

Synthesis and Properties of Secondary Thiocarbamoylsilanes

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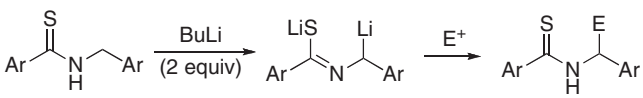
Secondary thioformamides were reacted with excess LDA and Me_3SiCl at −78 °C. The silyl group was selectively introduced to the thiocarbonyl carbon atom to give secondary thiocarbamoylsilanes. The use of $Me_2PhSiCl$ and *t*-$BuMe_2SiCl$ gave similar products in reduced yields. While a variety of *N*-arylmethylthioformamides participated in the silylation reaction, the yields of the products were influenced by the substituents on the aromatic ring: electron-withdrawing groups decreased the yield. No reaction occurred with thioformamides having secondary alkyl groups on the nitrogen atom, whereas the reaction of those with primary alkyl groups proceeded smoothly to form the corresponding thiocarbamoylsilanes. Initially, deprotonation takes place at the nitrogen atom to generate lithium thioimidates, which are then silylated with chlorosilanes to form silyl thioimidates. Excess LDA deprotonates silyl thioimidates at the imidate carbon atom to generate lithium silyl thioimidates, which undergo reverse Brook rearrangement to form lithium thioimidates bearing a silyl group at the imide carbon atom. Hydrolysis of the intermediates may lead to the formation of secondary thiocarbamoylsilanes. In UV–visible spectra of thiocarbamoylsilanes, the absorptions ascribed to n–π^* transitions were shifted to longer wavelengths by ca. 40–50 nm compared to those of thioformates. Finally, the structures of thioformamide and silylated product and their oxygen counterparts were elucidated by DFT calculations. Elongation of the C=O and C=S bonds in carbamoyl- and thiocarbamoylsilanes is discussed in relation to secondary orbital interactions.

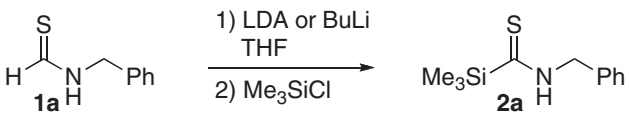
The replacement of formyl protons with silyl groups in carbonyl compounds provides compounds that exhibit unique properties and reactivities. One of the most characteristic features is the decrease in the energy gap between HOMO and LUMO of the carbonyl groups, to give a higher reactivity silyl-substituted carbonyl compounds. In this context, a wide variety of acylsilanes are synthesized and used as synthetic tools.[1] The synthesis[2] and reactions[3] of sulfur isologues of acylsilanes, i.e., thioacylsilanes, have also been well documented. However, the lability of the thiocarbonyl groups has hampered the isolation of aliphatic thioacylsilanes, which are in equilibrium with enethiols.[4] Alternatively, thioacylsilanes undergo cycloaddition reactions with 1,3-dipoles, α,β-unsaturated ketones, alkenes, and dienes.[5] The introduction of heteroatom-containing functional groups such as alkoxy, amino, and alkylthio groups to the carbon atom of thiocarbonyl groups enhances the stability of the compounds, but they still possess characteristics of thiocarbonyl groups. While tertiary thiocarbamoylsilane[6] and dithiocarboxylsilanes[7] have been isolated, they have been much less explored.

In contrast, while sulfur isologues of amides, i.e., thioamides have been studied in great depth,[8] their unique properties have not yet been fully disclosed. Along these lines, we have developed new synthetic reactions using thioamides.[9] For example, we found that the deprotonation of aromatic *N*-arylmethylthioamides with excess BuLi selectively gives thioamide dianions (Scheme 1).[10] The initial deprotonation takes place at the nitrogen atom, and the protons at the benzylic carbon atoms are then eliminated. We applied this protocol to *N*-arylmethylthioformamides, but the generation of similar dianions was not observed. We report herein the first synthesis of secondary thiocarbamoylsilanes from secondary thioformamides with a base and chlorosilanes. UV-spectra of the products and DFT calculations of the starting thioformamide and the product are also reported.

Initially, to confirm the generation of thioformamide dianion, thioformamide **1a** was treated with excess BuLi (Scheme 2). Me_3SiCl was then used as an electrophile. However, the reaction with BuLi gave a complex mixture containing a butyl group. Therefore, lithium diisopropylamide (LDA) was used as a base to avoid the nucleophilic introduction of a base. The reaction of **1a** with LDA (2 equiv) at 0 °C for 5 min, followed by the reaction with Me_3SiCl at 0 °C for 15 min resulted in the recovery of **1a**. After several surveys of the reaction conditions, the reaction at −78 °C for 10 min, followed by the reaction with Me_3SiCl at that temperature for 24 h, gave thiocarbamoylsilane **2a** as a yellow oil in 62% yield. To the best of our knowledge, **2a** is the first example of a



Scheme 1. Generation and reaction of thioamide dianions.



Scheme 2. Reaction of thioformamide **1a** with LDA and Me_3SiCl.

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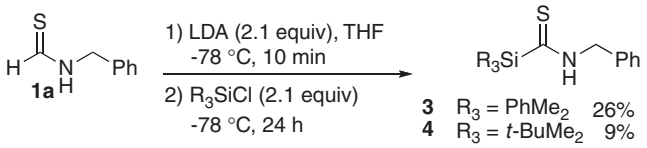


Scheme 3. Reaction of thioformamide **1a** with LDA and $PhMe_2SiCl$ and *t*-$BuMe_2SiCl$.

secondary thiocarbamoylsilane, although the synthesis[11] and synthetic applications[12] of several tertiary carbamoylsilanes and studies on tertiary thiocarbamoylsilanes[6,13] have been reported. Secondary carbamoylsilanes are prepared by the addition reaction of silyl groups to isocyanates as colorless compounds, and have been reported to be labile at room temperature.[14] Silyl groups in secondary carbamoyl groups are prone to shift to nitrogen or oxygen atoms to form *N*-silylformamides or silyl imidates. In contrast, the thiocarbamoylsilane **2a** is stable at room temperature and can be stored in the refrigerator for at least 3 months. As chlorosilanes, $Me_2PhSiCl$ and *t*-$BuMe_2SiCl$ were also used, but they gave the corresponding thiocarbamoylsilanes **2a′** and **2a″** in reduced yields (Scheme 3).

Second, a range of thioformamides were used as a starting material (Table 1). The reaction of *N*-arylmethylthioformamides **1b**–**1h** proceeded in a similar manner, but the yields of the products **2** were highly dependent on the substituents in the aromatic groups (Entries 1–8). The introduction of a methoxy group did not influence the efficiency (Entry 1), whereas the introduction of electron-withdrawing groups such as a chlorine and trifluoromethyl reduced the yield of **2** and led to recovery of the starting thioformamides (Entries 2 and 3). The methoxy group at the ortho position also retarded the silylation (Entry 4). The reaction of *N*-2-arylethylthioformamides **1i** and **1j** proceeded in a similar manner, but an electron-withdrawing group such as a chlorine atom still influenced the yield of **2j** (Entries 8 and 9). *N*-Cinnamylthioformamide (**1k**) and *N*-*n*-hexylthioformamide (**1l**) participated in the silylation reaction. In the former case, the product **2k** was obtained in only 8% yield (Entry 10). For the latter case, the use of a large excess of Me_3SiCl improved the efficiency to give the product **2l** in 82% yield (Entry 11). In other cases, a large excess of Me_3SiCl was not effective at improving the yields of the products **2**. In addition, thioformamides **1m**–**1p** did not give the corresponding silylated products at all. In most cases, the starting thioformamides were recovered. Therefore, the methylene group in thioformamides appears to be a prerequisite to lead to thiocarbamoylsilanes **2**.

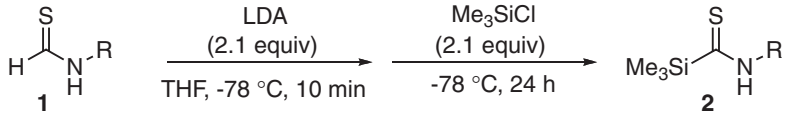
Thiocarbamoylsilanes **2** were characterized by IR, NMR, and mass spectra. In ^{13}C NMR spectra, the signals due to thiocarbonyl carbon atoms of the starting thioamides were observed at around δ 190. They were shifted to lower fields by more than 30 ppm by the introduction of silyl groups. A similar downfield shift was observed for *N*,*N*-dimethylformamide and *N*,*N*-dimethylcarbamoyl(trimethyl)silane, and the difference in the chemical shift was 22.9 ppm.[11g] Theoretical calculations for silylketones and -thioketones have also supported these types of large downfield shifts for the carbonyl and thiocarbonyl groups.[15]

A plausible reaction pathway is outlined in Scheme 4. Initially, the deprotonation of **1a** with LDA takes place at the nitrogen atom to generate lithium thioimidate **5**. Further deprotonation of **5** may lead to dianions **10** and **11**, similar to the reaction of *N*-benzylthioamides shown in Scheme 1. However, the deprotonation of **1a′** with LDA followed by silylation resulted in the formation of **2a′** (Scheme 5). No protonation at the benzylic carbon atom of **1a′** was observed. Similarly, the deprotonation of **1a** with LDA and deuteration with D_2O leads to the partly deuterated **1a**, where 60% deuterium was incorporated to the nitrogen atom of **1a**. Additionally, the use of aldehydes as an electrophile instead of chlorosilanes resulted in recovery of the starting formamide **1a**. These results appear to exclude the formation of dianions **10** and **11**. The generated anion **5** may then be silylated with Me_3SiCl to give *S*-silyl thioimidate **6**.[16] At this stage, the deprotonation of **6** with excess LDA, which is present in the reaction mixture, proceeds at the imide carbon atom to form anion **7**.[17] Subsequent silylation at this carbon atom occurs to give disilylated product **8** (path a). Alternatively, **7** undergoes reverse Brook rearrangement to form lithium thioimidate **9** (path b) possibly because a negative charge may be preferably located on a more electronegative atom. To confirm whether path a or path b is more plausible, thioformamide **1a** was reacted with various amounts of LDA and Me_3SiCl (Scheme 6). The use of one equiv of Me_3SiCl led to the product **2a**, whereas the reaction with one equiv of LDA resulted in the recovery of the starting **1a**. In the latter case, silylated product **7** may be formed, but it readily undergoes hydrolysis during the aqueous workup. Nevertheless, these results are consistent with path b in Scheme 4. Reverse Brook rearrangement similar to that in Scheme 4 is observed for the siloxyvinyllithium **13** derived by the lithium–tin exchange reaction of **12** (Scheme 7).[18] The silylation of **13** does not proceed, and instead **13** undergoes reverse Brook rearrangement to form lithium enolate **14**. Finally, silylation of **14** takes place at the oxygen atom to form enol silyl ether.

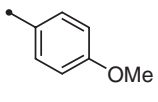
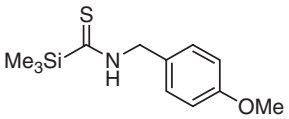
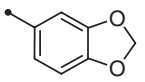
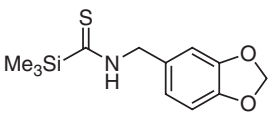
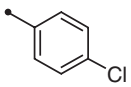
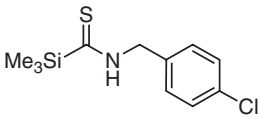
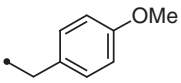
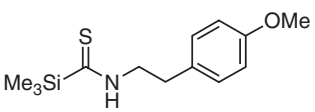
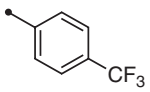
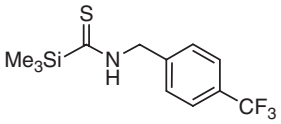
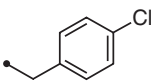
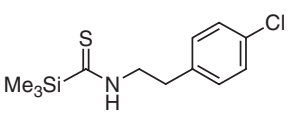
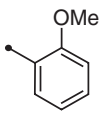
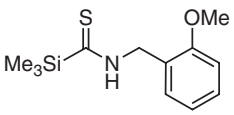
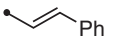
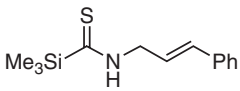
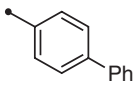
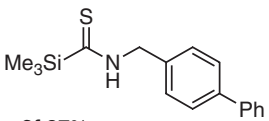
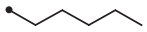
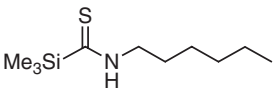
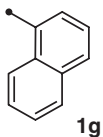
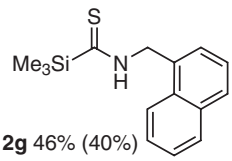
UV–visible spectra of thioformamides **1** and thiocarbamoylsilanes **2** are of interest, since **1** are colorless and **2** are yellow. Some are listed in Table 2. Notably, the absorptions at the longest wavelengths, which can be ascribed to n–π^* transitions of the thiocarbonyl group of **2**, were red-shifted by ca. 39–55 nm compared to those of **1**. This difference is smaller than those between ketones and acylsilanes, which are ca. 80 nm.[19] No previous studies have compared the UV spectra of secondary formamides and secondary carbamoylsilanes, probably because both compounds show absorptions only in the UV regions.

Geometry optimizations of the starting thioformamide **1a** and thiocarbamoylsilane **2a** were performed using B3LYP density functional theory (DFT)[20] with the 6-31+G(d) basis set. Representative bond distances of **1a** and **2a** are shown in Figure 1. For comparison, those of formamide **15** and carbamoylsilane **16** are also listed. Elongation of C=S bond distances by 0.019 Å was observed when a hydrogen atom in **1a** was replaced with a silyl group, whereas distances of C–N bonds remained nearly the same. A similar tendency was observed for **15** and **16**. The C=O bond distance was elongated by 0.015 Å upon moving from **15** to **16**. The elongation of the C=O bond between acetaldehyde and acetylsilane was con-

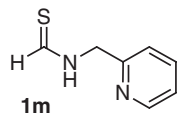
Table 1. Reaction of Various Thioformamides **1** with Me_3SiCl[a)]

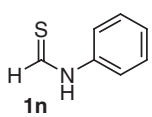


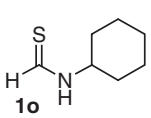
1 **2**

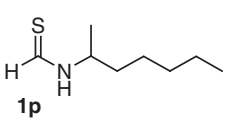
Entry	**1** R	Product[b)]	Entry	**1** R	Product[b)]
1	 **1b**	 **2b** 65% (19%)	7	 **1h**	 **2h** 18% (54%)
2	 **1c**	 **2c** 18%	8	 **1i**	 **2i** 67% (8%)
3	 **1d**	 **2d** 10% (53%)	9	 **1j**	 **2j** 28% (38%)
4	 **1e**	 **2e** 36% (30%)	10	 **1k**	 **2k** 8% (63%)
5	 **1f**	 **2f** 37%	11	 **1l**	 **2l** 82%[c)] (5%)
6	 **1g**	 **2g** 46% (40%)			

a) The reaction was carried out as follows unless otherwise noted: To a THF solution (5 mL) of LDA (2.1 mmol) was added thioformamide **1** (1.0 mmol), and the mixture was stirred at −78 °C for 10 min, and then, Me_3SiCl (2.1 mmol) was added, and the stirring was continued at −78 °C for 24 h. b) Yields of the recovered thioformamides **1** are shown in parentheses. c) Me_3SiCl (10 mmol) was used.


1m

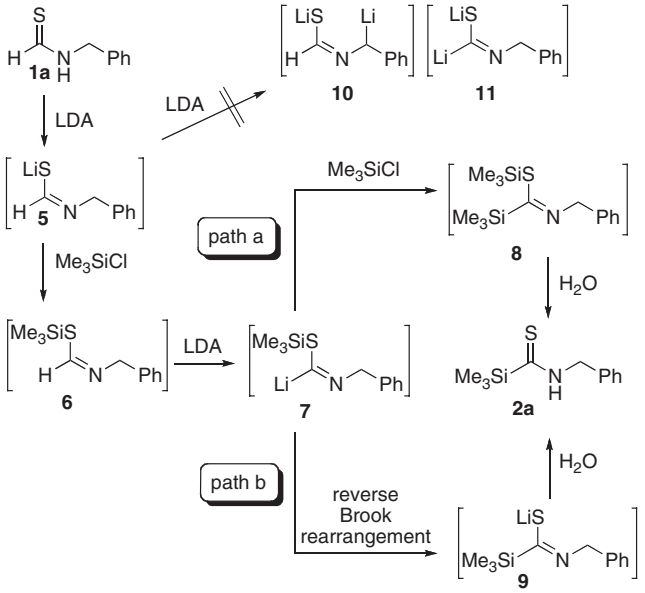

1n


1o

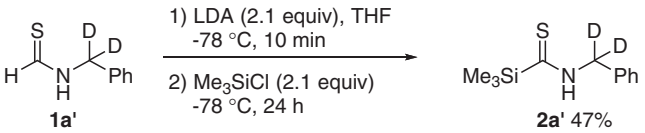

1p

firmed by molecular orbital calculations at the MP2/6-31G level.[21] To further elucidate the elongation of C=O and C=S bonds, NBO analyses of **1a**, **2a**, **15**, and **16** were performed, and some of the orbital interaction energies around the thiocarbamoyl and carbamoyl groups determined by NBO second-order perturbation analysis are listed in Table 3. Oxygen and sulfur atoms have two lone-pair electrons and the energy values are indicated as the sum of the two possible n_E (E = O and S) orbital interactions. The replacement of a hydrogen atom with a silicon atom almost has little affect on the orbital interaction energies of $n_E \rightarrow \sigma^*_{C-N}$ and $n_N \rightarrow \sigma^*_{C=E}$. In contrast, the energies of $n_E \rightarrow \sigma^*_{C-H}$ in **1a** and **15** are greater than those of $n_E \rightarrow \sigma^*_{C-Si}$ in **2a** and **16** by more than 4.5 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). These orbital interactions can finely attenuate the bond distances of C=O and C=S, and the weaker interaction of $n_E \rightarrow \sigma^*_{C-Si}$ leads to the elongation of C=O and C=S in **16** and **2a** compared to those in **15** and **1a**.[22]

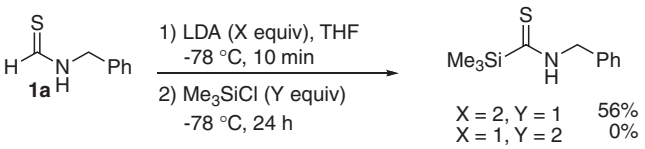
Finally, the energy levels of HOMO and LUMO or LUMO+1 of **1a**, **2a**, **15**, and **16** are shown in Figure 2 along with their orbital shapes. The introduction of a silyl group at the carbonyl carbon atom of **15** enhances the energy level of



Scheme 4. Plausible reaction pathway.

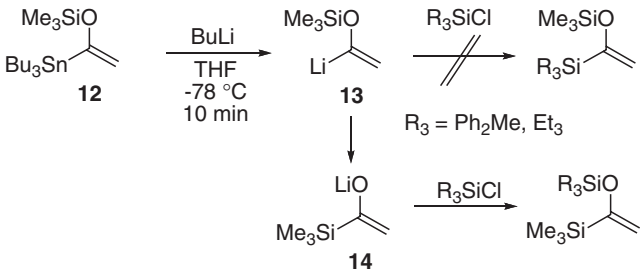


Scheme 5. Reaction of deuterated thioformamide **1a′**.



Scheme 6. Reaction of **1a** with different amounts of LDA and Me_3SiCl.

HOMO by 0.76, whereas the energy level of LUMO+1 is nearly equal in both cases. A similar trend in the change of orbital energies was also observed for **1a** and **2a**. The HOMO of **2a** is higher than that of **1a** by 0.30, and both LUMO have nearly the same energies. As a result, the energy gap between HOMO and LUMO of **2a** becomes smaller than that of **1a**, which is consistent with the red shifts of the UV–visible spectra of **2**. This is also in good agreement with the elongation of C=S bonds, which causes the less-efficient overlap of p orbitals of the carbon and sulfur atoms leading to a C–S π bond.



Scheme 7. Reverse Brook rearrangement of siloxyvinyllithium **13**.

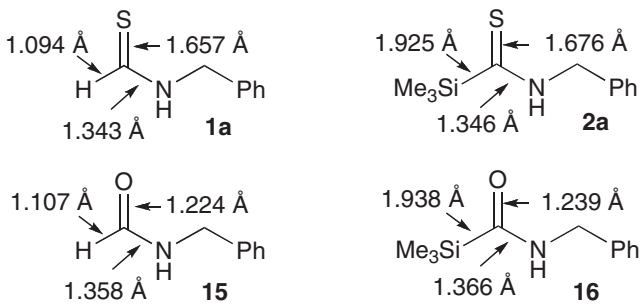


Figure 1. Bond distances of optimal structures of compounds **1a**, **2a**, **15**, and **6** at the B3LYP/6-31+G(d) level.

Table 2. UV–Visible Spectra of Thioamides **1** and **2**

	λ_{max} /nm	log ε		λ_{max} /nm	log ε
1a (R = $CH_2C_6H_5$)	226.0	3.44	**2a** (R = $CH_2C_6H_5$)	216.0	3.75
	265.0	4.22		241.0	3.87
	353.0	1.75		279.0	3.93
				392.0	1.64
1b (R = $CH_2C_6H_4OMe$-4)	229.0	3.95	**2b** (R = $CH_2C_6H_4OMe$-4)	234.0	4.07
	266.0	4.15		278.0	4.07
	356.0	1.67		398.0	1.65
1d (R = $CH_2C_6H_4CF_3$-4)	265.0	4.19	**2d** (R = $CH_2C_6H_4CF_3$-4)	213.0	3.79
	350.0	1.75		262.0	3.70
				400.0	1.84
1k (R = CH_2CH=$CHPh$)	226.0	1.41	**2k** (R = CH_2CH=$CHPh$)	223.0	1.44
	261.0	4.51		261.0	4.24
	348.0	1.86		402.0 (sh)	1.98
1l (R = *n*-Hexyl)	229.0	1.17	**2l** (R = *n*-Hexyl)	214.0	1.55
	261.0	4.09		261.0	4.00
	350.0	1.64		394.0	1.96

Table 3. Selected Orbital Interaction Energies Determined by NBO Second-Order Perturbation Analysis

	E	X	$n_E \rightarrow \sigma^*_{C-N}$ /kcal mol^{-1}	$n_E \rightarrow \sigma^*_{C-X}$ /kcal mol^{-1}	$n_N \rightarrow \sigma^*_{C=E}$ /kcal mol^{-1}
15	O	H	25.59	22.59	67.93
16	O	Si	24.87	14.09	65.96
1a	S	H	15.12	11.12	81.82
2a	S	Si	14.67	6.54	81.73

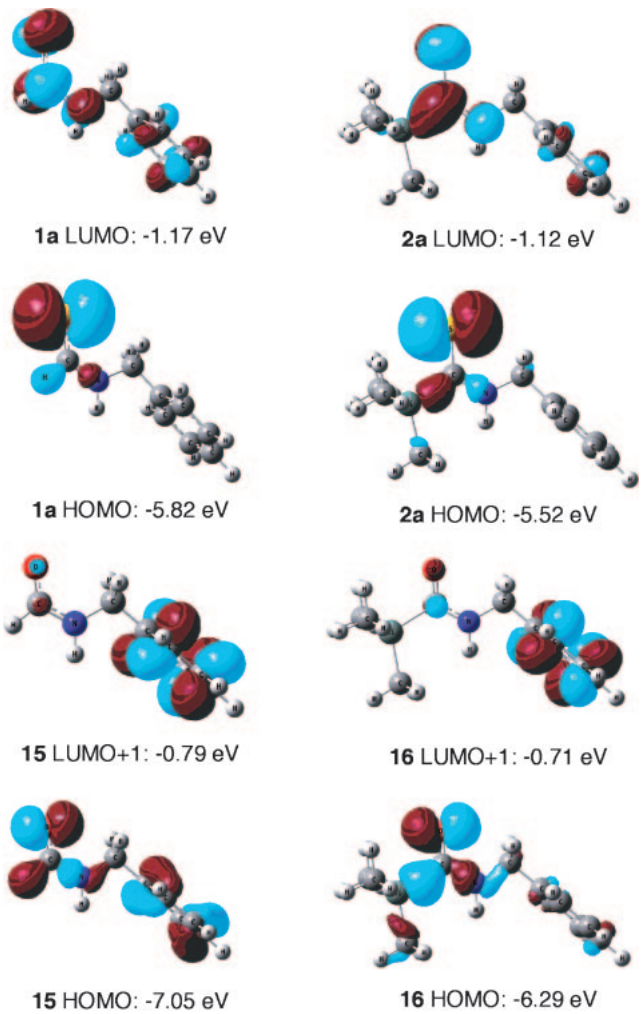


Figure 2. Energy levels of HOMO and LUMO or LUMO+1 of compounds **1a**, **2a**, **15**, and **16** at the B3LYP/6-31+G(d) level.

Conclusion

In summary, we have demonstrated the first synthesis of secondary thiocarbamoylsilanes by reacting thioformamides with LDA and chlorosilanes. The yellow products were stable at room temperature and could be stored in the refrigerator for at least 3 months. The reaction could be applied to thioformamides with a methylene group on the nitrogen atom. In the reaction, deprotonation at the nitrogen atom is followed by silylation at the sulfur atom to form silyl thioimidates, which undergo deprotonation at the imide carbon atom, followed by reverse Brook rearrangement to give lithium thioimidates with a silyl group at the imide carbon atom. In UV–visible spectra, red shifts of the absorptions ascribed to n–π^* transitions of thiocarbonyl groups were observed. This is in good agreement with DFT calculations, in which the energy gaps of HOMO and LUMO of thiocarbamoylsilanes are smaller than those of thioformamides. The elongation of C=O and C=S bond lengths by the attachment of silyl groups can be understood in terms of the efficiency of the secondary orbital interaction between the lone-pair electrons of oxygen and sulfur atoms and C–H or C–Si σ^* bonds. Further studies on new synthetic transformations using thiocarbonyl compounds and the applications of the resulting products are in progress.

Experimental

Typical Procedure for the Synthesis of Secondary Thiocarbamoylsilanes. To a solution of diisopropylamine (0.30 mL, 2.1 mmol) in THF (5 mL) was added *n*-butyllithium (1.6 M solution in hexane, 1.3 mL, 2.1 mmol) at −78 °C under an Ar atmosphere, and the mixture was stirred for 30 min. To the reaction mixture was added a solution of *N*-phenylmethylthioformamide (**1a**) (0.15 g, 1.0 mmol) in THF (1 mL) at −78 °C, and the mixture was stirred for 10 min. To the reaction mixture was added chlorotrimethylsilane (0.27 mL, 2.1 mmol) at −78 °C, and the mixture was stirred for 24 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (hexane: EtOAc = 8:1) to give trimethyl(*N*-phenylmethylthiocarbamoyl)-silane (**2a**) (0.14 g, 0.62 mmol, 62%, $R_f = 0.40$) as a yellow oil; IR (neat): 3302, 2956, 1498, 1454, 1368, 1317, 1247, 958, 849, 751, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 9H, $SiCH_3$), 4.92 (d, $J = 5.4$ Hz, 2H, CH_2), 7.30–7.39 (m, 5H, Ar), 7.74 (br, 1H, NH); ^{13}C NMR ($CDCl_3$): δ −1.79 ($SiCH_3$), 49.1 (CH_2), 128.0, 128.3, 128.9, 129.0 (Ar), 224.4 (C=S); MS (EI): m/z: 223 [M^+]; Anal. Calcd for $C_{11}H_{17}NSSi$: C, 59.14; H, 7.67; N, 6.27%. Found: C, 59.10; H, 7.52; N, 6.34%.

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Supporting Information

Detailed experimental procedures and spectroscopic data for new compounds, and Cartesian coordinates for the optimized geometries of all the calculated compounds; these materials are available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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