Reactivity and electrochemical behavior of ruthenium dithiolene complexes with coordinatively unsaturated metal centers: cycloaddition and dimerization reactions

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Abstract

The novel ruthenium dithiolene complexes $[(arene)Ru\{S_2C_2(COOMe)_2\}]$ (arene = C_6H_6 (**1a**), $C_6H_4(Me)(iPr)$ (**1b**), C_6Me_6 (**1c**)) were synthesized. The equilibrium between complex **1a** and the corresponding dimer $[(C_6H_6)Ru\{S_2C_2(COOMe)_2\}]_2$ (**1a′**) was confirmed in solution. The reaction of complex **1a** with dimethyl- or diethylacetylene dicaboxylate gave the alkene-bridged adducts $[(C_6H_6)Ru\{S_2C_2(COOMe)_2\}\{C_2(COOR)_2\}]$ (R = Me (**2a**), Et (**3a**)) as [2 + 2] cycloaddition products formally. The reactions of complex **1a** with diazo compounds also gave the alkylidene-bridged adducts $[(C_6H_6)Ru\{S_2C_2(COOMe)_2\}(CHR)]$ (R = H (**4a**), SiMe$_3$ (**5a**), COOEt (**6a**)) as [2 + 1] cycloaddition products. The electrochemical behavior of complex **1a** was investigated. The reductant of complex **1a** was a stable species for several minutes. The oxidant of complex **1a** was very unstable; the cation **1a**$^+$ formed was immediately converted to the corresponding cationic dimer **1a′**$^+$. The cationic dimer **1a′**$^+$ was stable for several minutes, and it was rapidly and quantitatively converted to the neutral complex **1a** when it was reduced.
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1. Introduction

A metalladithiolene ring is a five-membered ring consisting of one metal, two sulfur atoms and two unsaturated carbons. Metalladithiolene complexes are unique and interesting compounds because of their ability to exhibit both the aromatic and the unsaturated characters [1]. The former property exhibits substitution reactions in the metalladithiolene ring [2], and the latter property allows addition reactions of Lewis bases (e.g. PR$_3$) to the unsaturated metal center [3] and a dimerization of metalladithiolene complexes [4] (Scheme 1). In addition,

we have expanded the study of the unsaturation of metalladithiolene ring: namely, the metal–sulfur bond of metalladithiolene ring also has the unsaturated character. This chemical property induces cycloaddition reactions into the metal–sulfur bond. In the studies of the half-sandwich type of cobalta- and rhodia-dithiolene complexes, we have reported the alkylidene- [5] (Scheme 1), the imido- [6], the alkene- [7], and the norbornene-bridged metalladithiolene adducts [8]. In general, metalladithiolene complexes with a penta-coordinated and 16-electron (coordinatively unsaturated) metal center form the corresponding 18-electron (coordinatively saturated) complexes. Similar reactivities have been confirmed by the studies of the half-sandwich type of *o*-carborane dithiolato metal complexes by Kang [9] and by Herberhold [10].

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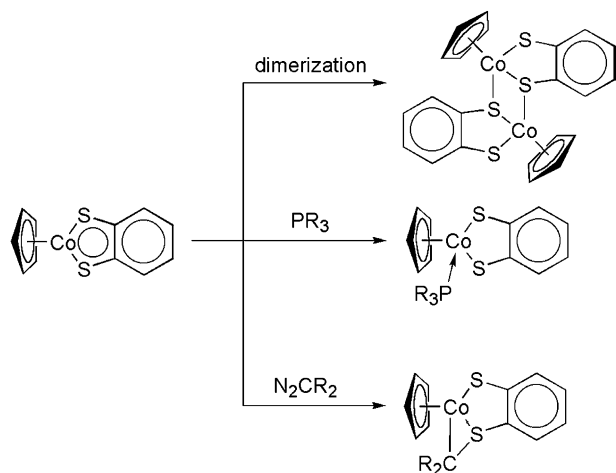
Scheme 1.

Half-sandwich types of ruthenium dithiolene complexes have been reported in a few cases: the ruthenium dithiolene complexes with cyclopentadienyl ligand [CpRu(PPh$_3$)(dithiolene)] [11], [Cp*Ru(NO)(dithiolene)] [12], and the dimeric complex [Cp*Ru{μ$_2$-η^4-(S$_2$C$_6$H$_4$)-Ru(P(OMe)$_3$)Cp*}] [13], whose metal centers are coordinatively saturated. Mashima et al. [14] have reported the ruthenium dithiolene complex with coordinatively unsaturated metal center, [(arene)Ru(S$_2$C$_6$H$_4$)] (arene = C$_6$H$_6$, C$_6$H$_4$(Me)(iPr), C$_6$Me$_6$). They reported the addition reactions of Lewis bases (PR$_3$, CNR [14a] and NH$_2$NH$_2$ [14b]) to the ruthenium center, and reported the dimerization of the ruthenium dithiolene complex due to its unsaturated character.

In present paper, we report on the reactivities of the novel ruthenium dithiolene complexes [(arene)-Ru{S$_2$C$_2$(COOMe)$_2$}]. We focused on the unsaturated character of the ruthenium–sulfur bond in the dithiolene ring, and we report on the novel cycloaddition reactions into the unsaturated bond. Furthermore, metalladithiolene complexes are sometimes promoted to undergo the dimerization reactions by an oxidation [15,16]. One example, which is reported by Fourmigué et al. [16] is shown in Scheme 2. We also report on the novel dimer-
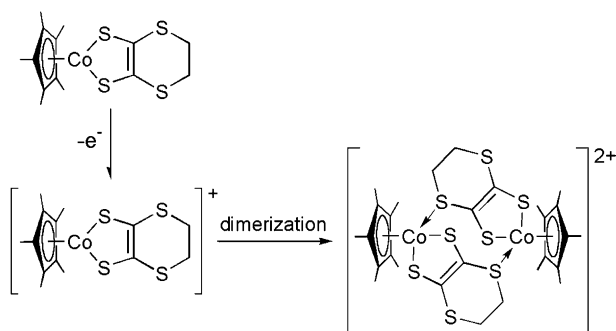
Scheme 2.

ization reaction of ruthenium dithiolene complexes induced by an electrochemical oxidation.

2. Results and discussion

### 2.1. Preparations of ruthenium dithiolene complexes

Dimethyl 1,3-dithiole-2-one-4,5-dicarboxylate was treated with 2 equivalents of sodium methoxide in methanol solution; next, the ruthenium complex dimer [(C$_6$H$_6$)Ru(Cl)(μ-Cl)]$_2$ was added into this solution. The solution color was changed from yellow to brown. The reaction mixture was stirred at room temperature for 24 h. The brown product was isolated as the novel ruthenium dithiolene complex [(C$_6$H$_6$)Ru{S$_2$C$_2$(COO-Me)$_2$}] (**1a**) in 80% yield (Scheme 3). The analogous ruthenium complexes [{C$_6$H$_4$(Me)(iPr)}Ru{S$_2$C$_2$(COO-Me)$_2$}] (**1b**, 74% yield) (p-cymene = C$_6$H$_4$(Me)(iPr)) and [(C$_6$Me$_6$)Ru{S$_2$C$_2$(COOMe)$_2$}] (**1c**, 75% yield) were obtained from [{C$_6$H$_4$(Me)(iPr)}Ru(Cl)(μ-Cl)]$_2$ and [(C$_6$Me$_6$)Ru(Cl)(μ-Cl)]$_2$, respectively.

The elemental compositions of complexes **1a–c** were determined by elemental analyses. However, the ^{1}H NMR spectrum of complex **1a** showed the signals of two species. The major signals appeared at 5.87 (singlet, 6H, C$_6$H$_6$) and 3.89 (singlet, 6H, OMe) ppm, and the minor signals appeared at 5.41 (singlet, 6H, C$_6$H$_6$), 3.93 (singlet, 3H, OMe), and 3.77 (singlet, 3H, OMe) ppm. The minor signals suggest the existence of the corresponding dimer [(C$_6$H$_6$)RuS$_2$C$_2$(COOMe)$_2$]$_2$ (**1a′**) in the solution (Scheme 4). The molar ratio of complexes **1a** and **1a′** was 20:1 (30 °C in CDCl$_3$). The proposed structure of dimer **1a′** is the structure dimerized by a sulfide coordination (Scheme 4); such a structure is suggested by two different ^{1}H NMR signals of OMe groups. On the other hand, complexes **1b** and **1c** are presented in solution only as the monomer complexes. The cobalt and rhodium dithiolene dimers having such structures: [CpCo(S$_2$C$_6$H$_4$)]$_2$ [4a], [Cp*Rh(S$_2$C$_6$H$_4$)]$_2$ [17], [Cp*Rh(mnt)]$_2$ [4b], and [Cp*Rh(dmit)]$_2$ [18] have been reported in X-ray structure studies. In addition, Mashima et al. [14] have reported the dimer of ruthenium dithiolene complexes containing 1,2-benzenedithiolate ligand [(arene)Ru(S$_2$C$_6$H$_4$)] (arene = C$_6$H$_6$, C$_6$H$_4$(Me)(iPr)).

The X-ray crystal structure of complex **1c** was shown in Fig. 1. The structure of complex **1c** is similar to the 1,2-benzenedithiolate ruthenium complex [(C$_6$Me$_6$)-Ru(S$_2$C$_6$H$_4$)] [14] previously reported. Complex **1c** has monomeric and two-legged piano stool structure. The ruthenium center is coordinatively unsaturated, and the five-membered ruthenadithiolene ring is extremely planar (mean deviation from ruthenadithiolene plane = 0.0018 Å). The ruthenadithiolene plane and arene ligand crosses at right angles.
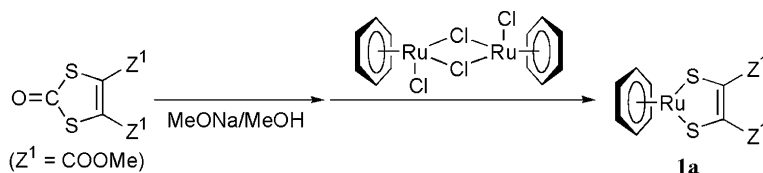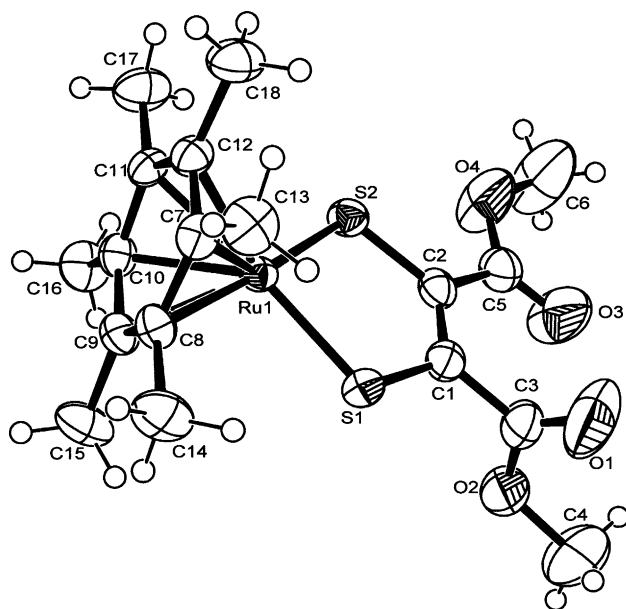
Scheme 3.
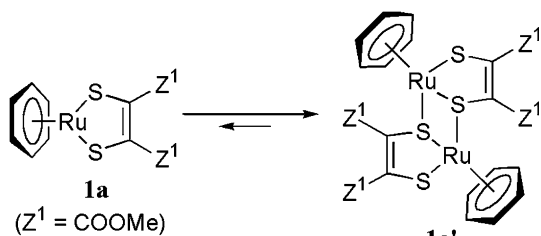
Scheme 4.

Fig. 1. ORTEP drawing of complex **1c**, [(C$_6$Me$_6$)Ru{S$_2$C$_2$-(COOMe)$_2$}]. Selected bond lengths (Å): Ru1–S1 2.252(1), Ru1–S2 2.2451(6), S1–C1 1.735(3), S2–C2 1.742(4), C1–C2 1.338(5). Selected bond angles (deg): S1–Ru1–S2 86.98(3), Ru1–S1–C1 106.0(1), Ru1–S2–C2 106.3(1), S1–C1–C2 120.9(3), S2–C2–C1 119.9(2).

2.2. Cycloaddition reactions of ruthenium dithiolene complexes

2.2.1. Formation and thermal decomposition of alkene-bridged adduct

Complex **1a** reacted with dimethylacetylene dicarboxylate (DMAD) or diethylacetylene dicarboxylate (DEAD) at room temperature, and the alkene-bridged adducts [(C$_6$H$_6$)Ru{S$_2$C$_2$(COOMe)$_2$}{C$_2$(COOR)$_2$}] were obtained in good yields (R = Me (**2a**); 90%, R = Et (**3a**); 77%). Elemental analyses of adducts **2a**–

3a indicated the 1:1 adduct between complex **1a** and alkynes. These spectroscopic data revealed that the alkene moiety was formally bridged to the ruthenium–sulfur bond by a [2 + 2] cycloaddition of an alkyne. These adducts were the dithiolene complex with 18-electron and coordinatively saturated metal center (Scheme 5). Phenylacetylene and dimethyl maleate did not react with complex **1a** at all. Therefore, an electron-poor alkyne efficiently forms the corresponding alkene-bridged adduct, and this indicates an electrophilic attack of alkynes on the electron-rich sulfur atom of dithiolene ring.

Thermal reactions of adducts **2a**–**3a** under refluxing xylene (140 °C) gave several products. One of them was isolated and identified as the thiophene derivative in 25% yield. In the thermal decomposition of adduct **2a**, the thiophene derivative having four methyl ester groups (Z^1) was obtained. In the case of adduct **3a**, the thiophene derivative having two Z^1 and two ethyl ester groups (Z^2) was formed. Namely, the thiophene derivatives are formed by the alkene moiety in the dithiolene ring, the bridged alkene, and the sulfur atom. In a previous report, our group has reported the catalytic formation of thiophene derivative in the one-pot reaction of the cobalt or the rhodium dithiolene complex, elemental sulfur and an acetylene [7].

2.2.2. Formation of alkylidene-bridged adduct

We attempted that the reactions of the ruthenium dithiolene complex with 1,3-dipoles as nucleophiles. The reaction of complex **1a** with excess diazo methane gave the methylene-bridged adduct [(C$_6$H$_6$)Ru{S$_2$C$_2$-(COOMe)$_2$}(CH$_2$)] (**4a**) in good yield. In addition, the alkylidene-bridged complexes with trimethylsilyl group, [(C$_6$H$_6$)Ru{S$_2$C$_2$(COOMe)$_2$}(CHSiMe$_3$)] (**5a**, 78% yield), was formed when trimethylsilyldiazomethane (N$_2$CHSiMe$_3$) was used. Complex **4a** was also obtained by a typical desilylation: the treatment of complex **5a** with tetrabutylammonium fluoride (TBAF). Ethyl diazoacetate (N$_2$CHCOOEt) reacted with complex **1a** to also give the alkylidene adduct [(C$_6$H$_6$)Ru{S$_2$C$_2$(COO-Me)$_2$}(CHCOOEt)] (**6a**, 94% yield) (Scheme 6). Analogous adducts [(arene)Ru{S$_2$C$_2$(COOMe)$_2$}(CHCOOEt)] (arene = C$_6$H$_4$(Me)(*i*Pr) (**6b**), C$_6$Me$_6$ (**6c**)) were synthesized by the reactions of complexes **1b** and **1c** with N$_2$CHCOOEt. These alkylidene adducts were efficiently formed under a mild condition in the reactions with diazo compounds having various scales of nucleophilicity
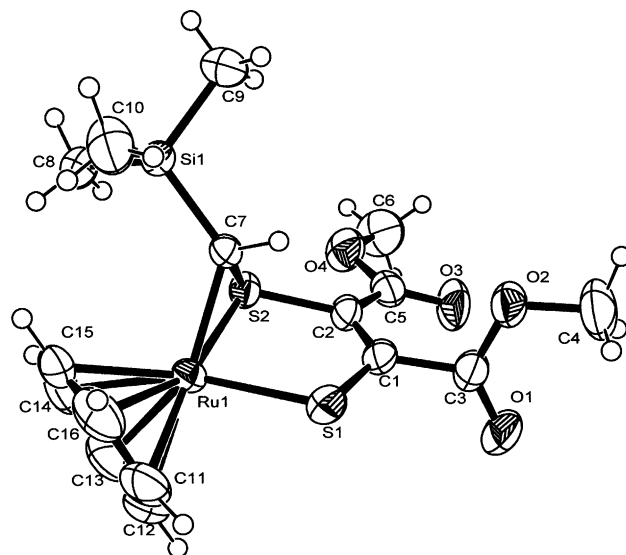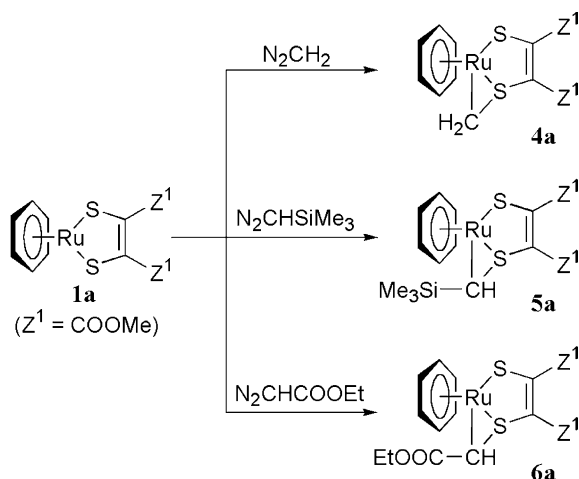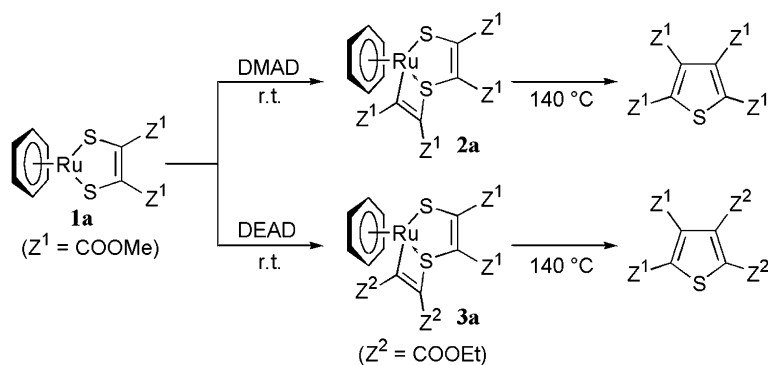
Scheme 5.

Scheme 6.

Fig. 2. ORTEP drawing of complex **5a**, [(C₆H₆)Ru{S₂C₂(COO-Me)₂}(CHSiMe₃)]. Selected bond lengths (Å): Ru1–S1 2.3447(8), Ru1–S2 2.3314(7), S1–C1 1.699(3), S2–C2 1.778(2), C1–C2 1.359(4), Ru1–C7 2.124 (2), S2–C7 1.775(2). Selected bond angles (deg): S1–Ru1–S2 85.55(2), Ru1–S1–C1 104.71(9), Ru1–S2–C2 105.04(9), S1–C1–C2 124.7(2), S2–C2–C1 118.0(2), Ru1–S2–C7 60.52(7), Ru1–C7–S2 72.82(6), C7–Ru1–S1 85.15(6), C7–Ru1–S2 46.66(6).

[19]. In general, 1,3-dipoles often undergo a [2 + 3] cyclo-addition reaction toward unsaturated compounds to form a five-membered hetero cycle [20]. However, only the typical [2 + 1] cycloaddition product of the ruthenium dithiolene complexes was observed.

The structure of the alkylidene-bridged complex **5a** was determined by X-ray crystal structure analysis. The ORTEP drawing, the selected bond lengths and angles of complex **5a** are shown in Fig. 2. This structure is analogous to the alkylidene-bridged adduct of a cyclopentadienyl cobaltadithiolene complex, [CpCo{S₂C₂-(COOMe)₂(CHSiMe₃)₃}] [5a]. Complex **5a** was three-legged piano stool structure and 18-electron complex. The three-membered ring of the bridging alkylidene moiety is almost perpendicular to the five-membered ruthenium dithiolene ring.

2.3. Electrochemical behavior of ruthenium dithiolene complexes

The cyclic voltammograms (CV) of complexes **1a–c** are shown in Fig. 3(a)–(c). The one-step reduction waves were confirmed in the reduction processes of complexes

1a–c. These reduction waves correspond to those of the monomer complexes **1a–c**. Although complex **1a** coexisted with the corresponding dimer **1a′** in ¹H NMR analysis (Scheme 4), the reduction wave of dimer **1a′** did not appear. This can be explained by arguing that either the reduction potential of dimer **1a′** is the outside of the potential window, or that the formation of the reductant **1a⁻** shifts the equilibrium between complexes **1a** and **1a′**. Complexes **1a–c** were easier to reduce in the sequence **1a > 1b > 1c** (Table 1). This can be explained by the effect of electron donor groups on the arene ligand, Me and *i*Pr groups. The reduction waves of complexes **1a–c** were chemically reversible (Scheme 7). This result reveals that the reductants of complexes **1a–c** were stable on the CV time scale. The redox potentials of the 18-electron adducts **2a** and **5a** were more negative than
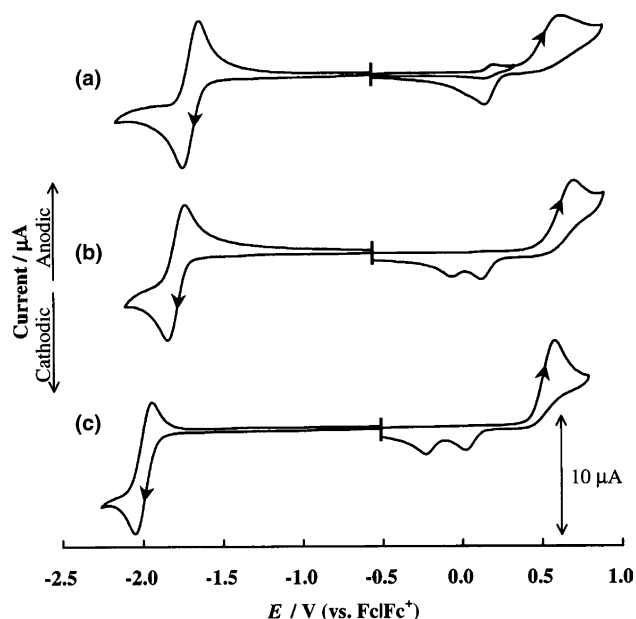
Fig. 3. Cyclic voltammograms ($v = 100$ mV s^{-1}, $\Phi = 1.6$ mm Pt disk) of 1 mM (a) complex **1a**, (b) complex **1b**, and (c) complex **1c** in TBAP-CH$_2$Cl$_2$ solution.

those of the corresponding 16-electron complex **1a**. In addition, the redox potentials of complex **2a** were more positive than those of complex **5a** (Table 1). This can be explained by a substituent effect on the bridged moiety.

Although the CV of complex **1a** showed two steps of oxidation wave, complexes **1b–c** showed only one oxidation wave (Fig. 3(a)–(c)). The first oxidation wave of complex **1a** corresponds to that of dimer **1a′** which slightly coexisted in the solution, and the second one corresponds to that of monomer **1a**. The oxidation wave of dimer **1a′** was chemically reversible, and that of monomer **1a** was chemically irreversible. Therefore, although cation **1a′⁺** is a stable species, the corresponding monomer cation **1a⁺** is unstable on the CV time scale. When the potential was scanned to negative after the oxidation of monomer **1a**, a re-reduction wave grew larger around +0.2 V. This wave corresponds to the reduction wave of the couple of dimer **1a′/1a′⁺**. This result reveals that monomer cation **1a⁺** rapidly reacted with the neutral complex **1a** present at the close electrode to form dimer cation **1a′⁺** (Scheme 7). Although the dimerizations of cobalt dithiolene complexes by an

Table 1
Redox potentials of ruthenium dithiolene complexes

Complex	Reduction				Oxidation			
	$E_{1/2}$/V	ΔE/mV	ΔE_p/mV	i_{pa}/i_{pc}	$E_{1/2}$/V	ΔE/mV	ΔE_p/mV	i_{pc}/i_{pa}
1a	−1.71[a]	76	104	0.97	0.56[b]	120	–	–
1a′	–[c]	–	–	–	0.18[a]	60	70	0.84
1b	−1.81[a]	72	112	0.89	0.64[b]	110	–	–
1c	−2.02[a]	74	104	0.84	0.53[b]	84	–	–
2a	−2.10[b]	173	–	–	0.55[b]	76	–	–
5a	−2.30[b]	178	–	–	0.23[a]	70	92	0.67

$E_{1/2} = (E_p + E_{p/2})/2$, $\Delta E = |E_p − E_{p/2}|$, $E_p = |E_{pc} − E_{pa}|$.
[a] reversible wave.
[b] irreversible wave.
[c] Not observed.
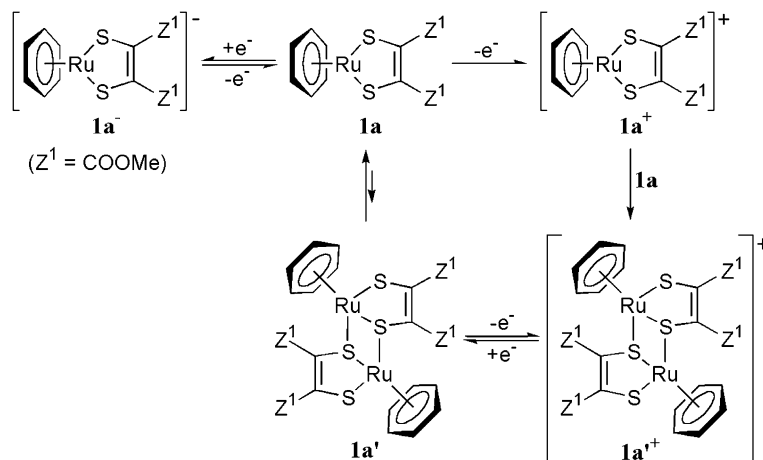
Scheme 7.

Fig. 4. Visible spectral changes of complex **1a** during (a) reduction (−2.0 V, sampling time 2 min, sampling interval 4 s); (b) re-oxidation (−0.5 V, sampling time 2 min, sampling interval 4 s) after reduction.

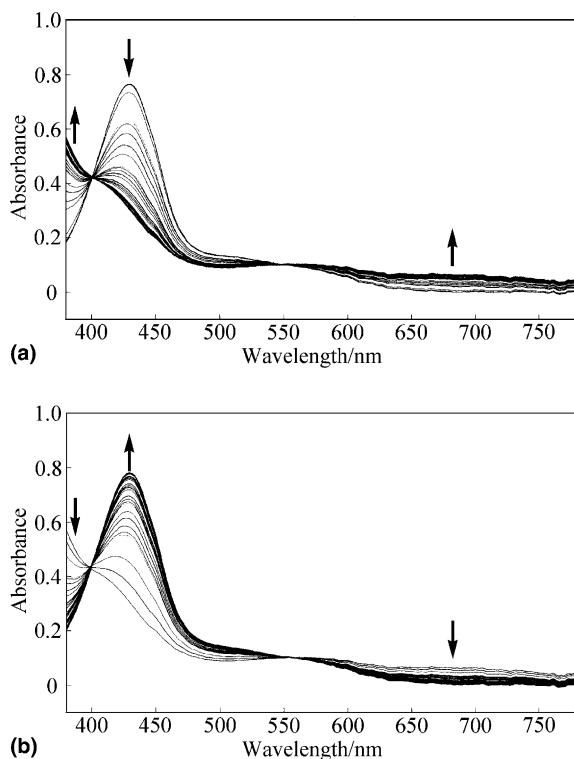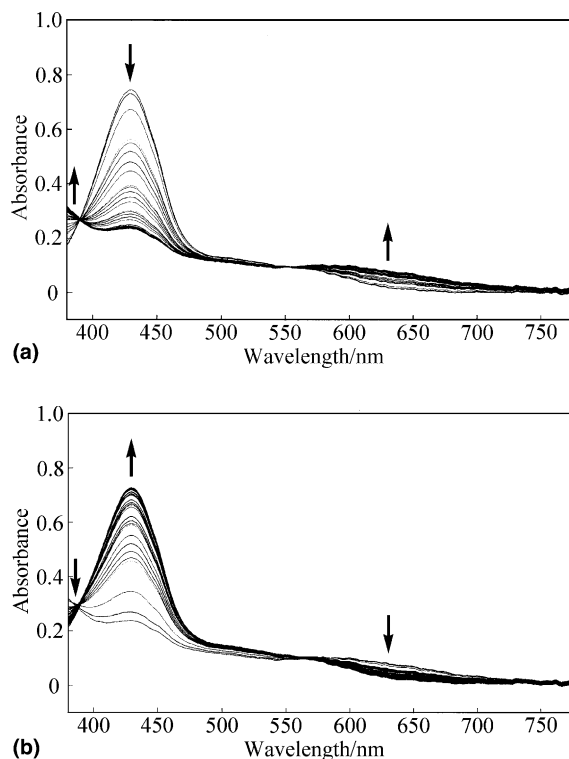Fig. 5. Visible spectral changes of complex **1a** during (a) oxidation (+0.8 V, sampling time 2 min, sampling interval 4 s); (b) re-reduction (−0.5 V, sampling time 2 min, sampling interval 4 s) after oxidation.

oxidation have been reported [15,16], our example is the first case of the electro-oxidative dimerization of a ruthenium dithiolene complex. In oxidation process, complexes **1b** and **1c** showed several re-reduction waves after oxidation. Therefore, the oxidants **1b$^+$** and **1c$^+$** were converted to some unknown products.

Visible absorption spectra during the electrolysis of complex **1a** were measured using optically transparent thin-layer electrode (OTTLE) cell. When complex **1a** was reduced at −2.0 V for 2 min, the π–π* absorption at 430 nm was decreased (Fig. 4(a)). The final spectrum corresponds to that of anion **1a$^-$**. When the potential was jumped to −0.5 V to re-oxidize anion **1a$^-$**, the spectrum was recovered to that of the neutral complex **1a** after 2 min (Fig. 4(b)). Therefore, the reductant of complex **1a** is also stable for several minutes order. We could not confirm the spectral changes of dimer **1a′**, because only a small amount of the dimer is contained in the solution.

When complex **1a** was oxidized at +0.8 V for 2 min, the π–π* absorption at 430 nm was decreased (Fig. 5(a)). Next, when the potential was jumped at −0.5 V to re-reduce an oxidant, the spectrum was completely recovered to that of the neutral complex **1a** after 2 min (Fig. 5(b)). These results prove two pieces of evidence. (1) The cationic dimer **1a′$^+$** formed by the oxidation of the neutral complex **1a** is stable for several minutes.

(2) When the cationic dimer **1a′$^+$** is re-reduced, the neutral dimer **1a′** is immediately and quantitatively converted to the corresponding monomer **1a**. Therefore, the oxidation behavior of complex **1a** can be described as an electrochemical square scheme [21] (Scheme 7).

2.4. Conclusion

The ruthenium dithiolene complexes having 16-electron (coordinatively unsaturated) metal center underwent the cycloaddition reactions between ruthenium and sulfur atoms. The [2 + 2] or [2 + 1] cycloaddition reaction was observed in the reactions with alkynes or diazo compounds, respectively. Furthermore, this complex underwent a dimerization reaction by an electrochemical oxidation. Therefore, the addition reactions of ruthenium dithiolene complexes to form the 18-electron (coordinatively saturated) species are classified into three categories: (1) the dimerization reactions [14] or the electro-oxidative dimerization reactions, (2) the addition reactions of Lewis bases to the metal center [14], and (3) the cycloaddition reactions of alkyne or alkylidene group to the metal–sulfur bond.

We have reported on the adduct formations of cobalt or rhodium dithiolene complexes due to their unsaturation [5–8]. To our knowledge, the unsaturation of the ruthenium dithiolene complex is stronger than those of

cobalt or rhodium dithiolene complexes. There are two pieces of evidence. (1) Although cobalt or rhodium dithiolene complexes are monomers in a solution [4,17,18], the monomeric ruthenium dithiolene complex coexists with the corresponding dimer species in solution. (2) The adducts of ruthenium dithiolene complexes are efficiently formed in a milder condition than that needed for the adduct formations of cobalt or rhodium complexes.

In other words, the aromaticity of ruthenium dithiolene complexes due to its 6π electron system is weaker than the aromaticity in cases of cobalt or rhodium. We propose that the balance between the aromaticity and the unsaturation in a metalladithiolene ring depends on the metal center.

3. Experimental

3.1. General remarks

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. Solvents were purified by ketyl distillation before use. The precursors of complexes **1a–c**, [(arene)Ru(Cl)(μ-Cl)]$_2$ (arene = C_6H_6, $C_6H_4(Me)(iPr)$ [22], C_6Me_6 [23]), were synthesized by literature methods. Dimethyl 1,3-dithiole-2-one-4,5-dicarboxylate was obtained from the reaction of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate (from Tokyo Kasei Kogyo Co., Ltd.) with $Hg(OAc)_2$ [24]. Silica gel (Wakogel C-300) was obtained from Wako Pure Chemical Industries, Ltd. Mass and IR spectra were recorded on a JEOL JMS-D300 and a Shimadzu model FTIR 8600PC, respectively. NMR spectra were measured with a JEOL LA500 spectrometer. UV–Vis spectra were recorded on a Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. Melting points were measured with a Yanaco Micro melting point apparatus.

3.2. Preparations of the ruthenium dithiolene complexes [(C_6H_6)Ru{$S_2C_2(COOMe)_2$}] (**1a**), [{$C_6H_4(Me)$-(iPr)}Ru{$S_2C_2(COOMe)_2$}] (**1b**) and (C_6Me_6)-Ru{$S_2C_2(COOMe)_2$}] (**1c**)

Dimethyl 1,3-dithiole-2-one-4,5-dicarboxylate (1.62 mmol), O=$CS_2C_2(COOMe)_2$, was treated with 2 equivalents of sodium methoxide in methanol solution (50 ml) at room temperature. The first colorless solution was changed to yellow after 1 h. When the ruthenium complex dimer [(C_6H_6)Ru(Cl)(μ-Cl)]$_2$ (0.62 mmol) was added into this solution, the yellow solution was changed to brown. The reaction mixture was stirred at room temperature for 24 h. After the solvent was removed under reduced pressure, the residue was extracted and the organic layer was purified by column chromatography (Wakogel C-300, eluent = dichloromethane). Complex **1a** was obtained as a brown solid in 80% yield. Complexes **1b** (74% yield) and **1c** (75% yield) were obtained from the corresponding ruthenium dimers [{$C_6H_4(Me)$-(iPr)}Ru(Cl)(μ-Cl)]$_2$ and [(C_6Me_6)Ru(Cl)(μ-Cl)]$_2$, respectively. Complex **1a**; mp > 300 °C (dec.). Mass (EI$^+$, 70 eV) m/z (rel. intensity) 386 (M$^+$, 54.6), 244 ((C_6H_6)RuS$_2^+$, 81.5), 212 ((C_6H_6)RuS$^+$, 9.2), 78 ($C_6H_6^+$, 100). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) monomer (**1a**): δ 5.87 (s, 6H, C_6H_6), 3.89 (s, 6H, OMe); dimer (**1a′**): δ 5.41 (s, 6H, C_6H_6), 3.93 (s, 3H, OMe), 3.77 (s, 3H, OMe). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ monomer (**1a**): 165.9 (C=O), 158.6 (dithiolene carbon), 81.0 (arene carbon), 52.9 (OMe); the signals of dimer (**1a′**) were very weak. IR (KBr disk) 3065, 2949, 1736, 1713, 1619, 1246 cm^{-1}. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon)$ 432 (6100), 303 (11000), 276 (11000). Anal. Calcd for $C_{12}H_{12}O_4S_2Ru_1$: C, 37.39; H, 3.14. Found: C, 37.17; H, 3.08%. Complex **1b**; mp 101.8–102.4 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 442 (M$^+$, 72.4), 411 (M$^+$–OMe, 6.0), 300 ({$C_6H_4(Me)(iPr)$}RuS$_2^+$, 61.8), 134 ({$C_6H_4(Me)(iPr)$}$^+$, 28.7), 119 ($C_9H_{11}^+$, 100). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 5.76 (m, 4H, C_6H_4), 3.84 (s, 6H, OMe), 2.60 (sept, J = 7.15 Hz, 1H, CHMe$_2$), 2.20 (s, 3H, C_6H_4Me), 1.30 (d, J = 7.15 Hz, 6H, CHMe_2). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 166.3 (C=O), 157.1 (dithiolene carbon), 106.5, 95.4, 81.4, 79.3 (arene carbon), 52.8 (OMe), 31.9 (CHMe$_2$), 23.5 (CHMe_2), 20.6 (C_6H_4Me). IR (KBr disk) 3578, 3508, 3076, 2953, 2873, 2841, 1720, 1651, 1636, 1501, 1435, 1244, 1084, 1022 cm^{-1}. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon)$ 432 (7100), 309 (14000), 274 (12000). Anal. Calcd for $C_{16}H_{20}O_4S_2Ru_1(H_2O)$: C, 41.82; H, 4.83. Found: C, 41.39; H, 4.71%. Complex **1c**; mp 248–249 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 470 (M$^+$, 100), 438 (M$^+$–OMe–1, 11.0), 328 ((C_6Me_6)RuS$_2^+$, 97.9), 162 ((C_6Me_6)$^+$, 13.0), 147 ((C_6Me_5)$^+$, 21.7). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 3.85 (s, 6H, OMe), 2.34 (s, 18H, C_6Me_6). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 166.8 (C=O), 154.2 (dithiolene carbon), 93.0 (arene carbon), 52.7 (OMe), 17.6 (Me). UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon)$ 428 (5500), 322 (12000), 276 (8800). Anal. Calcd for $C_{18}H_{24}O_4S_2Ru_1$: C, 46.04; H, 5.15. Found: C, 45.90; H, 5.11%.

3.3. Reactions of complex **1a** with acetylenes

A solution of complex **1a** (70 mg, 0.18 mmol) and DMAD (66 μl, 0.54 mmol) in benzene (10 ml) was stirred at room temperature for 3 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300, eluent = dichloromethane). The orange residue was purified by a re-crystallization (n-hexane/dichloromethane). Adduct **2a** was obtained as an orange solid in

90% (84 mg, 0.16 mmol) yield. Adduct **3a** was also obtained as an orange solid in 77% yield by the reaction of complex **1a** with DEAD. Complex **2a**; mp 162–163 °C (dec.). Mass (FAB$^+$, 70 eV, NBA) m/z 528 (M$^+$). Mass (EI$^+$, 70 eV) m/z (rel. intensity) 316 (SC$_4$(COOMe)$_4^+$, 14), 285 (SC$_4$(COOMe)$_4^+$–OMe, 100). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 5.72 (s, 6H, C$_6$H$_6$), 3.84 (s, 6H, OMe), 3.76 (s, 3H, OMe), 3.63 (s, 3H, OMe). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 179.01, 175.16, 172.19, 167.38 (C=O), 162.83, 157.97 (dithiolene carbon), 125.32, 106.63 (bridged-alkene carbon), 88.56 (arene carbon), 53.10, 52.23, 52.13, 52.11 (OMe). IR (KBr disk) 3076, 2947, 2839, 1726, 1707, 1692, 1246 cm^{-1}. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon)$ 360 (7200). Anal. Calcd for C$_{18}$H$_{18}$O$_8$S$_2$Ru$_1$: C, 40.98; H, 3.44. Found: C, 40.66; H, 3.43%. Complex **3a**; Mass (FAB$^+$, 70 eV, NBA) m/z 556 (M$^+$). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 5.70 (s, 6H, C$_6$H$_6$), 4.32–4.37 (m, 2H, OCH$_2$Me), 4.03–4.13 (m, 2H, OCH$_2$Me), 3.84 (s, 3H, OMe), 3.75 (s, 3H, OMe), 1.37 (t, J = 6.8 Hz, 3H, OCH$_2$Me), 1.19 (t, J = 7.2 Hz, 3H, OCH$_2$Me). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 179.19, 175.18, 171.66, 167.44 (C=O), 162.90, 157.60 (dithiolene carbon), 125.35, 108.65 (bridged-alkene carbon), 88.50 (arene carbon), 61.08, 61.03, 53.09, 52.19 (OMe or OCH$_2$Me), 14.54, 14.07 (OCH$_2$Me). Anal. Calcd for C$_{20}$H$_{22}$O$_8$S$_2$Ru$_1$: C, 43.24; H, 3.99. Found: C, 43.13; H, 3.82%.

3.4. Reactions of ruthenium dithiolene complexes with diazo compounds

3.4.1. Reaction of complex 1a with diazomethane

Diazo methane was prepared by a literature method [5d]. Excess diazo methane gas was blown into the dichloromethane solution of complex **1a** (98 mg, 0.254 mmol) at 0 °C. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300, eluent = dichloromethane). The orange residue was purified by re-crystallization (*n*-hexane/dichloromethane). Adduct **4a** was obtained as an orange solid in 80% (81 mg, 0.203 mmol) yield. Complex **4a**; Mass (EI$^+$, 70 eV) m/z (rel. intensity) 400 (M$^+$, 15.9), 340 (M$^+$–COOMe, 11.7), 212 ((C$_6$H$_6$)RuS$^+$, 13.3), 78 (C$_6$H$_6^+$, 100). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 5.52 (s, 6H, C$_6$H$_6$), 3.82 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.17 (d, J = 3.95 Hz, 1H, CH$_2$), 1.64 (d, J = 3.95 Hz, 1H, CH$_2$). UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon)$ 423 (5300), 275 (8800). HR-Mass (EI$^+$, 70 eV) Calcd for C$_{13}$H$_{14}$O$_4$S$_2$Ru$_1$: 399.9377. Found: 399.9388%.

3.4.2. Reaction of complex 1a with trimethylsiliydiazomethane

The 2.0 mmol dm^{-3} *n*-hexane solution of trimethyl-siliydiazomethane (1.9 ml, 3.8 mmol) was added into a

benzene solution (20 ml) of complex **1a** (100 mg, 0.26 mmol). The reaction mixture was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300, eluent = dichloromethane). The orange residue was purified by re-crystallization (*n*-hexane/dichloromethane). Adduct **5a** was obtained as an orange solid in 78% (94 mg, 0.20 mmol) yield. Complex **5a**; mp 161.5–162.0 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 472 (M$^+$, 100), 340 (M$^+$–SiMe$_3$–COOMe, 61.0), 212 ((C$_6$H$_6$)RuS$^+$, 34.0), 78 (C$_6$H$_6^+$, 73.9). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 5.53 (s, 6H, C$_6$H$_6$), 3.82 (s, 3H, OMe), 3.72 (s, 3H, OMe), 1.36 (s, 1H, CH), 0.10 (s, 9H, SiMe$_3$). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 171.8, 168.7 (C=O), 162.9, 115.3 (dithiolene carbon), 83.9 (arene carbon), 53.0, 52.1 (OMe), 31.3 (CH), 0.4 (SiMe$_3$). IR (KBr disk) 2993, 2943, 1726, 1686, 1472, 1429, 1238, 1090, 1026 cm^{-1}. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon)$ 412 (6000), 281 (9100). Anal. Calcd for C$_{16}$H$_{22}$O$_4$Si$_1$S$_2$Ru$_1$: C, 40.75; H, 4.70. Found: C, 40.48; H, 4.52%.

3.4.3. Reactions of complexes 1a–c with ethyl diazoacetate

A solution of complex **1a** (0.23 mmol) and ethyl diazoacetate (2.0 mmol) in benzene (90 ml) was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (Wakogel C-300, eluent = dichloromethane). The orange residue was purified by a re-crystallization (*n*-hexane/dichloromethane). Adduct **6a** was obtained as an orange solid in 94% yield. In the reactions of complexes **1b** and **1c** with ethyl diazoacetate, adducts **6b** and **6c** were also obtained as orange solids in 75% and 94% yields, respectively. Complex **6a**; mp 85–86 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 472 (M$^+$, 0.38), 386 (M$^+$–CHCOOEt, 77.0), 244 ((C$_6$H$_6$)RuS$_2^+$, 100), 78 (C$_6$H$_6^+$, 69.2). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 5.54 (s, 6H, C$_6$H$_6$), 4.11–4.22 (m, 2H, OCH$_2$Me), 3.83 (s, 3H, OMe), 3.73 (s, 3H, OMe), 2.34 (s, 1H, CH), 1.30 (t, J = 7.37 Hz, 3H, OCH$_2$Me). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 178.2, 174.2, 168.2 (C=O), 162.7, 128.3 (dithiolene carbon), 85.4 (arene carbon), 60.7, 53.1, 52.2 (OMe or OCH$_2$Me), 38.7 (CH), 14.7 (OCH$_2$Me). IR (KBr disk) 2951, 1732, 1690, 1481, 1433, 1248, 1142, 1086, 1024 cm^{-1}. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon)$ 400 (6100), 303 (7000). Anal. Calcd for C$_{16}$H$_{18}$O$_6$S$_2$Ru$_1$: C, 40.76; H, 3.85. Found: C, 41.08; H, 4.03%. Complex **6b**; Mass (EI$^+$, 70 eV) m/z (rel. intensity) 528 (M$^+$, 15.3), 454 (M$^+$–HCOOEt, 26.0), 300 ({C$_6$H$_4$(Me)(*i*Pr)}RuS$_2^+$, 22.7), 268 ({C$_6$H$_4$(Me)(*i*Pr)}RuS$^+$, 18.7), 134 ({C$_6$H$_4$(Me)(*i*Pr)}$^+$, 27.3), 119 (C$_9$H$_{11}^+$, 100). ^{1}H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 5.45 (d, J = 5.92 Hz, 1H, C$_6$H$_4$), 5.39 (d, J = 5.92 Hz, 1H, C$_6$H$_4$), 5.26 (d,

$J = 5.92$ Hz, 1H, C_6H_4), 4.95 (d, $J = 5.92$ Hz, 1H, C_6H_4), 4.12–4.19 (m, 2H, OCH_2Me), 3.82 (s, 3H, OMe), 3.73 (s, 3H, OMe), 2.70 (sept, $J = 6.95$ Hz, 1H, $CHMe_2$), 2.30 (s, 3H, C_6H_4Me), 2.27 (s, 1H, bridged-CH), 1.30 (t, $J = 6.99$ Hz, 3H, OCH_2Me), 1.30 (d, $J = 6.95$ Hz, 6H, $CHMe_2$). UV–Vis (CH_2Cl_2) $\lambda_{max}(\varepsilon)$ 405 (9800). Anal. Calcd for $C_{20}H_{26}O_6S_2Ru_1$: C, 45.53; H, 4.97. Found: C, 45.43; H, 5.09%. Complex **6c**; Mass $(EI^+, 70\ eV)$ m/z (rel. intensity) 556 (M^+, 42.7), 525 (M^+–OMe, 4.0), 482 (M^+–HCOOEt, 100), 328 $((C_6Me_6)RuS_2^+$, 25.7), 296 $((C_6Me_6)RuS^+$, 63.3), 162 $(C_6Me_6^+$, 38.7), 147 $(C_6Me_5^+$, 66.7). ^1H NMR (500 MHz, $CDCl_3$, vs. TMS) δ 4.05–4.21 (m, 2H, OCH_2Me), 3.82 (s, 3H, OMe), 3.70 (s, 3H, OMe), 2.35 (s, 1H, CH), 2.15 (s, 18H, C_6Me_6), 1.27 (t, $J = 7.92$ Hz, 3H, OCH_2Me). ^{13}C NMR (125 MHz, $CDCl_3$, vs. TMS) δ 177.5, 172.5, 169.3 (C=O), 163.5, 114.4 (dithiolene carbon), 96.1 (arene carbon), 60.1, 53.0, 52.0 (OMe or OCH_2Me), 39.9 (CH), 15.9 (OCH_2Me). UV–Vis (CH_2Cl_2) $\lambda_{max}(\varepsilon)$ 452 (5500). Anal. Calcd for $C_{22}H_{30}O_6S_2Ru_1$: C, 47.55; H, 5.44. Found: C, 47.40; H, 5.49%.

3.5. Thermal decompositions of adducts 2a and 3a

A xylene solution (10 ml) of adduct **2a** (26 mg, 0.05 mmol) or **3a** (4.7 mg, 0.008 mmol) was refluxed for 3 h. After the solvent was removed under reduced pressure, the residue was separated by thin-layer chromatography (Silica-gel, eluent; *n*-hexane/dichloromethane = 2:1). The thiophene derivatives were obtained in 25% yields. The thiophene derivative from adduct **2a**, $[SC_4(COOMe)_4]$: Mass $(EI^+, 70\ eV)$ m/z (rel. intensity) 316 (M^+, 7.0), 285 (M^+–OMe, 53.3). ^1H NMR (500 MHz, $CDCl_3$, vs. TMS) δ 3.92 (s, OMe). The thiophene derivative from adduct **3a**, $[SC_4(COOMe)_2(COOEt)_2]$: Mass $(EI^+, 70\ eV)$ m/z (rel. intensity) 344 (M^+, 21), 299 (M^+–OEt, 48), 239 (M^+–S(COOEt), 100).

3.6. X-ray diffraction study

Single crystals of complexes **1c** and **5a** were obtained by recrystallization from the dichloromethane solutions and then vapor diffusion of *n*-hexane into those solutions. The crystal data of complexes **1c** and **5a** are summarized in Table 2. The measurement was made on a Rigaku MERCURY diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All the calculations were carried out using the Crystal Structure crystallographic software package.

Table 2
Crystallographic data for complexes **1c** and **5a**

	1c	**5a**
Formula	$C_{18}H_{24}O_4Ru_1S_2$	$C_{16}H_{22}O_4Ru_1S_2Si_1$
Formula weight (g mol^{-1})	469.58	471.62
Crystal color	Brown	Brown
Crystal habit	Platelet	Block
Crystal size (mm)	$0.18 \times 0.10 \times 0.06$	$0.12 \times 0.12 \times 0.06$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}(\#2)$	$P\bar{1}(\#2)$
a (Å)	8.81930(10)	8.4398(5)
b (Å)	10.7369(4)	10.2943(5)
c (Å)	11.6571(2)	12.7899(8)
α (°)	83.442(6)	103.217(1)
β (°)	68.928(5)	102.264(1)
γ (°)	78.610(6)	106.356(1)
V (Å^3)	1008.60(4)	991.37(10)
Z	2	2
D_{calc} (g cm^{-3})	1.546	1.580
μ (Mo Kα) (cm^{-1})	10.03	10.78
T (K)	296	296
$2\theta_{max}$ (°)	55.0	54.9
Unique data (R_{int})	4392 (0.014)	4302 (0.014)
Number of observations	3628	3635
Number of variables	250	239
R_1, wR_2 ($I > 3.00\sigma(I)$)	0.027, 0.039	0.024, 0.033
Goodness-of-fit on F^2	0.941	0.804
Largest difference peak and hole (e A^{-3})	0.59, −0.44	0.45, −0.47

3.7. Electrochemical measurements

All electrochemical measurements were performed under argon atmosphere. Solvents for electrochemical measurements were dried by molecular sieve 4A before use. A platinum wire served as a counter electrode, and the reference electrode is Ag|AgCl corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium $(Fc|Fc^+)$ couple. Cyclic voltammetry were measured with model CV-50W of BAS Co. Visible absorption spectra during electrolysis were measured with models MCPD-7000 and MC-2530 of Otsuka Electronics Co. Ltd.

3.7.1. CV measurements

CV measurements were done in 1 mmol dm^{-3} dichloromethane solutions of complexes containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode.

3.7.2. Visible absorption spectral measurements during electrolysis

The visible and near-IR absorption spectra during electrolysis were obtained for 1 mmol dm^{-3} dichloromethane solutions of complexes containing 0.1 mol dm^{-3} TBAP at 25 °C in an optically transparent thin-layer electrode (OTTLE, thin-layer thickness = 0.4 mm) cell by using a Photal MCPD-7000 rapid scan spectrometer.

The working electrode was stationary platinum mesh in thin-layer form.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 256457 (**1c**) and 256458 (**5a**). Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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