

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

Aminosilanetrithiol  $\text{RSi}(\text{SH})_3$ : An Experimental and Quantum-Chemical Study

Cite this: DOI: 10.1039/x0xx00000x

Yan Li,<sup>a,c</sup> Hongping Zhu,<sup>\*a</sup> Diego M. Andrada,<sup>b</sup> Gernot Frenking,<sup>\*b</sup> Herbert W. Roesky<sup>\*c</sup>Received 00th January 2012,  
Accepted 00th January 2012

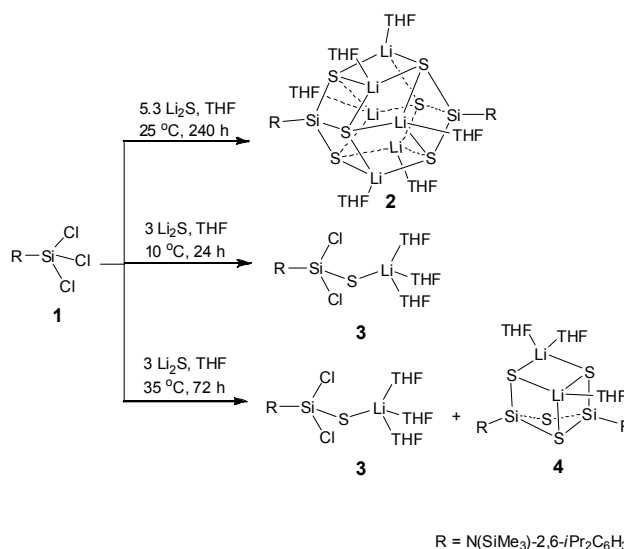
DOI: 10.1039/x0xx00000x

www.rsc.org/

An interesting aminosilanetrithiol  $\text{RSi}(\text{SH})_3$  ( $\text{R} = \text{N}(\text{SiMe}_3)\text{-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) 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  $\text{LSi}[\text{Ni}(\text{CO})_3]\text{SH}$  ( $\text{L} = \text{HC}[\text{C}(\text{Me})\text{CN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3]_2$ ) has been achieved by 1,4-addition of  $\text{H}_2\text{S}$  to  $\text{L}'\text{Si}[\text{Ni}(\text{CO})_3]$  ( $\text{L}' = \text{HC}[\text{C}(\text{Me})\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3][\text{C}(\text{CH}_2)\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3]$ ).<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 organosilanetrithiol by reacting the  $\text{R}'\text{SiCl}_3$  ( $\text{R}' = \text{Me}_2i\text{PrC}$  or  $\text{Me}$ ) precursor with  $\text{Li}_2\text{S}$ <sup>10</sup> or  $\text{H}_2\text{S}/\text{NEt}_3$  in the presence of  $\text{MeCl}_2\text{SiSiCl}_2\text{Me}$ <sup>11</sup> was not successful, and instead the silylsulfide clusters  $(\text{Me}_2i\text{PrCSi})_4\text{S}_6$  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.



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

The  $\text{RSi}(\text{OH})_3$  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**,  $\text{R} = \text{N}(\text{SiMe}_3)\text{-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) in the presence of 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 ( $\text{NEt}_3$ ,  $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$ , or pyridine) at various temperatures.<sup>13</sup> However, no reaction was observed.

Subsequently, we employed 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  $\text{Li}_2\text{S}$ <sup>6</sup> 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

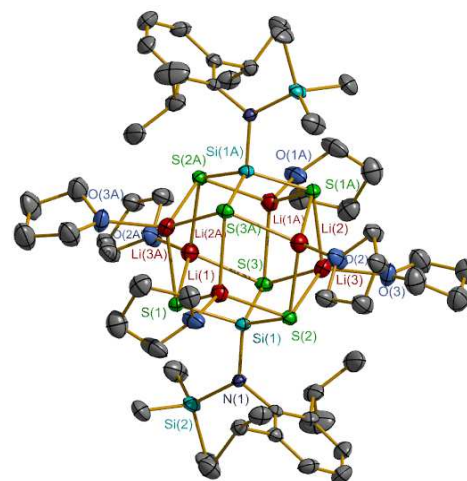
crystals in high yield (85%). However, changing the temperature, time, and ratio of the precursors the reaction only resulted in products  $\text{RSiCl}_2\text{SLi}(\text{THF})_3$  (**3**) and  $\text{RSi}[\text{SLi}(\text{THF})](\mu\text{-S})_2\text{Si}[\text{SLi}(\text{THF})_2]\text{R}$  (**4**). Compound **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 literature,<sup>10,11</sup> it is worth to note 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**.

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  $\text{Si}(\text{SLi})_3$  are assembled into a metal cage cluster which is comparable to those of the organosilanetriol-derived metallocloxanes 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 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.

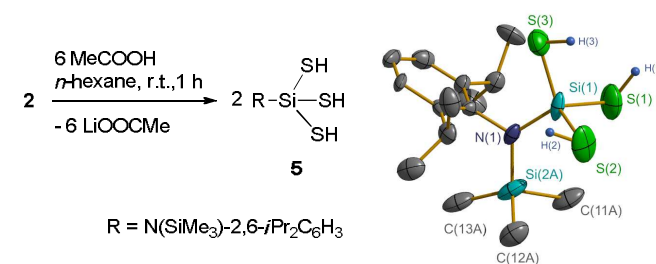
Compound **2** is a potential precursor for preparing aminosilanetrihiol. As expected, treatment of **2** with MeCOOH easily produced  $\text{RSi}(\text{SH})_3$  (**5**) as colorless crystals in 40% yield (Scheme 2). The alternative use of  $\text{CF}_3\text{COOH}$ ,  $\text{C}_6\text{H}_5\text{COOH}$ , 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 °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  $\text{SiS}$  silicon resonance (2.7 ppm) is remarkably lowfield shifted even to positive value in contrast to those of the  $\text{SiO}$  ones of the organosilanetriols (-40 to -90 ppm).<sup>13,3d</sup> A strong SH absorption band is observed at  $\bar{\nu}$  2543  $\text{cm}^{-1}$  in the IR spectrum.

The structural analysis unambiguously reveals **5** 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 appearance (see Figure S4 in ESI). Treatment with a splitting mode results in a setting of the related bond lengths (Si-S, 2.10-2.25  $\pm$  0.01; Si-C, 1.86  $\pm$  0.01;  $\text{Si}_{\text{SiMe}_3}$ -N, 1.76  $\pm$  0.01;  $\text{Si}_{\text{SiS}}$ -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)-2.110(7) Å; S-H, 1.31-1.34(3) Å;  $\angle$  Si-S-H, 94(4)-109(2)°) 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>



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



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

To further understand the bonding matrix of compound **5**, we have 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-TZVPP20 level,<sup>19</sup> the general structure (Figure S6 in ESI) calculated is basically in agreement with the results by the X-ray structural analysis (Figure S4 in ESI). The  $\text{Si}_{\text{Si}(\text{SH})_3}$ -N distance (1.712 Å) is computed to be ca. 0.020 Å longer than the experimental value while the  $\text{Si}_{\text{SiMe}_3}$ -N one (1.774 Å) 0.014 Å shorter. Both the experimental and theoretical data 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 an 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-TZVPP20. 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  $\nu$  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 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). The data point out that the former ( $P = 0.61-0.63$ ) has a higher bond order than the later ( $P = 0.56-0.58$ ). The former one can be explained by hyperconjugation of the lone pair orbital of the nitrogen, which is calculated by using second-order perturbation theory included in the NBO method. The  $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si}-\text{S})$  donation amounts to 17.8 kcal/mol while the  $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si}-\text{C})$  hyperconjugation is only 11.2 kcal/mol (Table S3 in ESI). Furthermore, application of the second-order perturbation theory revealed delocalization of three stabilizing two-electrons from the sulfur ( $\text{LP}(\text{S})$ ) to the anti-bonding orbital  $\sigma^*(\text{Si}-\text{S})$ , 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 kcal/mol for each of the  $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si}-\text{S})$  interaction.

In summary, we have successfully synthesized the aminosilanetriethyl  $\text{RSi}(\text{SH})_3$  (**5**) through a protonation of its precursor  $\{\text{RSi}[\text{SLi}(\text{THF})_3]_2$  (**2**) by  $\text{MeCOOH}$ . Precise control of the reaction condition 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. Corresponding NBO analysis shows that the  $\text{LP}(\text{N}) \rightarrow \sigma^*(\text{Si}-\text{S})$  and  $\text{LP}(\text{S}) \rightarrow \sigma^*(\text{Si}-\text{S})$  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>

This work is supported by the 973 Program (2012CB821704), the National Nature Science Foundation of China (91027014), and the Innovative Research Team Program (IRT1036 and 20923004). Support of the Deutsche Forschungsgemeinschaft (DFG) is highly acknowledged.

## Notes and references

<sup>a</sup> State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian, 361005, China. E-mail: hpzhu@xmu.edu.cn

<sup>b</sup> Fachbereich Chemie, Philipps-Universität Marburg Hans-Meerweinstrasse, 35032 Marburg, Germany. E-mail: frenking@chemie.uni-marburg.de

<sup>c</sup> Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraße 4, 37077-Göttingen, Germany. E-mail: hroesky@gwdg.de

† Electronic Supplementary Information (ESI) available: Experimental procedures, 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/c000000x/

- (a) S. Böhm, I. Senf, H.-D. Schädler and J. Kuthan, *J. Mol. Struct.: THEOCHEM*, 1992, **253**, 73-82; (b) S. Böhm, D. Antipova and J. Kuthan, *Int. J. Quantum Chem.*, 1996, **60**, 649-655; (c) R. Glaser, G. S.-C. Choy, G. S. Chen and H. Grützmacher, *J. Am. Chem. Soc.*, 1996, **118**, 11617-11628.
- (a) C. M. Marchand, U. Pidun, G. Frenking and H. Grützmacher, *J. Am. Chem. Soc.*, 1997, **119**, 11078-11085; (b) A. Herman and W. Wojnowski, *Structural Chemistry*, 1992, **3**, 239-244.
- See selected examples: (a) L. J. Tyler, *J. Am. Chem. Soc.*, 1955, **77**, 770-771; (b) R. Murugavel, V. Chandrasekhar and H. W. Roesky, *Acc. Chem. Res.*, 1996, **29**, 183-189 and references therein; (c) R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205-2236; (d) V. Chandrasekhar, R. Boomishankar and S. Nagendran, *Chem. Rev.*, 2004, **104**, 5847-5910.
- R. Piekos and W. Wojnowski, *Z. Anorg. Allg. Chem.*, 1962, **318**, 212-216.
- (a) J. E. Drake, B. M. Glavinčevski and R. T. Hemmings, *Can. J. Chem.*, 1980, **58**, 2161-2166; (b) J. Pikies and W. Wojnowski, *J. Organomet. Chem.*, 1989, **373**, 317-326.
- H. Lange and U. Herzog, *J. Organomet. Chem.*, 2002, **660**, 36-42.
- H. Beckers and H. Bürger, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1217-1224.
- (a) T. Tanabe, N. Takeda and N. Tokitoh, *Eur. J. Inorg. Chem.*, 2007, 1225-1228; (b) T. Tanabe, Y. Mizuhata, N. Takeda and N. Tokitoh, *J. Organomet. Chem.*, 2009, **694**, 353-365.
- A. Meltzer, S. Inoue, C. Präsang and M. Driess, *J. Am. Chem. Soc.*, 2010, **132**, 3038-3046.
- M. Unno, Y. Kawai, H. Shioyama and H. Matsumoto, *Organometallics*, 1997, **16**, 4428-4434.
- U. Herzog and G. Rheinwald, *J. Organomet. Chem.*, 2001, **628**, 133-143.
- R. Murugavel, V. Chandrasekhar, A. Voigt, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Organometallics*, 1996, **14**, 5298-5301.
- We have tried  $\text{H}_2\text{S}$  in the liquid form at ca.  $-100^\circ\text{C}$  and allowed it to slowly warm to room temperature in the course of the reaction.
- 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. CN2011115911 20110505). However, compound **5** is selected as a typical example in this manuscript for profound experimental and theoretical studies.
- D. J. Brauer, H. Bürger, G. R. Liewald and J. Wilke, *J. Organomet. Chem.*, 1985, **287**, 305-320.
- (a) M. Driess, G. Huttner, N. Knopf, H. Pritzkow and L. Zsolnai, *Angew. Chem., Int. Ed.*, 1995, **34**, 316-318; *Angew. Chem.*, 1995, **107**, 354-356; (b) M. Driess, C. Monsé and K. Merz, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1225-1230; (c) M. Driess, *Adv. Inorg. Chem.*, 2000, **50**, 235-284.
- L. Zsolnai, G. Huttner and M. Driess, *Angew. Chem., Int. Ed.*, 1993, **32**, 1439-1440; *Angew. Chem.*, 1993, **105**, 1549-1551.
- We tried  $\text{HCl}$  or  $\text{HCl}\cdot\text{NET}_3$  as the proton source. As a result, the chlorination happened and ionic  $(\text{RCl}_2\text{SiS})(\text{HNEt}_3)^+$  was isolated.
- (a) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241; (b) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
- P. Pyykkö and M. Atsumi, *Chem. Eur. J.*, 2009, **15**, 12770-12779.
- (a) K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251-8260; (b) M. W. Lodewyk, M. R. Siebert and D. J. Tantillo, *Chem. Rev.*, 2012, **112**, 1839-1862.
- (a) S. Miertuš, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117-129; (b) V. Barone, M. Cossi and J. Tomasi, *J. Comput. Chem.*, 1998, **19**, 404-417; (c) F. Jensen, *J. Chem. Theory Comput.*, 2008, **4**, 719-727; (d) N. C. Handy and A. J. Cohen, *Mol. Phys.*, 2001, **99**, 403-412; (e) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- (a) D. Cremer, L. Olsson and H. Ottosson, *J. Mol. Struct.: THEOCHEM*, 1994, **313**, 91-109; (b) L. Olsson, C.-H. Ottosson and D. Cremer, *J. Am. Chem. Soc.*, 1995, **117**, 7460-7479.
- (a) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899-926; (b) A. E. Reed, F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 1736-1740; (c) A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735-746.
- 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 monofunctional 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.