Synthesis and characterization of pentamethylcyclopentadienylrhodium(III) and -iridium(III) complexes with 1,2-benzenedithiolate $[(Cp^*Rh)_2(\mu(S)-1,2-C_6H_4S_2-S,S')_2]$, $[(Cp^*Rh)_2(\mu(S)-1,2-C_6H_4S_2-S,S')(\mu(S)-1,2-C_6H_4S(SO_2)-S,S')]$ and $[(Cp^*Ir)(1,2-C_6H_4S_2-S,S')]$ $(Cp^* = \eta^5-C_5(CH_3)_5)$ Professor Peter M. Maitlis on the occasion of his 65th birthday and in recognition of his pioneer contributions to this field

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Abstract

A reaction of the triple cubane-type organometallic polyoxomolybdate cluster, $[(Cp^*Rh)_4Mo_4O_{16}] \cdot 2H_2O$ $(1 \cdot 2H_2O)$, with 1,2-benzenedithiol gives a 1,2-benzenedithiolate-bridged dinuclear complex, $[(Cp^*Rh)_2(\mu(S)-1,2-C_6H_4S_2-S,S')_2]$ (2), and another dinuclear complex, $[(Cp^*Rh)_2(\mu(S)-1,2-C_6H_4S_2-S,S')(\mu(S)-1,2-C_6H_4S(SO_2)-S,S')]$ (3), both of which are characterized by the single-crystal X-ray diffraction method. The former complex, 2, is also obtained from a reaction of $[(Cp^*RhCl)_2(\mu-Cl)_2]$ with 1,2-benzenedithiol in the presence of $NaOCH_3$, and the latter, 3, from oxygenation of 2 with t-BuOOH. The ^1H NMR study in CD_2Cl_2 indicates that complex 2 changes gradually to a coordinatively unsaturated mononuclear complex, $[Cp^*Rh(1,2-C_6H_4S_2-S,S')]$ (4). An analogous mononuclear iridium(III) complex, $[Cp^*Ir(1,2-C_6H_4S_2-S,S')]$ (5), is also prepared and characterized by X-ray structural analysis. © 1997 Elsevier Science S.A.

1. Introduction

In previous papers [1-6], we have reported the synthesis and structure of the triple cubane-type organometallic polyoxomolybdate cluster, $[(Cp^*Rh)_4Mo_4O_{16}] \cdot 2H_2O$ $(1 \cdot 2H_2O$: $Cp^* = \eta^5-C_5(CH_3)_5)$ [1,2], and its reactivity toward methanol and
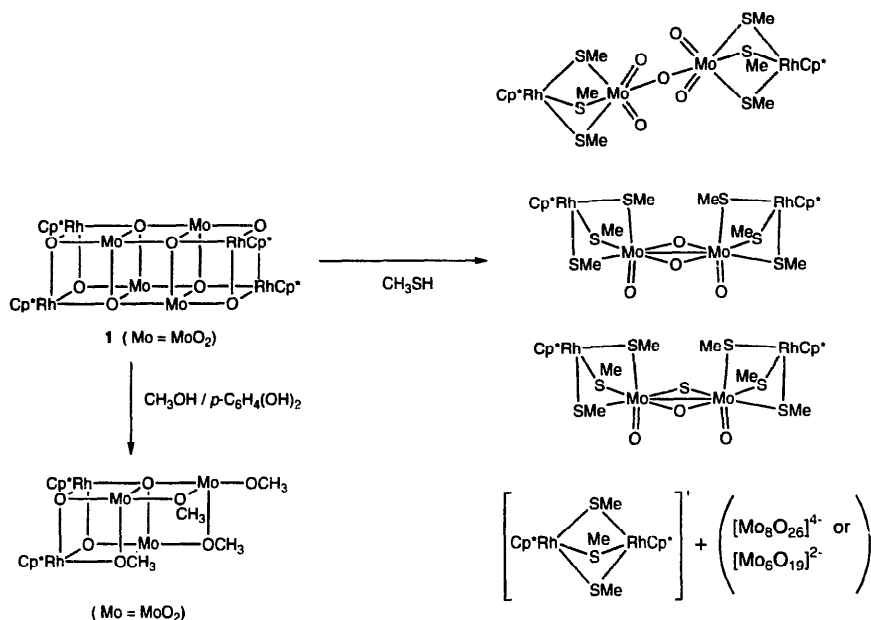
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methanethiol [3-6]. Cluster 1 in methanol in the presence of p-hydroquinone yielded the incomplete double cubane-type cluster, $[(Cp^*Rh)_2Mo_3O_9(OCH_3)_4]$ [3]. The reaction of 1 with methanethiol, in contrast, yielded three kinds of linear-type tetranuclear complexes, $[\{(Cp^*Rh)(\mu-SCH_3)_3MoO_2\}_2(\mu-O)]$, $[\{(Cp^*Rh)(\mu-SCH_3)_3MoO\}_2(\mu-O)_2]$ and $[\{(Cp^*Rh)(\mu-SCH_3)_3MoO\}_2(\mu-O)(\mu-S)]$, and two kinds of polyoxomolybdates of $[(Cp^*Rh)_2(\mu-SCH_3)_3]_2[Mo_6O_{19}]$ and $[(Cp^*Rh)_2(\mu-SCH_3)_3]_4[Mo_8O_{26}]$. The ratio of their formation is dependent on the reaction conditions (Scheme 1) [4-6]. These reactions seem to occur at first by attacking of protons on the basic bridging oxygen atoms of the triple cubane-type cluster. Therefore, we are interested in the reaction of 1 with 1,2-benzenedithiol, since it has two SH groups and the resulting dianion is expected to chelate a metal center.

Scheme 1.

2. Results and discussion

2.1. Reaction of triple cubane-type cluster 1 and 1,2-benzenedithiol

The reactions done in the present work are summarized in Scheme 2. The pure complexes isolated from the reaction mixture of 1 and 1,2-benzenedithiol do not have any oxomolybdate part, but consist of a dinuclear framework of the RhCp* groups bridged by 1,2-benzenedithiolate or 1,2-benzenethiolatesulfinate. Maitlis et al. studied the reaction of [(Cp*RhCl)₂(μ-Cl)₂] and sodium toluene-3,4-dithiolate and isolated the dinuclear complex of [(Cp*Rh)₂(S₂C₆H₃CH₃)₂] of which ¹H and ¹³C NMR spectra in CDCl₃ suggested that at least two isomers were present [7]. We have observed the same phenomena in the present study, and found that the dithiolatorhodium complex exists in a mononuclear and a dinuclear form that interconvert mutually in solution. A similar mononuclear–dinuclear interconversion in the 1,2-benzenedithiolate complexes was also reported by Rheingold et al. for [CpCo(1,2-C₆H₄S₂)] (Cp = η⁵-C₅H₅) [8]. We have isolated a mononuclear iridium(III) analogue, [Cp*Ir(1,2-C₆H₄S₂)], and found that the iridium complex exists in a mononuclear form and does not show any formation of dinuclear species in solution.
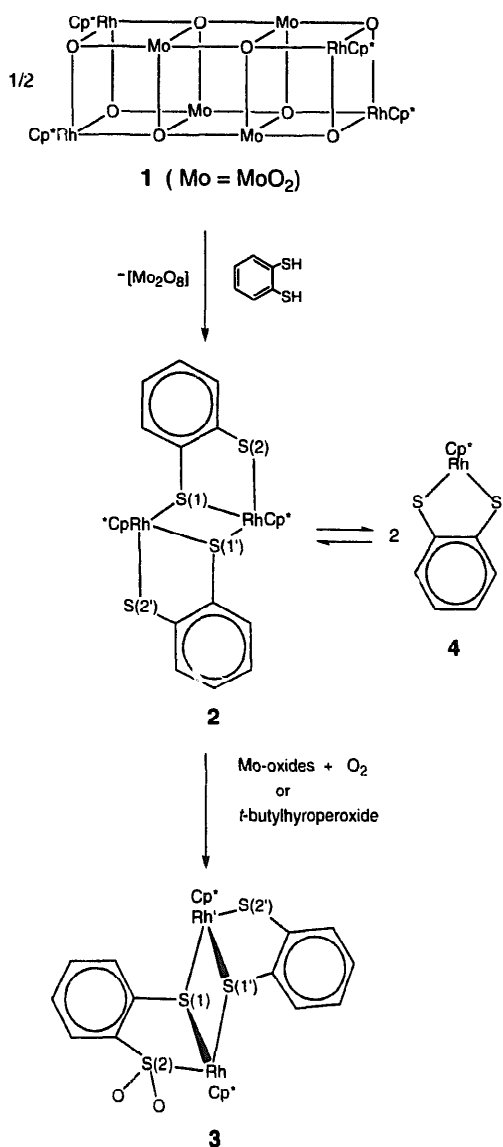
A reaction of 1·2H₂O with 1,2-benzenedithiol in methanol gives a yellow-brown precipitate consisting of several species including [(Cp*Rh)₂(μ(S)-1,2-C₆H₄S₂-S,S')₂] (2) and uncharacterized polyoxomolybdates which show a similar IR spectrum to that of [Mo₆O₁₉]²⁻.

The structure of 2 is confirmed by X-ray analysis (vide infra). When the crude precipitate is recrystallized directly from N,N-dimethylformamide (DMF) without purification using column chromatography, a different compound, [(RhCp*)₂(μ(S)-1,2-C₆H₄S₂-S,S')(μ(S)-1,2-C₆H₄S(SO₂)-S,S')] (3), is obtained. X ray analysis of 3 (vide infra) shows that it is a partially oxygenated dinuclear complex, which is probably formed by air-oxygenation of 2 during recrystallization. The bis(benzenedithiolate)-bridged complex, 2, can also be obtained in a nearly quantitative yield from a reaction of [(Cp*RhCl)₂(μ-Cl)₂] and 1,2-benzenedithiol in methanol in the presence of NaOCH₃. The partially oxygenated dinuclear complex, 3, can be prepared by oxygenation of 2 with t-butylhydroperoxide. However, recrystallization of pure 2 from DMF under the same conditions mentioned above does not give any crystal of 3; the obtained crystals are pure 2. This observation suggests that species formed during the reaction of 1 with 1,2-benzenedithiol, probably some polyoxomolybdate anions, may act as a catalyst for the oxygenation of 2 by oxygen in air to give 3.
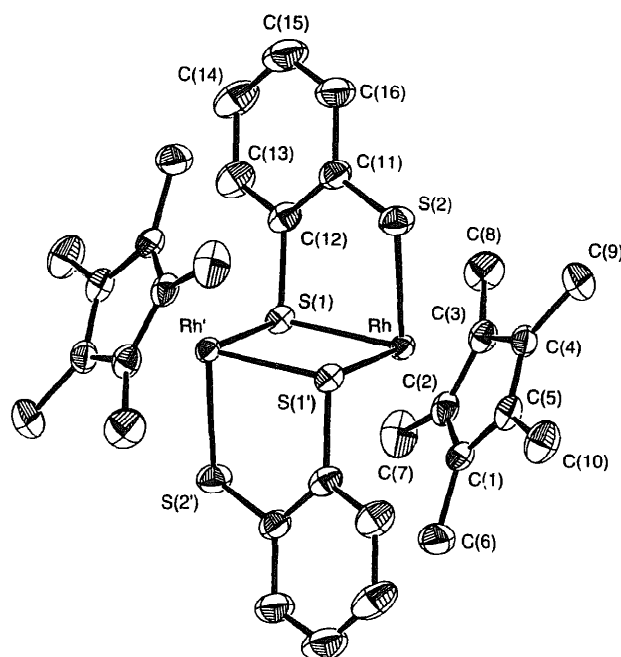
2.2. Crystal structures of 2 and 3

In Fig. 1, the structure of 2 confirmed by X-ray analysis is given with the atom-numbering scheme. The crystallographically-imposed center of symmetry makes the complex dinuclear; the 1,2-benzenedithiolate ligand acts both as a chelating ligand via S(1) and S(2) atoms and as a bridging one through the S(1) donor atom. The selected bond lengths and angles are collected in Table 1. The distance between two Rh atoms in the dinuclear

1 (Mo = MoO₂)

2

3

Scheme 2.

Fig. 1. Perspective drawing of [(Cp* Rh)₂(μ(S)-1,2-C₆H₄S₂-S,S')₂] (2).

The characterization of the partially oxygenated di-nuclear complex, **3**, was made by combination of elemental analysis, FAB-MS spectrometry, X-ray structural determination and infrared spectroscopy. The elemental analysis indicates the composition of Cp* Rh(C₆H₄S₂O), and the FAB-MS spectrum shows an isotopic distribution due to [Cp₂ Rh₂(C₆H₄S₂O)₂]⁺ (M = 788) at m/z = 788 (the most abundant mass ion peak). The results of the X-ray analysis give two possi-

structure (Rh · · · Rh' = 3.5307(8) Å) indicates no bonding interaction between them. The bond lengths between Rh and bridging S atoms are 2.356(1) Å for Rh–S(1) and 2.401(1) Å for Rh–S(1'). Although the former bond length is comparable to that of Rh–S(2) (2.358(1) Å, S(2) is not the atom bridging between two Rh atoms), the latter is quite long. This elongation seems to cause easy cleavage of the S-bridge in solution, giving the mononuclear complex (vide infra). In complex **2**, the Rh atom is not in the plane of 1,2-ben-zenedithiolate ligand; the dihedral angle between the plane defined by [Rh, S(1) and S(2)] and that by [S(1), S(2), C(11) and C(12)] is 30.0(1)°]. The non-planar structure of **2** is in contrast to the planar geometry of the iridium(III) mononuclear complex, [Cp* Ir(1,2-C₆H₄S₂-S,S')] (**5**: vide infra). The other structural parameters are normal, and the overall structure is very similar to that of [(CpCo)₂(μ(S)-1,2-C₆H₄S₂-S,S')₂] [8].

Table 1
Selected bond lengths (*l*/Å) and angles (*φ*/°) for **2**, **3** and **5**[a]

Complex	2	3	5
M · · · M'[b]	3.5307(8)	3.566(1)	–
M–S(1)	2.356(1)	2.353(2)	2.253(4)
M–S(2)	2.358(1)	2.340(3)	2.244(4)
M–S(1')	2.401(1)	2.398(2)	6.35(4)[c]
S(1)–C(12)	1.780(3)	1.770(9)	1.75(1)
S(2)–C(11)	1.761(4)	1.80(1)	1.75(1)
S(2)–O(1)	–	1.44(2)	–
S(2)–O(2)	–	1.39(1)	–
S(1)–M–S(2)	84.90(4)	85.00(9)	87.6(1)
S(1)–M–S(1')	84.15(4)	82.70(7)	–
S(2)–M–S(1')	84.59(4)	85.10(9)	–
M–S(1)–M'	95.85(3)	97.30(7)	–
M–S(1)–C(12)	102.0(2)	101.5(3)	105.6(5)
M'–S(1)–C(12)	109.4(2)	110.5(3)	–
M–S(2)–C(11)	102.1(1)	101.6(3)	106.0(5)
M–S(2)–O(1)	–	115.3(6)	–
M–S(2)–O(2)	–	119.4(6)	–

[a]M denotes Rh for **2** and **3**, and Ir for **5**.
[b]Intramolecular distance.
[c]The shortest intramolecular distance between the adjacent M and S atoms.
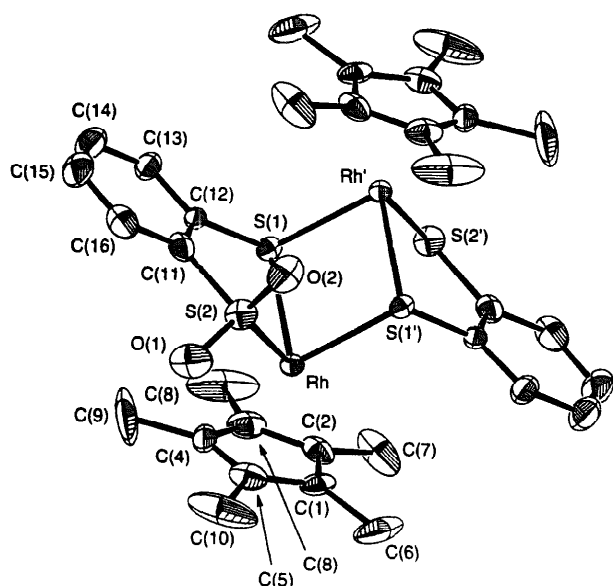
Fig. 2. Perspective drawing of one stereoisomer of [(Cp⁻Rh)₂(μ(S)-1,2-C₆H₄S₂-S,S')(μ(S)-1,2-C₆H₄S(SO₂)-S,S')] (3).

ble structures for complex 3: a bis(1,2-benzenethiolatesulfenate)-bridged dinuclear structure and a (1,2-benzenedithiolate)(1,2-benzenethiolatesulfinate)-

bridged one. In the former structure, two oxygen atoms are bound to S(2) and S(2') atom, separately and four possible stereoisomers are arranged at random in the crystal, giving the X-ray structural pattern. In the latter, both oxygen atoms are bound to one S(2) atom, but not the other S(2') atom of the dinuclear structure as shown in Scheme 2, and crystal-packing disorder of the dinuclear complex makes a crystallographically-imposed center of symmetry and the X-ray structural patterns. The obtained S–O bond lengths (1.44(2), 1.39(1) Å) are comparable with those of sulfinate complexes of cobalt(III) [9–11] and nickel(II) [12,13] (1.38–1.49 Å), but considerably shorter than those of sulfenate complexes (1.53–1.55 Å) [14,15]. Furthermore, the IR spectrum of 3 shows two strong absorption bands at 1061 and 1189 cm⁻¹ due to ν(S–O), the values correspond well to those of sulfinate complexes (two strong bands: 1090–1050 and 1220–1170 cm⁻¹) [9,13,15], not to those of sulfenate complexes which show only one strong band due to ν(S–O) vibration around 1010–950 cm⁻¹ [15,16]. Therefore, we conclude that 3 is a dinuclear sulfinate complex of [(Cp⁻Rh)₂(μ(S)-1,2-C₆H₄S₂-S,S')(μ(S)-1,2-C₆H₄S(SO₂)-S,S')]. The structure of 3 is shown in Fig. 2 (one of two possible stereoisomers), and the selected bond lengths and angles are collected in Table 1.
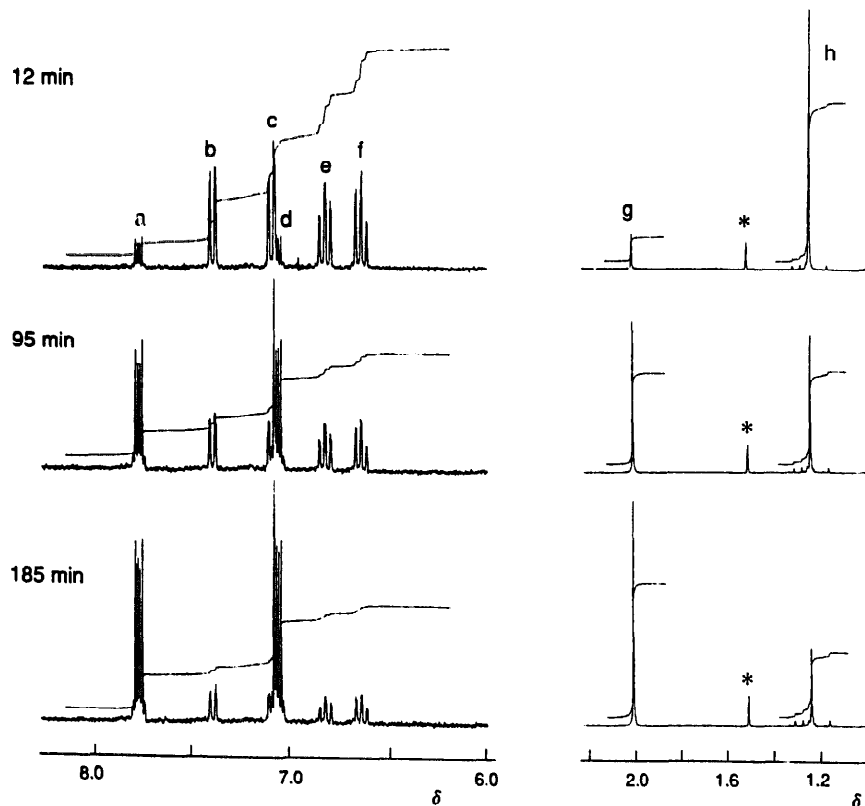
Fig. 3. The ¹H NMR spectral change for CD₂Cl₂ solution of 2 at 26°C, representing the 1,2-benzenedithiolate (left) and methyl (Cp⁻) signal regions. [2] = 3.3 × 10⁻² M. Signal assignment, b and c: 2- and 5-H (1,2-benzenedithiolate) for [(Cp⁻Rh)₂(μ(S)-1,2-C₆H₄S₂-S,S')₂]; e and f: 3- and 4-H (1,2-benzenedithiolate) for [(Cp⁻Rh)₂(μ(S)-1,2-C₆H₄S₂-S,S')₂]; a and d: 2,5- and 3,4-H (1,2-benzenedithiolate) for [(Cp⁻Rh)(1,2-C₆H₄S₂-S,S')]; g: CH₃ (Cp⁻) for [(Cp⁻Rh)(1,2-C₆H₄S₂-S,S')]; h: CH₃ (Cp⁻) for [(Cp⁻Rh)₂(μ(S)-1,2-C₆H₄S₂-S,S')₂]; an asterisk: water.

2.3. Behavior of 2 in solution

As shown in Fig. 3, top (12 min), the ^1H NMR spectrum taken 12 minutes after the single crystals of 2 were dissolved in CD_2Cl_2 at room temperature showed a dominant species consisting of four multiplet peaks at δ 7.39, (doublet, signal b), 7.09 (doublet, signal c), 6.83 (triplet, signal e), and 6.65 (triplet, signal f) assignable to the phenyl protons, along with a singlet peak at δ 1.25 for the methyl protons of the Cp^* rings (signal h). All of these signals are ascribed to the dinuclear structure of 2 determined by single-crystal X-ray analysis (vide supra). However, as seen in this spectrum, additional smaller peaks also exist: two virtually coupled quartet peaks at δ 7.78 (signal a) and 7.06 (signal d), and a singlet at δ 2.01 (signal g). The spectrum showed time-dependence; the latter set of signals grew up gradually with time, while the former decreased in intensity (Fig. 3, the middle (95 min) and the bottom (185 min)). Since the spectral pattern of virtual quartet peaks are similar to those of free 1,2-benzenedithiol, we assume that the latter species corresponds to a mononuclear 1,2-benzenedithiolate complex, $[Cp^*Rh(1,2\text{-}C_6H_4S_2\text{-}S,S')]$ (4). This assumption is derived from the X-ray analytical result of 2 described above: one of the Rh–$S_{bridging}$ bond length (2.401(1) Å for Rh–S(1')) is much longer than the other (2.356(1) Å for Rh–S(1)), which does indicate that the Rh–$S_{bridging}$ bond can be cleaved easily in solution. Further support to the mononuclear formula of 4 was obtained from the similarity in its ^1H NMR spectrum (the dominant set found in Fig. 3, the bottom) to that of the iridium(III) analogue, $[Cp^*Ir(1,2\text{-}C_6H_4S_2\text{-}S,S')]$ (5). The formation rate constant of the mononuclear complex 4 in CD_2Cl_2 was estimated to be $6.7 \times 10^{-5}\ s^{-1}$ at 26°C, and the activation parameters obtained between the temperature range from 26 to 38°C were $\Delta H^{\ddagger} = +128 \pm 13$ kJ mol^{-1} and $\Delta S^{\ddagger} = 103 \pm 43$ J $K^{-1}\ mol^{-1}$.

The mononuclear complex 4 is isolated by rapid precipitation on addition of diethyl ether to the CH_2Cl_2 solution containing the dinuclear and mononuclear mixture in an equilibrium (Scheme 2). The obtained red precipitate showed a different infrared spectrum from that of single crystal of 2 (dinuclear complex), especially for the absorption band due to in-plane bending of the ortho-disubstituted phenyl ring [17]. The crystal of dinuclear complex 2 showed a strong absorption band due to the bending vibration at 740 cm^{-1}, although the corresponding band of the precipitate appeared at 762 cm^{-1}. It should be noted that the dinuclear complex of 3 shows the band at 748 cm^{-1}, and the mononuclear iridium(III) complex (5) whose structure would be discussed in Section 2.4 showed at 761 cm^{-1}. We suggest that the absorption band is sensitive to the mononuclear–dinuclear structural change, and hence, the precipitate obtained from rapid addition of diethyl ether is

the mononuclear complex, 4. Throughout the X-ray, NMR and infrared spectroscopic studies, it is concluded that the complex of '$Cp^*Rh(1,2\text{-}C_6H_4S_2)$' in solution exists as an equilibrium mixture with the major species of the mononuclear 4 and the minor one of the dinuclear 2 complexes (equilibrium constant at 26°C: $K \approx 1.0 \times 10^{-1}$). The mixture deposits exclusively crystals of 2 by slow crystallization, but the rapid precipitation leads to form the solid of 4 selectively. In contrast to 2, the 1,2-dicyanoethene-1,2-dithiolate complex has the stable mononuclear form of $[Cp^*Rh(1,2\text{-}C_2(CN)_2S_2)]$ (1,2-$C_2(CN)_2S_2$ = 1,2-dicyanoethene-1,2-dithiolate) both in solid and solution [18].

Interestingly, complex 3 having a dinuclear structure similar to that of 2 does not show any conversion into mononuclear species in solution. The oxygenation of an S atom in two 1,2-benzenedithiolate ligands in the dinuclear structure might affect the electronic state of the whole molecule of 3 to prevent the interconversion.

2.4. Iridium(III) complex

Iridium(III) complexes are, in general, kinetically inert compared to the corresponding rhodium(III) complexes, and therefore, it may be possible to crystallize the mononuclear complex analogous to 4. Red-brown crystals of an iridium(III) complex with 1,2-benzenedithiolate was obtained from a similar method using $[(Cp^*IrCl)_2(\mu\text{-}Cl_2)_2]$. It is a mononuclear complex of $[Cp^*Ir(1,2\text{-}C_6H_4S_2\text{-}S,S')]$ (5) both in the solid state and in solution. The FAB-MS spectrum of 5 does not show any isotopic distribution envelope in the higher region than that of the mononuclear mother ion ($[Cp^*Ir(1,2\text{-}C_6H_4S_2)]^+$: $m/z = 468$). The crystal structure is confirmed by X-ray analysis; there is a crystallographically-imposed center of symmetry, but the symmetry does not make the complex dinuclear. The shortest intermolecular Ir · · · S distance is 6.35(4) Å. The structure is shown in Fig. 4, and selected bond lengths and angles are collected in Table 1. The complex seems

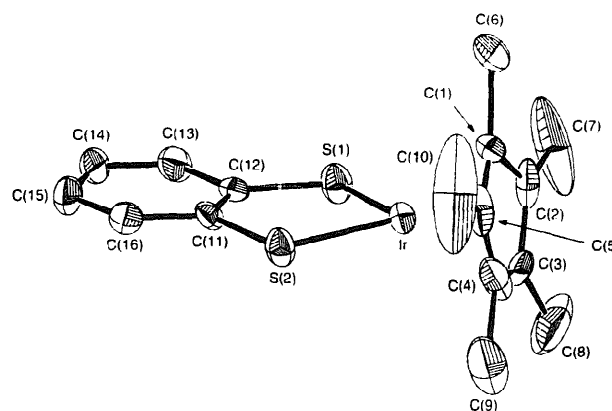Fig. 4. Molecular structure of $[Cp^*Ir(1,2\text{-}C_6H_4S_2\text{-}S,S')]$ (5).

to be coordinatively unsaturated five-coordinate species. The Ir–S bond lengths (Ir–S(1) = 2.253(4) Å, Ir–S(2) = 2.244(4) Å) are significantly shorter than the normal Ir^{III}–SR_2 bond length (2.35 Å) [19], or the Rh^{III}–S bond lengths in 2 and 3 (Table 1). A similar shortening of M–S bond is observed in the mononuclear $[CpCo(1,2-C_6H_4S_2-S,S')]$ and $[Ru(1,2-C_6H_4S_2-S,S')(PMe_3)_2]^n$ ($n = -1, 0$) [8,20], but not in $[Cp^*Rh(1,2-C_2(CN)_2S_2)_2]$ [18]. The short M–S bonds in the coordinatively unsaturated mononuclear complexes are interpreted by Sellmann's explanation [21]; in order to achieve the 18-electron configuration of the M^{III} (M = Ir, Co) center, the thiolate ligand donates its p-electron to the metal, and consequently, the M–S bonds have 1.5 bond character. The p-electron donation from S atoms of the chelated 1,2-benzenedithiol ligand should make the metallacyclic planar. In fact, the iridium atom is almost in the plane of the 1,2-benzenedithiolato ligand, and the dihedral angle between the plane defined by [Ir, S(1) and S(2)] and that by [S(1), S(2), C(11) and C(12)] is 7.3(4)°, the value being much smaller than the corresponding value of 2 or 3. The iridium(III) complex, 5, is stable in solution; no dimerization reaction is observed in the NMR spectrum. In the ^1H NMR spectrum, even at a week after the crystal was dissolved, only one singlet peak for methyl protons of the Cp^* ligand and two virtually coupled quintet peaks for phenyl protons were observed. The ^{13}C NMR spectrum also corresponds to the mononuclear structure: two and three resonances for Cp^*-ring and phenyl-ring carbons, respectively.

3. Conclusion

The reaction of the triple cubane-type cluster $[(Cp^*Rh)_4Mo_4O_{16}] \cdot 2H_2O$ with CH_3OH gives the incomplete double cubane-type cluster, $[(Cp^*Rh)_2Mo_3O_9(OCH_3)_4]$, where the OCH_3 groups bind selectively to hard molybdenum(VI) centers [3]. The reaction with methanethiol under mild conditions affords the tetranuclear complexes with the Mo-(μ-SCH_3)-Rh bridging system such as $[((Cp^*Rh)(\mu$-$SCH_3)_3MoO_2)_2(\mu$-$O)]$, $[((Cp^*Rh)(\mu$-$SCH_3)_3MoO)_2(\mu$-$O)_2]$ and $[((Cp^*Rh)(\mu$-$SCH_3)_3MoO)_2(\mu$-$O)(\mu$-$S)]$ [4,6]. As described in this paper, even under mild reaction conditions, 1,2-benzenedithiol induces a reconstruction of the cluster framework separating the organorhodium and oxide parts with formation of $[(Cp^*Rh)_2(\mu(S)$-$1,2$-$C_6H_4S_2$-$S,S')_2]$ (2) that displays the mononuclear–dinuclear interconversion in solution and uncharacterized oxo-molybdates that show a similar IR spectrum to that of $[Mo_6O_{19}]^{2-}$.

4. Experimental

All preparative procedures were performed under an Ar atmosphere unless otherwise noted. Methanol was distilled over magnesium. $[(Cp^*RhCl)_2(\mu$-$Cl)_2]$ [22] and the triple cubane-type oxide cluster, $[(Cp^*Rh)_4Mo_4O_{16}]$ [1], were prepared according to the literature procedures, respectively. 1,2-Benzenedithiol (96%, $d = 1.236$) was obtained from commercial source (Aldrich). Elemental analyses were performed by the IMS Chemical Material Center. IR spectra were measured in KBr pellets on a Perkin Elmer 1600 series FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on JEOL GX 400 NMR and JEOL EX-270 FT-NMR spectrometers in $CDCl_3$ and CD_2Cl_2, and the chemical shifts were referenced to TMS. FAB mass spectra were obtained with a Shimadzu/Kratos CONCEPT 1S mass spectrometer.

4.1. Reaction of triple cubane-type cluster 1 and 1,2-benzenedithiol

To an orange solution of $[(Cp^*Rh)_4Mo_4O_{16}] \cdot 2H_2O$ (1 · $2H_2O$) (1.00 g, 0.61 mmol) in methanol (25 cm^3) was added a methanolic solution (25 cm^3) of 1,2-benzenethiol (0.20 cm^3, 1.67 mmol) with stirring at room temperature; the mixture was stirred for an hour. The color of the mixture was changed to deep-red, and a yellow–brown precipitate was formed, which was collected by filtration and dried in air. The crude product was extracted with dichloromethane (2 cm^3). The remaining solid was used for the IR measurement and the solution was subjected on a column (ϕ 3 cm × 50 cm) of silica gel. Elution with a mixture of dichloromethane and acetone (20:1) gave three bands, and the fastest-moving purple band was collected. The eluate was evaporated to dryness under reduced pressure, giving purple crystals of $[(Cp^*Rh)_2(\mu(S)$-$1,2$-$C_6H_4S_2$-$S,S')_2]$ (2; 0.36 g, 39%). When the crude precipitate was recrystallized from N,N'-dimethylformamide (DMF), that is, the solution was allowed to stand for 2 weeks in air, a small amount of red crystals of $[(Cp^*Rh)_2(\mu(S)$-$1,2$-$C_6H_4S_2$-$S,S')(\mu(S)$-$1,2$-$C_6H_4S(SO_2)$-$S,S')]$ (3) were obtained.

4.2. Preparation of 2 from $[(Cp^*RhCl)_2(\mu$-$Cl)_2]$

A methanolic solution (40 cm^3) of 1,2-benzenedithiol (0.80 cm^3, 6.67 mmol) and sodium methoxide (0.70 g, 13.0 mmol) was added with stirring to a methanolic solution (60 cm^3) of $[(Cp^*RhCl)_2(\mu$-$Cl)_2]$ (2.00 g, 3.24 mmol), and the mixture was stirred for six hours. The resulting deep-purple precipitate was filtered, washed with methanol (5 cm^3), and then dried in air.

Recrystallization of the crude product from a mixture of dichloromethane and ethanol (1:2) gave purple crystals of **2** (1.90 g, 79%). (Found: C, 50.23; H, 4.97%; M^+ 756. $C_{32}H_{38}Rh_2S_4$ requires C, 50.79; H, 5.06%; M 756); $\tilde{v}_{max}$/cm^{-1} (KBr) 740s (in-plane bending of *ortho*-disubstituted benzene ring); δ_H (CD$_2$Cl$_2$, 23°C) 1.25 (30H, s, C_5Me_5), 6.65 (2H, m, $S_2C_6H_4$), 6.83 (2H, m, $S_2C_6H_4$), 7.09 (2H, m, $S_2C_6H_4$) and 7.39 (2H, m, $S_2C_6H_4$); δ_C (CD$_2$Cl$_2$, 23°C) 8.11 (s, C_5Me_5), 96.99 (d, C_5Me_5, J(RhC) = 4.6 Hz), 120.60 (s, $S_2C_6H_4$), 125.52 (s, $S_2C_6H_4$), 128.90 (s, $S_2C_6H_4$), 131.31 (s, $S_2C_6H_4$), 139.54 (s, $S_2C_6H_4$), 157.88 (s, $S_2C_6H_4$).

For the mononuclear complex of **4**, which exists in solution: δ_H (CD$_2$Cl$_2$, 23°C) 2.01 (30H, s, C_5Me_5), 7.06 (4H, virtually coupled quartet, $S_2C_6H_4$) and 7.78 (4H, virtually coupled quartet, $S_2C_6H_4$); δ_C (CD$_2$Cl$_2$, 23°C) 10.91 (s, C_5Me_5), 99.00 (d, J(RhC) = 7.7 Hz,

C_5Me_5), 122.51 (s, $S_2C_6H_4$), 130.11 (d, $S_2C_6H_4$), 153.26 (s, $S_2C_6H_4$).

4.3. Preparation of 3 by oxygenation of 2 with t-butyl-hydroperoxide

Complex **2** (0.30 g, 0.38 mmol) and *t*-butylhydroperoxide in dichloromethane (30 cm^3) were stirred for 24 hours at room temperature, and then the mixture was evaporated to dryness under reduced pressure. The reddish residue was dissolved in dichloromethane, and the solution was subjected on a column (ϕ3 cm × 50 cm) of silica gel. The chromatography using a mixture of dichloromethane and acetone (1:1) as an eluent gave three bands, and the third band was collected and evaporated to dryness under reduced pressure. Recrystallization from DMF gave red crystals of **3** (0.05 g, 16%). (Found: C, 48.16; H, 4.69%; M^+ 788.

Table 2
Crystallographic data and experimental conditions for **2**, **3** and **5**

Complex	2	3	5
Formula	$C_{32}H_{38}Rh_2S_4$	$C_{32}H_{38}O_2Rh_2S_4$	$C_{16}H_{10}IrS_2$
Formula weight	756.70	788.70	467.67
Crystal size/mm³	0.25 × 0.2 × 0.2	0.32 × 0.25 × 0.2	0.72 × 0.32 × 0.2
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Lattice constants			
a/Å	10.590(2)	11.386(4)	8.437(2)
b/Å	10.959(3)	9.767(4)	13.832(1)
c/Å	8.117(2)	14.310(3)	13.819(2)
α/°	111.12(2)	90	90
β/°	101.11(2)	98.04(2)	90.95(1)
γ/°	61.31(2)	90	90
V/Å³	770.6(4)	1575.6(8)	1612.47(4)
Z	1	2	4
D_x/g cm⁻³	1.63	1.66	1.93
μ(Mo K$_\alpha$)/mm⁻¹	1.36	1.30	8.52
$F(000)$	384	800	896
Scan type	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$
Scan width/°	1.15 + 0.5 tanθ	1.2 + 0.5 tanθ	1.0 + 0.5 tanθ
Scan speed/° min⁻¹ (in θ)	4	6	5
Octants measured	+h, ±k, ±l	+h, +k, +l	+h, ±k, ±l
No. reflns. collected	4729	5074	10032
No. independent reflns.	4500	4597	4719
R_{int}	0.027	0.042	0.100
Decay of standard intensities	0.02	0.02	0.04
Transmission coefficient, A	0.728–0.799	0.939–1.000	0.056–0.221
No. parameters refined	248	268	248
No. reflns. used for calculation	3529	2188	2722
Cutoff criteria	$|F_o| > 3\sigma(|F_o|)$	$|F_o| > 3\sigma(|F_o|)$	$|F_o| > 3\sigma(|F_o|)$
R^a	0.037	0.061	0.068
R_w^b	0.039	0.051	0.073
S^c	1.25(2)	1.27(2)	1.70(2)
$\Delta\rho$/eÅ⁻³	−0.47–0.88	−0.74–1.01	−4.73–3.73^d

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = (\Sigma_w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.
[c] $S = (\Sigma w(|F_o| - |F_c|)^2)^{1/2}/(n_{data} - n_{par})$.
[d] All intense residual peaks are close to the metal atom.

$C_{32}H_{38}O_2Rh_2S_4$ requires C, 48.73; H, 4.86%; M 788); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 748s (in-plane bending of *ortho*-disubstituted benzene ring), 1189s (SO), 1061s (SO); δ_H (CD$_2$Cl$_2$, 23°C) 1.24 (30H, s, C$_5$Me$_5$), 1.28 (30H, s, C$_5$Me$_5$), 7.87-6.67 (m, S$_2$(O)C$_6$H$_4$);λ_{max}/nm (ε/M^{-1} cm^{-1}): 474 (7.25 × 10^3), 354 (2.02 × 10^4), 257 (5.32 × 10^4).

4.4. Preparation of [(Cp*Ir)(1,2-C$_6$H$_4$S$_2$-S,S')] (5)

A methanolic solution (40 cm^3) of 1,2-benzenedithiol (0.60 cm^3, 5.0 mmol) and sodium methoxide (0.54 g, 10.0 mmol) was added dropwise with stirring to a methanolic solution (80 cm^3) of [(Cp*IrCl)$_2$(μ-Cl)$_2$] (2.00 g, 2.51 mmol), and the mixture was stirred for 15 hours. The volume of the mixture was reduced to ca. 10 cm^3 under reduced pressure, giving a red-brown precipitate of 5. The precipitate was collected by filtration, washed with diethyl ether and hexane, and then dried in vacuo. Recrystallization of the crude product from a mixture of methanol and dichloromethane gave red prismatic crystals of 5 (2.11 g, 90%). (Found: C, 40.83; H, 4.03%; M$^+$ 468. C$_{16}$H$_{19}$IrS$_2$ requires C, 41.09; H, 4.09; M 468); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 761s (in-plane bending of *ortho*-disubstituted benzene ring); δ_H (CD$_2$Cl$_2$, 23°C) 2.13 (15H, s, C$_5$Me$_5$), 6.99 (2H, virtually coupled quartet, S$_2$C$_6$H$_4$) and 7.97 (2H, virtually coupled quartet, S$_2$C$_6$H$_4$); δ_C (CD$_2$Cl$_2$, 23°C) 10.51 (s, C$_5$Me$_5$), 92.22 (s, C$_5$Me$_5$), 122.79 (s, S$_2$C$_6$H$_4$), 129.53 (s, S$_2$C$_6$H$_4$) and 153.54 (s, S$_2$C$_6$H$_4$); λ_{max}/nm (ε/M^{-1} cm^{-1}): 537 (1.93 × 10^3), 419 (1.28 × 10^4), 295 (sh). 289 (8.10 × 10^3), 251 (3.27 × 10^4).

4.5. Crystal structure determinations

Crystals of 2, 3, and 5 suitable for X-ray analyses were obtained from recrystallization from dichloromethane, DMF, and a mixture of dichloromethane and methanol, respectively, and were mounted on glass fibers. Crystal data and experimental conditions were collected in Table 2. Intensity data were obtained on a Rigaku AFC-5 four-circle diffractometer at 23°C with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The final lattice constants were determined by least-squares treatments using setting angles of 25 reflections in the 25° < 2θ < 30° range. The intensities were corrected for Lorentz and polarization effects and absorption corrections were made either by the numerical Gauss integration method [23] or by an empirical method based on a set of Ψ scan data [24]. The structures were solved by the usual heavy-atom method; the position of Rh or Ir atom was derived by Patterson function, and all the other non-hydrogen atoms were located by the Fourier technique. The positions of hydrogen atoms were located at the positions generated either by difference Fourier synthe-

ses or by theoretical calculations. The function, $\Sigma w||F_o| - |F_c||^2$, with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ was minimized by full-matrix least-squares methods using anisotropic and isotropic thermal parameters for all non-hydrogen and hydrogen atoms, respectively. Complex neutral-atom scattering factors were used [25]. All of the calculations were carried out on a Fujitsu S-4/IX workstation using Xtal 3.2 program packages [26]. Final atomic coordinates of 2, 3, and 5 are listed in Tables 3-5, respectively.

Table 3
Final atomic coordinates of non-hydrogen atoms for 2

Atom	x / a	y / b	z / c
Rh	0.59650(3)	0.06849(3)	0.43495(4)
S(1)	0.49306(9)	0.1104(1)	0.6943(1)
S(2)	0.3639(1)	0.2345(1)	0.3685(1)
C(1)	0.8344(4)	−0.0525(4)	0.4175(5)
C(2)	0.7960(4)	0.0746(4)	0.5683(5)
C(3)	0.7108(4)	0.2008(4)	0.5114(5)
C(4)	0.7022(4)	0.1510(4)	0.3221(5)
C(5)	0.7741(4)	−0.0045(4)	0.2634(5)
C(6)	0.9338(5)	−0.2063(5)	0.4181(9)
C(7)	0.8432(7)	0.0725(9)	0.7546(7)
C(8)	0.6499(6)	0.3574(5)	0.6261(7)
C(9)	0.6337(6)	0.2483(6)	0.2059(8)
C(10)	0.7938(7)	−0.1012(7)	0.0753(7)
C(11)	0.2918(4)	0.3411(4)	0.5801(5)
C(12)	0.3474(4)	0.2888(4)	0.7233(5)
C(13)	0.2871(5)	0.3745(5)	0.8902(6)
C(14)	0.1694(5)	0.5108(5)	0.9113(7)
C(15)	0.1108(6)	0.5626(5)	0.7666(8)
C(16)	0.1720(5)	0.4801(5)	0.6027(7)

Table 4
Final atomic coordinates of non-hydrogen atoms for 3

Atom	x / a	y / b	z / c
Rh	0.09567(6)	0.55224(7)	0.41805(5)
S(1)	0.1005(2)	0.5374(2)	0.5827(1)
S(2)	0.1557(3)	0.3230(3)	0.4283(2)
O(1)^a	0.248(2)	0.287(2)	0.373(1)
O(2)^a	0.071(1)	0.221(1)	0.429(1)
C(1)	0.0834(9)	0.766(1)	0.3651(9)
C(2)	0.190(1)	0.748(1)	0.4250(8)
C(3)	0.2576(9)	0.648(1)	0.3889(9)
C(4)	0.196(1)	0.605(1)	0.3027(8)
C(5)	0.090(1)	0.675(1)	0.2866(7)
C(6)	−0.011(2)	0.873(2)	0.374(2)
C(7)	0.222(4)	0.832(3)	0.518(1)
C(8)	0.379(2)	0.603(5)	0.437(4)
C(9)	0.243(3)	0.508(2)	0.234(2)
C(10)	0.003(3)	0.667(3)	0.195(2)
C(11)	0.2346(8)	0.315(1)	0.5461(8)
C(12)	0.2077(7)	0.4075(9)	0.6118(6)
C(13)	0.271(1)	0.404(1)	0.7035(8)
C(14)	0.355(1)	0.305(2)	0.726( )
C(15)	0.380(1)	0.210(1)	0.662(1)
C(16)	0.322(1)	0.213(1)	0.570(1)

^{a}Population of these atoms is 0.5.

Table 5
Final atomic coordinates of non-hydrogen atoms for **5**

Atom	x/a	y/b	z/c
Ir	0.68206(7)	0.32070(4)	0.25610(4)
S(1)	0.5501(5)	0.4038(3)	0.1400(3)
S(2)	0.5395(5)	0.4021(3)	0.3649(3)
C(1)	0.926(2)	0.299(1)	0.265(2)
C(2)	0.861(3)	0.238(1)	0.175(1)
C(3)	0.758(2)	0.176(1)	0.223(2)
C(4)	0.781(3)	0.189(2)	0.324(2)
C(5)	0.875(2)	0.258(2)	0.342(2)
C(6)	1.057(3)	0.375(2)	0.246(4)
C(7)	0.874(7)	0.246(5)	0.066(2)
C(8)	0.671(5)	0.104(2)	0.156(4)
C(9)	0.693(6)	0.127(3)	0.398(4)
C(10)	0.93(1)	0.294(6)	0.439(4)
C(11)	0.433(1)	0.489(1)	0.299(1)
C(12)	0.435(2)	0.488(1)	0.201(1)
C(13)	0.345(2)	0.560(1)	0.148(1)
C(14)	0.260(2)	0.627(1)	0.197(2)
C(15)	0.253(2)	0.626(1)	0.299(2)
C(16)	0.340(2)	0.559(1)	0.347(2)

4.6. Kinetics

The kinetic measurements were carried out by following the intensity change in the ^{1}H NMR spectra with time and temperature. A CD_2Cl_2 solution containing a certain amount of the dinuclear complex **2** was placed in the NMR cell compartment at room temperature and then the desired temperature was achieved. The kinetic measurements were run at 26, 30, 34, and 38°C at a certain time intervals. The rate constants were evaluated from the change in the relative integrated intensity ratio of the methyl singlets for [(Cp*Rh)$_2$(1,2-C$_6$H$_4$S$_2$-S,S')$_2$] (**2**) and [(Cp*Rh)(1,2-C$_6$H$_4$S$_2$-S,S')] (**4**) (Fig. 3, right).

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