



A mixed-valence dinuclear ruthenium complex composed of Ru(II)-acetylide and Ru(III)-tropolonato units: Acetylide–vinylidene interconversion in solution and solid state

Jun Yoshida*, Kyohei Kuwahara, Hidetaka Yuge

Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Minami-ku, Sagami-hara, Kanagawa 252-0329, Japan

ARTICLE INFO

Article history:

Received 17 December 2013

Received in revised form

6 January 2014

Accepted 17 January 2014

Keywords:

Ruthenium

Acetylide

Vinylidene

Protonation/deprotonation

Mixed-valence

Mechanochemical reaction

ABSTRACT

A dinuclear Ru(II)–Ru(III) complex, $[\text{Ru}(\text{acac})_2(\mu_2\text{-tropC}_2)\text{RuCp}(\text{dppe})]$ (**2a**, acac = acetylacetonato, Cp = cyclopentadienyl, dppe = 1,2-bis(diphenylphosphino)ethane, HtropC₂H = 5-acetylenyltropolone), has been newly synthesized and fully characterized. **2a** is composed of two hetero units, $[\text{Ru}^{\text{II}}\text{Cp}(\text{dppe})]$ and $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{trop})]$, and it showed a broad absorption in the NIR region, indicating the electronic communication between the two hetero units. **2a** quantitatively converted to the vinylidene form $[\mathbf{2aH}](\text{TsO})$ by the addition of p-toluenesulfonic acid monohydrate (TsOH·H₂O) to the chloroform solution of **2a**. The weak NIR absorption exhibited by **2a** disappeared in $[\mathbf{2aH}](\text{TsO})$. $[\mathbf{2aH}](\text{TsO})$ re-converted to the acetylide **2a** after the addition of triethylamine to the acetonitrile solution of $[\mathbf{2aH}](\text{TsO})$. ¹H NMR and UV–vis–NIR spectroscopy indicated the mutual interconversion and on/off behavior of the electronic communication between the two hetero units. Moreover, structural interconversion also proceeded in the solid state. **2a** swiftly converted to $[\mathbf{2aH}](\text{TsO})$ after grinding with solid TsOH·H₂O for 5 min. The conversion yield estimated from IR measurements was 70%. $[\mathbf{2aH}](\text{TsO})$ re-converted to **2a** after re-grinding with AcONa with a conversion yield of 84%. These results indicate the usability of **2a** as a molecular switch triggered by protonation/deprotonation both in solution and solid state.

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1. Introduction

Reversible response to protonation/deprotonation in organic and inorganic compounds is a simple but important approach for regulating structural and electronic properties [1]. The RuCp-acetylide (Cp = cyclopentadienyl) complex is one of the representative compounds that exhibits drastic structural and electronic changes upon protonation/deprotonation [2]; $[\text{RuCp}(\text{dppe})(\text{PhC}_2)]$ (dppe = 1,2-bis(diphenylphosphino)ethane, PhC₂H = phenylacetylene, Scheme 1) exhibits yellow color, while its protonated vinylidene form exhibits orange color. For example, the RuCp-acetylide complex has been used as a unit for switching nonlinear optical properties in response to protonation/deprotonation [3].

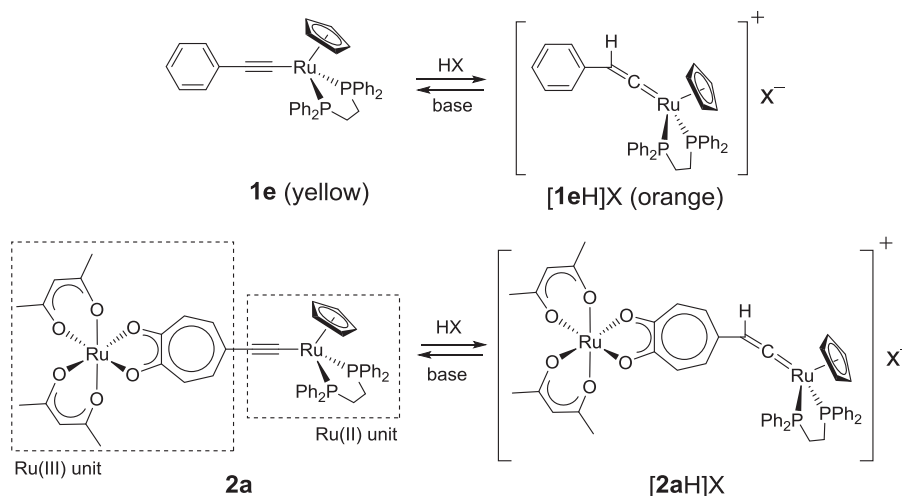
The conjugation of the RuCp-acetylide with other organometallic or transition metal compounds are also of great interest in terms of mixed-valence state, redox chemistry, electron-transfer, molecular wires, and nonlinear optical properties [3–5]. In

general, mixed-valence metal complexes, which change their characteristic electronic properties, such as NIR absorption, upon protonation/deprotonation, are attractive as molecular switches [6]. The acetylide–vinylidene structural conversion may also be utilized as a switch to turn intermetallic interactions on and off in mixed valence complexes. However, responsibility to protonation/deprotonation in di- or poly-nuclear complexes with RuCp-acetylide units has not been investigated and utilized. To date, $[\text{RuCp}(\text{PPh}_3)_2]$ connected with ruthenocene has been reported to exhibit intermetallic interactions in its *in situ* oxidized form [5]. Moreover, the conversion of the oxidized acetylide form to the vinylidene form was realized at –78 °C, while the reverse reaction to the acetylide form was not reported. The need of both *in situ* oxidation and protonation/deprotonation might make it difficult to establish a mixed valence complex with switching capability.

In this study, we report a new mixed valence diruthenium complex, $[\text{Ru}(\text{acac})_2(\mu_2\text{-tropC}_2)\text{RuCp}(\text{dppe})]$ (**2a**, acac = acetylacetonato, HtropC₂H = 5-acetylenyltropolone), which is composed of two hetero units with different valences, $[\text{Ru}^{\text{II}}\text{Cp}(\text{dppe})]$ and $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{trop})]$ (Htrop = tropolone). We expected the electronic communication between the two hetero units in the stationary state; we also expected the on/off behavior of this interaction to be

* Corresponding author. Tel.: +81 42 778 7980; fax: +81 42 778 9953.

E-mail addresses: yoshidaj@kitasato-u.ac.jp, yoshidajun.nasa@gmail.com (J. Yoshida).



Scheme 1. Acetylide–vinylidene interconversion in $[\text{RuCp}(\text{dppe})(\text{PhC}_2)]$ and **2a**.

triggered by protonation/deprotonation. In fact, **2a** showed a broad absorption in the NIR region in a chloroform solution, which indicates the electronic communication between the two hetero units, while the absorption peak disappeared upon conversion to the vinylidene form **[2aH](TsO)** ($\text{TsOH} = p$ -toluenesulfonic acid) (Scheme 1). The reversible acetylide–vinylidene structural conversion of **2a** was fully characterized in solution by UV–vis–NIR and ^1H NMR measurements. Then, we also examined the conversion of **2a** in the solid state by simply grinding it with solid $\text{TsOH}\cdot\text{H}_2\text{O}$ or sodium acetate as protonation and deprotonation sources, respectively. The response capability to external stimuli in the solid state is useful for applications as a molecular switch, gate, and in devices [7]. IR measurements clarified that the structural interconversion of **2a** proceeded even in the solid state.

2. Results and discussion

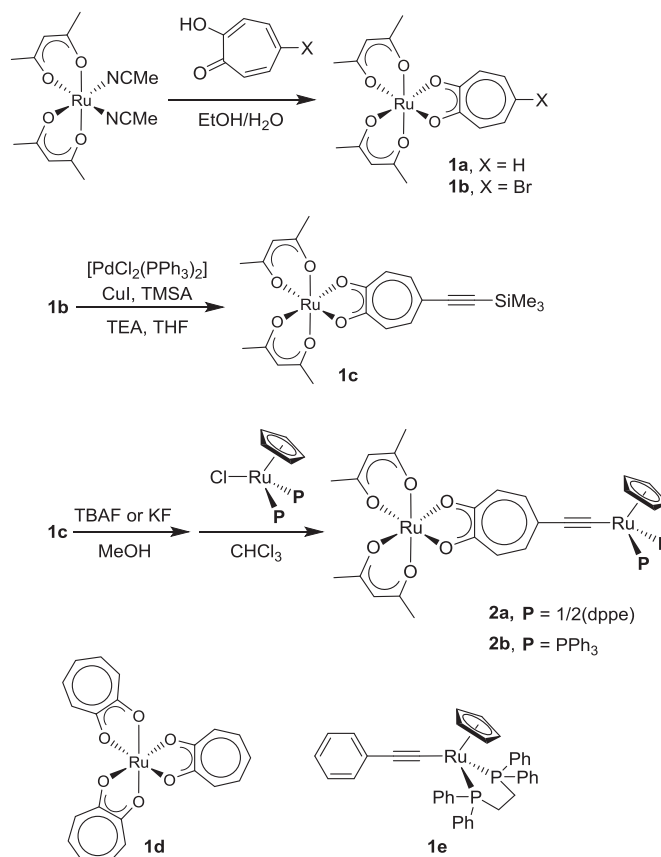
2.1. Synthesis and characterization

In the design of **2a**, we selected $[\text{Ru}(\text{acac})_2(\text{tropC}_2)]$ as a Ru^{III} unit conjugated with $\text{Ru}^{\text{II}}\text{Cp}$ -acetylide. We expected the electronic communication between the two ruthenium centers in **2a** through the alkyne and aromatic tropolone ring, where the latter is known as an acetylacetonate analog. Long-range electronic communication has already been reported between the two metal centers in tris(β -diketonato) $\text{Ru}(\text{III})$ complexes bridged by di-alkynes [8]. The overall synthetic procedure of **2a** is outlined in Scheme 2. For comparison, $[\text{Ru}(\text{acac})_2(\text{trop})]$ (**1a**), $[\text{Ru}(\text{acac})_2(\text{Brtrop})]$ (**1b**, $\text{HBrtrop} = 5$ -bromotropolone) in 80% and 90% yields, respectively. The palladium-catalyzed alkylation of **1b** with trimethylsilylacetylene (TMSA) under Sonogashira coupling conditions afforded $[\text{Ru}(\text{acac})_2(\text{tropC}_2\text{SiMe}_3)]$ (**1c**) in 90% yield [9]. The deprotection of the TMS group and following reaction with $[\text{RuCp}(\text{dppe})\text{Cl}]$ or $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$ proceeded in one pot and afforded $[\text{Ru}(\text{acac})_2(\text{tropC}_2)\text{RuCp}(\text{dppe})]$ (**2a**) and $[\text{Ru}(\text{acac})_2(\text{tropC}_2)\text{RuCp}(\text{PPh}_3)_2]$ (**2b**) with 80% and 57% yields, respectively. The newly synthesized complexes (**1a**, **1b**, **1c**, **2a**, and **2b**) were characterized by ^1H NMR, ESI-MS, and elemental analyses.

The treatment of $\text{cis-}[\text{Ru}(\text{acac})_2(\text{acetonitrile})_2]$ with tropolone and 5-bromotropolone afforded $[\text{Ru}(\text{acac})_2(\text{trop})]$ (**1a**) and $[\text{Ru}(\text{acac})_2(\text{Brtrop})]$ (**1b**, $\text{HBrtrop} = 5$ -bromotropolone) in 80% and 90% yields, respectively. The palladium-catalyzed alkylation of **1b** with trimethylsilylacetylene (TMSA) under Sonogashira coupling conditions afforded $[\text{Ru}(\text{acac})_2(\text{tropC}_2\text{SiMe}_3)]$ (**1c**) in 90% yield [9]. The deprotection of the TMS group and following reaction with $[\text{RuCp}(\text{dppe})\text{Cl}]$ or $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$ proceeded in one pot and afforded $[\text{Ru}(\text{acac})_2(\text{tropC}_2)\text{RuCp}(\text{dppe})]$ (**2a**) and $[\text{Ru}(\text{acac})_2(\text{tropC}_2)\text{RuCp}(\text{PPh}_3)_2]$ (**2b**) with 80% and 57% yields, respectively. The newly synthesized complexes (**1a**, **1b**, **1c**, **2a**, and **2b**) were characterized by ^1H NMR, ESI-MS, and elemental analyses.

2a and **2b** exhibited similar UV–vis–NIR spectra with relatively strong absorptions with peaks at 591 and 464 nm and broad

absorptions around 800–1000 nm in a chloroform solution (Fig. 1). In contrast, **1c** and **1e**, corresponding to the building components of **2a** and **2b**, respectively, did not show explicit absorption at wavelengths greater than 600 nm (Fig. 1). Therefore, the absorptions of **2a** and **2b** in the NIR region indicate the electronic communication between the two hetero units and weak delocalization of the mixed valence. Following ^1H NMR and CV measurements also indicated the presence of intermetallic interaction. On the other hand, **2a** and **2b** did not show much difference in their spectroscopic properties.



Scheme 2. Synthetic procedure of the ruthenium complexes investigated in this study.

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