

JOM 23619

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

Akeo Takahashi, Yasushi Mizobe, Hiroyuki Matsuzaka, Somanath Dev and Masanobu Hidai

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 (Japan)

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

Abstract

Reactions of $[\text{Cp}^*\text{RuCl}]_4$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with NaSR ($\text{R} = \text{iPr}, \text{tBu}, 2,6\text{-Me}_2\text{C}_6\text{H}_3$) in THF afforded dinuclear Ru^{II} complexes with two bridging thiolate ligands $[\text{Cp}^*\text{Ru}(\mu\text{-SR})_2\text{RuCp}^*]$ (**3**). An X-ray analysis of **3c** ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) has disclosed the folded Ru_2S_2 core structure with two equatorial $\text{C}_6\text{H}_3\text{Me}_2$ groups in a solid state, while the results of variable-temperature ^1H NMR study are diagnostic of the fluxional nature of complexes **3** in solution resulting from the Ru_2S_2 ring inversion. Complex **3a** ($\text{R} = \text{iPr}$) underwent oxidative addition of RX ($\text{R} = \text{PhCH}_2\text{CH}_2$ or PhCH_2 , $\text{X} = \text{Br}$; $\text{R} = \text{Me}$ or Et , $\text{X} = \text{I}$) and H_2 across the Ru_2 center to give $[\text{Cp}^*\text{RuR}(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*\text{X}]$ (**7**) and $[\text{Cp}^*\text{RuH}(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*\text{H}]$, respectively. The structure of **7a** ($\text{R} = \text{PhCH}_2\text{CH}_2$, $\text{X} = \text{Br}$) 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, $V = 3765(2)$ Å³, $Z = 4$; **7a**: space group $P2_1/c$, $a = 10.348(2)$ Å, $b = 15.113(2)$ Å, $c = 22.340(5)$ Å, $\beta = 93.10(2)^\circ$, $V = 3488(1)$ Å³, $Z = 4$.

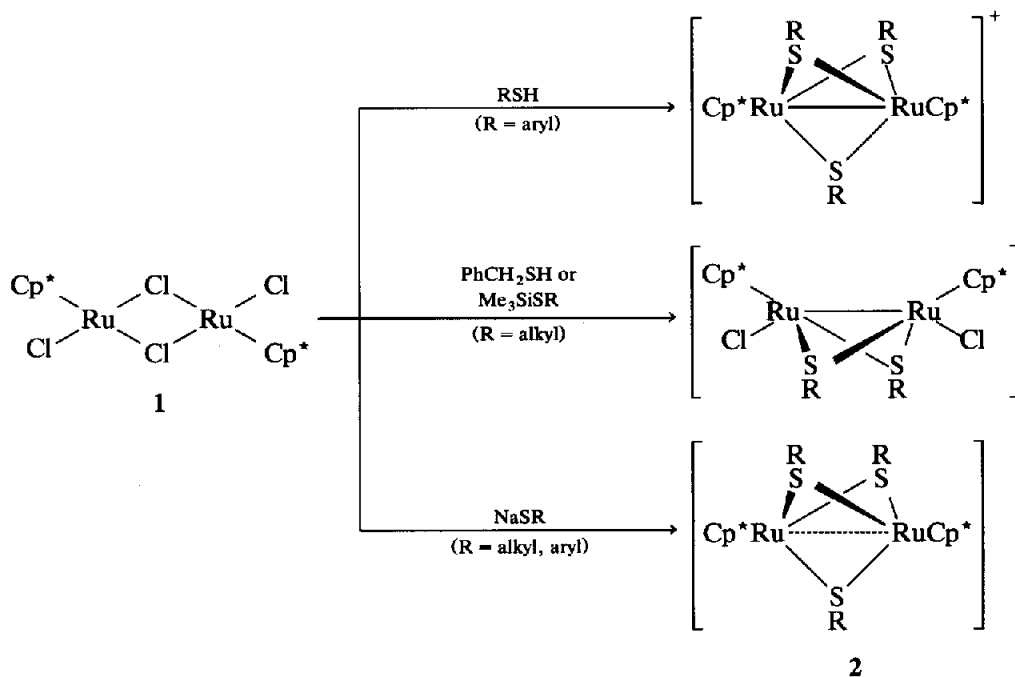
1. Introduction

The development of a convenient method to prepare $[\text{Cp}^*\text{RuCl}_2]_2$ (**1**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) [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 $[\text{Cp}^*\text{Ru}(\mu\text{-SR})_3\text{RuCp}^*]\text{Cl}$ and $[\text{Cp}^*\text{RuCl}(\mu\text{-SR})_2\text{RuCp}^*\text{Cl}]$ [**3**], and paramagnetic complexes $[\text{Cp}^*\text{Ru}(\mu\text{-SR})_3\text{RuCp}^*]$ (**2**) [4], depending upon the reaction conditions (Scheme

1). Among these diruthenium complexes, **2** involving a formal $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ pair exhibits the most intriguing reactivity. Thus $[\text{Cp}^*\text{Ru}(\mu\text{-S}^i\text{Pr})_3\text{RuCp}^*]$ (**2a**) reacts readily with a variety of molecules including CO, tBuNC , H_2 , and terminal alkynes to give either paramagnetic complexes $[\text{Cp}^*\text{Ru}(\text{S}^i\text{Pr})(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*(\text{L})]$ ($\text{L} = \text{CO}, \text{tBuNC}$) [4] or diamagnetic complexes $[\text{Cp}^*\text{RuR}'(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*\text{R}']$ ($\text{R}' = \text{H}, \text{alkynyl}$) [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 $[\text{Cp}^*\text{Ru}(\mu\text{-SR})_2\text{RuCp}^*]$ (**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 $[\text{Cp}^*\text{Ru}(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*]$ (**3a**) from $[\text{Cp}^*\text{RuCl}]_4$ (**4**) [7] or $[\text{Cp}^*\text{Ru}(\mu\text{-OMe})_2\text{RuCp}^*]$ (**5**) [2b,8] has been described briefly together with a novel oxidative trimerization reaction of $\text{Me}_3\text{SiC}\equiv\text{CH}$ promoted at the diruthenium

Correspondence to: Professor M. Hidai.



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

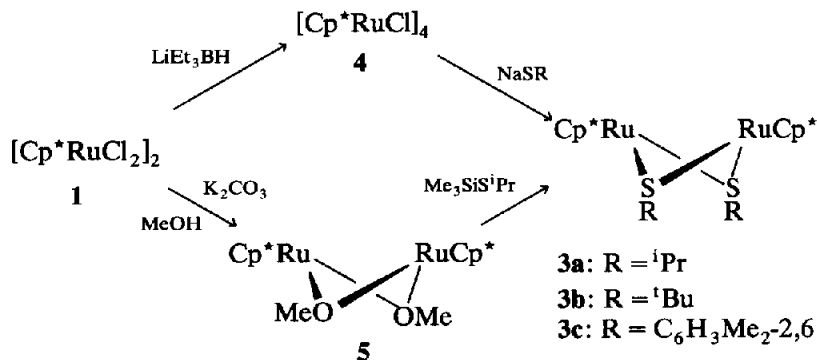
2.1. Syntheses of $[\text{Cp}^*\text{Ru}(\mu\text{-SR})_2\text{RuCp}^*]$ (**3**) and X-ray structure of $[\text{Cp}^*\text{Ru}(\mu\text{-SC}_6\text{H}_3\text{Me}_2\text{-2,6})_2\text{RuCp}^*]$ (**3c**)

We have previously reported that treatment of **1** with excess NaSR ($\text{R} = \text{Et}$, $i\text{Pr}$, PhCH_2 , C_6H_{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^tBu afforded a Ru^{II}

complex formulated as $[\text{Cp}^*\text{Ru}(\text{S}^t\text{Bu})]_n$ but the details remained unexplored. We have now found that Ru^{II} complexes $[\text{Cp}^*\text{Ru}(\mu\text{-SR})_2\text{RuCp}^*]$ (**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** ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$).

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

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



Scheme 2.

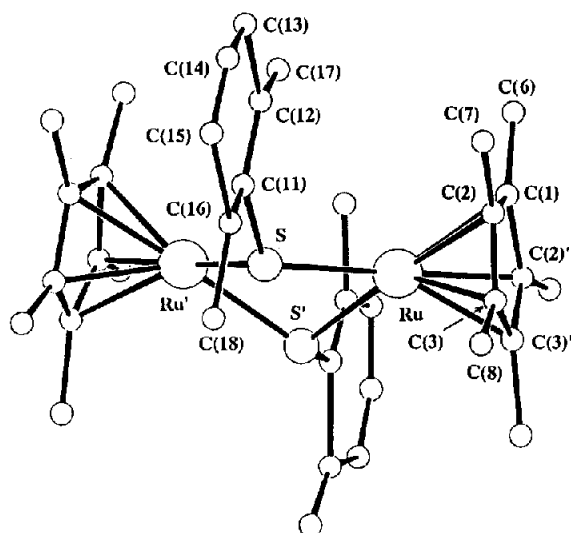


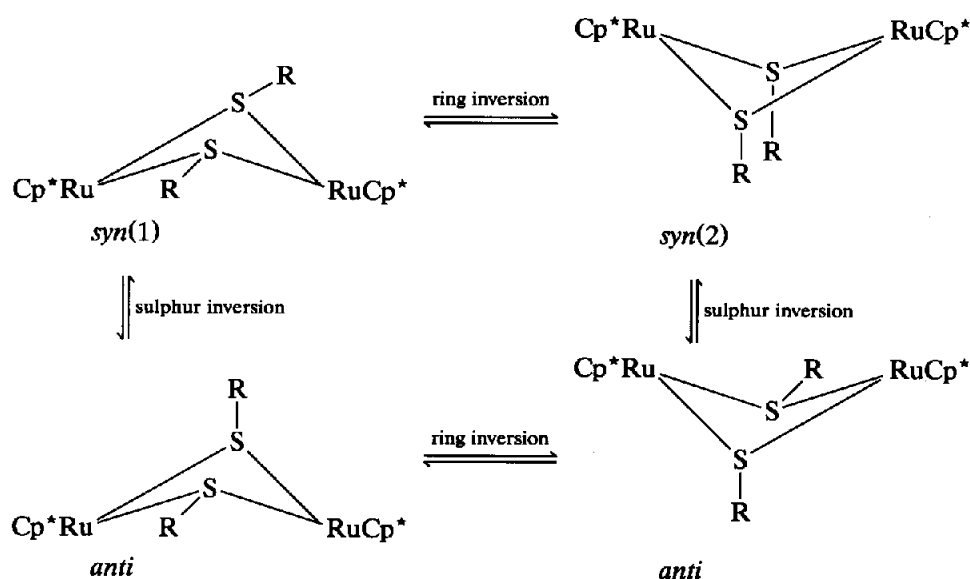
Fig. 1. The molecular structure of $[\text{Cp}^*\text{Ru}(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*]$ (**3c**).

yields as an air-sensitive blue or purple crystalline solid. Complex **5** also serves as a precursor for **3**; treatment of **5** with $\text{Me}_3\text{SiS}^i\text{Pr}$ in THF readily afforded **3a**. Formation of **3** ($\text{R} = \text{Et}$, ^iBu , $\text{Si}(\text{O}^i\text{Bu})_3$) 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 $\text{C}(1)$ and $\text{C}(6)$ 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 ($3.500(2) \text{ \AA}$) is much longer than those in diruthenium complexes with a Ru-Ru single bond bridged by two or three thiolate ligands as previously reported ($2.6\text{--}2.9 \text{ \AA}$) [3–5] and comparable to those without a Ru-Ru bond such as $[\text{Cp}^*\text{Ru}(\mu\text{-S}_2)(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*]$ ($3.590(2) \text{ \AA}$) [12], $[(\text{Me}_2\text{PhP})_3\text{Ru}(\mu\text{-SH})_3\text{Ru}(\text{SH})(\text{PMe}_2\text{Ph})_2]$ ($3.371(3) \text{ \AA}$) [13], and $[\text{Cp}'\text{Ru}(\mu, \eta^2\text{-S}_2)(\mu, \eta^1\text{-S}_2)\text{RuCp}']$ ($3.749(1) \text{ \AA}$; $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$) [14]. The Ru-S bond length of $2.350(4) \text{ \AA}$ in **3c** is slightly longer than the sum of the covalent radii of the Ru and S atoms ($2.28 \text{ \AA}$), 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 $[\text{Ru}(\text{SC}_6\text{Me}_4\text{H})_4(\text{MeCN})]$ and its derivatives (*ca.* $2.2 \text{ \AA}$) [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 C₆H₃Me₂-2,6 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)₂Rh(CO)₂] [17], [(COD)Ir(μ-SPh)₂Ir(COD)] (COD = 1,5-cyclooctadiene) [18], and [Rh(CO)₂(μ-SC₆H₄F-*p*)₂Rh(CO)₂] [19]. On the other hand, 18-electron Ru^{III} complexes with a Ru–Ru single bond [Cp* RuY(μ-SⁱPr)₂ RuCp*Y] previously reported (Y = H [4], C≡CC₆H₄Me-*p* [5]) and [Cp* Ru(CH₂CH₂Ph)(μ-SⁱPr)₂ RuCp*Br] (7a) described below have the *syn*(2) structure with two axial ⁱPr 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)₂FeCp(CO)] [20], [CpFe(CO)(μ-SMe)₂FeCp(CO)]⁺ [21], and [CpRh(μ-SPh)₂RhCp] [22] have the *syn*(1), *syn*(2), and *anti* structures, respectively. Furthermore, [CpW(CO)₂(μ-SⁱPr)₂WCp(CO)₂] comprises *cis* Cp ligands and two equatorial ⁱPr groups [23], presenting a sharp contrast to [CpMo(CO)₂(μ-SPh)₂MoCp(CO)₂] with *trans* Cp ligands and one equatorial and one axial Ph group [24]. In [CpNi(μ-SPh)₂NiCp], the Ni₂S₂ 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 Ru₂E₂ core (E = S, O) and the *syn*(1) form of the 2,6-Me₂C₆H₃, 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 RuE₂ planes along the E–E vector in 3c (139°) than in 6 (114°) and 5 (124°).

2.2. ¹H NMR study of complexes 3

¹H 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 SC₆H₃Me₂-2,6 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 Ru₂S₂ 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 com-

plexes with a M₂S₂ 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 ⁱPr group together with a sharp Cp* singlet. These ⁱPr 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 ^tBu 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 ^tBu peaks with 1:1 intensity ratio suggests the *anti* form having one axial and one equatorial ^tBu groups as the favorable structure of 3b at the slow exchange limit. The averaging of two ^tBu resonances at higher temperatures can be explained by the facile axial-equatorial interconversion due to the Ru₂S₂ ring inversion. This might occur more rapidly in 3a, which probably prevents the ⁱPr 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)₂Rh(COD)] (R = ^tBu, ⁱPr) with a rigid *anti* structure at low temperatures become fluxional at higher temperatures via Rh₂S₂ ring inversion, while the ¹H NMR spectra of [(COD)Rh(μ-SPh)₂Rh(CO)₂] are diagnostic of the *syn* structure. However, free energies of activation for ring inversion in the ^tBu and ⁱPr complexes (38–44 kJ mol^{–1}) are smaller than that of 3b (55 kJ mol^{–1} at 10°C) calculated from its ¹H 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-SCH₂Ph)₂RuCp(CO)] [27] and [(OC)₃Fe(μ-S^tBu)₂Fe(CO)₂(L)] (L = CO, P(OMe)₃, PPh₃) [28]. This isomerization requires sulphur inver-

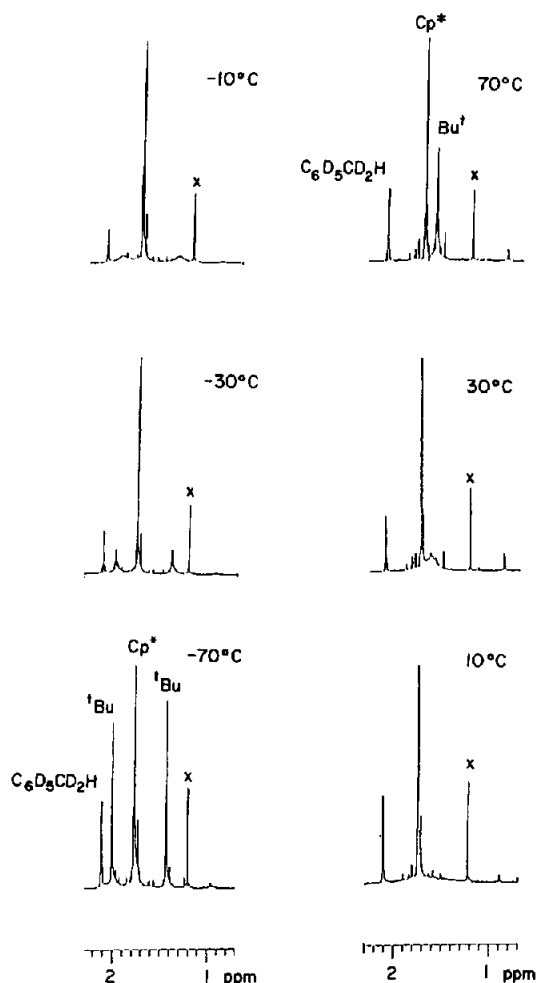


Fig. 2. Variable-temperature ^1H NMR spectra of $[\text{Cp}^*\text{Ru}(\mu\text{-SiPr})_2\text{RuCp}^*]$ (**3b**).

sion and the energy barriers for this process have been reported to be 58.7 kJ mol^{-1} for the former Ru complex and $65\text{--}77 \text{ kJ mol}^{-1}$ 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 $\text{Me}_3\text{SiC}\equiv\text{CH}$ [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 ^1H NMR spectrum of **3a**, we observed the quantitative formation of $[\text{Cp}^*\text{RuCl}(\mu\text{-SiPr})_2\text{RuCp}^*\text{Cl}]$ (**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 $[\text{Cp}^*\text{RuR}(\mu\text{-SiPr})_2\text{RuCp}^*\text{X}]$ (**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** ($\text{R} = \text{PhCH}_2\text{CH}_2$, $\text{X} = \text{Br}$) were obtained by recrystallization from benzene/hexane, an X-ray

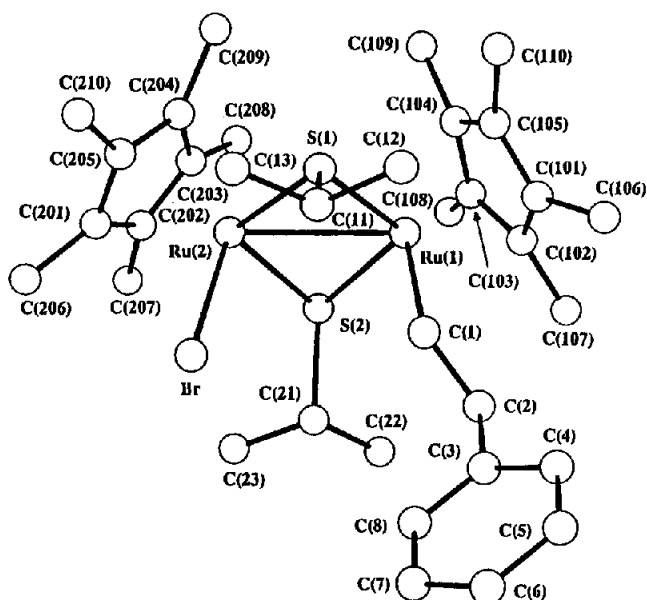
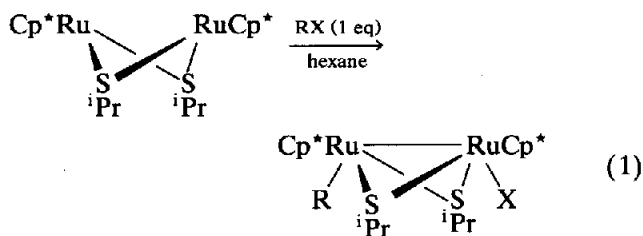


Fig. 3. The molecular structure of $[\text{Cp}^*\text{Ru}(\text{CH}_2\text{CH}_2\text{Ph})(\mu\text{-SiPr})_2\text{RuCp}^*\text{Br}]$ (**7a**).

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



7a: R = PhCH₂CH₂, X = Br

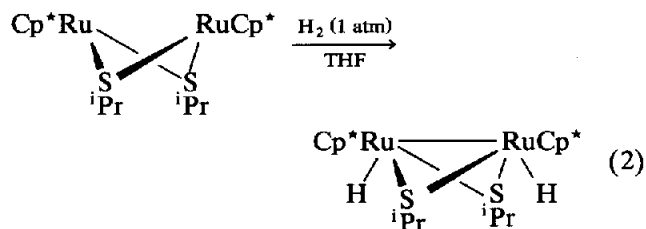
7b: R = PhCH₂, X = Br

7c: R = Me, X = I

7d: R = Et, X = I

bridged by two SⁱPr ligands and the remaining sites of two Ru atoms are occupied by PhCH₂CH₂ and Br ligands, respectively. The Ru₂S₂ 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(μ-SⁱPr)₂RuCp*Y] as described above (Ru–Ru distance: Y = H, 2.784(5) Å [4]; Y = C≡CC₆H₄Me-*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 SⁱPr 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 H₂ gas (1 atm) at room temperature to give a dinuclear oxidative addition product [Cp*RuH(μ-SⁱPr)₂RuCp*H] (**9**) (eqn. (2)).

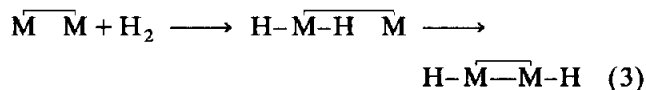


Synthesis of **9** from a paramagnetic complex **2a** and H₂ was reported previously [4], but the present reaction apparently demonstrates the more simple stoichiometry free from the elimination of a thiolate ligand. Although the positions of the hydrides in **9** were not

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(μ-H)₂(μ-O₂CR)₂RuCp*] derived from [Cp*Ru(μ-H)₄RuCp*] and RCOOH (R = CF₃, 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 H₂ 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 H₂ addition.

Related molecular H₂ addition to the dimetal center bridged by two thiolate ligands has been observed for the Ir complex [Ir(CO){P(OMe)₃}(μ-SⁱBu)₂Ir(CO){P(OMe)₃}], giving [IrH(CO){P(OMe)₃}(μ-SⁱBu)₂IrH(CO){P(OMe)₃}] [33]. The mechanism proposed for this reaction involves initial oxidative addition of H₂ 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 H₂ addition to d⁸/d⁸ metal centers (Ir/Ir or Rh/Rh) has demonstrated that this two-step mechanism initiated by

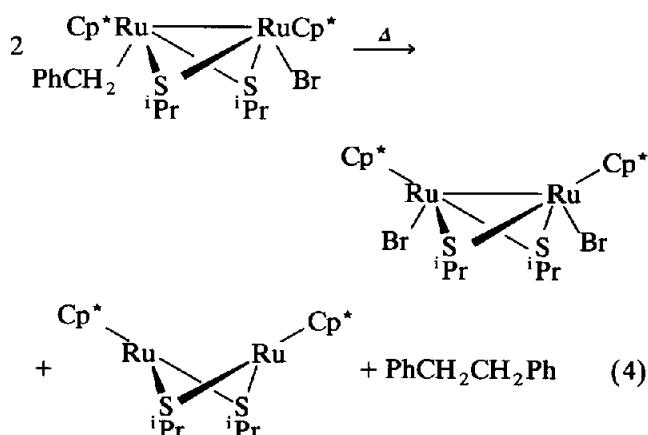


addition to a single metal is more realistic than the concerted addition to a dimetal center [34] and this result has been supported by experimental evidence in the analogous reactions of H₂ with Ir₂ complexes containing bridging diphosphine ligands [35]. By analogy, the reaction of [Rh(CO)(PMe₂Ph)(μ-SⁱBu)₂Rh(CO)(PMe₂Ph)] with one equiv of MeI is believed to proceed via initial oxidative addition at one Rh center, since a dirhodium complex [RhI(COMe)(PMe₂Ph)(μ-SⁱBu)₂Rh(CO)(PMe₂Ph)] can be isolated from the reaction mixture [36]. These may suggest that **3a** also undergoes oxidative addition of alkyl halides or H₂ 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(CH₂Ph)(μ-SⁱPr)₂RuCp*Br] (**7b**)

An interesting feature observed during the NMR study of **7** is that **7b** (R = PhCH₂, X = Br) in a solution

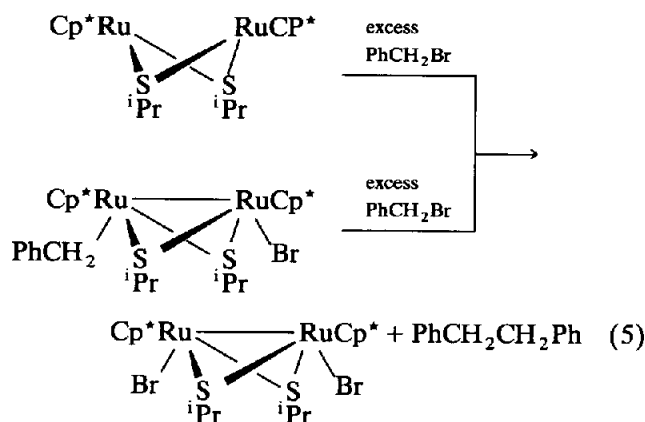
state is less stable than the other three. Thus **7b** dissolved in benzene-*d*₆ or THF-*d*₈ was gradually converted into a mixture of [Cp*RuBr(μ-S^{*i*}Pr)₂RuCp*Br] (**8b**) and **3a** even at room temperature. This reaction was substantially enhanced as the temperatures were raised and at 50°C it was 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 PhCH₂CH₂Ph 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 PhCH₂ group present in **7b** is converted into PhCH₂CH₂Ph. The stoichiometry of this reaction may therefore be described by eqn. (4), although the fate of the remaining 20% of the PhCH₂ moiety in **7b** could not be clarified. A radical trapping experiment demonstrated the formation of the ¹BuN(CH₂Ph)O radical upon warming a solution of **7b** in benzene containing a spin trap, ¹BuNO. 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].



Since the Ru^{II} complex **3a** is regenerated during this reaction, further addition of PhCH₂Br into this reaction mixture resulted in the conversion of **3a** into **7b** and finally to **8b**. Thus treatment of **3a** or **7b** with excess PhCH₂Br at 50°C afforded PhCH₂CH₂Ph in moderate yields together with **8b** as the only isolable product involving Ru (eqn. (5)); for example, the yields of **8b** and PhCH₂CH₂Ph from the reaction of **7b** with 6 equiv of PhCH₂Br 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.



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 Me₃SiS^{*i*}Pr [39] were prepared according to published methods. ¹H 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)₂RuCp*] (**3a**)

To a stirred suspension of **4** (720 mg, 0.662 mmol) in THF (30 cm³) 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. C₂₆H₄₄S₂Ru₂ calc.: C, 50.13; H, 7.12% [40*]. ¹H NMR (toluene-*d*₈, 100°C): δ 1.71 (s, 30H, Cp*), 1.62 (br d, 12H, SCHMe₂), 2.82 (br, 2H, SCHMe₂); see also text.

Treatment of **5** dissolved in THF with 2 equiv of Me₃SiS^{*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 ¹H 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 $[Cp^*Ru(\mu-S^iBu)_2RuCp^*]$ (**3b**)

This complex was prepared by the reaction of **4** (885 mg, 0.814 mmol) with NaSⁱBu (2.43 g, 19.9 mmol) in THF (15 cm³) or treatment of **1** (333 mg, 0.542 mmol) with NaSⁱBu (1.04 g, 8.19 mmol) in MeOH (5 cm³). 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 C₆H₆/MeCN afforded **3b** in an analytically pure form. Anal. Found: C, 51.48; H, 7.33. C₂₈H₄₈S₂Ru₂ calc.: C, 51.66; H, 7.43%. ¹H NMR (C₆D₆, 60°C): δ 1.78 (s, 30H, Cp*), 1.69 (s, 18H, SⁱBu); see also text.

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

This complex was prepared in an analogous manner by the reaction of **4** (60 mg, 0.055 mmol) with NaSC₆H₃Me₂-2,6 (54 mg, 0.34 mmol) in THF (4 cm³). 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. C₃₆H₄₈S₂Ru₂ calc.: C, 57.88; H, 6.48%. ¹H NMR (THF-*d*₈, r.t.): δ 1.27 (s, 30H, Cp*), 2.75 (s, 12H, C₆H₃Me₂-2,6), 7.09–7.23 (m, 6H, C₆H₃Me₂-2,6).

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

Into a solution of **3a** (486 mg, 0.78 mmol) in hexane (8 cm³) was added PhCH₂CH₂Br (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. C₃₄H₅₃BrS₂Ru calc.: C, 50.54; H, 6.61%. ¹H NMR (THF-*d*₈): δ 1.63 and 1.76 (s, 15H each, Cp*), 1.38 and 1.45 (d, 6H each, SCHMe₂), 3.81 (sep, 2H, SCHMe₂), 7.0 (m, 5H, Ph), 2.43 (*pseudo t*, 2H, PhCH₂), 1.04 (*pseudo t*, 2H, RuCH₂).

3.5. Preparation of $[Cp^*Ru(CH_2Ph)(\mu-S^iPr)_2RuCp^*Br]$ (**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 cm³) with PhCH₂Br (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. C₃₃H₅₁BrS₂Ru₂ calc.: C, 49.92; H, 6.37%. ¹H NMR (THF-*d*₈): δ 1.43 and 1.63 (s, 15H each, Cp*), 1.42 and

1.45 (d, 6H each, SCHMe₂), 4.30 (sep, 2H, SCHMe₂), 6.9 (m, 5H, Ph), 2.06 (s, 2H, RuCH₂).

3.6. Preparation of $[Cp^*RuMe(\mu-S^iPr)_2RuCp^*I]$ (**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 cm³) 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. C₂₇H₄₇IS₂Ru₂ calc.: C, 42.40; H, 6.19%. ¹H NMR (C₆D₆): δ 1.53 and 1.60 (s, 15H each, Cp*), 1.27 and 1.70 (d, 6H each, SCHMe₂), 4.50 (sep, 2H, SCHMe₂), 0.82 (s, 3H, RuMe).

3.7. Preparation of $[Cp^*RuEt(\mu-S^iPr)_2RuCp^*I]$ (**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 cm³) 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. C₂₈H₄₉IS₂Ru₂ calc.: C, 43.18; H, 6.34%. ¹H NMR (C₆D₆): δ 1.56 and 1.59 (s, 15H each, Cp*), 1.40 and 1.74 (d, 6H each, SCHMe₂), 4.26 (sep, 2H, SCHMe₂), 1.19–1.25 (m, 5H, Et).

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

Complex **3a**, prepared from **5** (670 mg, 1.23 mmol), and Me₃SiSⁱPr (375 mg, 2.51 mmol) were dissolved in THF (20 cm³) and H₂ 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 ⁱBu resonances in the variable-temperature ¹H 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* (Δ*H* = 53 kJ mol⁻¹, Δ*S* = -2.5 J mol⁻¹ deg⁻¹).

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

Complex **7b**, ⁱBuNO, 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 ⁱBuN(CH₂Ph)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 ($25 < 2\theta < 30^\circ$). 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 $[\text{Cp}^*\text{Ru}(\mu\text{-SC}_6\text{H}_3\text{Me}_2\text{-2,6})_2\text{RuCp}^*]$ (**3c**) and $[\text{Cp}^*\text{Ru}(\text{CH}_2\text{CH}_2\text{Ph})(\mu\text{-S}^i\text{Pr})_2\text{RuCp}^*\text{Br}]$ (**7a**)

	3c	7a
<i>(a) Crystal data</i>		
formula	$\text{C}_{36}\text{H}_{48}\text{S}_2\text{Ru}_2$	$\text{C}_{34}\text{H}_{53}\text{BrS}_2\text{Ru}_2$
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
$a/\text{\AA}$	15.307(4)	10.348(2)
$b/\text{\AA}$	15.307(4)	15.113(3)
$c/\text{\AA}$	16.070(4)	22.340(5)
$\beta/^\circ$	90	93.10(2)
$V/\text{\AA}^3$	3765(2)	3488(1)
Z	4	4
$D_{\text{calcd}}/\text{g cm}^{-3}$	1.32	1.54
$F(000)/\text{electrons}$	1536	1648
$\mu_{\text{calcd}}/\text{cm}^{-1}$	9.14	21.20
cryst dimens/mm	$0.35 \times 0.40 \times 0.50$	$0.30 \times 0.30 \times 0.08$
<i>(b) Data collection</i>		
diffractometer	MAC MXC-18	Rigaku AFC-5S
monochromator	graphite	
radn ($\lambda/\text{\AA}$)	Mo K α (0.7107)	
temp	room temperature	
2θ max/ $^\circ$	55	50
scan method	ω - 2θ scan	ω - 2θ scan
scan speed/ $^\circ \text{ min}^{-1}$	16	16
reflens measd	+h, +k, +l; $h \leq k$	+h, +k, ± 1
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 ($I > 3\sigma(I)$)
<i>(c) Structure solution and refinement</i>		
no of parameters	146	352
R^a	0.075	0.044
R_w^b	0.086	0.033
max residuals/ $e \text{\AA}^{-3}$	1.1	0.71

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

TABLE 2. Selected bond distances (Å) and angles (°) in [Cp*Ru(μ-SC₆H₃Me₂-2,6)₂RuCp*] (3c) and [Cp*Ru(CH₂CH₂Ph)(μ-SⁱPr)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 $20 < 2\theta < 30^\circ$. 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(CH₂Ph)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.

References and notes

- (a) T.D. Tilley, R.H. Grubbs and J.E. Bercaw, *Organometallics*, **3** (1984) 274; (b) N. Oshima, H. Suzuki and Y. Moro-oka, *Chem. Lett.*, (1984) 1161.
- (a) U. Koelle, J. Kossakowski, N. Klaff, L. Wesemann, U. Englert and G.E. Heberich, *Angew. Chem., Int. Ed. Engl.*, **30** (1991) 690; (b) U. Koelle and J. Kossakowski, *J. Organomet. Chem.*, **362** (1989) 383.
- (a) M. Hidai, K. Imagawa, G. Cheng, Y. Mizobe, Y. Wakatsuki and H. Yamazaki, *Chem. Lett.*, (1986) 1299; (b) T. Tanase, K. Imagawa, S. Dev, Y. Mizobe, S. Yano and M. Hidai, *New J. Chem.*, **12** (1988) 697; (c) S. Dev, K. Imagawa, Y. Mizobe, G. Cheng, Y. Wakatsuki, H. Yamazaki and M. Hidai, *Organometallics*, **8** (1989) 1232.
- S. Dev, Y. Mizobe and M. Hidai, *Inorg. Chem.*, **29** (1990) 4797.
- H. Matsuzaka, Y. Hirayama, M. Nishio, Y. Mizobe and M. Hidai, *Organometallics*, **12** (1993) 36.
- H. Matsuzaka, Y. Mizobe, M. Nishio and M. Hidai, *J. Chem. Soc., Chem. Commun.*, (1991) 1011.
- P.J. Fagan, M.D. Ward and J.C. Calabrese, *J. Am. Chem. Soc.*, **111** (1989) 1698.
- S.D. Loren, B.K. Campion, R.H. Heyn, T.D. Tilley, B.E. Bursten and K.W. Ruth, *J. Am. Chem. Soc.*, **111** (1989) 4712.
- Reactions of **3a** with terminal alkynes afford a variety of new diruthenium complexes, whose structures show a remarkable

- dependence on the alkyne substituent. See M. Nishio, H. Matsuzaka, Y. Mizobe and M. Hidai, *J. Chem. Soc., Chem. Commun.*, (1993) 375.
- 10 Complex **3a** was initially considered on the basis of EPR and ¹H NMR studies to be paramagnetic but this was probably due to impurities arising from its unintended reaction with air.
- 11 U. Koelle, Chr. Rietmann and U. Englert, *J. Organomet. Chem.*, **423** (1992) C20.
- 12 Y. Mizobe, M. Hosomizu, J. Kawabata and M. Hidai, *J. Chem. Soc., Chem. Commun.*, (1991) 1226.
- 13 K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka and Y. Sasada, *Inorg. Chim. Acta*, **105** (1985) L9.
- 14 T.B. Rauchfuss, D.P.S. Rodgers and S.R. Wilson, *J. Am. Chem. Soc.*, **108** (1986) 3114.
- 15 (a) S.A. Koch and M. Millar, *J. Am. Chem. Soc.*, **105** (1983) 3362; (b) M. Millar, T. O'Sullivan, N. de Vries and S.A. Koch, *J. Am. Chem. Soc.*, **107** (1985) 3714; (c) S.P. Satsangee, J.H. Hain, Jr., P.T. Cooper and S.A. Koch, *Inorg. Chem.*, **31** (1992) 5160.
- 16 E.W. Abel, S.K. Bhargava and K.G. Orrell, *Prog. Inorg. Chem.*, **32** (1984) 1.
- 17 H. Hill, B.A. Kelly, F.G. Kennedy, S.A.B. Knox and P. Woodward, *J. Chem. Soc., Chem. Commun.*, (1977) 434.
- 18 F.A. Cotton, P. Lahuerta, J. Latorre, M. Sanau, I. Solana and W. Schwotzer, *Inorg. Chem.*, **27** (1988) 2131.
- 19 C. Claver, A.M. Masdeu, N. Ruiz, C. Foces-Foces, F.H. Cano, M.C. Apreda, L.A. Oro, J. Garcia-Alejandre and H. Torrens, *J. Organomet. Chem.*, **398** (1990) 177.
- 20 G. Ferguson, C. Hannaway and K.M.S. Islam, *J. Chem. Soc., Chem. Commun.*, (1968) 1165.
- 21 N.G. Connelly and L.F. Dahl, *J. Am. Chem. Soc.*, **92** (1970) 7472.
- 22 N.G. Connelly, G.A. Johnson, B.A. Kelly and P. Woodward, *J. Chem. Soc., Chem. Commun.*, (1977) 436.
- 23 A. Shaver, B.S. Lum, P. Bird, E. Livingston and M. Schweitzer, *Inorg. Chem.*, **29** (1990) 1832.
- 24 I.B. Benson, S.D. Killops, S.A.R. Knox and A.J. Welch, *J. Chem. Soc., Chem. Commun.*, (1980) 1137.
- 25 N.-F. Ho, T.C.W. Mak and T.-Y. Luh, *J. Chem. Soc., Dalton Trans.*, (1990) 3591.
- 26 M.A. Ciriano, J.J. Perez-Torrente, F.J. Lahoz and L.A. Oro, *J. Chem. Soc., Dalton Trans.*, (1992) 1831.
- 27 S.D. Killops and S.A.R. Knox, *J. Chem. Soc., Dalton Trans.*, (1978) 1260.
- 28 G. Natile, L. Maresca and G. Bor, *Inorg. Chim. Acta*, **23** (1977) 37.
- 29 U. Koelle, B.-S. Kang, T.P. Spaniol and U. Englert, *Organometallics*, **11** (1992) 249.
- 30 (a) H.T. Schacht, R.C. Haltiwanger and M. Rakowski Dubois, *Inorg. Chem.*, **31** (1992) 1728; (b) K. Mashima, A. Mikami and A. Nakamura, *Chem. Lett.*, (1992) 1795.
- 31 H. Suzuki, T. Kakigano, M. Igarashi, M. Tanaka and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, (1991) 283.
- 32 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, in *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, p. 320.
- 33 J.J. Bonnet, A. Thorez, A. Maisonnat and R. Poilblanc, *J. Am. Chem. Soc.*, **101** (1979) 5940.
- 34 A. Sevin, Yu. Hengtai and P. Chaquin, *J. Organomet. Chem.*, **262** (1984) 391.
- 35 (a) B.A. Vaartstra, K.N. O'Brien, R. Eisenberg and M. Cowie, *Inorg. Chem.*, **27** (1988) 3668; (b) B.R. Sutherland and M. Cowie, *Organometallics*, **4** (1985) 1801; (c) A.L. Balch, B.J. Davis, F. Neve and M.M. Olmstead, *Organometallics*, **8** (1989) 1000.
- 36 A. Mayanza, J.-J. Bonnet, J. Galy, P. Kalck and R. Poilblanc, *J. Chem. Res. (S)*, (1980) 146.
- 37 For the other examples of dinuclear oxidative addition of MeI at bimetallic centers, see: (a) K.A. Beveridge, G.W. Bushnell, K.R. Dixon, D.T. Eadie, S.R. Stobart, J.L. Atwood and M.J. Zaworotko, *J. Am. Chem. Soc.*, **104** (1982) 920; (b) A.W. Coleman, D.T. Eadie, S.R. Stobart, M.J. Zaworotko and J.L. Atwood, *J. Am. Chem. Soc.*, **104**, (1982) 922; (c) C.-M. Che, W.P. Schaefer, H.B. Gray, M.K. Dickson, P.B. Stein and D.M. Roundhill, *J. Am. Chem. Soc.*, **104** (1982) 4253; (d) C.-M. Che, T.C.W. Mak and H.B. Gray, *Inorg. Chem.*, **23** (1984) 4386; (e) N.S. Lewis, K.R. Mann, J.G. Gordon II and H.B. Gray, *J. Am. Chem. Soc.*, **98** (1976) 7461; (f) J.D. Basil, H.H. Murray, J.P. Fackler, Jr., J. Tocher, A.M. Mazany, B. Trzcinska-Bancroft, H. Knachel, D. Dudis, T.J. Delord and D.O. Marler, *J. Am. Chem. Soc.*, **107** (1985) 6908; (g) R.G. Finke, G. Gaughan, C. Plerpont and J.H. Noordik, *Organometallics*, **2** (1983) 1481; (h) S. Fukuzumi, N. Nishizawa and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **56** (1983) 709.
- 38 (a) M. Tamura and J. Kochi, *J. Organomet. Chem.*, **29** (1971) 111; (b) Ref. 30, p. 94.
- 39 E.W. Abel, *J. Chem. Soc.*, (1960) 4406.
- 40 Elemental analysis data for **3a** and **3b** were not satisfactory even after repeated purifications, presumably due to the instability of these complexes.
- 41 G.R. Buettner, *Free Radical Biol. Med.*, **3** (1987) 259.
- 42 T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55** (1979) 69.
- 43 G.M. Sheldrick, SHELXS-86, *Program for Crystal Structure Determination*, Univ. of Goettingen, Germany (1986).
- 44 D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, England (1974).
- 45 TEXRAY *Structure Analysis Package*, Molecular Structure Corporation (1985).
- 46 C.J. Gilmore, MITHRIL, *an Integrated Direct Methods Computer Program*, University of Glasgow, UK, 1984.