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Preparation and Structural Characterization of Cationic Dinuclear Ruthenium(II)—Thiolate Complexes, $[Ru_2(SPh)_3(\eta^6\text{-}p\text{-cymene})_2]Y$ ($Y = Cl$ and PF_6)

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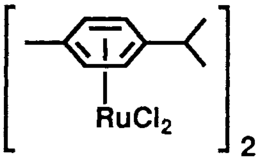
Treatment of $[RuCl_2(p\text{-cymene})]_2$ with sodium benzenethiolate in methanol afforded a cationic dinuclear ruthenium thiolate complexes, $[Ru_2(SPh)_3(p\text{-cymene})_2]Y$ (**2a** $Y = Cl$; **2b**: $Y = PF_6$), whose structure is determined by X-ray analysis of **2b**.

The chemistry of metal-sulfur compounds has attracted much interest recently for their importance in the field of metalloenzymes, material precursor, and catalyst. Although a large number of metal-thiolate compounds have been reported, a limited number of ruthenium complexes has been isolated and characterized.1—6) In our research to prepare the mononuclear ruthenium-thiolate complexes,7) we have synthesized two types of dinuclear ruthenium(II)-thiolate complexes6) which have η^6-*p*-cymene as a coligand.

Treatment of $[RuCl_2(p\text{-cymene})]_2$ (**1**) with three equiv. of sodium benzenethiolate in methanol afforded a cationic dinuclear complex $[Ru_2(SPh)_3(p\text{-cymene})_2]Cl$ (**2a**) as orange needles in 44% yield upon recrystallization of the product from a mixture of chloroform and hexane.8) The spectral data confirmed the presence of *p*-cymene and benzenethiolate in 2:3 ratio. Complex **2a** has a cationic complex part and the chloride anion is easily replaced by the PF_6 anion. Treatment of **2a** with KPF_6 in chloroform and the successive recrystallization of the product from acetonitrile and ether afforded **2b** as orange crystals in 77% yield.9)



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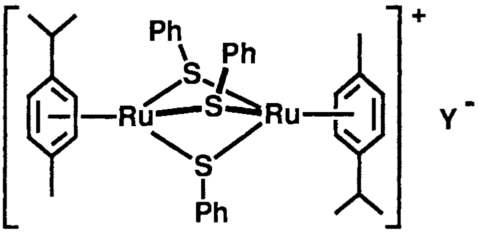

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a: Y = Cl
b: Y = PF_6

Complex **2b**, as shown in Fig. 1, contains a cationic dinuclear ruthenium(II) core triply bridged by sulfur atoms of benzenethiolate ligands.[10] The bond distances of Ru—S are normal. Two octahedral ruthenium(II) centers have the small deviation of Ru1—S—Ru2 angles (average 88.8°) from 90°. These angles are larger than the value (72.3 and 73.4°) of dinuclear Ru(II) complexes such as $[Ru_2(Et_2dtc)_5]^+$ (Et_2dtc = *N*,*N*-diethyldithiocarbamato).[11] The Ru1—Ru2 separation of 3.328 Å is well outside the range (2.28—2.95 Å) usually found for a Ru—Ru bond and is characteristic of triply-bridged diruthenium(II).[6,12] The Ru—Ru distance of the mixed valence Ru(II)Ru(III) complex, $(Cp^*Ru)_2(\mu\text{-S-}^i\text{Pr})_3$, is 2.968 Å,[3c] while that of Ru(III)Ru(III) has much shorter Ru—Ru distance in $[(Cp^*Ru)_2(\mu\text{-SPh})_3]^+$ (2.630 Å).[3b] Such tendency has been observed in the triply chloro-bridged dinuclear ruthenium complexes.[13] Two phenyl planes of *p*-cymene

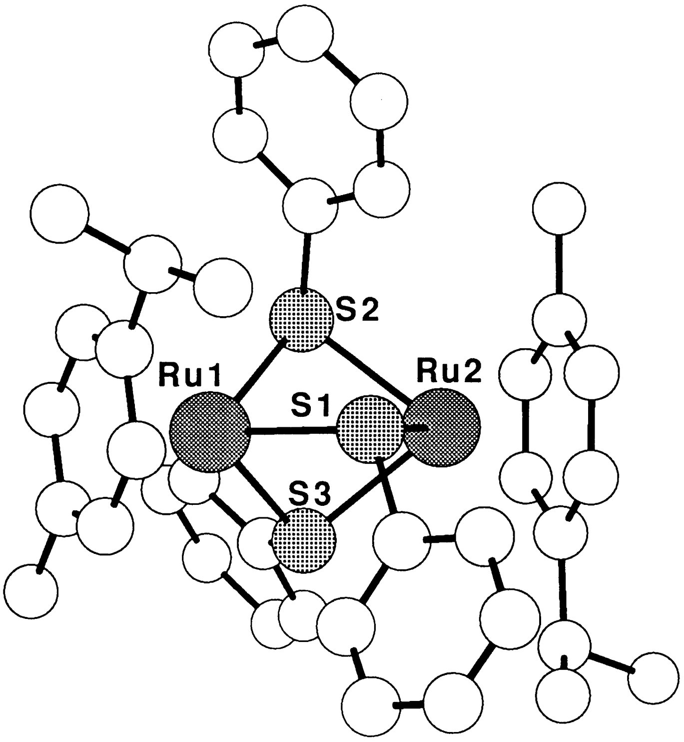

Fig. 1. A drawing of **2b** with a labeling scheme. Hydrogen atoms and PF_6 are omitted for simplicity. Selected bond distances (Å) and angles (degree): Ru1—S1 = 2.375(2), Ru1—S2 = 2.404(2), Ru1—S3 = 2.396(2), Ru2—S1 = 2.389(2), Ru2—S2 = 2.389(2), Ru2—S3 = 2.408(2); Ru1—S1—Ru2 = 89.32(5), Ru1—S2—Ru2 = 88.67(6), Ru1—S3—Ru2 = 88.39(6), S1—Ru1—S2 = 76.09(5), S1—Ru1—S3 = 76.71(6), S2—Ru1—S3 = 76.80(6), S1—Ru2—S2 = 76.10(6), S1—Ru2—S3 = 76.20(5), S2—Ru2—S3 = 76.85(6).

moieties are almost parallel (angle of the best planes = 4.0°) and a plane of three sulfur atoms occupies the middle between the two phenyl planes. The $Ru_2(\mu\text{-}SPh)_3$ part has a pseudo C_3 axis through the vector between two rutheniums, which is consistent with the observed NMR data, diastereotopic methyl on the isopropyl groups.$^{8,9)}$

It is of interest that the cationic dinuclear rhodium complex, $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3]^+$,$^{14)}$ has the similar structure to **2b**. These complexes are related by the idea of isolobal,$^{15)}$ (*p*-cymene)Ru vs. $(C_5Me_5)Rh$.

When a chelating ligand, 1,2-benzenedithiolate, was used instead of benzenethiolate, neutral dinuclear ruthenium complex **3** was obtained.$^{16)}$ Thus, treatment of **1** with sodium 1,2-benzenedithiolate in methanol afforded brownish red plates of complex **3** in 26% yield. The ratio of *p*-cymene to benzenedithiolate ligand (1:1) was revealed by ^1H NMR spectrum of **3**, in which two kinds of protons (A_2B_2 pattern) assignable to the benzenedithiolate moiety suggested that the symmetrical structure such as $Ru(\mu\text{-}\eta^1,\eta^1\text{-}S_2C_6H_4)_2Ru$ or $Ru(\mu\text{-}\eta^2,\eta^2\text{-}S_2C_6H_4)Ru$ might be favorable, but this point is still unclear. The FAB mass spectrum suggested the formation of a dinuclear complex. A base signal centered at *m/e* 753 corresponded to the mass of the protonated dinuclear molecule. Elemental analysis was also consistent with the product composition.

It was demonstrated here that the *p*-cymene acts as the supporting ligand for preparation of two types of dinuclear ruthenium—thiolate complexes depending on the kind of thiolate ligands.

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8) **2a**: Mp 132—137 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta = 0.78$ (d, CH*Me*Me, $J = 6.68$ Hz), 0.90 (d, CH*Me*Me, $J = 6.92$ Hz), 1.62 (s, Me), 1.93 (m, C*H*Me_2), 5.12 (d, $J = 5.44$ Hz), 5.15 (d, $J = 5.44$ Hz), 5.25 (d, $J = 5.44$ Hz), 5.44 (d, $J = 5.44$ Hz), 7.39 (m), and 7.91 (m) for aromatic protons: Anal. Found: C, 55.66; H, 5.47%. Calcd for ($C_{38}H_{43}ClS_3Ru_2$): C, 54.76; H, 5.20%.

9) **2b**: Mp 160—170 °C (decomp); ^{1}H NMR (CD_3CN): $\delta = 0.74$ (d, CH*Me*Me, $J = 6.92$ Hz), 0.86 (d, CH*Me*Me, $J = 6.68$ Hz), 1.57 (s, Me), 5.17 (d, $J = 5.94$ Hz), 5.21 (d, $J = 5.94$ Hz), 5.37 (d, $J = 5.94$ Hz), 5.49 (d, $J = 5.94$ Hz), 7.40 (m), and 7.91 (m) for aromatic protons; UV-vis ($CHCl_3$): $\lambda_{max} = 322$ nm; Anal. Found: C, 48.44; H, 4.55%. Calcd for ($C_{38}H_{43}F_6PS_3Ru_2$): C, 48.40; H, 4.60%.

10) *Crystal data* for **2b**: monoclinic space group $P2_1/n$, $a = 11.055(2)$, $b = 14.744(2)$, $c = 23.654(4)$ Å, $\beta = 98.68(1)°$, $Z = 4$, Mo-Kα radiation. Diffraction data were collected on a Rigaku AFC-5R diffractometer. The calculation was performed using TEXSAN. The structure was solved by conventional heavy-atom method and refined (difference Fourier synthesis; full matrix least squares), as isotropic temperature factors for all hydrogens and disordered four F of PF_6 and as anisotropic temperature factors for the remaining non-hydrogen atoms, to reach current residual values of $R = 0.040$ and $R_w = 0.056$ for unique 5022 reflections with $I > 3\sigma(I)$.

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16) **3**: Mp 145—151 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (d, CH*Me*$_2$, $J = 6.92$ Hz), 2.35 (s, Me), 2.71 (m, C*H*Me_2), 5.69 (d, $J = 6.55$ Hz) and 5.72 (d) for aromatic protons of *p*-cymene, 7.13 (m) and 8.03 (m) for aromatic protons; UV-vis ($CHCl_3$): $\lambda_{max} = 573$ and 443 nm; Anal. Found: C, 50.89; H, 4.92%. Calcd for ($C_{32}H_{36}S_4Ru_2$): C, 51.18; H, 4.83%.

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