Journal of Organometallic Chemistry, 456 (1993) 243–253

JOM 23619

Preparation and reactivity of dinuclear Ru^{II} complexes with bridging thiolate ligands [Cp*Ru(μ-SR)$_2$RuCp*] (Cp* = η^5-C$_5$Me$_5$; R = ^{i}Pr, ^{t}Bu, 2,6-Me$_2$C$_6$H$_3$). Oxidative addition of alkyl halides at the diruthenium center

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(Received November 28, 1992; in revised form February 18, 1993)

Abstract

Reactions of [Cp*RuCl]$_4$ (Cp* = η^5-C$_5$Me$_5$) with NaSR (R = ^{i}Pr, ^{t}Bu, 2,6-Me$_2$C$_6$H$_3$) in THF afforded dinuclear Ru^{II} complexes with two bridging thiolate ligands [Cp*Ru(μ-SR)$_2$RuCp*] (**3**). An X-ray analysis of **3c** (R = 2,6-Me$_2$C$_6$H$_3$) has disclosed the folded Ru$_2$S$_2$ core structure with two equatorial C$_6$H$_3$Me$_2$-2,6 groups in a solid state, while the results of variable-temperature ^{1}H NMR study are diagnostic of the fluxional nature of complexes **3** in solution resulting from the Ru$_2$S$_2$ ring inversion. Complex **3a** (R = ^{i}Pr) underwent oxidative addition of RX (R = PhCH$_2$CH$_2$ or PhCH$_2$, X = Br; R = Me or Et, X = I) and H$_2$ across the Ru$_2$ center to give [Cp*RuR(μ-S^{i}Pr)$_2$RuCp*X] (**7**) and [Cp*RuH(μ-S^{i}Pr)$_2$RuCp*H], respectively. The structure of **7a** (R = PhCH$_2$CH$_2$, X = Br) has been determined by X-ray crystallography. Crystal data for **3c**: space group $P4_2/mnm$, a = 15.307(4) Å, c = 16.070(4) Å, V = 3765(2) Å^3, Z = 4; **7a**: space group $P2_1/c$, a = 10.348(2) Å, b = 15.113(2) Å, c = 22.340(5) Å, β = 93.10(2)°, V = 3488(1) Å^3, Z = 4.

1. Introduction

The development of a convenient method to prepare [Cp*RuCl$_2$]$_2$ (**1**; Cp* = η^5-C$_5$Me$_5$) [1], which was initially formulated as a polymer or oligomer and then confirmed as a dimer [2], has led to recent rapid progress in the chemistry of Ru compounds containing the Cp*Ru unit. Because of our interest in the unique pattern of reactivity of the transition metal centers incorporated in metal-sulphur aggregates, transformations of **1** into novel Ru complexes with sulphur ligands have been studied in detail. As reported in previous papers, **1** can serve as a versatile precursor to synthesize a series of diruthenium complexes with bridging thiolate ligands; reactions of **1** with thiolate compounds afford diamagnetic complexes such as [Cp*Ru(μ-SR)$_3$RuCp*]Cl and [Cp*RuCl(μ-SR)$_2$RuCp*Cl] [3], and paramagnetic complexes [Cp*Ru(μ-SR)$_3$RuCp*] (**2**) [4], depending upon the reaction conditions (Scheme 1). Among these diruthenium complexes, **2** involving a formal Ru^{II}/Ru^{III} pair exhibits the most intriguing reactivity. Thus [Cp*Ru(μ-S^{i}Pr)$_3$RuCp*] (**2a**) reacts readily with a variety of molecules including CO, ^{t}BuNC, H$_2$, and terminal alkynes to give either paramagnetic complexes [Cp*Ru(S^{i}Pr)(μ-S^{i}Pr)$_2$RuCp*(L)] (L = CO, ^{t}BuNC) [4] or diamagnetic complexes [Cp*RuR′(μ-S^{i}Pr)$_2$RuCp*R′] (R′ = H, alkynyl) [4,5]. Initial steps of these reactions presumably involve the generation of a coordinatively unsaturated Ru^{II} center *in situ* upon dissociation of one bridging thiolate ligand from one Ru atom.

Diruthenium complexes [Cp*Ru(μ-SR)$_2$RuCp*] (**3**) are therefore another attractive set of candidates to be included in this class of ruthenium thiolate complexes inasmuch as they can provide a potential reaction site comprising two neighboring 16-electron Ru^{II} atoms. In a previous paper [6], facile formation of [Cp*Ru(μ-S^{i}Pr)$_2$RuCp*] (**3a**) from [Cp*RuCl]$_4$ (**4**) [7] or [Cp*Ru(μ-OMe)$_2$RuCp*] (**5**) [2b,8] has been described briefly together with a novel oxidative trimerization reaction of Me$_3$SiC≡CH promoted at the diruthenium

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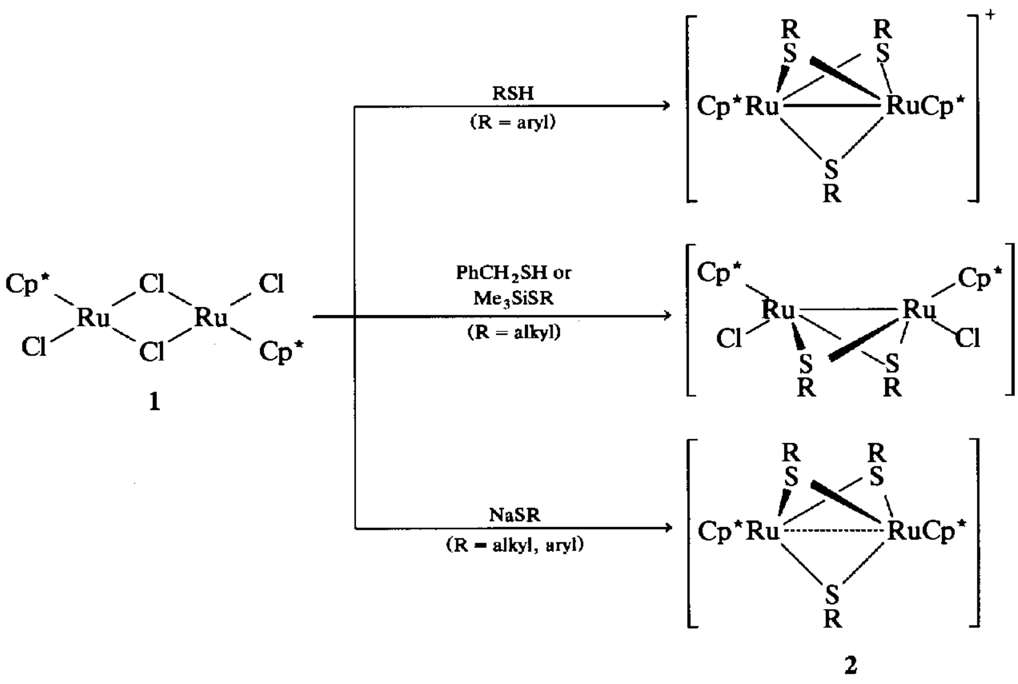


Scheme 1.

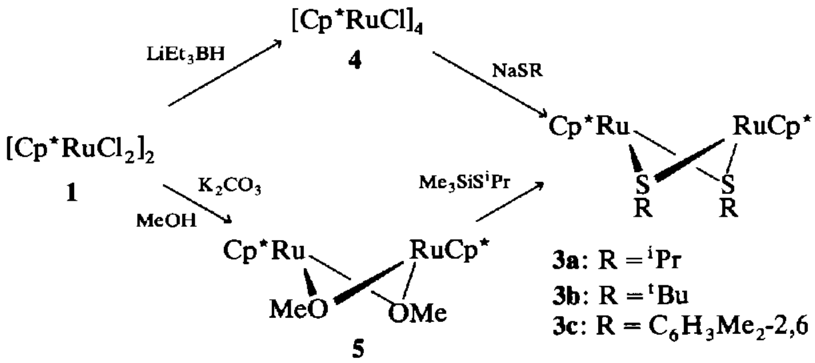
center in **3a** [9*]. Here we wish to report the preparation and detailed characterization of complexes **3** together with reactions of alkyl halides and H_2 with **3a**.

2. Results and discussion

*2.1. Syntheses of [Cp*Ru(μ-SR)$_2$RuCp*] (3) and X-ray structure of [Cp*Ru(μ-SC$_6$H$_3$Me$_2$-2,6)$_2$RuCp*] (3c)*

We have previously reported that treatment of **1** with excess NaSR (R = Et, ^{i}Pr, PhCH$_2$, C$_6$H$_{11}$, Ph) in MeOH gives paramagnetic diruthenium complexes **2**. This reaction involves reduction of one Ru^{III} atom in **1** to Ru^{II} by NaSR present in excess [4]. In contrast, reaction of **1** with excess NaS^{t}Bu afforded a Ru^{II} complex formulated as [Cp*Ru(S^{t}Bu)]$_n$ but the details remained unexplored. We have now found that Ru^{II} complexes [Cp*Ru(μ-SR)$_2$RuCp*] (**3**) can be readily prepared from the reactions of Ru^{II} complexes **4** or **5** with thiolate compounds (Scheme 2) and the dinuclear structure of **3** has been confirmed by the X-ray analysis of **3c** (R = 2,6-Me$_2$C$_6$H$_3$).

Complex **4**, dissolved in THF, rapidly reacted with excess NaSR at room temperature to give diamagnetic complexes **3** [10*] which were isolated in moderate



Scheme 2.

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* Reference number with an asterisk indicates a note in the list of references.

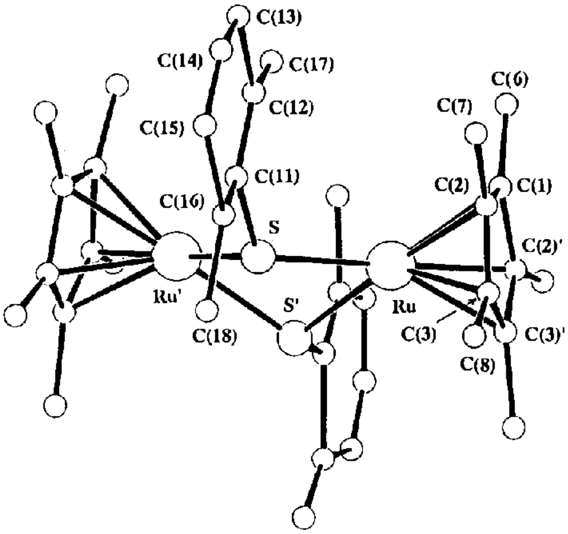
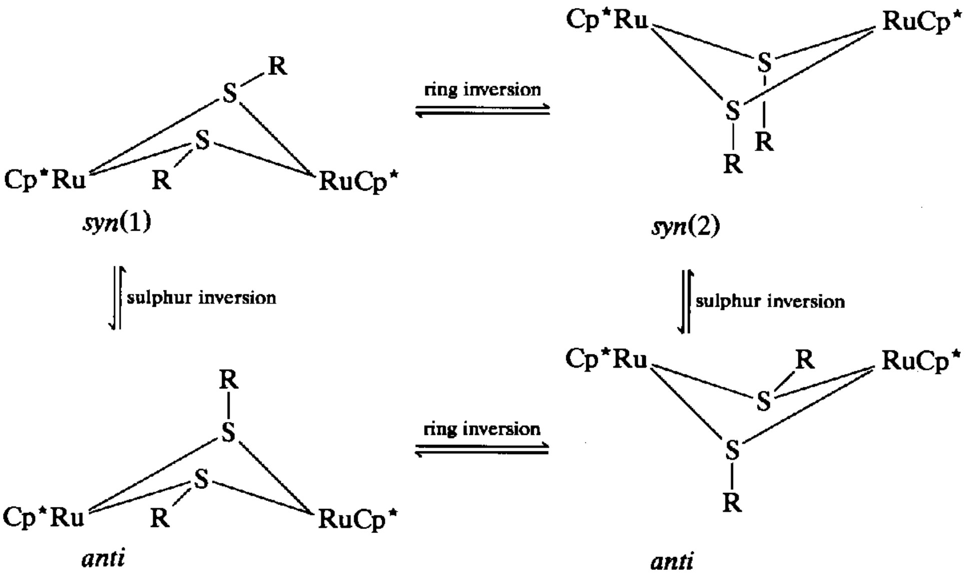


Fig. 1. The molecular structure of $[Cp^*Ru(\mu\text{-}S^iPr)_2RuCp^*]$ (**3c**).

yields as an air-sensitive blue or purple crystalline solid. Complex **5** also serves as a precursor for **3**; treatment of **5** with Me_3SiS^iPr in THF readily afforded **3a**. Formation of **3** (R = Et, ^tBu, $Si(O^tBu)_3$) from the reaction of **5** with RSH has recently been reported independently by Koelle and his coworkers in a preliminary form [11]. To clarify the structure of **3**, an X-ray analysis has been undertaken with a single crystal of **3c** grown from its THF solution at −20°C, the result of which is depicted in Fig. 1.

In **3c**, there exist two mutually perpendicular mirror planes, one of which includes a Ru–Ru vector bisected by the other. Two mutually eclipsed Cp^* ligands are distorted slightly to a *cis* direction (dihedral angle: 15°) and the C(1) and C(6) atoms in the Cp^* ligand are present on the former mirror plane, while all non-hydrogen atoms in the thiolate ligands are on the latter. The Ru–Ru distance (3.500(2) Å) is much longer than those in diruthenium complexes with a Ru–Ru single bond bridged by two or three thiolate ligands as previously reported (2.6–2.9 Å) [3–5] and comparable to those without a Ru–Ru bond such as $[Cp^*Ru(\mu\text{-}S_2)(\mu\text{-}S^iPr)_2RuCp^*]$ (3.590(2) Å) [12], $[(Me_2PhP)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2]$ (3.371(3) Å) [13], and $[Cp'Ru(\mu,\eta^2\text{-}S_2)(\mu,\eta^1\text{-}S_2)RuCp']$ (3.749(1) Å; Cp′ = $\eta^5\text{-}C_5Me_4Et$) [14]. The Ru–S bond length of 2.350(4) Å in **3c** is slightly longer than the sum of the covalent radii of the Ru and S atoms (2.28 Å), suggesting the absence of the π-bonding interaction. These structural features in **3c** are indicative of the coordinatively unsaturated 16-electron configuration for the Ru atoms in this complex. It is to be noted that much shorter Ru–S bond distances have been observed in some electron-deficient thiolate complexes such as $[Ru(SC_6Me_4H)_4(MeCN)]$ and its derivatives (*ca.* 2.2 Å) [15].

A four-membered Ru_2S_2 ring is folded with dihedral angles of 131 and 139° along the Ru–Ru′ and S–S′ vectors, respectively. Due to this folding of the Ru_2S_2 core, three isomers, *viz.*, *syn*(1), *syn*(2), and *anti* complexes, are anticipated for **3** with respect to axial and equatorial orientation of the substituents on the S atoms [16] (Scheme 3). The X-ray analysis shows that **3c** in a solid form exists as the *syn*(1) form with two



Scheme 3.

equatorial $C_6H_3Me_2$-2,6 groups exclusively. An analogous *syn*(1) structure has also been clarified for the closely related [Cp′Ru(μ-SEt)$_2$RuCp′] (**6**) reported recently [11] and other 16-electron dinuclear complexes [(COD)Rh(μ-SPh)$_2$Rh(CO)$_2$] [17], [(COD)Ir(μ-SPh)$_2$Ir(COD)] (COD = 1,5-cyclooctadiene) [18], and [Rh(CO)$_2$(μ-SC$_6$H$_4$F-*p*)$_2$Rh(CO)$_2$] [19]. On the other hand, 18-electron Ru^{III} complexes with a Ru–Ru single bond [Cp*RuY(μ-S^{i}Pr)$_2$RuCp*Y] previously reported (Y = H [4], C≡CC$_6$H$_4$Me-*p* [5]) and [Cp*Ru(CH$_2$CH$_2$Ph)(μ-S^{i}Pr)$_2$RuCp*Br] (**7a**) described below have the *syn*(2) structure with two axial ^{i}Pr groups. Although X-ray structures of several dinuclear complexes with two thiolate bridges are known, it is still difficult to rationalize the finely balanced factors determining the geometries. For example, complexes with mutually *cis* Cp ligands [CpFe(CO)(μ-SPh)$_2$FeCp(CO)] [20], [CpFe(CO)(μ-SMe)$_2$FeCp(CO)]$^+$ [21], and [CpRh(μ-SPh)$_2$RhCp] [22] have the *syn*(1), *syn*(2), and *anti* structures, respectively. Furthermore, [CpW(CO)$_2$(μ-S^{i}Pr)$_2$WCp(CO)$_2$] comprises *cis* Cp ligands and two equatorial ^{i}Pr groups [23], presenting a sharp contrast to [CpMo(CO)$_2$(μ-SPh)$_2$MoCp(CO)$_2$] with *trans* Cp ligands and one equatorial and one axial Ph group [24]. In [CpNi(μ-SPh)$_2$NiCp], the Ni_2S_2 core is planar and two Ph groups are *trans* to each other [25].

Comparison of the bonding parameters of **3c** with those in **6** [11] and a methoxide analogue **5** [8] is noteworthy. Although the structural features with respect to the folded Ru_2E_2 core (E = S, O) and the *syn*(1) form of the 2,6-$Me_2C_6H_3$, Et, and Me groups are analogous in these three complexes, the Ru–Ru distance in **3c** (3.500(2) Å) is significantly longer than those in **6** (3.075(1) Å) and **5** (2.961(1) Å). This results in the much larger folding angle of two RuE_2 planes along the E–E vector in **3c** (139°) than in **6** (114°) and **5** (124°).

2.2. ^{1}H NMR study of complexes 3

^{1}H NMR spectra of complexes **3** show one sharp singlet assignable to the methyl protons in the Cp* ligands. In addition to this resonance, **3c**, in THF-d_8 exhibits another singlet at 2.75 ppm due to the methyl protons as well as the peaks attributable to the aromatic protons in $SC_6H_3Me_2$-2,6 ligand at room temperature. The spectrum recorded at −70°C is essentially the same. This spectral feature of **3c** suggests the presence of the fast interconversion between the *syn*(1) and *syn*(2) isomers due to a Ru_2S_2 ring reversal in this whole temperature region which results in the averaging of two methyl groups in the thiolate ligand, although the *syn*(2) structure might be less favorable on steric grounds. Fluxional behavior of this class of complexes with a M_2S_2 core has been demonstrated already, which can be interpreted in terms of a ring reversal and a sulfur inversion (Scheme 3) [16]. In the complexes without a metal–metal bond, a ring reversal is commonly the lower energy process than a sulfur inversion, and non-rigidity observed for the related Rh [17,26] and Ir [18] complexes [(COD)M(μ-SPh)$_2$M(COD)] cited above has been ascribed to the rapid ring inversion.

In contrast to **3c**, the spectra of **3a** and **3b** are temperature-dependent, indicating unequivocally the fluxional nature of these complexes in a solution state. Thus in the spectrum of **3a** recorded at 100°C in toluene-d_8 there appeared a broad methyl doublet at 1.62 and a very broad methine peak at 2.82 ppm assignable to the ^{i}Pr group together with a sharp Cp* singlet. These ^{i}Pr resonances broadened further as the temperature decreased, and after collapsing at around 10°C they were no longer detectable at lower temperatures or even at −70°C, although the Cp* resonance remained unchanged. In the spectra of **3b**, the singlet at 1.69 ppm due to the ^{t}Bu group observed at 80°C also broadened upon cooling but then it split into two singlets at 1.99 and 1.43 ppm with the same intensity. The sharp Cp* singlet did not vary over the whole temperature range investigated (Fig. 2). Appearance of only one Cp* resonance together with two ^{t}Bu peaks with 1 : 1 intensity ratio suggests the *anti* form having one axial and one equatorial ^{t}Bu groups as the favorable structure of **3b** at the slow exchange limit. The averaging of two ^{t}Bu resonances at higher temperatures can be explained by the facile axial-equatorial interconversion due to the Ru_2S_2 ring inversion. This might occur more rapidly in **3a**, which probably prevents the ^{i}Pr resonances assignable to the static *anti* species from detection on the NMR time scale even at −70°C.

These findings about **3** are quite analogous to the result of variable-temperature NMR study of Rh complexes reported previously [17], which has shown that complexes [(COD)Rh(μ-SR)$_2$Rh(COD)] (R = ^{t}Bu, ^{i}Pr) with a rigid *anti* structure at low temperatures become fluxional at higher temperatures via Rh_2S_2 ring inversion, while the ^{1}H NMR spectra of [(COD)Rh(μ-SPh)$_2$Rh(CO)$_2$] are diagnostic of the *syn* structure. However, free energies of activation for ring inversion in the ^{t}Bu and ^{i}Pr complexes (38–44 kJ mol^{-1}) are smaller than that of **3b** (55 kJ mol^{-1} at 10°C) calculated from its ^{1}H NMR spectra.

It is to be noted that *syn-anti* interconversion has also been suggested to occur in several complexes such as *trans*-[CpRu(CO)(μ-SCH$_2$Ph)$_2$RuCp(CO)] [27] and [(OC)$_3$Fe(μ-S^{t}Bu)$_2$Fe(CO)$_2$(L)] (L = CO, P(OMe)$_3$, PPh$_3$) [28]. This isomerization requires sulphur inver-

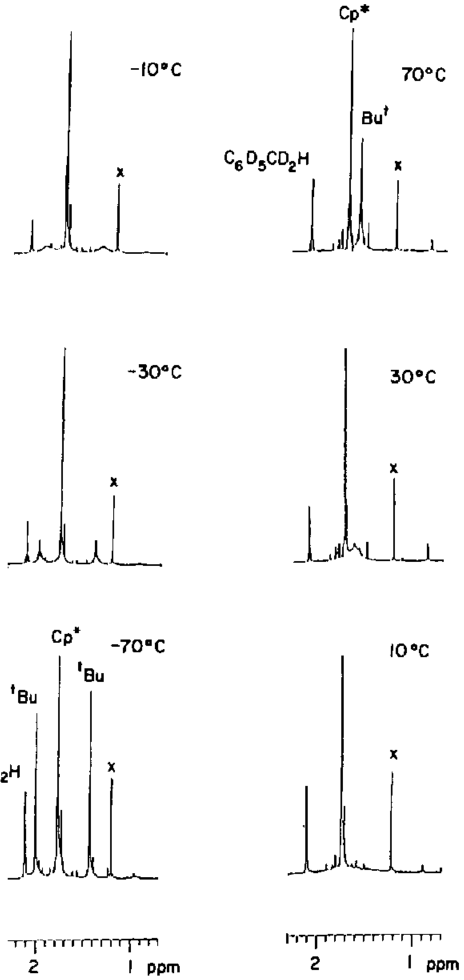


Fig. 2. Variable-temperature ^{1}H NMR spectra of [Cp*Ru(μ-S^{t}Bu)$_2$RuCp*] (**3b**).

sion and the energy barriers for this process have been reported to be 58.7 kJ mol^{-1} for the former Ru complex and 65–77 kJ mol^{-1} for the latter Fe complexes. Two mechanisms might operate in the sulfur inversion; one involves the planar transition state of the sulfur atom, while the other proceeds via an initial metal–sulfur bond dissociation and a subsequent rotation about the resulting terminal metal–sulfur bond followed by a metal–sulfur bond regeneration. However, in both *syn-anti* isomerizations referred to above, the latter mechanism is suggested to be plausible because it has a much lower energy barrier than the former. In **3**, isomerization involving a sulfur inversion might hardly take place because the latter lower energy process requires the formation of a 14-electron intermediate.

2.3. Oxidative additions of alkyl halides and hydrogen gas at the diruthenium center in **3a**

Because of the presence of two adjacent coordinatively unsaturated Ru atoms, **3** might be expected to exhibit intriguing reactivities. As reported briefly, we have already found that **3a** facilitates the novel oxidative oligomerization of $Me_3SiC{\equiv}CH$ [6], which has been extended further to a variety of alkynes. Now we report the oxidative addition of alkyl halides and H_2 gas to the diruthenium center in **3a**. Exploitation of the reactivity of the methoxide analogue **5** is progressing rapidly, which includes the reactions of **5** with molecules such as CO [2], olefins [29], *etc.*, but little is known about the reactions of **5** with halocarbons and H_2.

In our attempt to record the ^{1}H NMR spectrum of **3a**, we observed the quantitative formation of [Cp*RuCl(μ-S^{i}Pr)$_2$RuCp*Cl] (**8a**) [3] upon dissolution of **3a** in $CDCl_3$, although the other organic product(s) derived from $CDCl_3$ could not be clarified. Accordingly, we have studied the reactions of **3a** with a series of alkyl halides and found that treatment of **3a** dissolved in hexane with one equiv of RX smoothly affords diruthenium complexes [Cp*RuR(μ-S^{i}Pr)$_2$RuCp*X] (**7**) at room temperature (eqn. (1)). Complexes **7** precipitated from the reaction mixtures and were easily separated by filtration. Since the single crystals of **7a** (R = $PhCH_2CH_2$, X = Br) were obtained by recrystallization from benzene/hexane, an X-ray

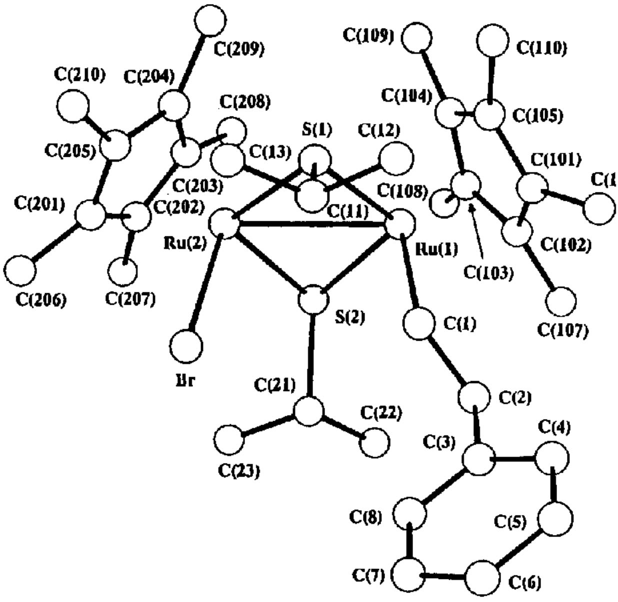
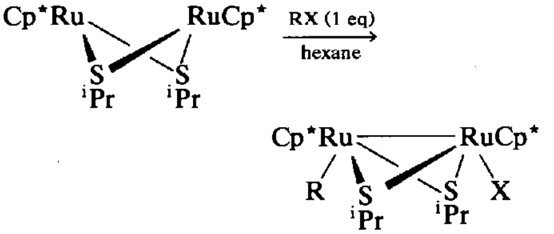


Fig. 3. The molecular structure of [Cp*Ru(CH_2CH_2Ph)(μ-S^{i}Pr)$_2$RuCp*Br] (**7a**).

analysis has been carried out to determine the structure. As shown in Fig. 3, **7a** has two Cp*Ru units



(1)

7a: R = $PhCH_2CH_2$, X = Br

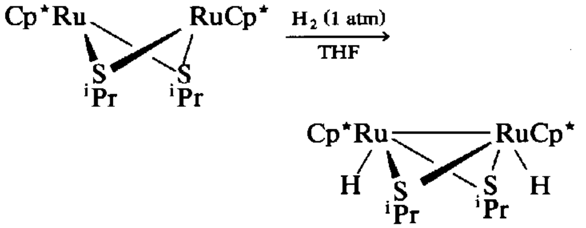
7b: R = $PhCH_2$, X = Br

7c: R = Me, X = I

7d: R = Et, X = I

bridged by two S^iPr ligands and the remaining sites of two Ru atoms are occupied by $PhCH_2CH_2$ and Br ligands, respectively. The Ru_2S_2 ring is folded but much closer to planar than in **3c**, with a dihedral angle of 171° along the Ru(1)–Ru(2) vector. The Ru–Ru distance of 2.844(1) Å is indicative of the presence of a Ru–Ru single bond, which is consistent with the diamagnetic nature of **7** despite the formal oxidation state of +3 for both Ru atoms. These structural features as well as the mutually *cis* configuration of two Cp* ligands and the *syn*(2) orientation with respect to two ^iPr groups are also observed in the other diruthenium complexes $[Cp^*RuY(\mu\text{-}S^iPr)_2RuCp^*Y]$ as described above (Ru–Ru distance: Y = H, 2.784(5) Å [4]; Y = $C\equiv CC_6H_4Me\text{-}p$, 2.809(3) Å [5]). The Ru–S distances of 2.28–2.33 Å are comparable to those in the previously reported thiolate-bridged diruthenium complexes with Ru^{III} and Ru^{II} centers [3–5,30]. The ^1H NMR spectra of **7** are diagnostic of this structure clarified for **7a**. Since neither two Cp* ligands nor two methyl groups in each S^iPr ligand are equivalent in **7**, the resonances attributable to the Cp* and ^iPr methyl protons appear as two singlets and two doublets, respectively.

Complex **3a** also reacted with H_2 gas (1 atm) at room temperature to give a dinuclear oxidative addition product $[Cp^*RuH(\mu\text{-}S^iPr)_2RuCp^*H]$ (**9**) (eqn. (2)).



(2)

Synthesis of **9** from a paramagnetic complex **2a** and H_2 was reported previously [4], but the present reaction apparently demonstrates the more simple stoichiometry free from the elimination of a thiolate ligand. Although the positions of the hydrides in **9** were not determined by the X-ray analysis due to the poor *R* values, not only the clarified bonding scheme of non-hydrogen atoms but the appearance of the medium ν(Ru–H) band at 1950 cm^{-1} in its IR spectrum strongly suggested the presence of two terminal hydrides in mutually *cis* positions. Interestingly the related carboxylate-bridged diruthenium complexes $[Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}O_2CR)_2RuCp^*]$ derived from $[Cp^*Ru(\mu\text{-}H)_4RuCp^*]$ and RCOOH (R = CF_3, Ph, *etc.*) have two bridging hydride ligands [31].

Reactivity of polynuclear complexes is a subject of significant interest, since it can provide a new method for activating substrates on cooperating metal centers and oxidative addition of H_2 and alkyl halides at a dimetal center is one of the interesting topics included in this area [32]. Formations of **7** and **9** from the Ru^{II} complex **3a** reported here therefore provide an interesting example of alkyl halide and H_2 addition.

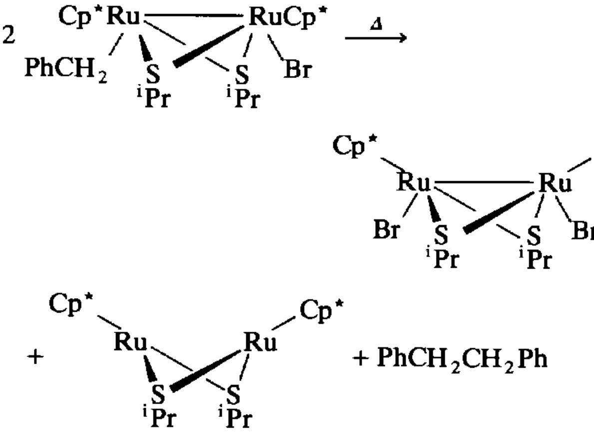
Related molecular H_2 addition to the dimetal center bridged by two thiolate ligands has been observed for the Ir complex $[Ir(CO)\{P(OMe)_3\}(\mu\text{-}S^tBu)_2Ir(CO)\{P(OMe)_3\}]$, giving $[IrH(CO)\{P(OMe)_3\}(\mu\text{-}S^tBu)_2IrH(CO)\{P(OMe)_3\}]$ [33]. The mechanism proposed for this reaction involves initial oxidative addition of H_2 at one Ir atom and successive migration of one hydride to the other Ir atom associated with formation of a Ir–Ir bond (eqn. (3)). The MO study of H_2 addition to d^8/d^8 metal centers (Ir/Ir or Rh/Rh) has demonstrated that this two-step mechanism initiated by

$$\overline{M\quad M} + H_2 \longrightarrow H\text{-}\overline{M\text{-}H\quad M} \longrightarrow H\text{-}\overline{M\text{—}M}\text{-}H \qquad (3)$$

addition to a single metal is more realistic than the concerted addition to a dimetal center [34] and this result has been supported by experimental evidence in the analogous reactions of H_2 with Ir_2 complexes containing bridging diphosphine ligands [35]. By analogy, the reaction of $[Rh(CO)(PMe_2Ph)(\mu\text{-}S^tBu)_2Rh(CO)(PMe_2Ph)]$ with one equiv of MeI is believed to proceed via initial oxidative addition at one Rh center, since a dirhodium complex $[RhI(COMe)(PMe_2Ph)(\mu\text{-}S^tBu)_2Rh(CO)(PMe_2Ph)]$ can be isolated from the reaction mixture [36]. These may suggest that **3a** also undergoes oxidative addition of alkyl halides or H_2 at one Ru center and then isomerizes to **7** and **9**. However, several trials to detect or isolate intermediate stages were not successful for the present reactions and the details are still uncertain [37].

2.4. *Thermal decomposition and related reactions of $[Cp^*Ru(CH_2Ph)(\mu\text{-}S^iPr)_2RuCp^*Br]$ (7b)*

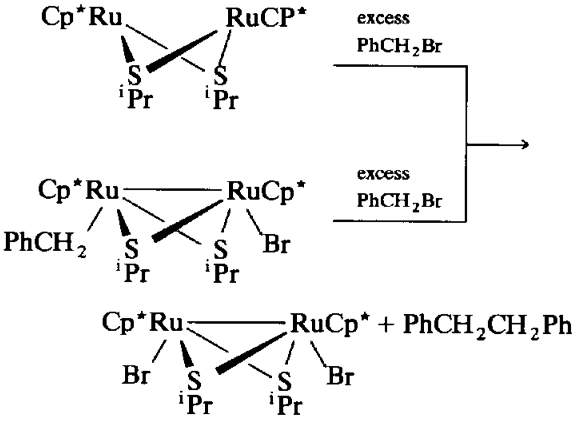
An interesting feature observed during the NMR study of **7** is that **7b** (R = $PhCH_2$, X = Br) in a solution state is less stable than the other three. Thus **7b** dissolved in benzene-d_6 or THF-d_8 was gradually converted into a mixture of [Cp*RuBr(μ-S^{i}Pr)$_2$RuCp*Br] (**8b**) and **3a** even at room temperature. This reaction was substantially enhanced as the temperatures were raised and at 50°C it was almost completed within 2 h. The former Ru^{III} complex **8b** is less soluble in these solvents and was easily isolated from the reaction mixture (0.40 mol/mol **7b**). This transformation of **7b** into a mixture of **8b** and **3a** was accompanied by the formation of $PhCH_2CH_2Ph$ as the only detectable organic product in the reaction mixture, the yield of which reached 0.40 mol/mol **7b**. This indicates that 80% of the $PhCH_2$ group present in **7b** is converted into $PhCH_2CH_2Ph$. The stoichiometry of this reaction may therefore be described by eqn. (4), although the fate of the remaining 20% of the $PhCH_2$ moiety in **7b** could not be clarified. A radical trapping experiment demonstrated the formation of the ^{t}BuN(CH$_2$Ph)O radical upon warming a solution of **7b** in benzene containing a spin trap, ^{t}BuNO. This suggests that the present reaction may be initiated by cleavage of the ruthenium–benzyl bond forming benzyl radical. It is of great interest that the ruthenium–benzyl bond in **7b** is readily cleaved, although mononuclear benzyl complexes of transition metals are commonly much more stable than alkyl complexes having β-hydrogens [38].



(4)

Since the Ru^{II} complex **3a** is regenerated during this reaction, further addition of $PhCH_2Br$ into this reaction mixture resulted in the conversion of **3a** into **7b** and finally to **8b**. Thus treatment of **3a** or **7b** with excess $PhCH_2Br$ at 50°C afforded $PhCH_2CH_2Ph$ in moderate yields together with **8b** as the only isolable product involving Ru (eqn. (5)); for example, the yields of **8b** and $PhCH_2CH_2Ph$ from the reaction of **7b** with 6 equiv of $PhCH_2Br$ were 0.97 and 0.74 mol/mol **7b**, respectively.

Further study is now in progress to clarify the details of the reactivities of alkyl groups in complexes **7** as well as dialkyl complexes derived from **7**, which will be reported in a subsequent paper.



(5)

3. Experimental section

All manipulations were carried out under nitrogen. Solvents and alkyl halides were dried and distilled before use. Compounds **4** [7], **5** [2b,8], and Me$_3$SiS^{i}Pr [39] were prepared according to published methods. ^{1}H NMR spectra were measured on a JEOL JNM-GX-400 spectrometer and EPR spectra were obtained at X-band frequencies on a JEOL JEX-FEIX spectrometer. GLC analyses were performed with a Shimadzu GC-14A Gas Chromatograph equipped with a HiCap-CBP10-M25-025 capillary column.

3.1. Preparation of [Cp*Ru(μ-S^{i}Pr)$_2$RuCp*] (3a)

To a stirred suspension of **4** (720 mg, 0.662 mmol) in THF (30 cm^3) was added NaS^{i}Pr (520 mg, 5.30 mmol) at room temperature. A rapid color change from orange to greenish blue was observed. After stirring overnight, the mixture was dried *in vacuo* and the residue was extracted with hexane. A blue crystalline solid precipitated from the concentrated extract after storage at −20°C, which was collected by filtration and recrystallized from hexane (108 mg, 13%). Anal. Found: C, 49.10; H, 6.94. $C_{26}H_{44}S_2Ru_2$ calc.: C, 50.13; H, 7.12% [40*]. ^{1}H NMR (toluene-d_8, 100°C): δ 1.71 (s, 30H, Cp*), 1.62 (br d, 12H, SCH*Me*$_2$), 2.82 (br, 2H, SC*H*Me$_2$); see also text.

Treatment of **5** dissolved in THF with 2 equiv of Me$_3$SiS^{i}Pr at room temperature resulted in an immediate change from wine red to blue. Evaporation of all volatile materials from the product solution *in vacuo* afforded **3a** as a blue solid, whose ^{1}H NMR spectrum showed that **3a** thus obtained in almost quantitative yield is sufficiently pure to be employed in the subsequent reactions.

3.2. Preparation of [$Cp^*Ru(\mu\text{-}S^tBu)_2RuCp^*$] (3b)

This complex was prepared by the reaction of **4** (885 mg, 0.814 mmol) with NaS^tBu (2.43 g, 19.9 mmol) in THF (15 cm^3) or treatment of **1** (333 mg, 0.542 mmol) with NaS^tBu (1.04 g, 8.19 mmol) in MeOH (5 cm^3). Analogous workup of the reaction mixtures to that for **3a** afforded **3b** as a blue microcrystalline solid in 66 and 80% yields, respectively. Subsequent recrystallization from C_6H_6/MeCN afforded **3b** in an analytically pure form. Anal. Found: C, 51.48; H, 7.33. $C_{28}H_{48}S_2Ru_2$ calc.: C, 51.66; H, 7.43%. ^{1}H NMR (C_6D_6, 60°C): δ 1.78 (s, 30H, Cp*), 1.69 (s, 18H, S^tBu); see also text.

3.3. Preparation of [$Cp^*Ru(\mu\text{-}SC_6H_3Me_2\text{-}2,6)_2RuCp^*$] (3c)

This complex was prepared in an analogous manner by the reaction of **4** (60 mg, 0.055 mmol) with $NaSC_6H_3Me_2$-2,6 (54 mg, 0.34 mmol) in THF (4 cm^3). A purple crystalline solid obtained from the hexane extract at −20°C was recrystallized from cold THF, giving 19 mg of **3c** as single crystals (23%). Anal. Found: C, 56.11; H, 6.24. $C_{36}H_{48}S_2Ru_2$ calc.: C, 57.88; H, 6.48%. ^{1}H NMR (THF-d_8, r.t.): δ 1.27 (s, 30H, Cp*), 2.75 (s, 12H, $C_6H_3Me_2$-2,6), 7.09–7.23 (m, 6H, $C_6H_3Me_2$-2,6).

3.4. Preparation of [$Cp^*Ru(CH_2CH_2Ph)(\mu\text{-}S^iPr)_2RuCp^*Br$] (7a)

Into a solution of **3a** (486 mg, 0.78 mmol) in hexane (8 cm^3) was added $PhCH_2CH_2Br$ (174 mg, 0.94 mmol) at −78°C and the mixture was stirred at room temperature for 7 h. A brown-yellow solid deposited was filtered off, washed with hexane, and then dried *in vacuo*. Recrystallization from benzene/hexane afforded 283 mg of **7a** (43%). Anal. Found: C, 50.24; H, 6.56. $C_{34}H_{53}BrS_2Ru$ calc.: C, 50.54; H, 6.61%. ^{1}H NMR (THF-d_8): δ 1.63 and 1.76 (s, 15H each, Cp*), 1.38 and 1.45 (d, 6H each, $SCHMe_2$), 3.81 (sep, 2H, $SCHMe_2$), 7.0 (m, 5H, Ph), 2.43 (*pseudo* t, 2H, $PhCH_2$), 1.04 (*pseudo* t, 2H, $RuCH_2$).

3.5. Preparation of [$Cp^*Ru(CH_2Ph)(\mu\text{-}S^iPr)_2RuCp^*Br$] (7b)

This complex was isolated according to the procedure for **7a** as a brown solid from the reaction of **3a** (322 mg 0.515 mmol) in hexane (10 cm^3) with $PhCH_2Br$ (88.5 mg, 0.515 mmol) for 15 min (303 mg, 74%). Complex **7b** was always contaminated with a trace of **8b** which was formed by decomposition of the former (*vide supra*). Anal. Found: C, 48.05; H, 6.37. $C_{33}H_{51}BrS_2Ru_2$ calc.: C, 49.92; H, 6.37%. ^{1}H NMR (THF-d_8): δ 1.43 and 1.63 (s, 15H each, Cp*), 1.42 and 1.45 (d, 6H each, $SCHMe_2$), 4.30 (sep, 2H, $SCHMe_2$), 6.9 (m, 5H, Ph), 2.06 (s, 2H, $RuCH_2$).

3.6. Preparation of [$Cp^*RuMe(\mu\text{-}S^iPr)_2RuCp^*I$] (7c)

This complex was isolated as a purple solid by an analogous method, by reaction of **3a** (142 mg, 0.228 mmol) in hexane (5 cm^3) with MeI (32.3 mg, 0.228 mmol) for 1 h. The product was recrystallized from THF/hexane (80 mg, 46%). Anal. Found: C, 41.63; H, 5.98. $C_{27}H_{47}IS_2Ru_2$ calc.: C, 42.40; H, 6.19%. ^{1}H NMR (C_6D_6): δ 1.53 and 1.60 (s, 15H each, Cp*), 1.27 and 1.70 (d, 6H each, $SCHMe_2$), 4.50 (sep, 2H, $SCHMe_2$), 0.82 (s, 3H, RuMe).

3.7. Preparation of [$Cp^*RuEt(\mu\text{-}S^iPr)_2RuCp^*I$] (7d)

This complex was isolated in an analogous way, as a purple solid, by treatment of **3a** (393 mg, 0.63 mmol) in hexane (10 cm^3) with EtI (217 mg, 1.39 mmol) for 3 h. The product was recrystallized from toluene/hexane (82 mg, 11%). Anal. Found: C, 42.56; H, 6.05. $C_{28}H_{49}IS_2Ru_2$ calc.: C, 43.18; H, 6.34%. ^{1}H NMR (C_6D_6): δ 1.56 and 1.59 (s, 15H each, Cp*), 1.40 and 1.74 (d, 6H each, $SCHMe_2$), 4.26 (sep, 2H, $SCHMe_2$), 1.19–1.25 (m, 5H, Et).

3.8. Preparation of [$Cp^*RuH(\mu\text{-}S^iPr)_2RuCp^*H$] (9) from 5 via 3a

Complex **3a**, prepared from **5** (670 mg, 1.23 mmol), and Me_3SiS^iPr (375 mg, 2.51 mmol) were dissolved in THF (20 cm^3) and H_2 gas was bubbled through the solution for 10 min. After removal of the solvent *in vacuo*, the resultant solid was purified by chromatography through alumina eluting with benzene/hexane (2/1). Evaporation of the solvent from a single blue-green band afforded **9** [4] as a green solid (560 mg, 73% based on **5**).

3.9. Dynamic NMR calculations

The rate constants k were determined from the line widths at half-height observed for the ^{t}Bu resonances in the variable-temperature ^{1}H NMR spectra, where the line width at −70°C (2.7 Hz) was employed as the value of the slow exchange limit. Parameters of the activation energy were derived from a plot of $\ln(k/T)$ *vs.* $1/T$ ($\Delta H = 53$ kJ mol^{-1}, $\Delta S = -2.5$ J mol^{-1} deg^{-1}).

3.10. Thermal decomposition of 7b in the presence of a spin trap

Complex **7b**, ^{t}BuNO, and benzene were charged in a quartz tube at −196°C and the tube was sealed *in vacuo*. The EPR spectrum of this mixture recorded at 50°C exhibited a strong septet with an intensity ratio of 1:2:2:2:2:2:1 assignable to $^tBuN(CH_2Ph)O$ radical.

The coupling constants observed ($A_N = 14.6$ G and $A_H = 7.3$ G) are in good agreement with those reported previously [41].

3.11. *X-ray crystallography of 3c*

A single crystal of **3c** obtained from its saturated solution in THF at −20°C was sealed in a glass capillary under Ar and mounted on a MAC MXC-18 diffractometer. The orientation matrices and unit cell parameters were calculated by least-squares treatment of 19 machine-centred reflections ($25 < 2\theta < 30°$). Data collection was carried out at room temperature and three check reflection intensities measured every 100 reflections exhibited no decay. Intensity data were corrected for the Lorentz-polarization effect and for absorption. Crystallographic data are summarized in Table 1.

Structure solution and refinement were performed by using the UNIX-III program package [42] at the Computer Center of the University of Tokyo. The positions of the Ru and S atoms were revealed by the direct methods program SHELXS-86 [43] and all remaining non-hydrogen atoms were found by successive difference Fourier maps. These atoms were refined anisotropically by using block-diagonal least-squares techniques. Atomic scattering factors were taken from ref. 44. Structure solution and refinement were tried by selecting the space group of both $P4_2/mnm$ and $P4_2nm$, which afforded essentially the same results and the space group of the higher symmetry ($P4_2/mnm$) was chosen. Selected bond distances and angles are shown in Table 2.

3.12. *X-ray crystallography for 7a*

A single crystal of **7a** obtained from benzene/hexane was sealed in a glass capillary under Ar and mounted on a Rigaku AFC-5S diffractometer. The orientation matrices and unit cell parameters were

TABLE 1. Details of X-ray crystallography for $[Cp^*Ru(\mu\text{-}SC_6H_3Me_2\text{-}2,6)_2RuCp^*]$ (**3c**) and $[Cp^*Ru(CH_2CH_2Ph)(\mu\text{-}S^iPr)_2RuCp^*Br]$ (**7a**)

	3c	**7a**
(a) Crystal data		
formula	$C_{36}H_{48}S_2Ru_2$	$C_{34}H_{53}BrS_2Ru_2$
fw	747.0	808.0
cryst system	tetragonal	monoclinic
space group	$P4_2/mnm$ (No. 136)	$P2_1/c$ (No. 14)
cryst color	purple-blue	violet
a/Å	15.307(4)	10.348(2)
b/Å	15.307(4)	15.113(3)
c/Å	16.070(4)	22.340(5)
β/°	90	93.10(2)
V/Å^3	3765(2)	3488(1)
Z	4	4
D_{calcd}/g cm^{-3}	1.32	1.54
$F(000)$/electrons	1536	1648
μ_{calcd}/cm^{-1}	9.14	21.20
cryst dimens/mm	0.35 × 0.40 × 0.50	0.30 × 0.30 × 0.08
(b) Data collection		
diffractometer	MAC MXC-18	Rigaku AFC-5S
monochromator	graphite	
radn (λ/Å)	Mo Kα (0.7107)	
temp	room temperature	
2θ max/°	55	50
scan method	ω–2θ scan	ω–2θ scan
scan speed/° min^{-1}	16	16
reflecns measd	+h, +k, +l; h ≧ k	+h, +k, ±l
absorptn correctn	Gaussian integration method	ψ scan method
transmission coeff	0.784–0.802	0.67–1.0
data used	1262 ($F_o > 3\sigma(F_o)$)	2994 ($I > 3\sigma(I)$)
(c) Structure solution and refinement		
no of parameters	146	352
R [a]	0.075	0.044
R_w [b]	0.086	0.033
max residuals/e Å^{-3}	1.1	0.71

[a] $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1$ for **3c** and $1/\sigma^2(F_o)$ for **7a**.

TABLE 2. Selected bond distances (Å) and angles (°) in $[Cp^*Ru(\mu\text{-}SC_6H_3Me_2\text{-}2,6)_2RuCp^*]$ (3c) and $[Cp^*Ru(CH_2CH_2Ph)(\mu\text{-}S^iPr)_2RuCp^*Br]$ (7a)

3c			
Ru ··· Ru	3.500(2)	S–Ru–S′	74.9(2)
Ru–S	2.350(4)	Ru–S–Ru′	96.8(4)
Ru–C(1)	2.15(2)	Ru–S–C(11)	121.0(4)
Ru–C(2)	2.14(1)		
Ru–C(3)	2.12(1)		
S–C(11)	1.78(2)		
7a			
Ru(1)–Ru(2)	2.844(1)	S(1)–Ru(1)–S(2)	104.25(9)
Ru(1)–S(1)	2.296(2)	S(1)–Ru(2)–S(2)	102.12(9)
Ru(1)–S(2)	2.284(3)	Ru(1)–S(1)–Ru(2)	76.04(8)
Ru(1)–C(1)	2.152(8)	Ru(1)–S(2)–Ru(2)	76.15(8)
Ru(2)–Br	2.575(1)	S(1)–Ru(1)–C(1)	86.8(2)
Ru(2)–S(1)	2.321(3)	S(2)–Ru(1)–C(1)	92.1(2)
Ru(2)–S(2)	2.327(3)	S(1)–Ru(2)–Br	92.81(7)
Ru(1)–C(101)	2.208(9)	S(2)–Ru(2)–Br	93.82(7)
Ru(1)–C(102)	2.196(9)	Ru(1)–S(1)–C(11)	120.2(3)
Ru(1)–C(103)	2.283(8)	Ru(2)–S(1)–C(11)	117.3(3)
Ru(1)–C(104)	2.384(9)	Ru(1)–S(2)–C(21)	121.1(3)
Ru(1)–C(105)	2.298(9)	Ru(2)–S(2)–C(21)	117.4(4)
Ru(2)–C(201)	2.24(1)	Ru(1)–C(1)–C(2)	126.6(7)
Ru(2)–C(202)	2.23(1)	C(1)–C(2)–C(3)	112.2(8)
Ru(2)–C(203)	2.20(1)		
Ru(2)–C(204)	2.20(1)		
Ru(2)–C(205)	2.18(1)		
S(1)–C(11)	1.841(9)		
S(2)–C(21)	1.838(9)		

derived from the least-squares fit of 25 machine-centered reflections with $20 < 2\theta < 30°$. No significant decay was observed for three check reflections measured every 150 reflections. Intensity data were corrected for the Lorentz-polarization effect and for absorption. Crystallographic data are listed in Table 1.

All calculations were performed with TEXSAN crystallographic software [45]. The structure was solved by the direct methods program MITHRIL [46]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were included at their calculated positions with fixed isotropic temperature factors. Selected bond distances and angles are summarized in Table 2.

4. Supplementary material available

A figure of the EPR spectrum of $^tBuN(CH_2Ph)O$ radical, tables of atomic coordinates, anisotropic temperature factors, and extensive bond lengths and angles in **3c** and **7a**, and listings of observed and calculated structure factors for **3c** and **7a** are available from the author (M.H.) upon request.

Acknowledgments

We thank Professor Yasuhiro Yamamoto and Dr. Tomoaki Tanase (Department of Chemistry, Toho University) for the X-ray analysis of **7a** and Mr. Junichi Tsuchiya (Engineering Research Institute, The University of Tokyo) for the EPR measurement. Financial support by the Japan Ministry of Education, Science and Culture is appreciated.

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