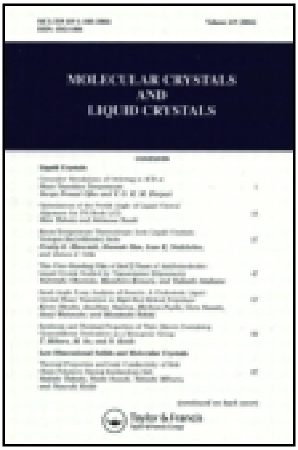

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Synthesis and Structural Characterization of a Photochromic Dirhodium Dithionite Complex: $[(Cp^{Ph}Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)]$ ($Cp^{Ph} = \eta^5\text{-}C_5Me_4Ph$)

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Synthesis and Structural Characterization of a Photochromic Dirhodium Dithionite Complex: $[(Cp^{Ph}Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)]$ ($Cp^{Ph} = \eta^5\text{-}C_5Me_4Ph$)

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*A rhodium dinuclear complex having phenyltetramethylcyclopentadienyl ($Cp^{Ph} = \eta^5\text{-}C_5Me_4Ph$) and photosensitive dithionite ($\mu\text{-}O_2SSO_2$) ligands, $[(Cp^{Ph}Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)]$ (**1**), has been synthesized. The crystal of complex **1** (monoclinic, C2/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 Cp^{Ph} ligands. The flexibility, volume, and shape of the reaction cavities for the dithionite unit of **1-cis** and **1-trans** in the crystal are discussed.*

Keywords: crystal structure; dithionite complex; photochromic complex

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

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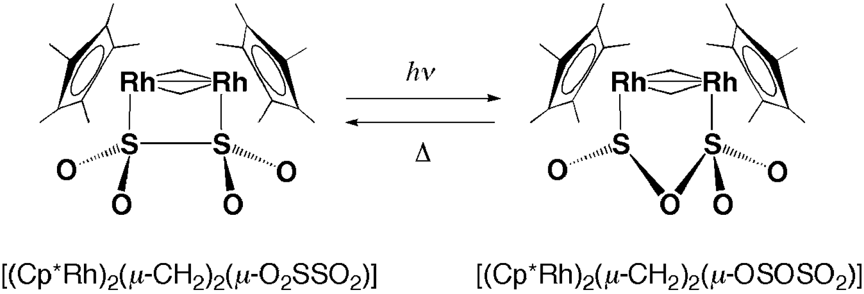
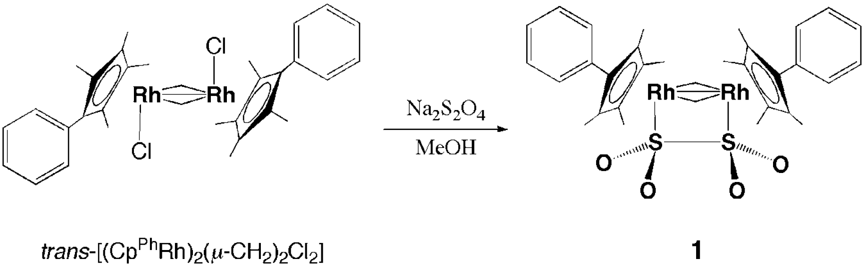


SCHEME 1 Single crystalline photochromism.

reactivity in the crystalline-state. We have recently found that a new class of photochromic compound, rhodium dinuclear complex with two Cp* ($=\eta^5$-C_5Me_5) and photo-reactive dithionite (μ-O_2SSO_2) ligands [$(Cp^*Rh)_2(\mu$-$CH_2)_2(\mu$-$O_2SSO_2)$], 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 [$(Cp^*Rh)_2(\mu$-$CH_2)_2(\mu$-$\mathbf{O_2S}SO_2)$] and [$(Cp^*Rh)_2(\mu$-$CH_2)_2(\mu$-$\mathbf{OSO}SO_2)$] 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 [$(Cp^*Rh)_2(\mu$-$CH_2)_2(\mu$-$O_2SSO_2)$]. Herein we report the synthesis and structural characterization of a new dithionite complex with phenyltetramethylcyclopentadienyl ligands, [$(Cp^{Ph}Rh)_2(\mu$-$CH_2)_2(\mu$-$O_2SSO_2)$] ($Cp^{Ph}=\eta^5$-C_5Me_4Ph) (**1**) (Scheme 2).



SCHEME 2 Synthesis of complex **1**.

EXPERIMENTAL

Synthesis of 1

The phenyl tetramethylcyclopentadinene derivative, HCp^{Ph} = eta^5-C$_5$Me$_4$Ph, was synthesized by literature procedures [5]. The dichloro dirhodium complex, *trans*-[(Cp^{Ph}Rh)$_2$(μ-CH$_2$)$_2$Cl$_2$], was synthesized by modifying the procedure for the corresponding Cp* analogue [6].

A mixture of *trans*-[(Cp^{Ph}Rh)$_2$(μ-CH$_2$)$_2$Cl$_2$] (200 mg, 0.29 mmol) and Na$_2$S$_2$O$_4$ (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$_2$Cl$_2$ and the insoluble solid was filtered off. Removal of the solvent gave [(Cp^{Ph}Rh)$_2$(μ-CH$_2$)$_2$(μ-O$_2$SSO$_2$)] (**1**) as a brown solid. This solid was washed with toluene and Et$_2$O. Yield 134 mg, 62%. ^{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$_5$Me$_4$*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$_5$Me$_4$*Ph*), 130.3 (C$_5$Me$_4$*Ph*), 128.5 (C$_5$Me$_4$*Ph*), 128.3 (C$_5$Me$_4$*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. Calcd for [(Cp^{Ph}Rh)$_2$(μ-CH$_2$)$_2$(μ-O$_2$SSO$_2$)]·0.6C$_7$H$_8$: C, 53.55; H, 5.31. Found: C, 53.32; H, 5.47.

X-ray Crystallography

All measurements were made on a Reigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). A single crystal of dimensions $0.19 \times 0.11 \times 0.06$ mm^3 was mounted on a glass fiber. The data were collected at −150°C 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 fai = 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 was 35.31 mm, and detector swing angles were 10.01°. The exposure rates were 30.0 [sec/°].

Of the 41903 reflections that were collected, 8738 were unique ($R_{int} = 0.045$); equivalent reflections were merged. Data were collected and processed using CrystalClear [7] software (Rigaku). The absorption coefficient, μ, for Mo-Kα radiation was 10.95 cm^{-1}. A numerical absorption correction was applied and resulted in transmission factors ranging from 0.89 to 0.97. The data were corrected for Lorentz and polarization effects.

Crystallographic data for **1**·$0.5CH_2Cl_2$·C_7H_8: $C_{39.50}H_{38}ClO_4Rh_2S_2$, $M = 882.12$, monoclinic, space group $C2/m$ (No. 12), $a = 24.805(2)$ Å, $b = 29.111(2)$ Å, $c = 10.8475(11)$ Å, $\beta = 105.9830(7)^\circ$, $V = 7530.0(12)$ Å^3, $Z = 8$, $D_{\mathrm{calced}} = 1.556$ g/cm^3.

The structure was solved by a direct method (SHELXL-97)[8] and expanded using a Fourier technique. All calculations were performed using the CrystalStructure [9,10] 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. The final cycle of full-matrix least-squares refinement of F^2 was based on 8738 observed reflections and 472 variable parameters. The final R_1 [$I > 2\sigma(I)$], wR_2 (all reflections) and GOF values were 0.057, 0.123 and 1.155, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.00 and –1.84 e$^-$/Å^3, respectively. CCDC reference number: 282559.

RESULTS AND DISCUSSION

The reaction of *trans*-[$(Cp^{Ph}Rh)_2(\mu\text{-}CH_2)_2Cl_2$] 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 (Scheme 2). 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**, one

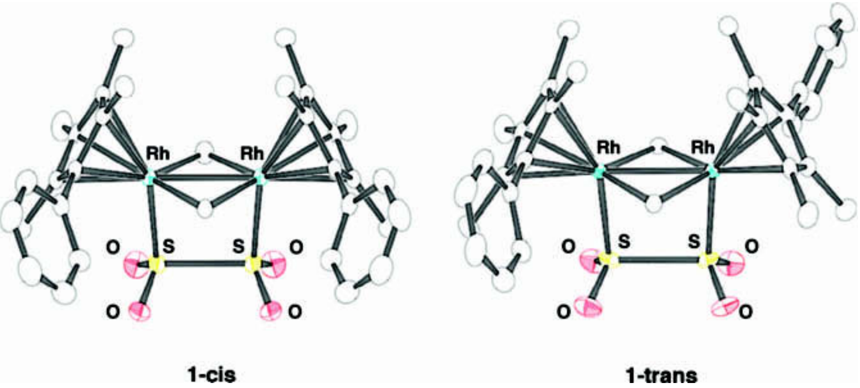


FIGURE 1 Solid-state molecular structures of **1-cis** (left) and **1-trans** (right) in crystals of **1**·$0.5CH_2Cl_2$·C_7H_8. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity, thermal ellipsoids are at 50% probability.

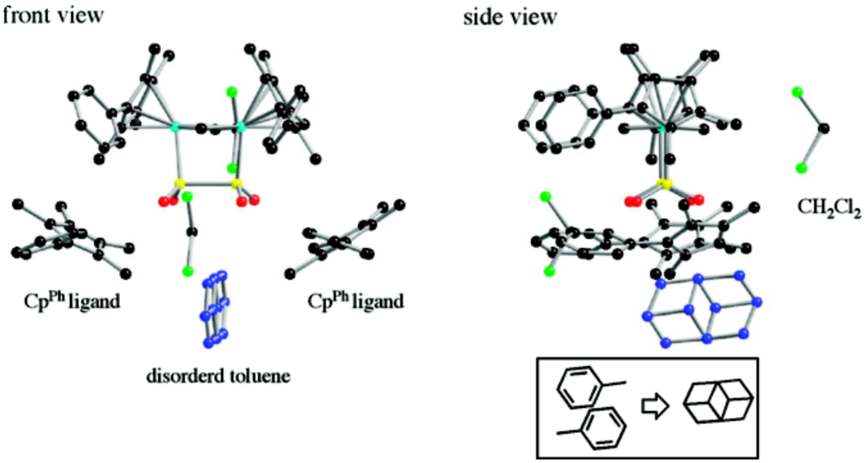


FIGURE 2 The Cp^{Ph} ligands and solvent molecules around the dithionite unit of **1-cis** viewed from front (left) and side (right) of **1-cis**. Disorder model for a toluene molecule (inset).

dichloromethane molecule, and three independent toluene molecules (Fig. 1). 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. 2). 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 (**1**·$0.5CH_2Cl_2{\cdot}C_7H_8$).

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

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 *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 *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 fragments 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

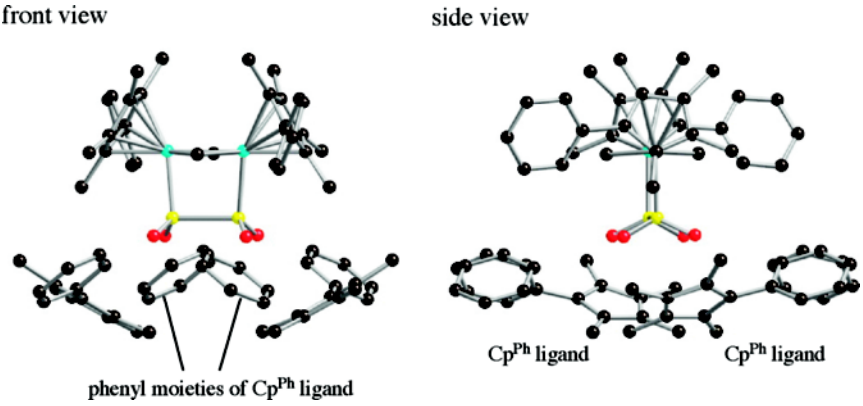


FIGURE 3 The $\mathrm{Cp^{Ph}}$ ligands and phenyl moieties of $\mathrm{Cp^{Ph}}$ ligand around the dithionite unit of **1-trans** viewed from front (left) and side (right) of **1-trans**.

(2.330(2) Å). This implies that the dithionite ligand in **1** has an electronic structure and photo-reactivity different from that in the $\mathrm{Cp^{*}}$ analogue.

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 $\mathrm{Cp^{Ph}}$ ligands of neighboring complexes and flexible co-crystalized solvents (dichloromethane and

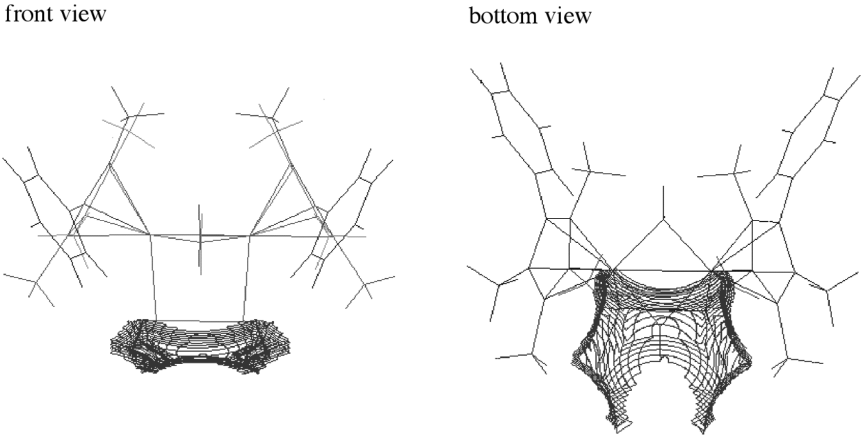


FIGURE 4 Front (left) and bottom (right) views of the reaction cavity for the dithionite unit of **1-cis**. The contours are drawn in sections separated by 0.10 Å.

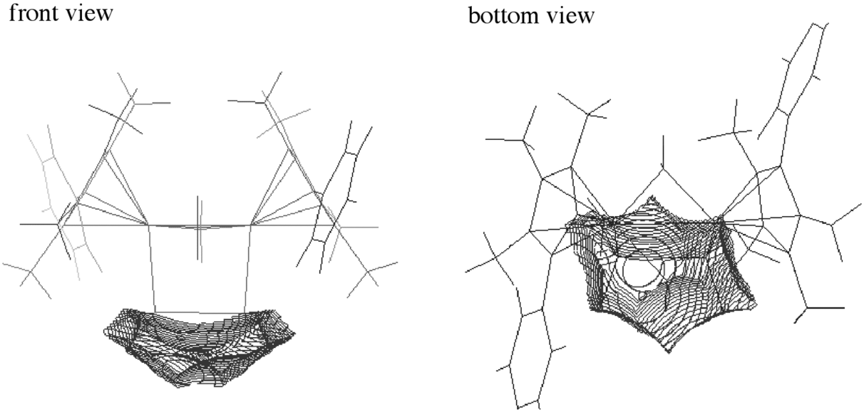


FIGURE 5 Front (left) and bottom (right) views of the reaction cavity for the dithionite unit of **1-trans**. The contours are drawn in sections separated by 0.10 Å.

disorderd toleune) (Fig. 2). In contrast, the dithionite unit of **1-trans** is only surrounded by rigid Cp^{Ph} ligands of neighboring complexes (Fig. 3). 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 [11,12]: 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 [13]. Figures 4 and 5 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:

$$\text{Flexibility}: \mathbf{1\text{-}cis} > \mathbf{1\text{-}trans}$$

$$\text{Volume}: \mathbf{1\text{-}cis} < \mathbf{1\text{-}trans}$$

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.

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