

## Unusual Coordination Modes of Arylthiolates in $\text{Mo}\{\eta^5\text{-SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}_2\{\eta^7\text{-SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}$

Takashi Komuro,<sup>†</sup> Tsukasa Matsuo,<sup>‡</sup> Hiroyuki Kawaguchi,<sup>\*,‡</sup> and Kazuyuki Tatsumi<sup>\*,†</sup>

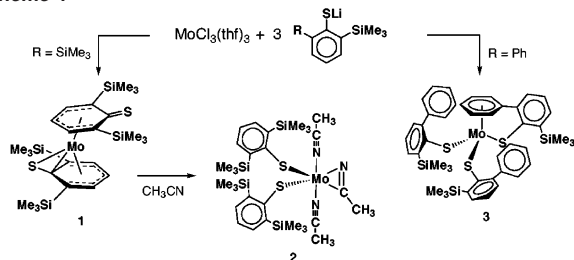
Research Center for Materials Science, and Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan, and Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received December 2, 2002; E-mail: i45100a@nucc.cc.nagoya-u.ac.jp; hkawa@ims.ac.jp

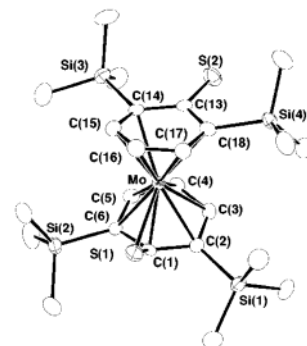
Although arylthiolate ligands are ubiquitous in transition-metal coordination chemistry, they are invariably S-bonded for either terminal or bridging coordination. This is probably because the affinity of transition-metal elements for thiolate sulfurs is strong relative to the metal–aryl  $\pi$  interactions. In contrast, analogous aryloxy complexes have occasionally been found to assume  $\pi$  coordination geometries at the aryl substituents, in an  $\eta^5$ -pentadienyl or an  $\eta^3$ -allyl bonding manner, leaving the C=O portion intact.<sup>1</sup> As a part of our ongoing study on activation of small molecules by means of coordinatively unsaturated transition-metal complexes,<sup>2</sup> we were interested in preparation of molybdenum complexes of the 2,6-disubstituted arylthiolates,  $\text{SC}_6\text{H}_3\text{-2-Ph-6-SiMe}_3$  and  $\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2$ . This contribution describes the reactions of  $\text{MoCl}_3\text{(thf)}_3$  with the lithium salts of these arylthiolates, which resulted in isolation of the unexpected  $\pi$ -sandwiched bis-aryltiolato complex,  $\text{Mo}\{\eta^5\text{-SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}_2\{\eta^7\text{-SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}$  (**1**). We also report here that the  $\pi$ -bonding in **1** is labile and that the reaction with acetonitrile gave rise to the S-bonded bis-aryltiolato complex carrying three acetonitrile molecules, one of which is coordinated in an  $\eta^2$ -mode,  $\text{Mo}\{\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}_2(\eta^1\text{-CH}_3\text{CN})_2(\eta^2\text{-CH}_3\text{CN})$  (**2**).

Treatment of  $\text{MoCl}_3(\text{thf})_3$  with 3 equiv of  $\text{LiSC}_6\text{H}_3\text{-2-Ph-6-SiMe}_3$  in  $\text{Et}_2\text{O}$ , and subsequent removal of  $\text{LiCl}$ , afforded the expected tris-aryltiolato complex of Mo(III),  $\text{Mo}(\text{SC}_6\text{H}_3\text{-2-Ph-6-SiMe}_3)_3$  (**3**) (see Scheme 1), as an analytically pure dark-purple crystalline solid in 67% yield.<sup>3</sup> According to the X-ray analysis, complex **3** has a three-legged piano-stool structure with three arylthiolate sulfurs and a  $\pi$ -bonded phenyl substituent of one arylthiolate ligand.<sup>4</sup> The coordination geometry at molybdenum(III) is similar to that of  $\text{Mo}(\text{SC}_6\text{H}_3\text{-2,6-Mes}_2)_3$ ,<sup>4a</sup> and the geometric parameters are not unusual.

### Scheme 1



On the other hand, we isolated reddish-brown crystals from the analogous reaction between  $\text{MoCl}_3(\text{thf})_3$  and 3 equiv of  $\text{LiSC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2$ . The product was formulated as  $\text{Mo}\{\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}_2$  (**1**), based on the elemental analysis,<sup>5</sup> the EI mass spectrum showing an isotope cluster of the parent ion centered at



**Figure 1.** Molecular structure of **1**. Selected bond distances [Å]: Mo–S(1) 2.562(1); Mo–C(1) 2.111(4); Mo–C(2) 2.339(4); Mo–C(3) 2.360(4); Mo–C(4) 2.280(4); Mo–C(5) 2.335(4); Mo–C(6) 2.317(4); Mo–C(13) 2.448(4); Mo–C(14) 2.302(4); Mo–C(15) 2.313(4); Mo–C(16) 2.327(4); Mo–C(17) 2.295(4); Mo–C(18) 2.369(4); S(1)–C(1) 1.754(4); S(2)–C(13) 1.709(4).

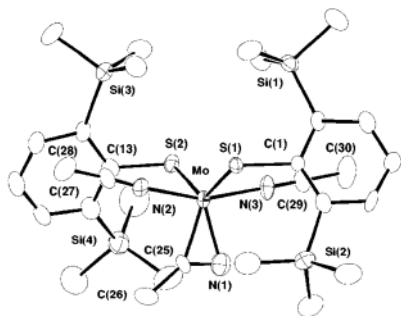
$m/z$  604, and the IR spectrum indicating the absence of an SH moiety. Obviously reduction from Mo(III) to Mo(II) took place during the reaction, and the yield of **1** is relatively low (29%), partly because we were forced to rinse the crude product with HMDSO repeatedly to remove the disulfide,  $\{\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}_2$ .

The X-ray crystal structure analysis confirmed the formulation of **1** and revealed its unusual coordination geometry (Figure 1). There are two immediate observations in the structure: (1) the aryl group of each ligand is  $\pi$ -bonded to Mo, and (2) one C=S group bends significantly toward Mo while the other is far away from the metal center, and thereby the molecule is unsymmetric. Close inspection of the C–C bond distances in either of the arylthiolates suggests that they are classified into two groups: four short C–C bonds among C(2)–C(6) (or C(14)–C(18)) (1.382(7)–1.426(6) Å) vs two long C(1)–C(2), C(1)–C(6), (or C(13)–C(14), C(13)–C(18)) bonds (1.450(6)–1.459(6) Å). Thus, the aryl rings behave like pentadienyl ligands. This bonding feature would provide 16 electrons at the Mo(II) center, and the additional  $\pi$ -coordination of one C=S bond makes the complex an 18-electron system. The  $\eta^7\text{-SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2$  ligand is folded by  $14.9^\circ$  at the C(2)–C(6) vector due to the coordination of the C=S group. Consequently the C(1)–S(1) bond is elongated, while the Mo–C(1) bond (2.111(4) Å) is substantially shorter than the other Mo–C bonds. In the  $\eta^5\text{-SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2$  ligand, the C(13)–S(2) bond length of 1.709(4) Å is between single and double bonds, indicating  $\pi$ -electron delocalization over the five “pentadienyl” carbon atoms and the C=S bond. The C=S group bends away from the metal center by  $10.8^\circ$ , resulting in the long Mo–C(13) distance of 2.449(5) Å.

The Mo(II) complex **1** is diamagnetic, and the  $^1\text{H}$  NMR spectrum in benzene- $d_6$  shows two sets of proton signals in a 1:1 intensity

<sup>†</sup> Nagoya University.

<sup>‡</sup> Institute for Molecular Science.



**Figure 2.** Molecular structure of **2**. Selected bond distances [Å] and angles (deg): Mo–S(1) 2.355(3); Mo–S(2) 2.352(3); Mo–N(1) 1.98(2); Mo–N(2) 2.14(1); Mo–N(3) 2.15(1); Mo–C(25) 1.98(2); S(1)–C(1) 1.81(1); S(2)–C(13) 1.78(1); N(1)–C(25) 1.24(2); N(2)–C(27) 1.15(2); N(3)–C(29) 1.16(2); S(1)–Mo–S(2) 128.5(1); N(2)–Mo–N(3) 162.1(5); Mo–S(1)–C(1) 110.2(3); Mo–S(2)–C(13) 108.7(4); N(1)–C(25)–C(26) 141(1).

ratio for both the aromatic and trimethylsilyl groups. The  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra also indicate that the two  $\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2$  ligands are chemically inequivalent.<sup>5</sup> The aryl ring proton resonances are all shifted upfield compared with those of  $\text{HSC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2$  (7.45(d) and 7.06(t) ppm). A similar trend was noticed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, except for one resonance at 174.0 ppm, which may be assigned to the uncoordinated thiocarbonyl carbon.<sup>6</sup> These observations suggest that the unsymmetric  $\pi$ -sandwich structure of **1** is preserved and rigid in solution.

Although the unsymmetric  $\pi$ -sandwich structure of **1** appears to be rigid at the NMR time scale, lability of the aryl–Mo bond was manifested by its reaction with acetonitrile. Thus, dissolution of **1** in  $\text{CH}_3\text{CN}$  at room temperature led to a rapid color change to deep green. A diamagnetic sky-blue crystalline product, formulated as  $\text{Mo}\{\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2\}_2(\text{CH}_3\text{CN})_3$  (**2**),<sup>7</sup> was obtained from the  $\text{CH}_3\text{CN}$  solution in 76% yield. The X-ray derived structure of **2** is given in Figure 2, which reveals a trigonal bipyramidal coordination geometry of Mo(II) with two S-bonded arylthiolates and three acetonitrile molecules. Interestingly, one acetonitrile molecule adopts an  $\eta^2$ -coordination mode at an equatorial site, while the other two show normal  $\eta^1$ -coordination at the axial sites. The  $\pi$ -bonded  $\text{CH}_3\text{CN}$  orients perpendicular to the equatorial plane, and the C(25)–N(1) bond is longer by 0.08 Å than the corresponding bonds of  $\eta^1$ - $\text{CH}_3\text{CN}$ . This upright conformation is electronically favored for a  $d^4$  configuration of Mo(II), and can be rationalized in terms of the optimal  $\pi$ -back-bonding.<sup>8b</sup> This bonding feature is analogous to the Mo(II) alkyne complexes,  $\text{Mo}(\text{S}^i\text{Bu})_2(\text{CN}^i\text{Bu})_2(\text{RC}\equiv\text{CR}')$  ( $\text{R}, \text{R}' = \text{Ph}, \text{H}$ ).<sup>8</sup>

The IR spectrum of **2** exhibits bands at 2261 and 1673  $\text{cm}^{-1}$ , assignable to the N–C stretching modes of the  $\eta^1$ - and  $\eta^2$ - $\text{CH}_3\text{CN}$  ligands, respectively. The  $^1\text{H}$  NMR spectrum in toluene- $d_8$  consists of three  $\text{CH}_3\text{CN}$  singlets and two sets of the arylthiolate ligands up to 70 °C,<sup>7</sup> at the temperature of which **2** starts to decompose. Thus, the molecule is not fluxional, and its solid-state structure is retained in solution. The  $\eta^2$ - $\text{CH}_3\text{CN}$  nitrile carbon resonance at 226.9 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shifts downfield considerably, relative to the  $\eta^1$ - $\text{CH}_3\text{CN}$  nitrile carbons, and falls in the region where  $\text{CH}_3\text{CN}$  has been thought to act as a four-electron-donor ligand.<sup>9</sup> Thus, the second  $\pi$  orbital<sup>10</sup> may also participate in the bonding with Mo(II) for **2**.

We have established for the first time that the 2,6-disubstituted arylthiolate ligand  $\text{SC}_6\text{H}_3\text{-2,6-(SiMe}_3)_2$  can bind to a metal center

at the aryl portion to form a  $\pi$ -sandwich Mo(II) complex, which would open a new facet of transition-metal thiolate chemistry. Lability of the  $\pi$ -aryl coordination of **1** and the presence of  $\eta^1$ - and  $\eta^2$ - $\text{CH}_3\text{CN}$  ligands in **2** suggest that these complexes are useful for exploration of the chemistry of coordinatively unsaturated low-valent molybdenum complexes.<sup>4,8,11</sup> Further study of the reactivity of **1** and **2** is currently underway.

**Acknowledgment.** This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 14078101, 14078211 “Reaction Control of Dynamic Complexes”) from Ministry of Education, Culture, Sports, Science, and Technology, Japan.

**Supporting Information Available:** Experimental procedures, analytical data, spectroscopic data (PDF), and X-ray crystallographic files (in CIF format) for **1**, **2**, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Cámpora, J.; Reyes, M. L.; Mereiter, K. *Organometallics* **2002**, *21*, 1014–1016. (b) Le Bras, J.; El Amouri, H.; Vaissermann, J.; *Organometallics* **1996**, *15*, 5706–5712. (c) Koelle, U.; Wang, M. H.; Raabe, G. *Organometallics* **1991**, *10*, 2573–2577. (d) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712–4718. (e) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Torroni, S.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Organomet. Chem.* **1980**, *188*, C31–C35. (f) Bennet, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87–93. (g) Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1995–1976.
- (2) Kawaguchi, H.; Matsuo, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2792–2794.
- (3) Data for **3**: Anal. Calcd for  $\text{C}_{45}\text{H}_{51}\text{MoS}_3\text{Si}_3$ : C, 62.25; H, 5.92; S, 11.08. Found: C, 61.90; H, 6.00; S, 10.82. Crystal data: monoclinic,  $P2_1/n$  (No. 14),  $a = 12.395(5)$  Å,  $b = 17.433(6)$  Å,  $c = 20.061(8)$  Å,  $\beta = 90.849(5)^\circ$ ,  $V = 4334(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_1 [I > 2\sigma(I)] = 0.055$  ( $wR_2$  (all data) = 0.142, GOF = 1.01 on  $F^2$ ).
- (4) (a) Buyuktas, B. S.; Olmstead, M. M.; Power, P. P. *Chem. Commun.* **1998**, 1689–1690. (b) Bishop, P. T.; Dilworth, J. R.; Zubieta, J. *J. Chem. Soc.* **1985**, 257–258. (c) Bishop, P. T.; Dilworth, J. R.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1985**, 257–258.
- (5) Data for **1**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.73 (d, 2H), 5.19 (t, 1H), 5.12 (d, 2H), 3.09 (t, 1H), 0.48 (s, 18H,  $\text{SiMe}_3$ ), 0.28 (s, 18H,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  174.0, 125.9, 110.1, 106.0, 104.4, 103.2, 95.5, 93.6, 2.9 ( $\text{SiMe}_3$ ), 1.6 ( $\text{SiMe}_3$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.9, –0.5. Anal. Calcd for  $\text{C}_{24}\text{H}_{42}\text{MoS}_2\text{Si}_4$ : C, 47.80; H, 7.02; S, 10.64. Found: C, 47.69; H, 7.07; S, 10.57. Crystal data: monoclinic,  $P2_1/n$  (No. 14),  $a = 11.960(5)$  Å,  $b = 19.135(8)$  Å,  $c = 13.097(5)$  Å,  $\beta = 99.847(5)^\circ$ ,  $V = 2953.1(20)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_1 [I > 2\sigma(I)] = 0.050$  ( $wR_2$  (all data) = 0.129, GOF = 1.03 on  $F^2$ ).
- (6) (a) Fisher, H.; Flick, K. H.; Troll, C. *Chem. Ber.* **1992**, *125*, 2675–2680. (b) Schenk, W. A.; Stur, T.; Dombrowski, E. *Inorg. Chem.* **1992**, *31*, 723–724.
- (7) Data for **2**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.47 (dd, 1H), 7.41 (dd, 1H), 7.38 (dd, 1H), 7.30 (dd, 1H), 6.94 (t, 1H), 6.90 (t, 1H), 3.02 (s, 3H), 1.05 (s, 3H), 0.78 (s, 3H), 0.69 (s, 9H), 0.63 (s, 9H), 0.242 (s, 9H), 0.237 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  226.9 ( $\eta^2$ -NCMe), 165.5 ( $\eta^1$ -NCMe), 164.9 ( $\eta^1$ -NCMe).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  –3.1, –3.5, –3.7, –4.6. Anal. Calcd for  $\text{C}_{30}\text{H}_{51}\text{MoN}_3\text{S}_2\text{Si}_4$ : C, 49.62; H, 7.08; N, 5.79; S, 8.83. Found: C, 49.26; H, 7.02; N, 5.67; S, 8.35. Crystal data: monoclinic,  $P2_1$  (No. 4),  $a = 11.496(8)$  Å,  $b = 15.287(9)$  Å,  $c = 13.237(9)$  Å,  $\beta = 114.96(1)^\circ$ ,  $V = 2108(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_1 [I > 2\sigma(I)] = 0.059$  ( $wR_2$  (all data) = 0.168, GOF = 1.01 on  $F^2$ ).
- (8) (a) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Hoffmann, R. *Organometallics* **1982**, *1*, 227–230. (b) Kamata, M.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Yoshida, T.; Otsuka, S. *Inorg. Chem.* **1983**, *22*, 2416–2424.
- (9) (a) Thomas, S.; Young, C. G.; Tiekink, E. R. T. *Organometallics* **1998**, *17*, 182–189. (b) Barrera, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8178–8180.
- (10) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.*, **1982**, *21*, 466–468.
- (11) (a) Chisholm, M. H.; Davidson, R. R.; Huffman, J. C.; Quinlan, K. B. *J. Am. Chem. Soc.* **2001**, *123*, 9652–9664. (b) Agapie, T.; Odom, A. L.; Cummins, C. C. *Inorg. Chem.* **2000**, *39*, 174–179. (c) Blower, P. J.; Dilworth, J. R.; Zubieta, J. *Inorg. Chem.* **1985**, *24*, 2886–2868.

JA029541+