

Preparation and properties of diruthenium complexes with bridging disulfide and thiolate ligands $[\text{Cp}^* \text{Ru}(\mu\text{-S}_2)(\mu\text{-SR})_2 \text{RuCp}^*]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{R} = \text{Pr}^i$ and PhCH_2)

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Abstract

Reactions of $[\text{Cp}^* \text{RuCl}(\mu\text{-SR})_2 \text{RuCp}^* \text{Cl}]$ (**2**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with Li_2S_2 in toluene at room temperature afforded the diruthenium complexes bridged by one disulfide and two thiolate ligands $[\text{Cp}^* \text{Ru}(\mu\text{-S}_2)(\mu\text{-SR})_2 \text{RuCp}^*]$ (**3a**, $\text{R} = \text{Pr}^i$; **3b**, $\text{R} = \text{PhCH}_2$), whose structures have been determined by X-ray crystallography. Crystal data for **3a**: tetragonal, space group $P4_12_12$ (No. 92), $a = 15.368(5)$, $c = 25.863(8)$ Å, $V = 6108(4)$ Å³, $Z = 8$, and $R(Rw) = 0.055$ (0.066) for 2582 reflections ($|F_o| > 3\sigma(F_o)$). **3b**: monoclinic, space group $P2_1/n$ (No. 14), $a = 10.607(1)$, $b = 23.214(3)$, $c = 14.107(3)$ Å, $\beta = 90.56(1)^\circ$, $V = 3473(1)$ Å³, $Z = 4$, and $R(Rw) = 0.067$ (0.074) for 5744 reflections ($|F_o| > 3\sigma(F_o)$). Cyclic voltammograms of **3** each exhibit two consecutive oxidation waves and one reduction wave that are all reversible.

Keywords: Ruthenium; Thiolate; Disulfide; X-ray structure; Cyclic voltammogram

1. Introduction

Our intensive studies on the reactivities of a dinuclear Ru(III) complex $[\text{Cp}^* \text{RuCl}(\mu\text{-Cl})_2 \text{RuCp}^* \text{Cl}]$ (**1**) and a tetranuclear Ru(II) complex $[(\text{Cp}^* \text{Ru})_4(\mu_3\text{-Cl})_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) towards various thiolate compounds led to preparation of a series of diruthenium complexes containing two or three bridging thiolate ligands [1] which involve the Ru(III)/Ru(III) complexes $[\text{Cp}^* \text{Ru}(\mu\text{-SR})_3 \text{RuCp}^* \text{Cl}]$ ($\text{R} = \text{aryl}$) and $[\text{Cp}^* \text{RuCl}(\mu\text{-SR})_2 \text{RuCp}^* \text{Cl}]$ (**2**; $\text{R} = \text{alkyl}$) [2], the Ru(II)/Ru(III) complexes $[\text{Cp}^* \text{Ru}(\mu\text{-SR})_3 \text{RuCp}^*]$ ($\text{R} = \text{alkyl, aryl}$) [3], and the Ru(II)/Ru(II) complexes $[\text{Cp}^* \text{Ru}(\mu\text{-SR})_2 \text{RuCp}^*]$ ($\text{R} = \text{alkyl, aryl}$) [4]. Activation and transformations of substrate molecules on multimetallic sites have been attracting significant interest in recent years. Reactivities of these thiolate-bridged diruthenium complexes towards various substrates have been investigated in this context, which has already resulted in

exploitation of the rich chemistry displayed at the bimetallic sites in these and related diruthenium complexes; e.g. the novel oligomerization reactions of terminal alkynes [5], the dinuclear oxidative addition reactions of alkyl halides and H_2 [4a], and the catalytic disproportionation of N_2H_4 into NH_3 and N_2 [6].

Recently we have also found that a new class of diruthenium complexes containing a bridging disulfide ligand together with two bridging thiolate ligands $[\text{Cp}^* \text{Ru}(\mu\text{-S}_2)(\mu\text{-SR})_2 \text{RuCp}^*]$ (**3**) can be obtained by the reactions of **2** with $[\text{NH}_4]_2[\text{MS}_4]$ ($\text{M} = \text{W, Mo}$) or Li_2S_2 . It is to be noted that complexes **3** have proved to serve as versatile precursors to prepare novel mixed metal sulfide clusters. Thus the trinuclear and tetranuclear clusters $[(\text{Cp}^* \text{Ru})_2(\mu\text{-SPr}^i)_2(\mu\text{-S})_2 \text{Pt}(\text{PPh}_3)_2]$ and $[(\text{Cp}^* \text{Ru})_2(\mu_3\text{-S})_2 \text{Pd}_2(\mu\text{-SPr}^i)(\text{SPr}^i)(\text{PPh}_3)]$ have been derived quite recently through the oxidative addition of the zero-valent Pt and Pd metal centers in $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pt, Pd}$) across the S–S bond in **3a** ($\text{R} = \text{Pr}^i$) [7]. In this paper, we wish to report the details of synthesis and characterization of the potential diruthenium complexes **3** along with their electrochemi-

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cal properties. A part of this work has appeared previously in a preliminary form [8].

2. Results and discussion

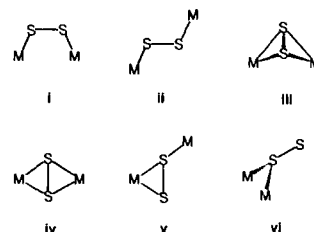
2.1. Preparation of $[\text{Cp}^*\text{Ru}(\mu\text{-S}_2)(\mu\text{-SR})_2\text{RuCp}^*]$ (**3**)

Treatment of **2** (**2a**: R = Prⁱ; **2b**: R = PhCH₂) with excess Li₂S₂ in toluene at room temperature produced the dark green products **3a** and **3b** (R = PhCH₂) in 25 and 20% yields respectively. Reactions of **2a** with [NH₄]₂[MS₄] (M = W, Mo) in THF at reflux, which were attempted with the aim of preparing mixed metal sulfide–thiolate compounds, also resulted in the formation of **3a** as the only isolable product. The isolated yields of **3a** from the reactions using [WS₄]²⁻ and [MoS₄]²⁻ were 11 and 8.3% respectively. Analogous extrusion of S₂²⁻ from MS₄²⁻ was observed in the reactions of **1** with [MS₄]²⁻ in THF at reflux to give $[(\mu\text{-S}_2)(\text{Cp}^*\text{Ru})_2(\mu_3\text{-S})(\mu_2\text{-S})_2\text{MS}]$ (M = W, Mo) [8,9]. Formation of diselenide complex $[(\eta^2\text{-Se}_2)\text{Ni}(\mu\text{-Se})_2\text{WSe}_2]^{2-}$ from the reaction of [Ni(acac)₂] with [WSe₄]²⁻ [10], which has been demonstrated to proceed via the degradation of [Se₂W(μ-Se)₂Ni(μ-Se)₂WSe₂]²⁻ initially generated, may also correlate with the present reaction. It has further been shown that **3a** can be obtained in 21% yield from the reaction of $[\text{Cp}^*\text{Ru}(\mu\text{-SPr}^i)_2\text{RuCp}^*]$ (**4**) with S₈ in toluene at room temperature. These three reaction courses affording **3** are summarized in Scheme 1. Reaction pathway towards $[\text{Cp}^*\text{Ru}(\mu\text{-S}_2)(\mu\text{-S}^i\text{Bu})_2\text{RuCp}^*]$ from $[\text{Cp}^*\text{-Ru}(\mu\text{-S}^i\text{Bu})_2\text{RuCp}^*]$ by treatment with S₈ has recently been demonstrated independently by Koelle and coworkers [4b]. Complexes **3** are highly soluble into both polar and non-polar organic solvents, which may be responsible, at least in part, for the unsatisfactory isolated yields of **3**.

The ¹H NMR spectrum of **3a** exhibits a singlet assignable to the Cp* methyl protons together with one septet and one doublet due to the Prⁱ group. In the spectrum of **3b**, both the Cp* methyl protons and the benzyl methylene protons appear as one singlet respectively. These spectral features are indicative of the equivalence of the two Cp* and two SR ligands, and

therefore the structure containing the two symmetrically bridged Cp* Ru units as well as the two R groups in a mutually *syn* orientation are plausible for **3**, which has been confirmed by X-ray crystallography (vide infra).

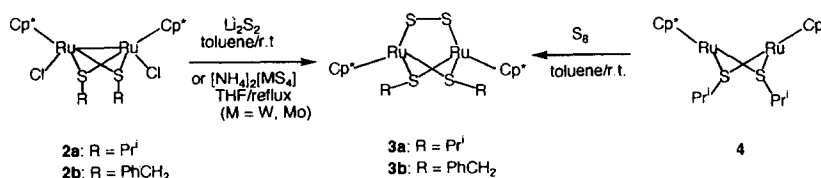
A number of disulfide complexes has already been reported for a wide range of transition metals. In addition to a simple η² coordination mode to a single metal center, the S₂ ligand is known to display a variety of bridging modes between multimetallic centers [11].



With respect to the μ₂-S₂ ligand, structural types (i)–(vi) shown above have been observed in the well-defined complexes. These include the diruthenium complexes containing the type (i) ligand such as $[\{\text{RuCl}(\text{P}(\text{OMe})_3)_2\}_2(\mu\text{-S}_2)(\mu\text{-Cl})(\mu\text{-N}_2\text{H}_4)]$ [12] and $[\{\text{RuCl}(\text{P}(\text{OMe})_3)_2\}_2(\mu\text{-S}_2)(\mu\text{-Cl})_2]$ (**5**) [13] and those having the type (ii) ligand, $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-S}_2)]^{4+}$ [14], $[\{(\text{MeCp})\text{Ru}(\text{PPh}_3)_2\}_2(\mu\text{-S}_2)_2]$ [15], $[\{\text{CpRu}(\text{PMe}_3)_2\}_2(\mu\text{-S}_2)]^{2+}$ [16], $[\{\text{Ru}(\text{PPh}_3)(\text{S}_4')\}_2(\mu\text{-S}_2)]$ (‘S₄’ = SC₆H₄SCH₂CH₂SC₆H₄S) [17], and $[\{\text{Ru}(\text{MeCN})_3(\text{P}(\text{OMe})_3)_2\}_2(\mu\text{-S}_2)]^{3+}$ [18], while the type (v) ligand has been found in $[(\text{Cp}^*\text{Ru})_2(\mu\text{-S}_2)(\mu\text{-S}_3)(\text{CO})]$ [19]. In addition, $[\{(\text{C}_5\text{Me}_4\text{Et})\text{Ru}\}_2(\mu\text{-S}_2)_2]$ (**6**) has been shown to consist of both the type (i) and type (iii) ligands [20]. It should be noted that diiron complexes related to **3**, $[\text{CpFe}(\mu\text{-S}_2)(\mu\text{-SR})_2\text{FeCp}]$ (**7**) [21], have been prepared previously from the reactions of either $[\text{CpFe}(\text{CO})_2]_2$ with Et₂S_n (n = 3, 4) or $[\text{CpFe}(\text{CO})(\text{SR})]_2$ with S₈, although the yields via both the synthetic routes were poor [21d].

2.2. Description of the X-ray structures of **3**

X-ray analyses have been carried out for both **3a** and **3b** to clarify their detailed structures. ORTEP drawing of **3a** and **3b** are shown in Figs. 1 and 2, while selected bond distances and angles are listed in Table 1.



Scheme 1.

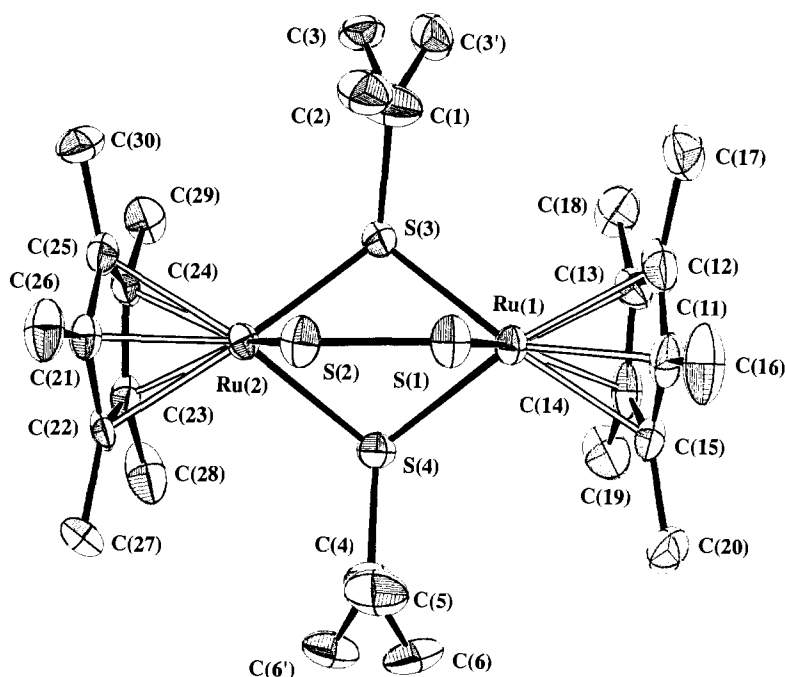


Fig. 1. Molecular structure of **3a**. The C(3') and C(6') atoms relate to the C(3) and C(6) atoms respectively by the disorder with 50% occupancy.

The structures of **3a** and **3b** are essentially the same, despite the presence of slight differences in the corresponding structural parameters. As expected, complexes **3** consist of two Cp*Ru units symmetrically bridged by one *cis*- η^1, η^1 -S₂ ligand of type (i) and two SR ligands. The distances between two Ru atoms of 3.591(2) Å in **3a** and 3.558(1) Å in **3b** are comparable with that linked by one *cis*- η^1, η^1 -S₂ and two Cl ligands in **5** (3.579(1) Å) [13] but significantly shorter than that in **6**

(3.749(1) Å) with the *cis*- η^1, η^1 -S₂ and η^2, η^2 -S₂ ligands [20]. The Ru–Ru distances in **3** are much elongated from those in the complexes containing two Ru(III) centers connected by an Ru–Ru single bond surrounded by two or three SR ligands, such as **2a** (2.853(2) Å) and [Cp*Ru(μ -SPh)₃RuCp*]⁺ (2.630(1) Å) [2], indicating the absence of any bonding interaction between two Ru atoms in **3**.

The S–S bond of the S₂ ligand in **3** is parallel to the

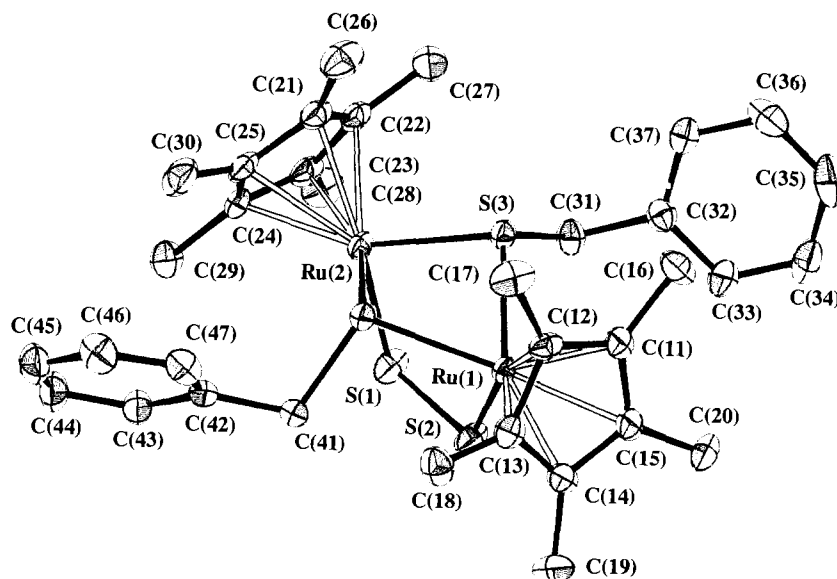


Fig. 2. Molecular structure of **3b**.

Ru–Ru vector and the S–S bond lengths (**3a**: 2.008(6) Å; **3b**: 2.020(4) Å) are slightly shorter, if compared with the S–S bond length in HSSH (2.055 Å) and MeSSMe (2.038 Å) [22]. The Ru–S distances in the Ru–S–S–Ru linkages (2.20–2.22 Å) are significantly shorter than those of the Ru–SR moieties (2.38–2.43 Å), which can be ascribed to the strong π -donating ability of the S₂ ligand, as suggested for the other S₂ complexes [12,16]. The diamagnetic nature of **3**, despite the presence of two Ru(III) atoms without metal–metal interaction, can be interpreted in terms of electron-pairing through the *cis*- η^1, η^1 -S₂ ligand with metal–sulfur $d\pi$ - $p\pi$ interaction, as was previously proposed for **7** [21c] and [(CpFe)₂(μ - η^1, η^1 -S₂)(μ - η^2, η^2 -S₂)] [23]. Two Prⁱ groups in **3a** and two benzyl groups in **3b** are both in the *syn*-equatorial orientation, which is consistent with the results of the ¹H NMR spectra described

above. Two almost eclipsed Cp* ligands are distorted to the direction opposite to the S₂ ligand, displaying the mutually *cis* disposition with respect to the Ru–Ru vector. Dihedral angles between the two cyclopentadienyl planes are 27° in **3a** and 39° in **3b** respectively.

2.3. Electrochemical properties of **3**

Under cyclic voltammetric conditions, complexes **3** dissolved in CH₂Cl₂-[ⁿBu₄N][BF₄] exhibit three successive reversible waves, which are assignable to the redox processes [3]⁻ (Ru(II)/Ru(III)) \rightleftharpoons [3]⁰ (Ru(III)/Ru(III)) \rightleftharpoons [3]⁺ (Ru(IV)/Ru(III)) \rightleftharpoons [3]²⁺ (Ru(IV)/Ru(IV)). The potentials observed for **3** are summarized in Table 2, together with those of the Fe analogues **7** reported previously [24]. As shown in Table 2, the Ru complexes **3** undergo one-electron oxidation and reduc-

Table 1
Selected bond distances and angles in **3a** and **3b**

Bond distances (Å)			
3a		3b	
Ru(1)–S(1)	2.215(4)	Ru(1)–S(1)	2.219(3)
Ru(1)–S(3)	2.417(4)	Ru(1)–S(3)	2.397(2)
Ru(1)–S(4)	2.430(4)	Ru(1)–S(4)	2.386(2)
Ru(1)–C(11)	2.19(2)	Ru(1)–C(11)	2.24(1)
Ru(1)–C(12)	2.23(2)	Ru(1)–C(12)	2.22(1)
Ru(1)–C(13)	2.32(2)	Ru(1)–C(13)	2.21(1)
Ru(1)–C(14)	2.27(2)	Ru(1)–C(14)	2.22(1)
Ru(1)–C(15)	2.23(2)	Ru(1)–C(15)	2.24(1)
Ru(2)–S(2)	2.209(5)	Ru(2)–S(2)	2.214(3)
Ru(2)–S(3)	2.423(4)	Ru(2)–S(3)	2.390(2)
Ru(2)–S(4)	2.424(4)	Ru(2)–S(4)	2.412(2)
Ru(2)–C(21)	2.20(2)	Ru(2)–C(21)	2.23(1)
Ru(2)–C(22)	2.22(2)	Ru(2)–C(22)	2.20(1)
Ru(2)–C(23)	2.30(1)	Ru(2)–C(23)	2.21(1)
Ru(2)–C(24)	2.29(1)	Ru(2)–C(24)	2.24(1)
Ru(2)–C(25)	2.21(2)	Ru(2)–C(25)	2.26(1)
S(1)–S(2)	2.008(6)	S(1)–S(2)	2.020(4)
S(3)–C(1)	1.91(2)	S(3)–C(31)	1.85(1)
S(4)–C(4)	1.93(2)	S(4)–C(41)	1.86(1)
Ru(1)–Ru(2)	3.591(2)	Ru(1)–Ru(2)	3.558(1)
Bond angles (°)			
3a		3b	
S(1)–Ru(1)–S(3)	93.1(2)	S(1)–Ru(1)–S(3)	91.0(1)
S(1)–Ru(1)–S(4)	93.6(2)	S(1)–Ru(1)–S(4)	90.9(1)
S(3)–Ru(1)–S(4)	70.0(1)	S(3)–Ru(1)–S(4)	74.3(1)
S(2)–Ru(2)–S(3)	93.6(2)	S(2)–Ru(2)–S(3)	90.8(1)
S(2)–Ru(2)–S(4)	93.7(2)	S(2)–Ru(2)–S(4)	91.1(1)
S(3)–Ru(2)–S(4)	70.0(1)	S(3)–Ru(2)–S(4)	73.9(1)
Ru(1)–S(1)–S(2)	111.2(2)	Ru(1)–S(1)–S(2)	110.2(1)
Ru(2)–S(2)–S(1)	110.8(2)	Ru(2)–S(2)–S(1)	110.4(1)
Ru(1)–S(3)–Ru(2)	95.8(1)	Ru(1)–S(3)–Ru(2)	96.1(1)
Ru(1)–S(3)–C(1)	111.5(7)	Ru(1)–S(3)–C(31)	110.3(4)
Ru(2)–S(3)–C(1)	117.7(7)	Ru(2)–S(3)–C(31)	105.0(3)
Ru(1)–S(4)–Ru(2)	95.4(2)	Ru(1)–S(4)–Ru(2)	95.7(1)
Ru(1)–S(4)–C(4)	115.3(8)	Ru(1)–S(4)–C(41)	105.6(3)
Ru(2)–S(4)–C(4)	113.7(7)	Ru(2)–S(4)–C(41)	111.5(3)

Table 2
Electrochemical data of complexes **3** and **7**^a

Complex	R	$E_{1/2}(\text{red})$	$E_{1/2}(\text{ox})$	$E_{1/2}(\text{ox})$
3 ^b	Pr ¹	-1.49	-0.16	0.93
	PhCH ₂	-1.37	-0.09	0.97
7 ^c	Et	-1.2 ^d	0.21	0.90 ^f
	PhCH ₂	n.d. ^e	0.28	0.99 ^f

^a V vs. SCE; reversible processes. ^b In CH₂Cl₂-[ⁿBu₄N][BF₄] (0.1 M). ^c In CH₃CN-[NH₄][PF₆] (0.1 M); Ref. [24]. ^d Anodic peak potential of irreversible wave. ^e Not described. ^f Quasi-reversible at slow scan rates and reversible at high scan rates.

tion at more negative potentials than their Fe analogues **7**. This indicates that the energy levels of both HOMO and LUMO in **3**, including the second-row transition metal, are higher than those in **7** containing the first-row transition metal in the same triad, as commonly observed in other complexes. It is noteworthy that the Ru species generated by both one-electron reduction and two-electron oxidation of **3** are more stable than the corresponding Fe species; both of these redox processes are reversible for **3** under cyclic voltammetric conditions, although it has been reported that the former

process is irreversible and the latter is quasi-reversible for **7**. It should also be noted that the reversible one-electron oxidation occurs at the more positive potentials in the chloride complexes **2** [2] than in the S₂ complexes **3**, which is consistent with the stronger electron donating ability of the S₂ ligand.

3. Experimental details

3.1. General

All experiments were carried out under dry nitrogen atmosphere by using standard Schlenk techniques. Compounds **2** [2b], **4** [4a], [NH₄]₂[MS₄] [25], and Li₂S₂ [26] were prepared according to the literature methods. ¹H NMR spectra were recorded on a JEOL JMN-GX-400 or EX-270 spectrometer. Electrochemical measurements were made by Hokuto Denko instrumentation (HA-501 potentiostat and HB-105 function generator) by using a glassy carbon electrode and a Pt wire counter electrode; potentials were measured vs. a saturated calomel electrode as reference.

Table 3
X-ray crystallographic data for **3a** and **3b**

	3a	3b
<i>Crystal data</i>		
Formula	C ₂₆ H ₄₄ S ₄ Ru ₂	C ₃₄ H ₄₄ S ₄ Ru ₂
FW	687.0	783.2
Crystal color	green	green
Crystal system	tetragonal	monoclinic
Space group	<i>P</i> 4 ₁ 2 ₁ 2 (No. 92)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	15.368(5)	10.607(1)
<i>b</i> (Å)	15.368(5)	23.214(3)
<i>c</i> (Å)	25.863(8)	14.107(3)
β (°)	90.00	90.56(1)
<i>V</i> (Å ³)	6108(4)	3473(1)
<i>Z</i>	8	4
<i>D</i> _{calc} (g cm ⁻³)	1.494	1.497
μ (cm ⁻¹)	12.46	11.06
<i>F</i> (000)	2816	1600
Crystal dimensions (mm ³)	0.38 × 0.30 × 0.38	0.20 × 0.30 × 0.35
<i>Data collection</i>		
Diffractometer	MAC MXC18	Rigaku AFC6A
Radiation (λ (Å))	Mo K α (0.7107)	Mo K α (0.7107)
Max 2θ (°)	50	55
Scan method	$\omega/2\theta$	$\omega(2\theta < 30^\circ)$, $\omega/2\theta(2\theta < 30^\circ)$
Scan speed (° min ⁻¹)	16	4
Reflections measured	+ <i>h</i> , + <i>k</i> , + <i>l</i> , <i>h</i> ≥ <i>k</i>	± <i>h</i> , + <i>k</i> , + <i>l</i>
Absorption correction	Gaussian integration method	
Transmission factor	0.677–0.710	0.721–0.810
<i>Structure refinement</i>		
No. of data used	2582 ($ F_o > 3\sigma(F_o)$)	5744 ($ F_o > 3\sigma(F_o)$)
No. of parameters refined	308	538
<i>R</i>	0.055	0.067
<i>R</i> _w	0.066	0.074
Max residual (eÅ ⁻³)	0.60 (around C(25))	1.3 (around Ru(2))

3.2. Preparation of $[Cp^*Ru(\mu-S_2)(\mu-SPr^i)_2RuCp^*]$ (**3a**)

(a) A mixture of **2a** (1.07 g, 1.54 mmol) and Li_2S_2 (0.50 g, 6.4 mmol) in toluene (15 cm³) was stirred at room temperature for 24 h and the resulting green suspension was filtered. The filtrate was dried in vacuo and the residue was extracted with hexane (35 cm³), which was evaporated to dryness to give a green solid of **3a**. The product obtained here was satisfactorily pure from NMR criteria. Analytically pure **3a** was available after dissolving a solid in minimum CH_2Cl_2 , followed by addition of MeOH with stirring (265 mg, 25%). Anal. Found: C, 44.69; H, 6.24. $C_{26}H_{44}S_4Ru_2$. Calc.: C, 45.45; H, 6.45%. ¹H NMR ($CDCl_3$): δ 1.80 (s, 30H, Cp*), 1.05 (sep, 2H, SCHMe₂), 0.34 (d, 12H, SCHMe₂).

(b) A mixture of **2a** (104 mg, 0.149 mmol) and $[NH_4]_2[WS_4]$ (303 mg, 0.871 mmol) in THF (5 cm³) was refluxed for 3 h and the resultant suspension was filtered. The green filtrate was dried in vacuo and the residue was extracted with hexane (12 cm³). The extract was concentrated and cooled to $-20^\circ C$, affording crystals of **3a** (11 mg, 11%). Analogous treatment of **2a** with $[NH_4]_2[MoS_4]$ also gave **3a** in 8.3% yield.

(c) A mixture of **4** (84.5 mg, 0.136 mmol) and S_8 (8.3 mg, 0.032 mmol) in toluene (4 cm³) was stirred at room temperature for 8 h. After removing the solvent in vacuo, the green residue was extracted with hexane (15 cm³). The extract was dried and crystallized from ether at $-20^\circ C$ (19.5 mg, 21%).

3.3. Preparation of $[Cp^*Ru(\mu-S_2)(\mu-SCH_2Ph)_2RuCp^*]$ (**3b**)

To a purple suspension of **2b** (453 mg, 0.574 mmol) in toluene (10 cm³) was added Li_2S_2 (105 mg, 1.34 mmol) and the mixture was stirred overnight at room temperature. The green suspension was filtered and the filtrate was dried in vacuo. The residue was extracted with ether and the concentrated extract was stored at $-20^\circ C$. Green crystals precipitated were collected and dried (90 mg, 20%). Anal. Found: C, 52.10; H, 5.57; S, 16.83. $C_{34}H_{44}S_4Ru_2$. Calc.: C, 52.14; H, 5.67; S, 16.38%. ¹H NMR (C_6D_6): δ 1.56 (s, 30H, Cp*), 2.21 (s, 4H, SCH₂), 6.8–7.1 (m, 10H, Ph).

3.4. X-ray crystallography

Single crystals of **3** suitable for X-ray analyses were obtained from their ether solutions at $-20^\circ C$ and sealed in the glass capillaries. Diffraction data were collected at room temperature with the use of graphite-monochromatized Mo K α radiation. Unit cell parameters and orientation matrices were obtained for 20 machine-

Table 4
Coordinates of non-hydrogen atoms in **3a** and **3b**

Atom	x	y	z
3a			
Ru(1)	0.73532(8)	0.75248(8)	0.78799(4)
Ru(2)	0.76972(8)	0.90752(7)	0.68613(5)
S(1)	0.7623(4)	0.8837(3)	0.8196(2)
S(2)	0.7801(3)	0.9707(3)	0.7626(2)
S(3)	0.8334(2)	0.7723(3)	0.7159(2)
S(4)	0.6561(3)	0.8085(3)	0.7138(2)
C(11)	0.711(1)	0.692(1)	0.8631(6)
C(12)	0.785(1)	0.652(1)	0.8431(8)
C(13)	0.757(1)	0.604(1)	0.7957(6)
C(14)	0.669(1)	0.620(1)	0.7903(7)
C(15)	0.640(1)	0.674(1)	0.8327(7)
C(16)	0.713(2)	0.741(1)	0.9152(6)
C(17)	0.882(2)	0.640(2)	0.8647(8)
C(18)	0.812(1)	0.548(1)	0.7596(9)
C(19)	0.611(1)	0.582(1)	0.7485(9)
C(20)	0.545(1)	0.698(1)	0.8473(9)
C(21)	0.797(1)	1.029(1)	0.6438(6)
C(22)	0.710(1)	0.9961(9)	0.6282(6)
C(23)	0.724(1)	0.914(1)	0.6014(6)
C(24)	0.817(1)	0.897(1)	0.6026(6)
C(25)	0.859(1)	0.965(1)	0.6284(6)
C(26)	0.818(2)	1.118(1)	0.6665(7)
C(27)	0.625(1)	1.046(1)	0.6324(7)
C(28)	0.648(2)	0.858(1)	0.5766(8)
C(29)	0.862(1)	0.816(1)	0.5777(6)
C(30)	0.957(1)	0.979(1)	0.6300(9)
C(1)	0.952(1)	0.774(2)	0.7380(9)
C(2)	0.979(1)	0.854(2)	0.7663(9)
C(3) ^a	1.007(2)	0.737(3)	0.703(1)
C(3') ^a	0.997(3)	0.699(2)	0.732(1)
C(4)	0.547(1)	0.865(2)	0.7295(9)
C(5)	0.552(2)	0.929(2)	0.768(1)
C(6) ^a	0.474(2)	0.807(3)	0.719(2)
C(6') ^a	0.490(2)	0.856(3)	0.691(2)
3b			
Ru(1)	0.25776(7)	0.57930(3)	0.83499(5)
Ru(2)	0.46308(6)	0.64212(3)	0.66587(5)
S(1)	0.4084(3)	0.5176(1)	0.7962(2)
S(2)	0.5262(3)	0.5538(1)	0.7017(2)
S(3)	0.4026(2)	0.6583(1)	0.8264(1)
S(4)	0.2451(2)	0.6134(1)	0.6756(1)
C(11)	0.1633(9)	0.6073(5)	0.9687(7)
C(12)	0.0801(9)	0.6162(5)	0.8911(7)
C(13)	0.0542(9)	0.5619(5)	0.8481(7)
C(14)	0.1221(9)	0.5187(4)	0.9003(7)
C(15)	0.1901(9)	0.5466(5)	0.9746(6)
C(16)	0.206(1)	0.6532(6)	1.0378(8)
C(17)	0.021(1)	0.6727(5)	0.864(1)
C(18)	-0.038(1)	0.5529(6)	0.7684(8)
C(19)	0.114(1)	0.4540(5)	0.8838(9)
C(20)	0.266(1)	0.5172(6)	1.0523(8)
C(21)	0.4673(9)	0.7337(4)	0.6186(7)
C(22)	0.5905(9)	0.7164(4)	0.6547(7)
C(23)	0.6361(9)	0.6722(5)	0.5947(7)
C(24)	0.5429(9)	0.6609(5)	0.5227(6)
C(25)	0.4398(9)	0.6995(4)	0.5377(6)
C(26)	0.390(1)	0.7820(5)	0.6588(9)
C(27)	0.663(1)	0.7449(5)	0.7329(8)
C(28)	0.764(1)	0.6430(6)	0.5999(9)
C(29)	0.560(1)	0.6218(6)	0.4384(7)
C(30)	0.323(1)	0.7059(5)	0.4770(8)

Table 4 (continued)

Atom	x	y	z
C(31)	0.5460(9)	0.6428(5)	0.8980(6)
C(32)	0.5347(8)	0.6630(5)	1.0003(7)
C(33)	0.542(1)	0.6228(4)	1.0735(7)
C(34)	0.534(1)	0.6398(5)	1.1672(7)
C(35)	0.521(1)	0.6975(6)	1.1887(8)
C(36)	0.519(1)	0.7277(5)	1.1163(8)
C(37)	0.523(1)	0.7204(5)	1.0221(8)
C(41)	0.2121(9)	0.5487(4)	0.6018(6)
C(42)	0.1798(9)	0.5645(4)	0.5012(7)
C(43)	0.261(1)	0.5489(5)	0.4299(7)
C(44)	0.235(1)	0.5650(6)	0.3371(8)
C(45)	0.128(2)	0.5962(6)	0.3149(9)
C(46)	0.044(1)	0.6094(6)	0.387(1)
C(47)	0.070(1)	0.5943(6)	0.4797(8)

^a Atom multiplicity of 0.5.

centered reflections ($25 < 2\theta < 35^\circ$). Data collection and crystal parameters are listed in Table 3. Three check reflections monitored every 100 reflections exhibited no significant decay during data collections. Lorentz and polarization corrections as well as the absorption correction were applied.

Two Ru atoms in **3** were located by a direct methods program (SHELXS 86) and the positions of all remaining non-hydrogen atoms were determined by cycles of Fourier maps and block-diagonal least-squares refinements using the UNIX-III program package [27] at the Computer Center of The University of Tokyo. For **3a**, since one methyl carbon in each Prⁱ group was located in two positions with almost the same electron densities due to the disorder, these two pairs, denoted C(3)/C(3') and C(6)/C(6'), were refined by assuming 50% occupancy for each atom. Hydrogen atoms were placed at the calculated positions and refined isotropically for **3b**, but are not included for **3a**. Atomic coordinates of non-hydrogen atoms in **3** are listed in Table 4.

4. Supplementary material

Tables of coordinates and isotropic temperature factors for hydrogen atoms in **3b**, anisotropic temperature factors of non-hydrogen atoms and extensive bond lengths and angles in **3a** and **3b** (7 pages), and a listing of observed and calculated structure factors for **3a** and **3b** (22 pages) are available from M.H. upon request.

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