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COMMUNICATION

Donor-acceptor stabilized silaformyl chloride[†]‡

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Formyl chloride (H(Cl)C=O) is unstable at room temperature and decomposes to HCl and CO. Silicon analogue of formyl chloride, silaformyl chloride IPr \cdot SiH(Cl)=O \cdot B(C₆F₅)₃ (3) (IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene), wasstabilized by Lewis donor-acceptor ligands. Compound 3 is not only the first stable acyclic silacarbonyl compound but also the first silacarbonyl halide reported so far.

The last three decades have witnessed considerable progress in the chemistry of compounds with multiple bonds with heavier group 14 elements.^{1–11} This is not only because of the experimental curiosity but also because they possess frontier orbitals with small energy separation and can activate small molecules and therefore mimic transition metals.2

Compounds with double bonds between group 14 and group 16 elements are of special interest.⁶⁻¹¹ Ketones (R₂C=O) are ubiquitous in organic chemistry, biochemistry, and material science but their silicon analogues are still scarce.¹²⁻¹⁵ In contrast to the carbonyl systems, derivatives with a Si=O bond show an extraordinarily high tendency to oligomerize with no activation barrier.¹⁶ This is due to the high polarity of the Si=O bond and weak p_{π} - p_{π} interaction. Therefore, silicon analogues of ketones remained elusive until recently.¹²⁻¹⁵ Intramolecular coordination of group 14 elements with nitrogen donor ligands allows the stabilization of such reactive species. We have isolated the first N-donor supported germathiocarboxylic acid (LGe(=S)OH) (L = CH(MeCNAr)₂, Ar = 2,6-Prⁱ₂C₆H₃) analogue with a monoanionic chelating β -diketiminate (L) ligand.¹⁷ Driess and co-workers reported some interesting silicon heterocycles featuring Si=O bonds supported by donor-acceptor ligands.¹²⁻¹⁵ However, to the best of our knowledge no silicon analogue of an acyclic- as well as a halo-carbonyl compound has been reported so far.

Lewis base stabilization of highly reactive species with low-valent main group elements using N-heterocyclic carbenes (NHCs) is an exciting area of research activity in NHC chemistry.¹⁸⁻²⁰ We have exploited this feature not only to stabilize highly reactive dichlorosilylene as monomeric $IPr \cdot SiCl_2$ (1) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) but also since NHC acts as a reducing agent for HSiCl₃.¹⁹ Starting from 1, some exciting stable silicon compounds have been isolated,^{20,21} which were supposed to exist as intermediates in many chemical transformations. Very recently a zwitterionic stable silicon analogue of an acid anhydride was isolated supported by donor-acceptor ligands.²²

Syntheses of stable silicon compounds have been motivated almost exclusively by their relationship with organic congeners.^{1–5} Formaldehyde ($H_2C=O$) is the simplest carbonyl compound and its mono-chlorinated derivative, formyl chloride A (Scheme 1), is a useful formylating agent.²³ Interestingly, formyl chloride A is unstable at room temperature and decomposes to HCl and CO.²⁴ Isolation of a stable silicon analogue B of formyl chloride with a Si=O bond is evidently more challenging due to the instability of A.²⁴

Herein we report on a stable silaformyl chloride IPr- $SiH(Cl) = O \cdot B(C_6F_5)_3$ (3), which was prepared by the reaction of $IPr \cdot SiCl_2$ (1) with $H_2O \cdot B(C_6F_5)_3$ in the presence of NHC as a HCl scavenger (Scheme 2). The mechanism for the formation of 3 is at present not known. Insertion of silvlene 1 into the O-H bond of $H_2O \cdot B(C_6F_5)_3$ to form 2 is plausible, which under the elimination of HCl yields a stable silaformyl chloride 3 (Scheme 2).^{25a} Compound 3 features a significant double bond character between Si and O atoms, however contribution of the resonating structure 3' cannot be ruled out. Compound 3 is the first haloas well as acyclic-silacarbonyl compound reported so far. Colorless crystals of 3 were obtained from a toluene solution in 26% yield.^{25a} Compound **3** is soluble in common organic solvents and stable under an inert atmosphere for appreciable time. The molecular structure of 3 was established by single crystal X-ray measurement.



Scheme 1 Formyl chloride (A) and its silicon analogue (B).

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Scheme 2 Synthesis of silaformyl chloride (3) from dichlorosilylene (1) (Ar = 2,6-diisopropylphenyl).

The ¹H NMR spectrum of **3** shows resonances for the IPr ligand, which are quite different from those found in **1**. A broad resonance at δ 5.55 ppm is assigned to Si*H* proton and further supported by ¹H-²⁹Si HSQC (HSQC = Heteronuclear Single Quantum Coherence) experiment. ¹¹B, ¹³C, and ¹⁹F NMR spectra of **3** exhibit resonances as expected for compound **3**. The ²⁹Si{¹H} NMR spectrum of **3** shows a singlet at δ –49.78 ppm consistent with the values reported for compounds with a four-coordinate²⁶ silicon atom. The ²⁹Si NMR resonance for **3** shows a significant upfield shift relative to dichlorosilylene **1**, which is comparable to those of reported silicon compounds with an Si=O bond.¹²

Compound **3** crystallizes in the monoclinic space group P2(1)/c with two molecules in the asymmetric unit.^{25b} Presence of the centrosymmetric space group indicates that both enantiomers (*R* and *S*) are present in the structure. The silicon atom in **3** is four-coordinate and features a distorted tetrahedral environment (Fig. 1). All coordination sites are occupied with four different atoms; one hydrogen, one chlorine, one oxygen, and one carbon atom of the NHC ligand. The Sil–O1 bond



Fig. 1 Representation of the molecular structure of **3** with 50% probability level for the displacement ellipsoids; isopropyl groups and H atoms (except the one on the Si atom as located in the difference Fourier map) were omitted for clarity. Only the non-disordered of the two molecules in the asymmetric unit^{25b} and the ipso-C atoms of the C₆F₅ groups are shown. Selected bond lengths [Å] and angles [°] with calculated values at BP86/SVP given in brackets: Si1–O1 1.568(15) [1.609], Si1–C1 1.911(2) [1.949], Si1–Cl1, 2.049(8) [2.087], O1–B1 1.492(3) [1.523]; O1–Si1–C1 110.90(9) [107.4], O1–Si1–Cl1 112.65(6) [115.7], C1–Si1–Cl1 103.08(7) [105.5].

length (1.568(15) Å) is smaller than the Si–O single bond (1.64 Å) but longer than the Si=O bond calculated for $H_2Si=O(1.53 Å)$.²⁷ This may be due to the higher coordination at the silicon.^{13–16} The Si1–O1 bond length is in agreement with those found in compounds with four-coordinate silicon.^{12–15} NBO analysis for compound **3** as well as for free SiH(Cl)O suggests a strongly polarized Si⁺–O⁻ bond as illustrated by **3'** (Scheme 2). As expected for Si(IV) compounds,^{19,20} the Si1–Cl1 (2.049(8) Å) and Si1–C1 (1.911(2) Å) bonds in **3** are shorter than those of Si(II) compound **1**. The O1–Si1–C1 features the bond angle of 110.90(9)°.

We carried out DFT calculations at the BP86/TZVPP-SVP level (see ESI[‡]) for compound 3 and associated donor and acceptor moieties. The calculated structures are shown in Fig. S4 (see ESI[‡]). The optimized geometry of 3 is very similar to the experimental structure shown in Fig. 1, where the calculated bond lengths and angles are also given. The theoretical distances are always somewhat longer than the experimental values, but otherwise the agreement between theory and experiment is quite good. The calculated Si=O bond in free SiH(Cl)O is shorter (1.545 Å) than in 3 (1.568 Å). The NBO analysis suggests that the Si=O double bond in free SiH(Cl)O is strongly polarized towards oxygen. The σ bond is 79% at O and 21% at Si while the π bond is 81% at O and 19% at Si. The polarization of the Si=O bond in 3 toward the oxygen end is even larger. In the compound 3, the σ bond is 85% at O and 15% at Si while the π bond is 96% at O and only 4% at Si. Thus, the π electrons are better described as Si⁺-O⁻ (as depicted for 3'). This is in agreement with the atomic partial charges which are q(Si) = +1.56 and q(O) = -1.04in free SiH(Cl)O while they are q(Si) = +1.58 and q(O) =-1.03 in 3.

We calculated the strength of the donor-acceptor bonds in IPr \rightarrow SiH(Cl)O \rightarrow B(C₆F₅)₃ **3** yielding the three fragments IPr, SiH(Cl)O and B(C₆F₅)₃ as separate moieties. The theoretically predicted values are shown in Table 1. The overall bond dissociation energy (BDE) of **3** is rather high. Separate calculations of the two donor-acceptor bonds show that the IPr \rightarrow SiH(Cl)O interactions in **3** are much stronger than the SiH(Cl)O \rightarrow B(C₆F₅)₃ donation. The former bond is about twice as strong as the latter. The calculated data also show that the two donor-acceptor bonds in **3** mutually enhance each other. The BDEs of the free acid-base pairs IPr \rightarrow SiH(Cl)O and SiH(Cl)O \rightarrow B(C₆F₅)₃ are a bit smaller than in **3**. The inclusion of dispersion interactions in the calculations gives larger values for the bond energies but the trends remain the same.

Table 1 Calculated bond dissociation energies ΔE and free energies ΔG^{298} at BP86/TZVPP//BP86/SVP of the calculated compounds [kcal mol⁻¹]. The dispersion corrected values at BP86-D3/TZVPP//BP86/SVP are given in parentheses

Reaction	ΔE	ΔG
$\begin{array}{l} \hline \textbf{3} \rightarrow \mathrm{IPr} + \mathrm{SiH}(\mathrm{Cl})\mathrm{O} + \mathrm{B}(\mathrm{C}_{6}\mathrm{F}_{5})_{3} \\ \textbf{3} \rightarrow \mathrm{IPr} \cdot \mathrm{SiH}(\mathrm{Cl})\mathrm{O} + \mathrm{B}(\mathrm{C}_{6}\mathrm{F}_{5})_{3} \\ \textbf{3} \rightarrow \mathrm{IPr} + \mathrm{SiH}(\mathrm{Cl})\mathrm{O} \cdot \mathrm{B}(\mathrm{C}_{6}\mathrm{F}_{5})_{3} \\ \mathrm{IPr} \cdot \mathrm{SiH}(\mathrm{Cl})\mathrm{O} \rightarrow \mathrm{IPr} + \mathrm{SiH}(\mathrm{Cl})\mathrm{O} \\ \mathrm{SiH}(\mathrm{Cl})\mathrm{O} \cdot \mathrm{B}(\mathrm{C}_{6}\mathrm{F}_{5})_{3} \rightarrow \\ \mathrm{SiH}(\mathrm{Cl})\mathrm{O} + \mathrm{B}(\mathrm{C}_{6}\mathrm{F}_{5})_{3} \end{array}$	70.6 (106.3) 23.2 (44.2) 51.1 (77.9) 47.4 (62.1) 19.5 (28.4)	36.8 (72.5) 6.5 (27.5) 32.2 (59.0) 30.2 (44.9) 4.6 (13.5)

The NBO atomic charges suggest that the SiH(Cl)O moiety in **3** is essentially neutral, the calculated partial charge is -0.01 e. Thus, the extent of charge exchange and charge acceptance at the SiH(Cl)O moiety in **3** does not correlate with the associated energy contributions, where IPr \rightarrow SiH(Cl)O donation is stronger than SiH(Cl)O \rightarrow B(C₆F₅)₃ donation.

In conclusion we have synthesized and characterized a remarkably stable silaformyl chloride IPr·SiH(Cl)=O·B(C₆F₅)₃ (**3**), whose carbon homologue formyl chloride is unstable at room temperature. Compound **3** is the first acyclic silacarbonyl compound reported so far. Moreover, **3** represents the first stable halo-silacarbonyl compound. Theoretical calculations support the experimental results.

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 (4) was also isolated, which separates out as an oil in non-polar solvents and can be easily removed. Further details are given in the ESI.[‡] Attempts to isolate Lewis acid–base adduct of siliconmonoxide IPr·Si=O·B(C₆F₅)₃, using 3 and IPr and also by the reaction of 1 with H₂O·B(C₆F₅)₃ in the presence of two equivalents of IPr were not successful. In both cases formation of 4 and free IPr was observed. (b) The asymmetric unit of 3 contains two molecules. Only one molecule of 3 was non-disordered. The second molecule of 3 (80% occupancy) was disordered and superposed to a molecule of the imidazolium-borate salt 4 with 20% occupancy (see ESI[‡] for more details).
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