4148 *Organometallics* **2010,** *29,* 4148–4153
DOI: 10.1021/om100689f

ORGANOMETALLICS
Article

Preparation and Reactivity of a Ruthenium Complex Bearing a 2,6-Bis(trimethylsilyl)benzenethiolate Ligand

Masahiro Yuki, Yoshihiro Miyake, and Yoshiaki Nishibayashi*

Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

Received July 13, 2010

The reaction of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with ArSK (ArS = 2,6-$(Me_3Si)_2C_6H_3S$) gives the mononuclear ruthenium complex with π-arenethiolate ligand $[Cp^*Ru(\eta^5\text{-}SAr)]$ via $[Cp^*Ru(\mu\text{-}SAr)]_2$. Further reactions of $[Cp^*Ru(\eta^5\text{-}SAr)]$ with HCl and $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ give the corresponding monoruthenium complex $[Cp^*Ru(\eta^6\text{-}HSAr)]Cl$ and diruthenium complex $[Cp^*Ru(\mu\text{-}\eta^5\text{:}\eta^1\text{-}SAr)RuClCp^*]$ in high yields, respectively.

Introduction

Since the first report on the ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with nucleophiles to give the corresponding propargylic-substituted products in good to high yields with complete selectivity,[1,2] we have found novel transformations of propargylic alcohols catalyzed only by thiolate-bridged diruthenium complexes $[Cp^*RuCl(\mu_2\text{-}SR)]_2$ (R = Me, Et, ^{n}Pr, ^{i}Pr).[3,4] More recently, we have developed enantioselective versions of these catalytic reactions by using chiral thiolate-bridged diruthenium complexes $[Cp^*RuCl(\mu_2\text{-}SR^*)]_2$ (SR* = (*R*)-SCH(Et)$C_6H_2Ph_3$ and (*R*)-SCH(Et)$C_6H_3Ph_2$) as catalysts.[5]

As an extension of our study, we have envisaged the preparation of a novel thiolate-bridged diruthenium complex bearing bulky 2,6-bis(trimethylsilyl)benzenethiolate[6] as a bridging ligand because the introduction of sterically demanding ligands is known to provide unique reactive sites on the transition-metal complexes.[7] The reaction of $[Cp^*RuCl(\mu_2\text{-}Cl)]_2$ with ArSH (ArS = 2,6-$(Me_3Si)_2C_6H_3S$) in tetrahydrofuran (THF) at room temperature for 12 h did not give the target dinuclear diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SAr)]_2$, but only a small amount of the corresponding mononuclear ruthenium complex with π-arenethiolate ligand $[Cp^*Ru(\eta^5\text{-}SAr)]$ (**1**) (Scheme 1). The unusual coordination mode of the benzenethiolate

*To whom correspondence should be addressed. E-mail: ynishiba@sogo.t.u-tokyo.ac.jp.

(1) (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (b) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393. (c) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 7900. (d) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 11846. (e) Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 15172. (f) Nishibayashi, Y.; Inada, Y.; Yoshikawa, M.; Hidai, M.; Uemura, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1495. (g) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2003**, *125*, 6060. (h) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Org. Chem.* **2003**, *69*, 3408. (i) Nishibayashi, Y.; Milton, M. D.; Inada, Y.; Yoshikawa, M.; Wakiji, I.; Hidai, M.; Uemura, S. *Chem.—Eur. J.* **2005**, *11*, 1433. (j) Inada, Y.; Yoshikawa, M.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. *Eur. J. Org. Chem.* **2006**, 881. (k) Nishibayashi, Y.; Shinoda, A.; Miyake, Y.; Matsuzawa, H.; Sato, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4835. (l) Daini, M.; Yoshikawa, M.; Inada, Y.; Uemura, S.; Sakata, K.; Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 2046. (m) Yamauchi, Y.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 48. (n) Fukamizu, K.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 2534.

(2) The result of the density functional theory calculation on the model reaction also supports the proposed reaction pathway of the ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with nucleophiles, where ruthenium−allenylidene complexes work as key intermediates; see: (a) Ammal, C. S.; Yoshikai, N.; Inada, Y.; Nishibayashi, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 9428. (b) Sakata, K.; Miyake, Y.; Nishibayashi, Y. *Chem. Asian J.* **2009**, *4*, 81.

(3) (a) The exact structure of these complexes by X-ray crystallographic analysis was not known at this stage: Dev, S.; Imagawa, K.; Mizobe, Y.; Cheng, G.; Wakatsuki, Y.; Yamazaki, H.; Hidai, M. *Organometallics* **1989**, *8*, 1232. (b) Qü, J.-P.; Masui, D.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1998**, 1003. (c) Hidai, M.; Mizobe, Y. *Can. J. Chem.* **2005**, *83*, 358, and references therein.

(4) (a) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 26. (b) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 5100. (c) Miyake, Y.; Endo, S.; Nomaguchi, Y.; Yuki, M.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 4017. (d) Miyake, Y.; Endo, S.; Yuki, M.; Tanabe, Y.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 6039. (e) Tanabe, Y.; Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 1138. (f) Kanao, K.; Tanabe, Y.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 2381.

(5) (a) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2003**, *22*, 873. (b) Inada, Y.; Nishibayashi, Y.; Uemura, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7715. (c) Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 6488. (d) Matsuzawa, H.; Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Org. Lett.* **2007**, *9*, 5561. (e) Kanao, K.; Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Synthesis* **2008**, 3869. (f) Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 2920. (g) Fukamizu, K.; Miyake, Y.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 10498. (h) Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 2126. (i) Ikeda, M.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, early view (DOI: 10.1002/anie.201002591).

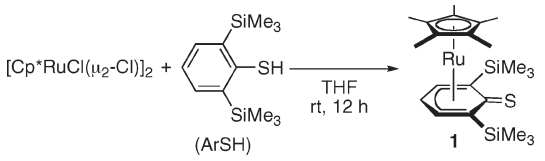
(6) (a) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654. (b) Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658. (c) Smith, K.; Lindsay, C. M.; Pritchard, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 665.

(7) (a) Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1178. (b) Ruhlandt-Senge, K. *Inorg. Chem.* **1995**, *34*, 3499. (c) MacDonnell, F. M.; Ruhlandt-Senge, K.; Ellison, J. J.; Holm, R. H.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 1815. (d) Ohta, S.; Ohki, Y.; Ikagawa, Y.; Suizu, R.; Tatsumi, K. *J. Organomet. Chem.* **2007**, *692*, 4792. (e) Ohki, Y.; Ikagawa, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2007**, *129*, 10457. (f) Ito, M.; Matsumoto, T.; Tatsumi, K. *Inorg. Chem.* **2009**, *48*, 2215.

(8) Gimeno, J.; Crochet, P. In *Comprehensive Organometallic Chemistry III*; Bruce, M., Ed.; Elsevier: Amsterdam, 2007; Vol. *6*, Chapter 14, pp 465−550.

 Published on Web 08/23/2010

Scheme 1. Reaction of $[Cp^*RuCl(\mu_2\text{-}Cl)]_2$ with ArSK



to the ruthenium atom in **1** prompted us to investigate the reactivity of **1** in detail.

It is well known that $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ ($Cp^* = \eta^5\text{-}C_5Me_5$) reacted with various arene derivatives including phenol to give the corresponding π-arene complexes $[Cp^*Ru(\eta^6\text{-arene})]Cl$ (Scheme 2).[8−11] In sharp contrast, reactions of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with benzenethiols did not give the corresponding π-arene complexes, but the corresponding benzenethiolate-bridged diruthenium complexes $[Cp^*Ru(\mu_2\text{-}SAr')]_2$ ($Ar' = Ph$, 2,6-$Me_2C_6H_3$, C_6F_5) because of high affinity between the ruthenium atom and thiolate sulfur.[12] Although the reaction with sterically demanding 2,6-dimesitylbenzenethiolate (DmpS) gave the corresponding mononuclear ruthenium complex $[Cp^*Ru(\eta^1\text{-}SDmp)]$,[13] no formation of the corresponding π-arene complexes was observed at all. As a new approach to the preparation of π-benzene complexes, we have now found that the reaction of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with ArSK gave **1** in good yield with complete selectivity. Herein, we describe the preparation and reactivity of **1** in detail.

Results and Discussion

Treatment of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with ArSK in THF at room temperature for 4 h gave the dinuclear ruthenium complex $[Cp^*Ru(\mu\text{-}SAr)]_2$ (**2**) in 72% isolated yield (Scheme 3). The ^{1}H NMR spectrum of **2** exhibits proton signals assignable to trimethylsilyl and Cp* moieties in 18:15 ratio, showing 1:1 complexation of the Cp*Ru fragment with the SAr moiety. The ring protons of the aryl moieties were observed in the normal region for aromatic protons (7.71−7.04 ppm), indicating that the thiolate ligand is bound to the ruthenium center through the sulfur atom in a general manner. ^{13}C NMR spectrum of **2** was also consistent with the structure. In addition, the mass spectral data for **2** support the dinuclear structure of **2** (see Experimental Section). Unfortunately, we have not yet characterized the molecular structure of **2** by X-ray crystallography.

The diruthenium complex **2** was unstable and gradually converted into π-arenethiolate complex $[Cp^*Ru(\eta^5\text{-}SAr)]$ (**1**). In fact, **1** was obtained in 80% isolated yield after a THF solution of **2** was stood at room temperature for 20 days. The ^{1}H NMR spectrum of **1** displays one set of trimethylsilyl and Cp* signals at 1.84 and 0.36 ppm in 18:15 ratio, respectively, showing 1:1 complexation of the Cp*Ru fragment with the SAr moiety. On the other hand, the ^{1}H NMR spectrum of **1** exhibits two high-field-shifted signals at 4.85 and 4.34 ppm ascribable to the aryl protons of the thiolate ligand. In the ^{13}C NMR spectrum of **1**, signals of aromatic carbons bound to the ruthenium center were observed at high field (97.5−82.3 ppm), whereas the signal of the carbon atom attached to the sulfur atom appeared at 152.0 ppm, suggesting η^5-coordination. A similar transformation was previously reported only in the reaction of the diruthenium complex bearing O-bonded 2,4-bis(*tert*-butyl)phenolate ligand $[Cp^*Ru(\mu_2\text{-}OC_6H_4\text{-}2,4\text{-}{}^tBu_2)]_2$ to give the corresponding mononuclear ruthenium complex with π-benzolate ligand $[Cp^*Ru(\eta^5\text{-}OC_6H_4\text{-}2,4\text{-}{}^tBu_2)]$.[9i]

The molecular structure of **1** was unequivocally determined by X-ray crystallography. The unit cell contains two independent molecules, but the structural parameters were almost the same. An ORTEP drawing and selected bond distances of **1** are shown in Figure 1. Evidently the 2,6-bis(trimethylsilyl)benzenethiolate ligand is bound to the ruthenium atom through the aromatic carbons. The sulfur atom is far away from the ruthenium center (Ru···S: 3.8 Å). The carbon atom attached to the sulfur atom has no or very weak interaction with the ruthenium center because the interatomic distance between ruthenium and the carbon atoms (2.37 Å (mean)) is longer than those between ruthenium and other carbon atoms (2.19−2.26 Å). These deviations of bond distances between ruthenium and carbon atoms indicate that the 2,6-bis(trimethylsilyl)phenyl moiety is coordinated to the ruthenium atom in a η^5-pentadienyl fashion rather than a η^6-arene fashion. The η^5-pentadienyl structure was analogous to the corresponding phenolate complexes.[9] The bond length between sulfur and the carbon atoms (1.72 Å (mean)) is shorter than those of general arenethiolato ligands (ca. 1.80 Å),[14] indicating a partial double-bond character between the sulfur and carbon atoms. The π-coordination of the 2,6-bis(trimethylsilyl)benzenethiolate ligand in **1** fulfills the 18-electron count for the ruthenium center. Only one example of the coordination mode of the η^5-pentadienyl structure bearing a thiolate ligand was previously reported for the molybdenum complex bearing two 2,6-bis(trimethylsilyl)phenyl thiolate ligands.[15]

On the other hand, the diruthenium complex **2** rapidly reacted with 2 equiv of isonitriles at room temperature for 20 min to give $[Cp^*Ru(\eta^1\text{-}SAr)(CNR)_2]$ (**3a**, R = ^{t}Bu; **3b**, R = *p*-$MeOC_6H_4$) in 66% and 75% yields (Scheme 3). IR spectra of **3** showed two ν_{CN} bands (**3a**: 2111 and 2045 cm^{-1}, **3b**: 2102 and 2030 cm^{-1}). The molecular structure of **3a** was unequivocally determined by X-ray crystallography. An ORTEP drawing and selected bond distances of **3a** are shown in Figure 2. The 2,6-bis(trimethylsilyl)benzenthiolate ligand was

(9) (a) Chaudret, B.; He, X.; Huang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1844. (b) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, D. T.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712. (c) He, X. D.; Chaudret, B.; Dahan, F.; Huang, Y.-S. *Organometallics* **1991**, *10*, 970. (d) Koelle, U.; Wang, M. H.; Raabe, G. *Organometallics* **1991**, *10*, 2573. (e) Vichard, D.; Gruselle, M.; Amouri, H. E.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1991**, 46. (f) Huang, Y.-S.; Sabo-Etienne, S.; He, X.-D.; Chaudret, B. *Organometallics* **1992**, *11*, 3031. (g) Koelle, U.; Hörnig, A.; Englert, U. *Organometallics* **1994**, *13*, 4064. (h) Hörnig, A.; Englert, U.; Kölle, U. *J. Organomet. Chem.* **1994**, *464*, C25. (i) Bücken, K.; Koelle, U.; Pasch, R.; Ganter, B. *Organometallics* **1996**, *15*, 3095. (j) Pasch, R.; Koelle, U.; Ganter, B.; Englert, U. *Organometallics* **1997**, *16*, 3950. (k) Morvan, D.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **2009**, *28*, 3161. (l) Trujillo, A.; Fuentealba, M.; Carrillo, D.; Manzur, C.; Ledoux-Rak, I.; Hamon, J.-R.; Saillard, J.-Y. *Inorg. Chem.* **2010**, *49*, 2750.

(10) Fish, R. H.; Fong, R. H.; Tran, A.; Baralt, E. *Organometallics* **1991**, *10*, 1209.

(11) Chaudret, B.; Jalon, F.; Perez-Manrique, M.; Lahoz, F. J.; Plou, F. J.; Sanchez-Delgado, R. *New J. Chem.* **1990**, *14*, 331.

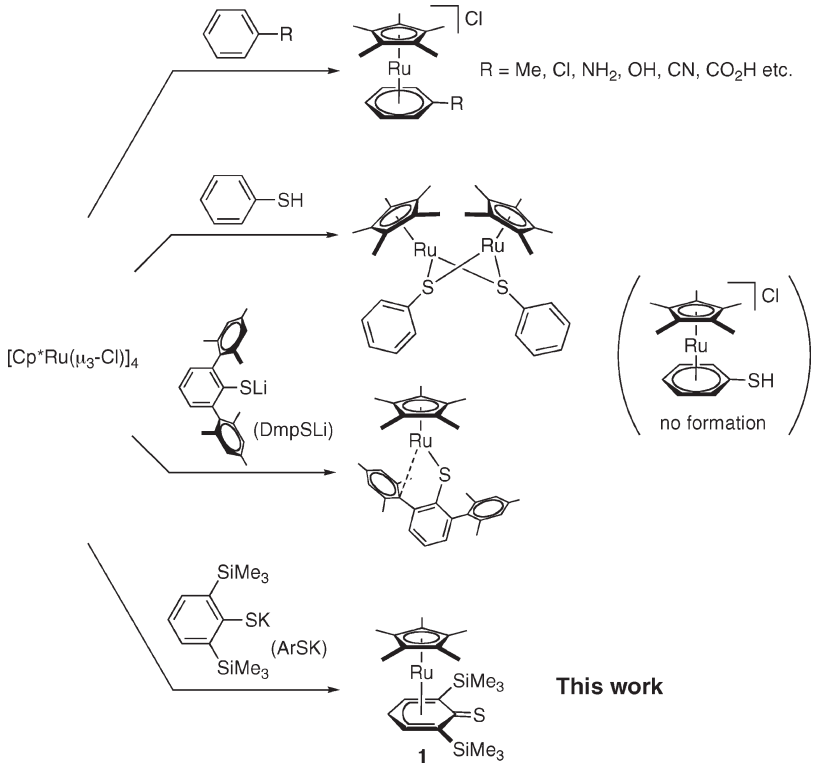
(12) (a) Koelle, U.; Rietmann, C.; Englert, U. *J. Organomet. Chem.* **1992**, *423*, C20. (b) Hörnig, A.; Rietmann, C.; Englert, U.; Wagner, T.; Kölle, U. *Chem. Ber.* **1993**, *126*, 2609. (c) Takahashi, A.; Mizobe, Y.; Matsuzaka, H.; Dev, S.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 243.

(13) Ohki, Y.; Sadohara, H.; Takikawa, Y.; Tatsumi, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 2290.

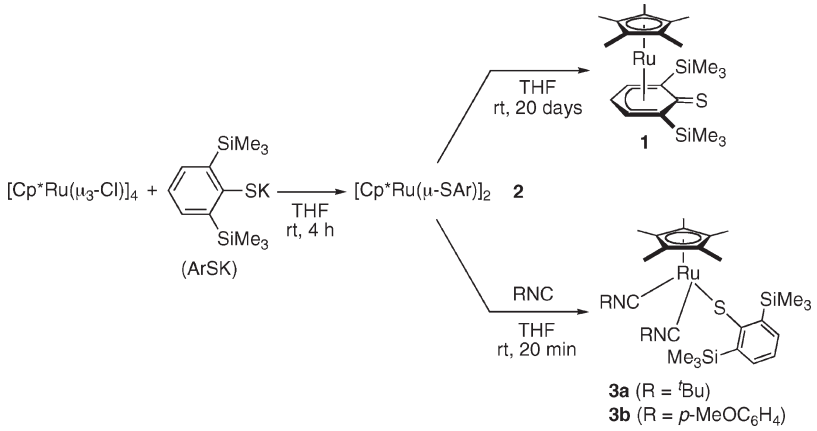
(14) (a) Ruhlandt-Senge, K.; Davis, K.; Dalal, S.; Englich, U.; Senge, M. O. *Inorg. Chem.* **1995**, *34*, 2587. (b) Chadwick, S.; Englich, U.; Ruhlandt-Senge, K.; Watson, C.; Bruce, A. E.; Bruce, M. R. M. *J. Chem. Soc., Dalton Trans.* **2000**, 2167. (c) Hildebrand, A.; Lönnecke, P.; Silaghi-Dumitrescu, L.; Silaghi-Dumitrescu, I.; Hey-Hwakins, E. *Dalton Trans.* **2006**, 967.

(15) Komuro, T.; Matsuo, T.; Kawaguchi, H.; Tatsumi, K. *J. Am. Chem. Soc.* **2003**, *125*, 2070.

Scheme 2. Reactions of [Cp*Ru(μ_3-Cl)]$_4$ with Arenes



Scheme 3. Reactions of [Cp*Ru(μ-SAr)]$_2$ (2)



bound to the ruthenium center through the sulfur atom. The ruthenium center adopts a three-legged piano stool geometry with one thiolate, two isonitriles, and one Cp* ligand. Two silyl groups of the 2,6-bis(trimethylsilyl)benzenthiolate moiety are highly bent away from the ruthenium center. The silicon atoms were displaced ca. 0.5 Å out of the least-squares plane defined by the six aromatic carbons, representing the severe steric repulsion between the trimethylsilyl group and the other ligands. A similar mononuclear ruthenium complex, [Cp*Ru(SDmp)-(CN^{t}Bu)$_2$], was previously obtained from the reaction of mononuclear ruthenium complex [Cp*Ru(SDmp)] with isonitriles.[13] In addition, the thiolate-bridged diruthenium complex [Cp*-Ru(S^{t}Bu)]$_2$ reacted with isonitriles to give the corresponding dinuclear complex [Cp*Ru(S^{t}Bu)(CN^{t}Bu)]$_2$.[12a]

Treatment of **1** with HCl in dichloromethane at room temperature for 1 h gave the corresponding mononuclear ruthenium complex [Cp*Ru(η^6-HSAr)]Cl (**4**) in 94% yield (Scheme 4). In the ^{1}H NMR spectrum of **4**, the thiol proton was observed at 3.42 ppm. In the ^{13}C NMR spectrum of **4**, all aromatic carbons of the 2,6-bis(trimethylsilyl)phenyl moiety including the carbon atom attached to the sulfur atom (102.7 ppm) are observed at high field (102.7−88.9 ppm) as typical for η^6-arene complexes. A similar change from η^5- to η^6-coordination is known for the protonation of the corresponding phenolate analogues.[9]

The molecular structure of **4** was unequivocally determined by X-ray crystallography. An ORTEP drawing and selected bond distances of **4** are shown in Figure 3. The sandwich structure of **1** is preserved in **4**. However, the bond distances between sulfur and carbon bonds are elongated to 1.79 Å (mean) by 0.07 Å compared to those of **1**. Bond distances between ruthenium and carbon atoms attached to sulfur atoms are 2.23−2.28 Å, which are ca. 0.1 Å shorter than those of **1** and are comparable to the distances between

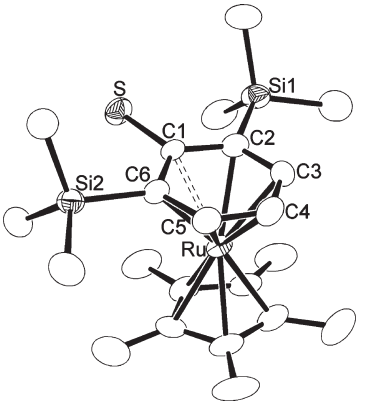


Figure 1. ORTEP view of **1**. Only one of two crystallographically independent molecules is shown. Selected interatomic distances (Å) for molecule A: Ru−C1 2.368(4), Ru−C2 2.263(4), Ru−C3 2.196(4), Ru−C4 2.185(4), Ru−C5 2.190(4), Ru−C6 2.257(4), S−C1 1.721(4). For molecule B: Ru−C1 2.378(4), Ru−C2 2.255(4), Ru−C3 2.190(4), Ru−C4 2.191(4), Ru−C5 2.192(4), Ru−C6 2.262(3), S−C1 1.727(4).

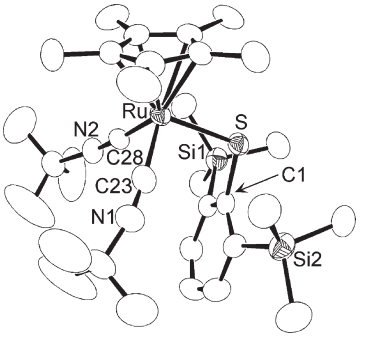
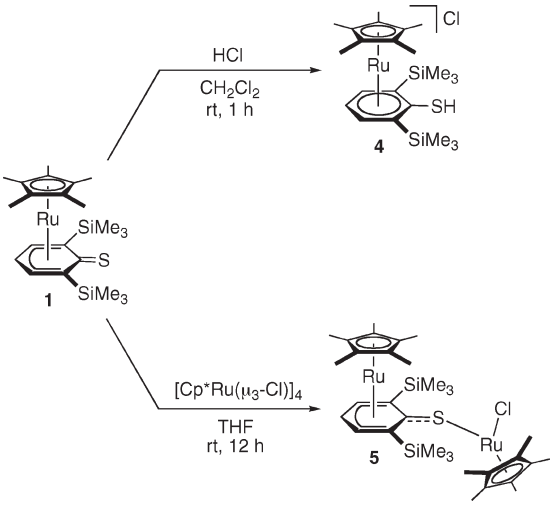


Figure 2. ORTEP view of **3a**. Only one of two crystallographically independent molecules is shown. Selected interatomic distances (Å) for molecule A: Ru−S 2.4354(12), Ru−C23 1.923(6), Ru−C28 1.925(5), S−C1 1.786(5). For molecule B: Ru−S 2.4398(13), Ru−C23 1.922(5), Ru−C28 1.896(7), S−C1 1.781(5).

Scheme 4. Reactions of [Cp*Ru(η^5-SAr)] (1)



ruthenium and other carbon atoms (2.19−2.27 Å) in **4**. These structural data indicate that the 2,6-bis(trimethylsilyl)phenyl moiety in **4** adopts a normal η^6-arene coordination mode.

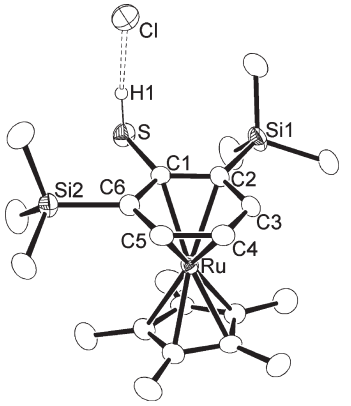


Figure 3. ORTEP view of **4**. Only one of two crystallographically independent molecules is shown. Selected interatomic distances (Å) for molecule A: Ru−C1 2.284(2), Ru−C2 2.269(3), Ru−C3 2.209(2), Ru−C4 2.192(2), Ru−C5 2.193(2), Ru−C6 2.257(3), S−C1 1.789(2). For molecule B: Ru−C1 2.231(2), Ru−C2 2.254(2), Ru−C3 2.211(2), Ru−C4 2.195(2), Ru−C5 2.211(2), Ru−C6 2.256(2), S−C1 1.787(2).

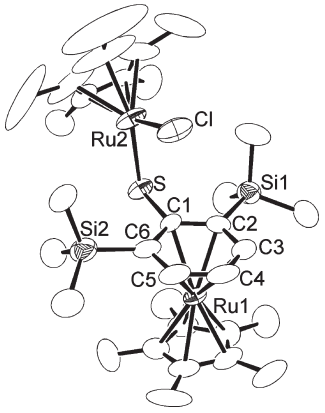


Figure 4. ORTEP view of **5**. Only one of two crystallographically independent molecules is shown. Selected interatomic distances (Å) for molecule A: Ru1−C1 2.319(5), Ru1−C2 2.275(5), Ru1−C3 2.205(6), Ru1−C4 2.204(6), Ru1−C5 2.194(6), Ru1−C6 2.271(6), S−C1 1.768(5), Ru2−S 2.3400(16). For molecule B: Ru1−C1 2.338(6), Ru1−C2 2.267(6), Ru1−C3 2.199(7), Ru1−C4 2.190(7), Ru1−C5 2.200(7), Ru1−C6 2.272(6), S−C1 1.758(6), Ru2−S 2.3440(16).

On the other hand, the reaction of **1** with [Cp*Ru(μ_3-Cl)]$_4$ in THF at room temperature for 12 h gave the corresponding diruthenium complex [Cp*Ru(μ-η^5:η^1-SAr)RuClCp*] (**5**) in 93% isolated yield (Scheme 4). In the ^{13}C NMR spectrum of **5**, the signal corresponding to the carbon atom attached to the sulfur atom appeared at 138.0 ppm, which was intermediate in value between **1** (152.0 ppm) and **4** (102.7 ppm). These observations indicate that coordination of the sulfur atom to a Cp*RuCl fragment in **5** results in the intermediate structure of the 2,6-bis(trimethylsilyl)benzenethiolate moiety between η^5-pentadienyl and η^6-arene character.

The molecular structure of **5** was unequivocally determined by X-ray crystallography. The unit cell contains two independent molecules. An ORTEP drawing and selected bond distances of **5** are shown in Figure 4. In the dinuclear complex, the [Cp*Ru(η^5-SAr)] moiety served as a sulfur donor ligand to the Cp*RuCl fragment. The bond distances between ruthenium and sulfur atoms (2.34 Å (mean)) were unusual. The bond distances between the carbon and sulfur

Table 1. Summary of Crystallographic Data

	1·0.25C_6H_{14}	**3a**·0.5C_6H_{14}	**4**	**5**
formula	$C_{23.5}H_{39.5}RuSi_2S$	$C_{35}H_{61}N_2RuSSi_2$	$C_{22}H_{37}ClRuSi_2S$	$C_{32}H_{51}Ru_2Si_2S$
fw	511.36	699.18	526.29	761.56
cryst size/mm	0.54 × 0.23 × 0.02	0.50 × 0.25 × 0.05	0.60 × 0.30 × 0.05	0.30 × 0.20 × 0.15
color, habit	yellow plate	orange plate	colorless plate	wine red prism
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a/Å	11.1331(4)	20.2705(8)	11.6073(8)	14.9562(5)
b/Å	15.9138(5)	18.1441(7)	14.0285(9)	26.9734(8)
c/Å	16.1451(5)	22.610(1)	16.641(1)	18.6671(7)
α/deg	92.964(1)	90	67.495(2)	90
β/deg	108.106(1)	104.327(1)	89.219(2)	109.586(1)
γ/deg	107.073(1)	90	89.219(2)	90
V/Å^3	2566.6(2)	8057.2(6)	2500.1(3)	7094.9(4)
Z	4	8	4	8
d_c/g cm^{-3}	1.323	1.153	1.398	1.426
μ(Mo Kα)/mm^{-1}	0.793	0.523	0.919	1.072
no. of data collected	25 328 ($2\theta < 55°$)	58 072 ($2\theta < 50°$)	24 112 ($2\theta < 55°$)	68 342 ($2\theta < 55°$)
no. of unique data (R_{int})	11 693 (0.041)	14 459 (0.097)	11 235 (0.031)	16 158 (0.085)
no. of params refined	518	742	517	707
R_1[a] ($F^2 > 2\sigma$)	0.039	0.065	0.031	0.060
wR_2[b] (all data)	0.108	0.199	0.081	0.192
goodness of fit indicator[c]	1.09	1.02	1.08	1.08
residual electron density/e Å^{-3}	+0.91 to −1.40	+1.88 to −1.07	+0.60 to −0.50	+1.21 to −1.45

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2]^{1/2}$. [c] $[\sum w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

atoms (1.76 Å (mean)) were elongated by coordination to the Cp*RuCl fragment, but were shorter than that of **4**. At the same time, the interatomic distances between ruthenium and the carbon atom attached to the sulfur atom (2.33 Å (mean)) are shorter than those of **1**, but still longer than those of **4**. Theses results indicate that the extent of donor−acceptor interaction of **1** at the sulfur atom influences the coordination structure of the 2,6-bis(trimethylsilyl)benzenethiolate moiety.

In summary, we have newly prepared and characterized a mononuclear ruthenium complex with π-arenethiolate ligand [Cp*Ru(η^5-SAr)] (**1**) from the reaction of [Cp*Ru(μ_3-Cl)]$_4$ with ArSK (ArS = 2,6-$(Me_3Si)_2C_6H_3S$). Further reactions of the monoruthenium complex **1** with HCl and [Cp*Ru(μ_3-Cl)]$_4$ gave the corresponding monoruthenium complex [Cp*Ru(η^6-HSAr)]Cl (**4**) and diruthenium complex [Cp*Ru(μ-η^5:η^1-SAr)RuClCp*] (**5**) in high yields, respectively.

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere using standard Schlenk-line techniques or in a glovebox. Solvents were dried over appropriate agents under an inert atmosphere. Compounds [Cp*RuCl]$_4$[16] and 2,6-bis(trimethylsilyl)benzenethiol[6] were prepared by the literature methods. Other reagents were purchased from commercial sources and were used as received. NMR spectra were recorded on JEOL JNM-EX270 spectrometers, and chemical shifts are quoted in ppm. Assignments of ^{13}C NMR signals were made by using DEPT and inverse-gated decoupling methods. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analyses were performed on an Exeter Analytical CE-440 elemental analyzer.

Preparation of [Cp*Ru(μ-SAr)]$_2$ (2). To a THF (2 mL) solution of 2,6-bis(trimethylsilyl)benzenethiol (128 mg, 0.501 mmol) was added a THF (3 mL) solution of KN$(SiMe_3)_2$ (100 mg, 0.501 mmol). After 30 min, the resulting yellow solution was dried *in vacuo* to remove HN$(SiMe_3)_2$. The white solid of ArSK was redissolved in THF (5 mL) and was transferred to an orange-brown THF (5 mL) solution of [Cp*RuCl]$_4$ (136 mg, 0.125 mmol). The resulting purple solution was stirred at room temperature for 4 h. The solution was concentrated to dryness, and the residue was extracted with hexane. Concentration of the hexane extract gave a purple powder of **2** (227 mg, 0.232 mmol). Recrystallization from cold hexane (−30 °C) afforded analytically pure **2** as purple microcrystals (176 mg, 0.180 mmol, 72%). Data for **2**: ^{1}H NMR (THF-d_8) δ 7.71 (d, J_{HH} = 7 Hz, 4H), 7.04 (t, J_{HH} = 7 Hz, 2H), 1.45 (s, 30H, Cp*), 0.09 (s with ^{29}Si satellites, $^3J_{HSi}$ = 6 Hz and 36H, $SiMe_3$); ^{13}C NMR (THF-d_8) δ 142.7 (3,5-positons of Ar), 127.5 (2,6-positions of Ar), 120.3 (4-position of Ar), 77.8 (C_5Me_5), 11.2 (C_5Me_5), 0.4 ($SiMe_3$); FAB MS (Xe, *m*-nitrobenzyl alcohol matrix) *m*/*z* 980 (18, M^+), 907 (29, $M^+ - SiMe_3$), 489 (100, Cp*RuSAr−H). Anal. Calcd for $C_{22}H_{36}RuSSi_2$: C, 53.94; H, 7.41. Found: C, 54.06; H, 7.13.

Preparation of [Cp*Ru(η^5-SAr)] (1). Complex **2** (41.7 mg, 0.0426 mmol) was dissolved in THF (5 mL). After 20 days at room temperature, the solution was concentrated to dryness. The dark yellow residue was washed with hexane to give a yellow crystalline solid of **1**·0.25C_6H_{14} (34.9 mg, 0.0682 mmol, 80%). Data for **1**: ^{1}H NMR (THF-d_8) δ 5.24−5.14 (m, 3H, Ar), 1.84 (s, 15H, Cp*), 0.36 (s with ^{29}Si satellites, $^3J_{HSi}$ = 7 Hz and 18H, $SiMe_3$); ^{13}C NMR (THF-d_8) δ 152.0 (1-position of Ar), 97.5 (2,6-position of Ar), 91.9 (C_5Me_5), 89.7 (3,5-position of Ar), 82.3 (4-position of Ar), 10.9 (C_5Me_5), 1.2 ($SiMe_3$). Anal. Calcd for $C_{23.5}H_{39.5}RuSSi_2$ (**1**·0.25C_6H_{14}): C, 55.19; H, 7.79. Found: C, 54.84; H, 7.66.

Preparation of [Cp*Ru(η^1-SAr)(CNR)$_2$] (3a; R = ^{t}Bu). To a THF (5 mL) solution of **2** (48.9 mg, 0.0499 mmol) was added ^{t}BuNC (27.2 mg, 0.327 mmol). The mixture was stirred at room temperature for 5 min. After filtration, the dark orange solution was concentrated to dryness. The residue was recrystallized from cold hexane (−30 °C). The orange platelet crystals were dried *in vacuo* to afford **3a** (42.9 mg, 0.0654 mmol, 66%). Data for **3a**: ^{1}H NMR (C_6D_6) δ 7.47 (d, J = 7 Hz, 2H, Ar), 7.05 (t, J = 7 Hz, 1H, Ar), 1.72 (s, 15H, Cp*), 1.05 (s, 18H, ^{t}Bu), 0.75 (s, 18H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 167.4 (1-position of Ar), 146.2 (2,6-positions of Ar), 134.5 (3,5-positions of Ar), 122.0 (4-position of Ar), 92.8 (C_5Me_5), 55.4 (CMe_3), 31.4 (CMe_3), 9.9 (C_5Me_5), 2.4

(16) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

($SiMe_3$); IR (KBr) ν_{CN} 2111 and 2045 cm^{-1}. Anal. Calcd for $C_{32}H_{54}N_2RuSSi_2$: C, 58.58; H, 8.30, N, 4.27. Found: C, 58.90; H, 8.36; N, 4.24.

Preparation of [Cp*Ru(η^1-SAr)(CNR)$_2$] (3b; R = *p*-MeOC$_6$H$_4$). To a THF solution (3 mL) of **2** (48.8 mg, 0.0498 mmol) was added *p*-methoxyphenylisonitrile (56.0 mg, 0.421 mmol) in THF (2 mL). The mixture was stirred at room temperature for 20 min. After filtration, the dark orange solution was concentrated to dryness. The oily residue was recrystallized from cold hexane (−30 °C), affording orange prisms of **3b** (56.2 mg, 0.0743 mmol, 75%). Data for **3b**: ^{1}H NMR (C_6D_6) δ 7.47 (d, J = 7.2 Hz, 2H, Ar), 7.22 (t, J = 7.2 Hz, 1H, Ar), 6.98 (d, J = 8.9 Hz, 4H, C_6H_4-OMe), 6.53 (d, J = 8.9 Hz, 4H, C_6H_4OMe), 3.11 (s, 6H, OMe), 1.85 (s, 15H, Cp*), 0.68 (s, 18H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 171.2 (*C*NR), 166.6 (1-position of Ar), 158.3 (4-position of R), 146.1 (2,6-positions of Ar), 135.3 (3,5-positions of Ar), 126.9 (2,6-positions of R), 124.5 (1-position of R), 122.5 (4-position of Ar), 114.5 (3,5-positions of R), 95.1 (C_5Me_5), 54.9 (OMe), 10.1 (C_5Me_5), 2.1 ($SiMe_3$); IR (KBr) ν_{CN} 2102 and 2030 cm^{-1}. Anal. Calcd for $C_{38}H_{50}N_2O_2RuSSi_2$: C, 60.36; H, 6.67, N, 3.70. Found: C, 59.98; H, 6.52; N, 3.57.

Preparation of [Cp*Ru(η^6-HSAr)]Cl (4). To a CH_2Cl_2 (5 mL) solution of **1**·0.25C_6H_{14} (51.2 mg, 0.100 mmol) was added etheral HCl (2 M solution, 0.07 mL, 0.14 mmol). After stirring at room temperature for 1 h, volatiles were removed under vacuum. Recrystallization from CH_2Cl_2 (1 mL)−hexane (7 mL) afforded colorless plates of **4** (49.3 mg, 0.0937 mmol, 94%). Data for **4**: ^{1}H NMR ($CDCl_3$) δ 6.86 (t, J = 6 Hz, 1H, Ar), 5.82 (d, J = 6 Hz, 2H, Ar), 3.42 (br, 1H, SH), 1.93 (s, 15H, Cp*), 0.40 (s with ^{29}Si satellite, $^3J_{HSi}$ = 6 Hz and 18H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 102.7 (1-position of Ar), 99.9 (2,6-positions of Ar), 96.2 (C_5Me_5), 91.3 (3,5-positions of Ar), 88.9 (4-position of Ar), 11.3 (C_5Me_5), 0.79 (s with ^{29}Si satellite, $^1J_{C-Si}$ = 55 Hz, $SiMe_3$). Anal. Calcd for $C_{22}H_{37}ClRuSSi_2$: C, 50.21; H, 7.09. Found: C, 49.97; H, 6.60.

Preparation of [Cp*Ru(μ-η^5:η^1-SAr)RuClCp*] (5). To a THF (5 mL) solution of **1**·0.25C_6H_{14} (23.0 mg, 0.0450 mmol) was added [Cp*RuCl]$_4$ (12.0 mg, 0.0110 mmol) with stirring. The resulting wine red solution was stirred at room temperature for 12 h. Concentration of the solution and recrystallization from THF−hexane afforded wine red prisms of **5**·0.5C_6H_{14} (34.2 mg, 0.0425 mmol, 93%). Data for **5**: ^{1}H NMR (THF-d_8) δ 5.41 (t, $^3J_{HH}$ = 6 Hz, 1H, Ar), 5.27 (d, $^3J_{HH}$ = 6 Hz, 2H, Ar), 1.90 (s, 15H, Cp*), 1.59 (s, 15H, Cp*), 0.42 (s, 18H, $SiMe_3$); ^{13}C{^{1}H} NMR (THF-d_8) δ 138.0 (1-position of Ar), 100.3 (2,6-positions of Ar), 93.3 (C_5Me_5), 90.8 (3,5-positions of Ar), 86.3 (4-position of Ar), 70.6 (C_5Me_5), 11.3 (C_5Me_5), 11.2 (C_5Me_5), 2.9 ($SiMe_3$). Anal. Calcd for $C_{35}H_{58}ClRu_2SSi_2$ (**5**·0.5C_6H_{14}): C, 52.24; H, 7.27. Found: C, 52.34; H, 7.18.

X-ray Crystallography. Crystallographic data are summarized in Table 1. Paraffin-coated crystals were placed on a nylon loop and mounted on a Rigaku RAXIS RAPID imagining plate system. Data were collected at −100 °C under a cold nitrogen stream using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Data were corrected for Lorenz, polarization, and absorption effects. Structures were solved by direct methods (SIR97)[17] and refined on F^2 by full-matrix least-squares techniques. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. The thiol hydrogen (H1) of **4** was located by difference-Fourier map and refined isotropically, while the remaining hydrogen atoms were placed in idealized positions and treated as riding atoms. In the crystal of **5**, the large anisotropy of thermal factors indicated the disordered structure of the Cp* ligands, but they could not be appropriately modeled. All calculations were carried out using WinGX/SHELXL software suites.[18,19] Thermal ellipsoid plots were drawn with ORTEP3.[20]

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research for Young Scientists (S) (No. 19675002) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(17) SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(18) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1998.

(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(20) Farrugia, L. J. ORTEP3 for Windows. *J. Appl. Crystallogr.* **1997**, *30*, 565.