



# Synthesis and reactivity of hydride-bridged ruthenium dithiolene complexes



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## ARTICLE INFO

### Article history:

Received 8 August 2017

Accepted 17 October 2017

Available online 27 October 2017

### Keywords:

Metalladithiolene complex

Ruthenium

Hydride

Carbon monoxide

Carbon dioxide

## ABSTRACT

Syntheses of two homonuclear hydride complexes, viz. hydride-bridged ruthenium dinuclear complex  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{S}_2\text{C}_6\text{H}_4)\text{RuClH}(\text{PPh}_3)_2]$  (**3**) and dihydride ruthenium dinuclear complex  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{S}_2\text{C}_6\text{H}_4)\text{RuH}_2(\text{PPh}_3)_2]$  (**4**), have been described. Complex **4** was obtained as a mixture of *cis*- and *trans*-dihydride isomers in a 10:1 M ratio, as indicated by the proton ratio in  $^1\text{H}$  NMR spectra. The dinuclear complex **4** reacted with carbon monoxide for 30 min and 1 day under similar conditions to produce dicarbonyl complex  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{S}_2\text{C}_6\text{H}_4)\text{Ru}(\text{CO})_2(\text{PPh}_3)]$  (**5**), and tetracarbonyl complex  $[\text{Ru}_2(\text{CO})_4(\text{PPh}_3)_2(\text{S}_2\text{C}_6\text{H}_4)]$  (**6**), respectively. On the other hand, treatment of **4** with carbon dioxide under ambient conditions was found to produce formic acid.

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## 1. Introduction

Transition metal hydride complexes have constituted a fascinating and active area of research for several decades owing to their unique reactivity in insertion and metathesis reactions [1–6]. Among these transition metals, sulfur-bridged group 8 bimetallic complexes with hydride ligands exhibit unique structure, and remarkable catalytic activity and reactivity with various chemical species [6–8]. For example, propanedithiolate and hydride-bridged ruthenium complex  $[\text{Ru}_2(\text{S}_2\text{C}_3\text{H}_6)(\mu\text{-H})(\text{H})(\text{CO})_3(\text{PCy}_3)_2]$  is reported to be a structure and reactivity based model for the Fe-only hydrogenase active site [7]. Holland and coworkers synthesized an iron sulfide complex with a bridging hydride  $[\text{NaCrypt-2.2.2}][\text{L}^{\text{Me}}\text{Fe}(\mu\text{-H})(\mu\text{-S})\text{FeL}^{\text{Me}}]$ , where  $\text{L}^{\text{Me}}$  is a bulky  $\beta$ -diketiminato ligand, which reacts with  $\text{CO}_2$  to produce a formate sulfide complex  $[\text{NaCrypt-2.2.2}][\text{L}^{\text{Me}}\text{Fe}(\mu\text{-CHOO})(\mu\text{-S})\text{FeL}^{\text{Me}}]$  [8].

Metalladithiolene complexes of group 8 transition metals are known to undergo addition reactions as the metal center contains a 16-electron unsaturated coordination state [9–16]. Such addition reaction between  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{S}_2\text{C}_6\text{H}_4)]$  and  $[\text{RuClH}(\text{PPh}_3)_3]$  produces a hydride-bridged rhodium-ruthenium heteronuclear complex  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{S}_2\text{C}_6\text{H}_4)\text{RuClH}(\text{PPh}_3)_2]$ , and between  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{S}_2\text{C}_6\text{H}_4)\text{RuClH}(\text{PPh}_3)_2]$  and potassium hydroxide in isopropyl alcohol produces a dihydride rhodium-ruthenium

heteronuclear complex  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{S}_2\text{C}_6\text{H}_4)\text{RuH}_2(\text{PPh}_3)_2]$  [17]. This dihydride compound is thermally stable up to 110 °C in toluene, and reacts efficiently with CO or ethynyl derivatives [17]. Although there have been some studies on synthesizing heteronuclear hydride complexes with metalladithiolene ligand, there have so far been very few reports on synthetic routes for asymmetric homonuclear hydride complexes. This triggers the quest to synthesize new homonuclear hydride complexes, which are expected to exhibit thermal stability and reactivity different from heteronuclear complexes. In this paper, we describe the synthesis and characterization of a hydride-bridged ruthenium dinuclear complex  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{S}_2\text{C}_6\text{H}_4)\text{RuClH}(\text{PPh}_3)_2]$  (**3**) and a dihydride ruthenium dinuclear complex  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{S}_2\text{C}_6\text{H}_4)\text{RuH}_2(\text{PPh}_3)_2]$  (**4**). The reaction of **4** with CO to form dicarbonyl complex  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{S}_2\text{C}_6\text{H}_4)\text{Ru}(\text{CO})_2(\text{PPh}_3)]$  (**5**) and tetracarbonyl complex  $[\text{Ru}_2(\text{CO})_4(\text{PPh}_3)_2(\text{S}_2\text{C}_6\text{H}_4)]$  (**6**) for different reaction times, and with  $\text{CO}_2$  to generate formic acid under ambient conditions are also described.

## 2. Experimental

**General:** Tetrahydrofuran (THF), diethyl ether ( $\text{Et}_2\text{O}$ ), hexane, isopropyl alcohol (*i*-PrOH), and toluene were purchased from KANTO Chemicals. Chloroform and methanol were purchased from Godo Co., Ltd. Dichloromethane was purchased from Wako Pure Chemical Industries, Ltd. Toluene and THF were distilled using Na, dried over 4 Å molecular sieves, and degassed with  $\text{N}_2$  before

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use. Isopropyl alcohol and methanol were dried over 3 Å molecular sieves and degassed with N<sub>2</sub> before use. Other solvents were distilled over calcium hydride, dried over 4 Å molecular sieves, and degassed with N<sub>2</sub> prior to use. Other chemicals were obtained from commercial sources. Complexes [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)Ru(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**1**) and [RuClH(PPh<sub>3</sub>)<sub>3</sub>] (**2**) were prepared using literature methods as reported previously [18,19].

All NMR spectra were recorded on an ECP-500 (500 MHz) spectrometer. <sup>1</sup>H NMR (500 MHz), <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz), and <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz) spectra were measured using tetramethylsilane as an internal standard. IR spectra were recorded using a JASCO FT-IR 6100 spectrometer. High-resolution electrospray ionization mass spectra (HR-ESI MS) were recorded on a JEOL JMS-T100CS “AccuTOF CS” spectrometer. Elemental analyses were performed using a PerkinElmer 2400II CHNS analyzer.

For structural determination, crystal data were collected using a Bruker AXS SMART APEX CCD X-ray diffractometer equipped with a rotating-anode X-ray generator emitting graphite-monochromatic Mo Kα (0.7107 Å) and Cu Kα radiation (1.5418 Å). Empirical absorption corrections and Lorentzian polarization correction were performed using equivalent reflections and the SADABS program, respectively [20]. All data were collected with SMART and Bruker SAINTPLUS (Version 6.45) software packages. The structures were solved using the SHELXS-97 [21] program and refined against F<sup>2</sup> using SHELXL-97 [22].

### 2.1. Synthesis of [Ru(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)RuClH(PPh<sub>3</sub>)<sub>2</sub>] (**3**)

Complexes **1** (0.081 g, 0.20 mmol) and **2** (0.19 g, 0.20 mmol) were suspended in THF (40 mL) and stirred at room temperature for 24 h. The crude product was then concentrated under reduced pressure, washed with Et<sub>2</sub>O, and collected by filtration. The final product was dried under reduced pressure to obtain complex **3** as dark green solid (yield: 0.16 g, 72%). Single crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from chloroform/hexane at –30 °C.

Experimental data for **3**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S1): –17.49 (t, J<sub>HP</sub> = 12 Hz, 1H, RuHRu), 1.65 (s, 18H, C<sub>6</sub>Me<sub>6</sub>), 6.60 (dd, J = 3.0, 6.0 Hz, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.92–6.99 (m, 18H, Ph), 7.36 (dd, J = 3.0, 6.0 Hz, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 7.60–7.64 (m, 12H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S2): 50.5 (s). IR (KBr): (ν<sub>C-H</sub>) 3052, 2907 cm<sup>-1</sup>, (ν<sub>P-C</sub>) 1631 cm<sup>-1</sup>. LRMS (LR-ESI-TOF) m/z: Calcd. for C<sub>54</sub>H<sub>53</sub>P<sub>2</sub>Ru<sub>2</sub>S<sub>2</sub> 1031 [M–Cl]<sup>+</sup>, Found: 1031. Anal. Calc. for C<sub>54</sub>H<sub>53</sub>ClP<sub>2</sub>Ru<sub>2</sub>S<sub>2</sub>: C, 60.86; H, 5.01. Found: C, 60.50; H, 5.05%.

### 2.2. Synthesis of [Ru(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**)

The hydride complex **3** (0.11 g, 0.10 mmol) and KOH (0.060 g, 1.1 mmol) were suspended in *i*-PrOH (10 mL) and heated at 60 °C for 2 h. The suspension was filtered and washed with methanol followed by extraction with toluene and reprecipitation from methanol. Finally, the precipitate was filtered and dried under reduced pressure to obtain complex **4** (*cis/trans* mixture) as orange solid (yield: 84 mg, 83%). The mixture was recrystallized from dichloromethane/hexane at room temperature to give *cis*-**4** isomer.

Experimental data for **4**: <sup>1</sup>H NMR for *cis*-**4** (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S2): –14.43 (t, J<sub>HH</sub> = 25 Hz, 1H, RuHRu), –9.61 (dd, J<sub>HP</sub> = 16 Hz, J<sub>HH</sub> = 25 Hz, 1H, RuH), 1.73 (s, 18H, C<sub>6</sub>Me<sub>6</sub>), 6.01 (t, J<sub>HH</sub> = 7.5 Hz, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.24 (d, J<sub>HH</sub> = 7.5 Hz, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.35 (d, J<sub>HH</sub> = 7.5 Hz, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 7.32 (d, J<sub>HH</sub> = 7.5 Hz, 1H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.89–7.75 (m, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR for *cis*-**4** (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S4): 63.7 (d, J<sub>PP</sub> = 65 Hz), 67.7 (d, J<sub>PP</sub> = 65 Hz). <sup>1</sup>H NMR for *trans*-**4** (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm): –8.74 to –8.59 (m, 1H, RuH), –8.35 to –8.33 (m, 1H, RuH), 1.83 (s, 18H, C<sub>6</sub>Me<sub>6</sub>), 6.89–7.75 (m, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR for *trans*-**4** (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm):

69.7 (s). HRMS (HR-ESI-TOF) m/z: Calc. for C<sub>54</sub>H<sub>53</sub>P<sub>2</sub>Ru<sub>2</sub>S<sub>2</sub> 1031.11509 [M–H]<sup>+</sup>, Found: 1031.11547.

### 2.3. Synthesis of [Ru(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Ru(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (**5**)

THF solution (10 mL) of **4** (0.052 mg, 0.050 mmol) was stirred at room temperature for 30 min under CO atmosphere. The solution was then concentrated under reduced pressure. The crude product was purified by aluminum gel column chromatography using toluene as eluent. The second reddish purple fraction that eluted from the column was collected. Subsequently, the solvent was evaporated and the final product was subjected under reduced pressure to obtain complex **5** as reddish purple solid (yield: 41 mg, 55%).

Experimental data for **5**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S5): 1.69 (s, 18H, C<sub>6</sub>Me<sub>6</sub>), 5.70 (dd, J = 3.0, 6.0 Hz, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.19 (dd, J = 3.0, 6.0 Hz, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.70–7.93 (m, 30H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S6): 38.7 (s). IR (KBr) (Fig. S9): (ν<sub>C-H</sub>) 3055, 2917 cm<sup>-1</sup>, (ν<sub>C=O</sub>) 2054, 1944 cm<sup>-1</sup>. HRMS (HR-ESI-TOF) m/z: Calcd. for C<sub>38</sub>H<sub>37</sub>O<sub>2</sub>P<sub>1</sub>Ru<sub>2</sub>S<sub>2</sub> 825.01560 [M+H]<sup>+</sup>, Found: 825.01397.

### 2.4. Synthesis of [Ru<sub>2</sub>(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**6**)

THF solution (10 mL) of **4** (0.052 mg, 0.050 mmol) was stirred at room temperature for 24 h under CO atmosphere. The solution was then concentrated under reduced pressure. The crude product was purified by aluminum gel column chromatography using toluene as eluent. The first pale yellow fraction that eluted from the column was collected and the solvent was evaporated. The final product was dried under reduced pressure to obtain complex **6** as yellow solid (42 mg, 86%).

Experimental data for **6**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S7): 5.71 (dd, 2H, J = 3.0, 6.0 Hz, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.21 (dd, J = 3.0, 6.0 Hz, 2H, S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 6.91–7.00 (m, 18H, Ph), 7.62–7.66 (m, 12H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) (Fig. S8): 38.4 (s). IR (KBr) (Fig. S9): (ν<sub>C-H</sub>) 3052 cm<sup>-1</sup>, (ν<sub>C=O</sub>) 2006, 1972, 1942 cm<sup>-1</sup>. LRMS (LR-ESI-TOF) m/z: Calcd. for C<sub>46</sub>H<sub>34</sub>O<sub>4</sub>P<sub>2</sub>Ru<sub>2</sub>S<sub>2</sub> 980 [M+H]<sup>+</sup>, Found: 980.

### 2.5. Reaction of [Ru(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**) and CO<sub>2</sub>

The dihydride complex **4** (0.052 mg, 0.050 mmol) was suspended in *i*-PrOH (10 mL) and stirred at room temperature for 24 h under CO<sub>2</sub> atmosphere. The solution was then concentrated under reduced pressure to collect the crude product and the distillate. The crude product was washed with hexane, filtered and subjected to reduced pressure to obtain a dark brown solid (16 mg). On the other hand, the distillate was confirmed to contain formic acid by GC–MS (Fig. S11).

## 3. Results and discussion

Complexes **1** and **2** were synthesized and single crystals of **2** were obtained by recrystallization in toluene in order to determine its molecular structure by single-crystal X-ray diffraction analysis (Fig. 1(a) and Table 1). The reaction of **2** with **1** produced the hydride-bridged ruthenium dinuclear complex **3** as dark green solid with 72% yield (Scheme 1). In the <sup>1</sup>H NMR spectrum (Fig. S1), the triplet signal at –17.49 ppm (J<sub>HP</sub> = 12 Hz) is assigned to the bridged hydride and a singlet at 1.65 ppm is assigned to methyl proton in the hexamethylbenzene ligand. Double doublets at 6.60 ppm and 7.36 ppm are assigned to protons in the benzenedithiolate ligand with lower chemical shift than those of **1** (7.03 and 7.81 ppm) [23] indicating a deformation of the

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