

# Coordination behavior of some bridge ligands having S–O bond bound to four-membered ring unit ( $\text{Ru}_2\text{O}_2$ ) of dinuclear areneruthenium complexes

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## Abstract

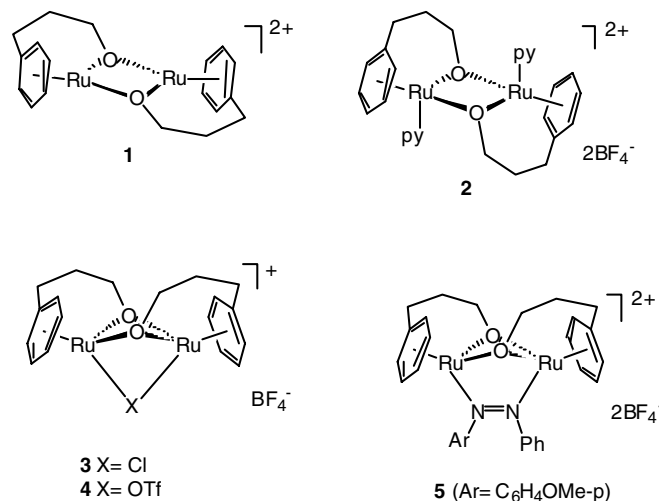
Visible light irradiation of *cis*-azobenzene bridging dinuclear  $\eta^6$ -areneruthenium complex  $[\text{Ru}_2(\eta^6\text{-}\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{cis-PhN}=\text{NC}_6\text{H}_4\text{OMe-p})](\text{BF}_4)_2$  in the presence of excess DMSO led to precipitation of a new dinuclear complex containing 1 equiv. DMSO ligand,  $[\text{Ru}_2(\eta^6\text{-}\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{DMSO})](\text{BF}_4)_2$  (**6**). A single crystal X-ray structural study of **6** revealed the presence of bridging DMSO ligand which uses O and S atoms as the donor. Treatment of **6** with 1 and 2 equiv.  $\text{NaBAR}_f$  ( $\text{BAR}_f = \text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-2,5}]_4$ ) afforded  $[\text{Ru}_2(\eta^6\text{-}\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{DMSO})(\text{BF}_4)(\text{BAR}_f)]$  and  $[\text{Ru}_2(\eta^6\text{-}\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{DMSO})(\text{BAR}_f)_2]$ , respectively, although the former was not isolated but assumed to exist only in solution by conductivity measurements. A neutral dinuclear areneruthenium complex with a bridging  $\text{SO}_4^{2-}$  ligand,  $[\text{Ru}_2(\eta^6\text{-}\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{SO}_4)]$  was prepared from the hydroxide  $[\text{Ru}_2(\eta^6\text{-}\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{OH})]\text{BF}_4$  and  $[\text{Et}_3\text{NH}](\text{HSO}_4)$ . The  $\text{SO}_4^{2-}$  ion in this complex coordinates to dicationic  $\text{Ru}_2$  center rather strongly in  $\text{CH}_2\text{Cl}_2$ , while in MeOH the complex lies in equilibrium with a complex formed by methanolysis reaction, namely methoxy bridging dinuclear complex  $[\text{Ru}_2(\eta^6\text{-}\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{OMe})]^+(\text{HSO}_4^-)$ .

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## 1. Introduction

Dinuclear metal complexes containing a four-membered unit,  $\text{M}_2\text{O}_2$  are now a ubiquitous class of complexes which play important roles in coordination chemistry. The  $\eta^5$ -cyclopentadienylruthenium and  $\eta^6$ -areneruthenium units can readily be utilized as a building block to construct a series of dinuclear ruthenium complexes with the  $\text{Ru}_2\text{O}_2$  framework made by alkoxy and hydroxy bridges [1,2]. Increasing attention has also been paid to synthesis and properties of metal complexes of the  $\eta^5$ -cyclopentadienyl and  $\eta^6$ -arene ligands having a certain functional group tethered to one of the five- and six-membered ring carbons [3,4].



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We have been studying synthesis, structure elucidation and catalytic application of dinuclear areneruthenium complexes with bridging alkoxy ligand which is tethered to the arene ring [5]. These complexes are composed of the dinuclear unit  $[\text{Ru}_2(\eta^6:\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2]^{2+}$  (**1**) containing the four-membered  $\text{Ru}_2\text{O}_2$  ring which is capable of accepting 4-electron donor groups. The 4-electron donors provide the metals with coordinative saturation, as represented by a set of two separate 2-electron donors in, e.g., **2**, bridging donors composed of one atom in, e.g., **3** and **4**, and other type of bridging donors in, e.g., **5**. Some of these dinuclear complexes are structurally rigid (e.g., **3**), so that their  $^1\text{H}$  NMR spectral feature can be understood in terms of the chiral nature of the molecule; the spectra of **3** exhibited five sets of arene proton resonances and six sets of sidearm proton resonances. In contrast, others undergo fluxional movement of ligand such as rapid dissociation–reassociation of the triflate ion in **4** to show  $^1\text{H}$  NMR spectra attributable to time-averaged non-chiral structure of the molecule; the spectra of **4** at the higher temperature exhibited three sets of both arene and sidearm proton resonances.

Here, we wish to report synthesis and solution behavior of dinuclear areneruthenium complexes composed of the dication  $[\text{Ru}_2(\eta^6:\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2]^{2+}$  and neutral, monoanionic and dianionic bridging ligands with S–O bond, namely  $\text{Me}_2\text{SO}$ ,  $\text{MeSO}_3^-$ , and  $\text{SO}_4^{2-}$ , respectively.

## 2. Results and discussion

In the previous report we found that the coordinatively unsaturated 4-electron acceptor  $[\text{Ru}_2(\eta^6:\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2]^{2+}$  (**1**) is generated by photoirradiation of *cis*-azobenzene bridging complex  $[\text{Ru}_2(\eta^6:\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{cis-PhN}=\text{NC}_6\text{H}_4\text{OMe-p})](\text{BF}_4)_2$  (**5**) [5b]. We now performed the photoirradiation of this complex in a  $\text{CH}_2\text{Cl}_2$  solution in the presence of excess DMSO to find precipitation of a new complex **6** composed of the dinuclear dicationic unit and 1 equiv. of DMSO molecule (Scheme 1). Although a speculation could be offered that the 1:1 stoichiometry of the complexation has arisen from the poor solubility of **6** in  $\text{CH}_2\text{Cl}_2$ , experiments employing the better soluble  $\text{BARf}^-$  salt ( $\text{BARf}^- = \text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-2,5}]_4$ ) (**6'**) described later suggested that the solubility issue is not the origin of the observed 1:1 stoichiometry of the complexation.

The  $\text{BF}_4^-$  salt **6** was converted to the  $\text{BARf}^-$  salt **6'** by the treatment of **6** with 2 equiv. of  $\text{NaBARf}$  in  $\text{CH}_2\text{Cl}_2$  (see Section 3). It is notable that the addition of only 1 equiv of  $\text{NaBARf}$  is enough to solubilize the dicationic complex **6**. Thus, upon a treatment of **6** (7.8 mg; 0.01 mmol) with 0.01 mmol of  $\text{NaBARf}$  all of solids of **6** dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL), where  $^1\text{H}$  NMR integrations indicated the presence of equimolar amounts of  $\text{BARf}^-$  and  $[\text{Ru}_2(\eta^6:\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{DMSO})]^{2+}$  ions. This NMR result could be explained by assuming that 0.005 mmol each of **6** and **6'** exist independently from each other in this  $\text{CD}_2\text{Cl}_2$  solution. However, this assumption can be excluded, because with the use of the same volume of  $\text{CD}_2\text{Cl}_2$ , 0.005 mmol of **6** is hardly soluble without adding  $\text{NaBARf}$ . These observations may lead us to propose the existence of a mixed anion salt  $[\text{Ru}_2(\eta^6:\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{DMSO})(\text{BF}_4)(\text{BARf})]$  as a discrete species which possesses a considerable equilibrium concentration and a good solubility. In this regard a Job plot was applied to conductivities of a series of solutions containing both  $\text{BF}_4^-$  salt **6** and  $\text{BARf}^-$  salt **6'** with the total concentration of **6** and **6'** being maintained constant (Fig. 1). The plot clearly shows that a line bends at the 50/50 ratio of **6/6'**, suggesting the occurrence of an equilibrium forming a 1:1 interaction product between **6** and **6'**. Then we tentatively suggest the formation of the mixed anion salt in solution (Scheme 2).

Attempted crystallization of the mixed anion salt by slow evaporation of solutions containing the 1:1 mixture of **6** and **6'** resulted in initial precipitation of **6**, followed by that of **6'**. An X-ray structural determination was

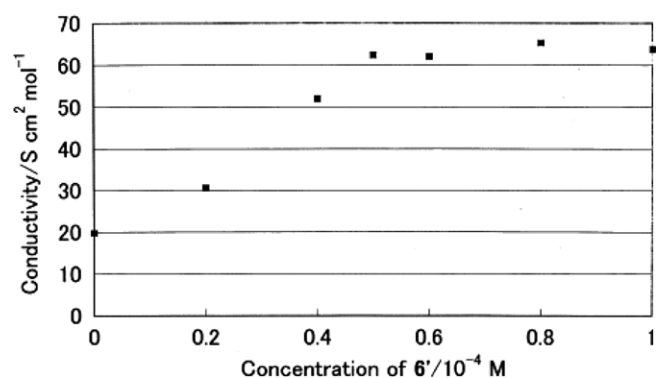
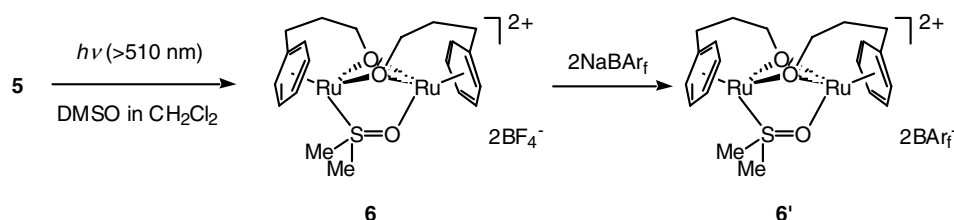
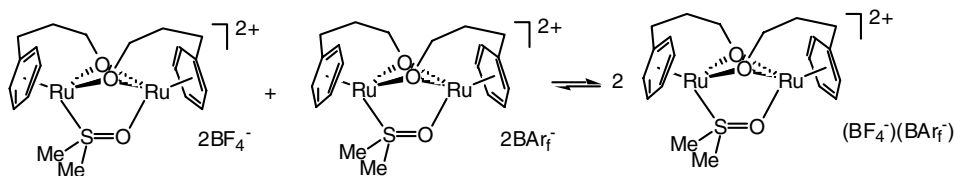


Fig. 1. Job plot for conductivity of  $\text{CH}_2\text{Cl}_2$  solutions containing **6** and **6'** at 25 °C. The total concentration of **6** and **6'** was adjusted to  $1 \times 10^{-4}$  M.



Scheme 1.



Scheme 2.

performed on a single crystal of **6** obtained from a solution of such mixture of **6** and **6'**. Although rather low quality of the crystal used and disorder of the trimethylene sidearms resulted in a structural refinement with somewhat limited accuracy regarding the geometrical parameters ( $R = 0.109$ ), the molecular connectivity was unambiguously established. The disorder is due to the existence of a pair of enantiomers in 6:4 ratio, with the major isomer being depicted in Fig. 2. In the minor isomer one trimethylene sidearm connected with O1 extends to the right arene bound to Ru2 and the other with O2 to the left arene, with the end of each arm being connected with the arene carbon meta to each ipso carbon of the major isomer. It is notable that the DMSO ligand bridges two ruthenium atoms by using *S* and *O* atoms. This type of DMSO bridge structure has been found in several dinuclear complexes such as those shown in Scheme 3, where all the examples contain the DMSO ligand bridging over two metals in the different coordination environments [6].

$^1\text{H}$  NMR spectra of the  $\text{BARf}^-$  salt **6'** were temperature dependent (Fig. 3). At 25 °C, the methyl resonances of DMSO ligand appeared as two different peaks (diastereotopic) at  $\delta$  3.31 and 3.32, suggesting that DMSO ligand is situated in a chiral environment of the dimeric areneruthenium unit. Furthermore, four multiplets integrating 2:4:2:4 (from the higher field peaks) were observed for the sidearm protons and four multiplets integrating 2:2:4:2 were observed for the arene proton resonances (see Section 3). These spectral features of the DMSO and  $\text{C}_6\text{H}_5(\text{CH}_2)_3\text{O}$  protons are not consistent with the rigid unsymmetrical structure such as shown in Fig. 2. The spectral features do not correspond to a dimeric unit having a time-averaged mirror symmetry either, which is induced by, e.g., a rapid dissociation and reassociation of DMSO ligand, as was the case of the triflate ion in complex **4** [5a]. Such a movement would have caused the complete loss of chirality of the molecule. The  $^1\text{H}$  NMR spectral features of **6'** at 25 °C are consistent with either a dimeric structure **A** having

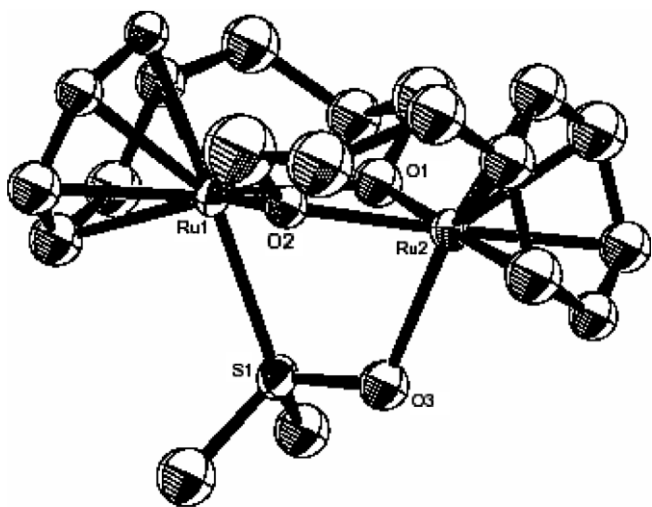
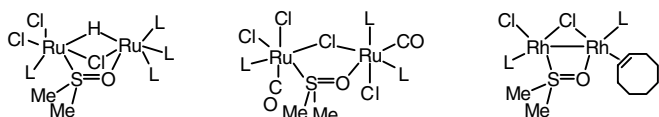


Fig. 2. ORTEP drawing of the major isomer of **6** with 50% probability level. The  $\text{BF}_4^-$  anions are not shown for clarity. Selected bond lengths (Å): Ru(1)–S(1) = 2.339(7), Ru(1)–O(1) = 2.05(2), Ru(1)–O(2) = 2.04(2), Ru(2)–O(1) = 2.08(2), Ru(2)–O(2) = 2.06(2), Ru(2)–O(3) = 2.17(2).



Scheme 3.

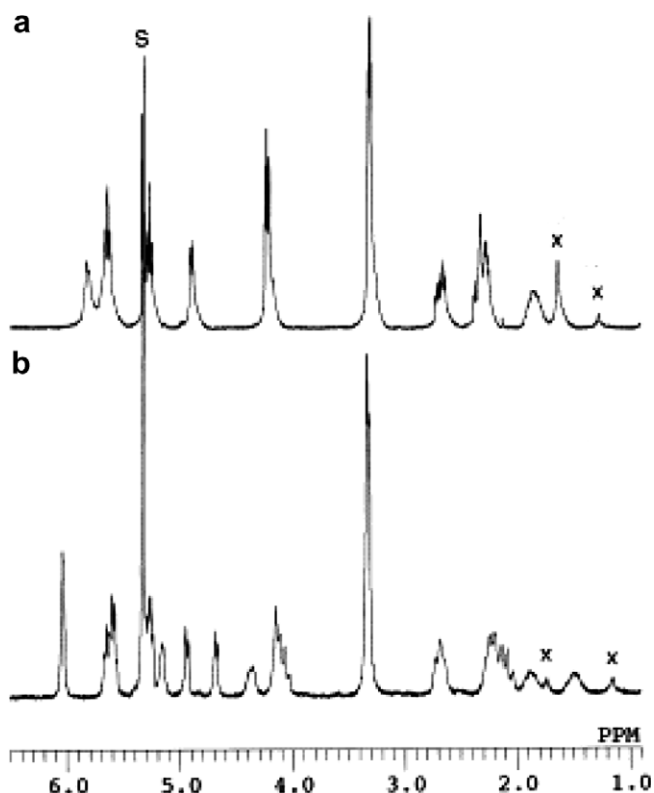
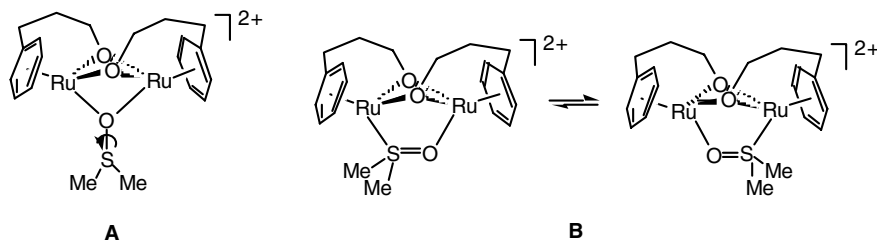
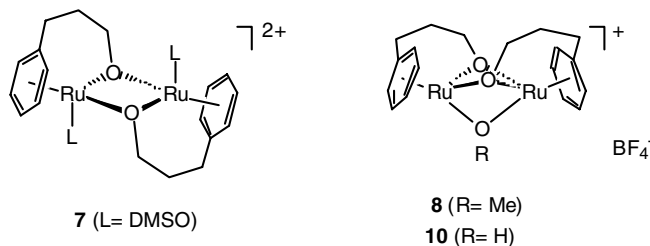


Fig. 3.  $^1\text{H}$  NMR spectra of **6'** in  $\text{CD}_2\text{Cl}_2$  at 25 °C (a) and  $-80$  °C (b). S denotes  $\text{CH}_n\text{D}_{2-n}\text{Cl}_2$  residue, and x denotes water and/or unidentified impurities.

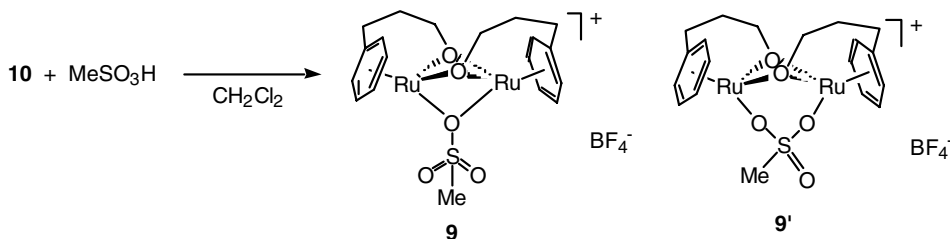
a DMSO bridge which utilizes only the oxygen atom accompanying rapid rotation about the S–O bond, or rapidly interconverting *S,O*-bridging dimers **B** (Scheme 4).

On lowering the temperature, some of the multiplets due to the sidearm and arene protons became very broad, disappeared, and reappeared at different chemical shift regions from the original to give a new set of resonances at  $-80\text{ }^{\circ}\text{C}$  as unresolved multiplets for the sidearm protons and six multiplets (integrating 1:1:1:2:3:2) for the arene protons. Unfortunately, it was not possible to correlate all of the lower temperature signals with the higher temperature signals because of appearance of many broad, overlapping signals at the intermediate temperature ranges. At the moment we cannot suggest to what fluxional movement the above  $^1\text{H}$  NMR spectral aspects of **6'** are attributed.

Next it should be pointed out that addition of an equivalent amount of free DMSO molecule to a  $\text{CD}_2\text{Cl}_2$  solution of the  $\text{BAR}_f$  complex **6'** resulted in no chemical shift change of the resonances of **6'**. In addition, the Me resonance of free DMSO also appeared separately ( $\delta$  2.55) from those of the coordinated DMSO ligand. Thus, there is no  $^1\text{H}$  NMR indication of formation of bis(DMSO) dinuclear complex (**7**), analogous to bis(acetonitrile) and bis(pyridine) complexes, as a discrete species lying in equilibrium with **6'**.



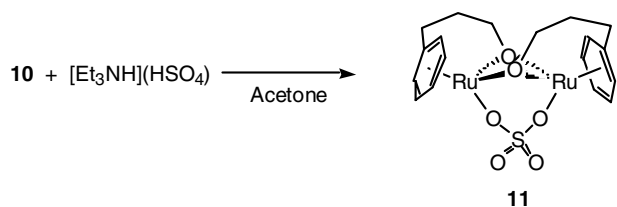
Scheme 4.



Scheme 5.

Previously, we prepared the very labile triflate bridge complex **4** from the reaction between Cl bridge complex **3** and  $\text{AgOTf}$  or MeO bridge complex **8** and triflic acid [5a]. As shown in Scheme 5, we now prepared the methanesulfonate complex **9** from methanesulfonic acid and hydroxyl bridge dinuclear complex **10** which was obtained from  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\text{Cl}_2]_2$  in a manner similar to that for obtaining the corresponding methoxy bridge complex [5a]. The  $^1\text{H}$  NMR spectra of **9** showed no temperature dependency down to  $-80\text{ }^{\circ}\text{C}$ . The spectra showed four sets of arene proton resonances integrating 4:2:2:2 and widely distributed multiplets for the sidearm proton resonances. These spectral features are not as simple as those of the triflate complex at the higher temperatures attributable to a time-averaged mirror-symmetric, non-chiral structure [5a]. We tentatively assign a rigid structure for **9** having  $\mu\text{-O}$  bridge of the methanesulfonate ligand [7]. An alternative  $\mu\text{-O,O'}$  bridge structure **9'** (Scheme 5) should have given, in principle, 12 and 10 multiplet signals for the sidearm and arene proton resonances, respectively.

Next we tried to prepare neutral dinuclear areneruthenium complex with dianionic ligands having S–O bond, e.g.,  $\text{SO}_4^{2-}$  or  $\text{SO}_3^{2-}$ . Several trials of reactions for synthesizing  $\text{SO}_4^{2-}$  bridging complex included photoirradiation of *cis*-azobenzene complex **5** in MeOH or  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{Na}_2\text{SO}_4$ , reaction of dichloride  $[\text{Ru}_2(\eta^6:\eta^1\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{Cl}_2]$  with  $\text{Ag}_2\text{SO}_4$  or  $[\text{Et}_3\text{NH}]_2(\text{SO}_4)$ . The last reaction indeed gave the desired complex in solution, but the isolation of this in a pure state turned out to be difficult. Finally, the use of  $\mu$ -hydroxy complex **10** and  $[\text{Et}_3\text{NH}](\text{HSO}_4)$  in acetone led to ready preparation of pure **11** (Scheme 6). Analogous sulfite complex was found to be too unstable to lead to its isolation [8].



Scheme 6.

Complex **11** is well soluble in  $\text{CH}_2\text{Cl}_2$  to show only a very low conductivity ( $0.7 \text{ S cm}^2 \text{ mol}^{-1}$  at  $10^{-4} \text{ M}$ ,  $25^\circ\text{C}$ ).  $^1\text{H NMR}$  spectra in  $\text{CD}_2\text{Cl}_2$  at room temperature showed the spectral pattern consistent with the chiral structure, thus indicating very rigid bridge bonding of  $\text{SO}_4^{2-}$  ion to  $[\text{Ru}_2\text{O}_2]^{2+}$  unit [9]. It should be pointed out that even addition of excess DMSO or pyridine molecule to **11** in  $\text{CD}_2\text{Cl}_2$  did not result in displacement of  $\text{SO}_4^{2-}$  by these donors. On the other hand, addition of  $\text{NaBARf}$  (2 equiv.) to **11** in wet  $\text{CD}_2\text{Cl}_2$  led to formation of white fine precipitates (probably  $\text{Na}_2\text{SO}_4$ ) and  $^1\text{H NMR}$  spectral change to show resonances attributable to a species having a time-averaged mirror symmetry. This solution readily reacted with 2 equiv. of pyridine to give bis(pyridine) coordinated dinuclear complex (Scheme 7). The aquated dicationic complex **12** might have been generated on treatment of **11** with  $\text{NaBARf}$  [10].

In the previous paper [5a] we demonstrated that the coordinatively unsaturated dication **1**, generated by either photoirradiation of **5** or treatment of the methoxy complex **8** with triflic acid, can catalyze isomerization of allyl alcohol to propionaldehyde under quite mild conditions. We now found that the similar catalysis was attained when a  $\text{CH}_2\text{Cl}_2$  solution of **11** (0.01 mmol) and allyl alcohol (0.4 mmol) was treated with 2 equiv of  $\text{NaBARf}$  at room temperature, where the catalytic efficiency was comparable to those of the previous experiments [5a]; ca. 67% yield of propionaldehyde was obtained after 20 h, while no such isomerization of allyl alcohol was induced by **11** itself without adding  $\text{NaBARf}$ . The key intermediate in this catalysis may be a bis(allyl alcohol) dicationic complex [5a] formed by replacement of the aquo ligands of **12** by allyl alcohol.

Finally, other intriguing solution behavior of **11** seems worthy of note. Thus,  $^1\text{H NMR}$  spectra of **11** dissolved in  $\text{CD}_3\text{OD}$  exhibited two sets of resonances, each attributable to a chiral dimeric unit where the relative ratio of two

Table 1  
Distribution of sulfate complex and methoxy complex in Scheme 8<sup>a</sup>

Initial concentration of <b>11</b> (M)	Sulfate complex (%)	Methoxy complex (%)
0.1	62	38
0.08	60	40
0.04	54	46
0.01	33	67
0.002	17	83

<sup>a</sup> By  $^1\text{H NMR}$  in  $\text{CD}_3\text{OD}$  at  $25^\circ\text{C}$ .

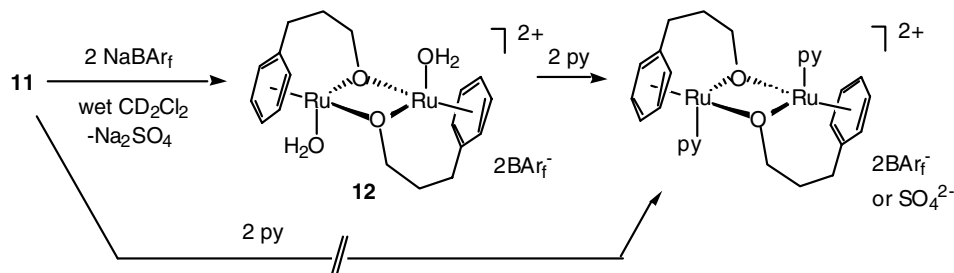
sets is dependent on the concentration of **11** dissolved initially (Table 1). One set of resonances, which dominates in the more concentrated solution, is similar to those of **11** measured in  $\text{CD}_2\text{Cl}_2$ , while the other set, which dominates in the more diluted solution, is the same as those of the authentic methoxy bridged dinuclear complex **8**. The conductivity of a methanol solution containing **11** was measured to be  $79 \text{ S cm}^2 \text{ mol}^{-1}$  at  $10^{-4} \text{ M}$ . From these results, we propose the occurrence of the following equilibrium involving methanolysis accompanied by ionic dissociation (Scheme 8). This is a very unique solvolysis reaction, and suggests that a considerably large stabilization energy should be gained by the methoxy bridge coordination to the  $[\text{Ru}_2(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2]^{2+}$  unit.

In summary, we found that the coordinatively unsaturated dinuclear areneruthenium dication is able to bind the neutral, monoanionic and dianionic ligands having S–O bond which bridge over two ruthenium atoms. Some unique solution behavior of the bridge ligands has been discussed.

### 3. Experimental section

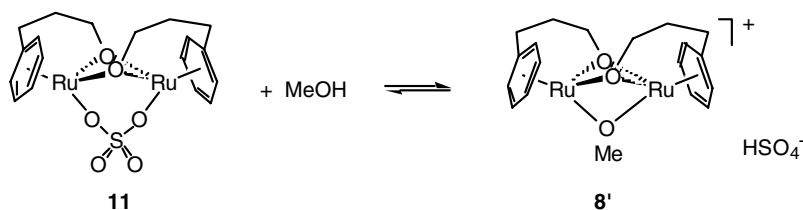
#### 3.1. General remarks

All manipulations were conducted under a nitrogen atmosphere using standard Schlenck or drybox techniques. The starting materials,  $[\text{Ru}\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}\text{Cl}_2]_2$  and **5** were prepared according to the reported methods [4h,5b].  $^1\text{H}$  nuclear magnetic resonance spectra were recorded on a JEOL GSX-270S spectrometer. The chemical shifts in the  $^1\text{H NMR}$  spectra were recorded relative to  $\text{Me}_4\text{Si}$  ( $\delta$  0.00), and residual proton peaks in deuterated solvents  $\text{CD}_2\text{Cl}_2$  ( $\delta$  5.32) and  $\text{CD}_3\text{OD}$  ( $\delta$  3.31).



Scheme 7.





Scheme 8.

### 3.2. $[Ru_2\{\eta^6:\eta^1-C_6H_5(CH_2)_3O\}_2(Me_2SO)](BF_4)_2$ (**6**)

A CH<sub>2</sub>Cl<sub>2</sub> solution (5 mL) of **5** (77 mg, 0.088 mmol) and DMSO (8.4 mg, 8 μL, 0.108 mmol) was irradiated by a tungsten lamp through a O-54 filter ( $\lambda > 510$  nm) for 5 min. Precipitates were filtered and washed by hexane. Yellow powders of **6** (58 mg, 0.080 mmol, 91%) were obtained. This compound was too insoluble in CD<sub>2</sub>Cl<sub>2</sub> to give clear <sup>1</sup>H NMR spectra. Anal. Calc. for C<sub>20</sub>H<sub>28</sub>O<sub>3</sub>S<sub>1</sub>-Ru<sub>2</sub>B<sub>2</sub>F<sub>8</sub>: C, 33.17; H, 3.90. Found: C, 33.45; H, 3.78%.

### 3.3. $[Ru_2\{\eta^6:\eta^1-C_6H_5(CH_2)_3O\}_2(Me_2SO)](BAR_f)_2$ (**6'**)

NaBAR<sub>f</sub> (85 mg, 0.096 mmol) was added to **6** (35 mg, 0.048 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the solution was filtered and evaporated under vacuum. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane to give 92 mg of yellow powders of **6'** (0.0404 mmol, 84%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 270 MHz, 25 °C):  $\delta$  1.86 (br s, 2H, sidearm), 2.25–2.38 (m, 4H, sidearm), 2.64–2.71 (m, 2H, sidearm), 3.31 (s, 3H, Me), 3.32 (s, 3H, Me), 4.22 (m, 4H, sidearm), 4.90 (d,  $J = 5.9$  Hz, 2H, ArH), 5.27 (t,  $J = 5.9$  Hz, 2H, ArH), 5.64 (t,  $J = 6.1$  Hz, 4H, ArH), 5.83 (br s, 2H, ArH), 7.58 (s, 8H, BAR<sub>f</sub>), 7.73 (s, 16H, BAR<sub>f</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 270 MHz, -80 °C)  $\delta$  1.50 (br, 1H, sidearm), 1.88 (br, 1H, sidearm), 2.03–2.24 (m, 4H, sidearm), 2.68 (br, 2H, sidearm), 3.31 (s, 3H, Me), 3.33 (s, 3H, Me), 4.07–4.14 (m, 3H, sidearm), 4.35 (br, 1H, sidearm), 4.68 (d,  $J = 5.6$  Hz, 1H, ArH), 4.94 (d,  $J = 6.1$  Hz, 1H, ArH), 5.16 (br, 1H, ArH), 5.26–5.32 (m, 2H, ArH), 5.58–5.65 (m, 3H, ArH), 6.04 (br s, 2H, ArH), 7.53 (s, 8H, BAR<sub>f</sub>), 7.72 (s, 16H, BAR<sub>f</sub>). Anal. Calc. for C<sub>84</sub>H<sub>52</sub>O<sub>3</sub>S<sub>1</sub>Ru<sub>2</sub>B<sub>2</sub>F<sub>48</sub>: C, 44.31; H, 2.30. Found: C, 44.22; H, 2.44%.

### 3.4. $[Ru_2\{\eta^6:\eta^1-C_6H_5(CH_2)_3O\}_2(MeSO_3)](BF_4)$ (**9**)

To a suspension of  $[Ru\{\eta^6-C_6H_5(CH_2)_3OH\}Cl_2]_2$  (500 mg, 0.81 mmol) in CH<sub>3</sub>CN (30 mL) was added a solution of NaOH (130 mg, 3.25 mmol) in H<sub>2</sub>O (1 mL) and NaBF<sub>4</sub> (90 mg, 0.82 mmol). After stirred for 12 h at room temperature, the mixture was filtered and the solvent was evaporated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the suspension was filtered. The filtrate was evaporated, and the residue was recrystallized from CH<sub>3</sub>CN and Et<sub>2</sub>O to give 355 mg (0.62 mmol, 76%) of yellow crystalline product  $[Ru_2\{\eta^6:\eta^1-C_6H_5(CH_2)_3O\}_2(OH)](BF_4)$  (**10**). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 270 MHz):  $\delta$  2.26 (m, 4H, sidearm), 2.45 (m,

4H, sidearm), 4.08 (m, 4H, sidearm), 4.91 (d,  $J = 5.9$  Hz, 2H, ArH), 5.04 (d,  $J = 5.7$  Hz, 2H, ArH), 5.19 (t,  $J = 5.4$  Hz, 2H, ArH), 5.42 (t,  $J = 5.7$  Hz, 2H, ArH), 5.52 (t,  $J = 5.5$  Hz, 2H, ArH). Anal. Calc. for C<sub>18</sub>H<sub>23</sub>O<sub>3</sub>B-F<sub>4</sub>Ru<sub>2</sub>: C, 38.66; H, 4.27. Found: C, 38.52; H, 4.29%. To a suspension of **10** (203 mg, 0.35 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added CH<sub>3</sub>SO<sub>3</sub>H (34 mg, 23 μL, 0.35 mmol). After stirred for 1 h at room temperature, the mixture was filtered and the solvent was evaporated. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane to give 123 mg (0.1875 mmol, 53%) of crystalline product **9**. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -80 °C, 270 MHz)  $\delta$  1.81–1.92 (m, 2H, sidearm), 2.27–2.51 (m, 6H, sidearm), 2.58 (s, 3H, Me), 4.39–4.67 (m, 4H, sidearm), 4.88 (m, 2H, ArH), 5.28 (m, 2H, ArH), 5.50–5.55 (m, 2H, ArH), 5.76–5.80 (m, 4H, ArH). Anal. Calc. for C<sub>19</sub>H<sub>25</sub>O<sub>5</sub>S<sub>1</sub>Ru<sub>2</sub>BF<sub>4</sub>: C, 34.87; H, 3.85. Found: C, 34.47; H, 3.90%.

### 3.5. $[Ru_2\{\eta^6:\eta^1-C_6H_5(CH_2)_3O\}_2(SO_4)]$ (**11**)

To a solution of **10** (576 mg, 1.0 mmol) in acetone (150 mL) was added [Et<sub>3</sub>NH][HSO<sub>4</sub>] (1.0 mmol) in acetone (50 mL) drop by drop. The mixture was stirred for 4.5 h at 0 °C to give precipitates. These were recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane to give 330 mg (0.56 mmol, 56%) of orange crystalline product. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 270 MHz):  $\delta$  2.33–2.50 (m, 8H, sidearm), 4.10–4.16 (m, 2H, sidearm), 4.31–4.38 (m, 2H, sidearm), 4.80 (d,  $J = 5.4$  Hz, 2H, ArH), 5.27 (d,  $J = 6.1$  Hz, 2H, ArH), 5.32–5.42 (m, 4H, ArH), 6.05 (t,  $J = 5.5$  Hz, 2H, ArH). IR (Nujol mulls; only peaks possibly associated with H<sub>2</sub>O and SO<sub>4</sub> groups are shown): 3433, 3490, 1233, 1220, 1189, 1061, 1032, 1011, 930 cm<sup>-1</sup>. Anal. Calc. for C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>S<sub>1</sub>Ru<sub>2</sub>·H<sub>2</sub>O: C, 36.86; H, 4.12. Found: C, 36.66; H, 3.89%.

### 3.6. $[Ru_2\{\eta^6:\eta^1-C_6H_5(CH_2)_3O\}_2(py)_2](BAR_f)_2$

Into an NMR tube containing a CD<sub>2</sub>Cl<sub>2</sub> solution (0.5 mL) of **11** (5.9 mg, 0.01 mmol) was added 17.7 mg (0.02 mmol) of NaBAR<sub>f</sub> to give white powdery precipitates. <sup>1</sup>H NMR spectrum showed resonances at  $\delta$  2.29 (br, 4H), 2.45 (br m, 4H), 4.18 (m, 4H), 5.03 (d,  $J = 5.7$  Hz, 4H), 5.30 (t,  $J = 5.5$  Hz, 2H), 5.56 (t,  $J = 5.5$  Hz, 4H), 7.57 (s, 8H), 7.72 (br s, 16H). To the suspension was added 2 μL of pyridine to result in a spectral change to show the resonances due to  $[Ru_2\{\eta^6:\eta^1-C_6H_5(CH_2)_3O\}_2(py)_2](BAR_f)_2$ .

The authentic sample of this complex was prepared by treatment of the corresponding  $\text{BF}_4$  salt  $[\text{Ru}_2\{\eta^6:\eta^1\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{O}\}_2(\text{py})_2](\text{BF}_4)_2$  [5b] with 2 equiv.  $\text{NaBARf}$  in  $\text{CH}_2\text{Cl}_2$ . Recrystallization from  $\text{CH}_2\text{Cl}_2$  and hexane gave orange crystalline product.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 270 MHz):  $\delta$  2.02–2.06 (m, 2H), 2.44–2.48 (m, 4H), 2.71–2.75 (m, 2H), 4.12 (m, 2H), 4.42 (m, 2H), 4.51 (d,  $J = 5.9$  Hz, 2H), 4.83 (t,  $J = 6.0$  Hz, 2H), 5.13 (t,  $J = 5.9$  Hz, 2H), 5.92 (d,  $J = 6.3$  Hz, 2H), 6.19 (t,  $J = 5.6$  Hz, 2H), 7.01 (t,  $J = 6.7$  Hz, 4H), 7.55–7.52 (m, 10H), 7.72 (s, 16H), 7.81 (d,  $J = 5.1$  Hz, 4H). Anal. Calc. for  $\text{C}_{92}\text{H}_{56}\text{O}_2\text{N}_2\text{B}_2\text{F}_{48}\text{Ru}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ : C, 46.30; H, 2.39; N, 1.17. Found: C, 45.85; H, 2.46; N, 1.39%.

### 3.7. Isomerization of allyl alcohol

To a  $\text{CD}_2\text{Cl}_2$  solution (0.5 mL) of **11** (5.9 mg; 0.01 mmol) and allyl alcohol (23 mg; 0.4 mmol) was added 17.7 mg (0.02 mmol) of  $\text{NaBARf}$ . The proceeding of the reaction was monitored by  $^1\text{H}$  NMR spectral measurements.

### 3.8. $[\text{Ru}_2\{\eta^6:\eta^1\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{O}\}_2\text{Cl}_2]$

To a suspension of  $[\text{Ru}_2\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}\text{Cl}_2]_2$  (1.85 g, 3 mmol) in  $\text{CH}_3\text{CN}$  (120 mL) was added  $\text{Et}_3\text{N}$  (0.607 g, 1  $\mu\text{L}$ , 7.17 mmol). After the mixture was stirred for 24 h at room temperature, the precipitate was washed by  $\text{Et}_2\text{O}$  to give 1.55 g (2.85 mmol, 95%) of orange products. Anal. Calc. for  $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Cl}_2\text{Ru}_2$ : C, 39.78; H, 4.08. Found: C, 39.70; H, 3.87%.

### 3.9. Crystal structure determination

All data were obtained on a Rigaku RAXIS RAPID diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation. All calculations were carried out with the TEXAN crystallographic software package of Molecular Structure Corp. A single crystal (0.15 mm  $\times$  0.13 mm  $\times$  0.10 mm) of **6** was obtained by cooling in a refrigerator a solution which had been prepared upon treatment of **6** with 1 equiv. of  $\text{NaBARf}$  in  $\text{CH}_2\text{Cl}_2$  followed by filtration. The structure was solved by direct methods and refined by full-matrix least-squares procedures, the function minimized being  $\sum w(|F_o| - |F_c|)^2$ . Due to the low quality of the crystal only two Ru, S and four F atoms of one  $\text{BF}_4$  group were refined anisotropically, while the other non-hydrogen atoms were refined isotropically. Part of the hydrogens was positioned by stereochemical consideration. *Crystal data for 6*:  $\text{C}_{20}\text{H}_{28}\text{O}_3\text{SB}_2\text{F}_8\text{Ru}_2$ ,  $M = 724.25$ , monoclinic, space group  $P2_1/c$  (#14),  $a = 10.5991(5)$  Å,  $b = 16.6980(8)$  Å,  $c = 14.1122(6)$  Å,  $\beta = 91.157(1)^\circ$ ,  $V = 2497.1(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1432$ ,  $D_c = 1.926$  g/cm<sup>3</sup>,  $\mu(\text{Mo K}\alpha) = 13.75$  cm<sup>-1</sup>, temperature =  $-120$  °C, 196 variables refined with 2547 reflections with  $I > 3\sigma(I)$  to  $R = 0.109$ .

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## Appendix A. Supplementary material

The CIF file for crystallographical details has been deposited at the Cambridge Crystallographical Data Center, CCDC, No.284184. Copies of this information can be obtained from the Director, CCDC, 12 Union Rd., Cambridge, CB2 1EZ, UK. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.073.

## References

- [1] (a) B. Chaudret, A. Duteil, X.D. He, J. Organometal. Chem. 391 (1990) C45; (b) U. Koelle, J. Kossakowski, J. Organometal. Chem. 362 (1989) 383.
- [2] (a) H. Le Bozec, D. Touchard, P.H. Dixneuf, Adv. Organometal. Chem. 29 (1989) 163; (b) V. Artero, A. Proust, P. Herson, P. Gouzerh, Chem. Eur. J. 7 (2001) 3901; (c) R.O. Gould, T.A. Stephenson, D.A. Tocher, J. Organometal. Chem. 263 (1984) 375; (d) R.O. Gould, C.L. Jones, T.A. Stephenson, D.A. Tocher, J. Organometal. Chem. 264 (1984) 365; (e) R.O. Gould, C.L. Jones, D.R. Robertson, D.A. Tocher, T.A. Stephenson, J. Organometal. Chem. 226 (1982) 199; (f) T. Arthur, D.R. Robertson, D.A. Tocher, T.A. Stephenson, J. Organometal. Chem. 208 (1981) 389.
- [3] (a) P. Jutzi, T. Redeker, Eur. J. Inorg. Chem. (1998) 663; (b) E. Becker, K. Mereiter, M. Puchberger, R. Schmid, K. Kirchner, A. Doppiu, A. Salzer, Organometallics 22 (2003) 3164; (c) A. Castro, M.L. Turner, P.M. Maitlis, J. Organometal. Chem. 674 (2003) 45; (d) Y. Matsushima, K. Onitsuka, T. Kondo, T. Mitsudo, S. Takahashi, J. Am. Chem. Soc. 123 (2001) 10405.
- [4] (a) J. Hannedouche, G.J. Clarkson, M. Wills, J. Am. Chem. Soc. 126 (2004) 986; (b) J. Soleimannejad, A. Sisson, C. White, Inorg. Chim. Acta 352 (2003) 121; (c) J. Soleimannejad, C. White, Organometallics 24 (2005) 2538; (d) P. Pinto, G. Marconi, F.W. Heinemann, U. Zenneck, Organometallics 23 (2004) 374; (e) K. Umezawa-Vizzini, I.Y. Guzman-Jimenez, K.H. Whitmire, T.R. Lee, Organometallics 22 (2003) 3059; (f) K.Y. Ghebreyessus, J.H. Nelson, Organometallics 19 (2000) 3387; (g) Y. Miyaki, T. Onishi, S. Ogoshi, H. Kurosawa, J. Organometal. Chem. 616 (2000) 135; (h) Y. Miyaki, T. Onishi, H. Kurosawa, Inorg. Chim. Acta 300–302 (2000) 369, and references therein.
- [5] (a) Y. Takai, R. Kitaura, E. Nakatani, T. Onishi, H. Kurosawa, Organometallics 24 (2005) 4729; (b) R. Kitaura, Y. Miyaki, T. Onishi, H. Kurosawa, Inorg. Chim. Acta 334 (2002) 142; (c) Y. Miyaki, T. Onishi, H. Kurosawa, Chem. Lett. (2000) 1334.
- [6] (a) T. Tanase, T. Aiko, Y. Yamamoto, J. Chem. Soc., Chem. Commun. (1996) 2341;

- (b) S. Geremia, S. Mestroni, M. Calligaris, E. Alessio, J. Chem. Soc., Dalton Trans. (1998) 2447;
- (c) R. Dorta, H. Rozenberg, D. Milstein, J. Chem. Soc., Chem. Commun. (2002) 710.
- [7] The rotation about the  $\mu$ -O-S bond in **9** is assumed to be rapid.
- [8] A dinuclear Rh complex with an *S,S'*-bridging thiosulfite ligand has been known: K. Shiomi, B.K. Breedlove, H. Kitayama, T. Nishioka, I. Kinoshita, N. Koga, K. Isobe, J. Chem. Soc., Chem. Commun. (2002) 1756.
- [9] The  $^1\text{H}$  NMR spectral pattern cannot distinguish between bidentate  $\mu$ -O,*O'* bridge structure and monodentate  $\mu$ -O bridge structure of  $\text{SO}_4^{2-}$  ligand. Also, the difficulty of unambiguous assignment of the IR bands of  $\text{SO}_4^{2-}$  ligand owing to the appearance of some medium to strong bands at the regions expected for this ligand cannot lead to determination of the correct  $\text{SO}_4^{2-}$  coordination mode.
- [10] The analogous bis(acetonitrile) and bis(methanol) complexes showed  $^1\text{H}$  NMR patterns attributable to the structure having a time-averaged mirror symmetry [5a,5b].