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.¹ 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 $\text{LMRu}_3(\mu\text{-H})(\text{CO})_{12}$ ($\text{M} = \text{W}$ and Mo ; $\text{L} = \text{Cp}$ and C_5Me_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.^{2,3} 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 μ_4 -CO ligands, as reported in the case of Ru_6 cluster chemistry⁴ and its heterometallic domain.⁵ In the meantime, reactivity studies have demonstrated that these multitopic-bound CO ligands can convert into carbide ligands through cleavage of C–O bond.⁶ In this communication, we extend the scope of these investigations, and report the first synthesis of WRu_6 compounds bearing three such uncommon μ_4 -CO ligands and a related cluster compound with two μ_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 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.⁷ 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.⁷ All of these products were characterized by IR and ¹H and ¹³C NMR spectroscopies and microanalysis. The X-ray structure of **1a** was determined to reveal its identity.⁷

As depicted in Figure 1, the molecule consists of a tetrahedral 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(SiMe₃) 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 Ru_3 basal triangle. Moreover, the Ru–Ru edges are each coordinated by a $\text{Ru}(\text{CO})_3$ pendant, forming three WRu_3 butterfly arrangements, supporting the observed μ_4 - η^2 -CO ligands. The associated metric parameters are similar to those of the tetrametallic butterfly clusters mentioned earlier^{2,3} and other polymetallic clusters bearing the same type of encapsulated μ_4 -CO ligand.⁸

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 ¹³C NMR data of **1a**, which exhibits five CO signals at δ 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 δ 288.1 with the characteristic ¹ J_{WC} coupling is assigned to the μ_4 -CO ligands. The signals at δ 200.5 and 189.6, which show the ² J_{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 δ 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 μ_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.⁷ 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 ¹H NMR data which exhibit three signals at δ –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.⁹

More striking behavior of **2** was found by VT NMR. For example, the μ_4 -CO ligands occur at δ 292.1 and 289.2 in the ¹³C NMR spectrum at 294 K. This observation agrees with

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

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Figure 1. Molecular structure of **1a** and the atomic numbering scheme; the methyl groups of the trimethylsilyl substituents were omitted for clarity. Selected bond lengths (Å): W–Ru(2) = 2.917(1), W–Ru(4) = 2.913(1), W–Ru(5) = 2.911(1), Ru(2)–Ru(4) = 2.801(1), Ru(2)–Ru(5) = 2.799(1), Ru(4)–Ru(5) = 2.815(1), Ru(1)–Ru(2) = 2.811(1), Ru(1)–Ru(5) = 2.828(1), Ru(2)–Ru(3) = 2.820(1), Ru(3)–Ru(4) = 2.804(1), Ru(4)–Ru(6) = 2.805(1), Ru(5)–Ru(6) = 2.820(1).

Figure 2. Molecular structure of **2** and the atomic numbering scheme; the methyl groups of the trimethylsilyl substituents were omitted for clarity. Selected bond lengths (Å): W–Ru(1) = 2.996(1), W–Ru(2) = 2.882(1), W–Ru(4) = 2.922(1), W–Ru(5) = 2.986(1), Ru(2)–Ru(4) = 2.838(1), Ru(2)–Ru(5) = 2.824(1), Ru(4)–Ru(5) = 2.740(1), Ru(1)–Ru(2) = 2.832(1), Ru(1)–Ru(5) = 2.741(1), Ru(2)–Ru(3) = 2.888(1), Ru(3)–Ru(4) = 2.827(1), Ru(4)–Ru(6) = 2.851(1), Ru(5)–Ru(6) = 2.727(1).

the asymmetric nature of the cluster skeleton indicated by the X-ray analysis. Upon raising of the temperature to 325 K, these CO signals coalesce to form a broad signal centered at δ 291.1. In addition, two of the three distinct olefinic hydrogen of the $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ substituent at δ 5.23 and 4.85 in its ^1H NMR spectrum at 294 K merge to form a broad signal at δ 5.06 at 325 K. These temperature-dependent behaviors are best interpreted in terms of the hydride hopping between the Ru(2)–Ru(3) edge and the Ru(5)–Ru(6) edge of the Ru_6 basal plane, forming a dynamic plane of mirror symmetry. Interestingly, the scrambling of the Ru–H–Ru hydride and the face-bridging hydride was also noted under the same conditions, suggesting that the proposed hydride hopping is relayed by the face-bridging hydride ligand (Scheme 1). Consistent with this

Scheme 1

observation, the signals at δ –14.70 and –20.71 are broaden extensively on warming to 303 K, suggesting the presence of pairwise exchange between these sites. The nonselective scrambling of all hydride ligands becomes possible only at the higher temperature, as the signal at δ –14.14, due to the third W–H–Ru hydride ligand, has turned much broader upon warming to 333 K, confirming the existence of such a higher energy process.

In summary, this paper reports the first example of transition metal clusters bearing three μ_4 -CO ligands. Two observations deserve additional comments. First, the formation of WRu_6 clusters **1a–c** is in sharp contrast to that of the condensation reactions using $\text{CpW}(\text{CO})_3\text{H}$ or $(\text{C}_5\text{Me}_5)\text{W}(\text{CO})_3\text{H}$, which gave only the tetrametallic counterparts $\text{LWRu}_4(\mu\text{-H})(\text{CO})_{12}$ ($\text{L} = \text{Cp}$ and C_5Me_5).³ The key factors leading to the formation of the WRu_6 compounds can be deduced by comparing the spectroscopic data of the substituted group 6 hydride complexes⁷ with those of their parent $\text{CpW}(\text{CO})_3\text{H}$. It suggests that the electronic effect imposed by the trimethylsilyl or isopropyl groups is minimal because the positions of their IR $\nu(\text{CO})$ absorptions and the ^1H NMR chemical shifts for hydrides are very similar. As a result, these cyclopentadienyl groups seem to exert their influence through steric interaction exclusively.¹⁰ However, this interligand repulsion is very subtle and can be depressed by removing of a CO ligand through ligand displacement.¹¹ Thus, complex **2** is available through hydrogenation of **1a**, demonstrating the elevation of such a steric interaction.

Second, the formation of the smaller, tetrametallic complex $\text{LWRu}_3(\mu\text{-H})(\text{CO})_{12}$ as the potential intermediate is also ruled out by the unsuccessful coupling experiment using $[\text{C}_5\text{H}_4(\text{CHMe}_2)]\text{WRu}_3(\mu\text{-H})(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ as reagents; the former was prepared from condensation of $\text{Ru}_3(\text{CO})_{12}$ and $[\{\text{C}_5\text{H}_4(\text{CHMe}_2)\}\text{W}(\text{CO})_3]\text{Na}$ in THF, followed by acidification.¹² Thus, the the formation of **1** occurs not via the expected step-by-step cluster building reaction

but via an unknown trimolecular coupling involving one tungsten hydride complex and two $\text{Ru}_3(\text{CO})_{12}$ molecules simultaneously.

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Supporting Information Available: Text describing experimental details and spectroscopic data for **1a–c** and **2** and tables of bond distances, atomic coordinates, and anisotropic thermal parameters for **1a** and **2** (17 pages). See any current masthead page for ordering and Internet access instructions.

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