

First Structural Characterization of Silanedithiol and Its Application toward the Synthesis of Silanedithiolato Complexes

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Keywords: Silanedithiol / Silanedithiolato complexes / Silaneselenol / Group 10 transition metal complexes / X-ray crystallography

In this paper, we report the synthesis and the structural characterization of stable examples of silanedithiol [Tbt(Mes)-Si(SH)₂ (**1**)], hydroxysilanethiol [Tbt(Mes)Si(OH)(SH) (**3**)], and hydroxysilaneselenol [Tbt(Mes)Si(OH)(SeH) (**7**)], which are kinetically stabilized by an effective combination of steric protection groups, Tbt (2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) and Mes (2,4,6-trimethylphenyl). Silanedichalcogenols **1**, **3**, and **7** are suggested to exist as a monomer without any intermolecular contact such as hydrogen bonds both in the solid state and in solution as judged by X-ray structural

analysis and IR spectroscopy. Treatment of **1** with 2 equiv. of butyllithium resulted in the quantitative formation of the corresponding dilithium silanedithiolate, Tbt(Mes)Si(SLi)₂ (**8**), the generation of which was confirmed by a trapping experiment using MeI. Furthermore, the addition of *cis*-[MCl₂(PPh₃)₂] (M = Pd, Pt) to a THF solution of **8** afforded the corresponding silanedithiolato complexes, [Tbt(Mes)Si(μ-S)₂M(PPh₃)₂] (**9a**: M = Pd; **9b**: M = Pt), respectively. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

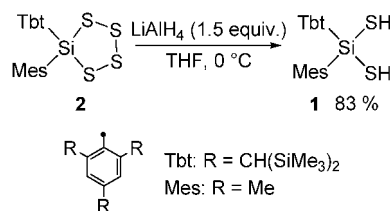
Introduction

Controlled synthesis of (chalcogenido)metal clusters has been one of the most attractive subjects in organometallic chemistry.^[1] Recently, silanethiolato or silanedithiolato complexes of late transition metals have been shown to be good precursors of (sulfido)mixed-metal clusters prepared by ligand exchange involving Si–S bond cleavage.^[2,3] However, chelating silanedithiolato complexes are less common due to the limitation of appropriate synthetic methodology. That is, an excess amount of 1,3,5,2,4,6-trithiatrisilinane (SSiMe₂)₃ should be required as a sulfur transfer reagent for the synthesis of such silanedithiolato complexes.^[4] On the other hand, silanedithiols, which should be a good precursor of silanedithiolato complexes, have attracted much interest from the viewpoint of their structure and properties. However, it is very difficult to isolate silanedithiols due to their high sensitivity toward moisture, and the properties remained little understood.^[5] As for the analogues of main group elements having two geminal SH groups, three examples are structurally characterized, i.e., TbtB(SH)₂,^[6] AlL(SH)₂,^[7] and Dep(Dip)Ge(SH)₂,^[8] {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, L (β-diketiminato) = [N(Dip)C(Me)₂CH, Dip = 2,6-diisopropylphenyl, Dep = 2,6-diethylphenyl}, where the reactive M–SH moieties are protected by bulky substituents. All of these compounds

could be easily converted into the heterodimetallic sulfido clusters.^[9] Thus, kinetic stabilization should be an appropriate method for the stabilization of M(SH)₂ species. In this paper, we present the synthesis and the first structural characterization of a silanedithiol, which is kinetically stabilized by an effective steric protection group, Tbt. In addition, its application as a building block toward the synthesis of silanedithiolato complexes will also be presented.

Results and Discussion

Silanedithiol **1** was synthesized by the reaction of the corresponding sterically hindered tetrathiasilolane **2**^[10] with 1.5 equiv. of LiAlH₄ at 0 °C as air- and moisture-stable crystals in 83% isolated yield (Scheme 1). When the reaction was carried out at room temperature, further reduction occurred to give a mixture of **1**, Tbt(Mes)Si(H)SH and Tbt(Mes)SiH₂.

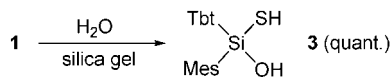


Scheme 1. Synthesis of **1**.

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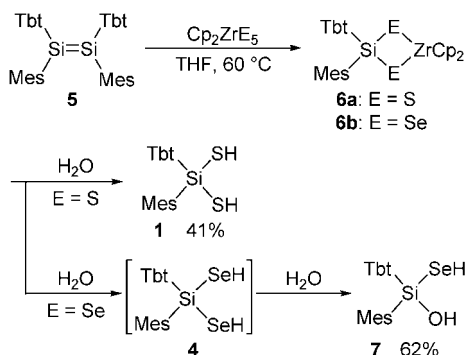
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Silanedithiol **1** is stable in [D₆]benzene solution even in the presence of H₂O for 1 d, reflecting the extreme bulkiness of the combination of Tbt and Mes groups. However, **1** underwent ready hydrolysis during preparative thin layer chromatography (SiO₂) to afford the corresponding hydroxysilanethiol **3** quantitatively (Scheme 2).



Scheme 2. Synthesis of **3** by hydrolysis of **1**.

The successful isolation of silanedithiol **1** prompted us to attempt the synthesis of the selenium analogue, silanediselenol, a stable example of which has been unknown. Unfortunately, tetraselenasilolane, the selenium analogue of **2**, is known to be not available.^[10] Another synthetic route is required to obtain the heavier analogue. We focused our attention on the (silanedichalcogenolato)zirconium complexes, which possess reactive Zr–E (E = S, Se) bonds. When disilene **5**^[10] was treated with Cp₂ZrE₅ at 60 °C, the corresponding silanedichalcogenolato complexes **6a,b** were obtained.^[11] Treatment of **6a** with H₂O followed by the separation afforded **1**, where the hydrolysis of the Zr–S bonds should occur selectively. Thus, the SiS₂Zr ring system (**6a**) was found to be another precursor for silanedithiol **1**. The selenium analogue **6b** should be a good precursor for silanediselenol. However, the reaction of **6b** with H₂O gave hydroxysilaneselenol **7**, which was probably formed by further hydrolysis of the initially generated silanediselenol **4** (Scheme 3).



Scheme 3. Reaction of **5** with Cp₂ZrE₅ (E = S, Se).

The molecular structures of the newly isolated silanedichalcogenols, **1**, **3**, and **7**, were fully determined by X-ray crystallographic analysis (Figure 1).^[12] To the best of our knowledge, these are the first examples of the X-ray structural analyses of a silanedithiol, a hydroxysilanethiol, and a hydroxysilaneselenol.^[13] The Si–E (E = O, S, Se) bond lengths of **1**, **3**, and **7** are within the range of those reported for the corresponding single bonds between silicon and chalcogen atoms. Absence of intermolecular hydrogen

bonding in the solid state was suggested by the packing view, where the observed intermolecular distances between chalcogen atoms are apparently longer than the sum of the van der Waals radii.^[14]

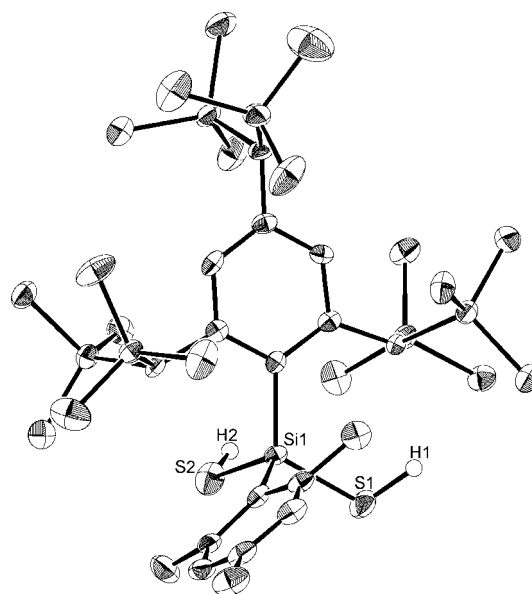
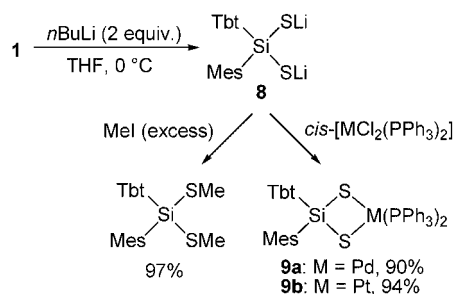


Figure 1. Crystal structure of **1** (ORTEF plot; thermal ellipsoids are shown at 50% probability; hydrogen atoms except for the S–H hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si(1)–S(1) 2.1576(16), Si(1)–S(2) 2.1436(15); S(1)–Si(1)–S(2) 101.73(6).

The IR spectra in the solid state for **1**, **3**, and **7** show sharp absorptions assigned to the E–H stretching vibrations [**1**: 2572 cm^{−1}; **3**: 2661 cm^{−1}, 3646 cm^{−1}; **7**: 2479 cm^{−1}, 3656 cm^{−1}], suggesting the absence of intra- and intermolecular interactions through hydrogen bonds.^[15] No change of the IR spectra in CCl₄ with several concentrations indicated their monomeric structure and almost no intermolecular contact even in solution.

The generation of dilithium silanedithiolate **8** in the reaction of **1** with 2 equiv. of *n*BuLi was confirmed by a trapping experiment with MeI. Compound **8** should be applicable toward the development of a new synthetic strategy for (silanedithiolato)transition-metal complexes. Addition of *cis*-[MCl₂(PPh₃)₂] (M = Pd, Pt) to a THF solution of **8** resulted in the almost quantitative formation of the corresponding silanedithiolato complexes **9a,b**, respectively (Scheme 4).^[16] The ²⁹Si NMR signals of the central silicon atoms in the silanedithiolato complexes **9a** (δ_{Si} = 15.3 ppm) and **9b** (δ_{Si} = 14.2 ppm), which appear in the characteristic region of silanedithiolato complex signals,^[4c] are in a lower-field region than that of **1** (δ_{Si} = −1.8 ppm). The structures of **9a,b** were revealed by X-ray crystallography. Both of the four-membered rings consisting of Si, S, and Pd or Pt atoms have puckered structures, though the SiS₂Pd ring of the reported (silanedithiolato)palladium complex, [Me₂Si(μ-S)₂-Pd(PEt₃)₂],^[4c] has an almost planar structure. This is probably due to the steric repulsion between the extremely bulky

Tbt group and the triphenylphosphane groups. The X-ray structural analysis of **9b**^[17] is the first example of a silanedithiolato complexes of platinum (Figure 2, Scheme 4).



Scheme 4. Synthesis of silanedithiolato complexes **9**.

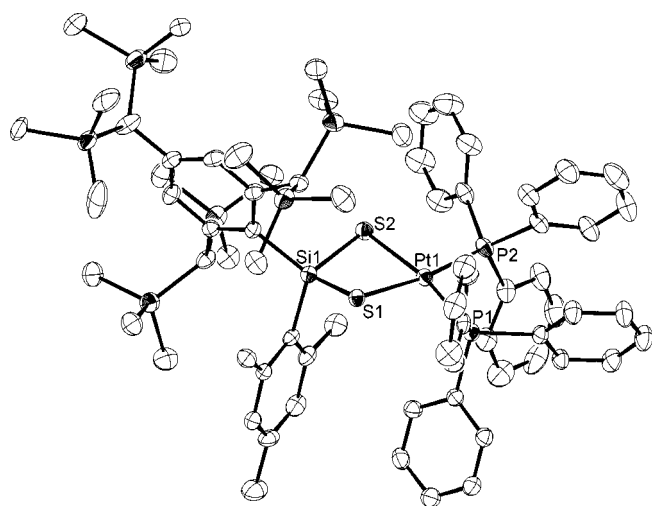


Figure 2. Crystal structure of **9b**-hexane (ORTEP plot; thermal ellipsoids are shown at 30% probability; hexane and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si(1)–S(1) 2.157(2), Si(1)–S(2) 2.115(2), Pt–S(1) 2.3667(15), Pt–S(2) 2.3333(17); S(1)–Si(1)–S(2) 94.92(9), S(1)–Pt–S(2) 84.09(6).

Conclusions

We have succeeded in the synthesis and characterization of a stable silanedithiol **1** and its application toward the synthesis of the silanedithiolato complexes of palladium and platinum. The stable silanedithiol should be a key species as a building block for several types of (sulfido)mixed-metal clusters. Further investigation on the reactivity of **8** and related compounds are currently in progress.

Experimental Section

General Procedure. All experiments were performed under anhydrous conditions under argon unless otherwise noted. All solvents used in the reactions were purified prior to use by standard meth-

ods and/or by an Ultimate Solvent System (Glass Contour Company).^[18] C₆D₆ used as a solvent was dried with Na, then with a K mirror. ¹H NMR (300 or 400 MHz) spectra were measured in CDCl₃ or C₆D₆ with a JEOL AL-400 or AL-300 spectrometer using residual CHCl₃ (δ = 7.25 ppm) or C₆D₅H (δ = 7.15 ppm) as an internal standard. ¹³C NMR (75 MHz) spectra were recorded with a JEOL JNM AL-300 spectrometer. ¹³C chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the carbon signal of CDCl₃ (δ = 77.0 ppm) or C₆D₆ (δ = 128.0 ppm). The multiplicity of signals in the ¹³C NMR spectra was determined by the DEPT technique. The ²⁹Si (59 MHz), ³¹P (120 MHz), ⁷⁷Se (95 MHz), and ¹⁹⁵Pt (64 MHz) NMR spectra were recorded with a JEOL JNM AL-300 spectrometer. IR spectra were recorded with a JASCO FT/IR-5300 spectrometer. High- and low-resolution mass spectrometric data were obtained with a JEOL JMS-700 spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. All melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. Wet column chromatography (WCC) and preparative thin-layer chromatography (PTLC) were performed using Wakogel C-200 and Merk Kieselgel 60 PF254, respectively. GLPC (gel permeation liquid chromatography) was performed on LC-908, LC-918 (Japan Analytical Industry Co., Ltd. Systems) equipped with JAIGEL 1H and 2H columns (eluent: toluene).

1: To a solution of **2** (165 mg, 238 μmol) in THF (15 mL) was added LiAlH₄ (13.5 mg, 356 μmol) at 0 °C. After the mixture was stirred at 0 °C for 1 h, ethyl acetate (5 mL) was added. After removal of the solvent, hexane was added to the residue. The suspension was filtered through Celite®, and the solvent was removed. The residue was separated by silica gel chromatography (*n*-hexane) to afford **1** (149.7 mg, 195.5 μmol, 83%); colorless crystals, m.p. 177–178 °C. ¹H NMR (300 MHz, CDCl₃): δ = −0.02 (s, 18 H), 0.00 (s, 18 H), 0.04 (s, 18 H), 1.18 (s, 2 H, S–H), 1.31 (s, 1 H), 2.22 (s, 3 H), 2.49 (s, 1 H), 2.57 (s, 6 H), 2.63 (s, 1 H), 6.24 (s, 1 H), 6.38 (s, 1 H), 6.76 (s, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 0.9 (q), 1.6 (q), 1.9 (q), 20.9 (q), 26.4 (q), 28.0 (d), 28.3 (d), 30.6 (d), 123.3 (d), 126.3 (s), 128.5 (d), 130.5 (d), 134.9 (s), 139.7 (s), 142.8 (s), 145.5 (s), 151.9 (s), 152.2 (s) ppm. ²⁹Si NMR (59 MHz, CDCl₃): δ = −1.8, 1.9, 2.9, 3.0 ppm. IR (KBr): ν̄ = 2572 [ν(S–H)] cm^{−1}. HRMS (FAB⁺): calcd. for C₃₆H₇₂S₂Si₇ [M]⁺ 764.3460, found 764.3472. C₃₆H₇₂S₂Si₇ (765.69): calcd. C 56.47, H 9.48, S 8.38; found C 56.51, H 9.57, S 8.81.

9b: To a solution of **1** (27.8 mg, 36.3 μmol) in THF (3 mL) was added *n*BuLi (1.64 N hexane solution, 51 μL, 82.1 μmol) at 0 °C. After the mixture was stirred at 0 °C for 30 min, a THF solution (15 mL) of *cis*-bis(triphenylphosphane)platinum dichloride (43.1 mg, 54.4 μmol) was added. After removal of the solvent, benzene (3 mL) was added to the residue. The mixture was filtered through Celite®, and the solvent was removed. The residue was separated with HPLC (toluene) to afford **9b** (50.5 mg, 34.1 μmol, 94%) as a pale yellow solid. Pale yellow crystals suitable for X-ray structural analysis were grown from hexane at −20 °C; pale yellow crystals, m.p. 250–252 °C (dec.). ¹H NMR (300 MHz, C₆D₆): δ = 0.21 (s, 18 H), 0.29 (s, 18 H), 0.34 (s, 18 H), 1.49 (s, 1 H), 2.11 (s, 1 H), 2.31 (s, 3 H), 2.53 (s, 1 H), 2.93 (s, 6 H), 6.50 (s, 1 H), 6.62 (s, 1 H), 6.83 (s, 2 H), 6.85–6.94 (m, 18 H, Ph₃P), 7.49–7.55 (m, 12 H, Ph₃P) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 1.2 (CH₃), 2.1 (CH₃), 2.5 (CH₃), 21.1 (CH₃), 25.3 (CH), 25.6 (CH), 26.9 (CH₃), 30.5 (CH), 127.8 (CH), 128.3 (CH), 128.5 (CH), 128.6 [d, ⁴J_{CP} = 1.2 Hz, CH, *p*-Ph(PPh₃)], 131.41 [d, ³J_{CP} = 1.9 Hz, CH, *m*-Ph(PPh₃)], 131.42 [dd, ¹J_{CP} = 54.9 Hz, ³J_{CP} = 6.8 Hz, C, *ipso*-Ph

(PPh₃), 135.3 [AA'X pattern, $1/2(^2J_{\text{CP}} + ^4J_{\text{CP}}) = 5.5$ Hz, CH, *o*-Ph (PPh₃), 136.6 (C), 137.9 (C), 141.9 (C), 143.1 (C), 143.3 (C), 151.3 (C), 151.6 (C) ppm. ²⁹Si NMR (59 MHz, C₆D₆): $\delta = 1.6, 2.5, 14.1$ ppm. ³¹P NMR (120 MHz, C₆D₆): $\delta = 21.2$ (s, with platinum satellites, $^1J_{\text{PPt}} = 3047$ Hz) ppm. ¹⁹⁵Pt NMR (64 MHz, C₆D₆, Na₂PtCl₄): $\delta = -4527.7$ (t, $^1J_{\text{PtP}} = 3047$ Hz) ppm. UV/Vis (*n*-hexane): $\lambda_{\text{max}} = 290$ (br., $\epsilon = 4 \times 10^4$), 269 (br., $\epsilon = 6 \times 10^4$), 232 (br., $\epsilon = 1 \times 10^5$), 209 ($\epsilon = 2 \times 10^5$) nm. HRMS (FAB⁺): calcd. for C₇₂H₁₀₀P₂¹⁹⁵PtS₂Si₇ [M]⁺ 1481.4774, found 1481.4771. C₇₂H₁₀₀P₂PtS₂Si₇ (1483.32): calcd. C 58.30, H 6.80, S 4.32; found C 58.39, H 6.89, S 4.31.

Supporting Information (see footnote on the first page of this article): Experimental procedures, spectroscopic data, and crystal data of **3**, **7**, **9a** and **9b**.

Acknowledgments

This work was supported in part by Grants-in-Aid for Creative Scientific Research (17GS0207), Scientific Research on Priority Area (No. 14078213), COE Research on Elements Science (No. 12CE2005), and the 21st Century COE Program, Kyoto University Alliance for Chemistry, from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We are grateful to Dr. Takahiro Sasamori, Institute for Chemical Research, Kyoto University, for the valuable discussions.

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- [12] Crystal data for **1**: The intensity data were collected with a Rigaku/MS Mercury CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71070$ Å). The structures were solved by direct methods (SIR-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97). Formula C₃₆H₇₂S₂Si₇, $MW = 765.69$; triclinic; space group $P\bar{1}$ (#2); $a = 9.2535(4)$, $b = 15.9925(5)$, $c = 15.8055(7)$ Å; $\alpha = 82.9726(15)$, $\beta = 81.7950(17)$, $\gamma = 81.365(4)^\circ$; $V = 2276.62(16)$ Å³; $Z = 2$; $\mu = 0.324$ mm^{−1}; $D_{\text{calcd.}} = 1.117$ g cm^{−3}; $2\theta_{\text{max}} = 51.0^\circ$; $T = 103(2)$ K; R_1 [$I > 2\sigma(I)$] = 0.0563; wR_2 (all data) = 0.1350; GOF = 1.049 for 8315 reflections and 427 parameters. CCDC-627421 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for **3** and **7** are given in the Supporting Information. CCDC-627422 (**3**) and -627425 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
- [13] We have already reported the synthesis of the stable silanethione and silaneselone, Tbt(Tip)Si=Ch (Ch = S, Se; Tip = 2,4,6-triisopropylphenyl). They should be related compounds to compounds **1**, **3**, and **7**, since the hydrolyzed products of the silanethione and silaneselone are Tbt(Tip)Si(OH)(SH) and Tbt(Tip)Si(OH)(SeH), which have already been reported. For reviews on heavy ketones, see: R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625–630.
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- [16] For the experimental procedure, spectral and crystal data for **9a**, see the Supporting Information. CCDC-627423 (**9a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
- [17] Crystal data for **9b** (**9b**-hexane): Formula C₇₈H₁₁₄P₂PtS₂Si₇, $MW = 1569.47$; triclinic; space group $P\bar{1}$ (#2); $a = 13.7853(8)$, $b = 16.8910(9)$, $c = 21.0444(17)$ Å; $\alpha = 113.276(7)$, $\beta = 102.504(4)$, $\gamma = 92.842(3)^\circ$; $V = 4344.4(5)$ Å³; $Z = 2$; $\mu = 1.833$ mm^{−1}; $D_{\text{calcd.}} = 1.200$ Mg/m³; $2\theta_{\text{max}} = 50.0^\circ$; $T = 173(2)$ K; R_1 [$I > 2\sigma(I)$] = 0.0511; wR_2 (all data) = 0.1272; GOF = 1.078 for 15211 reflections and 870 parameters. CCDC-627424 (**9b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
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Received: December 22, 2006

Published Online: February 13, 2007