

## Synthesis of the First Cluster Complexes Bearing Three Quadruply Bridging CO Ligands: X-ray Crystal Structure of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]\text{WRu}_6(\mu_3\text{-H})(\text{CO})_{18}$

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The transformation from a regular C-bonded, terminal, or bridging CO ligand to a quadruply bridging CO ligand is recognized as an essential requirement for the cleavage of the C–O bond in metal cluster compounds and on metal surfaces.<sup>1</sup> One of the interesting developments of recent years has been the realization that the tetrametallic butterfly clusters, such as  $[\text{Fe}_4(\mu\text{-H})(\text{CO})_{13}]^-$  or  $\text{LMRu}_3(\mu\text{-H})(\text{CO})_{12}$  ( $M = \text{W}$  and  $\text{Mo}$ ;  $L = \text{Cp}$  and  $\text{C}_5\text{Me}_5$ ), bearing one quadruply bridging CO ligand, are able to undergo equilibration in solution with the tetrahedral isomers possessing only the regular terminal or bridging CO ligands.<sup>2,3</sup> Thus, these isomerization studies provide explicit evidence for the rapid exchange between these two different types of CO ligands. Recently, this chemistry has been extended into the preparation of complexes possessing two  $\mu_4$ -CO ligands, as reported in the case of  $\text{Ru}_6$  cluster chemistry<sup>4</sup> and its heterometallic domain.<sup>5</sup> In the meantime, reactivity studies have demonstrated that these multisite-bound CO ligands can convert into carbide ligands through cleavage of C–O bond.<sup>6</sup> In this communication, we extend the scope of these investigations, and report the first synthesis of  $\text{WRu}_6$  compounds bearing three such uncommon  $\mu_4$ -CO ligands and a related cluster compound with two  $\mu_4$ -CO ligands, generated from direct hydrogenation.

The hydride complex  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]\text{W}(\text{CO})_3\text{H}$ , synthesized from  $\text{C}_5\text{H}_4(\text{SiMe}_3)_2$  and  $\text{W}(\text{CO})_3(\text{NCEt})_3$ , was added into a toluene solution of  $\text{Ru}_3(\text{CO})_{12}$  at reflux over a period of 3 h. Workup of the reaction mixture by routine TLC gave a  $\text{WRu}_6$  complex  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]\text{WRu}_6(\mu_3\text{-H})(\text{CO})_{18}$  (**1a**) in 28% yield.<sup>7</sup> The analogous  $\text{C}_5\text{H}_4(\text{SiMe}_3)$  and  $\text{C}_5\text{H}_4(\text{CHMe}_2)$  substituted

complexes **1b** and **1c** were obtained using the hydride complexes  $[\text{C}_5\text{H}_4(\text{SiMe}_3)]\text{W}(\text{CO})_3\text{H}$  and  $[\text{C}_5\text{H}_4(\text{CHMe}_2)]\text{W}(\text{CO})_3\text{H}$ , respectively.<sup>7</sup> All of these products were characterized by IR and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and microanalysis. The X-ray structure of **1a** was determined to reveal its identity.<sup>7</sup>

As depicted in Figure 1, the molecule consists of a tetrahedral  $\text{WRu}_3$  core with the tungsten atom located at the apical position and capped by a  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$  ligand, while the Ru atoms occupy the basal positions and each possess two terminal CO ligands. The W–Ru distances are nearly equal with distances 2.911(1)–2.917(1) Å, which are longer than the other Ru–Ru distances. The  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$  ligand seems to experience some steric congestion, as the W–C(SiMe<sub>3</sub>) distances (2.358(8)–2.368(8) Å) are relatively longer than the unsubstituted W–CH distances (2.324(7)–2.326(8) Å) of the  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$  ring. The hydride, which was located crystallographically, was found to span the  $\text{Ru}_3$  basal triangle. Moreover, the Ru–Ru edges are each coordinated by a  $\text{Ru}(\text{CO})_3$  pendant, forming three  $\text{WRu}_3$  butterfly arrangements, supporting the observed  $\mu_4$ - $\eta^2$ -CO ligands. The associated metric parameters are similar to those of the tetrametallic butterfly clusters mentioned earlier<sup>2,3</sup> and other polymetallic clusters bearing the same type of encapsulated  $\mu_4$ -CO ligand.<sup>8</sup>

Interestingly, the cluster framework of **1** possesses a virtual  $C_3$  axis which coincides with the vector linking the W atom and the hydride ligand. This symmetrical feature is best revealed by the <sup>13</sup>C NMR data of **1a**, which exhibits five CO signals at  $\delta$  288.1 ( $J_{\text{WC}} = 168$  Hz), 207.6, 200.5 ( $J_{\text{CH}} = 2.4$  Hz), 189.6 ( $J_{\text{CH}} = 12$  Hz), and 184.5 with an intensity ratio of 3:3:3:6 at room temperature. Thus, the signal at  $\delta$  288.1 with the characteristic <sup>1</sup> $J_{\text{WC}}$  coupling is assigned to the  $\mu_4$ -CO ligands. The signals at  $\delta$  200.5 and 189.6, which show the <sup>2</sup> $J_{\text{CH}}$  coupling, are due to the equatorial and the axial CO ligands associated with the Ru atoms on the inner metal triangle, while the signals at  $\delta$  207.6 and 184.5 with the ratio 3:6 are derived from the axial and the equatorial CO ligands of the  $\text{Ru}(\text{CO})_3$  pendants.

Some attempts were made to investigate the  $\mu_4$ -CO reactivity. Thus, treatment of **1a–c** with CO in toluene (1 atm, 5 h, 110 °C) resulted a slow decomposition. However, as a general example, hydrogenation of **1a** gave a trihydride complex  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]\text{WRu}_6(\mu\text{-H})_3(\text{CO})_{17}$  (**2**) in 71% yield.<sup>7</sup> The X-ray diffraction study disclosed that it now adopts a double edge-bridged trigonal bipyramidal core structure (Figure 2), which is formally derived from the previously mentioned, triple edge-bridged tetrahedra by generation of a W–Ru bond. Again, the hydride ligands are located, and they span the newly formed W–Ru(1) edge, the Ru(2)–Ru(3) edge, and the Ru(2)–Ru(4)–Ru(5) face, respectively. These assignments are fully consistent with the <sup>1</sup>H NMR data which exhibit three signals at  $\delta$  –14.14 ( $J_{\text{WH}} = 84.8$  Hz), –14.70, and –20.71; the last one is obviously due to the face-bridging hydride because of the large distinction in chemical shift.<sup>9</sup>

More striking behavior of **2** was found by VT NMR. For example, the  $\mu_4$ -CO ligands occur at  $\delta$  292.1 and 289.2 in the <sup>13</sup>C NMR spectrum at 294 K. This observation agrees with

(7) Complete experimental details and characterization data for all new complexes isolated during this work are provided as Supporting Information.

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