doi:10.1246/cl.2010.130

Published on the web January 16, 2010

An Acid-stable Organoruthenium Complex Suitable as a Bidentate Building Block

Chunbai Zheng,[1] Daisuke Inoki,[1] Takahiro Matsumoto,[1,2] and Seiji Ogo*[1,2]
[1]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395*
[2]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi 332-0012*

(Received November 17, 2009; CL-091016; E-mail: ogotcm@mail.cstm.kyushu-u.ac.jp)

A new, water-soluble organoruthenium(II) sulfato complex $[Ru^{II}(SO_4)(Bz^py)]$ {**1**, Bz^py = 2-(pentamethylbenzyl)pyridine} has been synthesized and is stable at pH from 2.0 to 8.0. This complex has a bidentate sulfato ligand as a leaving group and is a good building block for "*concerto* catalysis": a new way of thinking in catalysis that bridges hetero- and homogeneous catalysis.

The conceptual slicing of heterogeneous catalysts (e.g., polyoxometalate) into smaller, minimal fragments is a useful tool for designing relatively small, homogeneous catalysis (Figure 1a). These smaller molecules should have the catalytic properties of the bulk, solid-phase catalyst but have the ease of handling of homogeneous, soluble catalysts. Such an approach to cut a polyoxometalate into the corresponding simple organometallic oxide cluster, introduced by Isobe and co-workers,[1] Klemperer and co-workers,[2] and Finke and co-workers,[3] is the basis of the field of "*concerto* catalysis".[4]

This theoretical cutting up of the bulk-phase catalyst indicates useful starting points for the actual synthesis of soluble molecules. The catalyst can be "cut" into theoretical building blocks, which can then be realized in the laboratory. Joining these building blocks together should then enable researchers to construct large molecules capable of bridging the gap between hetero- and homogeneous catalysis.

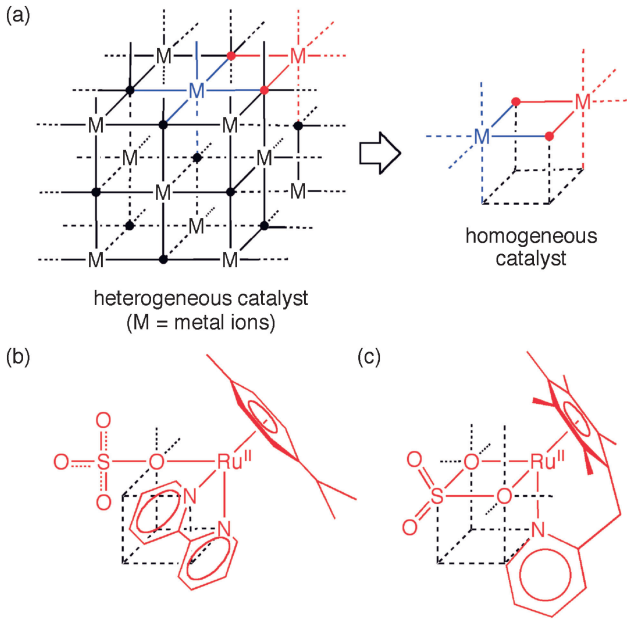

Figure 1. (a) Methodology to cut a block of heterogeneous catalyst into the corresponding simple homogeneous catalyst. (b) $[Ru^{II}(SO_4)$-(*p*-cymene)(bpy)] (bpy = 2,2′-bipyridine). (c) $[Ru^{II}(SO_4)(Bz^py)]$ {**1**, Bz^py = 2-(pentamethylbenzyl)pyridine}.

There are, however, a number of practical problems with the subsequent realization of metal clusters. First, the small building blocks are not very robust over a wide range of chemical conditions and decompose easily in acid, for example. In addition, the larger, multiunit molecules soon become insoluble in water.

Schlaf and co-workers reported the synthesis and crystal structure of a water-soluble, acid-stable Ru complex (Figure 1b).[5] This complex uses a monodentate sulfato ligand to stabilize the complex in acidic media, which confers both solubility and stability in H_2SO_4 solutions.[6]

In our laboratory, we have managed to develop many kinds of water-soluble, organometallic (Ru-, Rh-, Ir-, and Pd-based) complexes with one or more aqua ligands.[7] Even so, there are still few examples that are robust in acidic media, such as sulfuric acid.

To address these problems, we have constructed an acid-stable, water-soluble complex suitable for building up Ru-based metal clusters. The synthesis and characterization of this complex $[Ru^{II}(SO_4)(Bz^py)]$ {**1**, Bz^py = 2-(pentamethylbenzyl)-pyridine} (Figure 1c) are described herein. This complex has a bidentate leaving group, thus allowing it to form a good starting point for building *concerto* catalysts. In addition, the complex is both water-soluble and stable over a range of pH from 2.0 to 8.0.

The water-soluble, acid-stable organoruthenium(II) sulfato complex **1** was synthesized by the reaction of a dichloro Ru^{II} complex $[Ru^{II}Cl_2(Bz^py)]$[8] with Ag_2SO_4 in water at pH 7.0 at 25 °C (see Supporting Information).[9] The structure of **1** was determined by X-ray analysis (Figure 2).[10] Complex **1** adopts a distorted octahedral coordination with two perpendicular planes {the torsion angle between the least-squares plane of η^6-C_6Me_5 and that of NC_5H_4 is 88.50(8)°} as a result of the formation of the expected Ru^{II}–(η^6-C_6Me_5) and Ru^{II}–(NC_5H_4) bonds.

The sulfato Ru^{II} complex **1** was characterized by electrospray ionization mass spectrometry (ESI-MS) and IR and ^{1}H NMR spectroscopy.

A positive-ion ESI mass spectrum of **1** in water at pH 2.0 is consistent with the above formulation and mononuclearity (Figure 3a). A prominent signal at m/z 460.2 {relative intensity (I) = 100% in the range of m/z 200–1000} has a characteristic isotopic distribution (Figure 3b) that matches well with the calculated isotopic distribution for $[\mathbf{1} + Na]^+$ (Figure 3c).

The IR spectrum of **1** in the solid state shows a band at 1132 cm^{-1}, derived from the coordinated SO_4^{2-} in **1** (Figure S1 in Supporting Information).[9] The IR spectrum of an aqueous solution of **1** showed a band at 1100 cm^{-1}, responsible for the

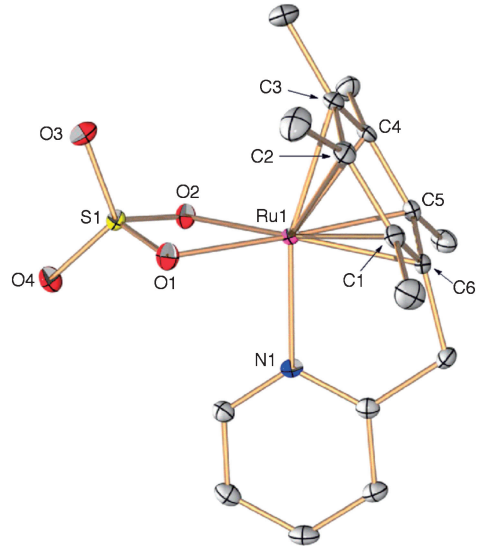

Figure 2. An ORTEP drawing of **1** with ellipsoids at 50% probability. The solvent (CH_2Cl_2) and the hydrogen atoms are omitted for clarity. Selected bond lengths (l/Å) and angles (ϕ/degree) as well as interatomic distance: Ru1–C1 = 2.170(2), Ru1–C2 = 2.157(2), Ru1–C3 = 2.212(2), Ru1–C4 = 2.196(2), Ru1–C5 = 2.184(2), Ru1–C6 = 2.101(2), Ru1–N1 = 2.133(2), Ru1–O1 = 2.130(2), Ru1–O2 = 2.126(2), O1–Ru1–O2 = 66.75(6), Ru1–O1–S1 = 95.47(8), Ru1–O2–S1 = 95.70(8), O1–S1–O2 = 100.08(9).

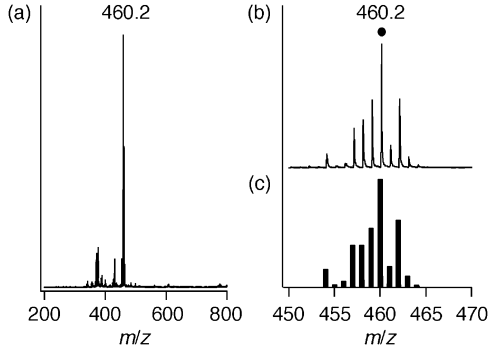

Figure 3. (a) Positive-ion ESI mass spectrum of **1** in water at pH 2.0, which was prepared by addition of Na^+ to an aqueous solution of **1**. (b) The signal at m/z 460.2 corresponds to $[\mathbf{1} + Na]^+$. (c) Calculated isotopic distribution for $[\mathbf{1} + Na]^+$.

coordination of SO_4^{2-} and is observed at pH 2.0–8.0 (Figures 4 and S2).[9]

It is confirmed by ^{1}H NMR that the structure of **1** remains at pD 2.0–8.0 (Figure S3).[9] The spectrum of **1** in D_2O at pD 2.0 shows the signals at 7.23–8.10 ppm corresponding to the pyridine protons of the Bz^py ligand; the signals observed at 4.53 ppm originate from the methylene group of the Bz^py ligand; the signals at 2.14–2.28 ppm arise the $C_6(CH_3)_5$ group of the Bz^py ligand.

In conclusion, **1** is not only stable in acid but also has two potentially vacant sites, factors which have two significant consequences. First, we can now increase the range of pH in which we can perform our chemistry, opening up a range of synthetic and mechanistic possibilities. Second, we can use the vacant sites as starting points for building up large frameworks

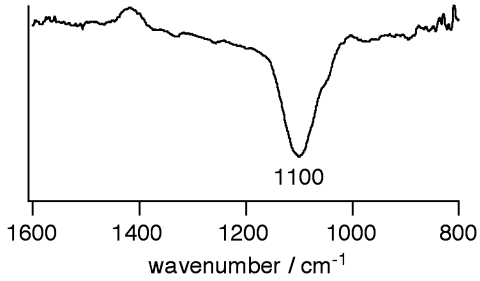

Figure 4. IR spectrum of **1** in water at pH 2.0.

of catalytic building blocks, an essential requirement for its use in *concerto* catalysis.

We thank Dr. Yuichi Kaneko for the synthesis of the Bz^py ligand. This work was supported by Grants-in-Aid: Nos. 17350027, 17655027, 18033041, and 18065017 (Chemistry of *Concerto* Catalysis), the Global COE Program, "Science for Future Molecular Systems" from the Ministry of Education, Culture, Sports, Science and Technology, Japan and the Basic Research Programs CREST Type, "Development of the Foundation for Nano-Interface Technology" from JST, Japan.

Dedicated to Prof. Kiyoshi Isobe on the occasion of his 65th birthday.

References and Notes

1 a) K. Isobe, A. Yagasaki, *Acc. Chem. Res.* **1993**, *26*, 524. b) Y. Do, X.-Z. You, C. Zhang, Y. Ozawa, K. Isobe, *J. Am. Chem. Soc.* **1991**, *113*, 5892.
2 a) H. K. Chae, W. G. Klemperer, T. A. Marquart, *Coord. Chem. Rev.* **1993**, *128*, 209. b) V. W. Day, W. G. Klemperer, *Science* **1985**, *228*, 533.
3 a) L. S. Ott, R. G. Finke, *Coord. Chem. Rev.* **2007**, *251*, 1075. b) R. G. Finke, S. Özkar, *Coord. Chem. Rev.* **2004**, *248*, 135.
4 The priority area "Chemistry of *Concerto* Catalysis" Web site, http://concerto.cstm.kyushu-u.ac.jp.
5 R. R. Dykeman, K. L. Luska, M. E. Thibault, M. D. Jones, M. Schlaf, M. Khanfar, N. J. Taylor, J. F. Britten, L. Harrington, *J. Mol. Catal. A: Chem.* **2007**, *277*, 233.
6 F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons, Inc., New York, **1999**, pp. 492–494.
7 a) H. Hayashi, S. Ogo, T. Abura, S. Fukuzumi, *J. Am. Chem. Soc.* **2003**, *125*, 14266. b) S. Ogo, H. Nishida, H. Hayashi, Y. Murata, S. Fukuzumi, *Organometallics* **2005**, *24*, 4816. c) S. Ogo, H. Nakai, Y. Watanabe, *J. Am. Chem. Soc.* **2002**, *124*, 597. d) S. Ogo, K. Uehara, T. Abuta, Y. Watanabe, S. Fukuzumi, *J. Am. Chem. Soc.* **2004**, *126*, 16520. e) H. Kanemitsu, K. Uehara, S. Fukuzumi, S. Ogo, *J. Am. Chem. Soc.* **2008**, *130*, 17141. f) S. Ogo, Y. Takebe, K. Uehara, T. Yamazaki, H. Nakai, Y. Watanabe, S. Fukuzumi, *Organometallics* **2006**, *25*, 331.
8 The details of $[Ru^{II}Cl_2(Bz^py)]$ will be reported elsewhere in a full paper.
9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
10 The crystal data for **1** have been deposited with Cambridge Crystallographic Data Center as a supplementary publication No. CCDC-753964.

