Conversion of Rectangular Tetrasulfide Ligand in Tetrarhodium Complex, $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu_4\text{-}S_4)]^{2+}$ ($Cp^* = \eta^5\text{-}C_5Me_5$), into Disulfide Ligands in Dirhodium Complex, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)]$ by Chemical Reduction

Takanori Nishioka,* Shigeyuki Nakamura, Yuichi Kaneko,*† Takayoshi Suzuki,††
Isamu Kinoshita, Syun-ichi Kiyooka,† and Kiyoshi Isobe*
Department of Material Science, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558
†Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780
††Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560

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Reaction of $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu_4\text{-}S_4)]^{2+}$ ($Cp^*=\eta^5\text{-}C_5Me_5$) (**1**) containing a rectangular S_4 ligand with the reducing agent of $NaBH_4$ affords $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)]$ (**2**) confirmed by FAB mass and ^1H NMR spectra. This disulfide complex is so air-sensitive that the S_2 ligand is easily oxygenated by oxygen to give an SSO ligand in $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO)]$ (**3**) whose structure is determined by X-ray analysis.

Rectangular S_4 being of interest for both experimental and theoretical chemists[1] has been found for the first time in a tetrarhodium complex, $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu_4\text{-}S_4)]^{2+}$ ($Cp^*=\eta^5\text{-}C_5Me_5$) (**1**), prepared by the oxidation of the bridging hydrosulfide dirhodium complex of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+$.[2] The S_4 unit in complex **1** has a cyclobutadiene-type structure: two long S–S bonds (2.702(1) Å, bond order; less than 1) parallel to the Rh–Rh bond and two short S–S bonds (1.979(1) Å, double bond character) perpendicular to the Rh–Rh bond. Charge population analysis from theoretical calculation shows that the S_4 unit has -1 net charge, not -2 counted simply by its formal oxidation state.[3] Thus, this novel cyclic S_4 unit has a unique geometrical and electronic structure that stimulates us to reveal its reactivities.

A cyclic voltammogram of **1** displayed a reduction wave at -0.70 V (vs. Ag/AgCl) and a re-oxidation wave at -0.21 V. Additional reduction wave at -0.27 V, corresponding to the reversible couple of the re-oxidation, appeared on the second cycle of the potential sweep of 0.0 V → -1.0 V → 0.0 V (Figure 1). It suggests that the reduction of **1** causes structure conversion and the reduced species may also be produced by chemical reduction and characterized. We describe here chemical reduction of the tetrarhodium complex to $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)]$ and its derivation of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO)]$ by oxygenation.

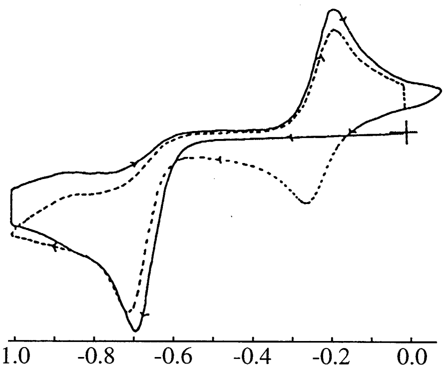
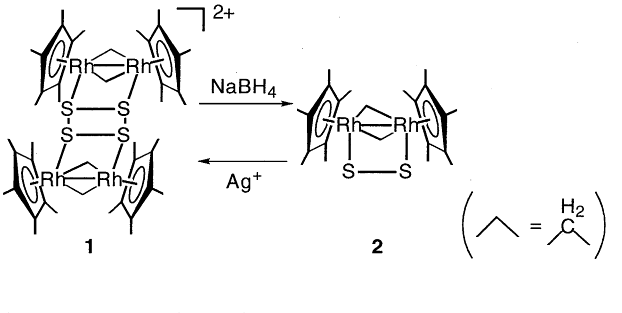


Figure 1. Cyclic voltammogram of **1** in 0.1 mol dm^{-3} $TBAPF_6$ in CH_2Cl_2 at a scan rate of 100 mV/s. Solid and dashed lines indicate the first and second cycles of potential sweep, respectively.

A sample made up by a portion of the reaction mixture of [**1**]Cl(OH) (10 mg, 0.084 mmol), and $NaBH_4$ (2 mg, 0.520 mmol) in diethanolamine (DEA; 0.1 cm^3) under Ar gas was submitted to the positive ion FAB mass spectral measurement where the amine was used directly as a matrix for the measurement; in the spectrum typical envelopes such as $[[(RhCp^*)_2(CH_2)_2(S_2)]$ (**2**)+ H$]^+$ (at m/z = 569), [**2**+ Na$]^+$ (at m/z = 591), and [**2**+ Na + DEA$]^+$ (at m/z = 696) and their characteristic isotopic distribution due to isotopes of ^{32}S and ^{34}S were observed to prove the formation of a neutral S_2 dinuclear complex.[4] ^1H NMR spectra of samples prepared in DEA and in CD_3OD, separately, by the above method have completely the same patterns each other except for the DEA peaks: the CH_3 signal of the Cp* ligands appears at around δ 1.7 as singlet and the μ-CH_2 signals at around δ 10 and 9 as double-triplets which suggests that the complex has a cis configuration.[5] Several attempts to isolate **2** were unsuccessful because **2** is highly air-sensitive and unstable. Complex **2** was oxidized by AgO_3SCF_3 to reproduce **1**. While **2** was oxygenated by oxygen quickly to give an SSO complex: a deep brown reaction mixture containing **2** (≈0.061 mmol) generated similarly in CH_3OH (3 cm^3) was poured into a 3:5 mixture of H_2O and CH_2Cl_2 (80 cm^3) and exposed to air with stirring. The separated organic layer was concentrated and purified by silica-gel column chromatography using a 49:1 mixture of CH_2Cl_2 and CH_3OH as an eluent. The concentrated eluate was again chromatographed carefully using a silica-gel column and a 4:6:1 mixture of CH_2Cl_2, CH_3CN, and CH_3OH as an eluent. From the second fraction[6] in the second chromatography $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO)]$ (**3**)[7] was obtained in a 39% yield and recrystallized by a slow diffusion of AcOEt to the CH_2Cl_2 solution to give brown red single crystals.

Scheme 1.



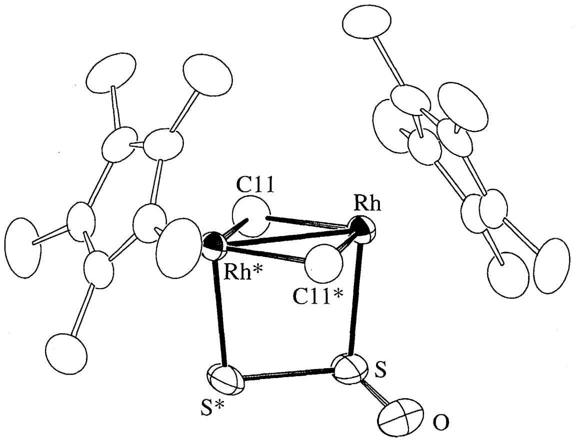
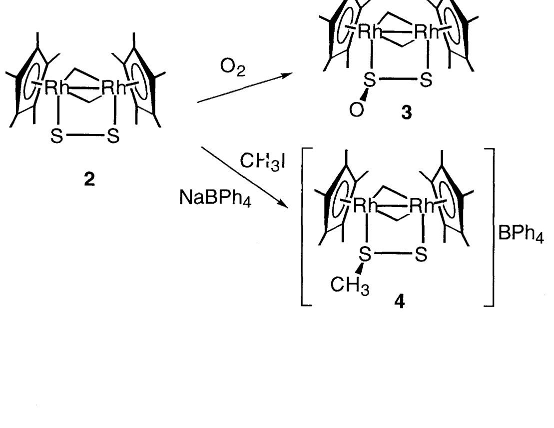


Figure 2. Molecular structure of $[(RhCp^*)_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SSO)]$ (**3**) drawing in 50% probability. Selected bond lengths (Å) and angles (°): Rh-Rh 2.605(1), Rh-S 2.322(2), S-S* 2.115(3), S-O 1.44(1), Rh*-Rh-S 83.87(6), Rh-S-S* 95.96(9), Rh-S-O 112.0(5), S*-S-O 110.7(7).
*symmetry operation: 1-x, y, 1/2-z.

The structure of **3** was determined by X-ray analysis.[8] The oxygen atom is disordered into two positions with 1/2 population in the molecule. The ^1H NMR spectrum of **3**, however, clearly shows that two Cp* ligands are magnetically nonequivalent and that, of course, **3** does not contain **2**. This means that complex **3**is not the mixture of OSSO and S_2 complexes but the SSO complex where the S–S bond bridges the Rh–Rh bond as shown in Figure 2. The Rh-Rh bond length is 2.605(1) Å corresponding to the single bond.[9] The S–O bond has double bond character because of its short bond distance (1.44(1) Å).[10] From the above results we conclude that the S_2 complex of **2** is a disulfide complex $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)]$ with a side-on bridging mode of the S_2 unit as described in Scheme 1. Although we need further experiments to know exactly which two S–S bonds in the cyclobutadiene-type S_4 unit in **1** are cleaved, the shorter S–S bonds, which have a double bond character, seem to split on the reduction. The results of the cyclic voltammogram (Figure 1) indicate that the reversible couple around 0.25 V should be corresponded to the redox of **2** produced by structure conversion of the neutral reduced form of **1** after the first reduction wave.

It is also worthwhile to note that generally S_2 ligands in many complexes are not oxygenated readily, but the strong oxidizing reagent of IO_4^- or *m*-chloroperbenzoic acid is able to oxygenate the S_2 ligand in $[Ir(dppe)_2(S_2)]^+$ or $[Mo(S_2)(S_2CNEt_2)_3]$ to give the SSO complex of $[Ir(dppe)_2(SSO)]^+$[11] or $[Mo(SSO)(S_2CNEt_2)_3]$.[12] Thus, the S_2 ligand in complex **2** has an unusual air-sensitivity to convert to the SSO ligand in **3** under mild conditions, which implies its electron rich character. The reaction of $[Co(dmpe)_2]^{2+}$ with elemental sulfur (S_8) gave also the SSO complex of $[Co(SSO)(dmpe)_2]^+$. It might be produced through air oxidation of an intermediate containing a S_2 ligand which was not detected in the reaction system.[13] Reaction of **2** with CH_3I as an electrophile proceeds readily in the presence of $NaBPh_4$ in CH_3OH to give $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSMe)](BPh_4)$ in a 50% yield (Scheme 2).[14]

Scheme 2.



References and Notes

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4 See supplementary material.

5 ^1H NMR (CD_3OD) δ 9.92 (dt, $^2J_{H\text{-}H}$ = 3.8 Hz, $^2J_{H\text{-}Rh}$ = 1.9 Hz, 2H, $\mu\text{-}CH_2$), 9.10 (dt, $^2J_{H\text{-}H}$ = 3.8 Hz, $^2J_{H\text{-}Rh}$ = 1.5 Hz, 2H, $\mu\text{-}CH_2$), 1.74 (s, 30H, C_5Me_5).
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6 From the first fraction we obtained $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO_2)]$ in a 22% yield. X-ray analysis of this is in progress.

7 ^1H NMR ($CDCl_3$) δ 9.72 (dt, $^2J_{H\text{-}H}$ = 2.1 Hz, $^2J_{H\text{-}Rh}$ = 2.1 Hz, 2H, $\mu\text{-}CH_2$), 8.89 (dt, $^2J_{H\text{-}H}$ = 2.1 Hz, $^2J_{H\text{-}Rh}$ = 1.2 Hz, 2H, $\mu\text{-}CH_2$), 1.82 (s, 15H, C_5Me_5), 1.74 (s, 15H, C_5Me_5); ^{13}C NMR ($CDCl_3$): δ 172.3 (dd, $^1J_{C\text{-}Rh}$ = 24 Hz, $^1J_{C\text{-}Rh}$ = 30 Hz, $\mu\text{-}CH_2$), 161.8 (t, $^1J_{C\text{-}Rh}$ = 25 Hz, $\mu\text{-}CH_2$) 101.8 (s, C_5Me_5), 100.3 (d, $^1J_{C\text{-}Rh}$ = 4 Hz, C_5Me_5), 9.9 (s, $C_5\mathit{Me}_5$), 9.6 (s, $C_5\mathit{Me}_5$); FAB mass spectrum (NBA) : *m/z* 585 $[M+H]^+$, 556 $[M\text{-}2(CH_2)]^+$, 504 $[M\text{-}S_2O]^+$; Anal. Found: C, 44.34; H, 5.68%. Calcd for $C_{22}H_{34}ORh_2S_2$: C, 44.01; H, 5.71%.

8 Crystal data for **3**: $C_{22}H_{34}ORh_2S_2$, M_w = 584.45, monoclinic, space group *C2/c*, *a* = 11.696(3), *b* = 12.930(4), *c* = 15.816(5) Å, β = 105.40(2)°, *V* = 2306(1) Å^3, *Z* = 4, D_x = 1.683 g/cm^3, μ(Mo*K*α) = 16.2 cm^{-1}. Intensity data were measured on a Rigaku AFC5S diffractometer using ω-2θ scan technique with graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). 3519 unique refractions within $4 \leq 2\theta \leq 60°$ were collected. The data were corrected for Lorentz and polarization effects. No decay correction was applied. The structure was solved and refined by using the Xtal programs. The current *R* value is 0.062 (R_w = 0.076) for 2699 independent absorption-corrected reflections ($I \geq 3\sigma(I)$) by empirical Ψ scan method.

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14 ^1H NMR (CD_2Cl_2) δ 9.72 (dt, $^2J_{H\text{-}H}$ = 1.5 Hz, $^2J_{H\text{-}Rh}$ = 1.5 Hz, 1H, $\mu\text{-}CH_2$), 9.58 (dt, $^2J_{H\text{-}H}$ = 1.6 Hz, $^2J_{H\text{-}Rh}$ = 1.5 Hz, 1H, $\mu\text{-}CH_2$), 9.14 (m, 2H, $\mu\text{-}CH_2$), 7.35 (m, 8H, BPh_4), 7.05 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 8H, BPh_4), 6.90 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, BPh_4), 2.36 (d, $^3J_{H\text{-}Rh}$ = 1.7 Hz, 3H, SSMe), 1.73 (s, 15H, C_5Me_5), 1.75 (s, 15H, C_5Me_5); ^{13}C NMR (CD_2Cl_2): δ 177.1 (dd, $^1J_{C\text{-}Rh}$ = 24 Hz, $^1J_{C\text{-}Rh}$ = 26 Hz, $\mu\text{-}CH_2$), 174.5 (t, $^1J_{C\text{-}Rh}$ = 24 Hz, $\mu\text{-}CH_2$), 164.4 (q, $^1J_{C\text{-}B}$ = 50 Hz, BPh_4), 136.3 (q, $^2J_{C\text{-}B}$ = 1 Hz, BPh_4), 125.9 (q, $^3J_{C\text{-}B}$ = 3 Hz, BPh_4), 122.0 (s, BPh_4), 103.3 (d, $^1J_{C\text{-}Rh}$ = 5 Hz, C_5Me_5), 102.8 (d, $^1J_{C\text{-}Rh}$ = 5 Hz, C_5Me_5), 31.4 (d, $^2J_{C\text{-}Rh}$ = 1 Hz, SSMe), 10.2 (s, $C_5\mathit{Me}_5$), 9.9 (s, $C_5\mathit{Me}_5$); FAB mass spectrum (NBA): *m/z* 583 $[M]^+$; Anal. Found: C, 61.80; H, 6.29%. Calcd for $C_{47}H_{57}BRh_2S_2$: C, 62.53; H, 6.36%.