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Journal of Organometallic Chemistry 692 (2007) 122–128
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structural characterization of a photoresponsive organodirhodium complex with active S–S bonds: $[(\mathrm{Cp}^{\mathrm{Ph}}\mathrm{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\mathrm{SSO}_2)]$ ($\mathrm{Cp}^{\mathrm{Ph}} = \eta^5\text{-C}_5\mathrm{Me}_4\mathrm{Ph}$)

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Received 28 February 2006; accepted 3 April 2006
Available online 30 August 2006

Abstract

A photoresponsive rhodium dinuclear complex having phenyltetramethylcyclopentadienyl ($\mathrm{Cp}^{\mathrm{Ph}} = \eta^5\text{-C}_5\mathrm{Me}_4\mathrm{Ph}$) and photosensitive dithionite ($\mu\text{-O}_2\mathrm{SSO}_2$) ligands, $[(\mathrm{Cp}^{\mathrm{Ph}}\mathrm{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\mathrm{SSO}_2)]$ (**1**), has been synthesized. The crystal of complex **1** (monoclinic, *C*2/*m* (No. 12), $a = 24.805(2)$ Å, $b = 29.111(2)$ Å, $c = 10.8475(11)$ Å, $\beta = 105.9830(7)°$, $V = 7530.0(12)$ Å^3, $Z = 8$) consists of two independent molecules, **1-cis** and **1-trans**, with different arrangement of the $\mathrm{Cp}^{\mathrm{Ph}}$ ligands. The flexibility, volume, and shape of the reaction cavities around the dithionite unit of **1-cis** and **1-trans** in the crystal are discussed. The crystal structures of the precursors of **1**, *trans*-$[(\mathrm{Cp}^{\mathrm{Ph}}\mathrm{Rh})_2(\mu\text{-Cl})_2\mathrm{Cl}_2]$ and *trans*-$[(\mathrm{Cp}^{\mathrm{Ph}}\mathrm{Rh})_2(\mu\text{-CH}_2)_2\mathrm{Me}_2]$, are also reported.

Keywords: Dithionite complex; Crystal structure; Photochromism

1. Introduction

Photochromic compounds, which show reversible crystalline-state reactions, have attracted remarkable attention because of their potential applications for optical memory media and optical switching devices [1–3]. Although a great number of photochromic compounds have been reported, little is known about compounds having photochromic reactivity in the crystalline-state. We have recently found that a new class of photochromic compound, rhodium dinuclear complex with two Cp* (= $\eta^5\text{-C}_5\mathrm{Me}_5$) and photoreactive dithionite ($\mu\text{-O}_2\mathrm{SSO}_2$) ligands $[(\mathrm{Cp}^*\mathrm{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\mathrm{SSO}_2)]$, shows intriguing photochromic performance, such as reversible 100% photo- and thermo-chemical conversions in the crystalline-state (Scheme 1) [4].

This reversible oxygen transfer reaction between $[(\mathrm{Cp}^*\mathrm{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-}\mathbf{O}_2\mathbf{S}\mathrm{SO}_2)]$ and $[(\mathrm{Cp}^*\mathrm{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-}\mathbf{OSO}\mathrm{SO}_2)]$ proceeds in the reaction cavities formed by the Cp* ligands in the crystal. We speculate that the key feature allowing the reversible crystalline-state reaction in this system is the flexibility of the reaction cavity. In order to find a role of the reaction cavity in reversible crystalline-state reactions, we are currently preparing various derivatives of dithionite complexes by chemical modification of the Cp* ligands of $[(\mathrm{Cp}^*\mathrm{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\mathrm{SSO}_2)]$. Herein, we report the synthesis and structural characterization of a new dithionite complex with phenyltetramethylcyclopentadienyl ligands, $[(\mathrm{Cp}^{\mathrm{Ph}}\mathrm{Rh})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\mathrm{SSO}_2)]$ ($\mathrm{Cp}^{\mathrm{Ph}} = \eta^5\text{-C}_5\mathrm{Me}_4\mathrm{Ph}$) (**1**) (Scheme 2), together with the crystal structures of its precursors, *trans*-$[(\mathrm{Cp}^{\mathrm{Ph}}\mathrm{Rh})_2(\mu\text{-Cl})_2\mathrm{Cl}_2]$ ($\mathbf{Rh}^{\mathbf{ClCl}}$) and *trans*-$[(\mathrm{Cp}^{\mathrm{Ph}}\mathrm{Rh})_2(\mu\text{-CH}_2)_2\mathrm{Me}_2]$ ($\mathbf{Rh}^{\mathbf{CH2Me}}$).

2. Results and discussion

The synthesis of the dithionite complex **1** is summarized in Scheme 2. The solid-state molecular structures of $\mathbf{Rh}^{\mathbf{ClCl}}$, $\mathbf{Rh}^{\mathbf{CH2Me}}$, and **1** were determined by X-ray

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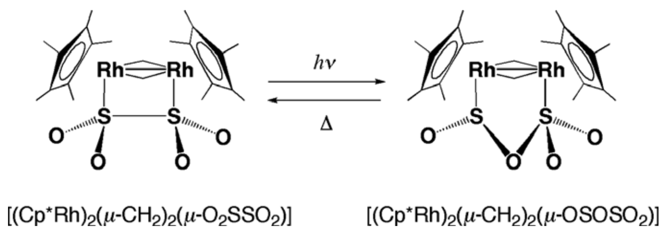
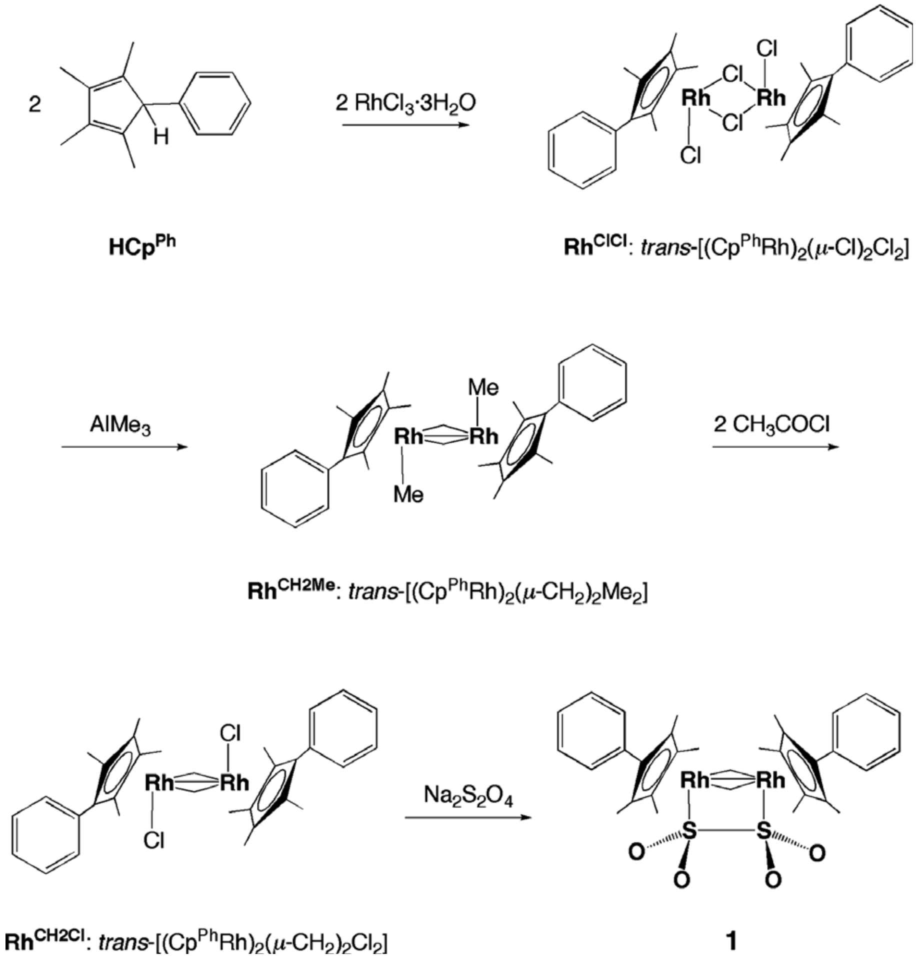
doi:10.1016/j.jorganchem.2006.08.063



Scheme 1. Crystalline-state photochromism.

diffraction analysis and are shown in Figs. 1 and 2. Crystal data are summarized in Table 1 and selected bond lengths and angles are listed in Table 2.

Although the synthesis of the dichloro–dimer complex, **Rh**$^{\mathbf{ClCl}}$, was reported in 2005 [5], this complex has not been structurally characterized. Recrystallization of **Rh**$^{\mathbf{ClCl}}$ from CH_2Cl_2/AcOEt at room temperature yields single crystals suitable for X-ray diffraction analysis. Fig. 1 (left) show the molecular structure of **Rh**$^{\mathbf{ClCl}}$. The bond distance and



Scheme 2. Synthesis of dithionite complex **1**.

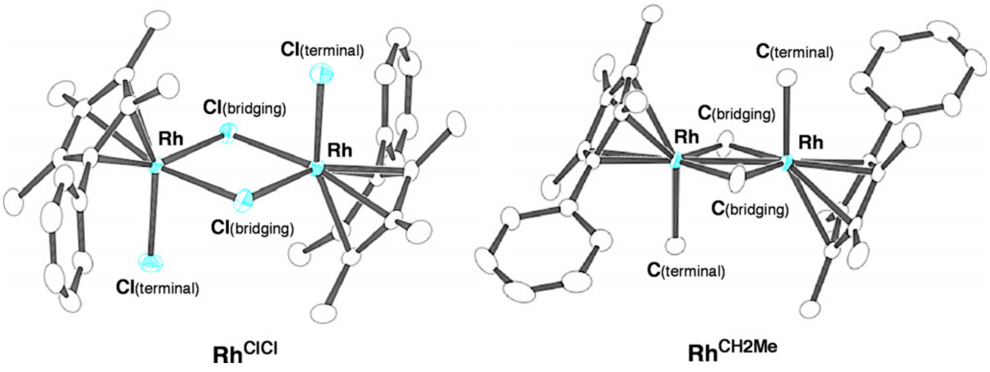
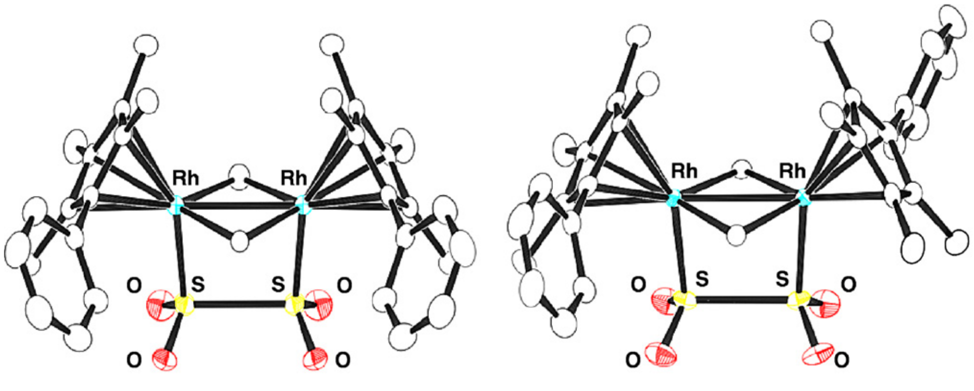


Fig. 1. Solid-state molecular structures of **Rh**$^{\mathbf{ClCl}}$ (left) and **Rh**$^{\mathbf{CH2Me}}$ (right). Hydrogen atoms are omitted for clarity, thermal ellipsoids are at 50% probability.



1-cis **1-trans**

Fig. 2. Solid-state molecular structures of **1-cis** (left) and **1-trans** (right) in crystals of **1** · $0.5CH_2Cl_2 \cdot C_7H_8$. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity, thermal ellipsoids are at 50% probability.

Table 1
Crystallographic data for $\mathbf{Rh}^{\mathbf{ClCl}}$, $\mathbf{Rh}^{\mathbf{CH2Me}}$, and **1**

	$\mathbf{Rh}^{\mathbf{ClCl}}$	$\mathbf{Rh}^{\mathbf{CH2Me}}$	**1** · $0.5CH_2Cl_2 \cdot C_7H_8$
Formula	$C_{30}H_{34}Cl_4Rh_2$	$C_{34}H_{44}Rh_2$	$C_{39.5}H_{38}ClO_4Rh_2S_2$
Fw	742.22	658.53	882.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$C2/m$ (No. 12)
a (Å)	12.4756(7)	10.299(1)	24.805(2)
b (Å)	15.7361(8)	11.508(1)	29.111(2)
c (Å)	14.7026(8)	12.267(2)	10.8475(11)
α (°)	90	90	90
β (°)	91.9430(5)	99.0088(9)	105.9830(7)
γ (°)	90	90	90
V (Å^3)	2884.7(3)	1435.9(3)	7530.0(12)
Z	4	2	8
μ (cm^{-1})	15.30	11.67	10.95
$F(000)$	1488	676	3568
D_{calc} (g/cm^3)	1.709	1.523	1.556
Temperature (K)	173	173	123
Reflections collected	31969	15987	41903
Independent reflections	31042 ($R_{int} = 0.019$)	3278 ($R_{int} = 0.026$)	8738 ($R_{int} = 0.045$)
Data/parameters	6551/326	3278/164	8738/472
R_1 [$I > 2\sigma(I)$]	0.026	0.029	0.057
wR_2 (all data)	0.069	0.075	0.123
Goodness-of-fit	1.053	1.078	1.155

angles of the $Rh_2(\mu\text{-}Cl)_2Cl_2$ unit in $\mathbf{Rh}^{\mathbf{ClCl}}$ compare well to those found for the corresponding Cp* analogue *trans*-$[(Cp^*Rh)_2(\mu\text{-}Cl)_2Cl_2]$ [6]. The average Rh–Cl(terminal): 2.3813(6) Å and Rh–Cl(bridging): 2.4460(6) Å distances in $\mathbf{Rh}^{\mathbf{ClCl}}$ are slightly shorter than those of the Cp* analogue (Rh–Cl(terminal): 2.3967(11) Å and Rh–Cl(bridging): 2.4586(11) Å). The Rh–Cl(bridging)–Rh and Cl(bridging)–Rh–Cl(bridging) angles in $\mathbf{Rh}^{\mathbf{ClCl}}$ are 3.6° more acute and obtuse, respectively, than those of the Cp* analogue. Thus, these results suggest that the electronic structure of the core unit in this system can be controlled by changing the ligand from Cp* to Cp^{Ph}.

The methylene–methyl complex, $\mathbf{Rh}^{\mathbf{CH2Me}}$, can be synthesized by modifying the procedure for the corresponding Cp* analogue *trans*-$[(Cp^*Rh)_2(\mu\text{-}CH_2)_2Me_2]$ [7]. Additionally, the molecular structure of $\mathbf{Rh}^{\mathbf{CH2Me}}$ having the *trans*-$Rh_2(\mu\text{-}CH)_2Me_2$ core unit can be unequivocally determined by X-ray diffraction technique (Fig. 1 (right)). Although the *trans*- and *cis*-isomer of the Cp* analogue $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2Me_2]$ are known, only the *cis*-isomer, *cis*-$[(Cp^*Rh)_2(\mu\text{-}CH_2)_2Me_2]$, has been structurally characterized so far. The dimetallacyclobutane (Rh_2C_2) ring in the *trans*-isomer, $\mathbf{Rh}^{\mathbf{CH2Me}}$, is planar while that in *cis*-$[(Cp^*Rh)_2(\mu\text{-}CH_2)_2Me_2]$ is puckered (angle of fold, 28° about Rh–Rh). The Rh–C(terminal) and average Rh–C(bridging) distances in $\mathbf{Rh}^{\mathbf{CH2Me}}$ are 2.075(3) and 2.019(3) Å, respectively. The Rh–C(bridging)–Rh and C(bridging)–Rh–C(bridging) angles in $\mathbf{Rh}^{\mathbf{CH2Me}}$ are 81.0(1) and 99.0(1)°, respectively.

Treatment of the methylene–methyl complex, $\mathbf{Rh}^{\mathbf{CH2Me}}$, with acetylchloride in CH_2Cl_2 yields the methylene–chloro complex, $\mathbf{Rh}^{\mathbf{CH2Cl}}$, as a red–brown powder (87%). This

Table 2
Selected bond lengths (Å) and angles (°) for $\mathbf{Rh^{ClCl}}$, $\mathbf{Rh^{CH2Me}}$, and **1**

	$\mathbf{Rh^{ClCl}}$	$\mathbf{Rh^{CH2Me}}$	**1-cis**	**1-trans**
Rh–Rh	3.5980(2)	2.6224(3)	2.6334(4)	2.6285(4)
Rh–Cl(terminal)	2.3785(6)			
	2.3840(6)			
Average	2.3813(6)			
Rh–Cl(bridging)	2.4506(6)			
	2.4447(5)			
	2.4366(5)			
	2.4522(6)			
Average	2.4460(6)			
Rh–C(terminal)		2.075(3)		
Rh–C(bridging)		2.017(3)	2.050(5)	2.054(5)
		2.020(3)	2.051(5)	2.043(4)
Average		2.019(3)	2.051(5)	2.049(5)
Rh–S			2.284(1)	2.283(1)
S–S			2.295(2)	2.299(2)
S–O			1.469(4)	1.449(4)
			1.456(4)	1.458(4)
Average			1.463(4)	1.454(4)
Rh–Cl–Rh	94.82(2)			
	94.57(2)			
Average	94.70(2)			
Rh–C–Rh		81.0(1)	79.9(2)	79.8(2)
			79.9(2)	
Average			79.9(2)	
Cl–Rh–Cl	85.23(2)			
	85.37(2)			
Average	85.30(2)			
C–Rh–C		99.0(1)	99.9(2)	99.9(2)

powder is contaminated with a very small amount of $\mathbf{Rh^{ClCl}}$ as a by-product; however, this material is enough purity for further reaction.

The reaction of the methylene–chloro complex, $\mathbf{Rh^{CH2Cl}}$, with $Na_2S_2O_4$ in MeOH under N_2 in the dark led to the formation of the dithionite complex, **1**, in good yield (62%) as a brown powder. Crystals of **1** suitable for X-ray diffraction analysis were grown from CH_2Cl_2/toluene (C_7H_8) in the dark at room temperature. The crystal of complex **1** consists of two independent dithionite complexes, **1-cis** and **1-trans** (Fig. 2) [8], one dichloromethane molecule, and three independent toluene molecules. One of three toluene molecules is ordered. Other two toluene molecules are disordered in the same fashion (a disorder model for these toluene molecules is shown in inset of Fig. 3). There are a 1/2 of **1-cis**, a 1/2 of **1-trans**, a 1/2 of CH_2Cl_2, a 1/2 of C_7H_8, and two 1/4 of C_7H_8 in an asymmetric unit ($\mathbf{1} \cdot 0.5CH_2Cl_2 \cdot C_7H_8$).

The solid-state molecular structures of the two independent dithionite complexes, **1-cis** and **1-trans**, in crystals of $\mathbf{1} \cdot 0.5CH_2Cl_2 \cdot C_7H_8$ are depicted in Fig. 2.

The molecule of **1-cis** has a mirror plane through two bridged methylene carbons and a center of the Rh–Rh bond. The phenyl rings of the Cp^{Ph} ligands of **1-cis** are arranged in a *cis* fashion to the Rh–Rh bond. The other molecule, **1-trans**, has a C_2 axis bisecting the Rh–Rh and S–S bonds. The phenyl rings in **1-trans** are arranged in a *trans* fashion to the Rh–Rh bond. Except for the arrangement of the Cp^{Ph} ligands, the solid-state structure of the $Rh_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)$ core fragment of **1-cis** is comparable to that found for **1-trans**. For instance, the Rh–Rh bond distances in **1-cis** and **1-trans** are 2.6334(4) and 2.6285(4) Å, respectively. The bond lengths and angles of the $Rh_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)$ core fragments of **1-cis** and **1-trans** are also similar to that found for the Cp^* analogue $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)]$ [4]. The S–S bond distances in **1-cis** (2.295(2) Å) and **1-trans** (2.299(2) Å), however, are clearly shorter than that in the Cp^* analogue (2.330(2) Å). This implies that the dithionite ligand in **1** has an electronic structure and photo-reactivity different from that in the Cp^* analogue.

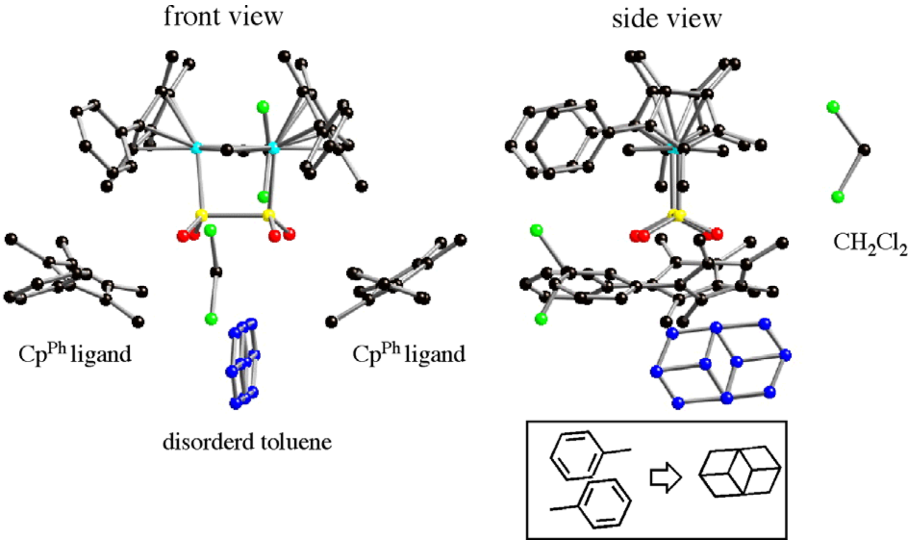


Fig. 3. The Cp^{Ph} ligands and solvent molecules around the dithionite unit of **1-cis** viewed from front (left) and side (right) of **1-cis**. Disorder model for a toluene molecule (inset).

It is worthwhile to note that the reaction cavities for the ditionite unit of **1-cis** and **1-trans** in the crystal have quite different character. The dithionite unit of **1-cis** is surrounded by rigid Cp^{Ph} ligands of neighboring complexes and flexible co-crystalized solvents (dichloromethane and disorderd toleune) (Fig. 3). In contrast, the dithionite unit of **1-trans** is only surrounded by rigid Cp^{Ph} ligands of neighboring complexes (Fig. 4). Consequently, **1-cis** has a more flexible reaction cavity than **1-trans** does.

There is some approach to explain the reactivity in the solid state [9,10]: the volume and shape of the void space around the reaction group (= reaction cavity) in the crystal are very informative in estimating the reactivity. The reaction cavities for the dithionite unit of **1-cis** and **1-trans** were calculated by using Cavity 5.0 [11]. Figs. 5 and 6 illustrate the cavities of **1-cis** and **1-trans**.

The cavities in **1-cis** and **1-trans** have the volume of 7.34 and 9.45 Å^3, respectively. Thus, the features of the reaction cavities of **1-cis** and **1-trans** in the crystal of $\mathbf{1} \cdot 0.5CH_2Cl_2 \cdot C_7H_8$ are summarized as follows:

Flexibility: **1-cis** > **1-trans**
Volume: **1-cis** < **1-trans**

Our preliminary experiment shows that new dithionite complex **1** has photochromic reactivity in the crystalline-state. We are currently investigating the correlation between the reaction cavities (flexibility, volume, and shape) and photochromic performance using the crystal of $\mathbf{1} \cdot 0.5CH_2Cl_2 \cdot C_7H_8$ containing the two kinds of reaction cavity as mentioned above.

3. Experimental

3.1. General

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents used were purified by distillation before use. Rhodium(III) chloride trihydrate, $RhCl_3 \cdot 3H_2O$, was purchased from Tanaka Kikinzoku Kogyo K.K. Sodium dithionite, $Na_2S_2O_4$, was purchased from Aldrich. All other chemicals were obtained from commercial sources and used as received unless otherwise noted. The phenyl derivative ligand, **HCp^{Ph}** = HC_5Me_4Ph, was synthesized by the literature procedures [12]. ^1H and ^{13}C NMR spectra were recorded on a JEOL Lambda 400 FT-NMR spectrometer

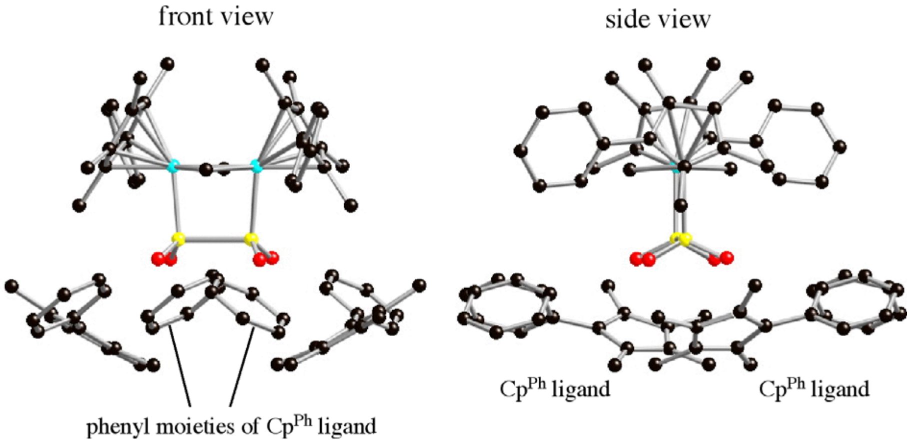


Fig. 4. The Cp^{Ph} ligands and phenyl moieties of Cp^{Ph} ligand around the dithionite unit of **1-trans** viewed from front (left) and side (right) of **1-trans**.

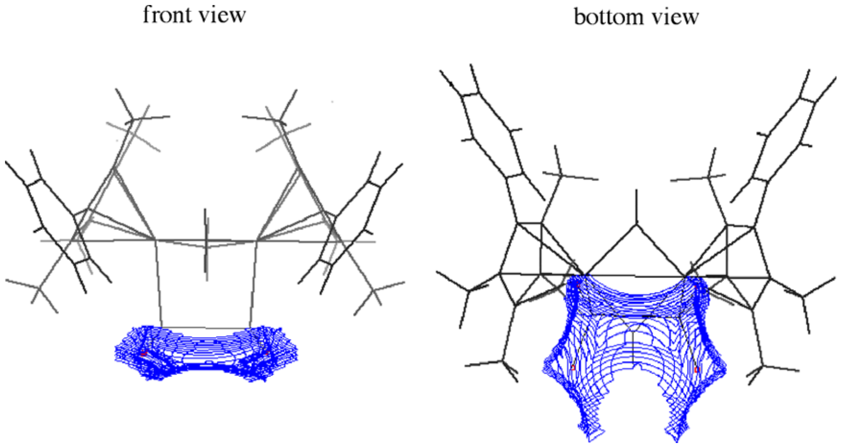


Fig. 5. Front (left) and bottom (right) views of the reaction cavity for the dithionite unit of **1-cis**. The contours are drawn in sections separated by 0.10 Å.

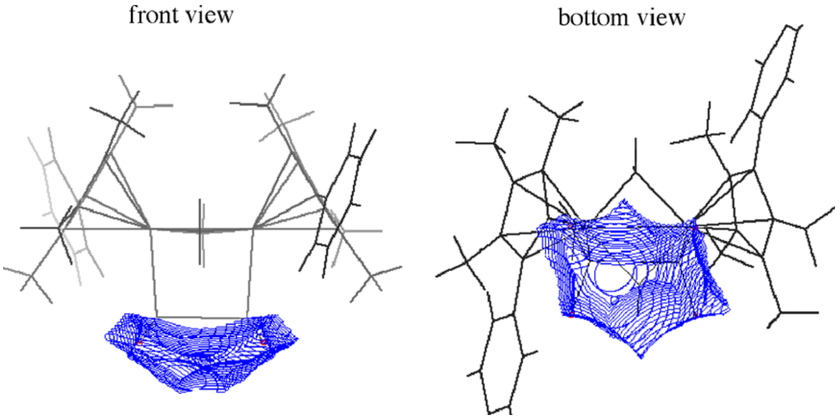


Fig. 6. Front (left) and bottom (right) views of the reaction cavity for the dithionite unit of **1-trans**. The contours are drawn in sections separated by 0.10 Å.

in $CDCl_3$. Chemical shifts were referenced to *protio* solvent impurities (^1H: δ 7.26, ^{13}C: δ 77.0 ($CDCl_3$)) and are reported in ppm. Elemental analyses were performed by the Advanced Science Research Center at Kanazawa University on a Yanaco MT-5 CHN autocorder.

3.2. Synthesis of trans-[($Cp^{Ph}Rh)_2(\mu$-$Cl)_2Cl_2$] (**Rh^{ClCl}**)

A mixture of $RhCl_3 \cdot 3H_2O$ (3.60 g, 13.7 mmol) and **HCp^{Ph}** (4.08 g, 20.6 mmol) in MeOH (30 ml) was refluxed for 24 h under N_2. After the reaction mixture was cooled to room temperature, the resulting red precipitate was filtered and washed with Et_2O. Yield 3.97 g, 78%. Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of AcOEt into a solution of **Rh^{ClCl}** in CH_2Cl_2 at room temperature.

^1H NMR (400 MHz, $CDCl_3$): δ 7.61–7.68 (4H, m, C_5Me_4*Ph*), 7.33–7.41 (6H, m, C_5Me_4*Ph*), 1.71 (12H, s, C_5*Me*$_4$Ph), 1.67 (12H, s, C_5*Me*$_4$Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.2 (C_5Me_4*Ph*), 128.9 (C_5Me_4*Ph*), 128.6 (C_5Me_4*Ph*), 128.3 (C_5Me_4*Ph*), 100.3 (*C*$_5$Me$_4$Ph), 100.2 (*C*$_5$Me$_4$Ph), 93.5 (*C*$_5$Me$_4$Ph), 93.4 (*C*$_5$Me$_4$Ph), 90.6 (*C*$_5$Me$_4$Ph), 90.5 (*C*$_5$Me$_4$Ph), 10.6 (C_5*Me*$_4$Ph), 9.6 (C_5*Me*$_4$Ph). Anal. Calc. for [$(Cp^{Ph}Rh)_2(\mu$-$Cl)_2Cl_2$]: C, 48.55; H, 4.62. Found: C, 48.18; H, 4.65%.

3.3. Synthesis of trans-[($Cp^{Ph}Rh)_2(\mu$-$CH_2)_2Me_2$] (**Rh^{CH2Me}**)

An 1.03 M solution of $AlMe_3$ in hexane (4.5 ml, 4.64 mmol) was added dropwise to a stirred suspension of **Rh^{ClCl}** (1.02 g, 1.38 mmol) in toluene (30 ml) at −40 °C. After stirring for 1 h at −40 °C, the resulting solution was allowed to warm up to room temperature. Acetone (4.5 ml) was slowly added and stirred for 12 h at room temperature. MeOH (30 ml) was added to the solution and the solvent was removed *in vacuo*. The red solid was washed with pentane (100 ml) and extracted with CH_2Cl_2 (100 ml). The extract was concentrated and washed with MeOH (50 ml) to give **Rh^{CH2Me}** as a red solid. Yield 538 mg, 59%. Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of MeOH into a solution of **Rh^{CH2Me}** in CH_2Cl_2 at room temperature.

^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (4H, t, μ-CH_2), 7.30–7.37 (4H, m, C_5Me_4*Ph*), 7.19–7.28 (6H, m, C_5Me_4*Ph*), 1.78 (12H, s, C_5*Me*$_4$Ph), 1.62 (12H, s, C_5*Me*$_4$Ph), −0.78 (6H, s, CH_3). ^{13}C NMR(100 MHz, $CDCl_3$): δ 164.0 (μ-CH_2), 134.9 (C_5Me_4*Ph*), 131.7 (C_5Me_4*Ph*), 127.8 (C_5Me_4*Ph*), 126.1 (C_5Me_4*Ph*), 103.3 (*C*$_5$Me$_4$Ph), 103.2 (*C*$_5$Me$_4$Ph), 101.4 (*C*$_5$Me$_4$Ph), 10.3 (C_5*Me*$_4$Ph), 10.0 (C_5*Me*$_4$Ph), −3.0 (CH_3). Anal. Calc. for [$(Cp^{Ph}Rh)_2(\mu$-$CH_2)_2(CH_3)_2$]: C, 62.01; H, 6.73. Found: C, 61.85; H, 6.84%.

3.4. Synthesis of trans-[($Cp^{Ph}Rh)_2(\mu$-$CH_2)_2Cl_2$] (**Rh^{CH2Cl}**)

Acetylchloride (0.26 ml, 1.80 mmol) was added to a solution of **Rh^{CH2Me}** (410 mg, 0.62 mmol) in CH_2Cl_2 (20 ml) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, allowed to warm up to room temperature, and then refluxed for 12 h. MeOH (10 ml) was added to the solution and the solvent was removed *in vacuo*. The red–brown solid was extracted with toluene (50 ml). The extract was concentrated and washed with Et_2O (10 ml) to give **Rh^{CH2Cl}** as a red–brown solid. Yield 380 mg, 87%.

^1H NMR (400 MHz, $CDCl_3$): δ 10.55 (4H, t, μ-CH_2), 7.20–7.46 (10H, m, C_5Me_4*Ph*), 1.79 (12H, s, C_5*Me*$_4$Ph), 1.52 (12H, s, C_5*Me*$_4$Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7 (μ-CH_2), 132.0 (C_5Me_4*Ph*), 131.0 (C_5Me_4*Ph*), 128.1 (C_5Me_4*Ph*), 127.5 (C_5Me_4*Ph*), 109.7 (*C*$_5$Me$_4$Ph), 102.5 (*C*$_5$Me$_4$Ph), 100.9 (*C*$_5$Me$_4$Ph), 10.6 (C_5*Me*$_4$Ph), 10.0 (C_5*Me*$_4$Ph).

3.5. Synthesis of [($Cp^{Ph}Rh)_2(\mu$-$CH_2)_2(\mu$-O_2SSO_2)] (*1*)

A mixture of **Rh^{CH2Cl}** (200 mg, 0.29 mmol) and $Na_2S_2O_4$ (68 mg, 0.39 mmol) in MeOH (30 ml) was stirred for 6 h under N_2 in the dark at room temperature. The solvent was removed under reduced pressure to give a reddish brown solid. The crude product was dissolved in 20 ml of

CH_2Cl_2 and the insoluble solid was filtered off. Removal of the solvent gave **1** as a brown solid. This solid was washed with toluene and Et_2O. Yield 134 mg, 62%. Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of toluene (C_7H_8) into a solution of **1** in CH_2Cl_2 at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (2H, s, μ-CH_2), 8.76 (2H, t, μ-CH_2), 7.31–7.51 (10H, m, C_5Me_4*Ph*), 1.86 (12H, s, C_5*Me*$_4$Ph), 1.76 (12H, s, C_5*Me*$_4$Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6 (μ-CH_2), 131.0 (C_5Me_4*Ph*), 130.3 (C_5Me_4*Ph*), 128.5 (C_5Me_4*Ph*), 128.3 (C_5Me_4*Ph*), 108.7 (*C*$_5$Me$_4$Ph), 107.3 (*C*$_5$Me$_4$Ph), 103.6 (*C*$_5$Me$_4$Ph), 9.9 (C_5*Me*$_4$Ph), 9.8 (C_5*Me*$_4$Ph). Anal. Calc. for $[(Cp^{Ph}Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)] \cdot 0.6C_7H_8$: C, 53.55; H, 5.31. Found: C, 53.32; H, 5.47%.

3.6. X-ray crystallography

All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). Single crystals of dimensions $0.32 \times 0.27 \times 0.20$ ($\mathbf{Rh^{ClCl}}$), $0.23 \times 0.20 \times 0.16$ ($\mathbf{Rh^{CH2Me}}$), and $0.19 \times 0.11 \times 0.06$ (**1**) mm^3 were mounted on a glass fiber. The data were collected at 173 ($\mathbf{Rh^{ClCl}}, \mathbf{Rh^{CH2Me}}$) or 123 (**1**) K to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A first sweep of data was done using ω scans from -80.0 to 100.0° in 0.50° step, at $\chi = 45.0°$ and $\phi = 0.0°$. A second sweep of data was made using ω scans from -80.0 to 100.0° in 0.50° step, at $\chi = 45.0°$ and $\phi = 90.0°$. The crystal-to-detector distances were 34.97 ($\mathbf{Rh^{ClCl}}, \mathbf{Rh^{CH2Me}}$) or 35.31 (**1**) mm, and detector swing angles were 10.03 ($\mathbf{Rh^{ClCl}}, \mathbf{Rh^{CH2Me}}$) or 10.01 (**1**) [°]. The exposure rates were 5.0 ($\mathbf{Rh^{ClCl}}$ and $\mathbf{Rh^{CH2Me}}$), or 30.0 (**1**) [sec/°].

Data were collected and processed using CrystalClear [13] software (Rigaku). A numerical absorption correction was applied and resulted in transmission factors ranging from 0.67 to 0.81 ($\mathbf{Rh^{ClCl}}$), 0.85 to 0.91 ($\mathbf{Rh^{CH2Me}}$), and 0.89 to 0.97 (**1**). The data were corrected for Lorentz and polarization effects.

The structure was solved by a direct method: SIR-92 [14] for $\mathbf{Rh^{ClCl}}$, $\mathbf{Rh^{CH2Me}}$, or SHELXL-97 [15] for **1** and expanded using a Fourier technique. All calculations were performed using the CrystalStructure [16,17] crystallographic software package except for refinement, which was performed using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except for those of solvent molecules, were placed in calculated idealized positions. Crystallographic data are summarized in Table 1 and have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC reference number: 299813 ($\mathbf{Rh^{ClCl}}$), 299814 ($\mathbf{Rh^{CH2Me}}$), and 282559 (**1**).

Acknowledgements

The present work was financially supported by the Grant-in-Aid for Scientific Research (KAKENHI) in Priority Area "Dynamic Complex", "Molecular Nano Dynamics", and "Chemistry of Coordination Space" from Ministry of Education, Culture, Sports, Science and Technology and Tokuyama Science Foundation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.063.

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