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Preparation and Reactions of Diruthenium Thiolate Complexes [Cp*Ru(μ-SR)$_3$RuCp*] (Cp* = η^5-C$_5$Me$_5$; R = *i*-Pr, Et, Cy, Bz, Ph)

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By treatment with excess NaSR (R = *i*-Pr, Et, Cy, Bz, Ph; Bz = benzyl, Cy = cyclohexyl), [Cp*RuCl$_2$]$_2$ (Cp* = η^5-C$_5$Me$_5$) gave paramagnetic diruthenium complexes [Cp*Ru(μ-SR)$_3$RuCp*] in moderate yields. An X-ray analysis of [Cp*Ru(μ-S-*i*-Pr)$_3$RuCp*] disclosed the dinuclear structure with three bridging thiolate ligands. Crystal data: $C_{29}H_{51}S_3Ru_2$, monoclinic, space group $P2_1/a$; a = 17.850 (9), b = 10.974 (4), c = 17.320 (13) Å; β = 112.56 (4)°; Z = 4. The Ru–Ru bond distance observed is 2.968 (2) Å, indicating the presence of a relatively long Ru–Ru bond. These complexes (R = *i*-Pr, Cy) reacted with CO or *t*-BuNC to give paramagnetic diruthenium complexes [Cp*Ru(SR)(μ-SR)$_2$RuCp*(L)] (R = *i*-Pr, L = CO, *t*-BuNC; R = Cy, L = CO), whereas treatment with H$_2$ gas or PhC≡CH afforded diamagnetic diruthenium complexes [Cp*RuR′(μ-SR)$_2$RuCp*R′] (R = *i*-Pr, R′ = H, C≡CPh; R = Cy, R′ = H).

Introduction

Transition-metal complexes with sulfur ligands are of significant interest as synthetic analogues for the active sites of metalloproteins, and we have been currently studying the chemistry of ruthenium thiolate complexes, which is still a relatively unexplored area compared with that of iron thiolate complexes. In previous papers, we reported the preparation and some reactivities of a series of the diamagnetic diruthenium complexes [Cp*Ru(μ-SAr)$_3$RuCp*]Cl (I; Ar = aryl) and [Cp*RuCl(μ-SR)$_2$RuCp*Cl] (II; R = alkyl), which have the Ru–Ru single bond surrounded by three and two bridging thiolate ligands, respectively (Scheme I).[1-3]

Here we wish to report the synthesis of the paramagnetic diruthenium complexes [Cp*Ru(μ-SR)$_3$RuCp*] (III; R = *i*-Pr, Et, Cy, Bz, Ph; Bz = benzyl, Cy = cyclohexyl) and the X-ray structure of [Cp*Ru(μ-S-*i*-Pr)$_3$RuCp*] (IIIA) together with some reactions of these complexes.

Experimental Section

General Data. All experiments were carried out under a nitrogen atmosphere. Solvents were dried and distilled under nitrogen. Thiols and *t*-BuNC were commercially obtained and used without further purification. Compounds [Cp*RuCl$_2$]$_2$ (IV)[4] and [Cp*RuCl(μ-SEt)$_2$RuCp*Cl] (IIA)[3] were prepared according to the published methods. IR spectra were measured with a Shimadzu IR-408 spectrometer by the KBr method. ^{1}H NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer. EPR spectra were obtained at X-band frequencies by using a JEOL JEX-FEIX spectrometer. Electrochemical measurements were made with HOKUTO DENKO instrumentation (HA-501 potentiostat and HB-105 function generator) using a glassy-carbon working electrode; potentials were measured vs a saturated calomel electrode as reference in CH$_2$Cl$_2$ and DMF or a pseudoreference electrode of a silver wire immersed in THF. Elemental analyses were performed at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of [Cp*Ru(μ-S-*i*-Pr)$_3$RuCp*] (IIIA). To a slurry of complex IV (738 mg, 1.20 mmol) in MeOH (5 mL) was added 13.5 mmol of NaS-*i*-Pr (from 310 mg of sodium and 1.26 mL of *i*-PrSH) in MeOH (5 mL) by a cannula. Immediate color change from brown to green was observed. The resultant suspension was stirred overnight at room temperature and then the liquid phase was filtered off. The remaining solid was dried and extracted with benzene. To a concentrated extract was added acetonitrile (volume ratio = 1:1), and the mixture was cooled overnight at −10 °C. The dark green crystals that deposited were filtered off and dried in vacuo (465 mg, 56%). Anal. Calcd for $C_{29}H_{51}S_3Ru_2$: C, 49.89; H, 7.36; S, 13.77. Found: C, 49.63; H, 7.25; S, 13.38. EPR: g = 1.97.

Scheme I

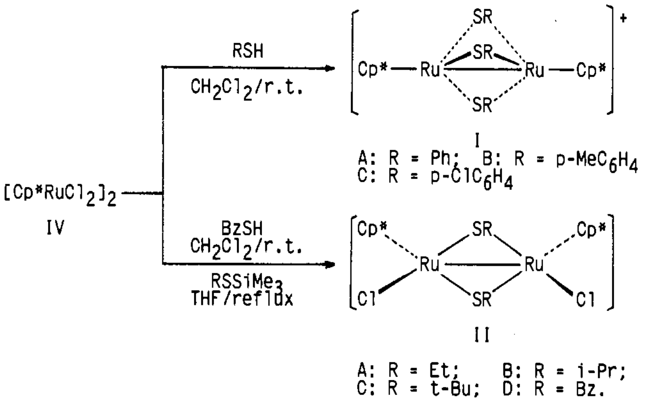

Table I. Crystallographic Data for [Cp*Ru(μ-S-*i*-Pr)$_3$RuCp*] (IIIA)

chem formula $C_{29}H_{51}S_3Ru_2$	space group $P2_1/a$ (No. 14)
fw 698.1	T = 30 °C
a = 17.850 (9) Å	λ = 0.7107 Å
b = 10.974 (4) Å	ρ_{calcd} = 1.48 g cm^{-3}
c = 17.320 (13) Å	μ = 11.54 cm^{-1}
β = 112.56 (4)°	transm coeff = 0.637–0.780
V = 3133 Å^3	R = 0.068
Z = 4	R_w = 0.075

Preparation of [Cp*Ru(μ-SEt)$_3$RuCp*] (IIIB) from Complex IV. The reaction was carried out analogously to the procedure described above by using sodium (128 mg, 5.56 mmol), EtSH (0.42 mL, 5.6 mmol), and complex IV (232 mg, 0.378 mmol). In this case, the resultant solid was extracted with THF and addition of acetonitrile afforded dark green crystals (137 mg, 55%). Anal. Calcd for $C_{26}H_{45}S_3Ru_2$: C, 47.61; H, 6.91; S, 14.66. Found: C, 47.34; H, 7.09; S, 13.62. EPR: g = 1.97.

Preparation of Complex IIIB from [Cp*RuCl(μ-SEt)$_2$RuCp*Cl] (IIA). To a solution of NaSEt prepared from sodium (115 mg, 5.00 mmol) and EtSH (0.40 mL, 5.4 mmol) in MeOH (5 mL) were added THF (20 mL) and complex IIA (104 mg, 0.156 mmol). The mixture was stirred overnight at room temperature, and acetonitrile was added to the concentrated product solution, which gave dark green crystals of complex IIIB (41 mg, 40%).

Preparation of [Cp*Ru(μ-SCy)$_3$RuCp*] (IIIC). This complex was prepared according to the procedure for complex IIIA by using sodium (121 mg, 5.26 mmol), CySH (0.75 mL, 5.3 mmol), and complex IV (221 mg, 0.359 mmol). The product was obtained as green microcrystals (185 mg, 62%). Anal. Calcd for $C_{38}H_{63}S_3Ru_2$: C, 55.24; H, 7.71. Found: C, 55.78; H, 7.76.

Preparation of [Cp*Ru(μ-SBz)$_3$RuCp*] (IIID). This complex was obtained as light green crystals by the method used for complex IIIB from sodium (150 mg, 6.52 mmol), BzSH (1.0 mL, 6.5 mmol), and complex IV (202 mg, 0.329 mmol). Yield: 157 mg (56%). Anal. Calcd for $C_{41}H_{51}S_3Ru_2$: C, 58.47; H, 6.10; S, 11.42. Found: C, 58.64; H, 5.90; S, 12.21. EPR: g = 1.97.

Preparation of [Cp*Ru(μ-SPh)$_3$RuCp*] (IIIE). This complex was obtained as a brown solid by the method used for complex IIIA from

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(2) Tanase, T.; Imagawa, K.; Dev, S.; Mizobe, Y.; Yano, S.; Hidai, M. *New J. Chem.* **1988**, *12*, 697.

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(4) Oshima, N.; Suzuki, H.; Moro-oka, T. *Chem. Lett.* **1984**, 1161.

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Table II. Atomic Parameters for Non-Hydrogen Atoms in [Cp*Ru(μ-S-i-Pr)$_3$RuCp*] (IIIA)[a]

atom	x	y	z
Ru(1)	2191 (1)	483 (1)	7615 (1)
Ru(2)	1768 (1)	−2140 (1)	7339 (1)
S(1)	3103 (2)	−1224 (3)	7895 (2)
S(2)	1648 (2)	−814 (2)	8378 (2)
S(3)	1332 (2)	−515 (3)	6376 (2)
C(1)	3560 (7)	−1730 (11)	9020 (7)
C(2)	4315 (9)	−2445 (15)	9146 (10)
C(3)	3747 (10)	−724 (14)	9660 (9)
C(4)	599 (8)	−563 (11)	8251 (9)
C(5)	570 (9)	151 (14)	8987 (10)
C(6)	39 (7)	−101 (13)	7416 (9)
C(7)	1793 (7)	−396 (13)	5598 (7)
C(8)	2519 (8)	−1132 (15)	5739 (8)
C(9)	1168 (10)	−496 (17)	4730 (9)
C(11)	2510 (9)	2127 (10)	8402 (9)
C(12)	1758 (8)	2369 (9)	7687 (9)
C(13)	1974 (7)	2281 (9)	6967 (8)
C(14)	2792 (10)	1968 (10)	7197 (8)
C(15)	3113 (8)	1928 (10)	8102 (9)
C(21)	2568 (13)	2267 (14)	9285 (10)
C(22)	995 (11)	2861 (13)	7685 (13)
C(23)	1380 (9)	2596 (11)	6096 (9)
C(24)	3277 (10)	1957 (14)	6669 (11)
C(25)	4031 (9)	1802 (15)	8624 (12)
C(31)	1984 (9)	−4033 (10)	7764 (9)
C(32)	1250 (10)	−3730 (11)	7725 (9)
C(33)	766 (7)	−3448 (10)	6903 (10)
C(34)	1219 (9)	−3603 (11)	6413 (8)
C(35)	2007 (8)	−3941 (11)	6923 (10)
C(41)	2685 (15)	−4569 (15)	8491 (15)
C(42)	1004 (19)	−3843 (16)	8443 (15)
C(43)	−128 (10)	−3247 (17)	6591 (18)
C(44)	904 (15)	−3563 (18)	5470 (10)
C(45)	2652 (12)	−4309 (17)	6629 (17)

[a] Multiplied by 10^4.

sodium (100 mg, 4.34 mmol), PhSH (0.60 mL, 4.4 mmol), and complex IV (194 mg, 0.316 mmol). Yield: 136 mg (53%). Anal. Calcd for $C_{38}H_{45}S_3Ru_2$: C, 57.05; H, 5.67; S, 12.02. Found: C, 57.36; H, 5.68; S, 12.59. EPR: g = 1.97.

X-ray Diffraction Study of [Cp*Ru(μ-S-i-Pr)$_3$RuCp*] (IIIA). A dark green crystal suitable for diffraction was sealed in a glass capillary under Ar and mounted on a Rigaku AFC-6 four-circle diffractometer equipped with a graphite monochromator. The orientation matrices and unit cell parameters were derived from a least-squares fit of 24 machine-centered reflections with 2θ values between 20 and 25°. The data collection was performed at room temperature, and no significant decay was observed for three check reflections measured every 100 reflections. Intensity data were corrected for the Lorentz–polarization effect, and absorption corrections were performed. Selected crystallographic data are shown in Table I.

Structure solution and refinement were performed by using the UNIX-III program at the computer center of The University of Tokyo.[5] Two Ru atoms in the asymmetric unit were found by the direct-methods program MULTAN. Subsequent block-diagonal least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms, which were refined by using anisotropic temperature factors taken from ref 6. Many of the hydrogen atom positions were visible in a final difference Fourier map, remaining hydrogen atoms being placed at the calculated positions. These hydrogen atoms were included in the final stage of refinement with isotropic thermal parameters, which converged with an R value $(\sum||F_o| - |F_c||/\sum|F_o|)$ of 0.068 and an R_w value $((\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2})$ of 0.075. Final atomic parameters of all non-hydrogen atoms are given in Table II. The final difference Fourier map contained several residual peaks around two Ru atoms, the maximal one of which is 3.0 e/Å^3 near the Ru(2) atom.

Reactions of Complexes IIIA and IIIC with CO. Through a solution of complex IIIA (66 mg, 0.095 mmol) in C_6H_6 (12 mL) was bubbled CO gas for 2 h. The initial green color smoothly changed to violet-red during this period. The solution was continuously stirred at room temperature under a CO atmosphere overnight. The product solution was reduced to ca. 1 mL, and acetonitrile was added to it (volume ratio = 1:1). The violet-red crystalline solid of [Cp*Ru(S-i-Pr)(μ-S-i-Pr)$_2$RuCp*(CO)] (VA) was filtered off and dried in vacuo (50 mg, 72%). Anal. Calcd for $C_{30}H_{51}OS_3Ru_2$: C, 49.62; H, 7.08; S, 13.24. Found: C, 49.43; H, 6.78; S, 11.72. EPR: g = 2.05. IR: $\nu_{C\equiv O}$ 1915 (s) cm^{-1}.

Table III. Selected Bond Distances and Angles in [Cp*Ru(μ-S-i-Pr)$_3$RuCp*] (IIIA)

Bond Distances (Å)			
Ru(1)–S(1)	2.406 (3)	Ru(2)–S(1)	2.420 (3)
Ru(1)–S(2)	2.386 (3)	Ru(2)–S(2)	2.387 (3)
Ru(1)–S(3)	2.372 (3)	Ru(2)–S(3)	2.360 (3)
Ru(1)–C(11)	2.20 (1)	Ru(2)–C(31)	2.19 (1)
Ru(1)–C(12)	2.23 (1)	Ru(2)–C(32)	2.20 (2)
Ru(1)–C(13)	2.23 (1)	Ru(2)–C(33)	2.19 (1)
Ru(1)–C(14)	2.22 (1)	Ru(2)–C(34)	2.21 (1)
Ru(1)–C(15)	2.21 (1)	Ru(2)–C(35)	2.20 (1)
Ru(1)--Ru(2)	2.968 (2)		
Bond Angles (deg)			
Ru(1)–S(1)–Ru(2)	75.9 (1)	S(2)–Ru(1)–S(3)	88.1 (1)
Ru(1)–S(2)–Ru(2)	76.9 (1)	S(1)–Ru(2)–S(2)	78.8 (1)
Ru(1)–S(3)–Ru(2)	77.7 (1)	S(1)–Ru(2)–S(3)	88.6 (1)
S(1)–Ru(1)–S(2)	79.1 (1)	S(2)–Ru(2)–S(3)	88.3 (1)
S(1)–Ru(1)–S(3)	88.6 (1)		

From complex IIIC (44 mg, 0.054 mmol) was prepared [Cp*Ru(SCy)(μ-SCy)$_2$RuCp*(CO)] (VB) analogously as a violet-red crystalline solid (28 mg, 61%). Anal. Calcd for $C_{39}H_{63}OS_3Ru_2$: C, 55.35; H, 7.50. Found: C, 55.36; H, 7.24. EPR: g = 2.04. IR: $\nu_{C\equiv O}$ 1910 (s) cm^{-1}.

Reaction of Complex IIIA with *t*-BuNC. To a stirred solution of complex IIIA (60 mg, 0.086 mmol) in THF (8 mL) was added t-BuNC (0.05 g, 0.6 mmol), and the mixture was stirred overnight at room temperature. The resultant red-violet solution was concentrated to ca. 1 mL, and a small amount of acetonitrile (ca. 1 mL) was added to it. The red-violet crystalline solid of [Cp*Ru(S-i-Pr)(μ-S-i-Pr)$_2$RuCp*(t-BuNC)] (VC) was filtered off and dried in vacuo (33 mg, 48%). Anal. Calcd for $C_{34}H_{60}NS_3Ru_2$: C, 52.27; H, 7.74; N, 1.79; S, 12.31. Found: C, 52.69; H, 7.62; N, 1.98; S, 12.72. EPR: g = 2.01. IR: $\nu_{N\equiv C}$ 2038 (s) cm^{-1}.

Reaction of Complex IIIC with *t*-BuNC. A treatment analogous to that described above was used. Complex IIIC (104 mg, 0.126 mmol) was treated with t-BuNC (29 mg, 0.35 mmol) in THF (5 mL) followed by the crystallization from THF/MeOH afforded violet-red diamagnetic crystals of [Cp*Ru(t-BuNC)(μ-SCy)$_2$RuCp*(t-BuNC)] (54 mg, 48%). Anal. Calcd for $C_{42}H_{70}N_2S_2Ru_2$: C, 58.03; H, 8.12; N, 3.22. Found: C, 57.83; H, 8.17; N, 2.37. ^{1}H NMR (C_6D_6; Cy protons omitted): δ 1.30 (s, 30 H, Cp*), 1.70 (s, 18 H, t-Bu). IR: $\nu_{N\equiv C}$ 2000 (s) cm^{-1}.

Reactions of Complexes IIIA and IIIC with H_2. The light green crystalline solid of [Cp*RuH(μ-S-i-Pr)$_2$RuHCp*] (VIA) was isolated by treatment of complex IIIA (62 mg, 0.088 mmol) in C_6H_6 (12 mL) with H_2 gas for 1 day at room temperature, followed by the addition of acetonitrile to the concentrated light green product solution (40 mg, 71%). Anal. Calcd for $C_{26}H_{46}S_2Ru_2$: C, 49.97; H, 7.42. Found: C, 49.25; H, 7.44. ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 30 H, Cp*), 1.14 (d, 12 H, CH*Me*; J = 7.0 Hz), 3.05 (sep, 2 H, C*H*Me; J = 7.0 Hz), −16.06 (s, 2 H, RuH). IR: ν_{Ru-H} 1948 (m) cm^{-1}.

[Cp*RuH(μ-SCy)$_2$RuCp*H] (VIB) could also be prepared from complex IIIC (25 mg, 0.31 mmol) according to the same procedure (15 mg, 70%). Anal. Calcd for $C_{32}H_{54}S_2Ru_2$: C, 54.51; H, 7.72; S, 9.09. Found: C, 55.02; H, 7.55; S, 8.16. ^{1}H NMR ($CDCl_3$, Cy protons omitted): δ 1.84 (s, 30 H, Cp*), −16.01 (s, 2 H, RuH). IR: ν_{Ru-H} 1950 (m) cm^{-1}.

Reaction of Complex IIIA with PhC≡CH. To a solution of complex IIIA (58 mg, 0.083 mmol) in THF (8 mL) was added PhC≡CH (185 mg, 1.82 mmol). Within several minutes, the initial green color changed to deep brown. The mixture was continuously stirred overnight. The product solution was reduced to ca. 1 mL and hexane (1 mL) added. The brown solid of [Cp*Ru(C≡CPh)(μ-S-i-Pr)$_2$Ru(C≡CPh)Cp*] (VIC) obtained was filtered off and dried in vacuo (15 mg, 21%). Anal. Calcd for $C_{42}H_{54}S_2Ru_2$: C, 61.14; H, 6.60; S, 7.77. Found: C, 61.15; H, 6.58; S, 7.77. ^{1}H NMR (C_6D_6): δ 1.50 (s, 30 H, Cp*), 1.48 (d, 12 H, CH*Me*; J = 6.4 Hz), 4.83 (sep, 2 H, C*H*Me; J = 6.4 Hz), 7.27–6.74 (d and 2 t, 10 H, Ph). IR: $\nu_{C\equiv C}$ 2100 (m) cm^{-1}.

Results

Treatment of complex IV with excess NaSR gave a series of paramagnetic diruthenium complexes III, as summarized in Scheme II. The result of an electrochemical study for complex IIIE is shown in Figure 1. A structure study was undertaken for complex IIIA, whose results are presented in Tables I–III and

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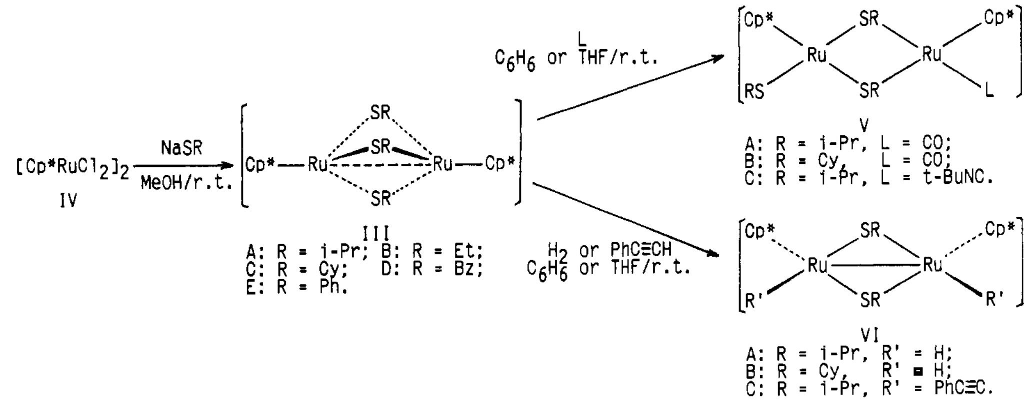
[5] Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* **1979**, *55*, 69.

[6] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1976; Vol. 3.

Scheme II



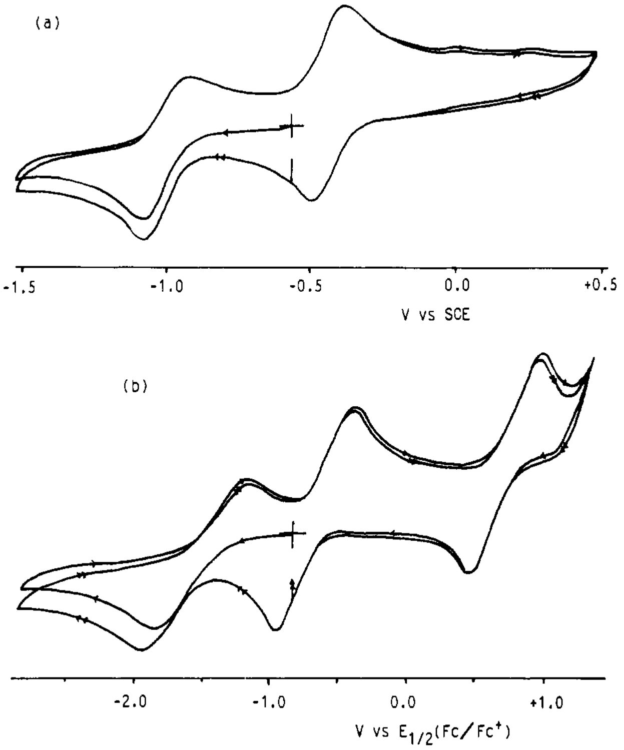


Figure 1. Cyclic voltammograms for complex IIIE in DMF–0.1 M [n-Bu$_4$N][BF$_4$] (a) and in THF–0.1 M [n-Bu$_4$N][BF$_4$] (b). Scan rate: 0.2 V s^{-1}.

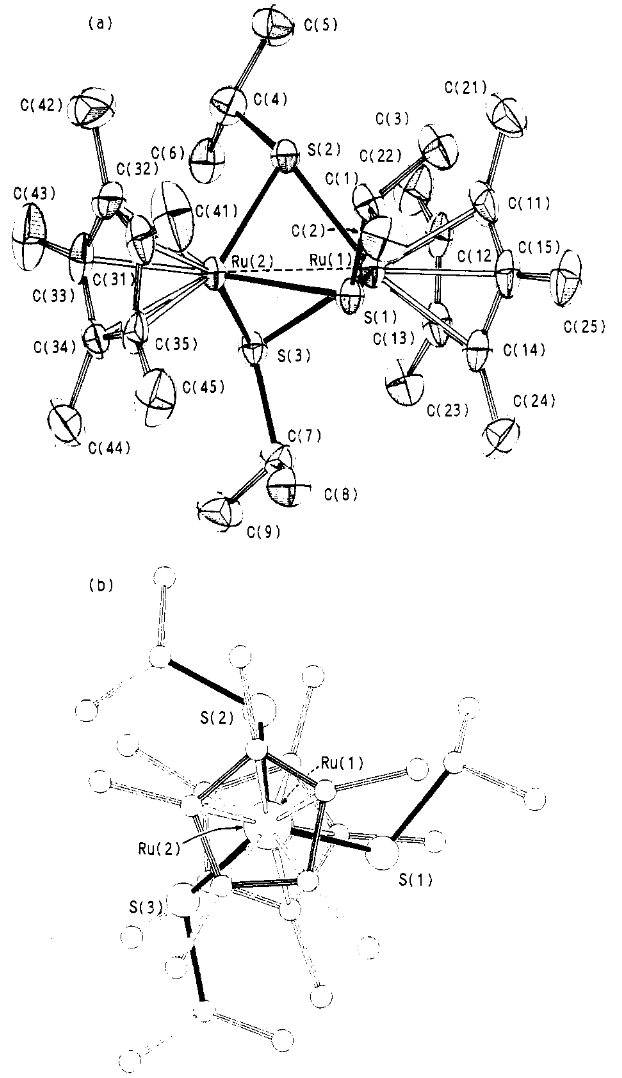


Figure 2. ORTEP view and atom-numbering scheme for [Cp*Ru(μ-S-i-Pr)$_3$RuCp*] (IIIA) (a) and the side view of complex IIIA from the direction of the Ru–Ru bond (b).

Figure 2. Complexes IIIA and IIIC reacted with CO or t-BuNC to give paramagnetic diruthenium complexes VA–C, whereas treatment with H$_2$ gas or PhC≡CH afforded diamagnetic diruthenium complexes VIA–C, which are also shown in Scheme II. The structure of complex VIA determined by the X-ray analysis is depicted in Figure 3. These will be introduced at appropriate places in the sections that follow.

Discussion

Preparation of Paramagnetic Diruthenium Complexes [Cp*Ru(μ-SR)$_3$RuCp*] (III). As reported already,[3] treatment of [Cp*RuCl$_2$]$_2$ (IV) with excess RSH (R = p-XC$_6$H$_4$; X = H, Me, Cl) in CH$_2$Cl$_2$ afforded the diamagnetic diruthenium complexes I, whereas complex IV reacted with excess BzSH in CH$_2$Cl$_2$ or Me$_3$SiSR (R = Et, i-Pr, t-Bu) in THF to give other types of diamagnetic diruthenium complexes II (Scheme I). The diamagnetic character of these complexes arises from a spin–spin pairing between two ruthenium atoms. Now we have found that complex IIA further reacts with excess NaSEt in THF/MeOH to give a paramagnetic diruthenium complex [Cp*Ru(μ-SEt)$_3$RuCp*] (IIIB). Novel diruthenium complexes of this type could be prepared more generally by treatment of complex IV with excess NaSR (R = i-Pr, Et, Cy, Bz, Ph) in MeOH (Scheme II). All of complexes III were isolated as substantially air-sensitive crystals or crystalline solids in moderate yields and show broad singlets in their EPR spectra.

Net stoichiometry for the formation of complexes III can be described by eq 1, in which a part of NaSR is consumed for the

$$[\mathrm{Cp^*RuCl_2}]_2 + 4\mathrm{NaSR} \rightarrow [\mathrm{Cp^*Ru}(\mu\text{-SR})_3\mathrm{RuCp^*}] + 4\mathrm{NaCl} + \tfrac{1}{2}\mathrm{RSSR} \quad (1)$$

reduction of a Ru(III)–Ru(III) pair in complex IV to a formal Ru(III)–Ru(II) pair in complexes III. This stoichiometry was confirmed by the GC analysis of the reaction mixture from the preparation of complex IIIC, which demonstrated the formation of CySSCy in more than 90% yield of that expected from eq 1.

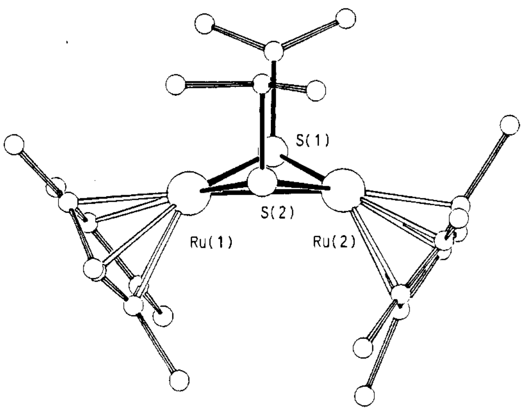


Figure 3. ORTEP drawing of [Cp*RuH(μ-S-*i*-Pr)$_2$RuCp*H] (VIA). Selected bond distances (Å) and angles (deg) are as follows: Ru(1)–Ru(2), 2.784 (5); Ru(1)–S(1), 2.28 (1); Ru(1)–S(2), 2.33 (1); Ru(2)–S(1), 2.22 (1); Ru(2)–S(2), 2.29 (1); Ru(1)–S(1)–Ru(2), 76.4 (3); Ru(1)–S(2)–Ru(2), 74.1 (4).

The cyclic voltammogram of complex IIIE was measured in DMF–0.1 M [*n*-Bu$_4$N][BF$_4$], which showed two simple successive redox processes, as shown in Figure 1a. As reported previously,[3] complex IA (R = Ph), which corresponds to the one-electron-oxidized species generated from complex IIIE, also shows two successive reduction waves at the analogous potentials under the same cyclic voltammetric conditions. Thus the redox process observed at $E_{1/2}$ = −0.45 V vs SCE is assignable to the Ru(II)–Ru(III)/Ru(III)–Ru(III) couple (complex IIIE ⇌ complex IA), whereas the other at $E_{1/2}$ = −1.05 V results from the Ru(II)–Ru(II)/Ru(II)–Ru(III) couple. An analogous electron-transfer series including the bimetallic species with the Mn(I)–Mn(I), Mn(I)–Mn(II), and Mn(II)–Mn(II) metal centers has also been observed for the oxidations of [(CO)$_3$Mn(μ-SR)$_3$Mn(CO)$_3$]$^-$.[7] On the other hand, when its spectrum was recorded in THF–0.1 M [*n*-Bu$_4$N][BF$_4$], complex IIIE showed the presence of another redox process at the more positive potential of +0.71 V vs the Fc/Fc$^+$ couple (Fc = ferrocene), as depicted in Figure 1b. This may be assignable to the Ru(III)–Ru(III)/Ru(IV)–Ru(III) couple, as observed clearly for complexes II in DMF around +0.50 V vs SCE.[3,8]

In contrast to the reactions of complex IV with NaSR (R = *i*-Pr, Et, Bz, Cy, Ph), treatment of complex IV with NaS-*t*-Bu gives the paramagnetic ruthenium(II) thiolate complex with the formula [Cp*Ru(S-*t*-Bu)]$_n$. The characterization of this new Ru(II) complex and its analogues, which may be closely related to the diruthenium complexes [Cp*Ru(μ-OR)$_2$RuCp*] (R = Me, Et) recently reported,[9] is now in progress.

X-ray Structure of [Cp*Ru(μ-S-*i*-Pr)$_3$RuCp*] (IIIA). The structure of complex IIIA determined by an X-ray analysis is shown in Figure 2, and selected bond distances and angles are summarized in Table III. Two Cp* ligands coordinate to the Ru atoms almost perpendicularly to the Ru–Ru vectors (85.0 and 89.7°), and the dihedral angle between the Cp* rings is 5.9°. The conformation of two Cp* rings is almost staggered as is observed for complex IA.[3] As shown in the side view of the molecule, three thiolate ligands coordinate to two Ru atoms in the manner that the Ru–Ru vector becomes a pseudo-C_3 axis. Thus there are no significant differences in the coordination geometry between the two Ru atoms, and the spin delocalization may occur over the two Ru atoms in complexes III. The Ru–Ru bond lengths depicted in Table III (2.968 (2) Å) may correspond to the bond order of around 0.5, if compared to the Ru–Ru distances of other diruthenium complexes having three bridging thiolate ligands with a Ru–Ru single bond (complex IA, 2.630 (1) Å) and without a Ru–Ru bond ([(Ru(μ-S-2-CH$_2$-3,5,6-Me$_3$C$_6$H)(S-2,3,5,6-Me$_4$C$_6$H)(NO))$_2$(μ-S-2,3,5,6-Me$_4$C$_6$H)]$^-$, 3.347 (1) Å;[10] [(Me$_2$PhP)$_3$Ru(μ-SH)$_3$Ru(SH)(PMe$_2$Ph)$_2$], 3.371 (3) Å[11]). This bond order observed for complex IIIA may closely relate to the spin delocalization over the two Ru atoms. The presence of such an interaction of the unpaired electron with two equivalent metal centers has already been demonstrated for the Mn(I)–Mn(II) species [(OC)$_3$Mn(μ-SPh)$_3$Mn(CO)$_3$].[7,12]

Reactions of Complexes III with CO and *t*-BuNC. Complex IIIA readily reacted with CO or *t*-BuNC in benzene or THF at room temperature to afford paramagnetic diruthenium complexes [Cp*Ru(S-*i*-Pr)(μ-S-*i*-Pr)$_2$RuCp*(L)] (L = CO (VA), *t*-BuNC (VC)) in moderate yields. The reaction of complex IIIC with CO also resulted in the formation of the complex [Cp*Ru(SCy)(μ-SCy)$_2$RuCp*(CO)] (VB) (Scheme II). These complexes show intense singlets in their EPR spectra, and the molar conductivity observed for complex VA (1.12 cm^2 mol^{-1} Ω^{-1} in 0.58 mM solution in benzene) is consistent with the structure having no charge shown in Scheme II. The $\nu_{C\equiv O}$ or $\nu_{N\equiv C}$ bands at 1915, 1910, and 2038 cm^{-1} for complexes VA, VB, and VC, respectively, are indicative of the terminal end-on coordination modes for these ligands. In the preceding paper,[3] we reported the preparation of closely related monocarbonyl and monoisocyanide complexes of the type [Cp*RuCl(μ-SR)$_2$RuCp*(L)]Cl (VII) derived from complexes II. The difference between complexes V and VII is in the oxidation state of the Ru atoms binding CO or *t*-BuNC, which results in the shift of the $\nu_{C\equiv O}$ and $\nu_{N\equiv C}$ bands to the lower frequency region in complexes V compared to those in complexes VII (R = Et, L = CO, 1983 cm^{-1}; R = *i*-Pr, L = CO, 1985 cm^{-1}; R = Et, L = *t*-BuNC, 2150 cm^{-1}).

On the other hand, when complex IIIC was treated with *t*-BuNC, a diamagnetic complex [Cp*Ru(*t*-BuNC)(μ-SCy)$_2$RuCp*(*t*-BuNC)] was isolated in 48% yield.[13] This complex showed the $\nu_{N\equiv C}$ band at 2000 cm^{-1} in its IR spectrum and two singlets assignable to the Cp* and *t*-Bu protons together with the multiplets for the Cy protons in its ^{1}H NMR spectrum. Details of the syntheses and characterization of this and related diruthenium complexes with Ru(II) centers will be reported in the subsequent paper.

Reactions of Complexes III with H$_2$ and PhC≡CH. Complexes IIIA and IIIC reacted with H$_2$ in benzene at room temperature to form the dinuclear diamagnetic complexes [Cp*RuH(μ-SR)$_2$RuCp*H] (R = *i*-Pr (VIA), Cy (VIB)) in about 70% yields. In the case of the reaction of complex IIIC, formation of CySH together with a small amount of CySSCy was detected by GLC analysis of the reaction solution. In the IR spectra of complexes VI the medium ν_{Ru-H} bands appear around 1950 cm^{-1}, whereas the ^{1}H NMR spectra of these complexes show singlet resonances assignable to the hydride protons at about −16 ppm with an intensity of 2 H per two Cp* ligands. The diamagnetic behavior of these complexes in the NMR study can be ascribed to the spin–spin pairing between two Ru(III) atoms, as was shown in complexes I and II. As for complexes II, we proposed the structure

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(8) Cyclic voltammograms of complexes IIIA–D could not be measured in DMF because of the rapid decomposition of these complexes in this solvent. On the other hand, the cyclic voltammograms recorded in THF or CH$_2$Cl$_2$ showed four or five uncharacterizable anodic and cathodic peaks, which presumably result from the low stability of the oxidized or reduced species generated from these complexes under the voltammetric conditions.

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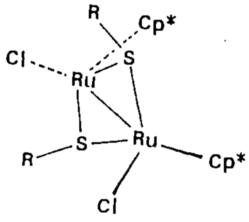
(13) A doubly bridged dinuclear structure with 18-electron Ru centers is plausible for this complex, since a set of peaks interpreted as the [Cp*Ru$_2$(SCy)(*t*-BuNC)]$^+$ fragment appeared intensely around *m/z* = 537 in its mass spectrum (see supplementary material), although a parent peak was not clear. Moreover, the ^{13}C NMR spectrum has disclosed that the structure having the mirror plane that bisects the Ru–Ru vector is plausible for this complex, since the ortho and meta carbon atoms in Cy rings appear as the singlets, respectively: ^{13}C NMR (C$_6$D$_6$) δ 10.41 (C$_5$*Me*$_5$), 27.25 (meta C in Cy), 27.46 (para C in Cy), 32.40 (*Me*$_3$CNC), 35.78 (ortho C in Cy), 47.21 (ipso C in Cy), 54.83 (Me$_3$*C*NC), 88.68 (*C*$_5$Me$_5$), 162.9 (*t*-BuN*C*).



II

with two Cp* ligands in mutually cis positions from the ^{1}H NMR criteria. Furthermore, we favored the structure in which two R substituents are present in mutually syn positions with respect to the Ru_2S_2 core in consideration of the steric repulsion between the R groups and the methyl groups in the Cp* ligands.[3] However, we could not discern the details of the structure of complexes II because the isolation of the crystals suitable for an X-ray analysis was not successful.

Now an X-ray analysis of complex VIA has been performed, which is expected to have the same structure as complexes II. Although the R and R_w values after the final refinement were still 0.11 and 0.15 because of the poor character of the crystals obtained here,[14] the structure of complex VIA with the expected cis configuration of two Cp* ligands and the syn configuration of two *i*-Pr substituents has been clearly demonstrated, which is depicted in Figure 3. The positions of the hydride atoms were unable to be located, but the mutually cis terminal dihydride structure must be most plausible, if the coordination geometry of the Cp* and the thiolate ligands around the Ru atom is taken into consideration. The Ru–Ru distance of 2.784 (5) Å in this complex is significantly shorter than those in the diruthenium complexes without a Ru–Ru bond referred to above and even than that in complex IIIA, which is indicative of the presence of a Ru–Ru single bond in complex VIA. The Ru_2S_2 core is not planar but has a butterfly structure, and the dihedral angle between the plane including the Ru(1), Ru(2), and S(1) atoms and that defined by the Ru(1), Ru(2), and S(2) atoms is 150°.

The reaction of complex IIIA with PhC≡CH also gave the diamagnetic diruthenium complexes with alkynyl ligands [Cp*Ru(C≡CPh)(μ-S-*i*-Pr)$_2$RuCp*(C≡CPh)] (VIC). There appeared no ν_{Ru-H} bands in its IR spectra and no hydride resonances in its ^{1}H NMR spectra. Therefore we formulated this product as above, which might have the same structure as that of complex VIA. However, only a small amount of H_2 gas (<5%) was evolved from the reaction mixture and the formation of PhCH=CH$_2$ was not observed. Thus the fate of the acetylene hydrogen atom after the reaction is not yet clear.

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Supplementary Material Available: Tables of X-ray crystallographic data, bond distances and angles, positional and isotropic thermal parameters for hydrogen atoms, and anisotropic thermal parameters for nonhydrogen atoms for complex IIIA and a figure of the observed and calculated mass spectra around m/z = 537 generated by the fragmentation of [Cp*Ru(*t*-BuNC)(μ-SCy)$_2$RuCp*(*t*-BuNC)] (6 pages); a listing of observed and calculated structure factor amplitudes for complex IIIA (25 pages). Ordering information is given on any current masthead page.

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(14) Crystal data for complex VIA: $C_{26}H_{46}S_2Ru_2$; monoclinic, space group $P2_1/a$; a = 17.931 (5), b = 8.917 (3), c = 19.101 (9) Å; β = 110.30 (3)°; Z = 4. Data collection and structure solution and refinement were undertaken by the method analogous to that for complex IIIA. Final R and R_w values were 0.11 and 0.15, based on 2534 unique data ($F > 5\sigma(F)$).

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Synthesis, Structure, and Characterization of Chlorobis(diethyldithiocarbamato)((2-mercaptophenyl)imido)molybdenum(VI)[†]

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The reaction of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ with 2-aminothiophenol produces the imido complex $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$. The structure of this complex has been determined by X-ray crystallography. The crystals are monoclinic, of space group $P2_1/c$, with a = 8.565 (3) Å, b = 16.461 (5) Å, c = 20.542 (8) Å, β = 125.60 (2)°, and Z = 4. The structure was refined to R = 3.34% and R_w = 2.95% by using 1351 independent reflections. The geometry of the complex is distorted pentagonal bipyramidal. The molybdenum–imido nitrogen distance is 1.744 (6) Å, and the imido linkage (Mo–N(1)–C(11)) has an angle of 137.7 (7)°, indicating that the imido nitrogen acts as a two-π-electron donor. The Cl(1)–Mo–N(1) angle is 159.9 (4)°. The molybdenum–chloride distance is 2.455 (2) Å, showing no bond lengthening due to a trans effect of the molybdenum–imido nitrogen bond. The molybdenum–sulfur distances average 2.510 (6) Å. The complex has two reduction peaks in the cyclic voltammogram, one irreversible at −0.64 V and the other quasi-reversible at −0.87 V. When reduced with one electron at −0.7 V, the red-brown complex turns into a green Mo(V) monomer. The Mo(V) compound has an EPR signal with g_0 = 1.992. The frozen-solution EPR spectrum at 96 K has three different g values, indicating rhombic symmetry of the Mo(V) complex. The Mo(V) monomer can be reduced with one electron at −0.9 V to form a brown Mo(IV) complex, which can be reoxidized to the green, EPR-active Mo(V) monomer. The molybdenum center of $Mo(NC_6H_4S)Cl(S_2CN(C_2H_5)_2)_2$ has a ^{95}Mo NMR signal at 292 ppm; i.e., the ^{95}Mo nucleus is about 500 ppm more deshielded than in $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$ or $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$. The imido nitrogen has a signal in the ^{14}N NMR spectrum at +70 ppm and is also more deshielded than the imido nitrogens in other seven-coordinate Mo(VI) imido complexes.

Introduction

Molybdenum(VI) compounds are of special interest because of the importance of molybdenum(VI) as a catalytic center in molybdenum hydroxylases, a group of enzymes that catalyze two-electron reduction and oxidation reactions.[1] The synthesis

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[†] Dedicated to Professor Jack T. Spence on the occasion of his retirement.

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