds, sequentially.[2] Our study reported in this paper highlights the role and action of the accessory ligands in responding to the creation of coordination unsaturation.

Treatment of tungsten acetylide $WCp(CO)_3C{\equiv}CPh$[3] with the triosmium alkyne complex $Os_3(CO)_{10}(C_2Tol_2)$[4] in refluxing toluene (110 °C, 30 min) yielded a novel heterometallic cluster (**1a**, 20%), while the analogous derivative (**1b**, 9%) was prepared from the reaction between $WC_5Me_5(CO)_3C{\equiv}CPh$ and $Os_3(CO)_{10}(C_2Me_2)$[5] under similar conditions (Scheme 1). Both complexes **1a** and **b** were initially characterized by mass, IR and NMR spectroscopy;‡ in addition, complex **1a** was examined by X-ray diffraction in an attempt to establish the exact molecular structure.§ The ORTEP diagram and some bond parameters are presented in Fig. 1. Consistent with its molecular structure, we deduce that the formation of these Os_3W clusters involves two unique processes. One is the scission of the acetylide carbon–carbon triple-bond and the other is the coupling of the acetylide α-carbon with the coordinated alkyne ligand, producing the observed alkylidyne and C_3 hydrocarbon ligands, respectively.

Reactions with disubstituted alkyne have also been examined. The reaction of **1a** with excess ditolylacetylene in toluene (110 °C, 50 h) led to the isolation of a dark green complex (**2a**, 53%)[6] and unreacted starting material **1a** (35%). On the other hand, reaction of the analogous compound **1b** with ditolylacetylene in refluxing xylene solvent (140 °C, 30 min) produced three cluster compounds **2b** (yellowish green), **3b** (red-brown) and **4b** (brown) in 14, 41 and 22% yields, respectively, in addition to about 8% starting material **1b** (Scheme 1). These cluster compounds were separated by TLC and purified by recrystallization, although we have observed that the silica gel tends to accelerate the decomposition of **3b** and **4b**. The structure of **2b** is closely related to **2a** as indicated by its spectral data, whereas the FAB mass and ^{13}C NMR data suggest that both **3b** and **4b** possess one carbonyl ligand less than that of complex **2b**.¶

Red-brown, air-stable, plate-shaped crystals of **3b** were obtained from a solution of CH_2Cl_2–heptane at room temperature and an X-ray diffraction study was carried out.** An ORTEP diagram is shown in Fig. 2, which also provides selected bond distances. The molecule contains a planar triangulated rhomboidal arrangement with W and Os(2) atoms at the bridgehead position, the dihedral angle between the W–Os(2)–Os(1) and W–Os(2)–Os(3) planes being 171.8(1)°. There is an alkylidyne ligand (μ_3-CPh) which is associated with the face defined by atoms Os(2), Os(3) and W and, on the opposite side of the alkylidyne ligand, is a C_5 hydrocarbon ligand which is coordinated to all four metal atoms. The central carbon atom C(12) is linked to three metal

‡ *Spectral data* for **1a**: MS (FAB, ^{192}Os, ^{184}W) *m/z* 1384(M^+); IR(C_6H_{12}) ν(CO)/cm^{-1} 2077s, 2048vs, 2036m, 2018s, 1997vw, 1974m, 1969m and 1909w; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.24–6.75 (m, 13H), 5.49 (s, 5H), 2.33 (s, 3H) and 2.19 (s, 3H). For **1b**: MS (FAB, ^{184}W, ^{192}Os), *m/z* 1302(M^+). IR(C_6H_{12}) ν(CO)/cm^{-1} 2072s, 2040vs, 2032m, 2012s, 1991vw, 1970m, 1952s and 1912br, w; ^1H NMR (400 MHz, CD_2Cl_2, 294 K) δ 7.09 (t, 2H, J_{H-H} 6.8 Hz), 6.70 (t, 1H, J_{H-H} 7.2 Hz), 6.91 (d, 1H, J_{H-H} 7.4 Hz), 6.84 (d, 1H, J_{H-H} 7.8 Hz), 3.21 (s, 3H), 2.07 (s, 3H) and 1.80 (s, 15H); ^{13}C NMR (100 MHz, CD_2Cl_2, 294 K), δ 187.8, 185.6, 181.3, 180.2, 177.2, 176.2 (3C), 172.7 and 239.5 (J_{W-C} 111 Hz, μ_3-CPh). Satisfactory elemental analyses were obtained for both **1a** and **b**.

§ *Crystal data* for **1a**: $C_{38}H_{24}O_9Os_3W_1$, M=1379.05, monoclinic, space group $P2_1/n$, a = 19.440(7), b = 9.655(2), c = 19.976(6) Å, β = 105.85(3)°, V = 3607(2) Å^3, Z = 4, D_c = 2.540 g cm^{-3}, F(000) = 2503, Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation, λ = 0.70930 Å, μ(Mo-Kα) = 13.85 mm^{-1}. The min. and max. transmission factors are 0.416 and 0.997, 6342 unique reflections were measured, and 4603 reflections with $I > 2.0\ \sigma(I)$ were used in refinement. Refinement of 75 atoms and 461 parameters converged to R_f = 0.037 and R_w = 0.032, goodness of fit (GOF) = 1.89. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre for **1a**, **3b** and **4b**. See Notice to Authors, Issue No. 1.

¶ *Spectral data* for **2b**: MS (FAB, ^{184}W, ^{192}Os), *m/z* 1480(M^+). IR(C_6H_{12}) ν(CO)/cm^{-1} 2066s, 2029vs, 2008s, 1992m, 1964m, 1959s, 1950m and 1943w; ^1H NMR (400 MHz, CD_2Cl_2, 250 K) δ 7.74 (d, 1H, J_{H-H} 8.2 Hz), 7.20–7.09 (m, 5H), 6.99 (t, 1H, J_{H-H} 7 Hz), 6.86–6.77 (m, 6H), 3.40 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H), 1.80 (s, 15H) and 1.37 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K): δ 189.8, 187.7, 182.3 (3C, br), 180.9, 178.6, 173.9 and 247.2 (J_{W-C} 118 Hz, μ_3-CPh). For **3b**: MS (FAB, ^{184}W, ^{192}Os), *m/z* 1452(M^+). IR(C_6H_{12}) ν(CO)/cm^{-1} 2064s, 2004vs, 1959s, 1940s and 1878m; ^1H NMR (400 MHz, CD_2Cl_2, 294 K) δ 7.22 (d, 2H, J_{H-H} 8 Hz), 7.12 (m, 2H), 7.03 (d, 2H, J_{H-H} 8 Hz), 7.01–6.95 (m, 5H), 6.67 (d, 2H, J_{H-H} 8 Hz), 3.15 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H), 1.87 (s, 15H) and 1.23 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 250 K) δ 209.2, 189.3, 189.2, 186.1, 181.3, 178.4, 171.9 (CO) and 257.0 (J_{W-C} 113 Hz, μ_3-CPh). For **4b**: MS (FAB, ^{184}W, ^{192}Os), *m/z* 1452(M^+). IR(C_6H_{12}) ν(CO)/cm^{-1} 2066s, 2029vs, 2008s, 1992m, 1964m, 1959s, 1950m and 1943w; ^1H NMR (400 MHz, CD_2Cl_2, 294 K) δ 7.37 (d, 2H, J_{H-H} 7.7 Hz), 7.27 (t, 2H, J_{H-H} 7.7 Hz), 7.14 (d, 2H, J_{H-H} 8.0 Hz), 7.02–6.91 (m, 7H), 3.27 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.09 (s, 3H) and 1.61 (s, 15H); satisfactory elemental analyses were obtained for compounds **2b**, **3b** and **4b**.

** *Crystal data* for **3b**: $C_{45}H_{40}O_7Os_3W_1$, M = 1447.26, monoclinic, space group $P2_1/n$, a = 14.532(2), b = 18.485(2), c = 15.654(2) Å, β = 91.52(1)°, V = 4203(1) Å^3, Z = 4, D_c = 2.287 g cm^{-3}, F(000) = 2671, μ(Mo-Kα) = 11.88 mm^{-1}. The min. and max. transmission factors are 0.396 and 0.999, 5482 unique reflections were measured, and 3523 reflections with $I > 2.0\ \sigma(I)$ were used in refinement. Refinement of 96 atoms and 501 parameters converged to R_f = 0.040 and R_w = 0.036, GOF = 1.81.

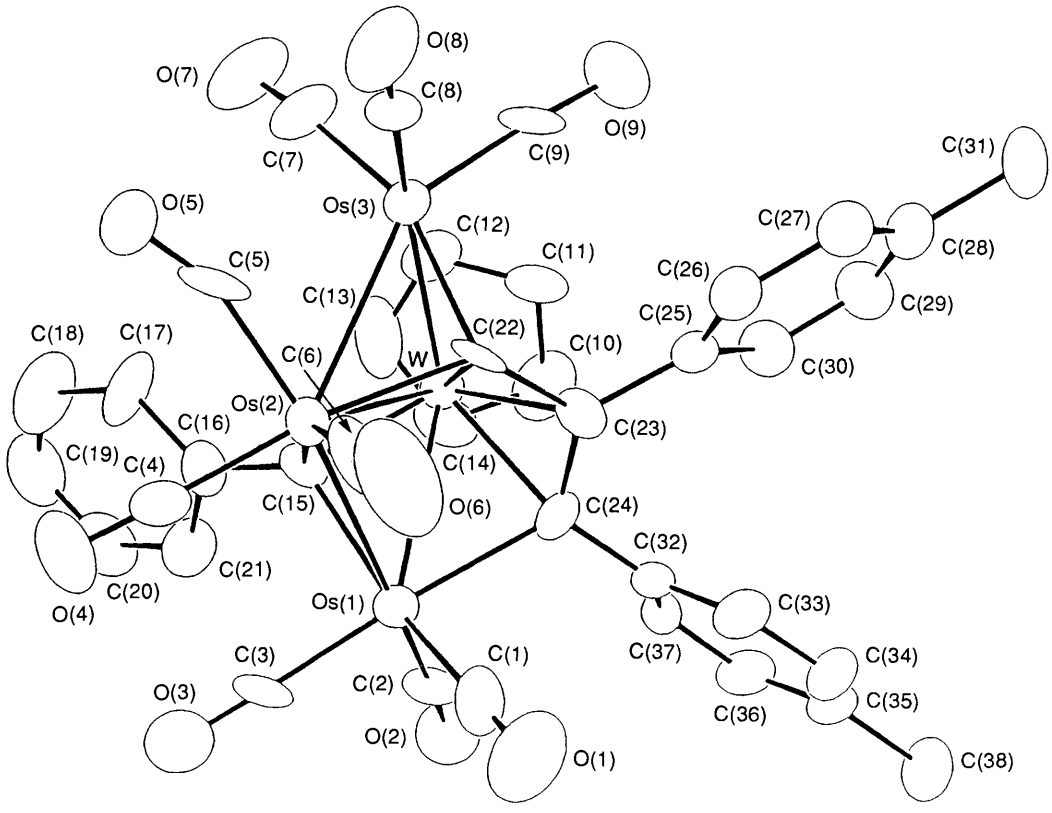


Fig. 1 The molecular drawing of **1a**. Bond lengths (Å): Os(1)–Os(2) 2.769(1), Os(1)–W 2.830(1), Os(2)–W 2.849(1), Os(3)–W 2.857(1), Os(2)–Os(3) 2.818(1), Os(1)–C(15) 2.16(1), Os(2)–C(15) 2.23(1), W–C(15) 1.96(1), Os(2)–C(22) 2.11(1), Os(3)–C(22) 1.97(1), W–C(22) 2.15(1), W–C(23) 2.29(1), Os(1)–C(24) 2.18(1), W–C(24) 2.21(1), C(22)–C(23) 1.44(2) and C(23)–C(24) 1.48(2). Dihedral angle between the planes Os(1)–Os(2)–W and Os(2)–Os(3)–W 162.1(1)°.

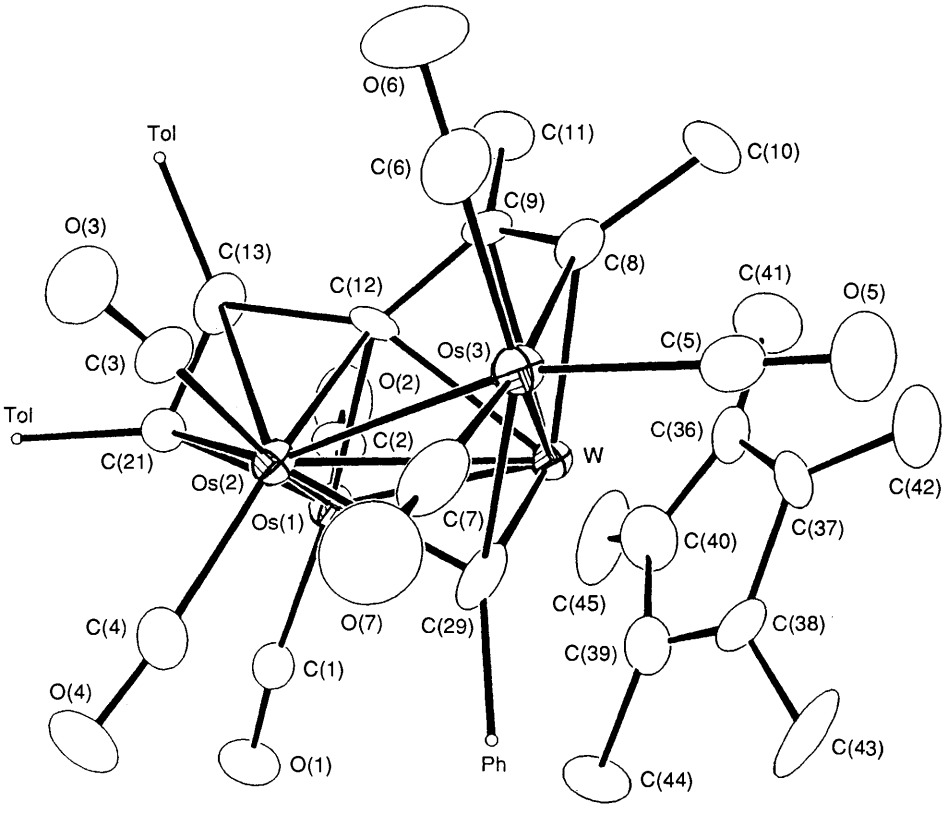


Fig. 2 The molecular drawing of **3b**. Bond lengths (Å): Os(1)–Os(2) 2.803(1), Os(1)–W 2.681(1), Os(2)–W 2.887(1), Os(3)–W 2.873(1), Os(2)–Os(3) 2.770(1), Os(2)–C(29) 2.19(2), Os(3)–C(29) 2.15(2), W–C(29) 2.04(2), Os(3)–C(8) 2.24(2), W–C(8) 2.27(2), W–C(9) 2.36(2), W–C(12) 2.19(2), Os(1)–C(12) 2.28(2), Os(2)–C(12) 2.17(2), Os(2)–C(13) 2.30(2), Os(1)–C(13) 2.56(2), Os(1)–C(21) 2.03(2), Os(2)–C(21) 2.14(2), C(8)–C(9) 1.32(3), C(9)–C(12) 1.44(2), C(12)–C(13) 1.54(3) and C(13)–C(21) 1.39(3). Dihedral angle between the planes Os(1)–Os(2)–W and Os(2)–Os(3)–W 171.8(1)°.

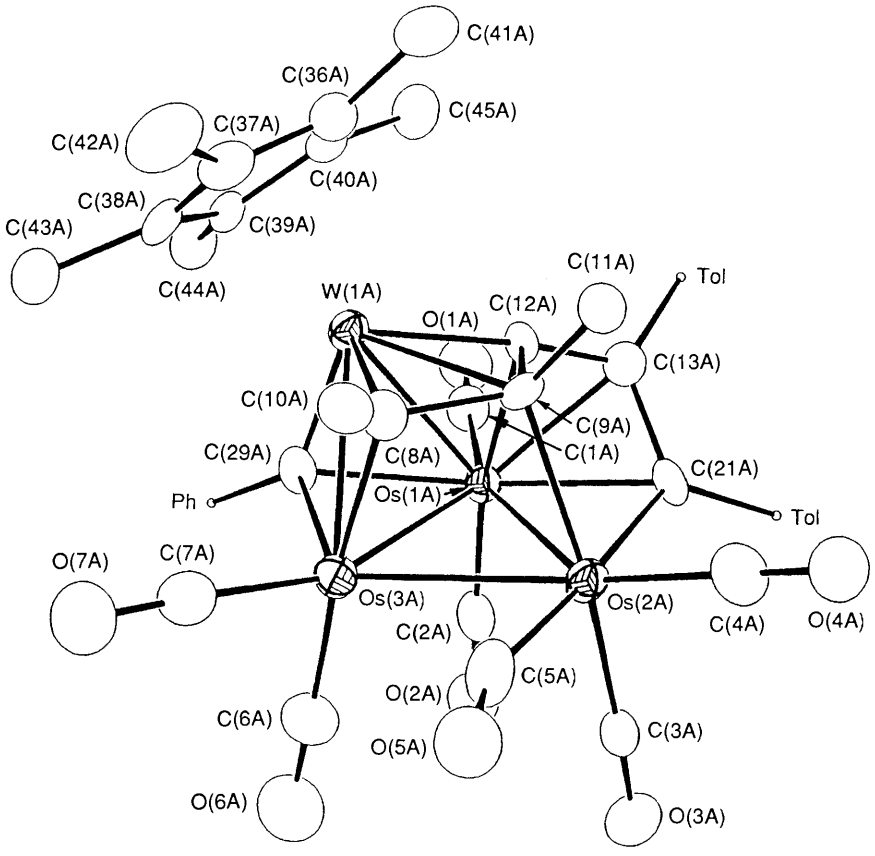


Fig. 3 The molecular drawing of **4b**. Bond lengths (Å): Os(1A)–Os(2A) 2.771(2), Os(1A)–Os(3A) 2.803(2), Os(1A)–W(1A) 2.791(2), Os(2A)–Os(3A) 2.723(2), Os(3A)–W(1A) 2.794(2), Os(1A)–C(29A) 2.18(2), Os(3A)–C(29A) 2.04(2), W(1A)–C(29A) 2.03(2), Os(3A)–C(8A) 2.19(2), W(1A)–C(8A) 2.02(2), Os(2A)–C(9A) 2.24(2), W(1A)–C(9A) 2.40(2), Os(1A)–C(12A) 2.17(2), W(1A)–C(12A) 1.94(2), Os(1A)–C(13A) 2.22(2), Os(2A)–C(21A) 2.14(2), Os(1A)–C(21A) 2.25(2), C(8A)–C(9A) 1.54(3), C(9A)–C(12A) 1.57(3), C(12A)–C(13A) 1.44(3), C(13A)–C(21A) 1.49(3), Os(2A)–C(5A) 1.92(3) and Os(3A)–C(5A) 2.48(3). Dihedral angle between the planes Os(1A)–Os(2A)–Os(3A) and Os(1A)–Os(3A)–W(1A) 108.9(1)°.

atoms W, Os(1) and Os(2), and two C_2 alkyne fragments. The C(9)–C(8) fragment is linked to the Os(3) atom *via* a σ-bonding and to the W atom *via* a π-bonding, whereas the C(13)–C(21) fragment is coordinated to Os(1) atom and the Os(2) atom *via* a σ-bonding and a π-bonding.

Basically, the core arrangement of **3b** is similar to that of the structurally characterized **2a**, except that the 'wing-tip' metal atom Os(1) in this case carries two CO ligands and that the W–Os(1) bond [2.681(1)Å] is much shorter than the respective W–Os distance of **2a** [3.004(1)Å].[6] Moreover, the conformation of the C(13)-C(21) fragment, with respect to the Os(1)–Os(2)–C(12) triangle, is reminiscent of the unusual μ_3 (η^2-⊥) alkyne arrangement observed in the unsaturated, 46-electron trinuclear alkyne complexes,[7] such as $Fe_3(CO)_9(C_2Ph_2)$[8] and $Cp_2W_2Fe(CO)_6(C_2Tol_2)$.[9] It is possible that the electron-donating ability of the C_5Me_5 ligand, the perpendicular arrangement of the alkyne fragment and the potential multiple-bonding character of the W–Os(1) bond contribute substantially to the remarkable stability of **3b**.

Crystals of **4b** suitable for X-ray diffraction study were obtained from a solution of CCl_4–heptane. According to the X-ray analysis,†† the unit cell contains two crystallographically distinct, but structurally similar molecules. An ORTEP diagram of one of these molecules is shown in Fig. 3. This molecule displays a 'butterfly' arrangement with Os(2A) and W(1A) defining the 'wing-tip' positions and with Os(1A) and Os(3A) atoms occupying the 'hinge' positions. The alkylidyne ligand is located at the exterior of the Os(1A)–Os(3A)–W(1A) surface, and the C_5 hydrocarbon ligand now adopts an S-shaped arrangement and is encapsulated in the interior of the butterfly core arrangement. Again, the C(8A)–C(9A) alkyne fragment of the coordinated C_5 ligand may also exhibit the uncommon μ_3 (η^2-⊥) bonding character.

After completion of the structural assignment, the relationship between complexes **2**, **3b** and **4b** can be readily understood and established. Thermolysis of **2a** in xylene solution (140 °C, 60 min) is fraught with much decomposition. However, thermolysis of its C_5Me_5 analogue **2b** under similar conditions (140 °C, 20 min) induced elimination of CO to produce **3b** in 85% yield; as expected, exposure of the toluene solution of **3b** to CO (1 atm, 110 °C, 5 min) regenerated **2b** in nearly quantitative yield. Further heating of **3b** in xylenes (65 min) led to **4b** in 25% yield, in addition to 48% unreacted **3b**. In contrast, carbonylation of **4b** in refluxing toluene (1 atm, 110 °C, 45 min) failed to produce its saturated, 62-electron precursor **2b**, but gave instead two additional cluster complexes. This result is clearly due to the fact that the metal skeleton has encountered extensive, irreversible rearrangement during the formation of **4b**.

We thank the National Science Council of the Republic of China for financial support of this research (Grant No. NSC80-0208-M007-60).

Received, 19th February 1991; Com. 1/00795E

†† *Crystal data* for **4b**: $C_{45}H_{40}O_7Os_3W_1$, M = 1447.26, monoclinic, space group $P\bar{1}$, a = 11.179(5), b = 17.689(4), c = 24.41(2) Å, α = 99.36(5), β = 96.92(5), γ = 88.75(3)°, V = 4728(5) Å^3, Z = 4, D_c = 2.033 g cm^{-3}, F(000) = 2671, μ(Mo-Kα) = 10.57 mm^{-1}. The min. and max. transmission factors are 0.478 and 1.000, 12326 unique reflections were measured, and 8668 reflections with $I > 2.0\,\sigma(I)$ were used in refinement. Refinement of 192 atoms and 940 parameters converged to R_f = 0.048 and R_w = 0.057, GOF = 3.68.

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