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Synthesis and Structure of Thiolate Complexes Containing $(\eta^5\text{-}C_5Me_5)Rh^{III}$ Groups

Zhaomin HOU, Yoshiki OZAWA,* and Kiyoshi ISOBE*
Institute for Molecular Science, Myodaiji, Okazaki 444

Reaction of $[Cp^*RhCl_2]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with NaSMe in H_2O—MeOH (1:1 by volume) gave $[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]Cl\cdot 2H_2O$ which was converted to $[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]_2[W_3S_9]$ by treatment with WS_4^{2-}. In the presence of MoO_3 the reaction led to formation of $[Cp^*RhCl(\mu\text{-}SMe)_2RhCp^*Cl]$. X-Ray structure analyses revealed that $[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]_2[W_3S_9]$ has three μ_2-bridged SMe ligands and that $[Cp^*RhCl(\mu\text{-}SMe)_2RhCp^*Cl]$ has a syn-planar conformation with two μ_2-bridged SMe ligands.

Thiolate complexes containing the Cp^*M or CpM group (M = Ti, V, Fe, Mo, Ru, Rh, and W; Cp = $(\eta^5\text{-}C_5H_5)$ have recently been synthesized and showed unique reactivities and electrochemical properties.[1] The thiolate ruthenium(III) complexes $[Cp^*Ru(\mu\text{-}SR)_3RuCp^*]Cl$ (R = aryl) and $[Cp^*RuCl(\mu\text{-}SR')_2RuCp^*Cl]$ (R' = alkyl and benzyl) were derived from $[Cp^*RuCl_2]_2$.[1a] Although there is the corresponding starting material $[Cp^*RhCl_2]_2$, the chemistry of the thiolate rhodium (III) complexes has been undeveloped.[2] This communication reports synthesis and structures of thiolate rhodium(III) complexes derived from $[Cp^*RhCl_2]_2$.

Reaction of $[Cp^*RhCl_2]_2$ (**1**) with 4 times molar amount of NaSMe in CH_3OH-H_2O (1:1 by volume) at room temperature for 1.5 h gave red crystals of $[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]Cl\cdot 2H_2O$ (**2**) in 90% yield after recrystallization from acetone—ether (Eq. 1). In the presence of equimolar amount of MoO_3

$$\underset{\mathbf{1}}{[Cp^*RhCl_2]_2} + 3NaSMe \xrightarrow[\text{in } CH_3OH—H_2O]{} \underset{\mathbf{2}}{[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]Cl} + 3NaCl \quad (1)$$

$$[Cp^*RhCl_2]_2 + 2NaSMe \xrightarrow[\text{in } CH_3OH—H_2O]{MoO_3} \underset{\mathbf{3}}{[Cp^*RhCl(\mu\text{-}SMe)_2RhCp^*Cl]} + 2NaCl \quad (2)$$

$$2[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]Cl + 3(NH_4)_2WS_4 \xrightarrow[\text{in } CH_3CN]{}$$

$$\underset{\mathbf{4}}{[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]_2[W_3S_9]} + 2NH_4Cl + (NH_4)_2S_2 + (NH_4)_2S \quad (3)$$

the reaction of **1** with 2 times molar amount of NaSMe in the same solvent formed red needle crystals of $[Cp^*RhCl(\mu\text{-}SMe)_2RhCp^*Cl]$ (**3**) (15% yield in Eq. 2) together with **2** as the main product.[3] The ^1H NMR signals of **2** and **3** in $CDCl_3$ appear at δ 1.92 (t, $J_{Rh\text{-}H}$ = 1.2 Hz, 9H, SMe) and

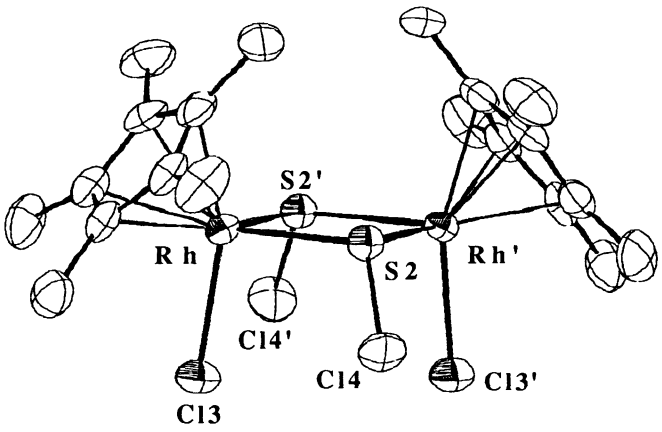

Fig. 1. ORTEP view for **3**. The molecule has a C_2 symmetry. Selected bond distances (Å) and angles (°): Rh·····Rh' = 3.640(1), Rh—S2 = 2.381(2), Rh—Cl3 = 2.387(2), S2—Cl4 = 1.828(7), Rh—Cp* (ring) = 2.19(av.), Rh—S2—Rh' = 99.85(6), S2—Rh—Cl3 = 96.06(6)

1.78 (s, 30H, Cp*), and δ 1.84 (t, $J_{Rh\text{-}H}$ = 1.1 Hz, 6H, SMe) and 1.74 (s, 30H, Cp*), respectively, which indicates that all of the three or two methylthiolate ligands in **2** or **3** are in bridge between two rhodium atoms. Treatment of **2** with $(NH_4)_2WS_4$ in CH_3CN under refluxing readily produced brick-red crystals of $[Cp^*Rh(\mu\text{-}SMe)_3RhCp^*]_2[W_3S_9]$ (**4**) in 85% yield (Eq. 3).[4] The $W_3S_9^{2-}$ anion shows characteristic metal-sulfur vibrations below 600 cm^{-1} due to the $(S)_2W(\mu\text{-}S)_2WS(\mu\text{-}S)_2W(S)_2$ framework.[5]

The molecular structures of complexes **3** and **4** have been determined by X-ray analysis and are shown in Fig. 1 and Fig. 2, respectively.[6, 7] These are the first examples of alkylthiolate rhodium(III) complexes of which structures have been revealed. Complex **3** has a dinuclear structure bridged by two SMe ligands and possesses a C_2 symmetry. The Rh·····Rh distance (3.640(1) Å) suggests no interaction between the Rh atoms which are surrounded by one terminal chlorine atom, two bridging sulfur atoms, and a Cp* ring to form a distorted octahedron with 18-electron configuration. The $Rh(\mu_2\text{-}S)_2Rh$ unit is planar and has a syn-conformation with respect to the disposition of methyl groups in the SMe ligands.[8] The same conformation was suggested for the corresponding ruthenium complex $[Cp^*RuCl(\mu\text{-}SCH_2Ph)_2RuCp^*Cl]$ from EXAFS and NMR spectroscopies.[1a] Complex **4** consists of two dinuclear cations $[RhCp^*(\mu\text{-}SMe)_3RhCp^*]^+$ and one anion $W_3S_9^{2-}$ formed by aggregation of three WS_4^{2-} units.[4] In two cations both Rh1·····Rh2 axes are nearly parallel to the W1·····W3 axis (Fig. 2). The molecule of complex **4** as a whole has a C_2 symmetry. Interestingly, two Cp* ligands coordinate to the Rh atoms perpendicularly to the Rh·····Rh axis in an eclipse conformation, not in a staggered one found in the ruthenium.[1a] The Rh·····Rh distance (3.235(2) Å) is quite longer, the Rh—S—Rh angles (85.8°(av.)) are much more obtuse, and the S—Rh—S angles (78.6°(av.)) are more acute than those in $[Cp^*Ru(\mu\text{-}SPh)_3RuCp^*]Cl$ which has the Ru—Ru bond (Ru—Ru = 2.630(1) Å,[1a] Ru—S—Ru = 68.2°(av.),[9] S—Ru—S = 91.6°(av.).[9] These data indicate that there is no bonding interaction between the two rhodium atoms. The $W_3S_9^{2-}$ anion in **4** has the same disorder as does $[PPh_4]_2W_3S_9$ and the anions in both complexes have almost identical structure parameters.[10]

There is a sharp contrast between Cp^*Ru^{III} and Cp^*Rh^{III} thiolate complexes with respect to the bridging mode of the thiolate ligand; in the former the nature of the thiolate sources

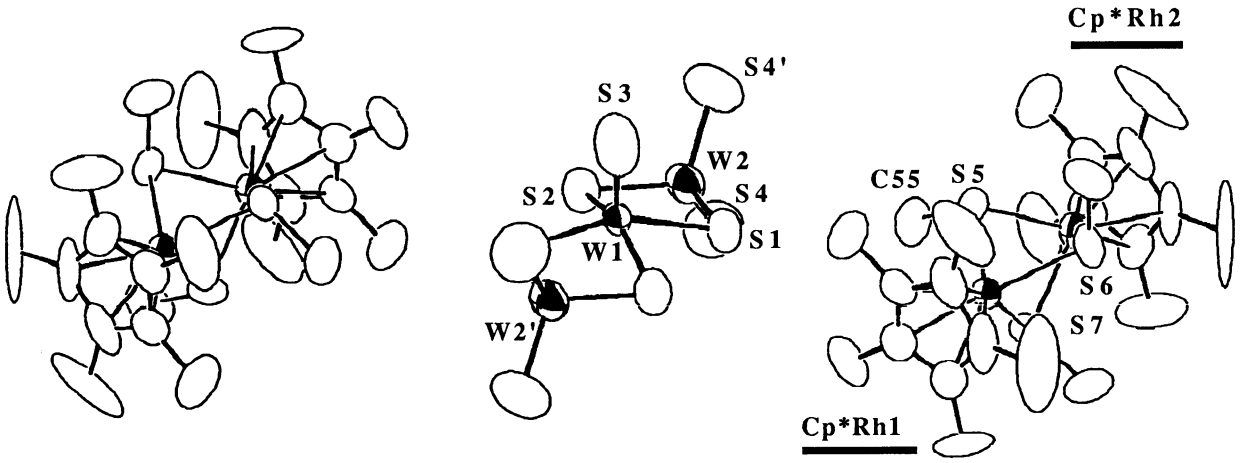

Fig. 2. ORTEP view for **4**. Selected bond distances (Å) and angles (°): Rh1—S5 = 2.373(7), Rh1—S6 = 2.389(9), Rh1—S7 = 2.356(7), S5—C55 = 1.80(3), Rh1—Cp* (ring) = 2.19(av.) Rh1—S5—Rh2 = 85.8(3), Rh1—S6—Rh2 = 85.1(3), Rh1—S7—Rh2 = 86.5(3), S5—Rh1—S6 = 78.4(3), S5—Rh1—S7 = 78.9(3), S6—Rh1—S7 = 79.4(3), W1—W2 = 2.964(1), W1—S3 = 1.86(3), W1—S1 = 2.398(6), W1-S2 = 2.410(8), W2—S4 = 2.135(7), W2—W1—W2' = 158.09(7), S1—W1—S2 = 94.9(2), S1—W2—S2 = 103.9(3), S4—W2—S4' = 112.2(3).

determine whether they take the di-μ_2-bridged $Ru(\mu\text{-}SR)_2Ru$ structure or the tri-μ_2-bridged $Ru(\mu\text{-}SR)_3Ru$ structure,[1a] the latter, however, can take both the structures with an identical thiolate source. This leads to the first example of the di-μ_2-bridged and the tri-μ_2-bridged dinuclear rhodium(III) complexes having the identical μ_2-SMe ligand. We are developing the thiolate rhodium(III) chemistry by use of other alkyl and arylthiolates for comparing with the thiolate ruthenium(III) chemistry.

References

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2) Some rhodium thiolate complexes being not well characterized, for example, $[Cp^*_2Rh_2Cl_2(SMe)_2MeSH]_n$ have already been reported: M. J. H. Russell, C. White, A. Yates, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, **1978**, 849.

3) We were not able to see any formation of **3** in the reaction without MoO_3, which gave **2** as well as the starting compound (**1**), and we don't know the role of MoO_3 in the formation of **3** at the present stage of the study.

4) **4**: Anal. Found: C, 26.68; H, 3.87%. Calcd for $C_{46}H_{78}Rh_4S_{15}W_3$: C, 26.62; H, 3.79%. ^1H NMR ($CDCl_3$) δ 1.84 (t, $J_{Rh\text{-}H}$ = 1.2 Hz, 18H, SMe), 1.70 (s, 60H, Cp*). IR (Nujol) 518(m), 500(m), 492(s), 466(m),

435(w) cm^{-1}.

5) W-H. Pan, M. E. Leonowicz, and E. I. Stiefel, *Inorg. Chem.*, **22**, 672 (1983).

6) Crystallographic data for $[RhCp^*Cl(\mu\text{-}SMe)_2RhCp^*Cl]$: *F. W.* = 577.248, monoclinic, *A2/a*, λ = 0.71069 Å, *a* = 19.015(2), *b* = 15.571(2), *c* = 8.541(1) Å, β = 98.70(1)°, *V* = 2499.8(16) $Å^3$, Z = 4, D_c = 1.704 g cm^{-3}, μ(Mo Kα) = 16.88 cm^{-1}. Total 2154 independent reflections with $|Fo| > 3.0\,\sigma(Fo)$ ($2° < 2\theta < 60°$) were used for calculation. The metal atoms were located by Patterson function. The other non-hydrogen atoms were found from successive Fourier syntheses. R/R_w = 0.035/0.046 was obtained by using block-diagonal least-squares anisotropically for all non-H atoms.

7) Crystallographic data for $[RhCp^*(\mu\text{-}SMe)_3RhCp^*]_2[W_3S_9]$: *F. W.* = 2075.522, monoclinic, *C2/m*, λ = 0.71069 Å, *a* = 26.149(4), *b* = 12.681(3), *c* = 11.136(1) Å, β = 113.30 (1)°, *V* = 3391(1) $Å^3$, Z = 2, D_c = 2.03 g cm^{-3}, μ(Mo Kα) = 65.88 cm^{-1}. Total 1562 independent reflections with $|F_o| > 3.0\,\sigma(F_o)$ ($2° < 2\theta < 60°$) were used for calculation. The crystal structure was solved by the Patterson–Fouier method as mentioned above. Final R/R_w = 0.050/0.057 was obtained.

8) Five different geometric isomers are in principle possible for di-μ_2-bridged thiolate complexes depending on whether the $M(\mu_2\text{-}SR)_2M$ unit is planar or folded and on the disposition of R. A. Muller and E. Diemann, "Comprehensive Coordination Chemistry," ed by G. Wilkinson Pergamon Press, Oxford (1987), Vol. 2, Chap. 16.1, pp. 527-528.

9) These bond angles have been calculated from the data in Ref. 1a.

10) A. Müller, H. Bogge, E. Krickemeyer, G. Henkel, and B. Krebs, *Z. Naturforsch.*, B, **37**, 1014 (1982).

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