Donor-Stabilized Silacyclobutanone: A Precursor of 1-Silaketene via Retro-[2 + 2]-Cycloaddition Reaction at Room Temperature

Thibault Troadec,[†] Morelia Lopez Reyes,[†] Ricardo Rodriguez,[†] Antoine Baceiredo,*[,†] Nathalie Saffon-Merceron,[‡] Vicenç Branchadell,[§] and Tsuyoshi Kato*[,†]

[†]Université de Toulouse, UPS, and CNRS, LHFA UMR 5069, F-31062 Toulouse, France
[‡]Université de Toulouse, UPS, and CNRS, ICT FR2599, 118 route de Narbonne, F-31062 Toulouse, France
[§]Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

S *Supporting Information*

ABSTRACT: The synthesis of donor-stabilized silacyclobutanone **2** was successfully realized by the reaction of silacyclopropylidene **1** with benzaldehyde in the presence of a Lewis acid catalyst. Of particular interest, silacyclobutanone **2** evolves at room temperature via a retro-[2 + 2]-cycloaddition reaction, leading to an original NHC-stabilized 1-silaketene **4** and *cis*-stilbene.

The carbonyl group is ubiquitous and one of the most important functional groups in organic chemistry. In contrast, the heavier silicon analogue is far less studied, and the corresponding silanones remain highly reactive transient species whose chemistry is underdeveloped compared with that of related ketones.[1] The situation has dramatically improved since the development of efficient stabilization techniques by Driess's group using donor (**I**)[2] or donor/acceptor (**II**)[3] systems (Chart 1). These techniques enabled the

Chart 1. Donor-Stabilized Silanones and Retro-[2 + 2]-Cycloaddition Reactions of Silicon-Containing Four-Membered Heterocycles
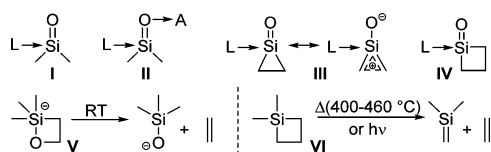

synthesis of several stable and easy-to-manipulate silanone derivatives.[4,5] Nevertheless, the types of available silanones are still highly limited, and there is only one example of a small cyclic silanone such as silacyclopropanone **III**, which was recently described by our group.[6] This three-membered cyclic silanone **III** shows a unique structure with electron delocalization of the cyclic C—C σ bond toward the silicon atom, inducing an original silacyclopropanone—oxyallyl hybrid structure. In the series of cyclic silanones, silacyclobutanone **IV** still remains elusive.

Thermally unstable four-membered metallacycles, which easily fragment into two unsaturated fragments via a formal retro-[2 + 2]-cycloaddition reaction, are well-known as the key intermediates of the olefin metathesis reaction.[7] In silicon chemistry, the thermally unstable cyclic anionic pentacoordi-

nate oxasiletanes **V** are the intermediates of the Peterson olefination reaction.[8] In marked contrast, the more closely related silacyclobutanes **VI**, silicon/carbon-based four-membered metallacycles, are thermally stable, and the retro-[2 + 2]-cycloaddition reaction requires significant thermal activation (400−460 °C).[9,10] Here we report the synthesis and isolation of the first example of a donor-stabilized silacyclobutanone **2** (type **IV**) which, under mild conditions (room temperature) undergoes a [2 + 2]-cycloreversion to generate a transient 1-silaketene derivative.

Over the past few years, we have developed the chemistry of the donor-stabilized silacyclopropylidene **1**[11] and reported the original reactivity with N_2O[6] and O_2[12] as well as a thermal ring-opening reaction giving a silene possessing unique properties.[13] The reaction of silacyclopropylidene **1** with 1 equiv of benzaldehyde in the presence of a magnesium salt (ClMgOCHMePh) as a Lewis acid catalyst (10 mol %) cleanly affords silacyclobutanone **2** stabilized by the intramolecular coordination of the imine fragment (Scheme 1). Cyclic silanone

Scheme 1. Reactions of 1 with Benzaldehyde in the Presence of a Magnesium Salt as a Lewis Acid Catalyst
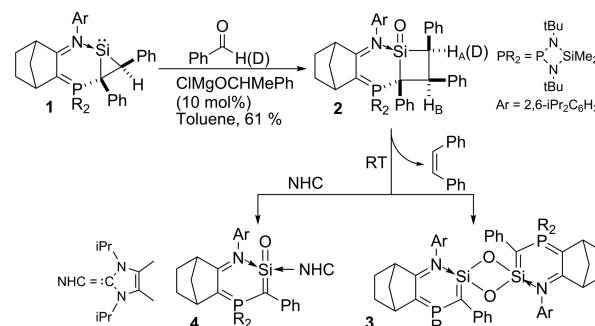

2 was isolated as colorless crystals from a toluene solution at −30 °C (61% yield). The reaction is stereospecific, as indicated by the presence of a singlet signal in the ^{31}P NMR spectrum (59.6 ppm). In the ^{29}Si NMR spectrum, the signal corresponding the silanone function (−37.3 ppm) appears at relatively low field compared with those of other cyclic

silanones with the same ligand system such as silacyclopropanone (−69.1 ppm)[6] and sila-β-lactone (−57.2 ppm)[12] or other base-stabilized silanones (−50 to −77 ppm).[1d,4] In the ^{1}H NMR spectrum, the two ring CH protons appear as a doublet [4.35 ppm (d, $^3J_{HH}$ = 11.5 Hz, H_A)] and a doublet of doublets [5.01 ppm (dd, $^3J_{HH}$ = 11.5, $^3J_{HP}$ = 26.5 Hz, H_B)], suggesting a cis configuration.[14] The X-ray structure of **2** reveals a slightly folded cyclobutanone ring [$\sum$(angles) = 354.3°] and a distorted tetrahedral geometry around the silicon atom due to the coordination of the imine fragment (Figure 1).[15] The
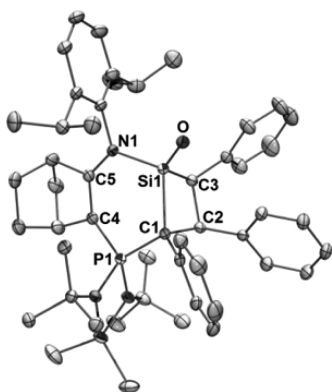
Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. Solvent molecules and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−O1 1.544(2), Si1−N1 1.798(2), Si1−C1 1.984(3), Si1−C3 1.897(3), C1−C2 1.611(3), C2−C3 1.572(3), C1−P1 1.833(3), P1−C4 1.733(3), C4−C5 1.386(4), C5−N1 1.357(3), Si1−C1−C2 85.71(14), C1−C2−C3 100.53(19), C2−C3−Si1 89.83(16), C3−Si1−C1 78.21(11), N1−Si1−C1 109.71(10), N1−Si1−C3 109.61(12).

significantly short Si1−O1 distance (1.544 Å) is comparable to those for previously reported base-stabilized silanones (1.532−1.542 Å).[1d,4] The three phenyl groups are located on the same side of the four-membered ring, in agreement with the NMR data.

Lewis acid-catalyzed rearrangements of organic oxaspiropentanes into the corresponding cyclobutanones have been reported to proceed by a simple cyclopropane ring expansion reaction triggered by the coordination of a Lewis acid to the oxirane ring (**A** → **B**, Figure 2).[16] Similarly, silacyclobutanone **2**
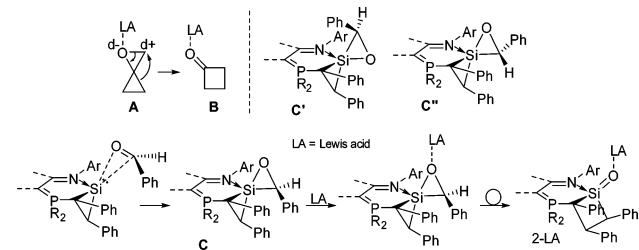

Figure 2. Plausible reaction mechanisms.

is probably obtained via a Lewis acid-assisted rearrangement of silaoxaspiropentane intermediate **C**, the [2 + 1]-cycloadduct between silylene **1** and benzaldehyde (Figure 2). The use of deuterated benzaldehyde (PhCDO) unambiguously demonstrated that the CHPh group belonging to benzaldehyde is connected to the silicon atom in **2** (Scheme 1). The very high stereoselectivity level achieved can most probably be attributed

to the selective formation of the sterically more favored intermediate **C** than other possible intermediates **C′** and **C″** having the phenyl group oriented toward more hindered sides (Figure 2).

Of particular interest, the base-stabilized silacyclobutanone **2** slowly evolves at room temperature to form the four-membered cyclic disiloxane **3** and cis-stilbene (Scheme 1). The formation of **3** was unambiguously confirmed by NMR spectroscopy and X-ray diffraction analysis (Figure 3).[15] This result is in good agreement with the transient formation of a 1-silaketene intermediate via [2 + 2]-cycloreversion of **2**.[17]
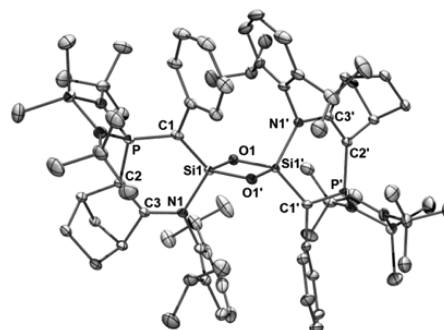

Figure 3. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Solvent molecules and H and disordered atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−O1′ 1.679(2), Si1−O1 1.680(2), Si1′−O1 1.680(2), Si1′−O1′ 1.679(2), Si1−N1 1.760(2), Si1−C1 1.806(3), C1−P 1.700(3), P1−C2 1.760(4), C2−C3 1.344(6), C3−N1 1.371(6), O1−Si1−O1′ 86.5(2), Si1−O1−Si1′ 93.5(2), Si1−O1′−Si1′ 93.6 (2), N1−Si1−C1 106.9(1), Si1−C1−P 122.1(2), C1−P−C2 108.1(2), P1−C2−C3 125.7(4), C2−C3−N1 129.0(5), C3−N1−Si1 123.1(3).

Indeed, in the presence of an N-heterocyclic carbene (NHC) the dimerization of the transient silacumulene was prevented, and 1-silaketene complex **4** was isolated as yellow crystals (87% yield). To the best of our knowledge, this is the first stable 1-silaketene derivative, although several persistent 2-silaketenes have been reported.[18,19] The ^{29}Si NMR spectrum exhibits a resonance for the central silicon atom of **4** (−49.6 ppm, J_{SiP} = 30.3 Hz) that is at higher field than those calculated for free silanones ($H_2Si{=}O$, 72 ppm; $(H)(H_2N)Si{=}O$, 13 ppm)[20] and a recently reported metallasilanone (170 ppm)[21] and persistent dialkylsilanone (129 ppm)[22] but is similar to those observed for donor-stabilized silanones (−50 to −77 ppm) and the 2-silaallene complexed with two ligands (−38 ppm),[23] which is in agreement with the double coordination of the silicon atom by the NHC and the imine fragment. In the ^{13}C NMR spectrum, the chemical shift for the silaketene carbon is strongly shifted to higher field (53.8 ppm, J_{CP} = 92.1 Hz), suggesting strong polarization of the Si=C bond toward the carbon atom. Furthermore, the structure was confirmed without any doubt by single-crystal X-ray diffraction analysis (Figure 4).[15]

Calculations on the retro-[2 + 2]-cycloaddition of **2**[24] demonstrated that the reaction is slightly but thermodynamically favored (ΔG_{5-2} = −3.4 kcal/mol) and reproduced a reasonably low Gibbs free energy barrier ($\Delta G^{\ddagger}_{5-2}$ = 28.0 kcal/mol) (Figure 5). The calculated energy barrier (gas-phase reaction) is somewhat higher than the expected one (ca. 24 kcal/mol) roughly estimated from the experimental observation ($t_{1/2} \approx$ 5 h at 25 °C), probably as a result of acceleration of the
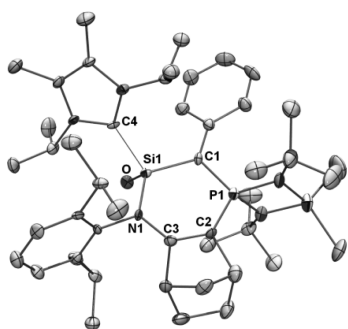
Figure 4. Molecular structure of **4**. Thermal ellipsoids represent 30% probability. Solvent molecules and disordered and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−C4 1.990(6), Si1−O 1.549(4), Si1−N1 1.786(4), Si1−C1 1.835(6), C1−P1 1.693(5), P1−C2 1.727(6), C2−C3 1.360(8), C3−N1 1.372(7), O−Si1−N1 113.3(2), O−Si1−C1 118.2(2), O−Si1−C4 104.1(2), N1−Si1−C1 107.6(2), Si1−C1−P1 120.7(3), C1−P1−C2 107.5(3), P1−C2−C3 129.4(4), C2−C3−N1 127.9(5), C3−N1−Si1 121.8(4).
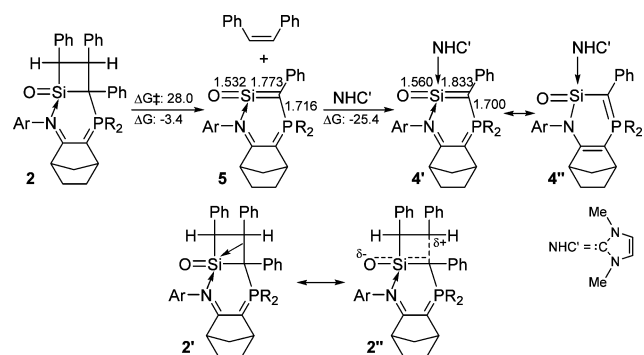
Figure 5. Calculated Gibbs free energy barrier ($\Delta G^{\ddagger}$ in kcal/mol) and Gibbs free energies (ΔG in kcal/mol) for the formation of 1-silaketene complexes (**5** and **4′**) and some calculated bond lengths (Å) of 1-silaketenes **3** and **4′** (M06-2X/6-311+G(d,p)//M06-2X/6-31G(d) level).

reaction in the condensed phase due to solvent effects. Indeed, calculations predict a nonsynchronous cleavage of the Si−C3 and C1−C2 bonds in **2** and the preceding heterolytic cleavage of the C1−C2 bond with strong charge separation ($C1^{\delta+}$−$C2^{\delta-}$) in the transition state (TS).[25] The significantly lower energy barrier for the retro-[2 + 2]-cycloaddition of **2** compared with that for silacyclobutane **VI** (Chart 1) probably results from the interaction of the strongly electrophilic silanone function with the C1−C2 σ bond, which weakens the C−C bond (**2′** and **2″** in Figure 5). This electronic effect should also stabilize the TS with strong charge separation. We previously reported the ring-opening reaction of the donor-stabilized silacyclopropanone **III** under mild conditions due to a similar silanone−C−C bond interaction.[6] Very few examples of retro-[2 + 2]-cycloaddition at ambient temperature without intervention of a transition metal have been reported. Reversible [2 + 2]-cycloaddition of distannyne with ethylene at room temperature has been reported by Power and co-workers.[26] In organic chemistry, a pair of strongly electron-rich and electron-deficient olefins are also known to undergo reversible [2 + 2]-cycloaddition, proceeding through the formation of a charge transfer complex as an intermediate.[27] Although the thermal [2 + 2]-cycloaddition of ketenes with an olefin under mild conditions is frequent, to the best of our

knowledge[28,29] the occurrence of the reverse reaction at room temperature has not been reported to date.

The particularly small difference of Gibbs free energy for the retro-[2 + 2]-cycloaddition of **2** (ΔG_{5-2} = −3.4 kcal/mol) suggests the reversibility of the reaction. In contrast, the coordination of the donating NHC′ ligand to the silicon center of 1-silaketene **5** to form complex **4′** is strongly favored ($\Delta G_{4′-5}$ = 25.4 kcal/mol), which should displace the equilibrium toward the formation of the 1-silaketene (Figure 5). It also suggests a remaining electrophilic character of 1-silaketene **5** already stabilized by the intramolecular coordination of the imine fragment. The calculated geometry of **5** shows a Si=O bond with a typical bond length for donor-stabilized silanones (1.532−1.542 Å)[4] and a shortened Si=C bond length (1.773 Å), which corresponds to the long-end values for those of silenes (1.702−1.775 Å).[30] In contrast, the corresponding NHC complex **4′** exhibits a significantly elongated Si1−C1 bond (1.833 Å) and a shortened C1−P1 bond (1.700 Å) compared with those of **3**, indicating an increased contribution of canonical structure **4″** (Figure 5), certainly resulting from enhanced polarization of the Si=C bond toward the carbon atom due to coordination of the NHC.

The presence of the silanone function in **2** is essential for the low-temperature retro-[2 + 2]-cycloaddition reaction. Indeed, addition of 1 equiv of diphenylsilane at −50 °C leads to the transient pentacoordinate silane **6**, which isomerizes via a ring-opening reaction to give stable eight-membered heterocycle **7** (Scheme 2). A similar ring-opening reaction induced by

Scheme 2. Reaction of Base-Stabilized Silacyclobutanone 2 with Diphenylsilane
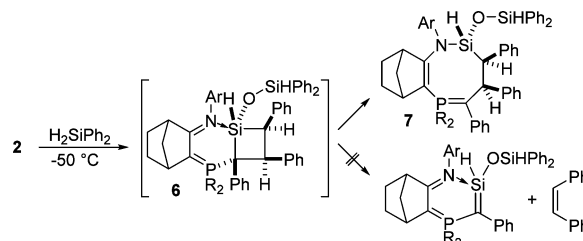
hydrosilylation of the silanone function was previously observed for silacyclopropanone **III**.[4] Hexacoordinate silacyclobutanes are also known to isomerize via ring-opening reactions.[31]

In conclusion, we have successfully synthesized and fully characterized the original base-stabilized silacyclobutanone **2**. Interestingly, this compound slowly evolves at room temperature via a retro-[2 + 2]-cycloaddition reaction to afford, in the presence of an N-heterocyclic carbene, the first isolable NHC-stabilized 1-silaketene **4** and *cis*-stilbene. The detailed mechanistic study of this unique room-temperature [2 + 2]-cycloreversion process and its applications for the metal-free, silicon-mediated olefin metathesis reaction are under active investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00631.

X-ray crystallographic data for **2** (CIF)
X-ray crystallographic data for **3** (CIF)
X-ray crystallographic data for **4** (CIF)

X-ray crystallographic data for **7** (CIF)

Procedures, characterization data, NMR spectra, crystallographic data, and DFT calculation details (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*baceired@chimie.ups-tlse.fr

*kato@chimie.ups-tlse.fr

Notes

The authors declare no competing financial interest.

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(24) Geometries were optimized using the M06-2X density functional with the 6-31G(d) basis set. The energy of each stationary point was recomputed using the 6-311+G(d,p) basis set. The reported Gibbs free energies (298.15 K and 1 atm) were computed from the total energies obtained with the 6-311+G(d,p) basis set and zero-point, thermal, and entropy corrections computed with the 6-31G(d) basis set.

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