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The Quest for Stable Silaaldehydes: Synthesis and Reactivity of a Masked Silacarbonyl

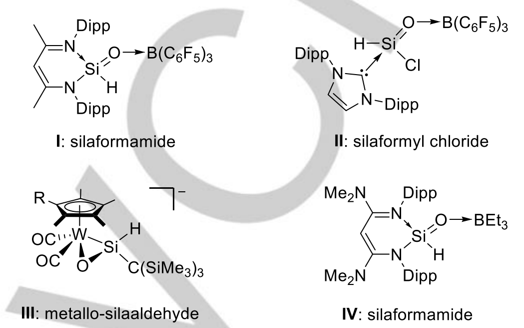
Debotra Sarkar,[a] Vitaly Nesterov,[a] Tibor Szilvási,[b] Philipp J. Altmann,[a] and Shigeyoshi Inoue*[a]

Abstract: First donor-acceptor complex of a silaaldehyde, compound with general formula $(NHC)(Ar)Si(H)OGaCl_3$, was synthesized using the reaction of silyliumylidene–NHC complex $[(NHC)_2(Ar)Si]Cl$ with water in the presence of $GaCl_3$. Conversion of this complex to the corresponding silacarboxylate dimer $[(NHC)(Ar)SiO_2GaCl_2]_2$, free silaacetal $ArSi(H)(OR)_2$, silaacyl chloride $(NHC)(Ar)Si(Cl)OGaCl_3$, and phosphasilene–NHC adduct (NHC)(Ar)Si(H)PTMS unveil its true potential as a synthon in silacarbonyl chemistry.

Carbonyl group is important and ubiquitous functionality in the field of organic chemistry, life sciences and beyond.[1] While aldehydes, ketones, and carboxylic acid derivatives are generally well-known stable organic compounds, the synthesis and isolation of their stable heavier group 14 analogues is challenging.[2] The instability and high tendency to oligomerize of the latter are attributed to the different nature of the heavier E=O bonds (E = Si–Pb), which exhibit higher zwitterionic character $E^{\delta+}$–$O^{\delta-}$ due to the significant decrease in electronegativity of heavier elements and their intrinsic propensity to form weaker π-bonds descending the group. Recent years have witnessed considerable advances in the isolation of monomeric silacarbonyl compounds including silanones (R_2SiO) and silanoic acid (RSi(O)OH) derivatives.[3-9] Rational steric and electronic protection, Lewis base or Lewis base/acid complex formation are the key approaches to achieve the required stabilization.[3-10] Nevertheless, despite this success our knowledge about the reactivity of silicon analogues of carbonyl compounds and their synthetic potential remains to be very scarce.

Among reported silacarbonyls, derivatives containing a silaformyl group (-Si(H)O) are rare (**I–IV**, Figure 1a),[6-9] while a stable analogue of an aldehyde (RSi(H)O) with three-coordinate silicon is not known. Driess and co-workers reported a silaformamide–borane complex (**I**) with essential Si=O double bond character synthesized by reacting corresponding hydroxysilylene with water–borane adduct $H_2O{\cdot}B(C_6F_5)_3$.[6] Several years later, Roesky, Frenking and co-workers described the isolation of silaformyl chloride complex (**II**)[7] via the reaction of the silylene dichloride–NHC adduct $(IDipp)Cl_2Si$: with $H_2O{\cdot}B(C_6F_5)_3$ and additional equivalent of the NHC. Hashimoto, Tobita and co-workers isolated anionic η^2-silaaldehyde complex (**III**) with a Si–O motif within coordination sphere of tungsten, considered as a three-membered metallacycle rather than a silaaldehyde π-complex.[8] More recently, the group of Aldridge in an elegant study demonstrated the synthetic utility of nacnac-supported chlorosilylene to access a number of silacarbonyls, including silaformamide **IV**.[9]

a) described compounds with silaformyl group (R = Me, Et):



b) present work:

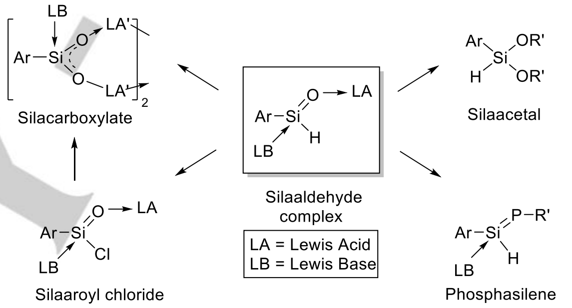


Figure 1. (a) Silaformyl compounds **I–IV**. (b) Present work.

Previously we succeeded in the isolation of stable three-coordinate imino(silyl) silanones $[(IDipp)N](R_3Si)SiO$ (IDipp = $[HC(DippN)]_2C$:, R = ^tBu, $SiMe_3$) with prolonged lifetime in solution.[3a] Our quest for a stable silaaldehyde started from the investigation of the reactivity of a NHC-stabilized silyliumylidene $[(IMe_4)_2(^{Mes}Ter)Si$:]Cl (**1**, ^{Mes}Ter = 2,6-$(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$, IMe_4 = $[(Me)C(MeN)]_2C$:)[11] and hydridosilylene $(IMe_4)(^tBu_3Si)(H)Si$: (**2**).[12] These compounds react with carbon dioxide affording NHC-stabilized silaacylium salt $[(IMe_4)_2(^{Mes}Ter)Si(O)][Cl]$ (**3**) with comparably high double bond character of the Si=O bond,[5c] and NHC-free cyclotrisiloxane $[(^tBu_3Si)(H)SiO]_3$ regarded as a trimer of silaaldehyde intermediate.[13] Exploration of the reactivity of silyliumylidene (**1**) towards chalcogens and H_2S enabled an access to NHC-stabilized heavier chalcogen silaacylium derivatives[14] and thiosilaaldehyde.[15] Herein, we report our study devoted to the synthesis of a silaaldehyde, isolated as a Si,O-donor-acceptor complex, and its unique reactivity showing strong relationship to the chemistry of carbonyl congeners (Figure 1b).

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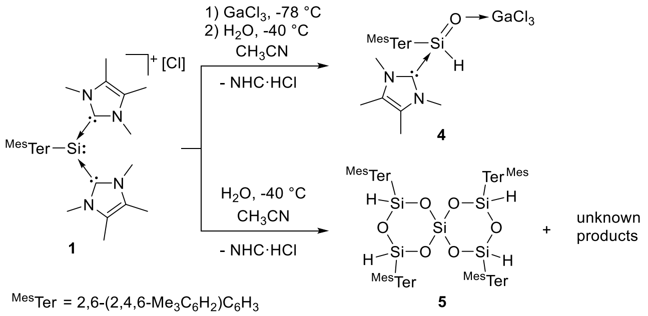
Treatment of sillyliumylidene complex **1** with equimolar amounts of gallium chloride and water in acetonitrile at low temperatures led to the formation of complex **4** together with corresponding imidazolium chloride (Scheme 1). Recrystallization of the row product from acetonitrile/toluene solution (2 : 1) at –30°C furnished colorless crystals of **4** in a moderate yield (61 %).



Scheme 1. Hydrolysis of silyliumylidene complex **1** in the presence and absence of the Lewis acid ($GaCl_3$).

The ^{1}H NMR spectrum of compound **4** in CD_3CN shows a distinct signal of silicon-bound hydrogen at 4.98 ppm ($^{1}J_{Si,H}$ = 234.2 Hz). It lies within the range of values reported for silaformyl compounds **I**, **II** (broad signals at 5.64 and 5.55 ppm, respectively)[6,7] and **III** (4.29 ppm,$^{1}J_{Si,H}$ = 190.6 Hz),[8] and considerably upfield shifted compared to the formyl proton of the corresponding aldehyde ^{Mes}TerCHO (9.65 ppm).[16] The ^{29}Si NMR spectrum of **4** exhibits a resonance at –45.0 ppm, which is very close to that of silaformyl chloride **II** (–49.8 ppm).[7]

The molecular structure of complex **4** was unambiguously confirmed by single crystal X-ray diffraction analysis (Figure 2), which revealed a distorted tetrahedral geometry of the silicon atom.

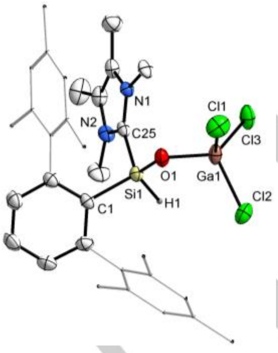


Figure 2. Molecular structure of **4**. Hydrogen atoms except H1 are omitted for clarity.

The Si–O bond distance in **4** is 1.605(3) Å. Surprisingly, it is only marginally shorter than Si–O single bonds in acyclic organodisiloxanes $(R_3Si)_2O$ (1.61–1.64 Å) or siloxanes R_3SiOR' (ca. 1.64 Å), and even slightly longer than those in halogenodisiloxanes $(X_3Si)_2O$ (1.58–1.59 Å, X = F, Cl).[17] This bond is also elongated compared to those in **I**, **II**, and **IV** (1.552(2), 1.568(15), and 1.5514(10) Å, respectively)[6,7,9] and in three-coordinate silanones (1.52–1.54 Å).[3]

In the solid state, the IR spectrum of **4** displayed a strong absorption band at 975 cm^{-1}. Although Si=O stretching vibrations of parent silaaldehydes in argon matrix are observed at higher wave numbers (H_2SiO, $\tilde{\nu}$ = 1202 cm^{-1}, and MeSi(H)O, $\tilde{\nu}$ = 1207 cm^{-1}),[18a] this value is large enough to distinguish it from the absorption of Si–O single bonds ($\tilde{\nu}$ = 800–900 cm^{-1}).[18b] Thus, the structural and IR data suggest strong dominance of the zwitterionic resonance structure **4B** or equivalent Lewis structure **4C** into the ground state of the molecule (Figure 3).

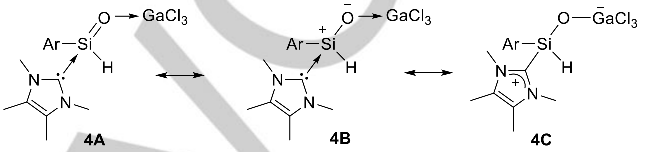


Figure 3. Resonance structures of silaaldehyde **4**.

DFT calculations at B97-D/def2-SVP level of theory showed a good agreement between calculated metric parameters, the ^{29}Si NMR as well as IR data (δ = –41.2 ppm, $\tilde{\nu}$ = 964 cm^{-1}) of **4** and the experimentally obtained data. HOMO and LUMO of **4** are mainly located at the aryl ligand/chlorine atom and NHC ligand/Si–C_{NHC} σ* orbital/aryl ligand, respectively (Figure S22). No indication of possible Si–O π-orbital was observed. Natural charges of Si and O atoms (1.67 and –1.22, respectively) indicate strong charge separation. Obtained Wiberg bond index (WBI), and Mayer bond order (MBO) of the Si–O bond (0.74 and 1.21, respectively) indicate a single bond with negligible double bond character. The computed mechanism of formation of **4** includes barrier-free protonation of **1** involving $H_2O{\cdot}GaCl_3$ complex and following transformations toward **4** with low energy barriers (Scheme S1).

Interestingly, the use of other Lewis acid reagents, such as $AlCl_3$, $B(C_6F_5)_3$, BX_3 (X = F, Cl, Br) or ZnX_2 (X = F, Cl), instead of gallium chloride in the reaction of **1** with water did not lead to any selective transformation. In an attempt to procure an acceptor-free silaaldehyde ^{Mes}Ter(IMe$_4$)Si(H)O, hydrolysis of **1** was also performed in the absence of any Lewis acid (Scheme 1). However, it resulted in the formation of a mixture of unidentified products, from which only sterically hindered spirosiloxane **5** was isolated in 9.2 % yield. The structure of **5** was confirmed using multinuclear NMR spectroscopy and single crystal X-ray diffraction analysis (see SI). Attempt to remove the NHC from **4** using BPh_3 at 80 °C led to the isolation of the corresponding borane–NHC adduct and unidentified decomposition products.

In order to access donor-acceptor complex of a silacarboxylic acid (**6**), silaaldehyde complex **4** was reacted with water in the presence of the NHC as a hydrogen scavenger (Scheme 2). Reaction led to the formation of an unprecedented gallium silacarboxylate complex (**7**) isolated in low yield (8 %) if one equivalent of the NHC was employed. The yield of **7** was improved to 22 % using two equivalents of the NHC. Corresponding 2,2-dihydroimidazolidine and imidazolium salt

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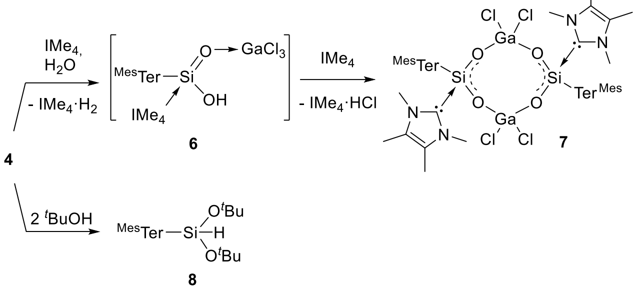
were identified as by-products. Additionally, alcoholysis of complex **4** with *tert*-butanol provided silaacetal **8** isolated in 79 % yield (Scheme 2).



Scheme 2. Synthesis of siladicarboxylate **7** and silaacetal **8**.

Molecular structures of **7** and **8** were confirmed using X-ray diffraction analysis. In the solid state, compound **7** exists as a centrosymmetric dimer containing two silacarboxylate ($^{Mes}TerSiO_2$) fragments bridged by two $GaCl_2$ units in a similar manner found in gallium(III) carboxylate complexes (Figure 4).[19] Each silicon center has a distorted tetrahedral geometry. The Si1–O2 (1.586(17) Å) and Si1–O1 (1.603(17) Å) bond distances are close to each other and to the Si–O distance found in **4**. These distances are also comparable to those in the donor-acceptor-stabilized silanoic acid (EtO)(D→)Si(O→A)OH (1.588(2)–1.626(2) Å) reported by Baceiredo, Kato and co-workers.[5e] Moreover, both Si–O bonds in **4** are sufficiently shorter than Si–O single bonds in gallium–siloxane complexes (1.62–1.70 Å).[20]

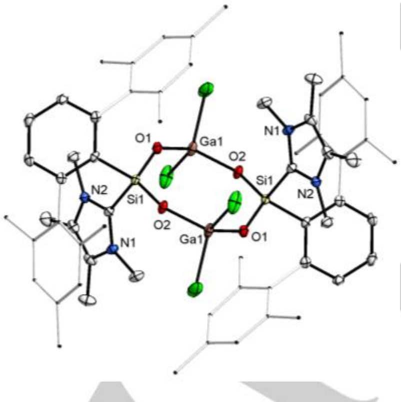
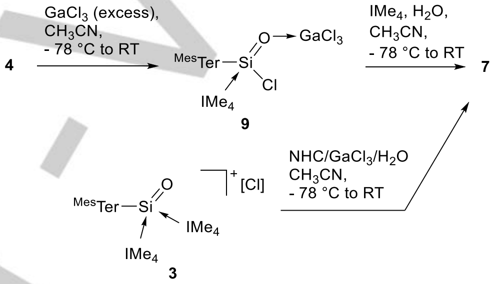


Figure 4. Molecular structure of **7**. Hydrogen atoms are omitted for clarity.

According to our DFT calculation, the Si–O bonds in SiO_2 moieties in **7** are almost identical within 0.02 Å. MBOs are same for all Si–O bonds (1.18) and the same as found in the starting material. Noteworthy, HOMO–40 of **7** (Figure S24) shows a cyclic delocalization through the oxygen atoms, thus supporting the heavy silacarboxylate analogy. Conversion of **4** into **7** involves intermediate formation of the acid **6** and starts from the nucleophilic attack of the silicon of **4** by the oxygen of H_2O·NHC complex (Scheme S2).

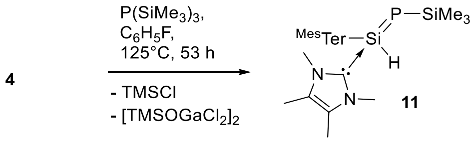
We used reaction of silaaldehyde complex **4** with an excess of gallium chloride to access novel silaaroyl chloride **9** (Scheme 3). Analytically pure sample of **9** was obtained in low yield (9 %) as a very moisture sensitive solid with low solubility in polar and non-polar solvents. All attempts to characterize single crystals of **9** led to their contamination with the corresponding acid $Ar(IMe_4)Si(O)(GaCl_3)OH$ (**10**) due to partial hydrolysis.

In order to examine a relationship to classical acyl transfer reactions, we performed hydrolysis of silaacyl derivatives **9** and **3** with water under various conditions. It was found, that reaction of silaaroyl chloride **9** with water in the presence of NHC leads to selective formation of siladicarboxylate dimer **7**, while the reaction of silaacylium salt **3**[5c] with a $NHC/GaCl_3/H_2O$ mixture (1:1:1) provides the same product in 43 % yield (Scheme 3).



Scheme 3. Synthesis of silaacyl chloride complex **9** and alternative approaches to siladicarboxylate complex **7**.

Aldehydes and ketones are known as important reagents not only in C–C bond forming reactions, but also for the construction of mono- and heteronuclear C=E double bonds (E = C, N, P).[1] We found, that reaction of **4** with *tris*(trimethylsilyl)phosphine at elevated temperature in fluorobenzene yields selectively thermally stable NHC-supported phosphasilene **11** (Scheme 4). While the mechanism of this transformation remains unclear, it may involve nucleophilic attack of the phosphorus reagent on the electropositive silicon, leading to elimination of transient $[TMSOGaCl_3]$ anion and following formation of $TMSOGaCl_2$ dimer,[22] TMSCl, and phosphasilene **11** (Scheme S3). Notably, analogous reaction of aldehydes RCHO with *bis*(trimethylsilyl)phosphines $R'PTMS_2$ in the presence of $AlCl_3$ is known to yield corresponding phosphaalkenes R(H)C=PR'.[21]



Scheme 4. Synthesis of phosphasilene **11** from silaaldehyde complex **4**.

The same phosphasilene complex **11** was obtained alternatively using a convenient two-step approach starting from

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^{Mes}TerSi(H)Cl$_2$ (see SI). Reaction products in both cases were identical and showed same spectroscopic data. Moreover, **11** was characterized by X-ray diffraction analysis (Figure 5). Obtained spectroscopic and structural data of **11** are in good agreement with those of the described previously similar phosphasilene–NHC complex bearing more bulky ^{Dipp}Ter aryl substituent at the silicon atom.[23,24]

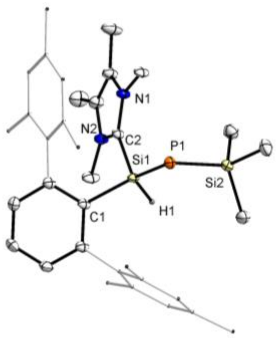

Figure 5. Molecular structure of **11**. Hydrogen atoms except H1 are omitted for clarity.

In summary, we have synthesized and characterized the first donor-acceptor complex of an aryl silaaldehyde. Notably, it reacts as masked silacarbonyl providing an access to a number of stable derivatives, thus showing a relationship to carbonyl chemistry. Difficulties in the preparation of the corresponding donor, and acceptor-free silaaldehyde complexes, as well as the isolation of free spirosiloxane underline low stability of the corresponding free silaaldehyde. Thus, the quest for stable free silaaldehydes remains challenging.

Acknowledgements

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Keywords: Silaaldehyde • Silanone • Silacarbonyl group • Silyliumylidene • N-Heterocyclic carbene

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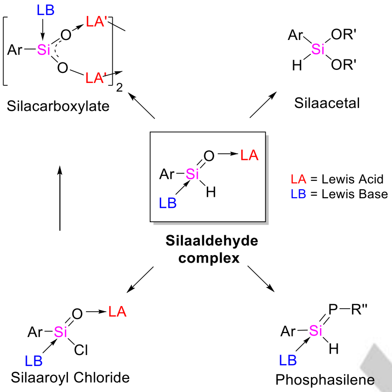
COMMUNICATION

First silicon analogue of an aldehyde stabilized with an external Lewis base and Lewis acid was successfully isolated and characterized. It shows unique reactivity mimicking behaviour of carbonyl congeners and provides an access to various classes of silacarbonyl derivatives.



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