Early High Oxidation State–Late Low Oxidation State Mixed-Metal Organometallics: Examples of Oxo-Bridged Tungsten–Ruthenium Acetylide Clusters

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Summary: The heterometallic complexes (C5Me5)W(O)2-Ru4(CO)13($\mu_4$-PPh)(CCPh) (1), (C5Me5)W(O)2Ru4(CO)13($\mu_4$-H)(C6H5)($\mu_4$-PPh)(CCPh) (2), and (C5Me5)W(O)2Ru5(CO)12($\mu_4$-PPh)(CCPh) (3) which contain examples of oxo-bridged tungsten–ruthenium bonds, have been prepared by condensation of Ru4(CO)13($\mu_4$-PPh) and (C5Me5)W(O)2($\mu_4$-O)(CCPh)Cl2 as eluent, followed by recrystallization from a mixture of CH2Cl2 and methanol at room temperature.

The molecular structure of 1 (Figure 1) consists of a distorted square of Ru atoms capped by a quadruply bridging phosphinidene ligand and the other by the tungsten dioxo acetylide fragment (C5Me5)W(O)2(PP)(CCPh). The latter is attached to the Ru4 fragment via the oxo-bridged W–Ru(1) bond (2.806(1) Å) and by the $\mu_4$-$\eta^2$-bound acetylide ligand. In common with previously reported reactions of Ru4(CO)13($\mu_4$-PPh) with small organic unsaturates, skeletal isomerization occurs to form an approximately square Ru4 face bound to an apical phosphinidene group. The Ru4–Ru metal distances span the range 2.962(1)–2.714(1) Å, of which the two shorter Ru4–Ru bonds are bridged by CO ligands. The coordination of the tungsten-substituted acetylene to all four metal atoms on the square Ru4 face closely resembles the mode of attachment of other alkenes on this surface.

Of particular interest is the nature of the (C5Me5)W(O)2 moiety and its bonding to the Ru4 framework. The local structural features of the (C5Me5)W(O)2 fragment resemble those in the 16-electron mononuclear oxo alkyl complexes LW(O)2(CH2SiMe3), L = Cp and C5Me5, formally containing tungsten in its highest oxidation state.

(4) Spectral data for 1: IR (CH2Cl2) ν(CO) 2069(m), 2045(vs), 2041(vs), 2020(vs), 2005(vs), 1974(m), 1964(w) cm$^{-1}$; 1H NMR (200 MHz, CD2Cl2, 294 K) δ = 2.93(4H, s, 2Ph), 1.66(15H, s, C5Me5); 31P NMR (121.5 MHz, CD2Cl2, 294 K) δ = 173.6(3P), δ = 10.0(1P), δ = 2.283 g cm$^{-3}$, F(000) = 2334, (MoKα) = 1.7017 Å, T = 298 K, μ = 49.0 cm$^{-1}$. The intensities were measured on a Nonius CAD-4 diffractometer at a crystal with dimensions 0.13 × 0.20 × 0.25 mm. The structure was solved by using the NRC-SDP-WAX package and refined to R = 0.032, Rw = 0.032, and GOF = 1.33 for 77 atoms and 469 parameters: weight scheme w = $\sigma^2$(F2) + 0.0001F2 and highest Δv/ơ ratio 0.007.

(5) Crystal data for 1: C56H22O12PRu4W, Mw = 1244.64, monoclinic, space group P21/n, a = 19.868(2) Å, b = 9.936(2) Å, c = 20.553(2) Å, β = 112.13(1)°, V = 3621.0(8) Å3, Z = 4, μ(MoKα) = 2.283 g cm$^{-3}$, F(000) = 2334, (MoKα) = 1.7017 Å, T = 298 K, μ = 49.0 cm$^{-1}$. The intensities were measured on a Nonius CAD-4 diffractometer at a crystal with dimensions 0.13 × 0.20 × 0.25 mm. The structure was solved by using the NRC-SDP-WAX package and refined to R = 0.032, Rw = 0.032, and GOF = 1.33 for 77 atoms and 469 parameters: weight scheme w = $\sigma^2$(F2) + 0.0001F2 and highest Δv/ơ ratio 0.007.
The reactivity of 1 was investigated in an attempt to synthesize closely related derivatives. Thus, the tolenesubstituted derivative [(C5Me5)W(O)(Ru(CO)2(C5H5)(µ4-PPh)](CCPPh) (2) and the hexametallocycle complex [(C5Me5)W(O)(Ru(CO)2(µ4-PPh)](CCPPh) (3) were prepared from the direct reaction of 1 with toluene (110 °C, 60 min, 42%) and with excess Ru3(CO)12 in toluene (110 °C, 15 min, 71%), respectively. These two clusters were fully characterized by NMR spectroscopy and by single-crystal X-ray analysis.11 As indicated in Scheme 1, the basic metal framework of 2 resembles that of 1 with an Ru(CO)2(µ-CO) fragment replaced by a newly formed Ru(µ4-toluene) moiety.12 The oxo-bridged tungsten-ruthenium bond in the precursor 1 is retained in 2 (Figure 2). Consistent with the solid-state structure, the 13C NMR spectrum of a 13CO-enriched sample of 2 exhibits one bridging CO signal at δ 256.5 and six sharp CO resonances in the region δ 202.8–192.4. The 1H NMR spectrum shows one methyl signal at δ 2.12 and five multiplets in the region δ 6.30–4.92, suggesting the incorporation of a toluene molecule.

On the other hand, the X-ray study of 3 reveals an identical arrangement for the [(C5Me5)W(µ-CO)] fragment, but the coordination of the acetylide ligand differs greatly from that observed in 1 and 2.13 The structure of 3 (Figure 3) consists of an Ru5P octahedral skeleton.
The octahedral Ru₃P core is analogous to that of the ruthenium phosphinidene clusters Ru₅(CO)₁₅(µ₄-PPh) and Ru₅(CO)₁₃(µ₄-PPh)(µ-H)(µ-PHOPr⁺).³⁵ While the acetylide–metal interaction with the triruthenium surface is reminiscent of the alkynyl bonding observed in the layer-segregated, face-shared biocatalytic alkynyl cluster Pt₃Ru₆(CO)₁₅(C₂Ph₂)(µ-H)₂.³⁶

In summary, the strategy of utilizing the strong σ-coordinating ability of an acetylide ligand to deliver a high oxidation state early-metal oxo fragment to a late-metal, low oxidation state carbonyl center has allowed the synthesis of mixed-metal clusters with oxo-bridged tungsten–ruthenium bonds. This methodology should be applicable to the generation of many other early–late metal oxo clusters. A particular aspect of interest for such oxide systems is the dilemma of providing an adequate description of bond orders and donor properties of the oxo ligands. In the present cases based on structural data and electron counting, we propose that both the bridging and the terminal oxo donor properties of the oxo ligands. In the present cases based on structural data and electron counting, we propose that both the bridging and the terminal oxo ligands possess W=O double bonds, which is in contrast to related monooxo tungsten-containing cluster complexes in which the terminal oxo ligand instead adopts a formal W=O triple bond.¹⁷ We believe that this unusual description of bonding is associated with the availability of only two valence orbitals on tungsten, which can be utilized to accept π-electrons from the oxo ligands.¹⁸ In support of this, MO calculations suggest much less multiple-bond character than in the monooxo relatives MOX₄.¹⁹ We are currently examining other oxide-bridged metal combinations to shed more light on the nature of metal–oxide–metal interactions, which are important for a better understanding of oxide-supported bimetallic catalysts.

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**Supporting Information Available:** Text describing the experimental details for complexes 1–3 and full details of crystal structure analyses, including tables of bond distances, atomic coordinates, and anisotropic thermal parameters (19 pages). Ordering information is given on any current masthead page.

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