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Structure and reactivity of a novel parallel thiosulfito (SSO_2-*S*:*S′*) rhodium dinuclear complex

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The parallel thiosulfite ligand (SSO_2) in a rhodium complex, which is formed by oxygenation of a bridging disulfide, is converted to a bridging hydrocarbyl thiolate ligand and sulfur dioxide gas by the reaction with hydrocarbyl halides.

Oxidation and oxygenation of sulfur are significant processes in biological, mineralogical, and industrial processes.[1] We have studied the oxidation and oxygenation of inorganic sulfur compounds bound on a rhodium dinuclear unit. For example, $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$) is oxidized by elemental sulfur or oxygen with excess hydrogen sulfide to give a cyclotetrasulfide rhodium tetranuclear complex, $[\{(Cp^*Rh)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$.[2] The tetrasulfide complex is reduced by $NaBH_4$ to afford a disulfide complex $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2)]$[3] which also can be prepared by the reaction of $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2Cl_2]$[4] and Li_2S_2. The bridging disulfide ligand coordinating to the rhodium dinuclear unit in parallel is easily oxygenated in the air. Previously, we reported the structure of a disulfurmonoxide (SSO) dirhodium complex, $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO\text{-}S{:}S')]$,[3] isolated from the oxygenation reaction. We report here the structure and the reactivity of a novel thiosulfito (SSO_2) complex $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO_2\text{-}S{:}S')]$ (**1**) isolated from the oxygenation reaction of the disulfide complex.† Since the two S atoms in the SSO_2 moiety have such different formal oxidation states (−1 for ***S***SO_2 and +3 for S***S***O_2), they should exhibit different reactivity, which should provide better understanding of sulfur chemistry in general.

Complex **1** shown in Fig. 1(a) is the first example of an SSO_2 ligand bridging between two metal atoms in parallel.‡ In most cases, the SSO_2 ligand bridges *via* the non-oxygenated S atom.[5] One published example of a complex having SSO_2-*S*:*S′* coordination, $[\{Co(CN)_5\}_2(SSO_2\text{-}S{:}S')]^{6-}$, was reported in which the metal atoms are arranged in a *trans* fashion about the S–S bond.[6] Even though the coordination geometries of the Co complex and **1** are different, they both have shorter M–S bond lengths involving the oxygenated S atom (2.255(2) Å for the Co complex and 2.311(3) Å for **1**) compared to the non-oxygenated S atoms (2.297(2) Å for the Co complex and 2.346(3) Å for **1**).

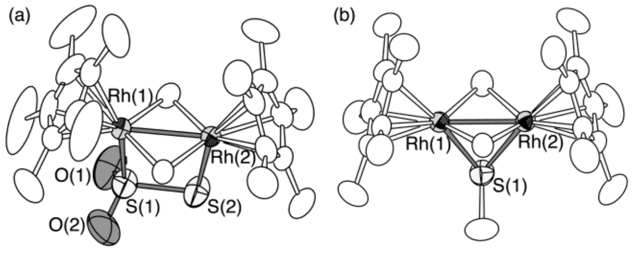

Fig. 1 (a) Molecular structure of complex **1**. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–Rh(2) 2.6137(9), Rh(1)–S(1) 2.311(3), Rh(2)–S(2) 2.346(3), S(1)–S(2) 2.102(4), S(1)–O(1) 1.441(9), S(1)–O(2) 1.455(10); Rh(1)–S(1)–S(2) 98.5(1), Rh(2)–S(2)–S(1) 94.2(1), S(2)–S(1)–O(1) 107.0(4), S(2)–S(1)–O(2) 109.8(4). (b) Structure of the cationic complex **2**. All hydrogen atoms have been deleted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–Rh(2) 2.5447(3), Rh(1)–S(1) 2.3712(9), Rh(2)–S(1) 2.3897(8); Rh(1)–S(1)–Rh(2) 64.62(2).

In order to estimate the charges on the S atoms in the SSO_2 ligand in **1**, B3LYP hybrid density functional theory calculations were performed on the model complex $[\{(\eta^5\text{-}C_5H_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO_2\text{-}S{:}S')]$, in which the C_5H_5 was used in place of Cp* for simplification.§ Natural population analysis showed that the sulfur atoms, ***S***SO_2 and S***S***O_2, have a charge of −0.318 e and +1.702 e, respectively. This difference in charge should greatly affect the reactivity of each S atom towards electrophiles, and herein, we present reactivity towards hydrocarbyl halides and I_2.

The reaction of **1** with MeI gave a MeS bridged dirhodium complex $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SMe)]^+$ (**2**) shown in Fig. 1(b) accompanied by the generation of SO_2 gas.¶ It is quite clear that the electrophile attacked the more electronegative non-oxygenated S atom, forming a C–S bond, with subsequent release of SO_2. In a similar reaction with the μ-S_2-*S*:*S′* complex, $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSMe\text{-}S{:}S')]$ was formed.[3] This shows that the oxidation state of the S atoms in **1** has a direct effect on the reactivity of **1**.

The structure of the BPh_4 salt of **2** was determined by X-ray crystallography.‡ The Rh–S–Rh angle (64.62(2)°) in **2** is acute, similar to other μ-CH_2 dirhodium thiolate compounds having a Rh–Rh bond, such as $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2\{\mu\text{-}SC(COOMe){=}CH(COOMe)\}]^+$ (63.53(3)°)[7] or $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+$ (64.3(1)°).[8] As the Rh–S–Rh angle depends on the Rh···Rh distance, the μ-CH_2 complexes with a shorter Rh–Rh bond have a smaller Rh–S–Rh angle.

When an organic dihalide, such as 1,4-dibromoxylene, was used, a tetranuclear complex consisting of two dirhodium units bridged by an organic dithiolate formed, Fig. 2.¶ The bond lengths and angles around the S atoms in **3** are slightly different from those in **2** due to a positioning disorder involving the S atoms.‡ While the reaction of **1** with 1,3-diiodopropane also gave a related derivative, that with 1,2-diiodoethane did not

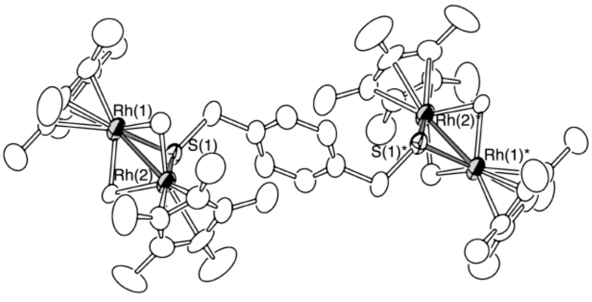

Fig. 2 Structure of the cationic complex **3**. All hydrogen atoms have been deleted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–Rh(2) 2.5549(8), Rh(1)–S(1) 2.387(2), Rh(2)–S(1) 2.413(2); Rh(1)–S(1)–Rh(2) 64.31(6).

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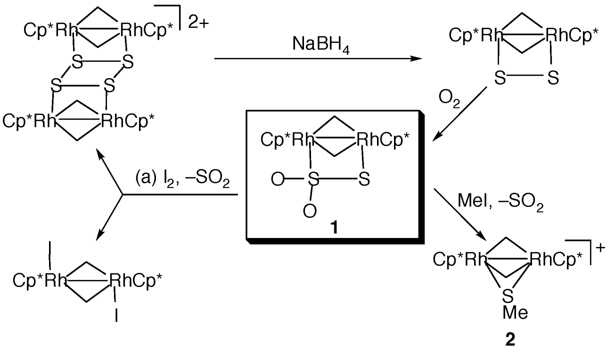

Scheme 1

give the corresponding tetranuclear complex probably because the shorter bridging ligand causes steric repulsion between the bulky dirhodium units. As well, the 1,2-diiodoethane is easily converted to I_2 and ethene under the reaction conditions.

In the reaction of **1** with 1,2-diiodoethane, $[\{(Cp^*Rh)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$ and $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2I_2]$ were observed, possibly due to the decomposition of the 1,2-diiodoethane which forms I_2. The source of three compounds was verified when a reaction of **1** with 2/3 equiv. of I_2 proceeded quantitatively to give the μ-S_4 and diiodide rhodium complexes accompanied by the generation of SO_2 gas (Scheme 1(a)). The iodine oxidizes both S atoms (S^{-I}–$S^{III}O_2$ to $(S^{-1/2})_4$ and $S^{IV}O_2$) but not the rhodium atoms.

The reactions of **1** are summarized in Scheme 1. From the oxygenation reaction of the disulfide complex, we have isolated two compounds other than the SSO and SSO_2 complexes. Spectral and analytical data suggested that the compounds were *trans*- and *cis*-OSSO complexes. Further theoretical and experimental investigations concerning with the reaction mechanisms and the related compounds are now in progress.

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Notes and references

† *Synthesis* of **1**: a solution of $NaBH_4$ (50 mg, 1.32 mmol) in methanol (5 mL) was added to a solution of $[\{(Cp^*Rh)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]Cl(OH)$ (500 mg, 0.42 mmol) in methanol (5 mL). After stirring for 15 min, the solution was exposed to the air and stirred for 5 h. The solvent was removed under reduced pressure to give a mixture of $[\{(Cp^*Rh)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-SSO-}S{:}S')]$ and **1**. These complexes were separated by silica-gel column chromatography using a mixed solvent of CH_2Cl_2 and ethylacetate (10 : 1). Yield: 80 mg (13%). Single crystals suitable for crystallography were obtained from a solution of **1** in CH_2Cl_2 by diffusion of ethyl acetate.

‡ *Crystallographic data*: for **1**: $C_{22}H_{34}O_2Rh_2S_2$, M = 600.44, monoclinic, space group $P2_1/n$, a = 8.517(6), b = 14.367(6), c = 19.674(5) Å, β = 96.30(1)°, V = 2392(2) Å^3, Z = 4, μ(Mo-Kα) = 1.565 mm^{-1}, 7679 reflections measured on a Rigaku AFC-5S diffractometer, 6974 unique (R_{int} = 0.075). An analytical absorption correction was applied (T = 0.630–0.811). The final $R1$ was 0.0757 for 3205 reflections ($I > 2.0\sigma(I)$) and $wR2$ (all data) was 0.1572 with GOF of 1.182.

For **2**·BPh_4: $C_{47}H_{57}BRh_2S$, M = 870.65, triclinic, space group $P\bar{1}$, a = 12.519(1), b = 14.582(1), c = 11.842(1) Å, α = 98.007(9), β = 95.297(7), γ = 85.428(8)°, V = 2126.6(3) Å^3, Z = 2, μ(Mo-Kα) = 0.854 mm^{-1}, 12918 reflections measured on a Rigaku AFC-7S diffractometer, 12389 unique (R_{int} = 0.024). An analytical absorption correction was applied (T = 0.805–0.920). The final $R1$ was 0.0348 for 7799 reflections ($I > 2.0\sigma(I)$) and $wR2$ (all data) was 0.0589 with GOF of 1.133.

For **3**·$(BPh_4)_2$·$2CH_2Cl_2$: $C_{102}H_{120}B_2Cl_4Rh_4S_2$, M = 1985.24, triclinic, space group $P1$, a = 11.5491(8), b = 12.315(1), c = 17.291(1) Å, α = 79.146(9), β = 83.98(1), γ = 87.84(1)°, V = 2401.6(3) Å^3, Z = 1, μ(Mo-Kα) = 0.873 mm^{-1}, 19067 reflections measured on a Rigaku/MSC Mercury CCD diffractometer, 10536 unique (R_{int} = 0.040). The final $R1$ was 0.0810 for 6499 reflections ($I > 2.0\sigma(I)$) and $wR2$ (all data) was 0.1941 with GOF of 1.074. Two orientations of the $\{Rh(\mu\text{-}CH_2)(\mu\text{-}SH)Rh\}$ core were observed. Both cores share the two rhodium atoms and the sulfur and carbon atoms of the bridging methylene were disordered into two positions with occupancies of 0.75 and 0.25, respectively.

All three structures were solved by direct method (SIR92).[9] The teXsan[10] and SHELX-97[11] packages were used for other calculations. CCDC reference numbers 186588–186590. See http://www.rsc.org/suppdata/cc/b2/b204765a/ for crystallographic data in CIF or other electronic format.

§ *Theoretical calculations*: we used Gaussian98 program[12] for the B3LYP calculations. In the calculations we used the LANL2DZ basis functions and effective core potential for the rhodium atoms and the 6-31G* and 6-31G basis functions for the SSO_2 and C_5H_5 groups, respectively. Part of the calculations was performed at the Research Center for Computational Science in Nagoya University.

¶ *Synthesis* of **2** and **3**: iodomethane (4.7 μL, 0.08 mmol) was added to a solution of **1** (30 mg, 0.05 mmol) in MeOH (5 mL). After stirring for 14 h, to the solution was added a solution of $NaBPh_4$ (50 mg, 0.15 mmol) in MeOH (5 mL) to give a red precipitate of **2**·BPh_4. The precipitate was collected on a filter and washed with MeOH. Yield: 27 mg (63%). The generation of SO_2 gas was checked by an SO_2 gas detector tube (Gastec Corporation). Single crystals suitable for crystallography were obtained from a solution of **2**·BPh_4 in CH_2Cl_2 by diffusion of toluene. Anal. Calc. for $C_{47}H_{57}BRh_2S$: C, 64.84; H, 6.60. Found: C, 64.43; H, 6.61%. MS(FAB): *m/z* 551 ($[M]^+$). Complex **3** was also obtained by a procedure similar to that described for **2** but 0.5 equiv. of 1,4-dibromoxylene was used instead of iodomethane. Yield: 61%. Single crystals suitable for crystallography were obtained from a solution of **3**·$(BPh_4)_2$ in CH_2Cl_2 by diffusion of MeOH. Anal. Calc. for $C_{100}H_{116}B_2Rh_4S_2$·$1.7CH_2Cl_2$: C, 62.33; H, 6.14. Found: C, 62.33; H, 6.15%. MS(ES): *m/z* 588 ($[M]^{2+}$).

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