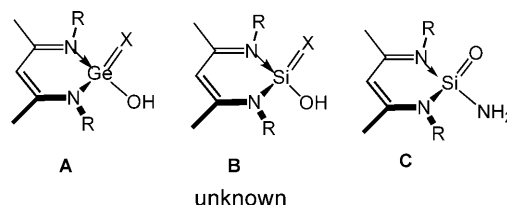


# Silicon Analogues of Carboxylic Acids: Synthesis of Isolable Silanoic Acids by Donor–Acceptor Stabilization\*\*

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In memory of Herbert Schumann and Pascal LeFloch

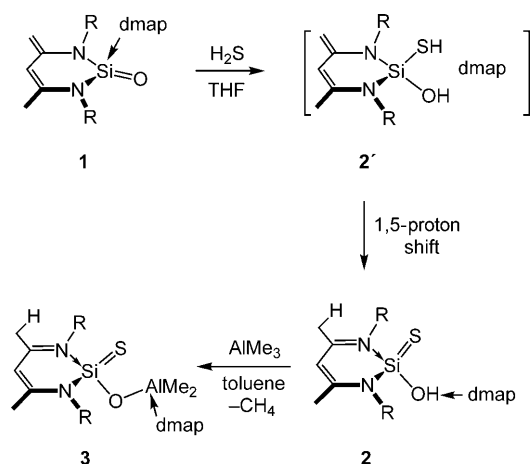
The carbonyl group in ketones, carboxylic acids, and related compounds is one of the most widely occurring functional groups in chemistry, biochemistry, and material science. In contrast, its silicon analogues  $\text{Si}=\text{X}$  ( $\text{X} = \text{chalcogen}$ ) and their related functional groups (e.g.  $\text{Si}(=\text{X})\text{OH}$ ) are difficult to realize or are even completely unknown in the condensed phase owing to their intrinsically weaker  $p_\pi-p_\pi$  bonding and higher polarities of the  $\text{Si}=\text{X}$  subunit, which gives rise to facile isomerization and self-polymerization reactions. However, in the last decades, milestones have been achieved for the synthesis and isolation of silanechalcogenones (heavier silaketones) by taking advantage of thermodynamic and kinetic stabilization. Among the early examples, isolable silaketone-like systems featuring donor-stabilized  $\text{Si}=\text{S}$  and  $\text{Si}=\text{Se}$  bonds with four-coordinate silicon atoms have been reported by Corriu and co-workers<sup>[1a]</sup> and more recently by the research groups of Wagler,<sup>[1b]</sup> West,<sup>[1c]</sup> and Roesky.<sup>[1d]</sup> Moreover, even silanechalcogenones with three-coordinate silicon atoms have been synthesized and structurally characterized by the research groups of Okazaki, Tokitoh, Iwamoto, Törring, and Kira.<sup>[2–5]</sup> However, stable compounds containing a  $\text{Si}=\text{O}$  bond and three-coordinate silicon atoms are still unknown. Likewise, experimental evidence about the existence of silacarboxylic (silanoic) acids  $\text{RSi}(=\text{O})\text{OH}$  is scarce and limited to low temperature studies under argon-matrix isolation conditions.<sup>[6a–c]</sup> Use of the monoanionic  $\beta$ -diketiminato chelate ligand  $\text{L}$  ( $\text{L} = \text{CH}[\text{C}(\text{Me})\text{NR}]_2$ , where  $\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ) led to the first isolable donor-supported germanium analogues of carboxylic acids,  $\text{LGe}(=\text{X})\text{OH}$  **A** ( $\text{X} = \text{S}, \text{Se}$ ; Scheme 1), which were prepared and structurally characterized by Roesky and co-workers.<sup>[6d–e]</sup> To our knowledge, the corresponding silicon analogues  $\text{LSi}(=\text{X})\text{OH}$  **B** (Scheme 1) are still unknown. However, our research group has reported a complete series of stable silacarboxylic silyl esters  $\text{LSi}(=\text{X})\text{OR}'$  ( $\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ;  $\text{R}' = \text{silyl}$ ),<sup>[7a–c]</sup> which are accessible through direct chalcogenation of the corresponding



**Scheme 1.** N-donor-stabilized germanium and silicon analogues of carboxylic acids **A**, **B**, and the silanoic amide **C**.  $\text{X} = \text{O}, \text{S}, \text{Se}$ ;  $\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ .

siloxo silylene precursors.<sup>[7d]</sup> Despite the presence of four-coordinate silicon atoms, the latter esters possess significant  $\text{Si}=\text{X}$  bond character.<sup>[7c]</sup>

Furthermore, we have synthesized peculiar types of donor-supported  $\text{Si}=\text{X}$  systems starting from the zwitterionic *N*-heterocyclic silylene  $\text{L}'\text{Si}$  ( $\text{L}' = \text{CH}[\text{C}(\text{Me})(\text{C}=\text{CH}_2)(\text{NR})_2]$ ,  $\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ).<sup>[7e]</sup> Thus, the latter species reacts directly with  $\text{H}_2\text{S}$  to give the isolable silathioformamide,  $\text{LSi}(=\text{S})\text{H}$ .<sup>[8]</sup> Moreover, starting from *N*-heterocyclic carbene (NHC) adducts of  $\text{L}'\text{Si}$ , a series of NHC-stabilized heavier ketone analogues  $\text{L}'\text{Si}(=\text{X})(\text{NHC})$  ( $\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ) have been successfully synthesized, including a silanone adduct.<sup>[9a–b]</sup> Accordingly, use of the readily accessible *dmap* complex of  $\text{L}'\text{Si}$  (*dmap* = 4-dimethylaminopyridine) enabled us to synthesize the stable silanone complex,  $\text{L}'\text{Si}(=\text{O})(\text{dmap})$  **1**<sup>[9c]</sup> (Scheme 2). Because the *dmap* ligand is only weakly coordinated, compound **1** can serve as a convenient silanone



**Scheme 2.** Synthesis of **2** from **1** and its metalation to the silathiocarboxylate **3**. *dmap* = 4-dimethylaminopyridine,  $\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ , THF = tetrahydrofuran.

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precursor. Strikingly, **1** is capable of reacting with ammonia under replacement of the dmap ligand and subsequent N–H addition to the Si=O bond to give the corresponding sila-hemiaminal  $\text{LSi}(\text{OH})\text{NH}_2$  and its silacarboxylic amide tautomer **C**  $\text{LSi}(=\text{O})\text{NH}_2$  (Scheme 1).<sup>[9c]</sup> The remarkable formation of **C** is due to the pronounced basicity of the exocyclic methylene group of the  $\text{C}_3\text{N}_2$  chelate ligand **L'**.

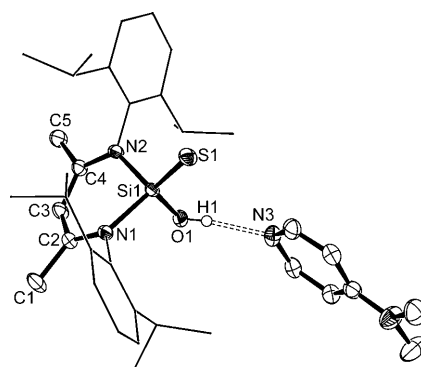
The latter results prompted us to probe whether **1** is capable of activating  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  to form the corresponding silacarboxylic acids **B** ( $\text{X} = \text{S}, \text{O}$ ; Scheme 1). Herein, we report the facile synthesis and structural characterization of the first stable silathiocarboxylic acid–base adduct and its metalation to form a silathiocarboxylate. In addition, we describe for the first time the formation of a donor–acceptor stabilized silacarboxylic acid.

Treatment of a pale yellow suspension of **1** in THF with an excess of dry hydrogen sulfide gas at room temperature led to a clear yellow solution, from which complex **2** could be obtained as yellow crystals in 90% yield (Scheme 2).

The mechanism is unknown but we assume that **2** is formed via the intermediate **2'**, which results from the addition of  $\text{H}_2\text{S}$  to the Si=O bond in **1**. Subsequent isomerization of **2'** by a 1,5-proton shift from the thiol group to the exocyclic methylene group affords **2** as the final product. The driving force for the tautomerization process originates both from the pronounced Brønsted acidity of the SH group and the basicity of the methylene group of the  $\text{C}_3\text{N}_2$  ligand in **2'**. The 1,5-proton shift is akin to that observed for the formation of **C**<sup>[9c]</sup> (Scheme 1) and the silathioformamide,  $\text{LSi}(=\text{S})\text{H}$ .<sup>[8]</sup>

Compound **2** is soluble in THF and dichloromethane, marginally soluble in toluene but insoluble in *n*-hexane. The constitution of **2** could be determined by multinuclear NMR and IR spectroscopy, and its composition was proven by electron-impact (EI) mass spectrometry and elemental analysis. The EI mass spectrum of **2** shows a base signal for the dmap-free species at  $m/z$  495 [ $\text{LSi}(=\text{S})\text{OH}$ ] + H. Meanwhile, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2** (see the Supporting Information) for the  $\beta$ -diketiminato ligand **L** exhibit similar chemical shifts to those reported for the germanium analogue **A**. The proton of the OH group in **2** resonates at  $\delta = 6.35$  ppm, that is, at a significantly lower field than that in  $\text{LGe}(=\text{S})\text{OH}$  **A** ( $\delta = 2.0$  ppm).<sup>[6d]</sup> The  $^{29}\text{Si}$  NMR spectrum of **2** reveals a resonance signal at  $\delta = -30.0$  ppm akin to the value observed for the silathiocarboxylic silylester  $\text{LSi}(=\text{S})\text{OR}$ , which bears the same  $\beta$ -diketiminato ligand **L** ( $\delta = -41$  ppm).<sup>[7b]</sup>

The molecular structure of **2** has been elucidated by single-crystal X-ray diffraction analysis. The compound crystallized in THF as a mono-THF solvate in the triclinic space group  $P\bar{1}$ . The compound bears one dmap ligand connected to the silathiocarboxylic acid through an O–H $\cdots$ N hydrogen bond, and the O $\cdots$ N distance of 2.703 Å falls into the normal range of O–H $\cdots$ N hydrogen bonds (Figure 1). Obviously, the hydrogen bridge stabilizes the system and prevents the dimerization process, which is usually observed for carboxylic acids and has also been observed for the “base-free” germanium analogues **A**.<sup>[6d]</sup> The six-membered  $\text{SiN}_2\text{C}_3$ -ring in **2** is strongly puckered and the silicon atom possesses a distorted tetrahedral coordination environment. The Si–N



**Figure 1.** Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms, except that at O1, are omitted for clarity. The bridging hydrogen atom at O1 could be localized in the difference Fourier maps. Selected bond lengths [Å] and angles [°]: Si1–S1 1.993(1), Si1–O1 1.620(2), Si1–N2 1.809(2), Si1–N1 1.827(2), C1–C2 1.514(3), C2–C3 1.394(3), C3–C4 1.389(3), C4–C5 1.499(3), O1–N3 2.703; O1–Si1–N2 102.63(9), O1–Si1–N1 102.27(8), N2–Si1–N1 97.46(8), O1–Si1–S1 120.49(7), N2–Si1–S1 114.90(7), N1–Si1–S1 115.76(7), O1–H1–N3 172.0.

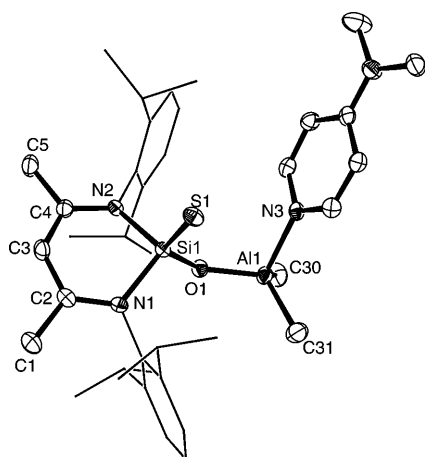
bond lengths of 1.827(2) and 1.809(2) Å, respectively, are similar to the corresponding values observed in the silathiocarboxylic silylester  $\text{LSi}(=\text{S})\text{OR}$  (1.819(3), 1.833(4) Å).<sup>[7b]</sup> The bond lengths of C1–C2 (1.514(3) Å) and C4–C5 (1.499(3) Å) confirm the presence of two exocyclic methyl groups. Accordingly, the short Si–S bond length of 1.993(1) Å is akin to those in the silathiocarboxylic silylester  $\text{LSi}(=\text{S})\text{OR}$  (1.980(2) Å)<sup>[7b]</sup> and  $\text{LSi}(=\text{S})\text{H}$  (1.985(1) Å).<sup>[8]</sup> and indicates a significant Si=S bond character. In contrast, the Si1–O1 distance of 1.620(2) Å in **2** is much larger than the Si=O length in the starting material **1** (1.545(2) Å) and thus represents a Si–O single bond.

Notably, **2** does not undergo a 1,3-proton shift to give the possible  $\text{LSi}(=\text{O})\text{SH}\cdots\text{dmap}$  isomer. It seems unlikely that the isomerization is prevented by the presence of a base because base-free **A** remains stable in solution.<sup>[6d]</sup> In contrast, thiocarboxylic acids  $\text{RC}(=\text{S})\text{OH}$  are in equilibrium with the corresponding isomers  $\text{RC}(=\text{O})\text{SH}$  in solution through rapid proton migration between the oxygen and the sulfur atoms.<sup>[10]</sup> The preference of  $\text{LSi}(=\text{S})\text{OH}$  **2** over  $\text{LSi}(=\text{O})\text{SH}$  is most likely a result of the weaker  $p_\pi$ – $p_\pi$  bond and the higher bond polarity of the Si=O compared with the Si=S subunit.<sup>[7c]</sup>

Compound **2** reacts easily with organometallic bases to form metal silathiocarboxylates. Thus, treatment of **2** with one molar equivalent of  $\text{AlMe}_3$  in toluene at ambient temperature furnished the silathiocarboxylate  $\text{LSi}(=\text{S})\{\text{OAlMe}_2(\text{dmap})\}$  **3** with the dmap coordinated at the aluminum atom (Scheme 2), as confirmed by  $^1\text{H}$  NMR spectroscopy. Reaction of **2** with MeLi or  $\text{LiN}(\text{SiMe}_3)_2$  resulted only in the formation of inseparable mixtures. Complex **3** was isolated in high yield (91%) in the form of colorless crystals and could be fully characterized ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR, IR, EI-MS, and elemental analysis). Compound **3** is soluble in benzene, toluene, and THF, but insoluble in *n*-hexane. In the  $^1\text{H}$  NMR spectrum of **3**, a typical high-field singlet can be observed for the two methyl groups of the  $\text{AlMe}_2$  moiety at  $\delta = -0.57$  ppm. The  $^{29}\text{Si}$  NMR spectrum shows a slightly up-field-shifted

resonance at  $\delta = -40.0$  ppm for **3** compared to that of **2** ( $\delta = -30.0$  ppm). While the molecular-ion signal of **3** and (**3**-dmap) did not appear in the EI mass spectrum, however, the fragment ion  $[\text{LSi}(=\text{S})(\text{OAlMe}_2)]^+$ , which indicated loss of a methyl group, could be detected as the most abundant species at  $m/z$  535.

Compound **3** crystallized at 4 °C from THF as yellow needles in the monoclinic space group  $P2_1/c$ . The aluminum atom in **3** is tetrahedrally coordinated to the N3 atom of the dmap ligand, the O1 atom, and the two carbon atoms of the methyl residues (Figure 2). The Al1–S1 distance of 3.967 Å



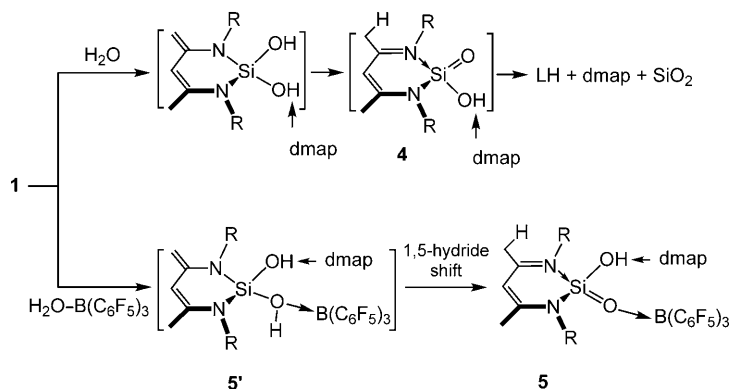
**Figure 2.** Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–S1 1.991(1), Si1–O1 1.589(1), Si1–N1 1.810(2), Si1–N2 1.819(2), Al1–O1 1.742(1), Al1–N3 1.961(2), Al1–C31 1.967(2), Al1–C30 1.967(2), C5–C4 1.501(3), C4–C3 1.388(3), C3–C2 1.397(3), C2–C1 1.488(3); O1–Si1–N1 106.2(1), O1–Si1–N2 104.9(1), N2–Si1–N1 98.0(1), O1–Si1–S1 120.9(1), N1–Si1–S1 111.6(1), N2–Si1–S1 112.7(1), O1–Al1–N3 104.2(1), O1–Al1–C31 111.2(1), N3–Al1–C31 106.9(1), O1–Al1–C30 113.4(1), N3–Al1–C30 103.8(1), C31–Al1–C30 116.2(1), Si1–O1–Al1 139.0(1).

clearly shows that there is no S→Al coordination. The bond length of 1.742(1) Å for Al1–O1 falls in the normal range for an Al–O single bond,<sup>[11]</sup> while the bond lengths for Al1–C30 and Al1–C31 (1.967(2) Å) are comparable to those found in  $\text{Al}_2\text{Me}_6$  (1.956(2), 1.949(2) Å)<sup>[12]</sup> and in the related  $\text{MeC}(=\text{O})(\text{OAlMe}_2)$  anion (2.01(1) to 2.05(1) Å).<sup>[11b]</sup> As expected, the bond length of 1.961(2) Å for Al1–N3 is longer than an Al–N bond in aluminum amides and thus indicative of a dative N→Al interaction.<sup>[13]</sup> Similar to the situation in precursor **2**, the tetrahedrally coordinated silicon atom in **3** is bonded to two nitrogen atoms from the chelate ligand, the sulfur atom, and an oxygen atom. The Si–N distances (1.810(2), 1.819(2) Å) do not vary significantly from those in **2** (1.809(2), 1.827(2) Å). The same is true for the Si=S bond length (1.991(1) Å vs. 1.993(1) Å in **2**), which indicates no electronic change in that subunit. In contrast, a slightly shorter Si–O distance (1.589(1) Å) can be observed in **3** compared with that in **2** (1.620(2) Å). This value for the Si–O bond length is

even close to the Si=O distance in **1** (1.545(2) Å),<sup>[9c]</sup> and this similarity presumably results from the strong electron donation of the dmap ligand to the aluminum center which weakens the Al–O interaction and hence significantly induces a stronger Si–O electrostatic interaction. A similar effect induced by dmap has also been observed for related Si=O→Al complexes, which resulted from the addition reactions of  $\text{AlMe}_3$  to **1**.<sup>[14]</sup>

Attempts to synthesize the analogous silacarboxylic acid–base complex **4** by exposing a pale yellow solution of **1** in THF to  $\text{H}_2\text{O}$  vapor at room temperature were unsuccessful (Scheme 3). Instead, the parent  $\beta$ -diketiminato ligand LH and “free” dmap resulted, along with the quantitative precipitation of  $\text{SiO}_2$ . At low temperature ( $<0$  °C), no significant reaction progress of **1** with  $\text{H}_2\text{O}$  could be observed. By increasing the acidity of the water molecule, a much faster addition reaction occurs even at low temperature; as shown by using the water–borane adduct  $\text{H}_2\text{O} \cdot \text{B}(\text{C}_6\text{F}_5)_3$ . Thus, conversion of **1** with  $\text{H}_2\text{O} \cdot \text{B}(\text{C}_6\text{F}_5)_3$  furnished the first isolable  $\text{LSi}(=\text{O})\text{OH}$  complex in the form of  $[\text{LSi}(\text{OH} \cdots \text{dmap})(=\text{O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3)]$  **5** in almost quantitative yield (Scheme 3). It is very likely that formation of **5** occurs via intermediate **5'**, which immediately undergoes a 1,5-proton shift to form a Lewis acid supported Si=O bond. The latter process is akin to the formation of the borane-stabilized silaformamide complex  $\text{LSi}(=\text{O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3)\text{H}$ .<sup>[7d]</sup> The composition and constitution of **5** have been unambiguously proven by multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{29}\text{Si}$ ), IR spectroscopy, and elemental analysis (see the Supporting Information). The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of **5** observed for the chelate ligand L and the borane subunit are similar to the respective values reported for  $\text{LSi}(=\text{O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3)\text{H}$ .<sup>[7d]</sup> The  $^1\text{H}$  NMR spectrum further proves that the dmap ligand remains coordinated by an O–H $\cdots$ N hydrogen bond and the chemical shift for the OH proton appears at  $\delta = 3.02$  ppm. The  $^{29}\text{Si}$  NMR spectrum of **5** shows a resonance signal at  $\delta = -73.2$  ppm, which is close to the values observed for the respective silyl esters ( $\delta = -85.1$ ,  $-85.8$  ppm).<sup>[7b]</sup> Compound **5** is fragile in aprotic organic solutions and decomposes slowly to give LH,  $\text{SiO}_2$ , and  $\text{dmap} \cdot \text{B}(\text{C}_6\text{F}_5)_3$ .

In summary, the formation and structural characterization of the first silathiocarboxylic acid–base adduct **2** has been



**Scheme 3.** Reaction of **1** with  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O} \cdot \text{B}(\text{C}_6\text{F}_5)_3$ . R = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ .

described featuring the unique Si(=S)OH subunit. Although the OH group in **2** is O–H...N coordinated, the moiety can be metalated using AlMe<sub>3</sub> to give, under concomitant deprotonation and migration of the dmap ligand to the Al center, the unprecedented silathiocarboxylate **3**. While similar attempts to form the corresponding silacarboxylic acid by addition of H<sub>2</sub>O to **1** failed, conversion of **1** with the H<sub>2</sub>O–B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct furnished the first isolable LSi(=O)OH complex **5**. The easily accessible silathiocarboxylic acid adduct **2**, containing the Si(=S)(OH) subunit, and the Si(=O)OH moiety in adduct **5** represent versatile new functional groups in silicon chemistry. With these compounds in hand, fundamental aspects regarding the chemistry of silacarboxylic and thio-silanoic acids (e.g. in metal coordination) as well as their suitability for the synthesis of functional materials (e.g. metal-organic-inorganic hybrid frameworks) could now be explored. These studies are currently in progress.

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