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Main-Group Chemistry

A Base-Stabilized Sila-β-Lactone and a Donor/Acceptor-Stabilized Silanoic Acid**

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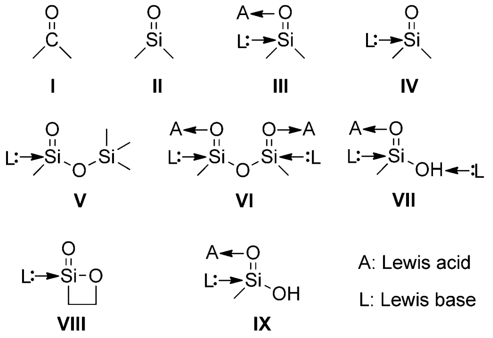
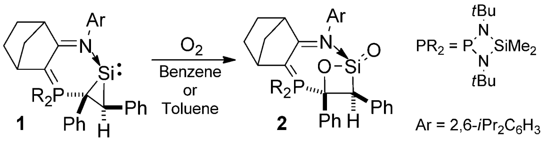
The carbonyl group **I** is ubiquitous and without doubt one of the most important functional groups in organic chemistry; it characterizes many compounds such as ketones, aldehydes, carboxylic acids, and many other related compounds. In marked contrast, the synthesis of the heavier silicon analogue **II** is still elusive owing to the weak and strongly polarized Si–O π bond, which accounts for a very strong tendency to give thermodynamically stable polysiloxanes.[1]



M. Driess and co-workers reported that the silanone function can be efficiently stabilized using a donor/acceptor system **III**.[2–3] A base-stabilized silanon complex with a transition metal (type III) has also recently been reported.[4] M. Driess and co-workers also demonstrated that the stabilization of such species can be achieved by coordination of electron-donating ligands on the silicon center (type **IV**), which allowed the isolation of the first examples of a base-supported silaurea[5] and a silanoic silyl ester **V**.[6] We have also recently reported the synthesis of the first donor-stabilized silacyclopropan-1-one of type **IV**.[7] Although these techniques allowed the synthesis of other silacarbonyl derivatives, such as silanoic acid anhydride **VI**[8] and pyridinium salts of silanoic acid **VII**,[9] only a few types of silacarbonyl compounds are available to date.[10] Here we present the synthesis of the first base-stabilized sila-β-lactone **VIII** and its unique reactivity with alcohols leading to the formation of a silanoic acid **IX**, more precisely, silicic acid monoethyl ester, which is a silicon analogue of monoethyl carbonate.

It was known that silylenes react with dioxygen (O_2) to generate the corresponding transient silaester.[11] Similarly, the base-stabilized silacycloprop-1-ylidene **1**[12] readily reacts with one equivalent of dioxygen at 5 °C to give selectively the corresponding base-supported sila-β-lactone **2** (Scheme 1).



Scheme 1. Reaction of silacyclopropylidene **1** with O_2.

The reaction proceeds regio- and diastereoselectively, which was indicated by the ^{31}P NMR spectrum showing only two signals for the β-lactone **2** in the same proportions as those for **1** (51.3 and 47.7 ppm; diastereomer ratio: 92:8). Derivative **2** is stable under inert conditions and was isolated as colorless crystals in 51 % yield. In the ^{29}Si NMR spectrum the signal corresponding to the silanone function appears as a doublet ($\delta = -52.7$ ppm, $^2J_{PSi} = 11.2$ Hz) at slightly lower field compared to **1** ($\delta = -87.5$ ppm), but in the range of base-stabilized silanones.[5,7] The two carbon atoms of the lactone ring were observed as two doublets at relatively low field ($\delta = 80.1$ ppm, $^1J_{CP} = 85.8$ Hz and $\delta = 47.4$ ppm, $^2J_{CP} = 13.6$ Hz). The ^{1}H NMR spectrum shows a doublet for the proton of the lactone ring with a large coupling constant ($\delta = 4.51$ ppm, $^3J_{PH} = 20.4$ Hz).

The structure of **2** was unambiguously confirmed by X-ray diffraction analysis (Figure 1).[13] The structure reveals an essentially planar β-lactone four-membered ring ($\Sigma° = 359.8°$) with an oxygen atom (O2) inserted between the silicon (Si1) and carbon (C1) atoms attached to the phosphorus atom. The silicon center presents a distorted tetrahedral geometry owing to the coordination of the imine fragment. The Si1–N1 bond

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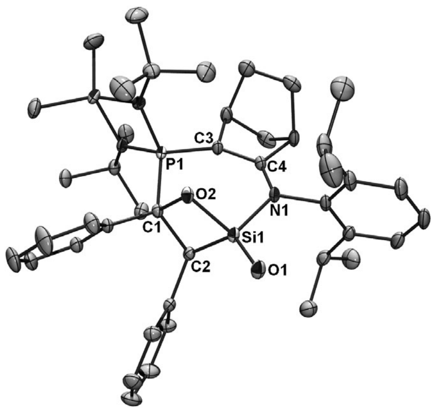
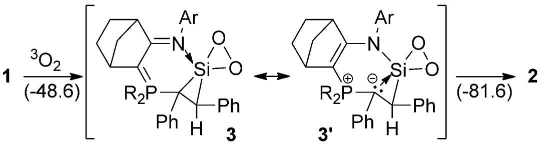


Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. H atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.539(2), Si1–O2 1.691(2), Si1–C2 1.894(2), C1–O2 1.463(3), C1–C2 1.590(3), Si1–N1 1.786(2), C1–P1 1.856(2), P1–C3 1.748(2), C3–C4 1.386(3), N1–C4 1.370(3); O1-Si1-O2 118.34(9), O1-Si1-C2 128.18(10), O1-Si1-N1 112.88(10), O2-Si1-N1 104.72(9), O2-Si1-C2 81.69(9), N1-Si1-C2 105.68(10), O2-C1-C2 100.54(17), C1-O2-Si1 94.47(13), C1-C2-Si1 83.05(13).

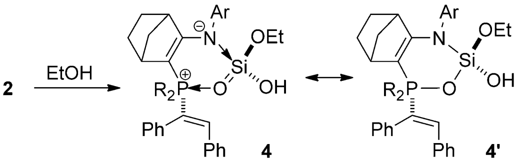
length (1.786 Å) corresponds to a single bond, thus indicating a strong coordination of the imine ligand to the silicon center, as observed for other imine–silanone complexes such as acyclic silaester **V** (1.768 Å)[6] or silacyclopropanone (1.764 Å).[7] The significantly short Si1–O1 distance (1.539 Å) is comparable to those reported for base-stabilized silaureas (1.532–1.542 Å)[5,7] and is much shorter than the endocyclic Si1–O2 single bond (1.691 Å), thus suggesting a double bond character.[14] Moreover, the significantly larger Wiberg bond order for the silanone function (1.194) than that for the single Si1–O2 bond (0.446) also indicates its multiple-bond character. The two phenyl groups are *syn* to each other like in the case of the starting silacycloprop-1-ylidene **1**,[12] thereby confirming that the oxidation takes place with retention of stereochemistry.

The formation of sila-β-lactone **2** from the silacyclopropylidene **1** probably proceeds in two steps in agreement with reported mechanisms;[5a,11] 1) formal side-on addition of dioxygen to generate the dioxasilirane intermediate **3**, 2) ring expansion of the silacyclopropane fragment through insertion of an oxygen atom (Scheme 2). Nevertheless the formation of **3** was not observed even at −100 °C. DFT calculations indicate the strongly thermally favored formation of the sila-β-lactone **2** from **1** (Scheme 2). As expected, the isomerization of **3** is strongly exergonic and proceeds with a low energy barrier ($\Delta G^{\neq} = 12.9\ \mathrm{kcal\,mol^{-1}}$). All attempts to find a reaction pathway for the direct formation of **2** from **1** have failed. The high regioselectivity of the reaction with the exclusive insertion of an oxygen atom (O2) between the C1 and Si1 atoms could be explained by a preferential migration of the C1 carbon atom owing to a large contribution of the ylide–dioxasilirane-complex-type canonical structure **3′** with a strongly polarized Si1−C1 bond.[15]



Scheme 2. Proposed mechanism via intermediacy of dioxasilirane **3**. In the parenthesis are the calculated Gibbs free energy values ($\mathrm{kcal\,mol^{-1}}$) for the reactions at the M06/6-311 + G(d,p)//M06/6-31G(d) level.

Owing to ring strain and the presence of the reactive silacarbonyl function, sila-β-lactone **2** should have a very high reactivity. Indeed derivative **2** readily reacts with ethanol at room temperature to afford the original donor/acceptor-stabilized silanoic acid **4** (Scheme 3). In this molecule, the silacarbonyl function is stabilized by a push-pull system with an amide as a donor and a phosphonio fragment as acceptor. A similar amidophosphorane-based push-pull system has recently been reported to capture a molecule of carbon dioxide.[16] In the ^{29}Si NMR spectrum, the chemical shift of the silacarbonyl function in **4** appears as a doublet at $\delta = -77.4$ ppm ($^2J_{\mathrm{SiP}} = 14.9$ Hz) in the range of the reported silanoic acid derivative (−73.2 ppm).[9] The pentacoordinate phosphorus center exhibits a drastic upfield shift in the ^{31}P NMR spectrum ($\delta = -57.5$ ppm) in comparison with **2** ($\delta = 51.3$ ppm). The formation of **4** involves a formal [2+2] retro-cycloaddition of sila-β-lactone **2**, and the presence of the phosphavinylic function in **4** is clearly indicated by two typical signals with large PC-coupling constants in the ^{13}C NMR spectrum ($\delta = 152.9$ ppm, $^1J_{\mathrm{PC}} = 171.2$ Hz and $\delta = 119.5$ ppm, $^2J_{\mathrm{PC}} = 20.0$ Hz) and by the vinyl proton observed in the ^{1}H NMR spectrum ($\delta = 6.82$ ppm, $^3J_{\mathrm{PH}} = 31.9$ Hz). Notably, there are very few reports concerning experimental[17] and theoretical[18] studies on silanoic acids to date. In almost all cases, such reactive species have been analyzed only in matrix system or gas phases, although Driess's group has recently reported the synthesis of a persistent silanoic acid stabilized by a donor/acceptor system (**VII**).[9] To our knowledge, this is the first example of a perfectly stable silanoic acid derivative in solution and in solid state.



Scheme 3. Reaction of **2** with EtOH, synthesis of silanoic acid **4**.

The structure of **4** reveals that the donor/acceptor binding of the ambiphilic amidophosphorane ligand is constituted by two interactions: N donor N→Si=O (Si1–N1 1.727 Å), and P acceptor P←O=Si (O1–P1 1.762 Å), forming a six-membered heterocycle (Figure 2).[13] Owing to the strong P←O = Si interaction, the P center adopts a distorted trigonal bipyramidal geometry (N2-P1-O1 172.4°, $\Sigma°_{\mathrm{equatorial}} = 360.0°$) with two long apical bonds (P1–O1: 1.762 Å and P1–N2: 1.827 Å). The P–O bond length is comparable to that in a reported CO_2 amidophosphorane complex (1.764–1.777 Å).[16] In spite of the strong donor/acceptor

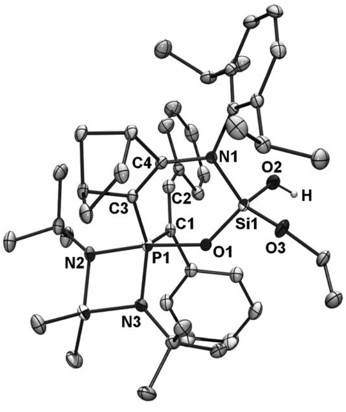
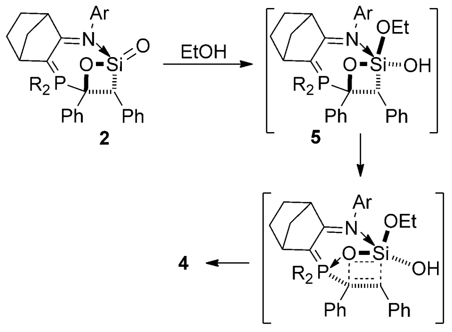


Figure 2. Molecular structure of **4**. Thermal ellipsoids represent 30% probability. H atoms, except for that on O2, solvent molecules, and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.588(2), Si1–O2 1.626(2), Si1–O3 1.615(2), Si1–N1 1.727(2), P1–O1 1.762(2), P1–N2 1.827(2), P1–N3 1.693(2), P1–C1 1.851(2), P1–C3 1.812(2), C3–C4 1.362(3), C4–N1 1.399(2), C1–C2 1.339(3); Si1-O1-P1 137.94(9), O1-P1-N2 172.43(8), N3-P1-C3 120.10(9), N3-P1-C1 119.13(9), C3-P1-C1 120.74(10), O1-Si1-O2 113.94(8), O1-Si1-O3 112.01(8), O2-Si1-O3 107.58(9), O1-Si1-N1 105.19(8).

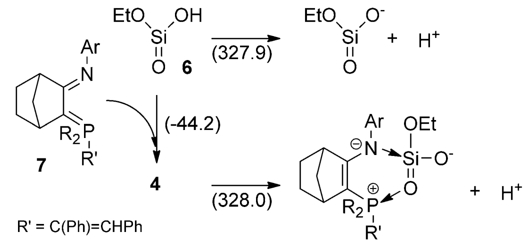
N$\rightarrow$Si=O$\rightarrow$P interactions, the Si1–O1 bond (1.588 Å) remains relatively short compared to other Si–O bonds (Si1–O2: 1.626 Å, Si1–O3: 1.615 Å), in agreement with a certain multiple bond character. This value is at the upper limit of those observed for other donor/acceptor-stabilized Si=O bonds (1.539–1.580 Å).[2–4,8,9] Furthermore, the quite similar Wiberg bond order for the Si1–O1 bond (0.640) compared to those for the other Si–O single bonds (0.601 and 0.565) indicates that the complexed Si = O function does not have a significant double-bond character. Thus, the stabilized silanoic acid derivative is well-described by the two canonical structures **4** and **4′** (Scheme 3). Compound **4** exists in the solid state as a dimer stabilized through hydrogen bonds involving the Si–OH group.[19]

As mentioned, the reaction is diastereoselective leading to exclusive formation of the isomer featuring the phosphavinyl function and silahydroxy group on the same side of the six-membered heterocycle plane (Figure 2). This diastereoselectivity suggests a 1,2-addition reaction of ethanol to the silacarbonyl function with an attack from the less-hindered side of the lactone ring (O-bridge side) to form the pentacoordinate silicon intermediate **5** (Scheme 4). Then, a [2+2] retro-cycloaddition, probably induced by a release of ring strain in the pentacoordinate intermediate **5**, similarly to the Perterson olefination reaction, affords **4**.[20,21]

The efficient stabilization of silanoic acid **6** by coordination of the donor/acceptor iminophosphorane ligand **7** on the silanone function was supported by DFT calculations revealing the strong exergonic nature of the reaction ($\Delta G = -44.2$ kcal mol^{-1}, Scheme 5). Interestingly, in spite of this stabilization, the coordination of ligand **7** does not affect the acidity in the gas phase. Indeed, both the free silanoic acid **6** and its complexed form **4** present similar ΔG values for the proton dissociation (**6**: 327.9 kcal mol^{-1}, and **4**: 328.0 kcal mol^{-1}). In contrast, a significant decrease of acidity is predicted when **6** is complexed by the Lewis pair $Me_4P^+{\cdot}Me_2N^-$ (345.9 kcal mol^{-1}), thus demonstrating the specificity of ligand **7**.



Scheme 4. Proposed mechanism for the formation of silanoic acid **4**.



Scheme 5. Reaction of silanoic acid **6** with an iminophosphorane ligand **7** and proton dissociation of free silanoic acid **6** and of its complex **4**. In parenthesis are the Gibbs free energies [ΔG (kcal mol^{-1}) in the gas phase] calculated at the M06/6-311+G(d,p)//M06/6-31G(d) level.

In conclusion, we have synthesized the first stable base-stabilized sila-β-lactone. Interestingly, this silalactone shows a unique reactivity with ethanol, thereby allowing the isolation of the first donor/acceptor-stabilized silanoic acid. Of particular interest, the DFT calculation on the complexed silanoic acid indicates that the coordination of the donor/acceptor ligand on the silanone function stabilizes efficiently the acid but does not modify its acidity. This feature could be important for developing further the chemistry of silicon-based carboxylic acid analogues, which has been difficult to realize because of their instability. More detailed studies on the influence of donor/acceptor ligands on the acidity as well as applications of the original reactivity of sila-β-lactones are under investigation.

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