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Donor−Acceptor-Stabilized Silicon Analogue of an Acid Anhydride

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S *Supporting Information*

ABSTRACT: A stable silicon analogue of an acid anhydride $\{PhC(Bu^tN)_2\}Si\{{=}O\cdot B(C_6F_5)_3\}O{-}Si(H)\{{=}O\cdot B(C_6F_5)_3\}\{(NBu^t)(HNBu^t)CPh\}$ (**4**) with a O=Si−O−Si=O core has been prepared by treating monochlorosilylene $PhC(Bu^tN)_2SiCl$ (**1**) with $H_2O\cdot B(C_6F_5)_3$ in the presence of NHC (NHC = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). Compound **4** has been characterized by elemental analysis and multinuclear NMR spectroscopic investigations. The molecular structure of **4** has been established by single-crystal X-ray diffraction studies, and DFT calculations support the experimental results.

The chemistry of compounds containing silicon−heteroatom multiple bonds has been one of the interesting areas of research in main group chemistry.[1−6] Compounds with formal double bonds to silicon (Si=X) of group 16 elements (X = O, S, Se, Te) are considered to be very reactive due to the highly polarized Si=X bond as well as weak $p_\pi - p_\pi$ interactions. This behavior is more pronounced in compounds with a formal silicon−oxygen double bond (Si=O) owing to oxygen having the highest electronegativity among the group 16 elements.

Nevertheless, some silicon compounds with Si=X double bond have been isolated[3−12] by taking advantage of kinetic and thermodynamic stabilization using specially designed ligands on silicon. The first successful attempt in this direction was made by Corriu et al.[3] with the isolation of base-stabilized silicon compounds containing Si=S and Si=Se bonds. Contributions to stabilize silicon compounds with Si=X bonds by the research groups of Wagler,[4] West,[5] Okazaki,[6,7] Tokitoh,[6,7] Kira,[8] and Driess[9−12] are noteworthy. Owing to the highly polarized nature of the Si=O bond, incorporation of a second substituent (OR, where R = H, alkyl, or aryl) is a challenge.[12,13]

We have reported a base-stabilized silicon thioester analogue ($PhC(Bu^tN)_2Si({=}S)SBu^t$), **A** (Scheme 1).[14] Furthermore, base-stabilized germanium analogues of carboxylic acids LGe(=X)OH, **B** (X = S, Se; Scheme 1), supported by β-diketiminate ligand L (L = $CH(MeCNAr)_2$, Ar = $2,6\text{-}Pr^i{}_2C_6H_3$) were synthesized and completely characterized.[15] Silicon analogues of carboxylic acid RSi(=O)OH are transient species and have been studied at low temperature in an argon matrix.[16] Driess and coworkers have explored the chemistry of silicon compounds[9−12] containing Si=X bonds that are stabilized by the β-diketiminate ligand. In a recent paper, they reported the isolation of the first silicon analogue of carboxylic acid LSi(=O)OH, **C** (Scheme 1), by donor−acceptor stabilization. A single-crystal X-ray structure analysis of **C** is still missing.[12]

In contrast to silicon, related carbon compounds with C=O functionality are ubiquitous and well-known. An acid anhydride (**D**) is shown in Scheme 2. Compounds of this type exhibit important roles in many industrial processes. To the best of our knowledge, a silicon analogue (**E**) of an acid anhydride so far has not been reported. We have used N-heterocyclic carbenes (NHCs) as dehydrochlorinating agents for the preparation of dichlorosilylene,[17] germylene,[18] and metal hydroxides.[19] We successfully eliminated HCl from a silyl halide containing a secondary amino group using NHC to form an unstable compound with a Si=N double bond, which further dimerizes to a four-membered Si_2N_2 ring.[20] In view of the above results, we became interested in preparing a compound with a Si=O bond starting from a chlorosilylene[21] $PhC(Bu^tN)_2SiCl$ (**1**) and $H_2O\cdot B(C_6F_5)_3$ in the presence of NHC as a HCl scavenger.

Herein, we report on a silicon analogue of an acid anhydride $\{PhC(Bu^tN)_2\}Si\{{=}O\cdot B(C_6F_5)_3\}O{-}Si(H)\{{=}O\cdot B(C_6F_5)_3\}\{(NBu^t)(HNBu^t)CPh\}$ (**4**; Scheme 3) containing the O=Si−O−Si=O moiety. Compound **4** was synthesized by treatment of a base-stabilized monochlorosilylene[21] $PhC(Bu^tN)_2SiCl$ (**1**) with $H_2O\cdot B(C_6F_5)_3$ in the presence of NHC (NHC is IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). The mechanism for the formation of **4** is not known; however we presume the involvement of a silaformaldehyde (**2b**) and a silacarboxylic acid (**3**) as depicted in Scheme 3. Formation of a monohydroxylsilylene $PhC(Bu^tN)_2Si(HO\cdot B(C_6F_5)_3)$ **2a** by the elimination of HCl as IPr·HCl on reaction of **1** with $H_2O\cdot B(C_6F_5)_3$ and its subsequent rearrangement to **2b** seems to be plausible.[22] Due to the high electronegativity of the oxygen atom and propensity of Si=O bonded compounds to exist as $^+Si{-}O^-$, **2b** can isomerize to **2c**. Cationic silicon in **2c** may abstract oxygen from $\{HOB(C_6F_5)_3\}^-$, formed by the reaction of IPr and $H_2O\cdot B(C_6F_5)_3$, with elimination of $\{HB(C_6F_5)\}^-$ to result in silacarboxylic acid **3**. Protonation of the amino nitrogen of the amidinate ligand of **2b** by silacarboxylic acid **3** affords acid anhydride **4**. Compound **4** is a zwitterion in which anionic silacarboxylate oxygen coordinates to the second silicon atom that contains the protonated amidinate ligand. Compound **4** was isolated as colorless crystals and characterized by elemental analysis and NMR spectroscopy. The molecular structure of **4** was unequivocally established by single-crystal X-ray diffraction.

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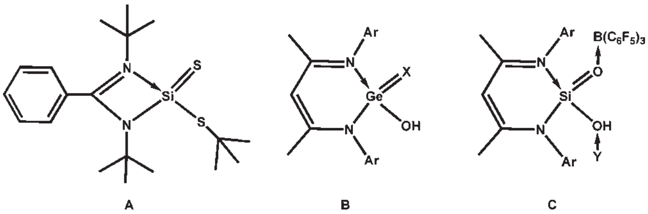
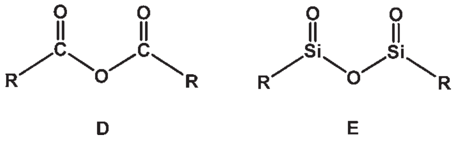
Scheme 1. Base-Stabilized Silicon or Germanium Analogues of Thioester (A), Thio- and Seleno-Carboxylic Acid (B; X = S or Se), and Carboxylic Acid (C)[a]



[a] Ar = 2,6-$Pr^i_2C_6H_3$, *Y* = 4-dimethylaminopyridine.

Scheme 2. An Acid Anhydride (D) and Its Silicon Analogue (E)[a]



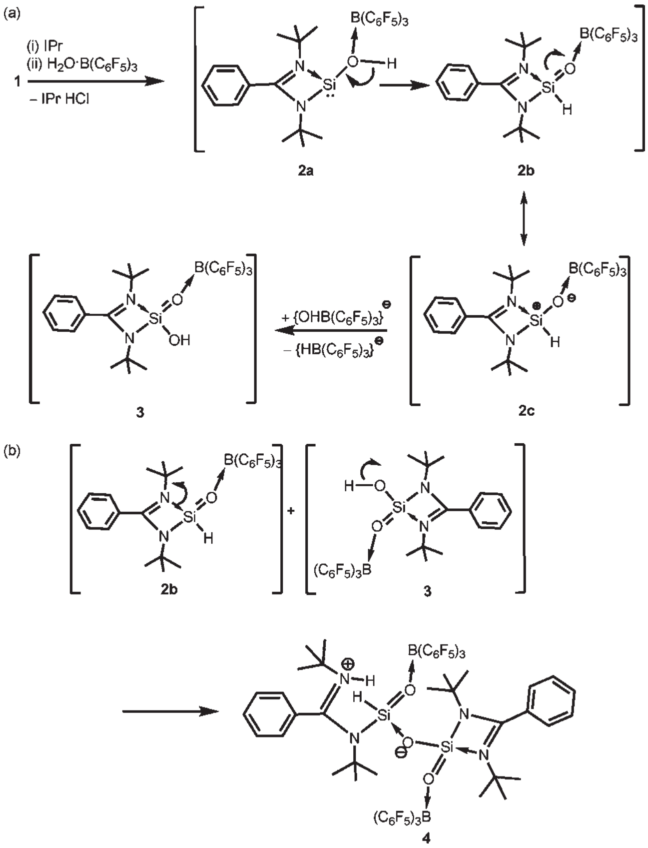
[a] R = alkyl or aryl group.

Compound **4** is stable under an inert atmosphere of nitrogen and soluble in common organic solvents. The ^{1}H NMR spectrum of **4** shows three sets of resonances for Bu^t groups along with a complex multiplet for phenyl protons. A broad resonance at δ 10.27 ppm is tentatively assigned for the N*H* proton. The Si*H* proton appears as a broad resonance at δ 4.10 ppm.[23] The ^{29}Si{^{1}H} NMR spectrum of **4** exhibits two resonances at δ −72.02 and −75.91 ppm. These resonances are consistent with those observed for compounds with a four-coordinate silicon atom.[12]

The molecular structure of compound **4** has been established by single-crystal X-ray diffraction and is shown in Figure 1. Compound **4** crystallizes as colorless crystals in the triclinic space group $P\bar{1}$. The asymmetric unit contains one molecule of **4** and one and a half toluene molecules. Compound **4** features an interesting bonding situation and constitutes two functionalities within a single molecule. These are interpreted as a deprotonated silacarboxylic acid and silaaldehyde moieties. Alternatively, two Si═O (silacarbonyl) groups are bridged by an oxygen atom, and therefore **4** represents the first silicon analogue of acid anhydride with an O═Si−O−Si═O core. Compound **4** is a zwitterionic species; this is characteristic for an amino acid.

Each of the silicon atoms in **4** is four-coordinate and centered at the distorted tetrahedron. One of the amidinate ligands chelates a silicon atom in a bidentate fashion with the N1−Si1−N2 bite angle of 72.09(13)°. Another amidinate ligand at the second silicon atom is arranged in a monodentate fashion, exhibiting a protonated amino group. Bonds to divalent silicon atom are expected to be longer in comparison to those of tetravalent silicon.[24] Therefore, the Si1−N1 (1.797(3) Å) and Si1−N2 (1.773(3) Å) bond lengths are slightly shorter than those found in compound **1**.[21] The silicon−oxygen bond lengths range from 1.5392(19) to 1.6272(19) Å and support the presence of an O═Si−O−Si═O core in **4**. They vary according to the electronic environment around the silicon atoms. The Si1−O1 bond length (1.5392(19) Å) is very close to the Si═O distance (1.545(2) Å) reported for

Scheme 3. Synthesis of Silicon Analogue of Acid Anhydride 4 (IPr = 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene): (a) Formation of Silaformaldehyde (2b) and Silacarboxylic Acid (3) as Intermediates; (b) Interaction of 2b and 3 Result in the Formation of 4



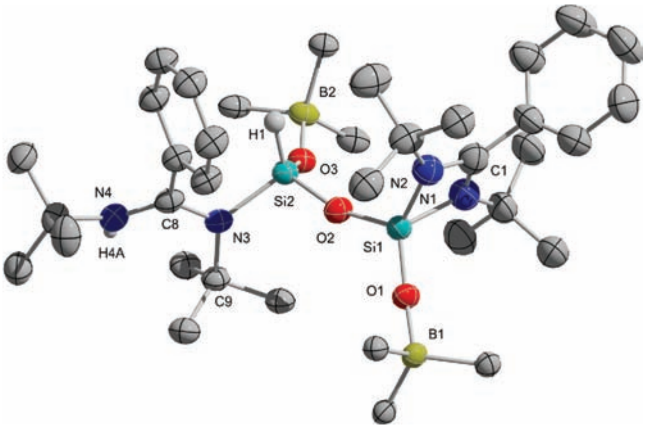


Figure 1. ORTEP representation of molecular structure with displacement ellipsoids of **4**; anisotropic displacement parameters depicted at 50% probability. Only *ipso* carbon atoms of C_6F_5 rings of $B(C_6F_5)_3$ and H atoms on Si2 and N4 are shown for clarity. Selected bond lengths [Å] and angles [deg]: Si1−O1 1.5392(19), Si2−O3 1.5804(18), Si1−O2 1.5829(19), Si2−O2 1.6272(19), Si1−N1 1.797(3), Si1−N2 1.773(3), Si1−N3 1.816(2), O1−B1 1.493(3), O3−B2 1.488(3); O1−Si−O2 115.12(10), Si1−O2−Si2 163.20(14), O2−Si2−O3 112.08(10), O1−Si1−N1 114.28(12), N1−Si1−O2 112.78(12), O2−Si2−N3 106.00 (10), N1−Si1−N2 72.09(13).

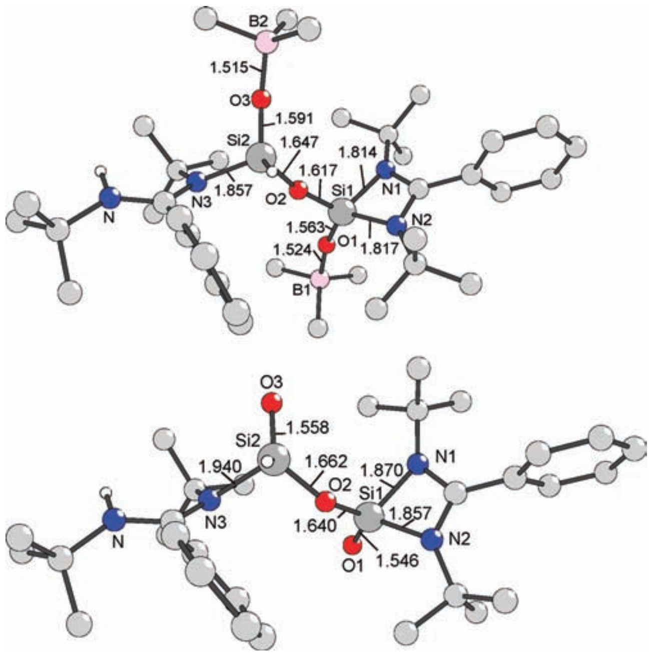


Figure 2. Calculated geometries (BP86/TZVPP-SVP) of **4** (top) and **4M** (bottom). Selected bond lengths are given in Å.

the compound with a four-coordinate silicon atom.[11c] The Si2−O2 bond length (1.6272(19) Å) is consistent with the Si−O single bond.[12] The Si2−O3 (1.5804(18) Å) and Si1−O2 (1.5829(19) Å) bond lengths are shorter than the Si−O single bond but longer than the Si=O double bond distances. Slight elongation of Si2−O3 and shortening of Si1−O2 bond lengths may be due to steric hindrance or to the electronic interaction of the Lewis acid $B(C_6F_5)_3$.[12] The Si1−O2−Si2 (163.20(14)°) bond features the largest bond angle.

We carried out DFT calculations at the BP86/TZVPP-SVP level (see Supporting Information) for compound **4** and the uncomplexed parent system **4M** without the $B(C_6F_5)_3$ molecules. Figure 2 shows the optimized geometries of **4** and **4M**. The calculated bond lengths of **4** are in good agreement with those of the experiment. The computed Si−O distances are 0.01−0.03 Å longer than the X-ray values. The calculated Si1−O1 bond length (1.563 Å) is shorter than the Si2−O3 distance (1.591 Å), while the Si1−O2 (1.617 Å) and Si2−O2 bonds (1.647 Å) are still longer, which concurs with the experiment. The complexation of **4** with two $B(C_6F_5)_3$ molecules at the terminal oxygen atoms complicates the assignment of the Si−O linkages as single or double bonds. The calculated bond lengths of **4M** give a much clearer picture of the bonding situation. The terminal Si1−O1 (1.546 Å) and Si2−O3 bonds (1.558 Å) are much shorter than the bridging Si1−O2 (1.640 Å) and Si2−O2 bonds (1.662 Å). The former distances agree with the classification of double bonds, while the latter values concur with typical Si−O single bonds. Complexation of **4** with $B(C_6F_5)_3$ molecules at the terminal oxygen atoms lengthens the Si1−O1 and Si2−O3 bonds, and it shortens the Si1−O2 and Si2−O2 bonds.

Moreover, we analyzed the nature of the Si=O bond in **4** and in **4M** with the NBO method. The π-bond in **4** is strongly polarized toward the oxygen end. The NBO data suggest that 91.7% of the Si=O π bond is at oxygen, while only 8.3% is at silicon. The most appropriate Lewis structure for **4** should thus be written with a negative partial charge at O(−) and a positive charge at Si(+). The nature of the π bond changes very little after complexation with the Lewis acid at oxygen. The Si=O π bond in **4M** is a bit more polarized toward oxygen (95.5%), while only 4.5% is at silicon. It follows that the Si=O bonding situations in **4** and in **4M** are very similar.

In summary, we report here for the first time a stable silicon analogue of an acid anhydride $\{PhC(Bu^tN)_2\}Si\{=O\cdot B(C_6F_5)_3\}-O-Si(H)\{=O\cdot B(C_6F_5)_3\}\{(NBu^t)(HNBu^t)CPh\}$ (**4**). Compound **4** was prepared by the reaction of monochlorosilylene $PhC(Bu^tN)_2SiCl$ (**1**) with the water−borane adduct $H_2O\cdot B(C_6F_5)_3$ in the presence of NHC. NHC serves as a HCl scavenger. Compound **4** was characterized by elemental analysis and multinuclear NMR spectroscopic investigations. The molecular structure of **4** was established by single-crystal X-ray diffraction study. DFT calculations support the experimental results.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures and X-ray crystallographic and computational information of compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) All manipulations were carried out in strictly anhydrous and oxygen-free atmosphere using glovebox or Schlenk-line techniques. Reaction of **1** with H_2O results in the formation of amidinate salt $PhC(Bu^tNH)_2 \cdot HCl$ with no silicon in the toluene-soluble part, most probably due to the formation of (SiO_2).

(23) Due to rapid hydrogen exchange on the NMR time scale even at low-temperature, it was not possible to measure $^{29}Si-^{1}H$ coupling. Therefore, ^{29}Si NMR resonances for both silicon atoms in **4** appear almost in the same region.

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