Substitution Effects of Cp Ring Benzyl Groups on Photoisomerization of a Rhodium Dithionite Complex in the Crystalline State

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Crystalline-state photoisomerization of a rhodium dithionite complex with benzyltetramethylcyclopentadienyl ligand, $[(\mathrm{Cp^{Bn}Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SSO_2})]$ ($\mathrm{Cp^{Bn}} = \eta^5\text{-}\mathrm{C_5Me_4Bn}$), is studied by X-ray crystallography and CP/MAS ^{13}C NMR spectroscopy. The disorder of the $\mathrm{Cp^{Bn}}$ ring in the crystal and the crystal packing of the molecules of isomers produced by photoreaction play an important role for stabilization of the whole crystal.

To date, chemists have shown that most photoreactive crystals tend to collapse and degrade as the reaction proceeds.[1] Fortunately, we have recently found that a new class of photochromic compounds, a rhodium dinuclear complex with two Cp* ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) and photoreactive dithionite ($\mu\text{-}\mathrm{O_2SSO_2}$) ligands, $[(\mathrm{Cp^*Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SSO_2})]$, shows intriguing photochromic performance, such as 100% reversible photo- and thermo-chemical isomerization in the crystalline state.[2] This reversible isomerization between $[(\mathrm{Cp^*Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SSO_2})]$ and $[(\mathrm{Cp^*Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SOSO})]$ proceeds in the crystal coupled with rotation of the Cp* rings.[3] We assume that the key feature allowing the reversible crystalline-state reaction in this system is the dynamics of the Cp* rings. In order to find the role of the dynamics of the Cp* rings and its derivatives in the crystalline-state reactions, we are currently preparing various derivatives of dithionite complexes by chemical modification of the Cp* ligands in $[(\mathrm{Cp^*Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SSO_2})]$.[4] The crystalline-state of the corresponding $\mathrm{Cp^{Et}}$ complex, $[(\mathrm{Cp^{Et}Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SSO_2})]$ ($\mathrm{Cp^{Et}} = \eta^5\text{-}\mathrm{C_5Me_4Et}$), where the ethyl substituent arrangement in the crystal forms rigid packing and the $\mathrm{Cp^{Et}}$ rings can not rotate, was degraded during photoirradiation:[3b] the crystal was broken by the stress produced by the photoreaction. Herein, we report the study of the crystalline-state photoisomerization of $[(\mathrm{Cp^{Bn}Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SSO_2})]$ ($\mathrm{Cp^{Bn}} = \eta^5\text{-}\mathrm{C_5Me_4Bn}$) (**1**), in which the rings have a more bulky substituent.

The benzyl derivative ligand precursor, $\mathrm{HCp^{Bn}}$, was synthesized according to modified literature procedures.[5,6] The dithionite complex **1** was obtained by a method similar to that for the Cp* complex.[2,7] Crystals of **1** suitable for X-ray diffraction analysis were grown from solution in hexane/dichloromethane at room temperature in the dark. The crystal structure of **1** is shown in Figure 1a and has a rectangular framework with a Rh–Rh single bond of 2.6212(2) Å and an S–S bond of 2.3120(10) Å.[8] These values are close to those of the Cp* complex.[2]

On irradiation with visible light, the red-brown crystals ($\lambda_{\max} = 511$ nm) of **1** change with almost 100% interconversion ratio to orange-brown crystals ($\lambda_{\max} = 498$ nm) of the new oxysulfur complex (Figure S1),[7] $[(\mathrm{Cp^{Bn}Rh})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SOSO})]$ (**2**), which has a five-membered framework of the $\mathrm{Rh_2S_2O}$ with a Rh–Rh single bond of 2.6145(6) Å and an S···S distance of 2.948(2) Å (Figure 1b).[9] It was determined on the basis of mixed sample experiments that the relative speed of photoisomerization of **1** is slow compared with that of the Cp* complex (Figures S1 and S2).[7] The crystals of **2** isomerize with almost 100% interconversion ratio to **1** in the dark. Thus, this photochromism is T-type.[10] We could not measure the quantum yield of the photoreaction of **1** in the crystalline state, however, in an acetonitrile solution 0.13 ± 0.01 yield at 405 nm was obtained.

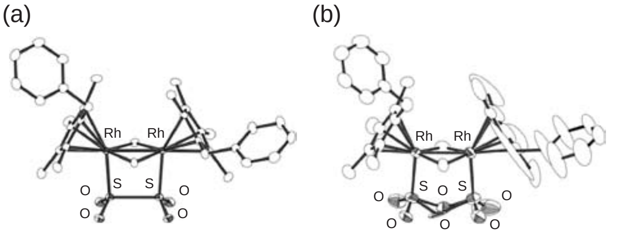

Figure 1. ORTEP drawings of (a) **1** and (b) **2** showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. ORTEP drawing of (b) is the disordering structure containing the four isomers of **2**.

The photoisomerization of **1** to **2** proceeds without degradation of the single-crystal form, though complex **1** has a considerable bulky ligand of $\mathrm{Cp^{Bn}}$ ring which can not rotate in the crystal,[3a] as indicated from the crystal packing (Figure S3)[7] and the solid-state ^{13}C NMR spectra, as shown in Figure 2a. It shows no temperature dependence of the signals at 148–293 K.

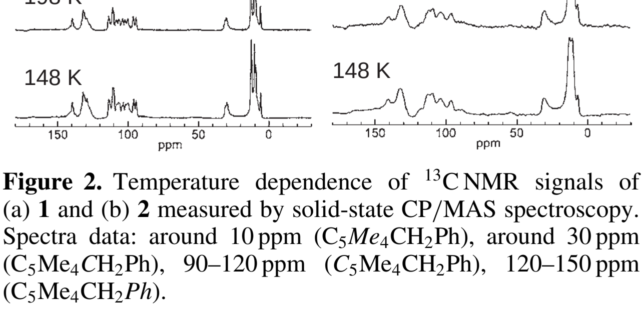

Figure 2. Temperature dependence of ^{13}C NMR signals of (a) **1** and (b) **2** measured by solid-state CP/MAS spectroscopy. Spectra data: around 10 ppm ($\mathrm{C_5}\mathit{Me}_4\mathrm{CH_2Ph}$), around 30 ppm ($\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2Ph}$), 90–120 ppm ($\mathit{C}_5\mathrm{Me_4CH_2Ph}$), 120–150 ppm ($\mathrm{C_5Me_4CH_2}\mathit{Ph}$).

During formation of **2**, how do the crystals solve the local

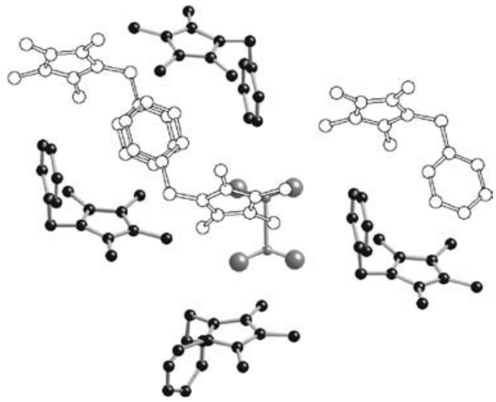

Figure 3. The cavity of the dithionite ligand of **1** formed by seven $\mathrm{Cp^{Bn}}$ ligands of other molecules. The white and black $\mathrm{Cp^{Bn}}$ ligands correspond to the right- and left-hand $\mathrm{Cp^{Bn}}$ ligands in **1** illustrated in Figure 1a, respectively. The white $\mathrm{Cp^{Bn}}$ ligand at the center of this figure is the nearest ligand to the central dithionite ligand.

stress[1] induced by photoisomerization without rotation of the ring? We have carefully inspected the thermal parameter change of the carbon atoms in the $\mathrm{Cp^{Bn}}$ rings with temperature and the occupancy change of the oxygen atoms before and after irradiation in the X-ray analysis. Figure 1a indicates that the thermal parameters of the carbon atoms in both right- and left-hand $\mathrm{Cp^{Bn}}$ rings in **1** have a similar value: similar size and shape of the thermal ellipsoids. After irradiation the ellipsoids of the left-hand $\mathrm{Cp^{Bn}}$ ring did not change appreciably (Figure 1b). In contrast, those of the right-hand $\mathrm{Cp^{Bn}}$ ring became elongated and enlarged along with the five-rotation axis of the Cp ring due to some disorder. Why does only the right-hand $\mathrm{Cp^{Bn}}$ ring have disorder?

The photosensitive dithionite ligand, which is located near the center of the cavity, produces local stress by oxygen atom transfer. Interestingly, the right-hand $\mathrm{Cp^{Bn}}$ ring (white in Figure 3) is closely on the dithionite ligand, as shown in Figure 3. Thus, its ring is more sensitive to the stress in the cavity than the left one. The generated stress might be compensated by the disordering of the right-hand $\mathrm{Cp^{Bn}}$ ring to stabilize the whole crystal.

The temperature dependence of the size and shape of the ellipsoids was examined by X-ray diffraction analysis (Figure S4).[7] The results show that they did not vary noticeably between 123 and 293 K. In addition, broadening of the solid-state ^{13}C CP/MAS signals of **2** with temperature elevation (Figure 2b), particularly due to the $\mathrm{CH_2}$ carbon that has a large compressed ellipsoid is very small. These results indicate that the disorder of the right-hand $\mathrm{Cp^{Bn}}$ ring of **2** is static. Difference in temperature dependence of the line shape between **1** and **2** (Figure 2) reflects the difference in the rigidity of the crystal packing: that of **2** is less rigid than that of **1** which has smaller unit cell volume (**1**: 3143.6(10) Å^3, **2**: 3165.0(8) Å^3).

The crystal of **2** consists of a mixture of stereochemical isomers (Figure S5),[7] which are detected by analysis of the dithionite oxygen disorder (Figure 1b) in the Fourier map. In the dithionite ligand of **1**, the terminal four oxygen atoms are stereochemically nonequivalent in the cavity formed by seven $\mathrm{Cp^{Bn}}$ ligands of the neighboring molecules. Upon photoirradiation, each terminal oxygen atom moves in a different ratio to the bridging position to form four stereochemically independent isomers of **2** in the crystal. When several photoreactions for separate crystals are performed under similar reaction conditions with respect to temperature, size and shape of the crystals, and the intensity of irradiation light, the resulting crystals of **2** in each photoreaction usually contain four isomers in a ratio of nearly 3:24:60:13 (Figure S5) despite the prolonged irradiation.[11] The crystal packing with this isomer ratio is the most stable packing and is also an important factor to stabilize the whole crystal of **2**.

A focus of our research is to elucidate the factors that enable the photoreaction of the Rh–Cp derivatives to progress in the crystalline state. In Rh–Cp*, the rotational motion of the ring is the key feature.[3] In contrast, in this work we determined that without the rotational motion the disordering of the $\mathrm{Cp^{Bn}}$ ring and the crystal packing of the isomer molecules are the key aspects. The substituent on the Cp ring governs the factors allowing the photoreaction to proceed in the crystalline state.

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8 Crystal data for **1** at 123 K: Crystal size $0.32 \times 0.18 \times 0.17\,\mathrm{mm}^3$, $\mathrm{C_{34}H_{42}O_4Rh_2S_2}$: fw 784.63, Space group $P2_1/c$, $a = 9.0227(17)$, $b = 13.993(2)$, $c = 25.049(5)$ Å, $\beta = 96.2991(14)^\circ$, $V = 3143.6(10)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.658\,\mathrm{g/cm^3}$, Number of reflections 7123, R_1 ($I > 2\sigma(I)$) 0.0275, wR_2 (all data) 0.0794, CCDC-686764.

9 Crystal data for **2** at 123 K: Crystal size $0.24 \times 0.22 \times 0.19\,\mathrm{mm}^3$, $\mathrm{C_{34}H_{42}O_4Rh_2S_2}$: fw 784.63, Space group $P2_1/c$, $a = 9.1916(13)$, $b = 14.2278(18)$, $c = 24.323(4)$ Å, $\beta = 95.7350(11)^\circ$, $V = 3165.0(8)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.647\,\mathrm{g/cm^3}$, Number of reflections 6980, R_1 ($I > 2\sigma(I)$) 0.0709, wR_2 (all data) 0.1629, CCDC-686763.

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11 In the case of the Cp* derivative, only one stereoisomer was formed at the final stage of the photoreaction.[2]