

Aminosilanetrithiol  $\text{RSi}(\text{SH})_3$ : an experimental and quantum-chemical study†Cite this: *Chem. Commun.*, 2014, 50, 4628Received 4th February 2014,  
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An interesting aminosilanetrithiol  $\text{RSi}(\text{SH})_3$  ( $\text{R} = \text{N}(\text{SiMe}_3)\text{-}2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ) has been prepared by the reaction of lithium aminosilanetrithiolate  $\{\text{RSi}[\text{SLi}(\text{THF})_3]_2\}$  with  $\text{MeCOOH}$ . Theoretical calculations indicate that the  $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si-S})$  and  $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si-S})$  electron donations remarkably contribute to the stabilization of the  $\text{Si}(\text{SH})_3$  part of the molecule.  $\text{RSi}(\text{SH})_3$  is the first example of a stable molecule containing three SH groups attached to one element.

Orthoformic acid ( $\text{HC}(\text{OH})_3$ ) and its sulfur congener ( $\text{HC}(\text{SH})_3$ ) are hypothetical molecules. Aqueous formic acid possibly contains  $\text{HC}(\text{OH})_3$  which is considered to be extremely unstable.<sup>1</sup> The analogous silicon species  $\text{HSi}(\text{OH})_3$  and  $\text{HSi}(\text{SH})_3$  have also been proposed and theoretically studied.<sup>2</sup>  $\text{RSi}(\text{OH})_3$  compounds with the bulky R substituents ( $\text{R} = \text{alkyl, aryl, aryloxy, or aryl-substituted amide group or a metal cluster}$ ) have already been reported since the 1950s.<sup>3</sup> They are extensively employed as building blocks for assembling lipophilic three-dimensional Si-O metal clusters.<sup>3b-d</sup> However, the sulfur analogue  $\text{RSi}(\text{SH})_3$  has not been prepared so far.

It has been documented that some of the triorganosilanethiols ( $\text{R}_3\text{SiSH}$ ) and diorganosilanedithiols ( $\text{R}_2\text{Si}(\text{SH})_2$ ) can be obtained by a variety of methods including alcoholysis of  $\text{SiS}_2$ ,<sup>4</sup> protonation of potassium silanethiolate,<sup>5</sup> insertion of sulfur into triorganosilane,<sup>6</sup> treatment of silylsulfide with hydrogen halide,<sup>7</sup> and  $\text{LiAlH}_4$  reduction of a silanepolysulfide.<sup>8</sup> More recently, a transition metal-trapped silylenylthiol  $\text{LSi}[\text{Ni}(\text{CO})_3]\text{SH}$  ( $\text{L} = \text{HC}[\text{C}(\text{Me})\text{CN-}2,6\text{-iPr}_2\text{C}_6\text{H}_3]_2$ ) has been achieved by 1,4-addition of  $\text{H}_2\text{S}$  to  $\text{L}'\text{Si}[\text{Ni}(\text{CO})_3]$  ( $\text{L}' = \text{HC}[\text{C}(\text{Me})\text{N-}2,6\text{-iPr}_2\text{C}_6\text{H}_3][\text{C}(\text{CH}_2\text{N-}2,6\text{-iPr}_2\text{C}_6\text{H}_3)]$ ).<sup>9</sup> In comparison

with the preparation of the organosilanols,<sup>3</sup> the synthesis of the organosilanethiols appears to be more complex. The approach to prepare organosilanetrithiol by reacting the  $\text{R}'\text{SiCl}_3$  ( $\text{R}' = \text{Me}_2\text{iPrC}$  or  $\text{Me}$ ) precursor with  $\text{Li}_2\text{S}^{10}$  or  $\text{H}_2\text{S}/\text{NET}_3$  in the presence of  $\text{MeCl}_2\text{Si-SiCl}_2\text{Me}^{11}$  was not successful, and instead the silylsulfide clusters  $((\text{Me}_2\text{iPrCSi})_4\text{S}_6$  and  $(\text{MeSi})_4\text{S}_5$ ) were produced. An intermediate in these reactions might be the Si-S-M ( $\text{M} = \text{Li, H}$ ) moiety, which further reacted to yield the Si-S-Si unit observed in the clusters.

$\text{RSi}(\text{OH})_3$  has been prepared by using  $\text{RSiCl}_3$  with a bulky R group which prevents the condensation shown in the previous work.<sup>3c</sup> Following the strategy of synthesizing  $\text{RSi}(\text{OH})_3$  by controlled hydrolysis of  $\text{RSiCl}_3$  (**1**,  $\text{R} = \text{N}(\text{SiMe}_3)\text{-}2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ) in the presence of an amine as the HCl-acceptor,<sup>12</sup> we used  $\text{H}_2\text{S}$  instead of  $\text{H}_2\text{O}$ . The experiments were carried out with different amines ( $\text{NET}_3$ ,  $2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{NH}_2$ , or pyridine) at various temperatures.<sup>13</sup> However, no reaction was observed.

Subsequently, we employed a salt metathesis reaction by treating **1** with  $\text{Na}_2\text{S}$  or  $\text{K}_2\text{S}$ , however, according to NMR analysis no transformation occurred. When we used a freshly prepared  $\text{Li}_2\text{S}^6$  obtained from the reaction of sulfur with  $\text{LiBET}_3\text{H}$ , the reaction proceeded and several products were formed depending on the amount of  $\text{Li}_2\text{S}$  and the reaction conditions. As illustrated in Scheme 1, the reaction of **1** with 5.3 equivalents of  $\text{Li}_2\text{S}$  in THF was carried out at 25 °C and stirred for 10 days, affording  $\{\text{RSi}[\text{SLi}(\text{THF})_3]_2\}$  (**2**) as colorless crystals in high yield (85%). However, upon changing the temperature, time, and ratio of the precursors, the reaction only resulted in products  $\text{RSiCl}_2\text{SLi}(\text{THF})_3$  (**3**) and  $\text{RSi}[\text{SLi}(\text{THF})](\mu\text{-S})_2\text{Si}[\text{SLi}(\text{THF})_2]\text{R}$  (**4**). Compound **3** is an incompletely sulfurized species which can be isolated as colorless crystals in 80% yield, when the reaction was conducted under stirring at 10 °C for 24 h using three equivalents of  $\text{Li}_2\text{S}$ . Increasing the reaction temperature to 35 °C and extending the reaction time to 72 h yielded a mixture of **3** and **4**. The latter shows the formation of a  $\text{Si}(\mu\text{-S})_2\text{Si}$  moiety, which is generated at a little higher temperature than 25 °C and is not observed during the formation of **2**. Compared with the results reported in the literature,<sup>10,11</sup> it is worth noting that a combination of the right  $\text{RSiCl}_3$ ,<sup>14</sup> restricted temperature, long reaction time, and excess of  $\text{Li}_2\text{S}$  is important to the successful and high yield production of **2**.

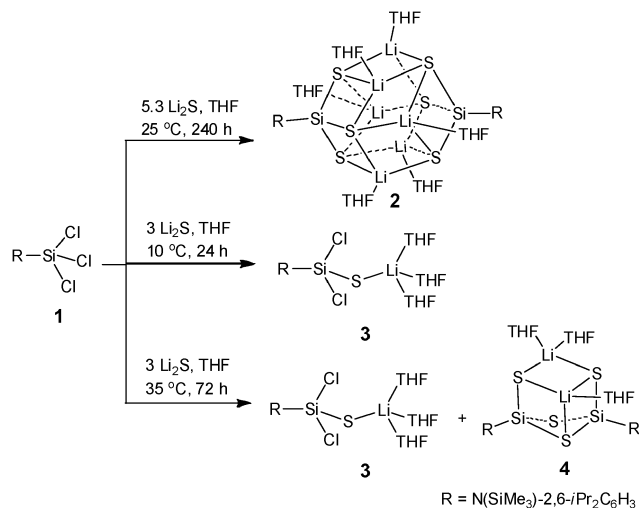
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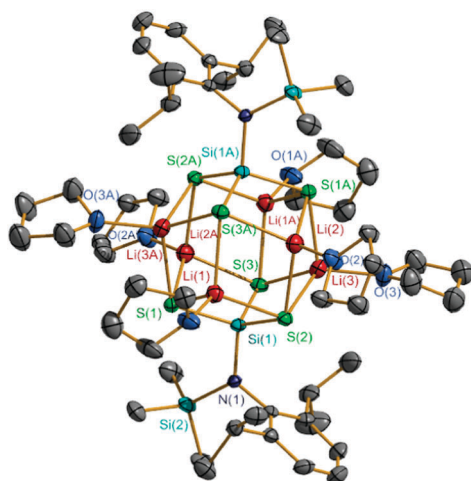
† Electronic supplementary information (ESI) available: Experimental procedures and X-ray crystallographic and computational information. CCDC 973535 (2), 973536 (3), 973538 (4), 979368 (5), and 987309 (6). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc00912f



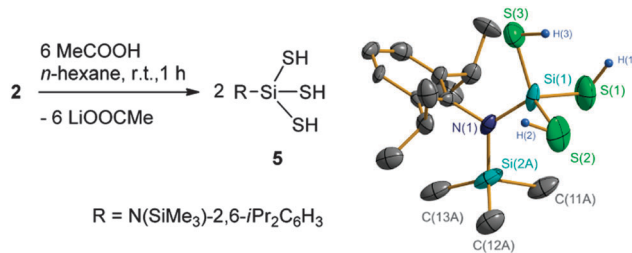


**Scheme 1** Reaction of **1** with freshly prepared  $\text{Li}_2\text{S}$  under different reaction conditions to produce compounds **2–4**.

Compounds **2–4** are air and moisture sensitive and have been characterized by NMR spectroscopy and X-ray crystallography. Compound **2** shows symmetric patterns in  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra in solution, indicating that all the R groups in **2** are equivalent. The  $\text{CHMe}_2$  resonance (4.05 ppm) of R in **2** is lowfield shifted when compared with those of **3** (3.60 ppm) and **4** (3.43 ppm). The  $^{29}\text{Si}$  NMR spectra of **2** display the respective resonances at  $\delta$  1.2 ( $\text{SiMe}_3$ ) and  $-4.2$  ppm ( $\text{SiS}$ ). The X-ray single-crystal structural analysis of **2** (Fig. 1) reveals that two  $\text{Si}(\text{SiLi})_3$  are assembled into a metal cage cluster which is comparable to those of the organosilanetriol-derived metallosiloxanes formed.<sup>3b–d</sup> The rhomboid-based dodecahedral  $\text{Si}_2\text{S}_6\text{Li}_6$  core of structure **2** contains six tetra-coordinate Li atoms each linked to one O atom from the THF molecule and three S atoms. Each of the six S atoms is located at the apex of a tetragonal pyramid and a  $\text{SiLi}_3$  four-membered ring forms the base of the pyramid. Similar structures containing  $\text{Si}_2\text{N}_6\text{Li}_6$ ,<sup>15</sup>  $\text{Si}_2\text{P}_6\text{Li}_6$ ,<sup>16</sup> and  $\text{Ge}_2\text{As}_6\text{Li}_6$ <sup>17</sup> frameworks have been reported. The congener  $\text{RSi}(\text{OX})_3$  (X = alkali metal) has not been prepared so far. The Si–S (2.1098(10)–2.1383(10) Å) and S–Li (2.398(5)–2.528(5) Å) bond



**Fig. 1** X-ray crystal structure of **2** with H atoms omitted for clarity.



**Scheme 2** Synthesis and the crystal structure of **5**.

lengths in **2** are comparable with those in **3** and **4**, respectively. The X-ray structures and detailed descriptions of **3** and **4** are given in the ESI†

Compound **2** is a potential precursor for preparing aminosilane-trithiol. As expected, treatment of **2** with  $\text{MeCOOH}$  easily produced  $\text{RSi}(\text{SH})_3$  (**5**) as colorless crystals in 40% yield (Scheme 2). The alternative use of  $\text{CF}_3\text{COOH}$ ,  $\text{C}_6\text{H}_5\text{COOH}$ , or  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$  is also possible but does not improve the yield.<sup>18</sup> Compound **5** is air and moisture sensitive. It has a melting point of  $154^\circ\text{C}$ , indicative of good thermal stability. In addition, **5** exhibits good solubility in common organic solvents such as *n*-hexane, toluene, diethyl ether, THF, and chlorinated hydrocarbons. The  $^1\text{H}$  NMR spectrum of **5** clearly shows the SH proton resonance at  $\delta$  1.18 ppm, which is comparable to those found in  $\text{Tbt}(\text{Mes})\text{Si}(\text{SH})_2$  and  $\text{Tbt}(\text{Mes})\text{Si}(\text{OH})\text{SH}$  (0.87–1.18 ppm).<sup>8</sup> The SiS silicon resonance (2.7 ppm) is remarkably lowfield shifted even to a positive value in contrast to those of the SiO ones of the organosilanetriols ( $-40$  to  $-90$  ppm).<sup>3d,13</sup> A strong SH absorption band is observed at  $\tilde{\nu}$   $2543\text{ cm}^{-1}$  in the IR spectrum.

The structural analysis unambiguously reveals **5** to be a monomeric molecule (Scheme 2). However, the refinements indicate a severe disorder for the N-bonded  $\text{SiMe}_3$  and  $\text{Si}(\text{SH})_3$  groups which are pseudo-symmetrically arranged along the N– $\text{C}_{\text{aryl}}$  axis, although the Me and SH groups show different appearances (see Fig. S4 in the ESI†). Treatment with a splitting mode results in a setting of the related bond lengths (Si–S,  $2.10\text{--}2.25 \pm 0.01$ ; Si–C,  $1.86 \pm 0.01$ ;  $\text{Si}_{\text{SiMe}_3}\text{--N}$ ,  $1.76 \pm 0.01$ ;  $\text{Si}_{\text{SiS}}\text{--N}$ ,  $1.72 \pm 0.01$ ; S–H,  $1.35 \pm 0.03$  Å) on the basis of the reported coordinate data. The final refinement gives convergence with bond parameters (Si–S,  $2.101(8)\text{--}2.110(7)$  Å; S–H,  $1.31\text{--}1.34(3)$  Å;  $\angle$  Si–S–H,  $94(4)\text{--}109(2)^\circ$ ) comparable to those found in  $\text{Tbt}(\text{Mes})\text{Si}(\text{SH})_2$ ,  $\text{Tbt}(\text{Mes})\text{Si}(\text{OH})\text{SH}$ ,<sup>8</sup> and  $\text{LSi}[\text{Ni}(\text{CO})_3]\text{SH}$ <sup>9</sup> as well as in the predicted  $[\text{Si}(\text{SH})_3]^+$ .<sup>2a</sup>

To further understand the bonding matrix of compound **5**, we carried out quantum chemical calculations on the basis of density functional theory (DFT). By optimizing the geometry of the molecule **5** at the M06-2X/def2-TZVPP level,<sup>19</sup> the general structure (Fig. S6, ESI†) calculated is basically in agreement with the results obtained by the X-ray structural analysis (Fig. S4, ESI†). The  $\text{Si}_{\text{Si}(\text{SH})_3}\text{--N}$  distance (1.712 Å) is computed to be *ca.* 0.020 Å longer than the experimental value while the  $\text{Si}_{\text{SiMe}_3}\text{--N}$  one (1.774 Å) is 0.014 Å shorter. Both the experimental and theoretical values are significantly shorter than the Si–N standard value (1.87 Å).<sup>20</sup> The experimental Si–S bond lengths range from  $2.101(8)$  to  $2.110(7)$  Å, which are a little shorter than the calculated distances (2.139–2.147 Å).

We also performed the calculation on the  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectroscopic data by means of DFT-GIAO calculations.<sup>21</sup>



Since the NMR measurements were carried out in solution ( $\text{CDCl}_3$ ), we optimized the geometry of **5** using the PCM (Polarized Continuum Model)<sup>22</sup> method in which the effect by solvent was considered. Therefore, the geometry of **5** optimized at the PCM( $\text{CHCl}_3$ )-M06-2X/def2-TZVPP level<sup>22</sup> is only slightly different from the one at the M06-2X/def2-TZVPP level. It is computed that the chemical shifts for the  $\text{Si}(\text{SH})_3$  group are at  $\delta$  2.02 ppm for the proton and 5.97 ppm for the silicon atom. The data for the hydrogen and silicon in the  $\text{SiMe}_3$  moiety are at  $\delta$  0.35 and 11.25 ppm, respectively. These data generally fit to the experimental<sup>5,9</sup> and the other related computational data.<sup>23</sup> Furthermore, the computed IR spectrum exhibits a band for the SH groups at  $\tilde{\nu}$  2753  $\text{cm}^{-1}$ , which is a little higher than the experimental value.

A natural bond orbital (NBO) analysis<sup>24</sup> was accomplished to investigate the bonding situation of **5**. The NBO results identify two N–Si bonds which are strongly polarized toward nitrogen (84% for the N atom and 16% for the Si atoms). The partial charges calculated suggest that the nitrogen atom carries a negative charge ( $-1.38 e$ ) in a large extent while the silicon atoms have strong positive charges, namely,  $+1.91 e$  (for  $\text{SiMe}_3$ ) and  $+1.46 e$  (for  $\text{Si}(\text{SH})_3$ ). The Wiberg bond order values  $P$  for  $\text{Si}_{\text{SiS}}\text{--N}$  and  $\text{Si}_{\text{SiMe}_3}\text{--N}$  bonds have been calculated at different levels of theory (Table S5, ESI<sup>†</sup>). The data point out that the former ( $P = 0.61\text{--}0.63$ ) has a higher bond order than the latter ( $P = 0.56\text{--}0.58$ ). The former one can be explained by hyperconjugation of the lone pair orbital of the nitrogen, which is calculated by using a second-order perturbation theory included in the NBO method. The  $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si--S})$  donation amounts to  $17.8 \text{ kcal mol}^{-1}$  while the  $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si--C})$  hyperconjugation is only  $11.2 \text{ kcal mol}^{-1}$  (Table S3, ESI<sup>†</sup>). Furthermore, application of the second-order perturbation theory revealed delocalization by three stabilizing two-electrons from the sulfur ( $\text{LP}(\text{S})$ ) to the anti-bonding orbital  $\sigma^*(\text{Si--S})$ , giving hints of a high conjugation of the  $\text{Si}(\text{SH})_3$  fragment. The computed associated energies ( $\Delta E(2)$ ) are 13.54, 12.81 and  $11.67 \text{ kcal mol}^{-1}$  for each of the  $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si--S})$  interactions.

In summary, we have successfully synthesized the amino-silanetriethyl  $\text{RSi}(\text{SH})_3$  (**5**) through protonation of its precursor  $\{\text{RSi}(\text{SLi}(\text{THF}))_3\}_2$  (**2**) by  $\text{MeCOOH}$ . Precise control of the reaction conditions is crucial for the synthesis of **2**, while varying the reaction conditions led to the products **3** and **4**. DFT calculations of **5** confirm the experimental data. The corresponding NBO analysis shows that the  $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si--S})$  and  $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si--S})$  donations remarkably contribute to the stabilization of the  $\text{Si}(\text{SH})_3$  fragment. Compound **5** shows a structure containing three SH groups attached to one element. The reactivity studies of **5** are now in progress.<sup>25</sup>

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- We have also tested the group tolerance in the syntheses of compounds **2** and **5**. Related results are shown in our recent patent which is still under authorization (CN10222598; Patent Application No. CN20111115911 20110505). However, compound **5** is selected as a typical example in this manuscript for profound experimental and theoretical studies.
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- Currently, we have obtained some preliminary results by isolating  $\text{Ag}_4$  clusters of composition  $[\text{R}(\text{HS})_2\text{SiSAg}]_4$  (**6**) and  $[\text{R}(\text{HS})_2\text{SiSAg}]_2(\text{AgMes})_2$  (**7**) from the reaction of **5** with  $(\text{AgMes})_4$ , which indicate a mono-functional reaction of the triethyl (**5**). Due to poor quality of the crystals of **7**, a preliminary structure of this compound was determined. The synthesis of these two compounds and crystallographic data of **6** are included in ESI<sup>†</sup>.

