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Supporting Information

# Aminosilanetrithiol RSi(SH)3: An Experimental and

# **Quantum-Chemical Study**

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#### **S1. Experimental section**

**Materials and Methods**. All manipulations were carried out under a dry argon or nitrogen atmosphere by using Schlenk line and/or glovebox techniques. The solvents toluene, *n*-hexane, and tetrahydrofuran were dried by reflux with sodium/potassium benzophenone under N<sub>2</sub> atmosphere prior to use. <sup>1</sup>H (500 MHz), <sup>13</sup>C (125 MHz), and <sup>29</sup>Si (99 MHz) NMR spectra were recorded on a Bruker Avance II 500 MHz spectrometer. Melting points of compounds were measured in a sealed glass tube using Büchi-540 instrument. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercially available reagents were purchased from Aldrich, Acros, Alfa-Assar and used as received. Anhydrous MeCOOH was dried by molecular sieves and distilled prior to use. RSiCl<sub>3</sub> (1, R = N(SiMe<sub>3</sub>)-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sup>S1a</sup> and (AgMes)<sub>4</sub> (Mes = 2,4,6-trimethylphenyl)<sup>S1b</sup> were prepared according to the published procedure.

 ${\rm RSi[SLi(THF)]_3}_2$  (2) To sublimed S (0.57 g, 17.8 mmol) was added LiBEt<sub>3</sub>H (32 mL of 1 M THF solution, 32 mmol) dropwise at room temperature. The generation of H<sub>2</sub> gas was observed. The mixture was stirred until the H<sub>2</sub>-generation had ceased. After additional stirring for 0.5 h, all volatiles were removed under reduced pressure. The as-formed light yellow solid of Li<sub>2</sub>S was kept for further reaction. At room temperature, a solution of 1 (1.15 g, 3.0 mmol) in THF (50 mL) was added to the forming Li<sub>2</sub>S. The mixture was kept at 25 °C and stirred for 10 d. The THF was removed under reduced pressure and the residue was extracted with toluene (20 mL). The extract was dried and dissolved in a mixture of THF and *n*-hexane (1 mL/ 10 mL). After the solution was stored at room temperature for 4 d, colorless crystals of 2 were formed. In the synthesis, an excess of Li<sub>2</sub>S (5.3 equivalents) was used in order to maximally complete the transformation of 1 to 2. The balanced equation for the formation of 2 is shown as follows:

$$2 \operatorname{RSiCl}_{3} + 6 \operatorname{Li}_{2}S \xrightarrow{|\mathsf{IH}|} \{\operatorname{RSi}[\operatorname{SLi}(\mathsf{THF})]_{3}\}_{2} + 6 \operatorname{LiCl}$$

$$1 \qquad 2$$

$$R = \operatorname{N}(\operatorname{SiMe}_{3}) - 2, 6 - i \operatorname{Pr}_{2}C_{6}\operatorname{H}_{3}$$

Yield: 1.55 g, 85% (based on 1). Mp: 90 °C (dec.). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  7.09–6.94 (m, 6 H, C<sub>6</sub>*H*<sub>3</sub>), 4.05 (sept, 4 H, <sup>3</sup>*J*<sub>HH</sub> = 6.5 Hz, C*H*Me<sub>2</sub>), 3.77 (t, 24 H, THF-OC*H*<sub>2</sub>CH<sub>2</sub>), 1.82 (m, 24 H, THF-OCH<sub>2</sub>C*H*<sub>2</sub>), 1.28 (d, 12 H, <sup>3</sup>*J*<sub>HH</sub> = 6.5 Hz, CH*Me*<sub>2</sub>), 1.14 (d, 12 H, <sup>3</sup>*J*<sub>HH</sub> = 6.5 Hz, CH*Me*<sub>2</sub>), 0.23 (s, 18

H, Si*Me*<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  149.0, 144.7, 123.6, 123.0 (*C*<sub>6</sub>H<sub>3</sub>), 68.3 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 25.6 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 27.9, 27.8, 26.7, 26.5, 25.4 (*C*H*Me*<sub>2</sub>), 4.8 (Si*Me*<sub>3</sub>). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  1.2 (*Si*Me<sub>3</sub>), -4.2 (*Si*S). Anal. calcd for C<sub>54</sub>H<sub>100</sub>Li<sub>6</sub>N<sub>2</sub>O<sub>6</sub>S<sub>6</sub>Si<sub>4</sub> (*M*<sub>r</sub> = 1218.60): C, 53.17; H, 8.26; N, 2.30. Found: C, 53.10; H, 7.99; N, 2.38.

**RSiCl<sub>2</sub>SLi(THF)**<sub>3</sub> (3) Li<sub>2</sub>S (18.0 mmol) was freshly prepared in a similar manner to that used in the synthesis of **2**. In a Schlenk flask (100 mL) the Li<sub>2</sub>S was cooled to 10 °C, and to it a solution of **1** (2.3 g, 6 mmol) in THF (60 mL) was added. The mixture was kept at this temperature and stirred for 24 h. The THF was removed under reduced pressure, and the residue was extracted with toluene (50 mL). The extract was dried and then dissolved in a mixture of THF and *n*-hexane (2 mL/10 mL). After the solution was stored at -20 °C for 3 d, colorless block crystals of **3** were formed. In the actual synthesis, an excess of Li<sub>2</sub>S (3 equivalents) was used in order to maximally complete the transformation of **1** to **3**. The balanced equation for the formation of **3** is shown as follows:

RSiCl<sub>3</sub> + Li<sub>2</sub>S 
$$\xrightarrow{\text{THF}}$$
 RSiCl<sub>2</sub>SLi(THF)<sub>3</sub> + LiCl  
1 3  
R = N(SiMe<sub>3</sub>)-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

Yield: 2.9 g, 80% (based on 1). Mp: 103 °C (dec.). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  7.11–7.06 (m, 3 H, C<sub>6</sub>H<sub>3</sub>), 3.83 (m, 12H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 3.60 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHMe<sub>2</sub>), 1.89 (m, 12 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 1.26 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHMe<sub>2</sub>), 1.21 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHMe<sub>2</sub>), 0.23 (s, 9 H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  147.6, 141.6, 125.0, 123.6 (C<sub>6</sub>H<sub>3</sub>), 68.5 (THF-O<sub>C</sub>H<sub>2</sub>CH<sub>2</sub>), 25.7 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 28.0, 25.5, 24.7 (CHMe<sub>2</sub>), 2.5 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  8.2 (SiMe<sub>3</sub>), -13.8 (SiS). Anal. calcd for C<sub>27</sub>H<sub>50</sub>Cl<sub>2</sub>LiNO<sub>3</sub>SSi<sub>2</sub> (M<sub>r</sub> = 602.76): C, 52.06; H, 7.98; N, 2.64. Found: C, 51.30; H, 8.07; N, 2.73.

**RSiCl<sub>2</sub>SLi(THF)<sub>3</sub> (3) and RSi[SLi(THF)](\mu-S)<sub>2</sub>Si[SLi(THF)<sub>2</sub>]R (4) Li<sub>2</sub>S (18.0 mmol) was freshly prepared in a similar manner to that used in the synthesis of 2. At room temperature, a solution of 1 (2.3 g, 6.0 mmol) in THF (60 mL) was added to Li<sub>2</sub>S. The mixture was allowed to heat to 35 °C and stirred for 72 h. After cooling to room temperature, the THF was removed under reduced pressure and the residue was extracted with toluene (50 mL). The extract was dried and dissolved in a mixture of THF and** *n***-hexane (2** 

mL/10 mL). After the solution was stored at  $-20 \,^{\circ}$ C for 3 d, colorless block crystals of **3** were formed and collected by filtration (0.18 g). The filtrate was kept at  $-20 \,^{\circ}$ C for another 2 d, and the second crop of a mixture of the crystals of **3** and **4** were formed (1.36 g). A collection of the crystals for X-ray diffraction study confirmed the formation of **4**. The reaction equation is shown for the formation of **3** and **4** as follows:

$$3 \operatorname{RSiCl}_3 + 5 \operatorname{Li}_2 S \xrightarrow{\text{THF}} \operatorname{RSiCl}_2 \operatorname{SLi}(\operatorname{THF})_3 + (\operatorname{RSiSSLi})_2 (\operatorname{THF})_3 + 7 \operatorname{LiCl}$$

$$3 \qquad 4$$

$$R = \operatorname{N}(\operatorname{SiMe}_3) - 2, 6 - i \operatorname{Pr}_2 \operatorname{C}_6 \operatorname{H}_3$$

The <sup>1</sup>H NMR spectra showed the data for the mixture of **3** and **4** (from the second crop) in a molar ratio of ca. 1:1 by the integral intensity analysis for one of the characteristic proton-containing groups (e.g.  $CHMe_2$ ). An attempt to separate the crystals was failed. The <sup>1</sup>H NMR spectral data of **4** was obtained by exclusion of the data of **3**. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  7.10–7.04 (m, 6 H, C<sub>6</sub>H<sub>3</sub>), 3.80 (m, 12 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 3.43 (sept, 4 H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHMe<sub>2</sub>), 1.86 (m, 12 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 1.28 (d, 12 H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CHMe<sub>2</sub>), 0.28 (s, 18 H, SiMe<sub>3</sub>).

**RSi(SH)**<sub>3</sub> (5) At room temperature, distilled anhydrous MeCOOH (0.43 g, 7.2 mmol) was added dropwise to a suspension of **2** (0.15 g, 1.2 mmol) in *n*-hexane (30 mL). A white precipitate was immediately formed. The mixture was stirred for 1 h. The solid was removed by filtration and the filtrate was concentrated to ca. 4 mL and stored at  $-20 \,^{\circ}$ C. Two days later, colorless crystals of **5** were formed. Yield: 0.36 g, 40%. Mp: 154 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  7.20–7.11 (m, 3 H, C<sub>6</sub>*H*<sub>3</sub>), 3.42 (sept, 2 H, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, C*H*Me<sub>2</sub>), 1.33 (d, 6 H, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, CH*M*e<sub>2</sub>), 1.24 (d, 6 H, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, CH*M*e<sub>2</sub>), 1.18 (s, 3 H, S*H*), 0.28 (s, 9 H, Si*M*e<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  147.4, 140.5, 126.2, 124.3 (*C*<sub>6</sub>H<sub>3</sub>), 28.3, 25.6, 24.9 (*C*H*M*e<sub>2</sub>), 2.7 (Si*M*e<sub>3</sub>). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  10.4 (*Si*Me<sub>3</sub>), 2.7 (*Si*S). IR (Nujol mull, cm<sup>-1</sup>):  $_{\vec{V}}$  2543 (SH). Anal. calcd for C<sub>15</sub>H<sub>29</sub>NS<sub>3</sub>Si<sub>2</sub> (*M*<sub>r</sub> = 375.76): C, 47.95; H, 7.78; N, 3.73. Found: C, 47.79; H, 7.70; N, 3.63.

[**R**(**HS**)<sub>2</sub>**SiSAg**]<sub>4</sub> (6) and [**R**(**HS**)<sub>2</sub>**SiSAg**]<sub>2</sub>(**AgMes**)<sub>2</sub> (7) At -78 °C, to a mixture of 5 (0.19 g, 0.5 mmol) and (AgMes)<sub>4</sub> (0.034 g, 0.375 mmol) was added toluene (30 mL) in dark. The mixture was allowed to warm to room temperature and stirred for 8 h. A colorless solution was obtained, which was concentrated (ca. 5 mL)

and stored at 4 °C. Three days later, colorless rectangular crystals of **6** were formed and collected by filtration. Yield: 0.06 g, 24% (based on **5**). The mother solution was kept at 4 °C for another three days. Colorless plate crystals of **7** were afforded in a very small amount, which were only subjected to the X-ray single-crystal diffraction study. Due to poor quality of the crystals of **7**, a preliminary structure of this compound was determined. For **6**, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  7.21–7.11 (m, 12 H, C<sub>6</sub>H<sub>3</sub>), 3.38 (sept, 8 H, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, *CH*Me<sub>2</sub>), 1.27-1.23 (m, 56 H, CH*Me*<sub>2</sub> plus S*H*), 0.26 (s, 36 H, Si*Me*<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  147.3, 138.9, 126.4, 124.4 (*C*<sub>6</sub>H<sub>3</sub>), 28.2, 25.3, 24.7 (*C*H*Me*<sub>2</sub>), 2.0 (Si*Me*<sub>3</sub>). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  6.9 (*Si*Me<sub>3</sub>), -43.9 (*Si*S). Anal. calcd for C<sub>60</sub>H<sub>112</sub>Ag<sub>4</sub>N<sub>4</sub>S<sub>12</sub>Si<sub>8</sub> (*M*<sub>r</sub> = 1930.49): C, 37.33; H, 5.85; N, 2.90; Found: C, 37.87; H, 6.02; N, 3.14.

#### S2. X-ray crystallography

X-ray Crystallographic Analysis. Crystallographic data for compounds 2, 3, 5 and 6 were collected on an Oxford Gemini S Ultra system, and the data for compound 4 was on a Rigaku R-Axis Spider IP system. For the measurement a graphite-monochromatic Mo-K<sub>a</sub> radiation ( $\lambda = 0.71073$  Å) was used. Absorption corrections were applied by the spherical harmonics program (multi-scan type). The structures were solved by direct methods  $(SHELXS-96)^{S2}$  and refined against  $F_2$  using SHELXL-97 program.<sup>S3</sup> The non-hydrogen atoms were generally located from the different Fourier synthesis and refined anisotropically, and the hydrogen atoms were included using a riding model with  $U_{\rm iso}$  tied to the  $U_{\rm iso}$  of the parent atoms unless otherwise specified. In 2, a half moiety was disclosed, and one of the three coordinated THF molecules was disordered and treated in a splitting mode. For 3, the crystal's diffracting intensity was weak, which affected the quality of the diffraction reflection data collected, and a low ratio (26%) of the observed/unique reflections was found. However, the data are sufficient to determine the structure which is in good agreement with the NMR and elemental analysis data. In the course of the structural analysis, the  $U_{eq}$  of the atoms from the SiMe<sub>3</sub> group and three coordinate THF molecules are large and a disordering treatment is applied by using a splitting mode, in which the non-hydrogen atoms of one of the THF molecules were refined isotropically. In 4, the SiMe<sub>3</sub> groups and three coordinated THF molecules are disordered and treated in a splitting mode, in which the non-hydrogen atoms of one of the THF molecules were refined isotropically. In 5, the SiMe<sub>3</sub> and Si(SH)<sub>3</sub> groups are disordered due to the structural similarity and were treated in a splitting mode. The SH hydrogen atoms were located from the different Fourier synthesis and refined isotropically. In the course of the refinement the bond lengths of Si-S  $(2.10-2.25 \pm 0.01 \text{ Å})$ , Si–C  $(1.86 \pm 0.01 \text{ Å})$ , Si<sub>SiMe3</sub>–N  $(1.76 \pm 0.01 \text{ Å})$ , Si<sub>Si(SH)3</sub>–N  $(1.72 \pm 0.01 \text{ Å})$ , and S–H  $(1.35 \pm 0.03 \text{ Å})$  are set, respectively, on the basis of the corresponding data reported.<sup>S1,S4</sup> The final refinement gave a convergence. In **6**, the SH hydrogen atoms were not able to be located due to the mediocre quality of the crystals.

	2	3	4	5	6
Empirical formula	C54H100Li6N2O6	C27H50Cl2LiNO3	C42H76Li2N2O3S	C15H29NS3Si2	C60H104Ag4N4S12
r	S <sub>6</sub> Si <sub>4</sub>	SSi <sub>2</sub>	4Si4	- 13 29 11 51 2	Si <sub>8</sub>
formula weight	1219.72	602.76	911.53	375.75	1922.39
CCDC No.	973535	973536	973538	979368	987309
crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
space group	$P2_{1}/n$	$P2_{1}/c$	$P2_{1}/n$	$Cmc2_1$	<i>P</i> -1
a/Å	11.2887(4)	12.2912(14)	14.035(3)	12.1294(9)	15.0310(6)
<i>b</i> /Å	12.5105 (5)	14.2850(18)	20.367(4)	12.0775(7)	15.0658(7)
c/Å	24.5874(10)	19.527(2)	18.446(4)	14.2602(8)	18.8598(6)
a/deg					95.478(3)
β/deg	97.663(4)	96.116(12)	90.00(3)		93.480(3)
γ/deg					98.395(4)
$V/\text{\AA}^3$	3441.4(2)	3409.0(7)	5272.8(18)	2089.0(2)	4193.7(3)
Ζ	2	4	4	4	2
$ ho_{ m calcd}/ m g\cdot  m cm^{-3}$	1.177	1.174	1.148	1.195	1.522
$\mu/\mathrm{mm}^{-1}$	0.312	0.348	0.306	0.465	1.370
<i>F</i> (000)	1312	1296	1968	808	1968
crystal size/mm <sup>3</sup>	0.35x0.35x0.35	0.30x0.28x0.25	0.40x0.20x0.12	0.30x0.18x0.18	0.30x0.30x0.10
$\theta$ range/deg	2.82-26.00	2.82-25.00	3.07-26.00	2.78-26.00	2.75-26.00
index ranges	$-13 \le h \le 13$	$-14 \le h \le 7$	$-17 \le h \le 17$	$-14 \le h \le 14$ ,	$-18 \leq h \leq 17$
	$-15 \le k \le 15$	$-16 \le k \le 16$	$-25 \le k \le 25$	$-14 \le k \le 13,$	$-18 \leq k \leq 18$
	$-29 \le l \le 30$	$-23 \le l \le 23$	$-22 \le l \le 22$	$-17 \le l \le 17$	$-23 \leq l \leq 23$
collected data	26155	14396	44405	7290	37940
unique data	6750	5984	10339	2077	16443
	$(R_{\rm int} = 0.0813)$	$(R_{\rm int} = 0.1321)$	$(R_{\rm int} = 0.2153)$	$(R_{int} = 0.0411)$	$R_{(int)} = 0.0646$
completeness to $\theta$	99.8%	99.9%	99.7%	99.9%	99.8%
Flack parameter				0.2(3)	
data/restraints/parameters	6750/195/396	5984/790/469	10339/946/696	2077/192/162	16443/0/821
GOF on $F^2$	0.817	0.716	0.936	1.004	0.782
final P indians $[I > 2]$ (D)	$R_1 = 0.0453$	$R_1 = 0.0663$	$R_1 = 0.0781$	$R_1 = 0.0442$	$R_1 = 0.0430,$
$\lim_{t \to \infty} 1 - 2  (1)$	$wR_2 = 0.0789$	$wR_2 = 0.1199$	$wR_2 = 0.1544$	$wR_2 = 0.0963$	$wR_2 = 0.0562$
R indices (all data)	$R_1 = 0.0985$	$R_1 = 0.2383$	$R_1 = 0.2065$	$R_1 = 0.0607$	$R_1 = 0.1059,$
	$wR_2 = 0.0864$	$wR_2 = 0.1525$	$wR_2 = 0.2042$	$wR_2 = 0.1051$	$wR_2 = 0.0617$
Largest diff	0.349/-0.290	0.776/-0.273	0.453/-0.694	0.290/-0.250	0.796/-0.573

Table S1. Crystal data and refinements for compounds 2-6

<sup>*a*</sup> All data were collected at 173(2) K using Mo K<sub>a</sub> ( $\lambda = 0.71073$  Å) radiation.  $R_1 = \sum (||F_o| - |F_c||) / \sum |F_o|$ ,  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ , GOF =  $[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_p)]^{1/2}$ .

Crystal structures of compounds 2-6



**Figure S1**. X-ray crystal structure of **2** containing disordering groups of the coordinated THF molecules. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)-S(1) 2.1276(10), Si(1)-S(2) 2.1098(10), Si(1)-S(3) 2.1383(10), Si(1)-N(1) 1.757(2), Si(2)-N(1) 1.752(2), S(1)-Li(1) 2.446(5), S(1)-Li(2A) 2.422(5), S(1)-Li(3A) 2.496(5), S(2)-Li(1) 2.427(5), S(2)-Li(2) 2.515(5), S(2)-Li(3) 2.398(5), S(3)-Li(1A) 2.528(5), S(3)-Li(2A) 2.425(5), S(3)-Li(3) 2.440(5), Li(1)-O(1) 1.922(5), Li(2)-O(2) 1.952(5), Li(3)-O(3) 1.940(5); S(1)-Si(1)-S(2) 111.95(4), S(2)-Si(1)-S(3) 109.74(4), S(1)-Si(1)-S(3) 108.19(4). Symmetry code for A: -x + 2, -y + 1, -2.



**Figure S2**. X-ray crystal structure of **3** containing disordering coordinated THF molecules and the SiMe<sub>3</sub> groups. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)-O(1) 1.885(20) (average), Li(1)-O(2) 1.955(20) (average), Li(1)-O(3) 1.914(20) (average), Li(1)-S(1) 2.468(10), Si(1)-S(1) 1.984(2), Si(1)-Cl(1) 2.104(2), Si(1)-Cl(2) 2.068(2), Si(1)-N(1) 1.709(4), Si(2)-N(1) 1.723(20) (average).



**Figure S3**. X-ray crystal structure of **4** containing disordering coordinated THF molecules and the SiMe<sub>3</sub> groups. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)-S(1)2.436(10), Li(1)-S(2) 2.458(10), Li(1)-S(4) 2.554(10), Li(1)-O(1) 1.896(12) (average), Li(2)-S(1) 2.491(10), Li(2)-S(2) 2.515(10), Li(2)-O(2) 1.940(30) (average), Li(2)-O(3) 1.985(30) (average), Si(1)-S(2) 2.0492(19), Si(1)-S(3) 2.171(2), Si(1)-S(4) 2.198(2), Si(2)-S(1) 2.049(2), Si(2)-S(3) 2.174(2), Si(2)-S(4) 2.196(2), Si(1)-N(2) 1.732(4), Si(2)-N(1) 1.729(4), Si(3)-N(2) 1.767(12) (average), Si(4)-N(1) 1.772(12) (average); S(1)-Li(1)-S(2) 105.6(4), Li(1)-S(2)-Li(2) 73.2(3), S(3)-Si(1)-S(4) 92.87(7), S(3)-Si(2)-S(4) 92.82(7), Si(1)-S(3)-Si(2) 82.38(7), Si(1)-S(4)-Si(2) 81.28(7).



**Figure S4**. X-ray crystal structure of **5** containing the disordering SH and SiMe<sub>3</sub> groups. The H atoms at the carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)-S(1) 2.110(7), Si(1)-S(2) 2.101(8), Si(1)-S(3) 2.101(7), Si(1)-N(1) 1.692(7), Si(2)-N(1) 1.788(8), S(1)-H(1) 1.34(3), S(2)-H(2) 1.31(3), S(3)-H(3) 1.34(3); Si(1)–S(1)–H(1) 103(3), Si(1)–S(2)–H(2) 94(4), Si(1)–S(3)–H(3) 109(2). Symmetry code for A: –x, y, z.



Figure S5. X-ray crystal structure of 6. The H atoms at the carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–S(1) 2.3821(14), Ag(4)–S(1) 2.3879(13), Ag(1)–S(2) 2.4008(14), Si(1)–S(1) 2.0843(19), Si(1)–S(11) 2.0672(17), Si(1)–S(12) 2.0403(18), Si(1)–N(1) 1.695(4); S(1)–Ag(1)–S(2) 168.80(5), Ag(1)–S(1)–Ag(4) 101.79(5).

The structure of **3** clearly reveals that only one Cl atom of **1** is replaced under the formation of  $(Cl_2)Si-S-Li(THF)_3$ . Compound **3** is a rare example containing a Si-S-Li unit and two Si-Cl bonds.<sup>S5</sup> Such compounds are generally unstable due to the elimination of LiCl. In **3** the Si-S bond length is 1.984(2) Å, which is a little shorter than those in  $[(4-MeC_6H_4)_3Si(\mu-S)AgPPh_3]_2$  (2.1060(12) Å)<sup>S6</sup> and Tbt(Mes)Si( $\mu$ -S)<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub> (2.115(2) and 2.157(2) Å).<sup>S7</sup> The S-Li bond distance is 2.468(10) Å. Compound **4** contains two  $\mu$ -S group bridging two Si atoms, and two terminal SLi moieties bound each to silicon. The coordination sphere of two Li atoms is different due to the number of THF molecule coordinated. The Si–S<sub>terminal</sub> bond lengths (2.049(2) and 2.0492(2) Å) are comparable to that found in **3**, but a little shorter than the Si- $\mu$ -S ones (2.171(2)-2.198(2) Å). The S–Li bond distances range from 2.436(10) to 2.554(10) Å.

#### **S3.** Computational Details

All geometry optimizations were computed using the functional M06-2X<sup>S4</sup> with the def2-TZVPP basis set.<sup>S8</sup> The stationary points were located with the Berny algorithm<sup>S9</sup> using redundant coordinates. Analytical Hessians were computed to determinate the nature of the stationary points.<sup>S10</sup> All the geometry optimizations computations were performed using the Gaussian 09 suite of programs.<sup>S11</sup>

In order to compute the chemical shifts, the geometry of the **5** compound was re-optimized by taking the solvent chloroform ( $\epsilon = 4.7113$ ) into account (PCM(CCl<sub>3</sub>H)-M06-2X/def2-TZVPP).<sup>S12</sup> Nonspecific solvent effects were described by using the self-consistent reaction field (SCRF) approach in Tomasi's formalism.<sup>S13</sup> The <sup>1</sup>H and <sup>29</sup>Si chemical shifts were calculated with GIAO<sup>14S</sup> method by a single point calculation at the functional OPBE<sup>S15</sup> and the pcS-3<sup>S16</sup> basis sets.

The NBO<sup>S17</sup> calculations were performed by using the GENNBO 5.9 program.<sup>188</sup> The energies associated with the donor-acceptor two-electron interactions have been computed according to the second-order perturbational theory.<sup>S17a</sup>



**Figure S6**. Optimized structure of compound **5**. Selected bond lengths [Å] and angles [°] at M06-2X/def2-TZVPP: Si(1)-S(1) 2.143, Si(1)-S(2) 2.147, Si(1)-S(3) 2.139, Si(1)-N(1) 1.712, Si(2)-N(1) 1.774, S(1)-H(1) 1.339, S(2)-H(2) 1.340, S(3)-H(3) 1.340; Si(1)–S(1)–H(1) 94.8, Si(1)–S(2)–H(2) 95.2, Si(1)–S(3)–H(3) 92.2. Selected bond lengths [Å] and angles [°] at PCM(CHCl<sub>3</sub>)-M06-def2-TZVPP: Si(1)-S(1) 2.144, Si(1)-S(2) 2.147, Si(1)-S(3) 2.139, Si(1)-N(1) 1.712, Si(2)-N(1) 1.776, S(1)-H(1) 1.339, S(2)-H(2) 1.339, S(3)-H(3) 1.341; Si(1)–S(1)–H(1) 94.9, Si(1)–S(2)–H(2) 95.6, Si(1)–S(3)–H(3) 92.6. Hydrogen atoms were omitted for clarity.

#### Natural Bond Orbital (NBO) analysis









MO-42

MO-43

MO-44







MO-95

MO-96

MO-97







MO-98

MO-99

MO-100



MO-101



MO-1066



MO-1068



**Figure S7**. NBOs (isocontour 0.045 au) of compound **5**. All the calculations were computed at the M06-2X/def2-TZVPP level. Hydrogen atoms were omitted for clarity.

 Table S2. Calculated NBO results

Orbital	Occupancy	Contribution from atoms to the orbitals
MO-1	1.97888	N(61.51%)-C(38.49%)
MO-2	1.95154	N(83.70%)–Si(16.30%)
MO-3	1.95797	N(83.04%)–Si(16.96%)
MO-42	1.97128	Si(29.53%)-S(70.47%)
MO-43	1.97178	Si(29.81%)–S(70.19%)
MO-44	1.97145	Si(30.26%)–S(69.74%)
MO-95	1.84627	N p 1.00(99.97%)
MO-96	1.97609	S s(60.83%) p(39.05%)
MO-97	1.90280	S s(0.54%) p( 99.14%)
MO-98	1.97546	S s(61.37%) p(38.51%)
MO-99	1.90366	S s(0.07%) p( 99.63%)
MO-100	1.97382	S s(62.89%) p(36.98%)
MO-101	1.90317	S s(0.11%) p(99.56%)
MO-1066	0.12979	N(16.96%)-Si(83.04%)
MO-1068	0.06518	N(16.30%)–Si(83.70%)
MO-1069	0.11194	Si(69.74%)-S(30.26%)
MO-1070	0.12574	Si(70.19%)–S(29.81%)
MO-1071	0.11092	Si(70.47%)-S(29.53%)

Donor NBO (i)	Acceptor NBO (j)	E <sup>(2)</sup> (kcal/mol)
LP(S) (MO-97)	σ*(Si-S) (MO-1069)	13.5
LP(S) (MO-97)	σ*(Si-S) (MO-1070)	4.1
LP(S) (MO-99)	σ*(Si-S) (MO-1069)	5.3
LP(S) (MO-99)	σ*(Si-S) (MO-1071)	1.1
LP(S) (MO-101)	σ*(Si-S) (MO-1070)	7.4
LP(S) (MO-101)	σ*(Si-S) (MO-1071)	11.7
LP(N) (MO-95)	σ*(Si-C)	7.4
LP(N) (MO-95)	σ*(Si-C)	1.1
LP(N) (MO-95)	σ*(Si-C)	2.7
LP(N) (MO-95) <sup>a</sup>	σ*(Si-S) (MO-1070)	10.9
LP(N) (MO-95) <sup>a</sup>	σ*(Si-S) (MO-1071)	6.9

Table S3. Second order perturbation theory analysis within NBO method

<sup>a</sup>Due to symmetry there are only two hyperconjugative interactions N(lp) $\rightarrow \sigma^*$ (Si-S).

**Table S4**. Atomic partial charges from the NBO calculations at the M06-2X/def2-TZVPP,BP86/def2-TZVPP and B3LYP/def2-TZVPP levels

Atom E	M06-2X	BP86	B3LYP
N(1)	-1.38	-1.32	-1.36
Si(1)	+1.46	+1.37	+1.43
Si(2)	+1.92	+1.83	+1.89
<b>S</b> (1)	-0.46	-0.44	-0.45
S(2)	-0.46	-0.44	-0.45
S(3)	-0.43	-0.42	-0.43
H(1)	+0.16	+0.17	+0.16
H(2)	+0.16	+0.16	+0.15
H(3)	+0.16	+0.16	+0.15

**Table S5**. Wiberg bond orders from the NBO calculations at the M06-2X/def2-TZVPP, BP86/def2-TZVPP and B3LYP/def2-TZVPP levels

Bond	M06-2X	BP86	B3LYP
Si <sub>SiMe</sub> -N	0.56	0.58	0.57
Si <sub>sis</sub> -N	0.61	0.63	0.62
Si-S	0.91	0.92	0.91
Si-S	0.92	0.93	0.92
Si-S	0.93	0.94	0.93
Si-C	0.78	0.80	0.78
Si-C	0.79	0.81	0.80
Si-C	0.79	0.81	0.79

 Table S6. Coordinates of the optimized structure of compound 5 at M06-2X/def2-TZVPP level

E= -2417	7.510795 Hartree		
Ν	0.327062000000	-0.104225000000	0.363806000000
С	-1.055115000000	0.132789000000	0.016383000000
С	-1.877907000000	-0.947851000000	-0.343431000000
С	-3.197594000000	-0.691725000000	-0.706212000000
Н	-3.836291000000	-1.519116000000	-0.988639000000
С	-3.703942000000	0.594431000000	-0.714843000000
Н	-4.730231000000	0.775363000000	-1.005398000000
С	-2.887843000000	1.649933000000	-0.346122000000
Н	-3.284884000000	2.657190000000	-0.354121000000
С	-1.563886000000	1.445219000000	0.026221000000
С	-1.397590000000	-2.386759000000	-0.331242000000
Н	-0.351360000000	-2.394817000000	-0.028177000000
С	-2.194573000000	-3.206926000000	0.687639000000
Н	-1.764522000000	-4.203813000000	0.796414000000
Н	-3.230371000000	-3.322756000000	0.363720000000
Н	-2.207559000000	-2.726515000000	1.667077000000
С	-0.714113000000	2.649837000000	0.385429000000
Н	0.228398000000	2.288766000000	0.800815000000
С	-0.399801000000	3.478608000000	-0.865708000000
Н	0.291985000000	4.288688000000	-0.626285000000
Н	-1.315536000000	3.923941000000	-1.259849000000
Н	0.025825000000	2.866406000000	-1.660463000000
Si	0.711250000000	-0.476545000000	2.055637000000
С	0.903349000000	-2.311387000000	2.375430000000
Н	1.647582000000	-2.768056000000	1.722285000000
Н	-0.032204000000	-2.858487000000	2.266518000000
Н	1.245552000000	-2.443640000000	3.404934000000

С	-0.691650000000	0.171180000000	3.098293000000
Н	-0.761154000000	1.256627000000	3.030830000000
Н	-0.519622000000	-0.092151000000	4.143590000000
Н	-1.652259000000	-0.246961000000	2.793298000000
С	2.313446000000	0.356880000000	2.528235000000
Н	2.286619000000	1.431815000000	2.348662000000
Н	3.163197000000	-0.054789000000	1.981644000000
Н	2.492367000000	0.189727000000	3.592788000000
Si	1.494258000000	-0.020407000000	-0.886407000000
S	2.695260000000	-1.789500000000	-0.739882000000
He	3.683276000000	-1.317066000000	-1.510702000000
S	2.960808000000	1.543700000000	-0.779186000000
Не	2.148770000000	2.504185000000	-1.240680000000
S	0.401837000000	0.165521000000	-2.715448000000
Не	1.526227000000	0.290144000000	-3.433796000000
С	-1.480951000000	-3.034175000000	-1.714860000000
Н	-0.885230000000	-2.485527000000	-2.442905000000
Н	-1.111915000000	-4.059769000000	-1.670166000000
Н	-2.512113000000	-3.065160000000	-2.071170000000
С	-1.382392000000	3.549038000000	1.428995000000
Н	-1.709439000000	2.988888000000	2.303769000000
Н	-0.687560000000	4.324006000000	1.755222000000
Н	-2.257196000000	4.049704000000	1.011954000000

**Table S7.** Coordinates for the optimized structure of compound **5** at PCM(CHCl<sub>3</sub>)-M06-2X/def2-TZVPP level

Ν	0.325205000000	-0.108697000000	0.363053000000
С	-1.053693000000	0.143014000000	0.012798000000
С	-1.887897000000	-0.929403000000	-0.346629000000
С	-3.204759000000	-0.659725000000	-0.712042000000
Н	-3.852792000000	-1.480293000000	-0.993502000000
С	-3.697235000000	0.632613000000	-0.722884000000
Н	-4.721305000000	0.824295000000	-1.014882000000
С	-2.870024000000	1.680137000000	-0.353532000000
Н	-3.256698000000	2.691423000000	-0.363019000000
С	-1.548457000000	1.461214000000	0.021406000000
С	-1.423436000000	-2.373583000000	-0.330381000000
Н	-0.376660000000	-2.392047000000	-0.029524000000
С	-2.227376000000	-3.182298000000	0.692319000000
Н	-1.810043000000	-4.184813000000	0.798445000000
Н	-3.266037000000	-3.282946000000	0.372425000000
Н	-2.227847000000	-2.702397000000	1.672101000000
С	-0.686586000000	2.657060000000	0.381150000000

Н	0.249822000000	2.286927000000	0.801949000000
С	-0.357892000000	3.478693000000	-0.871152000000
Н	0.341847000000	4.281171000000	-0.630288000000
Н	-1.267315000000	3.932542000000	-1.270303000000
Н	0.067186000000	2.860076000000	-1.661380000000
Si	0.699900000000	-0.481081000000	2.058777000000
С	0.885290000000	-2.316500000000	2.377270000000
Н	1.632659000000	-2.775560000000	1.729427000000
Н	-0.051980000000	-2.859086000000	2.260115000000
Н	1.218070000000	-2.448167000000	3.409919000000
С	-0.705354000000	0.170068000000	3.094470000000
Н	-0.781918000000	1.254197000000	3.014386000000
Н	-0.526740000000	-0.081245000000	4.141672000000
Н	-1.662967000000	-0.260269000000	2.797006000000
С	2.301223000000	0.350174000000	2.537953000000
Н	2.267583000000	1.427078000000	2.370699000000
Н	3.151808000000	-0.052496000000	1.985896000000
Н	2.478881000000	0.170668000000	3.600638000000
Si	1.496897000000	-0.036690000000	-0.882658000000
S	2.686936000000	-1.813710000000	-0.732392000000
Н	3.668179000000	-1.360559000000	-1.523989000000
S	2.974199000000	1.518042000000	-0.773845000000
Н	2.174375000000	2.490409000000	-1.231979000000
S	0.414647000000	0.147528000000	-2.718483000000
Н	1.537726000000	0.273985000000	-3.438813000000
С	-1.518207000000	-3.025272000000	-1.711424000000
Н	-0.920679000000	-2.483975000000	-2.443895000000
Н	-1.157544000000	-4.053756000000	-1.663999000000
Н	-2.551270000000	-3.049129000000	-2.062768000000
С	-1.348400000000	3.568069000000	1.418604000000
Н	-1.680324000000	3.016428000000	2.297101000000
Н	-0.645564000000	4.337501000000	1.740404000000
Н	-2.217743000000	4.074365000000	0.997085000000

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