Studies of the Synthesis, Structure, and Reactivity of a Tetranuclear Mixed-metal Imido Cluster, $(\eta^5\text{-}C_5H_5)WRu_3(CO)_9(\mu\text{-}NPh)(C{\equiv}CPh)$

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The title complex $(\eta^5\text{-}C_5H_5)WRu_3(CO)_9(\mu\text{-}NPh)(C{\equiv}CPh)$, containing a bridging imido ligand and a $\mu_4\text{-}\eta^2$-acetylide ligand, has been prepared by means of the condensation between $(\eta^5\text{-}C_5H_5)W(CO)_3C{\equiv}CPh$ and $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$, and its reactions with dihydrogen and disubstituted alkyne ligands are presented; the products have been fully characterized by spectroscopic methods and *X*-ray diffraction studies for two complexes.

The reactivity of mixed-metal clusters has been of interest for many years.[1] Research in this area is stimulated by a belief that the combination of metals having very different chemical properties within one compound may induce unique chemical transformations. In seeking to exploit the chemistry of the unsaturated hydrocarbyl ligand of polynuclear mixed-metal complexes we have treated the mononuclear acetylide complex $(cp)W(CO)_3C{\equiv}CR$ (cp = η^5-cyclopentadienyl) with $Os_3(CO)_{10}(MeCN)_2$ and $Ru_3(CO)_{12}$, with the goal of generating acetylide complexes of higher nuclearity.[2] However, the reactions with $Ru_3(CO)_{12}$ have produced only the trinuclear acetylide complexes, $(cp)WRu_2(CO)_8(C{\equiv}CR)$.[3] In order to overcome the problem of cluster fragmentation we decided to use the imido complex $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ (**1**) as the source of the triruthenium fragment, since the μ_3-NPh imido ligand may function as a 'protecting group' that can hold together the metal atoms.[4] Furthermore, because the chemistry of complex (**1**) with alkynes has been well documented,[5] it provides an opportunity, from the viewpoint of organometallic synthesis, to compare the chemical reactivity of the organic acetylides, $RC{\equiv}CR'$, with that of the analogous organometallic acetylide, $L_nMC{\equiv}CR$.

Treatment of $(cp)W(CO)_3C{\equiv}CPh$[6] with the triruthenium imido complex (**1**) in refluxing toluene (110 °C; 30 min) yielded a novel mixed-metal cluster, $(cp)WRu_3(CO)_9(\mu\text{-}NPh)(C{\equiv}CPh)$ (**2**), in 84% yield (Scheme 1). Complex (**2**) was separated on silica gel t.l.c. plates, and was characterized

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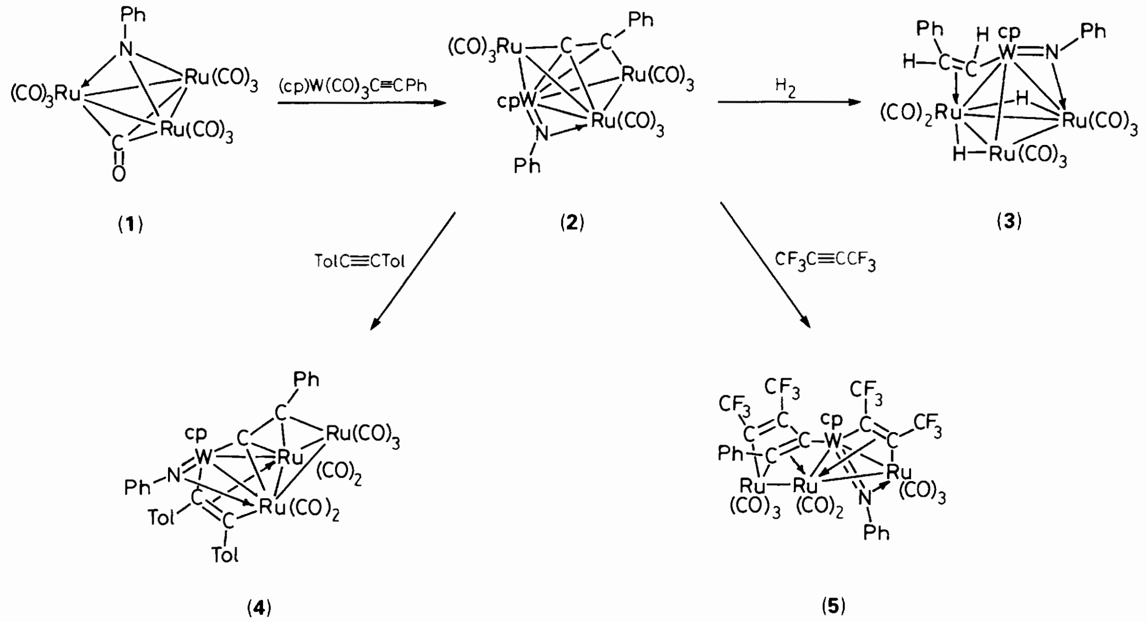
† For enquiries on the *X*-ray crystallography.



Tol = p-MeC$_6$H$_4$

Scheme 1

spectroscopically.‡ I.r. studies indicated the presence of only terminal CO ligands and the ^{13}C n.m.r. spectrum showed two signals at δ 232.4 and 194.6, assigned to the α- and β-carbons of the acetylide ligand, characteristic of a μ_4-η^2-bonding mode.[7]

Dark-red, air-stable, brick-shaped crystals of (**2**) were obtained from a layered CH$_2$Cl$_2$/hexane solution at −15 °C and an X-ray single-crystal diffraction study was carried out (Figure 1).§ The molecule consists of a WRu$_3$ core structure of a 'butterfly' arrangement, with Ru(2) and Ru(3) defining the 'wing-tip' positions and W and Ru(1) the 'hinge' positions. Each ruthenium atom is associated with three CO ligands and the tungsten atom is capped by a cp ligand. The acetylide ligand occupies the open face of the butterfly framework, and is co-ordinated in multi-site fashion with its α-carbon C(10) atom bound to three metal atoms W, Ru(1) and Ru(2), and the β-carbon atom C(11) linked to W and Ru(3) atoms; the Ru(2)–C(10)–C(11) angle is *ca.* 167°. This acetylide is, therefore, confirmed to adopt the μ_4-η^2 bonding mode similar to that observed in the butterfly cluster (cp)WOs$_3$(CO)$_{11}$(C≡CPh).[2]

The imido ligand (NPh) of this molecule is bridged, unsymmetrically, across the 'hinge' W–Ru(1) bond. The W–N

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‡ *Selected spectroscopic data*: complex (**2**): m/z (fast atom bombardment, f.a.b.; ^{102}Ru, ^{184}W), 999 (M^+); i.r. (C$_6$H$_{12}$) ν(CO) 2071s, 2039vs, 2032s, 2012s, 1977s, br., 1956m cm^{-1}; ^{1}H n.m.r. (CDCl$_3$; room temp.): δ 8.12 (d, 2H), 7.48 (t, 2H), 7.40 (t, 1H), 7.19 (m, 3H), 7.13 (m, 2H), 5.22 (s, 5H); ^{13}C{^{1}H} n.m.r. (CDCl$_3$; room temp.) δ 232.4 ($^1J_{\text{W-C}}$ 26 Hz, CCPh), 194.6 (CCPh), 163.9 ($^2J_{\text{W-C}}$ 24 Hz, 1C), 145.1 (1C), 129.4 (1C), 129.1 (2C), 128.7 (2C), 127.8 (2C), 125.8 (1C), 119.5 (2C), 96.2 (Cp).

Complex (**3**): m/z (f.a.b.; ^{102}Ru, ^{186}W), 974 (M^+); i.r. (C$_6$H$_{12}$) ν(CO) 2075s, 2037vs, 2021vs, 2010w, 1998m, 1981m, 1971vw, 1954vw cm^{-1}; ^{1}H n.m.r. (CDCl$_3$; room temp.): δ 7.98 (d, $J_{\text{H-H}}$ 12 Hz, 1H, CHCHPh), 7.31—6.69 (m, 10H, 2Ph), 5.87 (s, 5H, Cp), 4.92 (d, $J_{\text{H-H}}$ 12 Hz, 1H, CHCHPh), −11.64 (s, 1H) −18.78 (s, 1H); ^{13}C{^{1}H} n.m.r. (CDCl$_3$; room temp.): δ 203.3, 201.8, 198.6, 195.4, 194.0, 193.7, 192.8 (Ru–CO), 171.7 ($^1J_{\text{W-C}}$ 113 Hz, CHCHPh), 164.6 ($^2J_{\text{W-C}}$ 22 Hz, 1C), 147.6(1C), 129.1 (2C), 128.8 (2C), 125.9 (2C), 125.7 (2C), 122.4 (2C), 97.2 (cp), 77.0 (CHCHPh).

Complex (**4**): m/z (f.a.b.; ^{102}Ru, ^{184}W), 1121 (M^+ − CO); i.r. (CCl$_4$) ν(CO) 2069m,sh, 2065s, 2001s,br, 1992s, 1974vw, 1946w cm^{-1}; ^{1}H n.m.r. (CDCl$_3$; room temp.): δ 7.64 (d, 2H), 7.47 (t, 2H), 7.33 (t, 1H), 7.26 (d, 2H), 7.15 (d, 2H), 7.05 (t, 1H), 6.92 (d, 2H), 6.85 (d, 2H), 6.78 (d, 2H), 6.74 (d, 2H), 5.92 (s, 5H), 2.25 (s, 3H), 2.12 (s, 3H).

Complex (**5**): m/z (f.a.b.; ^{102}Ru, ^{186}W), 1239 (M^+ − 2CO); i.r. (C$_6$H$_{12}$) ν(CO) 2099s, 2088vs, 2042vs, 2032m, 2024m, 2017w cm^{-1}; ^{1}H n.m.r. (CDCl$_3$; room temp.): δ 7.81 (d), 7.33 (q), 7.22 (t), 7.10 (q), 6.78 (d), 6.74 (s, br), 6.52 (s, br.), 5.50 (s, 5H); ^{19}F{^{1}H} n.m.r. (CDCl$_3$; room temp.): δ − 42.73 (q, $^5J_{\text{F-F}}$ 16 Hz), −48.95 (q, br.), −49.93 (q, $^5J_{\text{F-F}}$ 15 Hz), −51.98 (q, $^5J_{\text{F-F}}$ 15 Hz) p.p.m. from CFCl$_3$. Satisfactory elemental analyses were obtained for (**2**), (**3**), and (**5**).

§ *Crystal data*: complex (**2**): C$_{28}$H$_{15}$O$_9$NRu$_3$W, M = 996.15, monoclinic, space group $P2_1/c$, a = 9.837(2), b = 21.088(2), c = 16.116(1) Å, β = 106.17(1)°, U = 3210.92 Å^3, Z = 4, D_c = 2.061 g/cm^3, F(000) = 1872, Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation, λ = 0.70930 Å, μ(Mo-K_α) = 5.05 mm^{-1}. The min and max transmission factors are 0.810 and 0.999, 5635 unique reflections were measured, and 4350 reflections with I > 2.5 σ(I) were used in refinement. Refinement of 57 atoms (15 H atoms fixed) and 380 parameters converged to R = 0.031 and R_w = 0.035, GOF = 1.666.

Complex (**3**): C$_{27}$H$_{19}$O$_8$NRu$_3$W, M = 972.18, triclinic, space group $P\bar{1}$, a = 12.088(2), b = 15.109(3), c = 17.613(2) Å, α = 100.33(1), β = 105.84(1), γ = 101.549(16)°, U = 2943.46 Å^3, Z = 4, D_c = 2.195 g/cm^3, F(000) = 18312, Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation, λ = 0.70930 Å, μ(Mo-K_α) = 5.51 mm^{-1}. The min and max transmission factors are 0.528 and 0.999, 10 125 unique reflections were measured, and 7452 reflections with I > 2.5 σ(I) were used in refinement. Refinement of 118 atoms and 721 parameters converged to R = 0.028 and R_w = 0.031, GOF = 1.247.

For both structures, atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

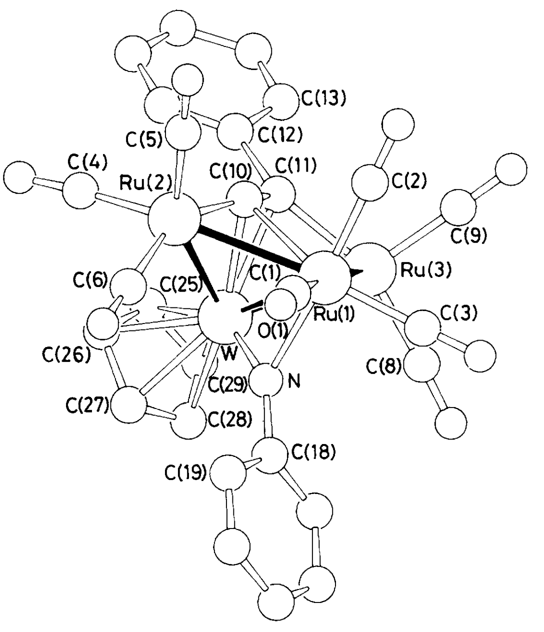

Figure 1. The molecular drawing of (**2**). Bond lengths (Å): W–Ru(1), 2.727(1); W–Ru(2), 2.816(1); W–Ru(3), 2.771(1); Ru(1)–Ru(2), 2.839(1); Ru(1)–Ru(3), 2.854(1); W–N, 1.83(1); Ru(1)–N, 2.20(1); W–C(10), 2.17(1); Ru(1)–C(10), 2.41(1); Ru(2)–C(10), 1.94(1); W–C(11), 2.39(1); Ru(3)–C(11), 2.09(1); C(10)–C(11), 1.20(1); C(11)–C(12), 1.66(2). Bond angles (°): Ru(2)–C(10)–C(11), 167(1); C(10)–C(11)–C(12), 111(1); W–N–Ru(1), 84.8(2); W–N–C(18), 147(1); Ru(1)–N–C(18), 128(1).

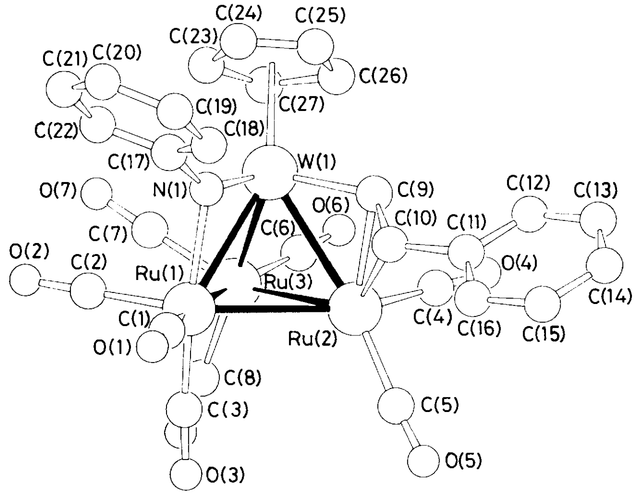

Figure 2. The molecular drawing of (**3**). Bond lengths (Å): W(1)–Ru(1), 2.930(1); W(1)–Ru(2), 2.813(1); W(1)–Ru(3), 2.716(1); Ru(1)–Ru(2), 2.996(1); Ru(1)–Ru(3), 2.805(1); Ru(2)–Ru(3), 2.833(1); W(1)–N(1), 1.81(1); Ru(1)–N(1), 2.19(1); W(1)–C(9), 2.06(1); Ru(2)–C(9), 2.19(1); Ru(2)–C(10), 2.26(1); C(9)–C(10), 1.40(1). Bond angles (°): W(1)–C(9)–C(10), 128(1); C(9)–C(10)–C(11), 124(1); W(1)–N(1)–Ru(1), 93.7(2); W(1)–N(1)–C(17), 144(1); Ru(1)–N(1)–C(17), 122(1); Ru(1)–Ru(2)–C(5), 106.8(2); Ru(2)–Ru(1)–C(1), 116.6(2); Ru(2)–Ru(3)–C(8), 112.8(3); Ru(3)–Ru(2)–C(5), 125.3(3).

[1.83(1) Å] and Ru(1)–N distances [2.20(1) Å] are inconsistent with a tungsten–nitrogen double bond and a ruthenium–nitrogen single bond, respectively. Consequently, the imido ligand is better described as having the novel W=N(Ph)→Ru bonding interaction.[8] The isoelectronic W=O→Os interaction in the closely related WOs_3 clusters has been reported.[9] In comparison, the lengths of the W–N and Ru–N single bond in the mixed metal imido complex (cp)-$WRu_2(CO)_8(\mu_3\text{-}NPh)(\mu\text{-}H)$[10] are 2.11 and 2.05 Å, respectively; the average Ru–N distances in (**1**), $Ru_3(CO)_8(dppm)$-$(\mu_3\text{-}NPh)$ (dppm = bisdiphenylphosphinomethane), and $Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}NPh)$ are in the range 2.06—2.07 Å.[11]

Hydrogenation of complex (**2**) in refluxing toluene solution (1 atm; 5 min) induced the elimination of one CO ligand and the addition of two molecules of H_2, giving the tetranuclear dihydrido-vinyl complex (**3**), (cp)$WRu_3(CO)_8(\mu\text{-}NPh)$-$(\mu\text{-}H)_2(CHCHPh)$, in 69% yield.‡ This reaction represents a rare example in which a *trans* vinyl group is produced from the hydrogenation of the co-ordinated acetylide ligand. In general, the hydrogenation of acetylide cluster complexes transfers both hydrogen atoms to the β-carbon to give an alkylidyne fragment ($\mu_3\text{-}CCH_2R$).[2,12]

Crystals suitable for single crystal *X*-ray diffraction study were obtained from acetone/heptane at room temperature. According to the *X*-ray crystal structure determination,§ the asymmetric unit contains two crystallographically distinct, but structurally similar molecules; Figure 2 shows one molecule. The molecule has a tetrahedral WRu_3 core in which W(1) is co-ordinated to a cp ring, whereas Ru(1) and Ru(3) are linked to three terminal CO ligands, and Ru(2) to two. The two bridging hydrides have not been located on the difference Fourier map, but we propose that they are associated with the Ru(1)–Ru(2) and the Ru(2)–Ru(3) bonds. These locations are in agreement with the ^1H n.m.r. data, the observed Ru–Ru distances, and the respective Ru–Ru–CO angles. The vinyl group (CH=CHPh) is both σ-bonded to W(1) with the W(1)–C(9) and C(10)–C(11) bonds *trans*, and π-bonded to Os(2). Finally, the bridging imido ligand (NPh) is associated with the W(1)–Ru(1) edge and rests on the extension of the W(1)–Ru(1)–Ru(3) plane. Its structural parameters are similar to those of the unsymmetrical imido group observed in complex (**2**).

Reactions of (**2**) with alkyne ligands have also been studied (Scheme 1). Treatment with excess of phenylacetylene in refluxing toluene solution produced only decomposition. However, reactions with excess of ditolylacetylene (110 °C; 45 min; 47% yield) and hexafluoro-but-2-yne (sealed tube, 110 °C, 10 min, 45% yield) in toluene induced the incorporation of one and two equivalents of the acetylene to give the complexes (**4**), (cp)$WRu_3(CO)_7(NPh)(C_2Tol_2)(CCPh)$, and (**5**), (cp)$WRu_3(CO)_8(NPh)[C(Ph)CC(CF_3)C(CF_3)]$-$[C_2(CF_3)_2]$ respectively. Complexes (**4**) and (**5**) were characterized by microanalysis and spectroscopic methods‡ and by single crystal *X*-ray diffraction studies.[13] The former consists of a butterfly cluster possessing a μ_4-η^2-acetylide ligand and an alkyne adapted in a typical 2σ + π bonding mode; the latter consists of a spiked triangular core structure possessing an alkyne ligand co-ordinated to the WRu_2 triangle, and a C_4 hydrocarbyl ligand produced from the coupling between the co-ordinated acetylide and the second incoming alkyne ligand. Interestingly, although the cluster core underwent extensive reorganization during the reaction with the alkyne ligand, the imido ligand acts as a spectator group and retains its W=N(Ph) → Ru bonding mode in the final products.

In summary, the condensation reaction reported provides a generalized strategy to prepare mixed metal cluster complexes of higher nuclearity; the complexes prepared represent a new class of clusters containing a doubly bridging imido ligand and complement those cluster complexes which contain a doubly bridging oxo ligand[9] or a triply bridging imido ligands.[11]

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