Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information (ESI) – Table of Contents

Molecular motion in organometallic crystals: photoinduced 2π/5 rotation of *n*-hexyltetramethylcyclopentadienyl ligand

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Experimental details

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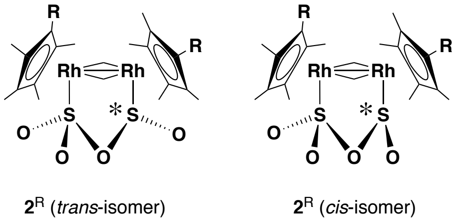
Experimental details

General: Solvents were purified by distillation before use. 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 crystals were irradiated using an LED lamp (Moritex, LLS2: 420-750 nm) ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance Neo 600 FT-NMR spectrometer in $CDCl_3$. Chemical shifts were referenced to *protio* solvent impurities (^{1}H: δ 7.26, ^{13}C: δ 77.16 ($CDCl_3$)). Infrared spectra were obtained with the KBr method on a JASCO 4600 FT-IR spectrometer. Absorption spectra in a microcrystalline powder film were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Elemental analyses were performed by A Rabbit Science Co., Ltd.

X-ray crystallography: All measurements were made on a Rigaku XtaLAB P200 diffractometer with confocal monochromated Mo Kα radiation (λ = 0.71070 Å). Data were collected and processed using CrysAlisPro[1] software (Rigaku). The data were corrected for Lorentz and polarisation effects. An emperical absorption corrections were applied. The structures were solved by a direct method: SIR92[2] for **1**$^{\text{Hex}}$ and SHELXT (Ver. 2014/5)[3] for **2**$^{\text{Hex}}$ and expanded using a Fourier technique. All calculations were performed using the CrystalStructure[4] crystallographic software package except for refinement, which was performed using SHELXL (Ver. 2014/7)[5]. All non-hydrogen atoms were refined anisotropically; two oxygen atoms (O2 and O6) in **2**$^{\text{Hex}}$ were refined isotropically. Hydrogen atoms were refined using the riding model.

The occupancy factors of the oxygen atoms of **2**$^{\text{Hex}}$ were fixed by the following treatments:

(1) The experimental occupancy factors of O1–O6 were obtained by refinement without any restriction: the sums of the occupancy factors (O1 + O3 + O5 and O2 + O4 + O6) were 2.0±0.1. Since no *cis*-isomer is present in our photochromic system,[6] ideal sum of the occupancy factors are 2.0000.



(2) In order to fit the experimental values to the ideal value, the experimental occupancy factors were multiplied by factors.

(3) If the calculated occupancy factor was more than 1.0000, the occupancy factor was fixed as 1.0000. The rests of the occupancy factors were treated with the same way.

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC). CCDC reference numbers: 2054887 (**1**$^{\text{Hex}}$) and 2054888 (**2**$^{\text{Hex}}$).

Syntheses

The *n*-hexyl derivative ligand precursor, HCp^{Hex} ($Cp^{Hex} = \eta^5$-C_5Me_4*n*-C_6H_{13}), was synthesized by modifying the procedure for HCp^{Pen} ($Cp^{Pen} = \eta^5$-C_5Me_4*n*-C_5H_{11}).[6] The starting material, *trans*-$[(RhCp^{Hex})_2(\mu\text{-}CH_2)_2Cl_2]$, was synthesized by modifying the procedure for the corresponding Cp^{Me} (η^5-C_5Me_5) analogue.[7]

$[(RhCp^{Hex})_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)]$ ($\mathbf{1}^{Hex}$): A mixture of *trans*-$[(RhCp^{Hex})_2(\mu\text{-}CH_2)_2\,Cl_2]$ (1.66 g, 2.32 mmol) and $Na_2S_2O_4$ (686 mg, 3.94 mmol) in MeOH (50 mL) was stirred for 4 h under Ar in the dark at room temperature. The solvent was removed under reduced pressure to give a reddish orange solid. The crude product was dissolved in 100 mL of CH_2Cl_2 and the insoluble solid was filtered off. Removal of the solvent afforded $\mathbf{1}^{Hex}$ as a red-orange solid. This solid was washed with Et_2O. Yield 1.22 g, 68%. Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of $\mathbf{1}^{Hex}$ in CH_3COOEt/CH_2Cl_2 (6/1) in the dark at room temperature.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.41 (2H, s, μ-CH_2), 8.54 (2H, s, μ-CH_2), 2.20 (4H, t, $C_5Me_4\mathit{CH_2}CH_2CH_2CH_2CH_2CH_3$), 1.84 (24H, s, $C_5\mathit{Me}_4$*n*-C_6H_{13}), 1.41-1.28 (16H, m, $C_5Me_4CH_2\mathit{CH_2CH_2CH_2CH_2}CH_3$), 0.87 (6H, t, $C_5Me_4CH_2CH_2CH_2CH_2CH_2\mathit{CH_3}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.6 (μ-CH_2), 107.5 (C_5Me_4*n*-C_6H_{13}), 104.5 (C_5Me_4*n*-C_6H_{13}), 104.0 (C_5Me_4*n*-C_6H_{13}), 31.7 (C_5Me_4*n*-C_6H_{13}), 29.7 (C_5Me_4*n*-C_6H_{13}), 29.4 (C_5Me_4*n*-C_6H_{13}), 24.8 (C_5Me_4*n*-C_6H_{13}), 22.6 (C_5Me_4*n*-C_6H_{13}), 14.1 (C_5Me_4*n*-C_6H_{13}), 9.71 ($C_5\mathit{Me}_4$*n*-C_6H_{13}), 9.64 ($C_5\mathit{Me}_4$*n*-C_6H_{13}). Anal. Calc. for $C_{32}H_{54}O_4Rh_2S_2$: C, 49.74; H, 7.04. Found: C, 49.56; H, 7.05%.

$[(\mathrm{RhCp}^{\mathrm{Hex}})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SOSO})]$ ($\mathbf{2}^{\mathrm{Hex}}$): The red-orange crystals of $\mathbf{1}^{\mathrm{Hex}}$ were irradiated with the LED lamp (420-750 nm, 0.4 $\mathrm{mW/cm^2}$) for 2 h under air at room temperature. The yellow-orange crystals of $\mathbf{2}^{\mathrm{Hex}}$ were obtained quantitatively.

^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ 9.50 (1H, s, μ-$\mathrm{CH_2}$), 9.04 (1H, s, μ-$\mathrm{CH_2}$), 8.61 (1H, s, μ-$\mathrm{CH_2}$), 8.13 (1H, s, μ-$\mathrm{CH_2}$), 2.27-2.03 (4H, m, $\mathrm{C_5Me_4C}\mathit{H_2}\mathrm{CH_2CH_2CH_2CH_2CH_3}$), 1.84 (12H, m, $\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 1.76 (12H, m, $\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 1.44-1.25 (16H, br, $\mathrm{C_5Me_4CH_2C}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 0.90 (6H, m, $\mathrm{C_5Me_4CH_2CH_2CH_2CH_2CH_2C}\mathit{H_3}$). ^{13}C NMR (150 MHz, $\mathrm{CDCl_3}$): δ 178.3 (μ-$\mathrm{CH_2}$), 168.8 (μ-$\mathrm{CH_2}$), 108.4 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 108.3 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 105.4 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 105.2 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 105.0 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 104.8 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 104.7 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 104.6 ($\mathit{C}_5\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_6H_{13}}$), 31.7 ($\mathrm{C_5Me_4}\mathit{n\text{-}C}_6\mathrm{H_{13}}$), 29.7 ($\mathrm{C_5Me_4}\mathit{n\text{-}C}_6\mathrm{H_{13}}$), 29.5 ($\mathrm{C_5Me_4}\mathit{n\text{-}C}_6\mathrm{H_{13}}$), 24.8 ($\mathrm{C_5Me_4}\mathit{n\text{-}C}_6\mathrm{H_{13}}$), 22.7 ($\mathrm{C_5Me_4}\mathit{n\text{-}C}_6\mathrm{H_{13}}$), 14.2 ($\mathrm{C_5Me_4}\mathit{n\text{-}C}_6\mathrm{H_{13}}$), 9.84 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 9.79 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 9.75 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 9.67 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 9.58 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 9.50 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$), 9.44 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_6H_{13}}$).

References

1 *CrysAlisPro*: Data collection and Processing Software, Rigaku Corporation (2015). Tokyo 196-8666, Japan.

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4 *CrystalStructure 4.2.2*: Crystal Structure Analysis Package, Rigaku Corporation (2000-2016). Tokyo 196-8666, Japan.

5 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

6 R. W. Seidel, C. Ganesamoorthy, S. Loerke, M. V. Winter, C. Gemel, R. A. Fischer, *Acta Cryst.*, 2013, **c69**, 573.

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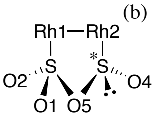
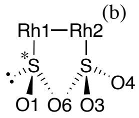
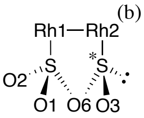
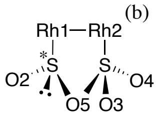
Tables

Table S1 Crystallographic data for $\mathbf{1}^{\mathrm{Hex}}$ and $\mathbf{2}^{\mathrm{Hex}}$

	$\mathbf{1}^{\mathrm{Hex}}$	$\mathbf{2}^{\mathrm{Hex}}$
Temperature (K)	100	100
Formula	$C_{32}H_{54}S_2O_4Rh_2$	$C_{32}H_{54}S_2O_4Rh_2$
Fw	772.71	772.71
Crystal system	orthorhombic	orthorhombic
Space group	Pbca	Pbca
a (Å)	19.7195(4)	19.7647(7)
b (Å)	8.9435(2)	8.9121(4)
c (Å)	37.5526(10)	38.0935(15)
α (deg)	90.0000	90.0000
β (deg)	90.0000	90.0000
γ (deg)	90.0000	90.0000
V (Å^3)	6622(3)	6710(5)
Z	8	8
μ (cm^{-1})	11.54	11.39
F(000)	3200	3200
D_{calcd}(g/cm^3)	1.550	1.530
Reflections collected	63875	34406
Independent reflection	9215 ($R_{\mathrm{int}} = 0.0699$)	8596 ($R_{\mathrm{int}} = 0.0651$)
Data/parameters	9215/371	8595/380
R_1 [$I > 2\sigma(I)$]	0.0473	0.0906
wR_2 (all data)	0.0922	0.1956
Goodness-of-fit	1.154	1.285

Table S2 Percentage population of the isomers, $\mathbf{1}^{\mathrm{Hex}}$, $\mathbf{2a}^{\mathrm{Hex}}$, $\mathbf{2b}^{\mathrm{Hex}}$, $\mathbf{2c}^{\mathrm{Hex}}$ and $\mathbf{2d}^{\mathrm{Hex}}$ in the crystal(a)

	$\mathbf{1}^{\mathrm{Hex}}$	 (b) $\mathbf{2a}^{\mathrm{Hex}}$ (R)	 (b) $\mathbf{2b}^{\mathrm{Hex}}$ (R)	 (b) $\mathbf{2c}^{\mathrm{Hex}}$ (S)	 (b) $\mathbf{2d}^{\mathrm{Hex}}$ (S)	$\mathbf{2}^{\mathrm{Hex}}$ (total)
$\mathbf{1}^{\mathrm{Hex}}$	100	0	0	0	0	0
$\mathbf{2}^{\mathrm{Hex}}$	2	9	86	3	0	98

(a) All the data have ±2% errors based on the errors of the experimental occupancy factors of the oxygen atoms. Although the crystal has mirror images of $\mathbf{2a}^{\mathrm{Hex}}$–$\mathbf{2d}^{\mathrm{Hex}}$, as a set, only one mirror image in the crystal is considered in this treatment (*Angew. Chem., Int. Ed.*, 2006, **45**, 6473; *J. Am. Chem. Soc.*, 2008, **130**, 17836). (b) The four stereoisomers, $\mathbf{2a}^{\mathrm{Hex}}$–$\mathbf{2d}^{\mathrm{Hex}}$, concerned with the μ-O_2SOSO unit. The Cp^{Hex} and μ-CH_2 ligands are omitted for clarity. The absolute configurations of the sulfur atoms are shown in parentheses.

The values of % for isomers $\mathbf{2a}^{\mathrm{Hex}}$–$\mathbf{2d}^{\mathrm{Hex}}$ were calculated from the simultaneous equations based on the occupancy of the oxygen atoms determined by X-ray diffraction analysis. The equations were as follows:

$$1.00\ (\text{occupancy of O1}) = \mathbf{2a}^{\mathrm{Hex}} + \mathbf{2b}^{\mathrm{Hex}} + \mathbf{2c}^{\mathrm{Hex}} + \mathbf{1}^{\mathrm{Hex}}$$

$$0.14\ (\text{occupancy of O2}) = \mathbf{2a}^{\mathrm{Hex}} + \mathbf{2c}^{\mathrm{Hex}} + \mathbf{2d}^{\mathrm{Hex}} + \mathbf{1}^{\mathrm{Hex}}$$

$$0.91\ (\text{occupancy of O3}) = \mathbf{2b}^{\mathrm{Hex}} + \mathbf{2c}^{\mathrm{Hex}} + \mathbf{2d}^{\mathrm{Hex}} + \mathbf{1}^{\mathrm{Hex}}$$

$$0.97\ (\text{occupancy of O4}) = \mathbf{2a}^{\mathrm{Hex}} + \mathbf{2b}^{\mathrm{Hex}} + \mathbf{2d}^{\mathrm{Hex}} + \mathbf{1}^{\mathrm{Hex}}$$

$$0.11\ (\text{occupancy of O5}) = \mathbf{2a}^{\mathrm{Hex}} + \mathbf{2d}^{\mathrm{Hex}}$$

$$0.87\ (\text{occupancy of O6}) = \mathbf{2b}^{\mathrm{Hex}} + \mathbf{2c}^{\mathrm{Hex}}$$

$$\mathbf{2a}^{\mathrm{Hex}} = 0.09,\ \mathbf{2b}^{\mathrm{Hex}} = 0.86,\ \mathbf{2c}^{\mathrm{Hex}} = 0.03,\ \mathbf{2d}^{\mathrm{Hex}} = 0.00,\ \mathbf{1}^{\mathrm{Hex}} = 0.02.$$

Figures

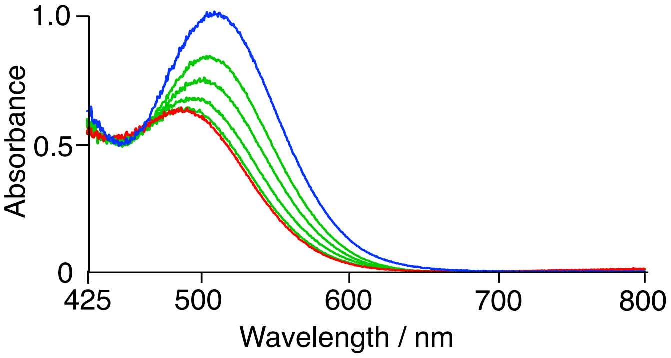


Fig. S1 The UV-vis spectral changes from $\mathbf{1}^{\mathrm{Hex}}$ (blue) to $\mathbf{2}^{\mathrm{Hex}}$ (red) in a microcrystalline powder film.

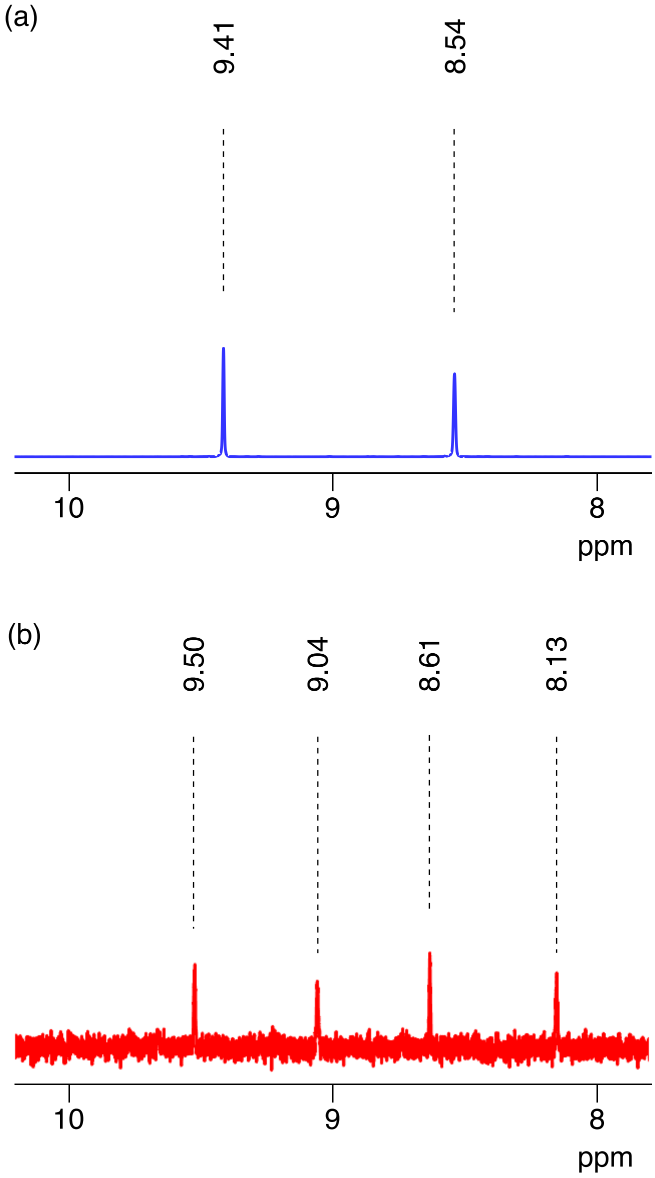
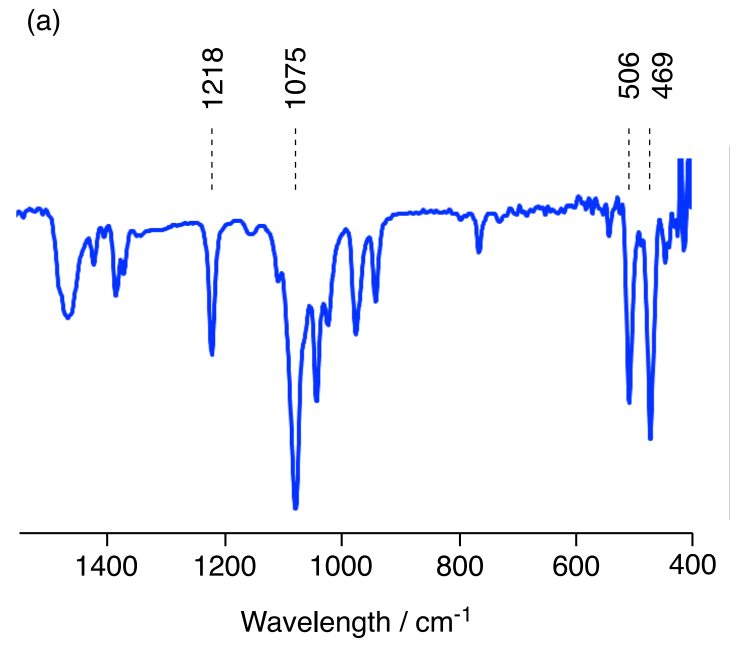


Fig. S2 ^{1}H NMR spectra of (a) **1**$^{\mathrm{Hex}}$ (blue) and (b) **2**$^{\mathrm{Hex}}$ (red) in $CDCl_3$ in the range of μ-CH_2 signals.



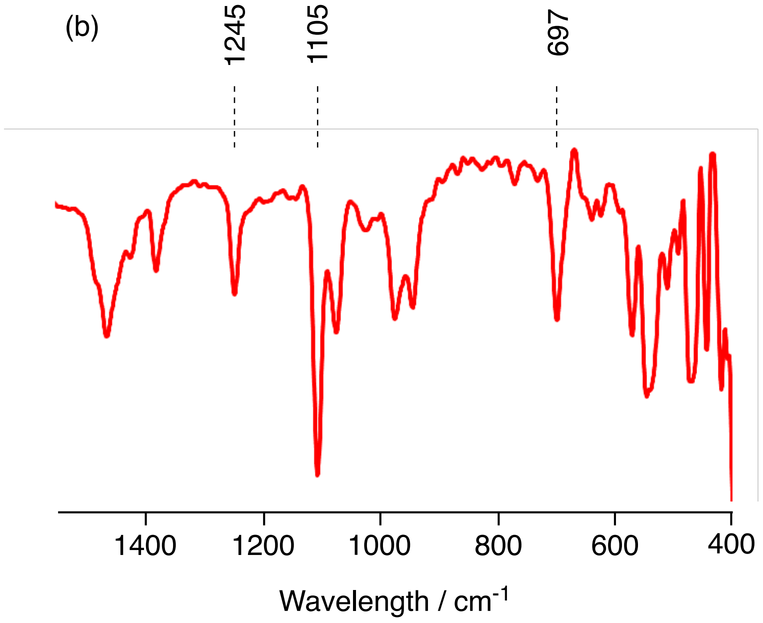


Fig. S3 IR spectra of (a) **1**$^{\mathrm{Hex}}$ (blue) and (b) **2**$^{\mathrm{Hex}}$ (red) in KBr.