

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

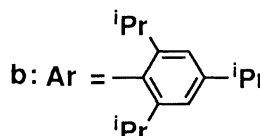
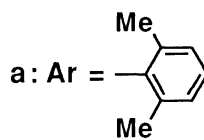
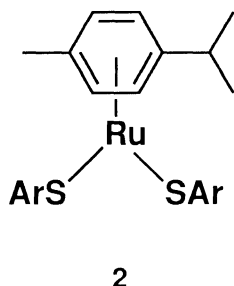
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Treatment of  $[\text{RuCl}_2(p\text{-cymene})]_2$  with sodium 2,6-dimethylbenzenethiolate or sodium 2,4,6-triisopropylbenzenethiolate in methanol afforded a mononuclear five-coordinated ruthenium thiolate complex,  $\text{Ru}(\text{SAr})_2(p\text{-cymene})$  (**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.<sup>1–4</sup> 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  $[\text{RuCl}_2(p\text{-cymene})]_2$  (**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.<sup>5</sup> Similarly, complex **2b** was prepared by the reaction of **1** with 6 equiv of sodium 2,4,6-triisopropylbenzenethiolate in THF.<sup>6</sup> Complex **2b** is more soluble in organic solvents and may be crystallized from a saturated hexane solution.



Structure of mononuclear Ru(II) complexes **2** was established by an X-ray crystallographic study of **2a**.<sup>7)</sup> 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)<sub>4</sub> (L = CO or CH<sub>3</sub>CN) (2.207(10)—2.409(3) Å),<sup>8)</sup> but shorter than the octahedral complexes such as RuH(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2.458(1) Å) and Ru(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2.470(2) Å).<sup>9)</sup> The bond lengths of Ru—C(η<sup>6</sup>) (2.17(3)—2.20(2) Å) are normal and the arene moiety coordinates to ruthenium atom in η<sup>6</sup>-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<sub>3</sub>CN)(S-2,3,5,6-tetramethylphenyl)<sub>4</sub> and Ru(CO)(S-2,3,5,6-tetramethylphenyl)<sub>4</sub>.<sup>8)</sup>

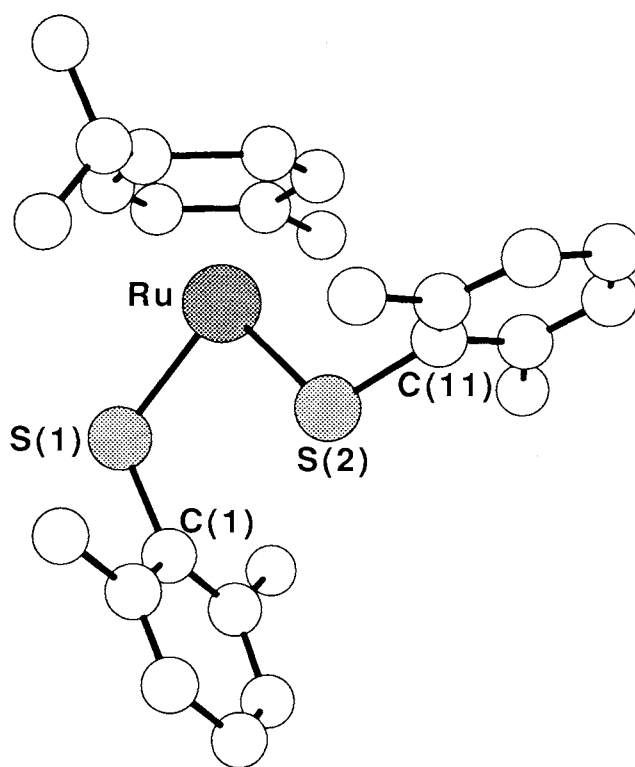
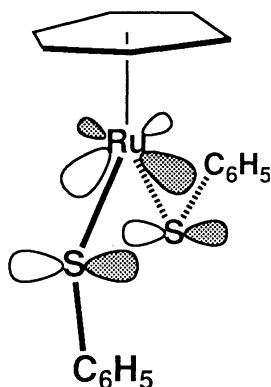


Fig. 1. A drawing of **2a** with a labeling scheme. Selected bond distances (Å) and angles (degree): Ru—S(1) 2.311(6), Ru—S(2) 2.263(7), Ru—C(cent) 1.673, S(1)—C(1) 1.77(2), S(2)—C(11) 1.82(2); S(1)—Ru—S(2) 89.0(2), S(1)—Ru—C(cent) 130, S(2)—Ru—C(cent) 140, Ru—S(1)—C(1) 114.2(8), Ru—S(2)—C(11) 108.9(8); 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.<sup>10)</sup> The planar geometry at the Ru—S—C part, e.g. the torsion angles of S(2)—Ru—S(1)—C(1) [ $-3(1)^\circ$ ] and S(1)—Ru—S(2)—C(11) [ $174(1)^\circ$ ], is attributed to the overlap between vacant  $d\pi$  orbital<sup>11,12)</sup> 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 $\rightarrow$ Ru charge-transfer transition.<sup>4)</sup> These red-shifted values are characteristic in comparison with the those of typical octahedral Ru(II) complexes (near 400 nm).<sup>9)</sup>

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); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ = 1.31 (d, *J* = 6.9 Hz, 6H; CHMe), 1.92 (s, 3H; Me), 2.35 (s, 12H; Me), 2.44 (m, 1H; CHMe), 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<sub>3</sub>): λ<sub>max</sub> = 676 nm; Elemental analysis: C, 61.13; H, 6.20%, calculated for (C<sub>26</sub>H<sub>32</sub>S<sub>2</sub>Ru): C, 61.26; H, 6.33%.
  - 6) **2b**: 57% yield; Mp 125—130 °C (decomp); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.17 (broad s, 24H; *o*-CHMe<sub>2</sub>), 1.25 (d, *J* = 6.3 Hz, 12H; *p*-CHMe<sub>2</sub>), 1.33 (d, *J* = 6.3 Hz, 6H; CHMe<sub>2</sub>), 1.88 (s, 3H; CH<sub>3</sub>), 2.44 (m, 1H; CHMe<sub>2</sub>), 2.86 (m, 2H; *p*-CHMe<sub>2</sub>), 3.57 (m, 4H; *o*-CHMe<sub>2</sub>), 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<sub>3</sub>): λ<sub>max</sub> = 686 nm; Elemental analysis: C, 67.28; H, 8.57%, calculated for (C<sub>40</sub>H<sub>60</sub>S<sub>2</sub>Ru): C, 68.04; H, 8.56%.
  - 7) Crystal data for **2a**: C<sub>26</sub>H<sub>32</sub>S<sub>2</sub>Ru, *M* = 509.73, monoclinic space group *P*2<sub>1</sub>/*n*, *a* = 7.675(5), *b* = 18.719(6), *c* = 17.215(6) Å, β = 92.65(4)°, *V* = 2471(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>calcd</sub> = 1.370 g cm<sup>-3</sup>, 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*<sub>w</sub> = 0.054 for unique 931 reflections with *I* > 3σ(*I*).
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