Reaction of 5-Phenyl-*3H*-1,2-dithiol-3-one and Thione with [Rh(Cp*)(CO)$_2$]. Formation of Metalladithiolene Rings *via* Rearrangement

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The reaction of [Rh(Cp*)(CO)$_2$] (**1**) with 5-phenyl-*3H*-1,2-dithiol-3-one (**2**) affords two rhodiadithiolene complexes, a dimer of (η^5-pentamethylcyclopentadienyl)(1-oxo-2-benzylidene-1,2-ethanedithiolato)rhodium(III) (**4**) and (η^5-pentamethylcyclopentadienyl)(1-phenyl-1,2-ethenedithiolato)rhodium(III) (**5**). 5-Phenyl-*3H*-1,2-dithiole-3-thione (**3**) reacts with **1** to afford only **5**. The formation of the complexes **4** and **5** is explained by a mechanism *via* the attack of coordinatively unsaturated "Rh(Cp*)(CO)" species to the S atom of **2**, followed by rearrangement.

The incorporation of a part of heterocyclic organic compounds in metal complexes as ligands is a useful method to prepare metal chelate complexes and metallacycles. An example of such type reactions to prepare metalladichalcogenollene complexes is the reaction of metal carbonyl with 1,2-dithiete.[1-4] 1,4-Dithiin can also be used as a souce of 1,2-ethenedithiolato ligand.[5] Using this type of reaction we synthesized a novel metallacycle, 1,2,5,3-cobaltadithiazole.[6,7] As such type reaction, we found an interesting reaction accompanying skeletal rearrangement in the course of complex formation. Meso-ionic 2,5-diaryl-1,3-dithiolylium-4-olate reacts with [Co(Cp)] species to give cobaltadithiolene complexes, accompanied by the rearrangement in the heterocyclic moiety.[8] Here we report other types of reactions to give rhodiadithiolene complexes *via* interesting rearrangements.

A xylene solution (300 cm^3) of [Rh(Cp*)(CO)$_2$] (**1**) (3.3 mmol) and 5-phenyl-*3H*-1,2-dithiol-3-one (**2**) (6.5 mmol) was refluxed for 3.5 h under Ar. As the products we obtained two substances: the major one is a red crystalline rhodium complex, (η^5-pentamethylcyclopentadienyl)(1-oxo-2-benzylidene-1,2-ethanedithiolato)rhodium(III) (**4**) (yield, 35% based on **1**) and the other minor one is (η^5-pentamethylcyclopentadienyl)(1-phenyl-1,2-ethenedithiolato)rhodium(III) (**5**) (yield, 8% based on **1**).

An X-ray crystal structural analysis of **4** (formula weight, 1103.56; space group, $P\bar{1}$(#2); unit cell dimensions: a = 10.953(2) Å, b = 11.777(3) Å, c = 9.754(3) Å, α = 97.68(3)°, β= 106.70(2)°, γ= 106.19(2)°, D_{calc} = 1.628 g cm^{-3}; R = 0.043) revealed that **4** has the structure shown in Figure 1. It is a dimer of 4-benzylidene-1,2,5-rhodiadithiol-3-one.

The complex **4** belongs to a family of metalladithiolenes but its structure is very unique. It has a dimer structure. The rhodium atom is bonded to one of the sulfur atoms of the other rhodiadithiolone as well as the two sulfur atoms of its own dithiolene ring. The rhodium atom has a piano stool coordination structure. The 1,2,5-rhodiadithiolone ring has a quinoid structure.

The dimer structure is probably due to the electron-deficiency (16 electron configuration) at the Rh atom in **4**. The delocalization of π-electrons in a rhodiadithiolene ring is lower than that in a cobaltadithiolene ring because of the longer Rh-S distance than Co-S and it causes the decrease of π-electron donation from S to the metal. Furthermore, the electron attracting C=O group in the 4-benzylidene-1,2,5-rhodiadithiol-3-one ring lowers the electron density at the rhodiadithiolene ring. The unsaturation is solved by the dimer formation.

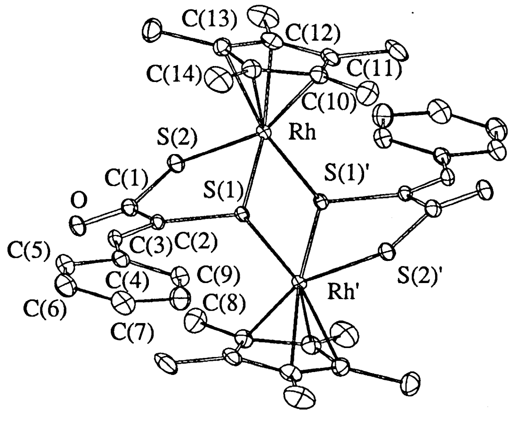
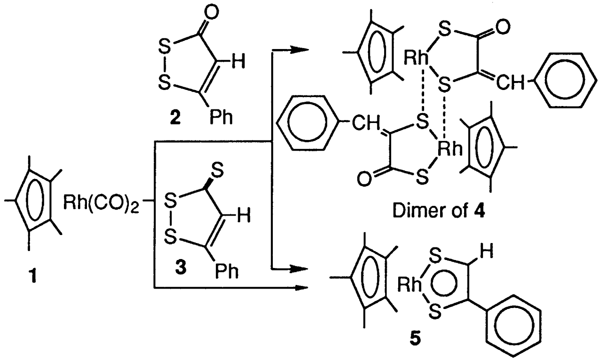


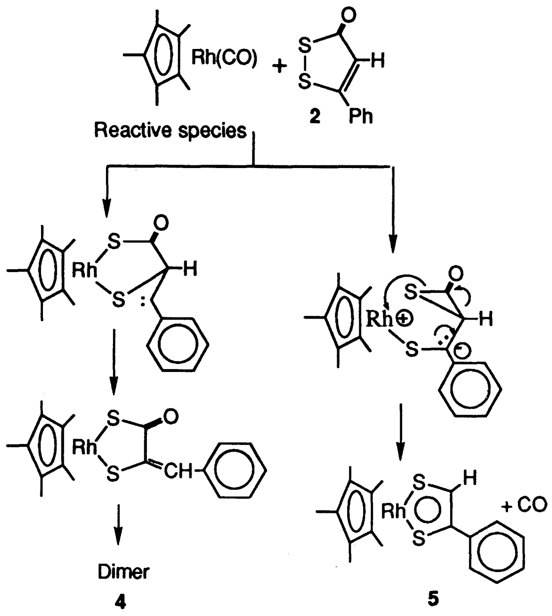
Figure 1. X-ray crystal structure of dimer of **4**
Selected bond lengths (Å) and angles (deg): Rh-S(1), 2.363(1); Rh-S(2), 2.345(1); Rh-S(1)', 2.403(1); S(2)-C(1), 1.739(5); S(1)-C(2), 1.76(4); C(1)-C(2), 1.514(7); C(1)-O, 1.217(6); C(2)-C(3), 1.336(7); S(1)-Rh-S(2), 85.80(5); S(1)-Rh-S(1)', 83.08(4); S(1)-C(2)-C(3), 124.9(4); S(1)-C(2)-C(1), 118.0(3); S(2)-C(1)-C(2), 118.1(3); C(2)-C(1)-O, 120.6(4)

The formation of the dithiolene having a quinoid structure is very specific for the reaction between [Rh(Cp*)(CO)$_2$] and *3H*-1,2-dithiol-3-one. The sulfur analog, 5-phenyl-*3H*1,2-dithiole-3-thione (**3**), gave no product similar to **4**, but only **5** in the reaction with [Rh(Cp*)(CO)$_2$] under similar conditions.



The carbonylcobalt complex, [Co(Cp*)(CO)$_2$] , gave no cobalt analog of **4** in the reaction with 5-phenyl-*3H*-1,2-dithiol-3-one but the cobaltadithiolene (**5b**: cobalt analog of **5**) in 59% yield. The reaction between [Co(Cp*)(CO)$_2$] and **3** gave also **5b** in 22% yield. Thus, the combination of **1** and **2** is the unique one to afford 4-benzylidene-1,2,5-metalladithiol-3-one.

The structures of the two products (**4** and **5**) from the reaction between **1** and **2** suggest that a molecule of the heterocyclic compound is incorporated in each product. The formation of **4** can be explained by a mechanism in which a coordinatively unsaturated "Rh(Cp*)(CO)" species inserts between S-S followed by a rearrangement. The formation of 5 would be initiated by the attack of "Rh(Cp*)(CO)" to the S followed by a rearrangement and extrusion of CO. A conceivable mechanism is shown in Scheme 1.



Scheme 1.

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9 The starting materials were synthesized according to the literature. The rhodium complex **1** was synthesized according to Herrmann *et al.* (W. A. Herrmann, J. Plank , and C. Bauer, *Z. Anorg. Allg. Chem.*, **487**, 85 (1982)) . The cobalt complex was obtained by the method in *Inorg. Synth.* (S. A. Frith and J. L. Spencer, *Inorg. Synth.*, **23**, 15 (1985)). 5-Phenyl-*3H*-1,2-dithiol-3-one (**2**) and its sulfur analog, 5-Phenyl-*3H*-1,2-dithiole-3-thione (**3**) were synthesized according to Klingsberg (E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2923 (1961)).
10 Spectral data of the dimer complex **4**: red crystals, mp > 270 ° C; UV($CHCl_3$) 278.4 (ε 40100), 318.0 (ε 41000), and 366.0 nm (sh, ε 28000) ; IR (KBr) 1604 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 1.45$ (15H, s, CH_3 in Cp*), 7.39 (3H, m, Ph), 7.78 (1H, s, benzylidene), and 8.09 (2H, d, $J = 7.93$ Hz, Ph) ; ^{13}C NMR ($CDCl_3$) $\delta = 8.69$ (CH_3), 97.98 (Cp*, 128.39 (Ph), 129.24 (Ph), 131.38 (Ph), 135.17 (Ph), 135.87 (Ph), 138.70 (benzylidene), and 208.06 (C=O); MS (70 V) *m/z* (rel intensity) 432 (90, M^+ (monomer)), 404 (33), 372 (100), 302 (100, Cp*RhS_2), 270 (89, Cp*RhS), 238 (54, Cp*Rh), 236 (87), 234 (33), 186 (25), 34 (79), and 119 (43).
The crystals of the dimer complex contains two molecules of $CHCl_3$ as the solvent of crystsallization. A part of the crystal solvent is lost during storage and we could not obtain a satisfactory results in elemental analysis.
11 The rhodiadithiolene **5**: Violet crystals; mp, 240 °C decomposition; UV (hexane) 259 (ε, 27000) , 277 (sh, 14600), and 565 nm (6950); ^{1}H NMR ($CDCl_3$) $\delta = 2.07$ (15H, d, $J_{Rh\text{-}H} = 1.22$ Hz, Cp), 7.29 (3H, m, Ph), 7.79 (2H, d, $J = 7.63$ Hz, Ph), and 8.35 (1H, d, $J_{Rh\text{-}H} = 5.49$ Hz, H in the rhodiadithiolene ring) ; ^{13}C NMR ($CDCl_3$) $\delta = 11$ (CH_3), 98 ($J_{Rh\text{-}C} = 7.4$ Hz, Cp), 127 ($J_{Rh\text{-}C} = 16.5$ Hz, rhodiadithiolene ring), 128 (rhodiadithiolene ring), 142 Ph); MS (70 V) *m/z* (rel intensity) 404 (100, M^+), 302 (55, Cp*RhS_2), and 238 (3, Cp*Rh) .Elemental analysis: Found: C, 53.44; H, 5.22; S, 15.29%.Calcd for $C_{18}H_{21}S_2Rh$: C, 53.46; H, 5.23; S, 15.86% .