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Generation of Oxo−Carbide Clusters from Direct Scission of a Coordinated Carbonyl Ligand: Molecular Structures of $Cp_2W_2Ru_3(CO)_{13}$ and $Cp^*W(O)Cp^*WRu_3(\mu_5\text{-}C)(CO)_{11}$

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The chemistry of carbido cluster compounds has developed in recent years to constitute a distinct research domain.[1] For the carbido clusters comprised of metals in low oxidation states, it has been established that the interstitial carbide atoms can be derived from the scission of the coordinated isonitrile[2] and acetylide ligands,[3] and the proton-induced reduction of CO,[4] or from the disproportionation of CO ligands.[5] The last studies have provided valuable insight into the activation of CO on metal surfaces.[6] However, there are only a few examples of generating carbide or related complexes in which the carbon and oxygen originating from CO are distinctly separated and remained in the coordination sphere. These examples include the nice work of Wolczanski on CO deoxygenation by tantalum siloxide complexes,[7] Chishlom on the reductive cleavage of CO using tungsten alkoxide clusters,[8] and the synthesis of carbido cluster $Ru_6C(CO)_{15}(C_{16}H_{16}\text{-}\mu_2\text{-}O)$ by Johnson and Braga[9] in which the departing oxo ligand is trapped by the [2,2]-paracyclophane ligand. In this paper, we report the synthesis and characterization of heterometallic carbonyl clusters $Cp_2W_2Ru_3(CO)_{13}$ and $LW(O)L'WRu_3(\mu_5\text{-}C)(CO)_{11}$, L, L′ = Cp, Cp*. Formation of the latter oxo−carbido clusters represents a unique example of direct scission of the C−O bond.

Treatment of the heterometallic cluster $CpWRu_3(CO)_{12}H$ with an excess of $CpW(CO)_3H$ in refluxing heptane followed by chromatography and recrystallization from CH_2Cl_2/CH_3OH afforded the dark brown pentanuclear cluster $Cp_2W_2Ru_3(CO)_{13}$ (**1**) in 29% yield.[10] The initial spectroscopic analysis confirmed that complex **1** is identical to the partially characterized cluster complex synthesized from the photochemical reaction of $[CpW(CO)_3]_2$ with $Ru_3(CO)_9BH_5$.[11]

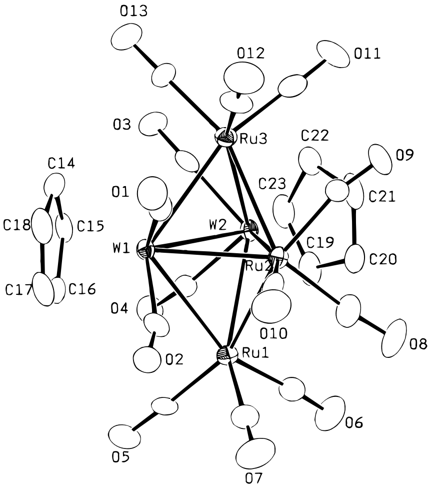

Figure 1. Molecular structure of **1** and the atomic numbering scheme. Selected bond lengths (Å): W(1)−W(2) = 2.941(1), W(1)−Ru(1) = 2.885(1), W(1)−Ru(2) = 2.880(1), W(1)−Ru(3) = 2.875(1), W(2)−Ru(1) = 2.913(1), W(2)−Ru(2) = 2.843(1), W(2)−Ru(3) = 2.905(1), Ru(1)−Ru(2) = 2.765(2), and Ru(2)−Ru(3) = 2.785(2).

Single crystal X-ray diffraction study of **1** revealed that the asymmetric unit contains two crystallographically distinct, but structurally similar molecules. A perspective view of one such molecule is indicated in Figure 1, which exhibits a distorted trigonal bipyramidal metal framework with both $CpW(CO)_2$ fragments occupying the equatorial sites. The unique W(1)−W(2) bond (2.941(1) Å) is considerably longer than the W−Ru distances (2.843(1)−2.913(1) Å) and the Ru−Ru distances (2.765(2) and 2.785(2) Å); the latter are the two shortest metal−metal bonds of the whole molecule. Similar variations of bond distances are observed in the analogous cluster $Cp_2Mo_2Os_3(CO)_{12}(\mu\text{-}H)_2$,[12] implying that the interligand repulsions around the W centers are much greater than those of the Ru atoms, which lead to the uneven expansion of the framework in the close proximity of W atoms.

In a remarkable further development we discovered that complex **1** slowly eliminated one CO in refluxing toluene solution (30 min) to afford an oxo−carbido complex $CpW(O)CpWRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2**) in 22% yield, based on the consumption of **1**. Two additional derivatives $LW(O)L'WRu_3(\mu_5\text{-}C)(CO)_{11}$ (**3**, L = L′ = Cp*, 26%; **4**, L = Cp and L′ = Cp*, 37%) except for **5** (L = Cp* and L′ = Cp) were obtained from the condensation of $LWRu_3(CO)_{12}H$ and $L'W(CO)_3H$ (L = L′ = Cp*; L ≠ L′ = Cp, Cp*) through the consecutive elimination of one H_2 and three CO ligands.[9] The X-ray diffraction study on **3** disclosed that it adopts a wingtip-bridged butterfly arrangement, which is formally derived from the trigonal bipyramid in **1** by scission of two equatorial metal−metal bonds. Now, the carbido atom is linked to all transition metal atoms, and the oxo ligand is coordinated to the Cp*W bridge and pointing toward the $Cp^*W(CO)_2$ fragment. The count of 76 valence electrons, consistent with that of the carbido clusters adopting the similar geometry,[13] is achieved by considering the oxo ligand as a four-electron donor. Since this donor ability

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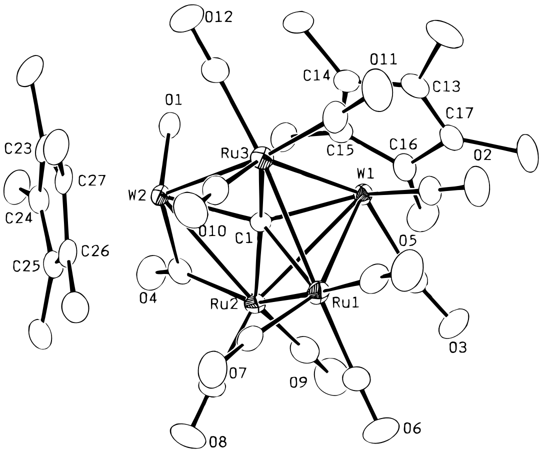


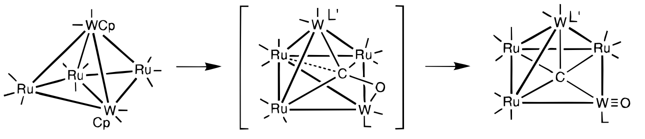
Figure 2. Molecular structure of **3** and the atomic numbering scheme. Selected bond lengths (Å): W(1)−Ru(1) = 2.846(1), W(1)−Ru(2) = 3.018(1), W(1)−Ru(3) = 3.031(1), Ru(1)−Ru(2) = 2.849(1), Ru(1)−Ru(3) = 2.810(1), W(2)−Ru(2) = 2.863(1), W(2)−Ru(3) = 2.942(1), W(1)−C(1) = 2.135(7), Ru(1)−C(1) = 2.200(7), Ru(2)−C(1) = 1.988(7), Ru(3)−C(1) = 2.016(7), W(2)−C(1) = 2.062(7), W(2)−O(1) = 1.697(5), and O(1)···C(1) = 2.960(8).

invokes W≡O multiple bonding interaction, a very short distance is observed, W(2)−O(1) = 1.697(5) Å.

The origin of the oxo and carbido ligands in **2**−**4** was explored in attempts to clarify the mechanism. First, we observed no formation of CO_2 from all reactions between $LWRu_3(CO)_{12}H$ and $L'W(CO)_3H$ by passing the exhaust into a saturated $Ca(OH)_2$ solution. This negative result suggests that the carbide is not produced from the CO disproportionation.[14] Secondly, the oxo ligand is produced from the direct scission of CO ligand, but not from the oxygen-containing impurities in the system.[15] In the latter experiment, the oxo−carbido clusters were examined by ^{17}O NMR spectroscopy on samples prepared from the ^{17}O enriched WRu_3 clusters and the normal tungsten hydride complexes. For **3**, the ^{17}O NMR spectrum consists of a broad W≡O signal at δ 832.9 and three CO signals at δ 388.1, 377.3, and 355.7 in a 1:6:2:3 ratio. These ^{17}O NMR chemical shifts are in good agreement with those of the W-bound oxo ligands[16] and the terminal CO ligands[17] reported in the literature.

Based on the above experimental evidence, one possible reaction path is proposed to account for the formation of the oxo−carbido clusters (Scheme 1). The facile conversion from **1** to **2** and the failure to obtain the mixed derivative **5** from the reactions between $LWRu_3(CO)_{12}H$ and $L'W(CO)_3H$ ($L \neq L'$ = Cp, Cp*) indicate that the trigonal bipyramidal clusters similar to that of **1** are the primary product, as the W atoms are located at the indistinguishable equatorial sites. After the generation of the trigonal bipyramidal cluster, it would further transfer to an intermediate (**A**) with a μ_4-η^2-CO or a μ_5-η^2-CO ligand through scission of the longest W−W bond to provide the unsaturation and to relieve the interligand repulsion. The detection of μ_4-η^2-CO in the closely related WRu_3, WRu_4, and W_2Ru_4 systems[18] and the isolation of ruthenium cluster compounds with the μ_6-η^2-CO ligand[19] provide the precedents for such postulation. The final conversion to the oxo−carbido clusters is accomplished by the cleavage of the η^2-CO ligand and the reorganization of cluster framework. The formation of the W≡O multiple bonding is undoubtedly crucial, providing an additional driving force for the C−O cleavage process described.

Scheme 1



(**1**) (**A**) (**2**), L = L' = Cp; (**3**), L = L' = Cp*

(**4**), L = Cp & L' = Cp*

(**5**), L = Cp* & L' = Cp; unknown

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Supporting Information Available: Text describing the experimental details and the spectroscopic data for **1**−**4**; full details of crystal structure analyses including tables of bond distances, atomic coordinates, and anisotropic thermal parameters for **1** and **3** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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