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16-Electron Half-sandwich Ru(II)—Thiolate Complexes, $Ru(SAr)_2(\eta^6\text{-}p\text{-cymene})$ (Ar = 2,6-dimethylphenyl and 2,4,6-triisopropylphenyl)

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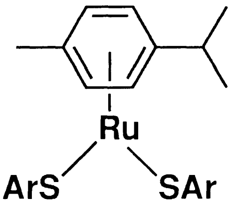
Treatment of $[RuCl_2(p\text{-cymene})]_2$ with sodium 2,6-dimethylbenzenethiolate or sodium 2,4,6-triisopropylbenzenethiolate in methanol afforded a mononuclear five-coordinated ruthenium thiolate complex, $Ru(SAr)_2(p\text{-cymene})$ (**2a:** Ar = 2,6-dimethylphenyl; **2b:** 2,4,6-triisopropylphenyl), whose structure is determined by X-ray analysis of **2a**.

The organometallic chemistry of metal complexes with sulfur ligands are of interest as the model for the active sites of metalloproteins. Although a number of synthetic studies of iron—sulfur complexes have been done, only a few ruthenium analogues have been synthesized. Polynuclear ruthenium-thiolate complexes bearing cyclopentadienyl and arene ligands have been prepared with bridging sulfur ligand atoms.[1—4] These Ru(II) complexes are mostly 18-electron formally hexa-coordinated ones and therefore of an "inert"-type. In this communication we describe the synthesis and characterization of mononuclear five-coordinated arene-ruthenium(II) thiolate complexes, which is 16-electron and labile.

Treatment of $[RuCl_2(p\text{-cymene})]_2$ (**1**) with 6 equiv. of sodium 2,6-dimethylbenzenethiolate in methanol afforded an intense blue solution, from which air-sensitive thiolate **2a** was isolated in 61% yield upon recrystallization from a chloroform—hexane solution.[5] Similarly, complex **2b** was prepared by the reaction of **1** with 6 equiv of sodium 2,4,6-triisopropylbenzenethiolate in THF.[6] Complex **2b** is more soluble in organic solvents and may be crystallized from a saturated hexane solution.



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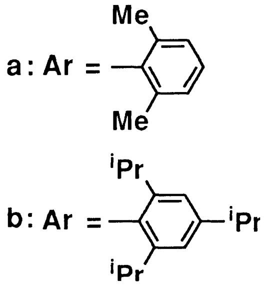


Structure of mononuclear Ru(II) complexes **2** was established by an X-ray crystallographic study of **2a**.7) Figure 1 shows the structure of **2a** with atom labeling scheme and selected interatomic distances and angles. Bond distances between a ruthenium and two sulfurs, Ru—S(1) 2.311(6) Å and Ru—S(2) 2.263(7) Å, are comparable to that of a five-coordinated tbp complex Ru(L)(S-2,3,5,6-tetramethylphenyl)$_4$ (L = CO or CH_3CN) (2.207(10)—2.409(3) Å),8) but shorter than the octahedral complexes such as $RuH(SC_6H_4CH_3)(CO)_2(PPh_3)_2$ (2.458(1) Å) and $Ru(SC_6H_4CH_3)_2(CO)_2(PPh_3)_2$ (2.470(2) Å).9) The bond lengths of Ru—C(η^6) (2.17(3)—2.20(2) Å) are normal and the arene moiety coordinates to ruthenium atom in η^6-coordination mode. Thus, the molecule **2a** is best represented as the two-legged piano stool geometry (Y-shape) and the mononuclear five-coordinated structure, though trigonal bipyramidal geometry has been observed for $Ru(CH_3CN)$(S-2,3,5,6-tetramethylphenyl)$_4$ and Ru(CO)(S-2,3,5,6-tetramethylphenyl)$_4$.8)

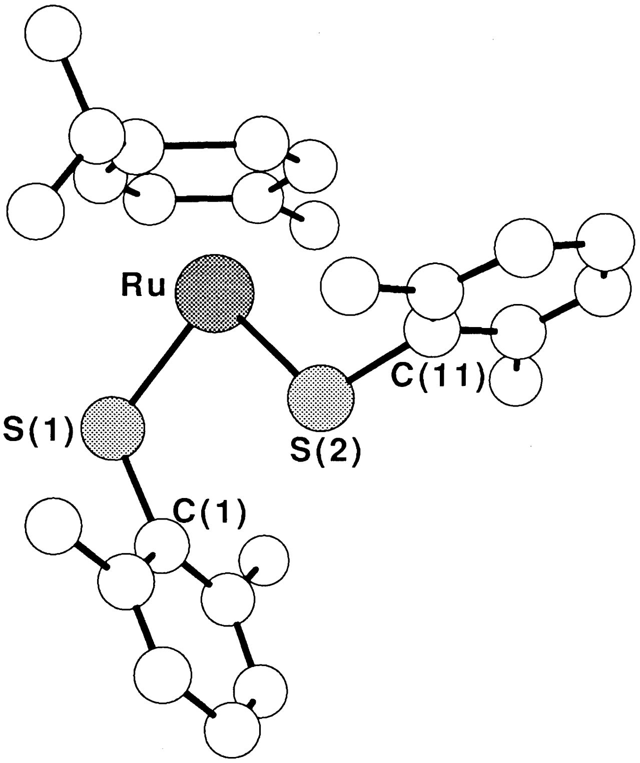
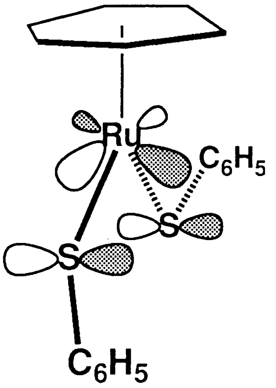


Fig. 1. A drawing of **2a** with a labeling scheme. Selected bond distances (Å) and angles (degree): Ru—S(1) 2.311(6), Ru—S(2) 2.263(7), Ru—C(cent) 1.673, S(1)—C(1) 1.77(2), S(2)—C(11) 1.82(2); S(1)—Ru—S(2) 89.0(2), S(1)—Ru—C(cent) 130, S(2)—Ru—C(cent) 140, Ru—S(1)—C(1) 114.2(8), Ru—S(2)—C(11) 108.9(8); where C(cent) is the centroid of phenyl ring of *p*-cymene.

The "half-sandwich" complexes of the type $(C_nH_n)ML_2$ having 16-electron configuration have been considered as the key intermediates in organometallic chemistry and most of such complexes with L = SR isolated is of 18-electron. Thus, **2** is the first example of the isolated mononuclear 16-electron ruthenium(II)-thiolate complex with Y-shaped geometry which was favored over the pyramidal one.10) The planar geometry at the Ru—S—C part, *e.g.* the torsion angles of S(2)—Ru—S(1)—C(1) [-3(1)°] and S(1)—Ru—S(2)—C(11) [174(1)°], is attributed to the ovelap between vacant $d\pi$ orbital11,12) of Ru and filled $p\pi$ orbital of sulfur, as illustrated schematically.



Solutions of the thiolate complexes **2** are characterized by deep blue colors due to an intense absorption near 680 nm, which is presumably a thiolate—>Ru charge-transfer transition.4) These red-shifted values are characteristic in comparision with the those of typical octahedral Ru(II) complexes (near 400 nm).9)

The new ruthenium—thiolate complexes **2** are a coordinatively unsaturated species expected to react with various substrates and should be a unique reagent for the synthesis of ruthenium—sulfur clusters such as $Ru_4S_4(L)_4$.

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5) **2a**: Mp 208—210 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.31$ (d, $J = 6.9$ Hz, 6H; CH*Me*), 1.92 (s, 3H; Me), 2.35 (s, 12H; Me), 2.44 (m, 1H; C*H*Me), 4.79 (d, $J = 6.1$ Hz, 2H; aromatic protons of *p*-cymene), 4.96 (d, 2H; aromatic protons of *p*-cymene), 7.00 (m, 2H; aromatic protons), 7.09 (m, 4H; aromatic protons); UV-vis ($CHCl_3$): $\lambda_{max} = 676$ nm; Elemental analysis: C, 61.13; H, 6.20%, calculated for ($C_{26}H_{32}S_2Ru$): C, 61.26; H, 6.33%.

6) **2b**: 57% yield; Mp 125—130 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta = 1.17$ (broad s, 24H; *o*-CHMe_2), 1.25 (d, $J = 6.3$ Hz, 12H; *p*-CHMe_2), 1.33 (d, $J = 6.3$ Hz, 6H; CHMe_2), 1.88 (s, 3H; CH_3), 2.44 (m, 1H; C*H*Me_2), 2.86 (m, 2H; *p*-C*H*Me_2), 3.57 (m, 4H; *o*-C*H*Me_2), 4.89 (d, $J = 5.4$ Hz, 2H; aromatic protons of *p*-cymene), 5.06 (d, 2H; aromatic protons of *p*-cymene), 6.96 (s, 4H; aromatic protons); UV-vis ($CHCl_3$): $\lambda_{max} = 686$ nm; Elemental analysis: C, 67.28; H, 8.57%, calculated for ($C_{40}H_{60}S_2Ru$): C, 68.04; H, 8.56%.

7) Crystal data for **2a**: $C_{26}H_{32}S_2Ru$, $M = 509.73$, monoclinic space group $P2_1/n$, $a = 7.675(5)$, $b = 18.719(6)$, $c = 17.215(6)$ Å, $\beta = 92.65(4)°$, $V = 2471(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.370$ g cm^{-3}, Mo-Kα radiation. Diffraction data were collected on a Rigaku AFC-5R diffractometer. The calculation was performed using TEXSAN. The structure was solved by conventional heavy-atom method and refined (difference Fourier synthesis; full matrix least squares), as anisotropic temperature factors for a Ru, two S, and 17 carbons and as isotropic temperature factors for the remaining 9 carbons and all hydrogens, to reach current residual values of $R = 0.059$ and $R_w = 0.054$ for unique 931 reflections with $I > 3\sigma(I)$.

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