A Novel Oxidatively Induced Structural Rearrangement of Diruthenocenyl Disulfide to the First Transition-metal Complex of 2,4-Cyclopentadien-1-thione

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The first transition metal-stabilized complex of 2,4-cyclopentadien-1-thione was synthesized in the oxidation of diruthenocenyl disulfide with p-BQ/$BF_3 \cdot OEt_2$.

Much attention is recently focused in an oxidatively induced rearrangement of the organic ligand in transition metal complexes.[1,2] 2,4-Cyclopentadien-1-thione, which is an extremely unstable compound because of the high reactivity of the thiocarbonyl group, was generated by gas phase pyrolysis and assigned only by photoelectron spectroscopy.[3] We here report the first synthesis of transition metal-stabilized 2,4-cyclopentadien-1-thione complex through a novel oxidatively induced structural rearrangement of diruthenocenyl disulfide.

Diruthenocenyl disulfide (**1**)[4] was prepared in 11 % yield from the reaction of lithioruthenocene with sulfur in THF at room temperature overnight. In the cyclic voltammogram of **1** (0.1M $n\text{-}Bu_4NClO_4$ solution in CH_2Cl_2), an irreversible two-electron oxidation wave was observed at +0.42 V (vs FcH/FcH$^+$), along with two irreversible reduction waves at -0.24 and -0.48 V (vs FcH/FcH$^+$). This is contrary to diferrocenyl diselenide which undergoes two reversible one-electron oxidations.[5] Moreover, the cyclic voltammogram remained unchanged in the repeat of oxidative and reductive scan. Then, complex **1** was oxidized with benzoquinone and $BF_3 \cdot OEt_2$ in CH_2Cl_2 at 0 °C. The reaction gave $[Ru(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^1{:}\eta^4\text{-}C_5H_4S)]_2(BF_4)_2$ (**2**)[4] as red brown crystals in 74% yield. The TOF-MS spectrum of **2** showed the molecular ion corresponding to $[Ru(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^1{:}\eta^4\text{-}C_5H_4S)]_2{}^{2+}$ at m/z 262 (M^{2+}). The ^1H NMR spectrum of **2** in CD_3CN at room temperature reveals the signals at δ 4.56 (dd, *J*=2 Hz, 1H), 5.49 (dd, *J*=2 Hz, 1H), and 6.11 (t, *J*=2 Hz, 2 H), along with one singlet at δ 5.84 (5 H). The shift of the Cp ring protons to a lower field (Δ 1.3 ppm) indicates the accumulation of the positive charge on the Ru atom in **2**. This is also supported by the appearance of the Cp ring carbon in a lower field region (δ 89.96) in the ^{13}C NMR spectrum. The fact that the protons of the 2,4-cyclopentadien-1-thione ligand in **2** are in asymmetric circumstances suggests a dimeric structure of complex **2** rather than a monomeric structure. The ^{13}C resonance of the thiocarbonyl carbon in **2** was observed at δ 161.82 ppm. This is a striking contrast to the observation that the signal of the thiocarbonyl carbon of diarylthioketones coordinated to a metal by the lone-pair electron of sulfur shifts only a little to a higher field (Δ ~5 ppm) than that of diarylthioketones (δ ~236).[6] This may be related to the high field shift (Δ ~20 ppm) observed in the carbonyl carbon of $[Ru(\eta^4\text{-}C_5H_4O)(\eta^5\text{-}C_5H_5)]_2{}^{2+}$ (**3**) in its origin (*vide infra*).[7b] It is noteworthy that complex **2** is more rigid than the 2,4-cyclopentadien-1-one complex **3**, because the latter shows a fluxional behavior in the solution at room temperature.[7b] This is probably due to the stronger coordination of the sulfur atom, compared with the oxygen atom, to the Ru atom.

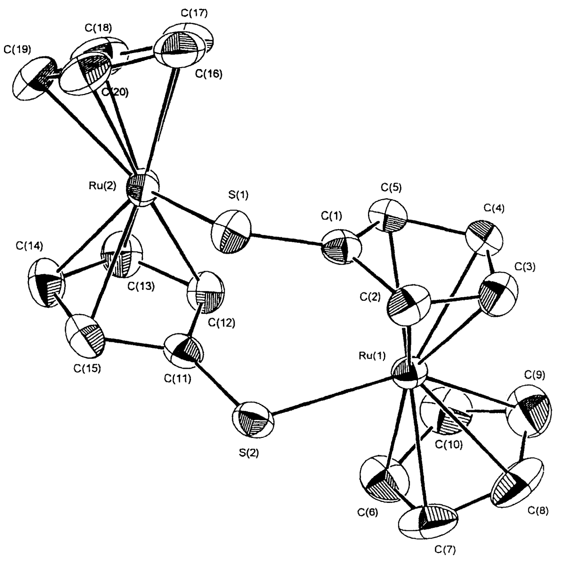
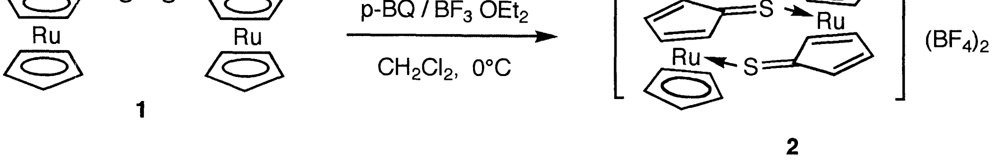


Figure 1. The ORTEP view of **2**. Selected bond distances and angles are as follows: C(1)-S(1) 1.684(6), Ru(1)-C(1) 2.421(6), Ru(1)-C(2) 2.247(6), Ru(1)-C(3) 2.191(6), Ru(1)-C(4) 2.191(7), Ru(1)-C(5) 2.261(6), S(1)-Ru(2) 2.395(2) Å; Ru(2)-S(1)-C(1) 106.4(3), Ru(1)-S(2)-C(11) 106.4(2)°.

A single crystal X-ray crystallographic analysis confirmed the structure of **2**.[8] The ORTEP view of the cation part of **2** is shown in Figure 1. As demonstrated clearly in the Figure, the complex **2** takes a dimeric structure, in which 2,4-cyclopentadien-1-thione coordinates as a η^4-ligand via the diene part to one Ru atom and as a η^1-ligand via the lone pair of the S atom to another Ru atom. The latter coordination seems to be required to comply with the 18e rule. The C(1)-S(1) [1.684(6) Å] is slightly longer than the corresponding distances [1.618(8) Å] in the thione complex, $(CO)_5CrS{=}CMe_2$[9] and considerably shorter than that in the complex having a thiolatocyclopentadiene ligand, for example, $(\eta^5\text{-}C_5H_4S)_2RuPPh_3$ [1.734(4) and 1.732(4) Å].[10] In the 2,4-cyclopentadien-1-thione ligand in **2**, a clear short-long-short pattern is observed [C(2)-C(3) = 1.410(9) Å, C(4)-C(5) =



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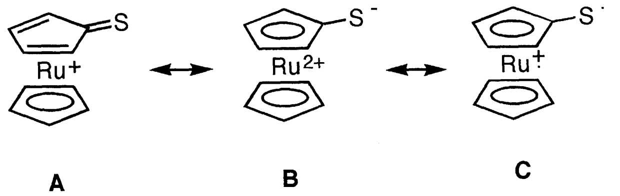
1.409(9) Å, and C(3)-C(4) = 1.450(1)], as is the case of cyclopentadienone complexes.[7,11,12] The plane S(1)-C(1)-C(2)-C(5) in the 2,4-cyclopentadien-1-thione ligand is folded by 9.9° from the plane C(2)-C(3)-C(4)-C(5) to the opposite side of the Ru metal.[13] The bond distances between Ru(1) and the butadiene fragment in complex **2** for C(3) and C(4) are shorter than for C(2) and C(5) by about 0.15 Å. These structural features is contrast to that in the complex having a thiolatocyclopentadiene ligand,$(\eta^5\text{-}C_5H_4S)_2RuPPh_3$, in which the C-C and Ru-C distances of the ruthenocenyl moiety are similar to each other and agree well with those for ruthenocene itself.[10] These findings support the $\mu\text{-}\eta^1{:}\eta^4$-coordination of the 2,4-cyclopentadien-1-thione ligand in complex **2**. However, the folding angle (9.9°) in complex **2** is considerably smaller than the corresponding angle in the cyclopentadienone complexes {e.g. 20.4° in $Ru(\eta^4\text{-}C_5H_4O)(\eta^5\text{-}C_5H_5)Br$[7a] and 18.0° in $[Ru(\eta^4\text{-}C_5H_4O)(\eta^5\text{-}C_5H_5)\text{-}(CH_3CN)]^+$}[7b] and the Ru(1)-C(1) distance [2.421(6) Å] is considerably shorter than the corresponding distance in $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)Br$ [2.60(1) Å][7a], and the carbon resonance of the thiocarbonyl group appears at a high field (δ 161.82 ppm). These findings suggest a certain interaction between the Ru atom and the thiocarbonyl group in **2**. The limited structure **B** and **C** other than the limited structure **A** may contribute to the structure of **2**. In connection with this, it is noteworthy that the S(1)-S(2) distance [3.010(3) Å] is fairly shorter than the sum of the van der Waals radii of sulfur [3.7 Å]. Complex **2** is reduced to diruthenocenyl disulfide with $(\eta^5\text{-}C_5H_5)_2Co$ in MeCN at 0°C for 4 hr in 93 % yield. The study concerning further reactivity of complex **2** is in progress.



References and Notes

1 D. Astruc, "*Electron Transfer and Radical Process in Transition-metal Chemistry*," VCH Publishers, Inc., New York (1995).

2 For a recent example, see M. Sato, A. Kudo, Y. Kawata, and H. Saitoh, *J. Chem. Soc., Chem. Commun.*, **1996**, 25.

3 R. Schulz and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **20**, 570 (1981).

4 All new complexes had a satisfactory elemental analysis.

5 P. Shu, K. Bechgaard, and D. C. Cowan, *J. Org. Chem.*, **41**, 1849 (1976).

6 H. Fischer and R. Märkl, *Chem. Ber.*, **115**, 1349 (1982).

7 a) T. P. Smith, K. S. Kwan, H. Taube, A. Bino, and S. Cohen, *Inorg. Chem.*, **23**, 1943 (1984). b) K. Kirchner, H. Taube, B. Scot, and R. D. Willett, *Inorg. Chem.*, **32**, 1430 (1993).

8 Crystal data for **2**, $C_{20}H_{18}B_2F_8S_2Ru_2$, FW=698.20, monoclinic, P $2_1/a$, a=14.715(2) Å, b=12.942(1) Å, c=12.382(2) Å, β=110.93(1)°, V=2202.2(5) $Å^3$, Z=4, D_c=2.11 g cm^{-3}, μ (MoKα)=16.027 cm^{-1}, T=298 K. 5688 measured reflections, 5055 unique reflections, 4224 reflections with $I \geq 3\sigma(I)$ used in refinement, empirical absorption correction (ψ-scan), R=0.0377 and Rw=0.0456.

9 B. A. Karcher and R. A, Jacobson, *J. Organomet. Chem.*, **132**, 387 (1977).

10 S. Akabori, T. Kumagai, T. Shirashige, S. Sato, K. Kawazoe, C. Tamura, and M. Sato, *Organometallics*, **10**, 2105 (1987). A similar feature was observed in ferrocene analogs.

11 a) L. S. Liebeskind and A. Bombrun, *J. Am. Chem. Soc.*, **113**, 8736 (1991). b) K. Mauthner, C. Slugovc, K. Mereiter, R. Schmid, and K. Kirchner, *Organometallics*, **15**, 181 (1996).

12 a) W. Reppe, H. Vetter, *Justus Liebigs Ann. Chem.*, **582**, 133 (1953). b) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, **1960**, 989.

13 The plane S(1)-C(1)-C(2)-C(5) is nearly planar, but the S(1)-C(1) bond is bent by 2.9° out of the plane C(1)-C(2)-C(5) toward the Ru atom.