J. Am. Chem. Soc. **1994**, *116*, 11578−11579

The First Genuine Silicon−Sulfur Double-Bond Compound: Synthesis and Crystal Structure of a Kinetically Stabilized Silanethione

Hiroyuki Suzuki,[†] Norihiro Tokitoh,[†] Shigeru Nagase,[‡] and
Renji Okazaki*[,†]

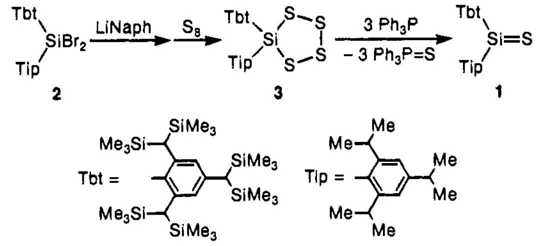
Departments of Chemistry
Graduate School of Science, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan
Faculty of Education, Yokohama National University
Yokohama 240, Japan

Received July 11, 1994

Recent years have witnessed dramatic developments in the chemistry of silicon-containing multiple-bonding compounds,[1] Si=Si,[2] Si=C,[3] and Si=Pn (Pr = N, P, As).[4] These species have been isolated by taking advantage of kinetic stabilization with bulky substituents. As for silicon−chalcogen double-bond species, however, there has been no example of the isolation using kinetic stabilization since bulky substituents for steric protection can be introduced only on the silicon atom and hence their oligomerization cannot be efficiently prevented. The isolation of a thermodynamically stabilized silanethione was reported by Corriu et al. in 1989,[5] but its X-ray structural analysis revealed that the central Si atom was tetracoordinate (because of the intramolecular coordination by a nitrogen lone pair) and the geometry around silicon was a distorted tetrahedral. Thus, any "genuine" silanethione has been still unknown. We previously reported the synthesis of germanethione[6] and stannanethione[7] stabilized by an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter). We now delineate the synthesis and structure of the first stable silanethione, **1**, having a "true" Si−S double bond.

Reaction of Tbt- and Tip-substituted dibromosilane **2** (Tip = 2,4,6-triisopropylphenyl) with lithium naphthalenide followed by addition of sulfur gave a novel cyclic polysulfide, 1,2,3,4,5-tetrathiasilolane **3** (31%) as pale yellow crystals (Scheme 1).[8,9] When a hexane solution of **3** was refluxed for 1 h in the presence of 3 molar equiv of triphenylphosphine, it turned yellow and a quantitative amount of triphenylphosphine sulfide precipitated. After filtration of the phosphine sulfide under argon, the filtrate was concentrated in a glovebox to give quantitatively pure silanethione **1** as yellow crystals.

Scheme 1



Silanethione **1** was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, Raman, and UV spectroscopy.[10] A chemical shift of δ_{Si} 166.56 for the silathiocarbonyl unit is much downfield shifted from that of the thermodynamically stabilized Corriu's silanethione (δ_{Si} 22.3),[5] clearly indicating a genuine Si=S double bond nature of **1** without any intra- or intermolecular coordination. The UV spectrum of **1** exhibited an absorption maximum at 396 nm which is assignable to the n−π^* transition, whereas its Raman spectrum in solid showed an absorption at 724 cm^{-1} attributable to the Si=S stretching.[11]

The molecular structure of **1** was finally determined by X-ray crystallographic analysis.[14] It was revealed that there are two nonidentical silanethiones in the unit cell, caused by the different dihedral angles between the Tbt−/Tip−aromatic ring planes and the silathiocarbonyl plane, in addition to the different direction of para-substituted bis(trimethylsilyl)methyl of Tbt group. There is, however, little difference in the geometry around the silicon atom between the two fragments. Figure 1 shows the ORTEP drawing of one of these silanethiones. The silathiocarbonyl unit of **1** has a completely trigonal-planar geometry, the sum of the bond angles around the silicon atom being 359.9°. Dihedral angles between the trigonal plane and two aryl planes are 41.8° for the Tbt ring and 67.8° for the Tip ring. The silicon−sulfur double-bond length is 1.948(4) Å, which is about 0.2 Å shorter than the typical Si−S single-bond length[16] (ca. 9% shortening), showing an unambiguous double-bond character between silicon and sulfur. The value for **1** is significantly shorter than that reported for Corriu's compound [2.013(3) Å],[5] indicative of the "true" double-bond nature of **1**.

[†] The University of Tokyo.

[‡] Yokohama National University.

(1) For a review, see: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(2) (a) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. (b) For a review, see: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

(3) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (b) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (c) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467. (d) For a review, see: Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(4) (a) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591. (b) Hesse, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 649. (c) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (d) van den Winkel, Y.; Bastiaans, H. M. M.; Bickelhaupt, F. *J. Organomet. Chem.* **1991**, *405*, 183. (e) Driess, M.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 316.

(5) Arya, P.; Boyer, J.; Carré, F.; Corriu, R.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016.

(6) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855.

(7) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065.

(8) For Tbt(Mes)SiS$_4$ (Mes = 2,4,6-trimethylphenyl), see: Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047.

(9) Physical properties of **2**−**6** are described in the supplementary material.

(10) **1**: yellow crystals, mp 185−189 °C; ^{1}H NMR (500 MHz, C$_6$D$_6$ at 360 K) δ 0.15 (s, 18H), 0.19 (s, 36H), 1.19 (d, J = 6.9 Hz, 6H), 1.40 (d, J = 6.5 Hz, 12H), 1.50 (s, 1H), 2.76 (sept, J = 6.9 Hz, 1H), 3.46 (br s, 2H), 3.51 (sept, J = 6.5 Hz, 2H), 6.58 (br s, 2H), 7.05 (s, 2H); ^{13}C NMR (125 MHz, C$_6$D$_6$ at 300 K) δ 1.13 (q), 1.49 (q), 1.83 (q), 22.53 (q), 24.00 (q), 27.67 (q), 30.33 (d), 30.98 (d), 31.98 (d), 34.88 (d), 38.13 (d), 121.93 (d), 123.87 (d), 131.22 (d), 139.03 (s), 148.35 (s), 151.00 (s), 151.16 (s), 151.26 (s), 152.77 (s), 153.01 (s); ^{29}Si NMR (53 MHz, C$_6$D$_6$ at 300 K) δ 2.44, 3.23, 166.56; UV (hexane) $\lambda_{\max}$ 396 nm (ϵ 100); FT-Raman spectrum in solid (excitation, Nd:YAG laser, 1064 nm) 724 cm^{-1} ($\nu_{\text{Si=S}}$).

(11) We have carried out density functional calculations at the B-LYP[12]/DZ+d[13] level to obtain the stretching frequency of Si−S of 689 cm^{-1} for H$_2$Si=S.

(12) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(13) The DZ basis sets (Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284) are augmented by a set of six d-type polarization functions (d exponents, 0.45 (Si), 0.246 (Ge), 0.183 (Sn), and 0.65 (S)), while the 6-31G* basis sets (Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257) are used for C and H.

(14) Crystallographic data for **1**: C$_{42}$H$_{84}$Si$_7$S, MW = 815.77, monoclinic, space group $P2_1/n$, a = 21.33(1), b = 13.82(1), and c = 36.13(2) Å, β = 92.50(5)°, V = 10639(12) Å^3, Z = 8, D_c = 1.018 g cm^{-3}, μ = 2.43 cm^{-1}. The intensity data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The structure was solved by direct method with SHELXS-86.[15] All the non-hydrogen atoms were refined anisotropically. The final cycle of the least-squares refinement was based on 5390 observed reflections [$I > 3\sigma(I)$] and 901 variable parameters with R (R_w) = 0.061 (0.051). Full details for the crystallographic analysis of **1** are described in the supplementary material.

(15) Sheldrick, G. M. *SHELX-86*; University of Göttingen: Göttingen, Germany, 1986.

(16) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compound*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, pp 227−304.

0002-7863/94/1516-11578$04.50/0

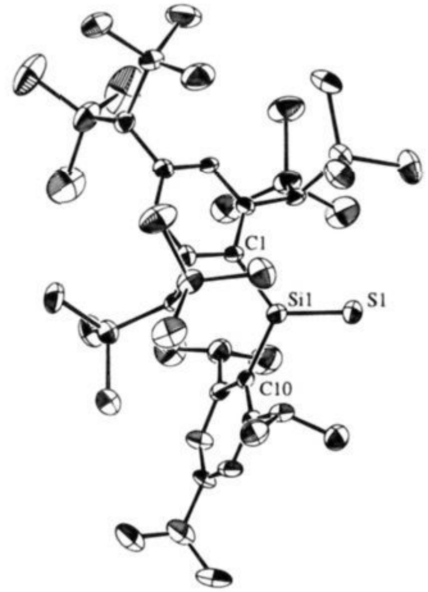
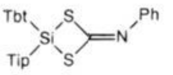
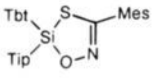


Figure 1. ORTEP drawing of silanethione **1** with thermal ellipsoid plot (30% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Si(1)−S(1), 1.948(4); Si(1)−C(1), 1.894(8); Si(1)−C(10), 1.867(9); Si(1)−Si(1)−C(1), 125.0(3); S(1)−Si(1)−C(10), 116.3(3); C(1)−Si(1)−C(10), 118.6(4).

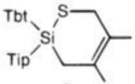
Though **1** is thermally stable up to its melting point (185−189 °C), **1** has a high chemical reactivity toward various reagents. Reactions of **1** with phenyl isothiocyanate, mesitonitrile oxide, and 2,3-dimethyl-1,3-butadiene gave the corresponding [2 + 2], [2 + 3], and [2 + 4] cycloadducts **4** (63%), **5** (54%), and **6** (74%), respectively.[9]



4



5



6

The synthesis of **1** has enabled us to compare the electronic spectra (n→π*) of a series of $R^1R^2M{=}S$ (M = C, Si, Ge, Sn) compounds. In Table 1 are listed observed spectra of these compounds, along with calculated spectra of $H_2M{=}S$ (M = C, Si, Ge, Sn) at the CIS[17]/DZ+d level[13] using the Gaussian 92/DFT program. One can see a very interesting change in the observed λ_{max} depending on the difference in group 14 elements; λ_{max} is much blue-shifted on going from thione **7** to silanethione **1**, whereas λ_{max} values for **1**, germanethione **8**, and stannanethione **9** are red-shifted with increasing atomic number of the group 14 elements. This trend is also found in calculated values for $H_2M{=}S$ (M = C, Si, Ge, Sn). Since calculated $\Delta\epsilon_{n\pi^*}$ values increase continuously from $H_2Sn{=}S$ to $H_2C{=}S$, a long-wavelength absorption for $H_2C{=}S$ (and hence for **7**) most likely results from a large repulsion integral ($J_{n\pi^*}$) for the carbon−sulfur double bond, as in the case of $H_2C{=}O$ vs $H_2Si{=}O$.[19]

Table 1. Electronic Spectra (n→π*) of Double-Bond Compounds between Group 14 Elements and Sulfur

observed[a]		calculated[e]		
compd	λ_{max}/nm	compd	λ_{max}/nm	$\Delta\epsilon_{n\pi^*}$/eV[f]
Tbt(H)C=S (**7**)	587[b]	$H_2C{=}S$	458	10.81
Tbt(Tip)Si=S (**1**)	396	$H_2Si{=}S$	345	10.39
Tbt(Tip)Ge=S (**8**)	450[c]	$H_2Ge{=}S$	363	9.97
Tbt(Tip)Sn=S (**9**)	473[d]	$H_2Sn{=}S$	380	9.30

[a] In hexane. [b] Reference 18. [c] Reference 6. [d] Reference 7. [e] CIS/DZ + d. [f] $\epsilon_{LUMO(\pi^*)} - \epsilon_{HOMO(n)}$.

Further investigation of physical and chemical properties of **1** is currently in progress.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 05236102) from the Ministry of Education, Science and Culture, Japan. We are grateful to Dr. Y. Furukawa, the University of Tokyo, for the measurement of the FT-Raman spectrum of **1**. We also thank Central Glass Co., Ltd., Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd. for the generous gifts of tetrafluorosilane, chlorosilanes, and alkyllithiums, respectively.

Supplementary Material Available: Physical properties of the starting material and reaction products **2**−**6**, and crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1** (54 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(17) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135.

(18) Tokitoh, N.; Takeda, N.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 7907.

(19) Kudo, T.; Nagase, S. *Chem. Phys. Lett.* **1986**, *128*, 507.