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A Neutral Five-coordinated Organoruthenium(0) Complex: X-ray Structure and Unique Solvatochromism

Kihun Jeong,[1] Harutaka Nakamori,[1,2] Shunsuke Imai,[2] Takahiro Matsumoto,[1,4] Seiji Ogo,*[1,3,4] and Hidetaka Nakai*[1,2,4]
[1]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,*
744 Moto-oka, Nishi-ku, Fukuoka 819-0395
[2]*Department of Chemistry, Graduate School of Natural Science and Technology, Kanazawa University,*
Kakuma-machi, Kanazawa, Ishikawa 920-1192
[3]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST),*
Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012
[4]*International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University,*
744 Moto-oka, Nishi-ku, Fukuoka 819-0395

(Received April 2, 2012; CL-120280; E-mail: nakai@mail.cstm.kyushu-u.ac.jp)

The structure of a neutral five-coordinated organoruthenium(0) complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}^0(\text{bpy})]$ (**1**, bpy: 2,2′-bipyridine) was determined by X-ray diffraction analysis. The solvent-induced reversible color change based on the interconversion between the purple Ru^0 complex **1** and a yellow Ru^{II}–hydride complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}^{\text{II}}(\text{bpy})\text{H}]^+$ is presented.

Five-coordinated d^8 metal complexes of the general composition $[(\pi\text{-arene})\text{M}(\alpha\text{-diimine})]^n$ ($\text{M} = \text{Ru}^0$, Os^0, Rh^{I}, Ir^{I}, etc.; *n*: charge of the complex) have received a great deal of attention because of their unique electronic structures and reactivities (Figure 1a).[1,2] For instance, the neutral Ir^{I} complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{I}}(\text{bpy})]$ (bpy: 2,2′-bipyridine) is known as a key intermediate in photocatalytic reactions.[1c,2] However, the studies on the five-coordinated d^8 metal complexes are limited because of their troublesome synthesis and instability.

With regard to the neutral Ru^0 complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}^0(\text{bpy})]$ (**1**), the isolation and preliminary characterization were reported by Kaim and co-workers in 1994.[3] However, this attractive complex has not been further characterized including X-ray diffraction analysis. During our study, we have successfully determined the X-ray structure of **1**. Furthermore, we have intriguingly found that, by dissolving **1** in MeOH, the purple Ru^0 complex **1** converts to a known yellow Ru^{II}–hydride complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}^{\text{II}}(\text{bpy})\text{H}]^+$ (**2**).[4] Removal of the solvent (MeOH) in vacuo leads to regeneration of **1** (Figure 1b). Herein we report the X-ray structure of **1** and unique solvatochromism between **1** and **2**.

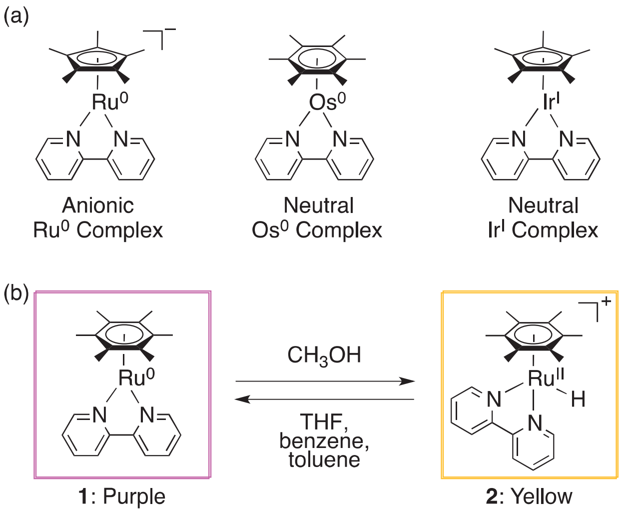

Figure 1. (a) Typical five-coordinated d^8 metal complexes, $[(\pi\text{-arene})\text{M}(\alpha\text{-diimine})]^n$. (b) Solvent-induced reversible conversion between the neutral Ru^0 complex **1** and the cationic Ru^{II}–hydride complex **2**.

The neutral five-coordinated Ru^0 complex **1** was prepared by a modified literature method via reduction of the Ru^{II}–chloro complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}^{\text{II}}(\text{bpy})\text{Cl}](\text{Cl})$[5] with sodium metal in THF at room temperature.[6] Whereas X-ray structures of an anionic Ru^0 complex and neutral Fe^0, Co^{I}, and Ir^{I} complexes for the five-coordinated d^8 metal complexes are known,[1] to the best of our knowledge, no X-ray structures of the corresponding neutral Ru^0 complexes have been reported so far. Fortunately, purple crystals of the neutral Ru^0 complex **1** suitable for X-ray diffraction analysis were grown from a saturated THF solution at −20 °C.

The structure of **1** is depicted in Figure 2, along with selected interatomic data.[6,7] The Ru^0 atom of **1** has a five-coordinate environment. The $\text{Ru–C}(\eta^6\text{-C}_6\text{Me}_6)_{\text{ring}}$ and Ru–N distances are $2.230(6)_{(\text{av.})}$ and $2.022(2)_{(\text{av.})}$ Å, respectively. The Ru1–N1–C17, Ru1–N2–C18, and N1–Ru1–N2 angles are 117.3(3), 116.8(3) and 77.68(17)°, respectively. The interplanar angle between the plane containing N1, Ru1, and N2 and the

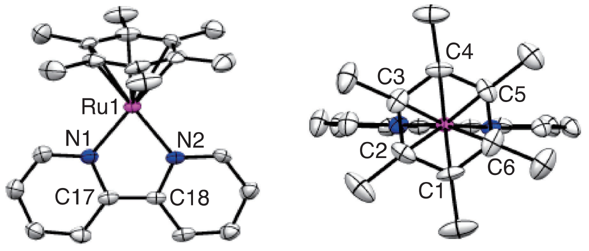

Figure 2. ORTEP drawing of **1** with 50% probability ellipsoids. Front view (left) and top view (right). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): $\text{Ru1–C}(\eta^6\text{-C}_6\text{Me}_6)_{\text{ring}}$ average: 2.230(6), Ru1–C1 = 2.211(5), Ru1–C2 = 2.225(6), Ru1–C3 = 2.242(5), Ru1–C4 = 2.236(5), Ru1–C5 = 2.235(5), Ru1–C6 = 2.232(6), Ru1–N1 = 2.024(4), Ru1–N2 = 2.020(4), C17–C18 = 1.399(7), Ru1–N1–C17 = 117.3(3), Ru1–N2–C18 = 116.8(3), N1–Ru1–N2 = 77.68(17), N1–C17–C18–N2 = 3.4(6).

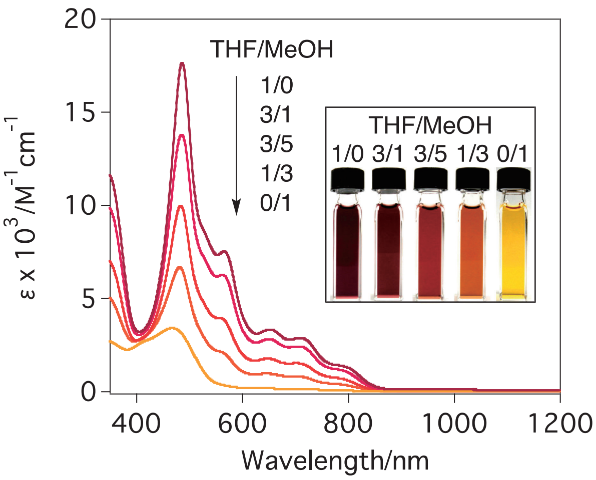

Figure 3. Change in the UV–vis–NIR absorption spectra of **1** (2.38×10^{-4} M) in THF, MeOH, and THF–MeOH mixed solvents with various THF/MeOH ratios (3/1, 3/5, and 1/3), together with photographs of the solutions (2.38×10^{-4} M).

$(C_6Me_6)_{ring}$ plane is 89.76°. These structural features, except for the Ru–C_{ring} distance, are similar to those found in the *anionic* Ru^0 complex $[(\eta^5\text{-}C_5Me_5)Ru^0(bpy)]^-$ which has Ru–C(η^5-C_5Me_5)$_{ring}$ distance of 2.161(7)$_{(av.)}$ Å.[1a] Notably, the coordinated bpy in **1** has a short C–C bond length of 1.399(7) Å between the pyridine moieties,[8] which is structural evidence for the ligand (bpy) reduction found in the structurally related $[(\eta^5\text{-}C_5Me_5)Ru^0(bpy)]^-$ (1.413(1) and 1.401(9) Å),[1a] $[(\eta^5\text{-}C_5Me_5)Co^I(bpy)]$ (1.419(3) Å),[1b] and $[(\eta^6\text{-}C_6H_4CH_3)Fe^0(bpy)]$ (1.417(3) Å).[1e]

Figure 3 displays the UV–vis–NIR absorption spectra of **1** (2.38×10^{-4} M) in THF, MeOH, and THF–MeOH mixed solvents with various THF/MeOH ratios (3/1, 3/5, and 1/3), together with photographs of the solutions (2.38×10^{-4} M). The color of **1** in THF, benzene, and toluene is purple which is the same color of **1** in the solid state (Figure S1).[6] Intriguingly, the color of **1** changes from purple to yellow on dissolving in MeOH. In order to find out the mechanism of this observation, the yellow solution was characterized by ^{1}H NMR and UV–vis–NIR spectroscopy. As a result, it was found that the yellow color comes from the formation of the Ru^{II}–hydride complex **2** in MeOH (Figure S2).[4,6] Removal of the solvent (MeOH) in vacuo leads to the purple solid of **1** being reformed. The color of the solution reversibly changes with changing the ratio of THF/MeOH. Thus, the solvatochromism based on the reversible conversion between the purple Ru^0 complex **1** and the yellow Ru^{II}–hydride complex **2** was observed.[9] This is a unique example for inorganic solvatochromism, since the solvatochromism of transition-metal complexes usually results from (i) coordination by the solvent onto the reactive metal center or (ii) interaction of the solvent with the ligand.[10]

It is noteworthy that the color of **1** (2.38×10^{-4} M) in EtOH is not yellow but red: the UV–vis–NIR spectrum of **1** in EtOH ($\varepsilon = 9200$ at 482 nm) is similar to that of **1** in THF/MeOH = 3/5 ($\varepsilon = 10000$ at 484 nm) (Figure S3).[6] This can be explained by the proton donor ability of the solvent: the pK_a values of MeOH and EtOH are 15.5 and 15.9, respectively.[11] As a consequence, an equilibrium between purple **1** and yellow **2** in EtOH more inclines toward **1** than that in MeOH, which shows red color.[12] Thus, in the solvatochromic system of **1**, the pK_a value of the solvent is one of the crucial factors to decide the color of the solution.

In conclusion, we have structurally characterized the neutral five-coordinated Ru^0 complex. This study constitutes the first X-ray structural determination of a $[(\eta^6\text{-}C_6Me_6)Ru^0(\alpha\text{-diimine})]$ complex. In addition, we have demonstrated the unique solvatochromism based on the reversible conversion between Ru^0 and Ru^{II}–hydride complexes. Stimuli-responsive compounds are of interest in wide areas of chemistry. We believe that our findings offer attractive new insight into the construction of novel switching devices, materials, and catalysts by organometallic compounds.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

7 Crystal data for **1**: $C_{22}H_{26}N_2Ru$, $M_r = 419.53$, orthorombic, $a = 9.059(5)$ Å, $b = 18.205(11)$ Å, $c = 21.953(13)$ Å, $V = 3621(4)$ Å^3, $T = 93 \pm 1$ K, space group *Pbca*, $Z = 8$, 25169 reflections measured, 4123 independent reflections ($R_{int} = 0.057$), $R_1 = 0.0699$ [$I > 2\sigma(I)$], $wR_2 = 0.1774$ (all data), GOF = 1.024. CCDC number CCDC 873615.

8 The uncoordinated bpy has the C–C bond length of 1.490(3) Å: M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress, W. H. Woodruff, *J. Am. Chem. Soc.* **1981**, *103*, 4945.

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12 The ^{1}H NMR spectrum of **1** in C_6D_6–CD_3OH (5:1) mixed solvent shows the signals from both **1** and **2** (Figure S4).