Syntheses and characterization of diruthenium(III) alkyl–alkyl and alkyl–alkynyl complexes with two bridging thiolate ligands [Cp*RuR(μ-SPr^i)$_2$RuCp*R'] (Cp* = η^5-C$_5$Me$_5$). X-ray structure of [Cp*Ru(CH$_2$CH$_2$Ph)(μ-SPr^i)$_2$RuCp*(CH$_2$CH$_2$Ph)]

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Abstract

Reactions of diruthenium alkyl–halido complexes containing two bridging thiolate ligands [Cp*RuR(μ-SPr^i)$_2$RuCp*X] (1; Cp* = η^5-C$_5$Me$_5$, R = PhCH$_2$CH$_2$, X = Br, R = Me, X = I) with R'MgX (R' = PhCH$_2$CH$_2$, X = Br; R' = PhCH$_2$, X = Cl) or R'Li (R' = Me, PhC≡C) in THF at room temperature afforded novel diruthenium alkyl–alkyl and alkyl–alkynyl complexes [Cp*RuR(μ-SPr^i)$_2$RuCp*R'] (2). In contrast, treatment of 1a (R = PhCH$_2$CH$_2$, X = Br) with EtMgBr resulted in the formation of an alkyl-hydrido complex [Cp*Ru(CH$_2$CH$_2$Ph)(μ-SPr^i)$_2$RuCp*H] as the only isolable product. X-ray analysis of 2a (R = R' = PhCH$_2$CH$_2$) has disclosed the structure as consisting of the two Cp*Ru(CH$_2$CH$_2$Ph) units connected by two μ-SPr^i ligands together with a Ru–Ru single bond, in which the two alkyl groups are oriented mutually *cis*. Crystal data for 2a: monoclinic, space group P2$_1$/c (No. 14) with a = 19.449(3) Å, b = 10.210(3) Å, c = 20.254(2) Å, β = 94.684(9)°, V = 4008(2) Å^3, Z = 4, and R(R$_w$) = 0.054 (0.041) for 2635 reflections [I > 3σ(I)]. Treatment of 2a with two equivalents of I$_2$ in THF resulted in the formation of PhCH$_2$CH$_2$I and [Cp*RuI(μ-SPr^i)$_2$RuCp*I] (7c) as the major products, while treatment with 1.2 equivalents of I$_2$ afforded a mixture of Ph(CH$_2$)$_4$Ph and PhCH$_2$CH$_2$I along with 7c and unidentified Ru species.

*Keywords:* Ruthenium; Thiolate; Alkyl; X-ray structure

1. Introduction

Carbon–carbon coupling reactions promoted by organometallic compounds are of great importance in organic syntheses and reactivities of the metal–carbon bonds in transition metal complexes have been widely studied in this context. Coupling of organic ligands proceeding at the dinuclear center is of particular interest, since it can give insight into processes occurring on solid metal catalysts, e.g. the Fischer–Tropsch polymerization, and, more importantly, such studies may lead to novel chemical transformations of organic compounds at multimetallic centers which are inaccessible through monometallic centers. However, despite the appearance of several systems that provide a potential bimetallic site for such reactions [1], the chemistry of dinuclear alkyl and alkynyl complexes is still relatively poorly explored in comparison with that of mononuclear complexes.

Recently we have reported a variety of diruthenium complexes containing Ru(II) and/or Ru(III) centers connected by two or three bridging thiolate ligands, which are prepared from the reactions of [Cp*RuCl$_2$]$_2$ (Cp* = η^5-C$_5$Me$_5$) with various thiolate compounds [2–4]. Subsequent studies have shown that the paramagnetic Ru(II)–Ru(III) complex [Cp*Ru(μ-SPr^i)$_3$RuCp*] (3) [3] can serve as a good precursor for diruthenium(III) alkynyl–alkynyl complexes. Thus, complexes [Cp*Ru-(C≡CR)(μ-SPr^i)$_2$RuCp*(C≡CR)] (4; R = Ph, 4-Me-C$_6$H$_4$) are readily derived from 3 by treatment with an excess of HC≡CR [3,5,6]. It should be noted that the two alkynyl ligands in 4 undergo unique coupling reactions to give either diruthenacyclopentadienoindane complexes or 1,3-butadiynes RC≡CC≡CR, depending upon the reaction conditions [6].

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1a: R = PhCH$_2$CH$_2$, X = Br
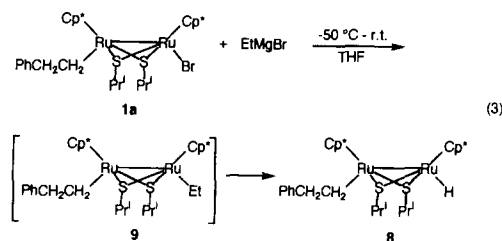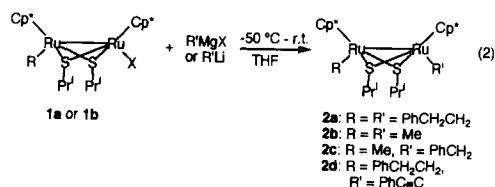1b: R = Me, X = I
1c: R = PhCH$_2$, X = Br
1d: R = Et, X = I
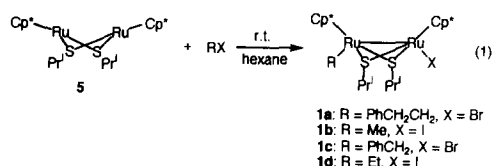
These observations have prompted us to exploit the more general route to synthesize various diruthenium complexes with σ-bonded alkyl, alkenyl and alkynyl ligands at the diruthenium center and to investigate their reactivities. This has led to the recent finding of dinuclear oxidative addition reactions of a diruthenium(II) complex [Cp* Ru(μ-SPr^i)$_2$RuCp*] (5) and alkyl halides to give novel diruthenium(III) monoalkyl complexes [Cp* RuR(μ-SPr^i)$_2$RuCp* X] (1) (Eq. (1)) [4]. In the present paper, we wish to report the reactions of 1 with R′Li and R′MgX, which afford a series of new diruthenium(III) alkyl–alkyl and alkyl–alkynyl complexes [Cp* RuR(μ-SPr^i)$_2$RuCp* R′] (2). Results of X-ray analysis of 2a (R = R′ = PhCH$_2$CH$_2$) and the reactions of 2a with iodine are also described.

2. Results and discussion

2.1. Preparation and properties of [Cp* RuR(μ-SPr^i)$_2$RuCp* R′] (2)

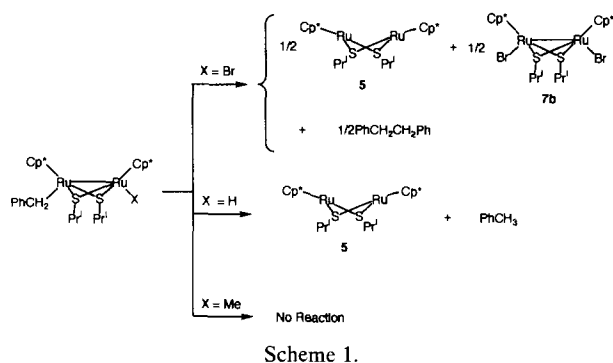When complexes 1a (R = PhCH$_2$CH$_2$, X = Br) and 1b (R = Me, X = I), prepared from oxidative addition reactions of RX across the diruthenium center in 5 (Eq (1)), were treated with 1–2 equivalents of either R′MgX (R′ = PhCH$_2$CH$_2$, X = Br; R′ = PhCH$_2$, X = Cl) or R′Li (R′ = Me, PhC≡C) in THF at room temperature, diruthenium(III) alkyl–alkyl and alkyl–alkynyl complexes 2 were obtained in moderate yields (Eq. (2)). This reaction may provide a versatile method to synthesize numerous symmetrical and nonsymmetrical diruthenium complexes containing the same or different hydrocarbyl ligands on each Ru atom. Preparation of mononuclear Ru(II) alkyl complexes [Cp* Ru(PMe$_3$)$_2$R] [7] and [CpRu(PPh$_3$)$_2$R] (6; Cp = η^5-C$_5$H$_5$) [8] by the analogous metathetical reactions of the corresponding Ru(II) chloro complexes with RMgX or RLi has already been reported. For the preparation of homoalkyl com-

plexes, reactions of diruthenium(III) dichloro complex [Cp* RuCl(μ-SPr^i)$_2$RuCp* Cl] (7a) [2b] with two equivalents of these carbon nucleophiles might serve as the more convenient method. However, neither PhCH$_2$CH$_2$MgBr nor MeLi reacted cleanly with 7a at room temperature and the isolation of the expected 2a or 2b (R = R′ = Me) from the resultant reaction mixtures was not successful.

Complexes 2a–2d are thermally stable; for example, no appreciable decomposition occurred even when the PhCH$_2$CH$_2$ complex 2a, which contains β-hydrogen atoms, was heated at 50 °C in benzene for 1 d. However, reaction of 1a with EtMgBr at room temperature gave an alkyl–hydrido complex [Cp* Ru(CH$_2$CH$_2$Ph) (μ-SPr^i)$_2$RuCp* H] (8) [9] as the only isolable product in 48% yield (Eq. (3)), which presumably results from the elimination of the β-hydrogen of the Et ligand within the [Cp* Ru(CH$_2$CH$_2$Ph)(μ-SPr^i)$_2$RuCp* Et] (9), formed prior to 8, although the amount of evolved ethylene has not been measured. It should be noted that the Et ligand in [Cp* RuEt(μ-SPr^i)$_2$RuCp* I] (1d) is fairly stable and remains intact even when heated in solution up to 50 °C. The thiolate bridges in 1d are presumably more firmly bound to the Ru atoms than those in 9 and the cis vacant site required for β-elimination [10] may be inaccessible for 1d. The higher reactivity of the Et group compared with the PhCH$_2$CH$_2$ group in 9 might be ascribed to less steric crowding around the β-carbon atom in the former. From 6 (R = Et, Pr^n, etc.) which contains the more dissociating PPh$_3$ ligand, a series of hydrido–alkene complexes [CpRu(PPh$_3$)(H)(η^2-alkene)] were readily obtained by warming their solutions. Isolation or detection of 9 was attempted by reacting 1d with PhCH$_2$CH$_2$MgBr, but this was unsuccessful due to the formation of a complicated mixture of several Cp* Ru species.

The stability of the PhCH$_2$ group in [Cp* RuMe(μ-SPr^i)$_2$RuCp* (CH$_2$Ph)] (2c) is also noteworthy. As reported previously, only the PhCH$_2$ complexes [Cp* Ru(CH$_2$Ph)(μ-SPr^i)$_2$RuCp* Br] [4] and [Cp* Ru(CH$_2$Ph)(μ-SPr^i)$_2$RuCp* H] [9] are exceptionally unstable among the alkyl–halido and alkyl–hydrido complexes prepared; the former is readily converted, even at room temperature, to a mixture of PhCH$_2$CH$_2$Ph, [Cp* RuBr(μ-SPr^i)$_2$RuCp* Br] (7b), and 5, and the

1a or 1b

2a: R = R′ = PhCH$_2$CH$_2$
2b: R = R′ = Me
2c: R = Me, R′ = PhCH$_2$
2d: R = PhCH$_2$CH$_2$, R′ = PhC≡C

Scheme 1.

Fig. 1. Molecular structure of [Cp*Ru(CH₂CH₂Ph)(μ-SPrⁱ)₂RuCp*(CH₂CH₂Ph)] (2a).

latter to the mixture of $PhCH_3$ and **5**. **2c** is quite stable under the same conditions (Scheme 1). Elucidation of the difference in reactivities of the benzyl ligands in [Cp*Ru(CH₂Ph)(μ-SPrⁱ)₂RuCp*X] associated with the nature of X (X = alkyl, H, halide) is now in progress. The results will be described elsewhere.

Despite the existence of the Ru(III) centers, complexes **2** are diamagnetic and show the sharp resonances in their ¹H NMR spectra. This suggests spin pairing between two Ru atoms. The ¹H NMR spectra of **2a** and **2b** exhibit one singlet assignable to the Cp* methyl protons as well as one doublet and one septet due to the SPrⁱ groups. Equivalence of the two PhCH₂CH₂ ligands in **2a** and the two Me ligands in **2b** is also demonstrated by their ¹H NMR spectra. These indicate the mutually cis disposition of two Cp* ligands and the syn orientation of the two Prⁱ groups in **2**, which is commonly observed in related diruthenium complexes such as **1**, **4** and **7a**, with two Ru(III) centers connected by a Ru–Ru single bond. In the ¹H NMR spectra of **2c** and **2d**, the Cp* methyl and Prⁱ methyl protons appear as two singlets and two doublets, respectively, which is consistent with the nonsymmetrical structure of these two complexes with respect to two Cp*RuR units. The medium $\nu(C\equiv C)$ band at 2081 cm⁻¹ in the IR spectrum of **2d** is typical for the σ-alkynyl ligand, as reported for mononuclear Ru complexes, e.g. [Cp(PR₃)₂Ru(C≡CR')] (R, R' = Me, Ph) (2068–2105 cm⁻¹) [11], dinuclear alkynyl–alkynyl complexes **4** (2100 cm⁻¹), and a dinuclear alkynyl–thiolate [6] or alkynyl–bromo [9] complexes [Cp*Ru(C≡CR)(μ-SPrⁱ)₂RuCp*X] (R = Buᵗ, Ph; X = SPrⁱ, Br) (2091–2110 cm⁻¹).

2.2. X-ray structure of [Cp*Ru(CH₂CH₂Ph)(μ-SPrⁱ)₂RuCp*(CH₂CH₂Ph)] (2a)

To confirm the structure of **2**, X-ray analysis was undertaken using a single crystal of **2a** grown from C₆H₆/MeCN at −20 °C. The ORTEP drawing of **2a** is depicted in Fig. 1 and some important bond lengths and angles are listed in Table 1. The structural parameters obtained for the {Cp*Ru(μ-SPrⁱ)₂RuCp*} moiety in
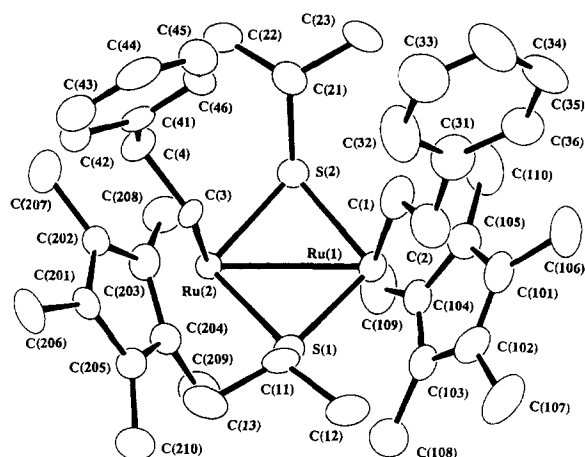
2a are in good agreement with those in **1a**. As expected from its ¹H NMR spectrum, **2a** has a dinuclear structure bridged by two SPrⁱ ligands. The two Cp* ligands are in mutually cis orientation. The Ru–Ru distance of 2.846(2) Å is consistent with the presence of a Ru–Ru single bond and comparable to those in doubly bridged Ru(III) complexes **1a** [2.844(1) Å] [4] and **4** (R = 4-MeC₆H₄) [2.809(3) Å] [6]. It should be noted that a considerably shorter Ru–Ru distance has been demonstrated for a Ru–Ru single bond surrounded by three SPh ligands in the Ru(III) complex [Cp*Ru(μ-SPh)₃RuCp*]Cl [2.630(1) Å] [2]. In contrast, a much larger separation of the two Ru atoms has been observed in the related Ru(II) complexes with no Ru–Ru interaction such as [Cp*Ru(μ-SC₆H₃Me₂-2,6)₂RuCp*] [3.500(2) Å] [4], [Cp'Ru(μ-SEt)₂RuCp'] (Cp' =

Table 1
Selected bond lengths and angles in **2a**

| Bond lengths (Å)			
Ru(1)–Ru(2)	2.846(2)		
Ru(1)–S(1)	2.304(1)	Ru(2)–S(1)	2.299(4)
Ru(1)–S(2)	2.314(3)	Ru(2)–S(2)	2.298(3)
Ru(1)–C(1)	2.15(1)	Ru(2)–C(3)	2.15(1)
Ru(1)–C(101)	2.21(1)	Ru(2)–C(201)	2.22(1)
Ru(1)–C(102)	2.20(1)	Ru(2)–C(202)	2.22(1)
Ru(1)–C(103)	2.28(1)	Ru(2)–C(203)	2.31(1)
Ru(1)–C(104)	2.38(1)	Ru(2)–C(204)	2.30(1)
Ru(1)–C(105)	2.27(1)	Ru(2)–C(205)	2.25(1)
S(1)–C(11)	1.82(1)	S(2)–C(21)	1.85(1)
C(1)–C(2)	1.53(1)	C(3)–C(4)	1.47(2)
Bond angles (°)			
Ru(2)–Ru(1)–C(1)	97.2(3)	Ru(1)–Ru(2)–C(3)	102.6(4)
S(1)–Ru(1)–S(2)	102.6(1)	S(1)–Ru(2)–S(2)	103.3(1)
S(1)–Ru(1)–C(1)	93.2(3)	S(1)–Ru(2)–C(3)	88.8(4)
S(2)–Ru(1)–C(1)	86.7(3)	S(2)–Ru(2)–C(3)	97.8(4)
Ru(1)–S(1)–Ru(2)	76.4(1)	Ru(1)–S(2)–Ru(2)	76.2(1)
Ru(1)–S(1)–C(11)	121.1(5)	Ru(1)–S(2)–C(21)	119.5(4)
Ru(2)–S(1)–C(11)	123.4(5)	Ru(2)–S(2)–C(21)	123.7(4)
Ru(1)–C(1)–C(2)	124.3(9)	Ru(2)–C(3)–C(4)	125(1)

η^5-C_5Me_4Et) [3.075(1) Å] [12], [Cp*Ru(CO)(μ-SBu^t)$_2$RuCp*(CO)] [3.751(1) Å] [13], and [(η^6-arene)Ru(μ-SPh)$_3$Ru(η^6-arene)]$^+$ (3.3–3.4 Å) [14], as well as in the Ru(II)–Ru(III) complex **3** which has a Ru–Ru bond order less than unity [2.968(2) Å] [3].

The Ru_2S_2 ring in **2a** is substantially puckered with a dihedral angle of 168° around the Ru–Ru bond, where the two SPr^i ligands are distorted in the direction opposite to the two Cp* ligands. The Ru–S distances (2.29–2.32 Å) are comparable to those in the thiolate-bridged diruthenium complexes containing Ru(II) and/or Ru(III) centers cited above. The staggered structure of the two Cp* ligands and the *syn* arrangement and axial–axial orientation of the two Pr^i groups are attributable to the steric crowding of the Cp* ligands. The two PhCH$_2$CH$_2$ ligands are mutually *cis* and the torsion angle of the C(1)–Ru(1)–Ru(2)–C(3) linkage is 10°. The Ru–C distance at 2.15(1) Å for both the Ru(1)–C(1) and Ru(2)–C(3) bonds is slightly longer than the sum of the covalent radii of the Ru and sp^3 C atoms (2.01 Å) and comparable to that of the Ru–Me linkages in [CpRuMe(μ-CHCH$_2$)(μ-CO)RuCp(CO)] [2.14(1) Å] [15] and [(OC)$_2$RuMe(μ-^{i}PrN=CH-CH=NPr^i)(μ-I)Ru(CO)$_2$] [2.12(1) Å] [16], as well as the Ru–η^1-CH$_2$ bonds in [CpRu(CO){μ-η^1,η^3-CH$_2$C-(CH$_2$)$_2$}(μ-CO)RuCp] [2.15(1) Å] [17] and **1a** [2.15(1) Å]. The Ru–C–C angles in the PhCH$_2$CH$_2$ ligands (124° and 125°) are considerably wider than the 109° expected for the ideal sp^3 carbon atom, which may be explained by steric crowding around the Ru center due to the Cp* and two SPr^i groups. Such distortion of the M–C–C angles in the alkyl ligands is observed in many transition metal complexes with bulky alkyl ligands and/or sterically congested metal centers [18] (e.g. 117°–124° in [WO(CH$_2$Bu^t)$_3$(NEt$_2$)] [19], 138° in [Cp*$_2$Hf(CH$_2$CHMe$_2$)(THF)][BPh$_4$] [20], 121° in [Cp$_2$-NbEt(η^2-MeC≡CMe)] [21], and 126° in [MoEt(NMe$_2$)-(μ-4-MeC$_6$H$_4$N$_3$C$_6$H$_4$Me-4)$_2$MoEt(NMe$_2$)] [22]). It should be noted, however, that this occurs even in some complexes with relatively unencumbered alkyl ligands (e.g. 121° in [RhEt(NH$_3$)$_5$]Br$_2$ [23]).

2.3. Reaction of **2a** with I_2

As described above, dialkyl complexes **2** are moderately stable and the alkyl ligands remain intact upon heating to 50°C. Such thermal stabilities are also observed for the dialkynyl complexes **4**. However, in the presence of 1.2 equivalents of I_2 in THF, complexes **4** smoothly afford 1,4-diaryl-1,3-butadiynes from coupling of the two alkynyl ligands in high yields, accompanied by quantitative formation of [Cp*RuI(μ-SPr^i)$_2$RuCp*I] (**7c**) (Scheme 2) [6].

We have found that an analogous treatment of **2a** with 1.2 equivalents of I_2 results in the formation of a mixture of Ph(CH$_2$)$_4$Ph and PhCH$_2$CH$_2$I, where 40%
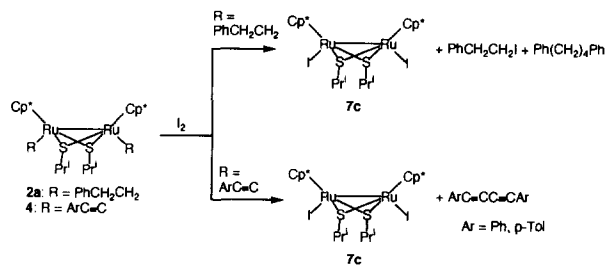
Scheme 2.

of the PhCH$_2$CH$_2$ ligands in **2a** are converted to the former and the remaining 60% to the latter. Complex **7c** was isolated from the reaction mixture as the only characterizable Ru compound in 43% yield (Scheme 2). However, the remaining Ru product(s) could not be identified, although the formation of Ru species not containing iodine is expected if the iodine balance is taken into account. As the molar ratio I_2 : **2a** was raised to 2, the yield of PhCH$_2$CH$_2$I increased to 77%, whereas that of Ph(CH$_2$)$_4$Ph decreased to a trace amount. In the reaction of **2a** with 1.2 equivalents of I_2 in which a substantial amount of the coupling product Ph(CH$_2$)$_4$Ph is formed, the intramolecular mechanism might not be operating, since an analogous treatment of **2c** did not give the coupling product PhCH$_2$CH$_3$ but resulted in the formation of PhCH$_2$CH$_2$Ph (34%). In this reaction, the fate of the remaining PhCH$_2$ group in **2c** is PhCH$_2$I. However, the product containing the Me group in **2c** could not be identified. Unfortunately, we are not yet able to demonstrate clearly the degradation pathways of the alkyl groups in **2** upon treatment with I_2, but it is of significant interest that the products derived from the I_2-induced Ru–C bond cleavage largely depend upon the nature of the carbon atoms attached to the Ru atoms.

3. Experimental details

3.1. General

All manipulations were carried out under dinitrogen using Schlenk tube techniques. Solvents were dried and distilled under dinitrogen before use. Complexes **1** were prepared as previously described [4], while PhCH$_2$CH$_2$-MgBr was prepared from PhCH$_2$CH$_2$Br and Mg in THF and used after determining the concentration by titration. Solutions of PhCH$_2$MgCl, MeLi, and Bu^{n}Li were obtained commercially and used without further purification. ^{1}H NMR spectra were recorded on a JEOL JNM-GX 400 spectrometer and IR spectra were obtained on a Shimadzu DR-8000 spectrometer. Quantitative GLC analyses were performed using a Shimadzu GC-14A gas chromatograph equipped with a CBP-10 capillary column.

3.2. Preparation of [Cp*Ru(CH₂CH₂Ph)(μ-SPr^i)₂-RuCp*(CH₂CH₂Ph)] (2a)

3.2. Preparation of [Cp*Ru(CH₂CH₂Ph)(μ-SPr^i)₂-RuCp*(CH₂CH₂Ph)] (2a)

To a suspension of **1a** (161 mg, 0.200 mmol) in THF (10 cm³) PhCH₂CH₂MgBr (0.20 mmol) was added at −50°C and the mixture was allowed to react at room temperature for 2.5 h. The resultant brown suspension was dried in vacuo and the residue was extracted with hexane. The extract was evaporated to dryness in vacuo and the resulting solid was crystallized from C₆H₆/MeCN affording 57 mg of **2a** as brown crystals (34%). Anal. Found: C, 59.64; H, 7.80. C₄₂H₆₂S₂Ru₂ Calc.: C, 60.54, H, 7.50%. ¹H NMR (C₆D₆): δ 1.71 (s, 30H, Cp*), 1.34 (d, 12H, SCH*Me*), 3.26 (sep, 2H, SC*H*Me), 0.75 (pseudo t, 4H, RuCH₂), 2.30 (pseudo t, 4H, RuCH₂C*H*₂), 6.82–7.13 (m, 10H, Ph).

3.3. Preparation of [Cp*RuMe(μ-SPr^i)₂RuCp*Me] (2b)

This compound was prepared by an analogous process from **1b** (323 mg, 0.423 mmol) and MeLi (0.845 mmol). The product was crystallized from toluene/MeCN. Yield, 94 mg (34%). Anal. Found: C, 50.67; H, 7.80. C₂₈H₅₀S₂Ru₂ Calc.: C, 51.50; H, 7.72%. ¹H NMR (C₆D₆): δ 1.62 (s, 30H, Cp*), 1.32 (d, 12H, SCH*Me*), 3.42 (sep, 2H, SC*H*Me), −0.12 (s, 6H, RuMe).

3.4. Preparation of [Cp*RuMe(μ-SPr^i)₂RuCp*(CH₂-Ph)] (2c)

This complex was also prepared from **1b** (369 mg, 0.483 mmol) and PhCH₂MgCl (ether solution; 1.0 mmol) in THF (5 cm³). The product was crystallized from hexane. Yield, 91 mg (26%). Anal. Found: C, 55.45; H, 7.42%. C₃₄H₅₄S₂Ru₂ Calc.: C, 56.01; H, 7.47%. ¹H NMR (C₆D₆): δ 1.36 and 1.60 (s, 15H each, Cp*), 1.33 and 1.46 (d, 6H each, SCH*Me*), 3.68 (sep, 2H, SC*H*Me), −0.41 (s, 3H, RuMe), 2.14 (s, 2H, RuCH₂), 7.08–7.36 (m, 5H, Ph).

3.5. Preparation of [Cp*Ru(CH₂CH₂Ph)(μ-SPr^i)₂-RuCp*(C≡CPh)] (2d)

Reaction was carried out analogously using **1a** (660 mg, 0.815 mmol) and PhC≡CLi [prepared in situ from PhC≡CH (674 mg, 6.7 mmol) and ⁿBuLi (hexane solution; 6.7 mmol) in THF (5 cm³)]. The product was crystallized from hexane. Yield, 714 mg (59%). Anal. Found: C, 60.93; H, 7.12%. C₄₂H₅₈S₂Ru₂ Calc.: C, 60.84; H, 7.05%. ¹H NMR (C₆D₆): δ 1.62 and 1.68 (s, 15H each, Cp*), 1.41 and 1.62 (d, 6H each, SCH*Me*), 1.28 (pseudo t, 2H, RuCH₂), 2.72 (pseudo t, 2H, RuCH₂C*H*₂), 3.94 (sep, 2H, SC*H*Me), 6.91–7.49 (m, 10H, Ph). IR (KBr disk, cm⁻¹): 2081(m) [ν(C≡C)].

3.6. Formation of [Cp*Ru(CH₂CH₂Ph)(μ-SPr^i)₂Ru-Cp*H] (8) from 1a and EtMgBr

To a solution of **1a** (211 mg, 0.261 mmol) in THF (3 cm³) EtMgBr (THF solution; 0.521 mmol) was added at −70°C and the mixture was stirred for 1 h at room temperature. After evaporating all volatile materials in vacuo, the residue was extracted with hexane and the extract was kept at −20°C. The crystalline solid deposited was collected by filtration and dried in vacuo, which has been characterized as **8** by IR and ¹H NMR spectra which are identical with those of the authentic compound [9] (92 mg, 48%).

3.7. Reaction of 2a with I₂

(a) To **2a** (168 mg, 0.202 mmol) was added I₂ (62.7 mg, 0.247 mmol, 1.2 equivalents of **2a**) in ether (5 cm³) and the mixture was stirred overnight at room temperature in the dark. The color of the reaction mixture changed from brown to purple. Quantitative GLC analysis of the product solution disclosed the formation of

Table 2
Details of X-ray crystallography for **2a**

(a) Crystal data	
formula	C₄₂H₆₂S₂Ru₂
formula wt.	833.2
crystal color	violet
crystal dimensions (mm)	0.25×0.25×0.10
crystal system	monoclinic
space group	P2₁/c
a (Å)	19.449(3)
b (Å)	10.210(3)
c (Å)	20.254(2)
β (°)	94.684(9)
V (Å³)	4008(2)
Z	4
D_calc (g cm⁻³)	1.380
F(000), electrons	1736
μ(Mo-Kα)(cm⁻¹)	8.65
(b) Intensity collection	
diffractometer	Rigaku AFC5S
radiation	Mo Kα (λ = 0.71069 Å)
temperature	room temperature
scan method	ω−2θ
scan rate (° min⁻¹)	16
max 2θ (°)	50
reflections measured	+h, +k, ±l
no. of unique reflections	7479
absorption correction	ψ-scan method
transmission factors	0.93–1.00
(c) Structure solution and refinement	
no. of reflections used [I > 3σ(I)]	2635
no. of variables	415
data/parameter ratio	6.35
R	0.054
R_w	0.041
max residual (e Å⁻³)	1.0

PhCH$_2$CH$_2$I (0.248 mmol) and Ph(CH$_2$)$_4$Ph (0.0813 mmol), which indicates that 60% of the PhCH$_2$CH$_2$ ligand in **2a** was converted to the former and the remaining 40% to the latter. The volume of the solution was then reduced to ca. a quarter in vacuo and hexane was added. Complex **7b** was deposited as a purple solid, filtered off and recrystallized from CH$_2$Cl$_2$/hexane (75.3 mg, 43%).

(b) Reaction of **2a** with 2 equivalents of I$_2$ was carried out analogously by the use of **2a** (87.3 mg, 0.105 mmol) and I$_2$ (51 mg, 0.202 mmol) in THF (5

cm^3). The GLC analysis showed the formation of PhCH$_2$CH$_2$I (0.163 mmol, 77%) and Ph(CH$_2$)$_4$Ph (trace), while **7b** was isolated in 46% yield from the reaction mixture.

3.8. X-ray Crystallography of 2a

A single crystal of **2a** sealed in a glass capillary under Ar was mounted on a Rigaku AFC5S diffractometer. The orientation matrices and unit cell parameters were derived from the least-squares fit of 25 machine-centered reflections with $20° < 2\theta < 30°$. Three check reflections measured every 150 reflections showed no significant decay during data collection. Intensity data were corrected for the Lorentz and polarization effects and for absorption. Crystallographic data are summarized in Table 2.

All calculations were performed by using the TEXSAN crystallographic software package [24]. The structure was solved by direct methods program MITHRIL [25]. 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. Atomic coordinates and equivalent temperature factors of non-hydrogen atoms are listed in Table 3.

4. Supplementary material available

Tables of hydrogen atom coordinates, anisotropic temperature factors of non-hydrogen atoms, and bond lengths and angles for **2a** (6 pages) as well as a listing of observed and calculated structure factors for **2a** (10 pages) are available from M.H. upon request.

Acknowledgments

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Table 3
Atomic coordinates and equivalent temperature factors of nonhydrogen atoms in **2a**

	x	y	z	B_{eq}
Ru(1)	0.68191(5)	0.1724(1)	0.45547(5)	2.87(5)
Ru(2)	0.82654(6)	0.2090(1)	0.45122(5)	3.43(6)
S(1)	0.7515(2)	0.1022(4)	0.3758(2)	4.1(2)
S(2)	0.7545(2)	0.3084(3)	0.5205(1)	3.4(2)
C(1)	0.6496(5)	0.345(1)	0.4006(6)	3.5(6)
C(2)	0.5962(6)	0.345(1)	0.3406(6)	4.5(7)
C(3)	0.8317(7)	0.366(1)	0.3814(7)	5.7(9)
C(4)	0.8563(8)	0.500(2)	0.398(1)	8(1)
C(11)	0.7354(7)	0.153(1)	0.2900(6)	4.8(8)
C(12)	0.6767(7)	0.071(1)	0.2599(6)	5.1(8)
C(13)	0.7979(8)	0.136(2)	0.2530(7)	8(1)
C(21)	0.7367(7)	0.487(1)	0.5209(6)	3.8(7)
C(22)	0.7983(8)	0.554(1)	0.5591(6)	5.5(8)
C(23)	0.6728(8)	0.513(1)	0.5572(7)	5.6(9)
C(31)	0.5852(7)	0.478(1)	0.3109(6)	3.7(7)
C(32)	0.6327(7)	0.532(2)	0.2734(7)	4.4(8)
C(33)	0.6217(8)	0.658(2)	0.2467(7)	6(1)
C(34)	0.566(1)	0.729(1)	0.2580(7)	6(1)
C(35)	0.5180(8)	0.676(2)	0.2967(7)	5.4(9)
C(36)	0.5272(7)	0.552(2)	0.3232(7)	4.7(8)
C(41)	0.865(1)	0.581(2)	0.333(1)	7(1)
C(42)	0.924(1)	0.581(2)	0.3042(9)	7(1)
C(43)	0.934(1)	0.661(2)	0.2538(9)	8(1)
C(44)	0.880(1)	0.738(2)	0.228(1)	9(1)
C(45)	0.821(1)	0.738(2)	0.256(1)	9(1)
C(46)	0.811(1)	0.661(2)	0.309(1)	9(1)
C(101)	0.5783(6)	0.151(1)	0.4919(6)	3.2(6)
C(102)	0.5861(7)	0.057(1)	0.4418(6)	3.4(7)
C(103)	0.6366(7)	−0.033(1)	0.4640(7)	3.9(8)
C(104)	0.6615(7)	−0.001(1)	0.5296(7)	3.9(8)
C(105)	0.6269(7)	0.115(1)	0.5456(7)	3.7(7)
C(106)	0.5223(7)	0.251(1)	0.4941(7)	6.0(9)
C(107)	0.5344(7)	0.035(1)	0.3822(7)	6(1)
C(108)	0.6546(7)	−0.156(1)	0.4285(7)	5.4(8)
C(109)	0.7019(8)	−0.084(1)	0.5793(7)	5.6(9)
C(110)	0.6347(7)	0.177(2)	0.6123(6)	5.9(8)
C(201)	0.9408(7)	0.197(2)	0.4543(9)	4.9(9)
C(202)	0.9232(8)	0.221(2)	0.5174(8)	5(1)
C(203)	0.8878(7)	0.108(2)	0.5396(8)	4.6(9)
C(204)	0.8810(7)	0.019(1)	0.4874(8)	4.4(8)
C(205)	0.9141(8)	0.073(2)	0.4341(8)	5(1)
C(206)	0.9921(7)	0.269(2)	0.4132(8)	8(1)
C(207)	0.9499(8)	0.330(2)	0.5585(8)	8(1)
C(208)	0.8660(8)	0.091(2)	0.6072(8)	8(1)
C(209)	0.8534(7)	−0.120(1)	0.4870(8)	7(1)
C(210)	0.9286(8)	0.003(2)	0.374(1)	9(1)

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