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Preparation of Thiolate-Bridged Diruthenium Complexes with Ru-Ru Single Bond

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Reactions of $[Cp^*RuCl_2]_n$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with ArSH (Ar = Ph, p-$ClC_6H_4$ or p-MeC_6H_4) in CH_2Cl_2 gave diruthenium complexes $[Cp^*_2Ru_2(SAr)_3]Cl$ in high yields. X-Ray analysis of the complex (Ar = Ph) disclosed the existence of the Ru-Ru bond triply bridged by SPh groups. On the other hand, analogous treatment of $[Cp^*RuCl_2]_n$ with $PhCH_2SH$ resulted in the formation of a neutral complex $[Cp^*_2Ru_2(SCH_2Ph)_2Cl_2]$.

The transition metal-thiolate complexes have recently attracted much attention in relevance to biological interest and a substantial number of metal-thiolate binary compounds and organometal-thiolate complexes have been reported. However, the metals are in common chosen from the elements of the first transition series except for Mo and W. Although the chemistry of iron-thiolate complexes, for example, is extensive,[1)] that of ruthenium analogues is the field that is still poorly investigated.[2)] In this paper are reported the preparation, structures and some selected properties of novel thiolate-bridged diruthenium complexes with Ru-Ru single bond.

Reaction of the complex $[Cp^*RuCl_2]_n$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) with excess PhSH in CH_2Cl_2 at room temperature for 24 h produced dark brown crystals of the diruthenium complex $[Cp^*_2Ru_2(SPh)_3]Cl$ (**2**) in 81% yield as mono CH_2Cl_2 solvate after crystallization from CH_2Cl_2-hexane.[3)] In spite of the oxidation state of Ru(III), the ^1H NMR spectrum of complex **2** exhibits two sharp resonances at 1.39

$$[Cp^*RuCl_2]_n \xrightarrow[CH_2Cl_2]{\text{excess ArSH}} [Cp^*Ru(SAr)_3RuCp^*]Cl$$

(s, 30H) and 7.28 - 7.38 ppm (m, 15H) assignable to the protons of Cp* and PhS ligands, respectively. Because of the diamagnetic character observed for complex **2**,$^{4)}$ this substitution reaction of chloride ligands by the thiolate anion was presumed to be accompanied with the formation of the spin-spin pair between two ruthenium atoms. The molecular structure of complex **2** has been determined by X-ray analysis and the structure of the cation component is shown in Fig.1.$^{5)}$ The Ru-Ru distance of 2.630(1) Å is compatible with the bond order of unity$^{6)}$ and

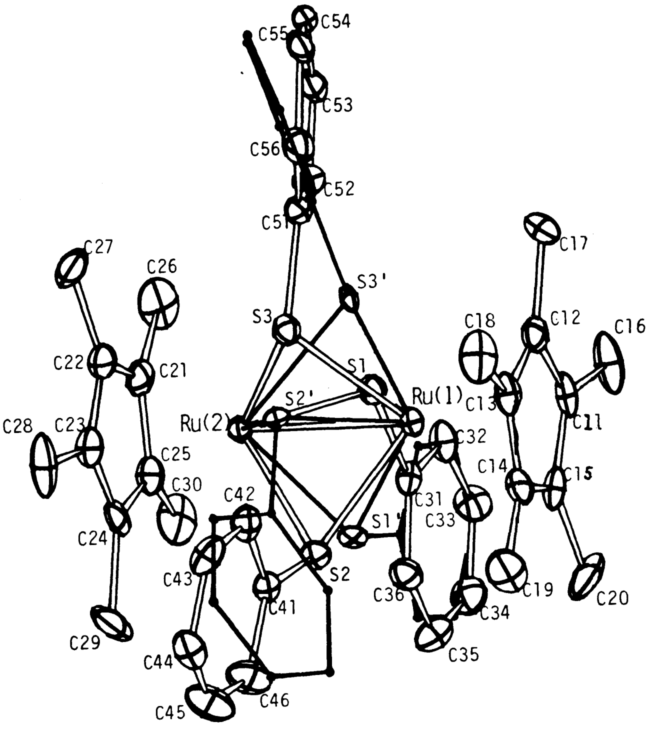
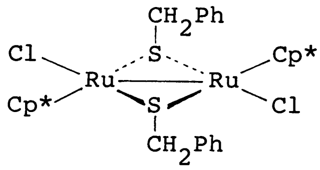


Fig. 1. ORTEP view and atom-labeling scheme for $[Cp^*_2Ru_2(SPh)_3]^+$. Singly primed atoms are related to the disordered thiolate ligands (15%). Selected bond distances and angles are Ru(1)-Ru(2) = 2.630(1), Ru(1)-S(1) = 2.356(4), Ru(1)-S(2) = 2.340(4), Ru(1)-S(3) = 2.358(4), Ru(2)-S(1) = 2.343(4), Ru(2)-S(2) = 2.351(4), Ru-S(3) = 2.330(4) Å, Ru(1)-S(1)-Ru(2) = 68.1(1), Ru(1)-S(2)-Ru(2) = 68.2(1), and Ru(1)-S(3)-Ru(2) = 68.3(1)°.

three thiolate ligands coordinate to two Ru atoms almost symmetrically in the manner that the Ru-Ru bond becomes a three-fold axis. Two Cp* ligands bind to two Ru atoms, each occupying the opposite side to the Ru-Ru bond. Both of two planes consisting of the Cp* carbon atoms are perpendicular to the Ru-Ru bond and two sets of five methyl groups are in staggered position to each other.

Treatment of complex **1** with p-XC_6H_4SH (X = Cl or Me) gave analogous complexes in high yields.7) These diruthenium complexes in DMF solution exhibit two succesive one-electron reductions that are reversible ($E_{1/2}^{red}$ = -0.52, -1.07 for X = Me; -0.48, -1.02 for X = H; -0.38, and -0.90 V vs. SCE for X = Cl).8) As expected, the reduction potential corresponding to the same redox process increases with increase in the Hammet σ constant of the para substituent.

Alkanethiols such as EtSH and Bu^tSH did not react with complex **1** under the same conditions as those for ArSH. However, the reaction of $PhCH_2SH$ with complex **1** occurred and another type of diruthenium complex $[Cp*_2Ru_2(SCH_2Ph)_2Cl_2]$ (**3**) was isolated as $1/2CH_2Cl_2$ solvate in 13% yield.9) This compound also shows sharp resonances in its ^1H NMR spectrum,10) which is indicative of the spin-spin pair between two Ru(III) atoms. Since the molar conductivity observed for complex **3** in CH_2Cl_2 solution is about 10^{-3} times smaller than that of complex **2**,11) the structure without an outer-sphere anion is plausible. The molecular geometry depicted below is one possible structure that is consistent with the observation described above and satisfies the 18-electron rule for the Ru atoms, but elucidation of the structure of complex **3** must await further investigation. Development of the synthetic routes to the higher Ru-S-heterometal aggregates starting from these diruthenium compounds is now in progress.



References

1) J. M. Berg and R. H. Holm, "Metal Ions in Biology," ed by T. G. Spiro, Wiley, New York (1982), Vol. 4, Chap. 1; P. T. Vergamini and G. J. Kubas, Prog. Inorg. Chem., 21, 261 (1977).

2) As for ruthenium thiolate complexes determined by X-ray analysis, see: M. M. Millar, T. O´Sullivan, N. de Vries, and S. A. Koch, J. Am. Chem. Soc., 107, 3714 (1985); S. A. Koch and M. Millar, ibid., 105, 3362 (1983); S. D. Killops, S. A. R. Knox, G. H. Riding, and A. J. Welch, J. Chem. Soc., Chem. Commun., 1978, 486; J.

A. K. Howard, F. G. Kennedy, and S. A. R. Knox, ibid., 1979, 839.

3) Found: C, 50.29; H, 5.19; Cl, 11.58; S, 10.23%. Calcd: C, 50.89; H, 5.17; Cl, 11.55; S, 10.45%.

4) Complex **2** is EPR-silent both at room temperature and 123 K, whereas complex **1** shows a singlet resonance at g = 2.07 at room temperature. Diamagnetic character of complex **2** was also confirmed by the Faraday method.

5) Space group $P\bar{1}$, a = 11.380(2)Å, b = 17.043(3)Å, c = 11.116(2)Å, α = 101.76(2)°, β = 105.76(2)°, γ = 87.66(2)°, V = 2031.1(7)$Å^3$, Z = 2, ρ_{calcd} = 1.504 g cm^{-3}. The data were collected on Rigaku automatic four-circle diffractometer with monochromatized Mo K_α (λ = 0.7107 Å) radiation using ω-2θ scans. With use of 4392 unique data, the structure was solved by three dimensional Patterson and Fourier techniques and refined by block-diagonal least squares. Final structure refinement converged to R = 6.8 and R_w = 5.9%.

6) The distance of two Ru(II) atoms linked by three bridging SH groups without Ru-Ru bond in $[Ru_2(SH)(\mu\text{-}SH)_3(PMe_2Ph)_5]$ is 3.371(3) Å: Private communication from Dr. K. Osakada. See also, K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka, and Y. Sasada, Inorg. Chim. Acta, 105, L9 (1985).

7) X = Cl: Found: C, 47.01; H, 4.85; Cl, 16.51; S, 9.24%. Calcd as 1/2 CH_2Cl_2 solvate: C, 47.12; H, 4.42; Cl, 18.06; S, 9.80%. ^1H NMR (CD_2Cl_2) δ 1.49 (s, 30H, Me), 7.28 ppm (s, 12 H, C_6H_4Cl). X = Me: Found: C, 48.42; H, 5.22; Cl, 16.46; S, 9.12%. Calcd as 3/2 $CHCl_3$ solvate: C, 48.31; H, 5.01; Cl, 18.45; S, 9.10%. ^1H NMR (CD_2Cl_2) δ 1.37 (s, 30H, C_5Me_5), 2.29 (s, 9H, $C_6H_4\underline{Me}$), 7.08, 7.22 ppm (d, 6H each, m- and o-H of $SC_6\underline{H}_4Me$).

8) About 1 mM solution in DMF-0.1 M $[Bu^n{}_4N][BF_4]$; Scan rate 0.2 V s^{-1}; The potential difference between the cathodic and anodic wave peaks were in the range of 90 - 100 mV for X = H and Cl and 130 - 150 mV for X = Me; Two irreversible oxidation waves were also observed for these three complexes.

9) Found: C, 50.48; H, 5.58; Cl, 12.66; S, 7.33%. Calcd: C, 49.78; H, 5.45; Cl, 12.79; S, 7.70%.

10) ^1H NMR ($CDCl_3$) δ 1.48 (s, 30H, Me), 4.38 (s, 4H, CH_2), 7.26 - 7.50 ppm (m, 10H, Ph). Complex **3** is EPR-silent both at room temperature and 123 K.

11) Λ = 1.01 x 10^0 and 8.11 x 10^2 S cm^2 mol^{-1} for complexes **3** and **2**, respectively, in 0.6 M CH_2Cl_2 solution.

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