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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 $(C_5Me_5)W(O)_2Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)$ (**1**), $(C_5Me_5)W(O)_2Ru_4(CO)_7(C_7H_8)(\mu_4\text{-}PPh)(CCPh)$ (**2**), and $(C_5Me_5)W(O)_2Ru_5(CO)_{12}(\mu_4\text{-}PPh)(CCPh)$ (**3**), which contain examples of oxo-bridged tungsten−ruthenium bonds, have been prepared by condensation of $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ and $(C_5Me_5)W(O)_2(CCPh)$. Their molecular structures demonstrate the coexistence of high oxidation state tungsten and low oxidation state ruthenium carbonyl fragments.*

Complexes of high oxidation state "oxophilic" metals and low oxidation state metals with π-acid ligands are usually considered to be at opposite extremes of the spectrum of transition metal organometallic compounds.[1] However, group VIII metals on oxide supports are some of the most widely used heterogeneous catalysts.[2] Thus, the combination of oxo early-metal organometallics with late-metal carbonyl compounds offers the opportunity to explore, *inter alia*, the generation of bimetallic or polymetallic models for oxide-supported platinum metal catalysts and the physical and chemical behavior of organometallic compounds of metals in highly disparate oxidation states. In this communication, we outline a strategy for the synthesis of oxo-bridged heterometallics which involves the coordination of an early-metal oxo acetylide with a late-metal carbonyl alkyne acceptor fragment.

When a toluene solution of $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$[3ab] and $(C_5Me_5)W(O)_2(CCPh)$[3c] in a 1:1.1 ratio was heated to reflux for 50 min, a pentanuclear complex (**1**) with the formula $(C_5Me_5)W(O)_2Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)$ was obtained in 46% yield, together with small amounts of $(C_5Me_5)W(O)_2Ru_4(CO)_7(C_7H_8)(\mu_4\text{-}PPh)(CCPh)$ (**2**) and $(C_5Me_5)W(O)_2Ru_5(CO)_{12}(\mu_4\text{-}PPh)(CCPh)$ (**3**).[4] Complex **1** is stable in both solution and the solid states and can be purified by thin-layer chromatography with pure CH_2Cl_2 as eluent, followed by recrystallization from a mixture of CH_2Cl_2 and methanol at room temperature.

The molecular structure of **1** (Figure 1)[5] consists of a distorted square of Ru atoms capped by a quadruply bridging phosphinidene ligand and the other by the tungsten dioxo acetylide fragment $(C_5Me_5)W(O)_2(CCPh)$. The latter is attached to the Ru_4 fragment via the oxo-bridged W−Ru(1) bond (2.806(1) Å) and by the μ_4-η^2-bound acetylide ligand.[6] In common with previously reported reactions of $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ with small organic unsaturates, skeletal isomerization occurs to form an approximately square Ru_4 face bound to an apical phosphinidene group.[7] The Ru−Ru metal distances span the range 2.962(1)−2.714(1) Å, of which the two shorter Ru−Ru bonds are bridged by CO ligands. The coordination of the tungsten-substituted acetylene to all four metal atoms on the square Ru_4 face closely resembles the mode of attachment of other alkynes on this surface.[8]

Of particular interest is the nature of the $(C_5Me_5)W(O)_2$ moiety and its bonding to the Ru_4 framework. The local structural features of the $(C_5Me_5)W(O)_2$ fragment resemble those in the 16-electron mononuclear oxo alkyl complexes $LW(O)_2(CH_2SiMe_3)$, L = Cp and C_5Me_5,[9] formally containing tungsten in its highest oxidation

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(4) Spectral data for **1**: IR (C_6H_{14}) ν(CO) 2069(m), 2045 (vs), 2041 (vs), 2020 (vs), 2001 (s), 1974 (m), 1964 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.28−6.66 (m, 10H, 2Ph), 1.66 (s, 15H, C_5Me_5); ^{31}P NMR (121.5 MHz, $CDCl_3$, 294 K) δ 172.6 (1P); ^{13}C NMR (100 MHz, CD_2Cl_2, 193 K) CO, δ 247.5 (1C), 224.8 (1C, br), 197.8 (d, 1C, $J_{P-C} = 39$ Hz), 195.7 (1C), 195.0 (1C, br), 194.7 (1C), 193.6 (1C, br), 192.3 (d, 1C, $J_{P-C} = 40$ Hz), 190.7 (1C), 189.0 (1C). Anal. Calcd for $C_{34}H_{25}O_{12}PRu_4W$: C, 32.81, H, 2.02. Found: C, 32.75, H, 1.98.

(5) Crystal data for **1**: $C_{34}H_{25}O_{12}PRu_4W$, $M_r = 1244.66$, monoclinic, space group $P2_1/n$, $a = 19.868(2)$ Å, $b = 9.936(2)$ Å, $c = 20.055(2)$ Å, $\beta = 113.85(1)°$, $V = 3621.0(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.283$ g cm^{-3}, $F(000) = 2334$, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $T = 298$ K, $\mu = 49.43$ cm^{-1}. The intensities were measured on a Nonius CAD4 diffractometer on a crystal with dimensions 0.13 × 0.20 × 0.25 mm. Of the 6369 unique reflections, 4648 with $I > 2\sigma(I)$ were used for the refinement. The structure was solved by using the NRCC-SDP-VAX package and refined to $R_F = 0.032$, $R_w = 0.032$, and GOF = 1.33 for 77 atoms and 469 parameters: weighting scheme $w^{-1} = \sigma^2(F_o) + 0.00001F_o^2$ and highest Δ/σ ratio 0.002.

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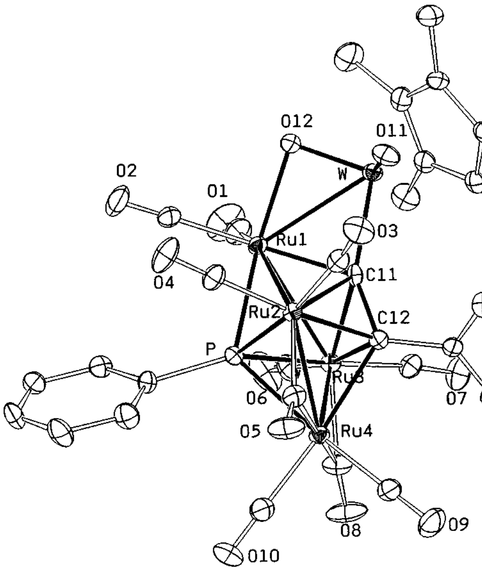
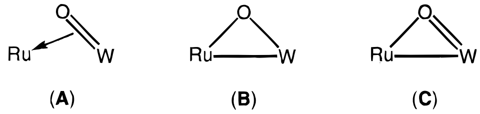


Figure 1. Molecular structure of **1**. Selected bond lengths (Å): W−Ru(1) = 2.806(1), Ru(1)−Ru(2) = 2.876(1), Ru(1)−Ru(3) = 2.962(1), Ru(2)−Ru(4) = 2.780(1), Ru(3)−Ru(4) = 2.714(1), W−O(11) = 1.709(5), W−O(12) = 1.793(5), Ru(1)−O(12) = 2.159(5), Ru(1)−P = 2.312(2), Ru(2)−P = 2.403(2), Ru(3)−P = 2.535(2), Ru(4)−P = 2.425(2), W−C(11) = 2.082(7), Ru(1)−C(11) = 2.124(7), Ru(2)−C(11) = 2.368(7), Ru(3)−C(11) = 2.463(7), Ru(2)−C(12) = 2.346(8), Ru(3)−C(12) = 2.306(7), Ru(4)−C(12) = 2.252(7), C(11)−C(12) = 1.42(1). The O(11)−W−O(12) angle is 106.8(3)°.

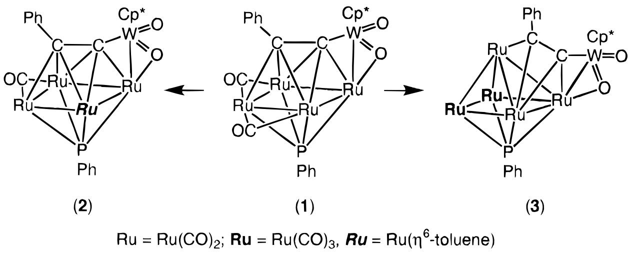
Chart 1



state of VI and showing the existence of two W=O double bonds. In addition, however, the W atom and one of the oxo ligands in **1** are at bonding distances from Ru(1). The apical coordination site on Ru(1) is occupied by the bridging W=O fragment, suggesting a dative bonding interaction from the W=O ligand to the Ru atom. Consequently, the W−O−Ru bonding can be represented by modes **A** and **B**, with the latter emphasizing covalent interactions (Chart 1). A third possibility may be that the oxo ligand is serving as a π-donor to the 16-electron W center (mode **C**). Indeed, the last assignment is supported by the short W−O(12) distance (1.793(5) Å), which is similar to that of the W=O→Os fragment in the $WOs_3(\mu\text{-}O)$ clusters[10] and suggests retention of W=O multiple bonding. The presence of such bonding is further confirmed by the modest lengthening (0.084(5) Å) of the W=O distance for the bridging oxo ligand vs the terminal oxo ligand in **1**.

It is interesting to note that the reactivity of the W(VI) dioxo center $Cp^*W(O)_2C_2Ph$ toward $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ leading to **1** is distinctly different from that of the W(II) center $Cp^*W(CO)_3(C_2Ph)$. In the latter, lower oxidation state case, a $Cp^*W(CO)(C_2Ph)$ fragment caps the nido Ru_4P framework with incorporation of the tungsten into an octahedral Ru_4WP skeleton.

Scheme 1



The reactivity of **1** was investigated in an attempt to synthesize closely related derivatives. Thus, the toluene-substituted derivative $(C_5Me_5)W(O)_2Ru_4(CO)_7(C_7H_8)(\mu_4\text{-}PPh)(CCPh)$ (**2**) and the hexametallic complex $(C_5Me_5)W(O)_2Ru_5(CO)_{12}(\mu_4\text{-}PPh)(CCPh)$ (**3**) were prepared from the direct reaction of **1** with toluene (110 °C, 60 min, 42%) and with excess $Ru_3(CO)_{12}$ 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 $Ru(CO)_2(\mu\text{-}CO)$ fragment replaced by a newly formed $Ru(\eta^6\text{-toluene})$ 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 ^{13}C NMR spectrum of a ^{13}CO-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 $(C_5Me_5)W(O)(\mu\text{-}O)$ 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 Ru_5P octahedral skeleton

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[11] Spectral data for **2**: IR (CH_2Cl_2) ν(CO) 2027 (m), 2006 (vs), 1987 (vs), 1941 (s, br), 1787 (w, br) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 294 K) δ 7.38−6.82 (m, 10H, 2Ph), 6.30 (d, 1H, J_{H-H} = 5.8 Hz), 6.02 (t, 1H, J_{H-H} = 5.6 Hz), 5.76 (t, 1H, J_{H-H} = 5.6 Hz), 5.36 (d, 1H, J_{H-H} = 5.8 Hz), 4.92 (t, 1H, J_{H-H} = 5.6 Hz), 2.12 (s, 3H, Me), 1.65 (s, 15H, C_5Me_5); ^{31}P NMR (122 MHz, $CDCl_3$) δ 240.5 (1P); ^{13}C NMR (100 MHz, CD_2Cl_2, 294 K) CO, δ 256.5 (1C), 202.8 (d, 1C, J_{P-C} = 6 Hz), 202.3 (d, 1C, J_{P-C} = 4 Hz), 200.9 (d, 1C, J_{P-C} = 5 Hz), 199.9 (d, 1C, J_{P-C} = 7 Hz), 197.9 (d, 1C, J_{P-C} = 5 Hz), 192.4 (d, 1C, J_{P-C} = 3 Hz). Anal. Calcd for $C_{38}H_{33}O_9PRu_4W$: C, 36.43; H, 2.66. Found: C, 36.33, H, 2.59. Spectral data for **3**: IR (CH_2Cl_2) ν(CO) 2077 (m), 2044 (s), 2027 (vs), 2013 (vs), 1980 (w, br) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 294 K) δ 7.88 (d, 2H, J_{H-H} = 8 Hz), 7.51 (t, 2H, J_{H-H} = 8 Hz), 7.36 (t, 2H, J_{H-H} = 7.5 Hz), 7.40−7.04 (m, 6H), 1.62 (s, 15H, C_5Me_5); ^{31}P NMR (122 MHz, $CDCl_3$) δ 320.4 (1P); ^{13}C NMR (75 MHz, $CDCl_3$, 294 K) CO, δ 208.7 (1C), 203.7 (d, 1C, J_{P-C} = 40 Hz), 200.8 (d, 1C, J_{P-C} = 23 Hz), 199.1 (1C), 198.4 (d, 3C, J_{P-C} = 11 Hz), 195.6 (d, 3C, J_{P-C} = 11 Hz), 192.4 (d, 1C, J_{P-C} = 3 Hz), 192.0 (d, 1C, J_{P-C} = 3 Hz). Anal. Calcd for $C_{36}H_{25}O_{14}PRu_5W$: C, 30.85; H, 1.80. Found: C, 30.83; H, 1.74.

[12] Crystal data for **2**: $C_{38}H_{33}O_9PRu_4W$, M_r = 1252.77, monoclinic, space group $P2_1/n$, a = 10.704(3) Å, b = 21.835(4) Å, c = 16.497(3) Å, β = 90.02(2)°, V = 3855.6(14) Å^3, Z = 4, ρ_{calcd} = 2.158 g cm^{-3}, F(000) = 2366, λ(Mo Kα) = 0.7107 Å, T = 298 K, μ = 46.38 cm^{-1}. The intensities were measured on a crystal with dimensions 0.25 × 0.25 × 0.50 mm. Of the 6775 unique reflections, 5810 with $I > 2\sigma(I)$ were used for the refinement. The structure was refined to R_F = 0.023, R_w = 0.022, and GOF = 1.56 for 89 atoms and 476 parameters: weighting scheme $w^{-1} = \sigma^2(F_o) + 0.00003F_o^2$ and highest Δ/σ ratio 0.001.

[13] Crystal data for **3**: $C_{36}H_{25}O_{14}PRu_5W\cdot{}^1/_2CH_2Cl_2$, M_r = 1443.2, monoclinic, space group $C2/c$, a = 22.763(3) Å, b = 12.337(2) Å, c = 31.407(4) Å, β = 106.57(1)°, V = 8454(2) Å^3, Z = 8, ρ_{calcd} = 2.266 g cm^{-3}, F(000) = 5386, λ(Mo Kα) = 0.7107 Å, T = 298 K, μ = 42.30 cm^{-1}. The intensities were measured on a crystal with dimensions 0.05 × 0.10 × 0.10 mm. Of the 5506 unique reflections, 3179 with $I > 2\sigma(I)$ were used for the refinement. The structure was refined to R_F = 0.037, R_w = 0.035, and GOF = 1.10 for 84 atoms and 533 parameters: weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0001F_o^2$ and highest Δ/σ ratio 0.0005.

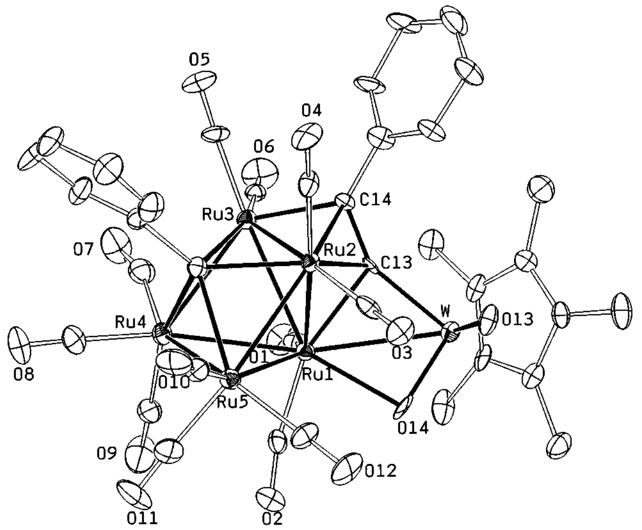

Figure 2. Molecular structure of **2**. Selected bond lengths (Å): W−Ru(1) = 2.804(1), Ru(1)−Ru(2) = 2.981(1), Ru(1)−Ru(4) = 2.827(1), Ru(2)−Ru(3) = 2.672(1), Ru(3)−Ru(4) = 2.808(1), W−O(8) = 1.724(3), W−O(9) = 1.799(3), Ru(1)−O(9) = 2.185(3), Ru(1)−P = 2.302(1), Ru(2)−P = 2.505(1), Ru(3)−P = 2.388(1), Ru(4)−P = 2.323(1), W−C(8) = 2.095(4), Ru(1)−C(8) = 2.112(4), Ru(2)−C(8) = 2.512(4), Ru(4)−C(8) = 2.293(4), Ru(2)−C(9) = 2.353(4), Ru(3)−C(9) = 2.247(4), Ru(4)−C(9) = 2.287(4), C(8)−C(9) = 1.413(6), average Ru(4)−C(arene) = 2.233(4). The O(8)−W−O(9) angle is 105.21(15)°.

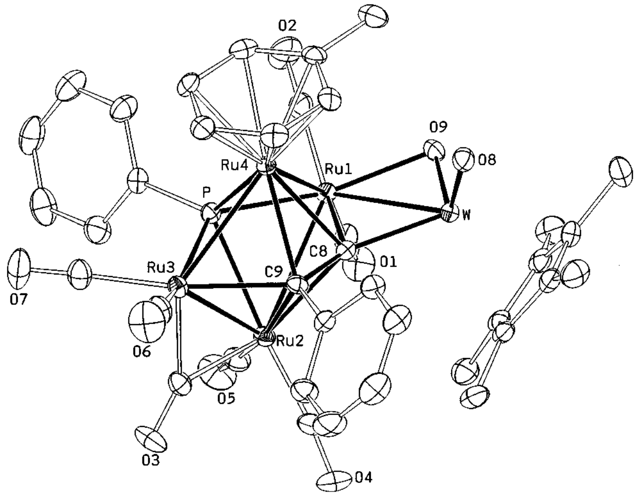

Figure 3. Molecular structure of **3**. Selected bond lengths (Å): W−Ru(1) = 2.945(1), Ru(1)−Ru(2) = 2.781(2), Ru(1)−Ru(3) = 2.869(2), Ru(1)−Ru(4) = 2.879(2), Ru(1)−Ru(5) = 2.870(2), Ru(2)−Ru(3) = 2.723(2), Ru(2)−Ru(5) = 2.840(2), Ru(3)−Ru(4) = 2.833(2), Ru(4)−Ru(5) = 2.878(2), W−O(13) = 1.728(8), W−O(14) = 1.77(1), Ru(1)−O(14) = 2.281(8), Ru(2)−P = 2.294(4), Ru(3)−P = 2.382(4), Ru(4)−P = 2.368(4), Ru(5)−P = 2.378(4), W−C(13) = 2.07(1), Ru(1)−C(13) = 2.17(1), Ru(2)−C(13) = 2.19(1), Ru(2)−C(14) = 2.24(1), Ru(3)−C(14) = 2.06(1), C(13)−C(14) = 1.37(2). The O(18)−W−O(14) angle is 108.1(4)°.

with one Ru$_3$ triangular face capped by the tungsten dioxo acetylide fragment via a $2\sigma + \pi$ attachment of the acetylide ligand[14] and a donor interaction of the bridging oxo ligand. Again, a Ru−O=W interaction is present. The octahedral Ru$_5$P core is analogous to that of the ruthenium phosphinidene clusters Ru$_5$(CO)$_{15}$(μ_4-PPh) and Ru$_5$(CO)$_{13}$(μ_4-PPh)(μ-H)(μ-PPhOPr^n),[15] while the acetylide−metal interaction with the triruthenium surface is reminiscent of the alkyne bonding observed in the layer-segregated, face-shared bioctahedral alkyne cluster Pt$_3$Ru$_6$(CO)$_{20}$(C$_2$Ph$_2$)(μ-H)$_2$.[16]

In summary, the strategy of utilizing the strong π-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 oxide 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 ligands possess W=O double bonds, which is in contrast to related monooxotungsten-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 that the Mo=O bonds in O$_2$MoX$_2$ complexes contain much less multiple-bond character than in the monooxo relatives OMoX$_4$.[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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