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Synthesis and behavior in solution of the triple cubane- and windmill-type framework isomers of an organorhodium tungsten oxide cluster $[(Cp^*Rh)_4W_4O_{16}]$†

Koji Nishikawa[1], Koichi Kido[1], Jun'ichi Yoshida[1], Takanori Nishioka[1], Isamu Kinoshita[1], Brian K. Breedlove[1], Yoshihito Hayashi[2], Akira Uehara[2] and Kiyoshi Isobe[1]*

[1] Department of Material Science, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan
[2] Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

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Two geometrical isomers of a $[(Cp^*Rh)_4W_4O_{16}]$ oxide cluster, a triple cubane-type and a windmill-type, are isolated selectively from the systems of $[Cp^*Rh]^{2+}$ and $[WO_4]^{2-}$ in CH_3CN using different reaction temperatures. Both isomers, which interconvert in certain solutions, are characterized by X-ray diffraction. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: organometallic oxide; tungsten oxide cluster; cubic framework; geometrical isomers; triple cubane-type; windmill-type; isomerization

INTRODUCTION

In the organometallic oxide cluster of $[(LM)_4M'_4O_{16}]$ (LM: organometallic groups; M′: Mo, W) two types of framework, triple cubane and windmill, have been found. Only one of the two isomers has been isolated for each oxide cluster to date. The cluster of $[(Cp^*Rh)_4Mo_4O_{16}]$ and its analogues[1,2] have been obtained as the triple cubane-type isomer, whereas $[(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPrRu)_4M'_4O_{16}]$ (M′ = Mo,[2,3] W[4,5]) have been isolated as the windmill-type isomer. Recently, Proust and coworkers[4,5] presented evidence for the existence of both isomers of $[(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPrRu)_4M'_4O_{16}]$ as an equilibrium mixture in $CHCl_3$ or CH_2Cl_2 using multinuclear magnetic resonance. Here, we report the first isolation and X-ray analysis of both isomers of the tungsten cluster $[(Cp^*Rh)_4W_4O_{16}]$.

DISCUSSION

The treatment of $[Cp^*RhCl(\mu\text{-}Cl)]_2$[6] with two equivalents of $[n\text{-}Bu_4N]_2[WO_4]$[7] in CH_3CN selectively produces the two isomers of $[(Cp^*Rh)_4W_4O_{16}]$, the triple cubane- (**1**) and the windmill-type (**2**) clusters, at different reaction temperatures. Cluster $\mathbf{1}\cdot nH_2O$ (the number of the crystalline water molecules n was determined to be 3.33 by X-ray analysis) is preferentially formed when the temperature is between 0 and 20 °C in acetonitrile at approximately 60% yield. On the other hand, when the temperature is 60 °C or above, cluster **2** is selectively formed with greater than 70% yield. At temperatures between 35 and 50 °C, mixtures of $\mathbf{1}\cdot nH_2O$ and **2** are produced. Whereas $\mathbf{1}\cdot nH_2O$ is only slightly soluble in CH_3CN, anhydrous **1** (which is obtained from $\mathbf{1}\cdot nH_2O$ in CH_2Cl_2 with anhydrous Na_2SO_4) is completely soluble in CH_3CN. Cluster **2** is insoluble in CH_3CN. The fast atom bombardment mass spectra (positive) of both **1** and **2** show the molecular ions at m/z 1944 with the expected envelopes of isotopic peaks, resulting from their composition. The IR spectra in the solid state of **1** and **2** differ from each other, as shown in Fig. 1a and b respectively: ν(W–O) bands for **1** at 943(s), 898(s) and 641(m) cm^{-1}, and for **2** at 929(s), 806(s), 741(s), 586(m) and 491(m) cm^{-1}. The peak pattern of **1** is similar to that of the triple cubane-type cluster $[(Cp^*Rh)_4Mo_4O_{16}]$,[1]

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*Correspondence to: Kiyoshi Isobe, Department of Material Science, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan.
E-mail: isobe@sci.osaka-cu.ac.jp

†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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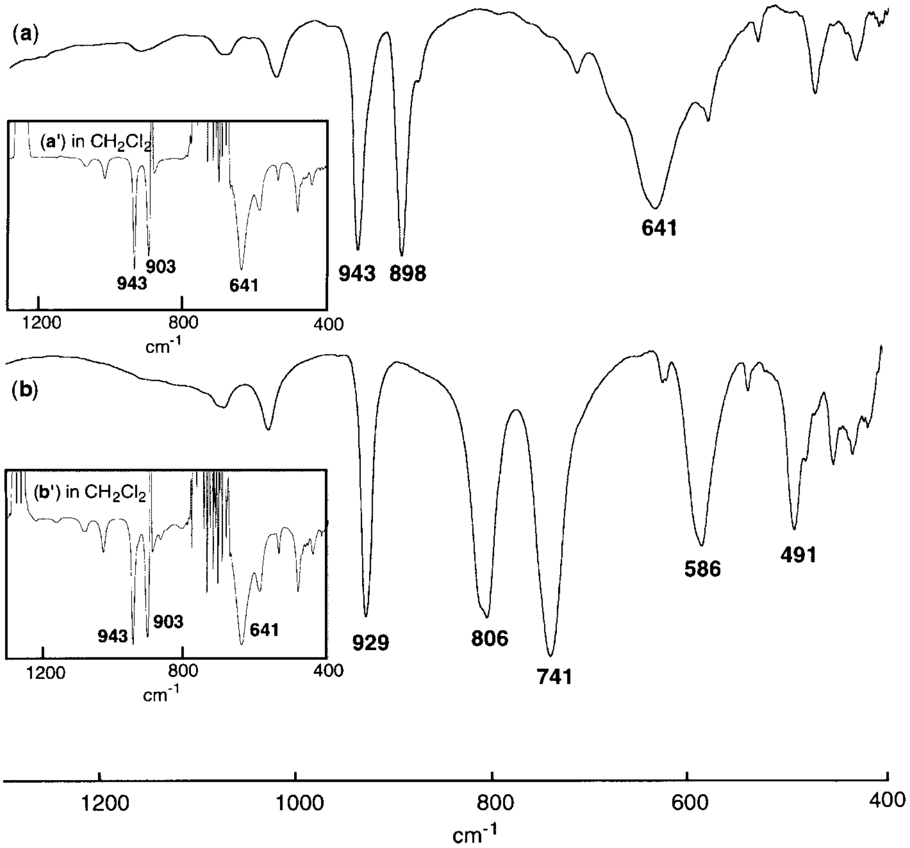

Figure 1. IR spectra of **1** (a) and **2** (b) by Nujol. Insets: IR spectra of **1** (a′) and **2** (b′) in CH_2Cl_2.

whereas the pattern of **2** is similar to that of the windmill-type clusters $[(\eta^6\text{-}p\text{-MeC}_6H_4{}^iPrRu)_4Mo_4O_{16}]$[2,3] and $[(\eta^6\text{-}p\text{-MeC}_6H_4{}^iPrRu)_4W_4O_{16}]$.[4,5]

The molecular structures of both isomers were confirmed by single-crystal X-ray analyses, shown in Fig. 2a for **1**·$n$$H_2O$ and Fig. 2b for **2**. Cluster **1** is isostructural with $[(Cp^*Rh)_4Mo_4O_{16}]$[1] and has a face-fused triple cubic framework consisting of two $Rh_2W_2O_8$ cores having S_4 symmetry. The central cube consists of W_4O_4. Each tungsten atom has a distorted octahedron with six oxygen atoms. In the cluster, there are three kinds of oxygen atom: terminal, triple bridging, and quadruple bridging. The molecular structure of **2** is similar to that of $[(\eta^6\text{-}p\text{-MeC}_6H_4{}^iPrRu)_4Mo_4O_{16}]$.[2,3] The structure consists of a central cubic core of W_4O_4 capped by four $[Cp^*Rh]^{2+}$ moieties to form a windmill-like shape. In this framework there are four chemically non-equivalent oxygen atoms: terminal, two kinds of double bridging (one is in the ladder framework of $W_2Rh_2O_4$, the other is in the plane of W_2RhO_3), and quadruple bridging. An interesting feature of **2** is that the W1–O1′ bond distance (2.366(5) Å; (there are three other equivalent W–O bonds (W1″–O1, W1*–O1″, and W1′–O1*) in **2**)), involving the quadruple bridging oxygen atoms, is the longest among the W–O bonds in **2** and **1**.

Even though heating the solid samples of **1** and **1**·$n$$H_2O$ to around 60 °C does not induce isomerization, in CH_3CN at 60 °C they quantitatively isomerize to **2**. Cluster **1** is easily solubilized in $CHCl_3$ or CH_2Cl_2. However, cluster **2** appeared to dissolve very slowly in $CHCl_3$ or CH_2Cl_2. A suspension of cluster **2** (100 mg in 30 ml of CH_2Cl_2) completely dissolved, resulting in an orange solution after stirring for approximately 20 h. The IR spectrum of the ν(W–O) absorption region for **1** in CH_2Cl_2 is similar to that in the solid state. However, the corresponding spectrum of **2** in the same solvent is different from that in the solid state, but similar to that of **1** in CH_2Cl_2. This is shown in the insets of Fig. 1, which also show that **1** in CH_2Cl_2 does not isomerize to **2**, but that **2** does isomerize to **1**. During the IR measurements, we also found that **1** is produced immediately after dissolution of **2**. Furthermore, the ^{17}O and ^1H NMR spectra indicate that, in $CHCl_3$, **1** exists in a single unchanged form and that **2** completely isomerizes to **1**. For **1** and **2**, three characteristic ^{17}O signals,[8,9] due to the triple cubane isomer, were observed (**1**: δ 679 (OW), 91 ($OWRh_2$), and 63 (OW_3Rh); **2**: δ 682 (OW), 88 ($OWRh_2$), 65 (OW_3Rh))[4,5] as well as a single ^1H signal at δ 1.76 (CH_3) for both **1** and **2**. No signals representative of **2** were observed in either $CHCl_3$ or CH_2Cl_2. Only **1** could be isolated from these solutions.

The thermodynamic stability of **1** and **2**, in solution, depends upon the solvent used. In CH_3CN, **2** is more stable than **1**. However, in $CHCl_3$ or CH_2Cl_2, **1** is more stable than **2**.

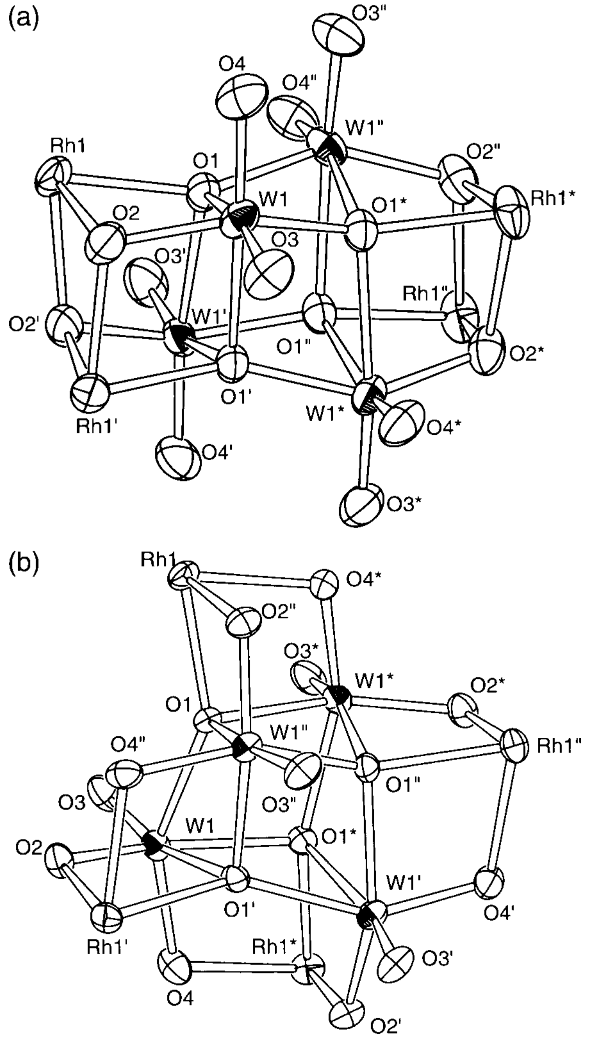

Figure 2. ORTEP drawings of the frameworks of $\mathbf{1}\cdot n\mathrm{H_2O}$ (a) and **2** (b). All Cp* rings in both clusters are omitted for clarity and the crystalline water molecules in **1** are also omitted for clarity.

Interestingly, both **1** and **2** are simultaneously obtained from a CH_3OH solution of **1** or **2** at 25 °C. The further study of the behavior of these clusters in CH_3OH is now in progress.

EXPERIMENTAL

As an example, the synthesis of $\mathbf{1}\cdot n\mathrm{H_2O}$ is presented: to a suspension of $[\mathrm{Cp^*RhCl}(\mu\text{-Cl})]_2$ (0.50 g, 0.81 mmol) in CH_3CN (5 ml) was added a solution of $[n\text{-}\mathrm{Bu_4N}]_2[\mathrm{WO_4}]$ (1.20 g, 1.60 mmol) in CH_3CN (20 ml) at 0 °C. The red suspension turned into a red solution, which formed an orange precipitate. After stirring for 6 h at 0 °C, the resulting orange solid was collected by filtration while the mixture was cold, and washed with acetonitrile and ether (yield: 0.50 g; 61.6% based on rhodium). Anal. Found C, 23.90; H, 3.36. Calc. for $\mathrm{C_{40}H_{66.67}O_{19.33}Rh_4W_4}$ ($\mathbf{1}\cdot 3.33\mathrm{H_2O}$): C, 23.97; H, 3.35%. At 60 °C cluster **2** was similarly prepared in CH_3CN in 73.4% yield. Anal. Found: C, 24.70; H, 3.09. Calc. for $\mathrm{C_{40}H_{60}O_{16}Rh_4W_4}$ (**2**): C, 24.72; H, 3.11%.

CRYSTALLOGRAPHY

For $\mathbf{1}\cdot 3.33\mathrm{H_2O}$ (MW: 2003.98), orange, prism, $0.20 \times 0.15 \times 0.10\ \mathrm{mm}^3$, cubic, space group $I\bar{4}3d$, $a = 25.255(5)$ Å, $V = 16\,108.2(6)$ Å^3, $Z = 4$, $D_c = 2.48\ \mathrm{g\ cm^{-3}}$, $F(000) = 11\,248.00$, $T = 193$ K, Rigaku/MSC Mercury CCD, Mo Kα radiation ($\lambda = 0.7107$ Å), $\mu = 98.03\ \mathrm{cm^{-1}}$, ω-scans, 2θ range $2\theta \leq 55.2°$, 3083 observed reflections; residuals: R_1 (0.034), wR_2 (0.078), $I > 2.00\sigma(I)$, 157 refined parameters, structure solution by directed methods (SIR92).

For **2** (MW: 1944.93), orange, platelet, $0.20 \times 0.20 \times 0.10\ \mathrm{mm}^3$, tetragonal, space group $I\bar{4}$, $a = 12.959(2)$ Å, $c = 14.741(3)$ Å, $V = 2475.3(7)$ Å^3, $Z = 2$, $D_c = 2.61\ \mathrm{g\ cm^{-3}}$, $F(000) = 1808.00$, $T = 193$ K, Rigaku/MSC Mercury CCD, Mo Kα radiation ($\lambda = 0.7107$ Å), $\mu = 106.23\ \mathrm{cm^{-1}}$, ω-scans, 2θ range $2\theta \leq 55.0°$, 2760 observed reflections; residuals: R_1 (0.028), wR_2 (0.069), $I > 2.00\sigma(I)$, 145 refined parameters, structure solution by directed methods (SIR92).

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