J|A|C|S
COMMUNICATIONS

An Isolable Silanoic Ester by Oxygenation of a Stable Silylene

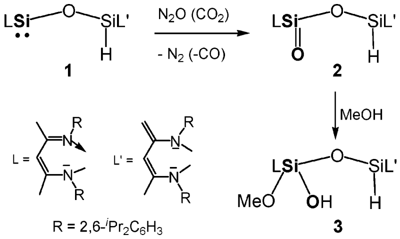
Shenglai Yao, Yun Xiong, Markus Brym, and Matthias Driess*

Institute of Chemistry: Metalorganics and Inorganic Materials Technische Universität Berlin, Strasse des 17. Juni 135, Sekr. C2, D-10623 Berlin, Germany

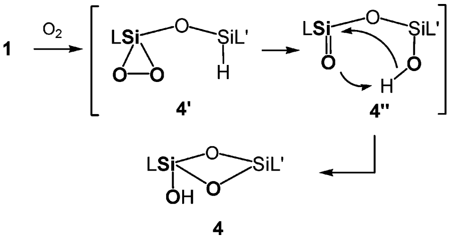
Received April 6, 2007; E-mail: matthias.driess@tu-berlin.de

The chemistry of stable main-group element compounds with silicon-heteroatom double bonds has witnessed tremendous progress over the past 25 years. This is evident by the fact that $Si{=}X$ compounds (X = group 13 to 16 elements) possess a unique reactivity and thus serve as indispensable building blocks in both organosilicon chemistry and organic synthesis.[1] However, stable silicon homologues of ubiquitous ketones ($R_2Si{=}O$) and carboxylic acids ($RSi({=}O)OH$) are still elusive. This is mainly due to the pronounced polarity of the $Si{=}O$ double bond which accounts for the extraordinary high tendency of silanones to undergo oligomerization.[2] Additionally, silanoic acids ($RSi({=}O)OH$; R = H, alkyl) tend to isomerize to their divalent silylene tautomers (RO(OH)Si:).[3] Therefore, silanones[4] and silanoic acid derivatives[5] are elusive species which have predominantly been investigated in cryogenic argon matrices. Recently, we succeeded in the synthesis of an isolable silaformamide−borane complex, $LSi(H){=}O{\rightarrow}BR_3$,[6] by a borane-assisted addition of water to the corresponding stable silylene.[7] The concept of donor−acceptor stabilization of the $Si{=}O$ double bond has now prompted us to challenge the discouraging attempts to synthesize an isolable silanoic ester. To synthesize a silanoic ester stable at room-temperature we probed the suitability of the $N{\rightarrow}Si$ donor supported siloxysilylene **1**[6] as possible precursor for gentle monooxygenation at the divalent silicon atom. In line with that, we also examined the dioxygenation of **1** with dioxygen which led to an unexpected new type of strained cyclodisiloxane. Here, we describe the first silanoic silylester **2** and the striking cyclodisiloxane **4** which resulted from convenient oxygenation of the siloxysilylene HSi(L′)-O-(L)Si:**1** {L = HC[CMeN(aryl)]$_2$; L′ = [L-H]; aryl = 2,6-diisopropylphenyl} with N_2O, CO_2, and O_2, respectively (Schemes 1 and 2). Exposure of a brown solution of the siloxysilylene **1** in toluene to N_2O at −78 °C leads to a gradual decoloration. Crystallization from the solution at −20 °C furnishes colorless plates of the desired silanoic silylester **2** in 79% yield. Remarkably, employing CO_2 as a cheaper monooxygen source leads to the same result.

Scheme 1. Synthesis of the Silanoic Silylester **2** by Oxygenation of **1** and Formation of the MeOH Adduct **3**



Scheme 2. Formation of **4** via the Proposed Intermediates **4′** and **4″**



Crystals of **2** are soluble in hydrocarbons and ethereal solvents. They are stable in dry-air and remain unchanged up to 200 °C in an anaerobic atmosphere. The composition of **2** is supported by multinuclear NMR, IR spectroscopy, correct combustion analysis, and EI-MS (M = 924 au). Its ^1H NMR spectrum exhibits two sets of the expected proton types and, thus, proves the presence of two rotational isomers, similar to the situation observed for the starting material **1**.[6] In addition, the ^{29}Si NMR spectrum shows two sets of resonances for the two chemically inequivalent ^{29}Si nuclei at $\delta = -55.0, -55.5$ ppm (each a doublet, siloxy group, ^1J Si,H = 281 Hz) and −85.1, −85.8 ppm (each a singlet, $LSi({=}O)$), respectively. As expected, the ^{29}Si chemical shift of the siloxy group in **2** is only marginally different from the respective values of the isomeric mixture of **1** ($\delta = -53.7, -54.2$ ppm). Remarkably, the ^{29}Si nucleus in the $LSi{=}O$ moiety is even higher-field shifted than that in the silaformamide−borane complex $LSi(H){=}O{\rightarrow}B(C_6F_5)_3$ ($\delta = -61.5$ ppm). This indicates substantial $Si{=}O$ π-bonding interaction in spite of the presence of tetracoordinate silicon and, thus, proves similar electronic features as present in the related silaformamide−borane complex.[6] Apparently, the favorable $Si{=}O$ π-bonding interaction through the oxygen lone-pair $n_\pi{\rightarrow}Si{-}N$ σ^*_π population (σ^*_π-acceptor orbitals mainly located at silicon) is more effective than that in the aforementioned silaformamide complex. The latter possesses a Si−O bond order of ca. 1.8 based on its $Si{=}O$ stretching vibration/force constant in comparison to the reference system $H_2Si{=}O$ with a bond order set to 2.0. Unfortunately, the $Si{=}O$ stretching vibration mode in **2** could not be unequivocally identified because of superimposition of signals in the characteristic region of the IR and Raman spectrum (1000−1200 cm^{-1}), respectively. However, in line with the presence of a $Si{=}O$ double bond, **2** reacts with methanol to give the corresponding Si(OMe)-OH adduct **3** in almost quantitative yield (Scheme 1).

The latter has been characterized by multinuclear NMR spectroscopy and EI-MS (M = 956 au). The molecular structure of **2** has been confirmed by a single-crystal X-ray diffraction analysis (Figure 1). The two almost planar six-membered C_3N_2Si rings in **2** prefer a gauche-conformation and are linked by the O2 atom. The structure is most notable for its silanoic silylester array Si1(═O1)−O2−Si2 with the remarkably short Si1−O1 distance of 157.9(3) pm, which is a little longer than that in the related silaformamide complex $LSi(H){=}O{\rightarrow}B(C_6F_5)_3$ (155.2(2) pm). Likewise, the relatively short Si1═O1 distance in **2** can also be explained by the contribution of resonance betaine structures as previously suggested for related systems.[6,8] Expectedly, the Si1−O2 (162.9(2) pm) and Si2−O2 bond lengths (162.6(2) pm) represent typical Si−O single bond values in siloxanes which are slightly shorter than those

10.1021/ja072425s CCC: $37.00

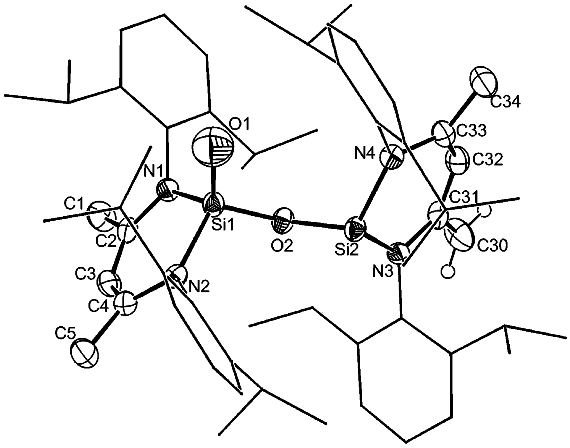


Figure 1. Molecular structure of **2**. Thermal ellipsoids (C1−C5, C30−C34, N1−N4, O1, O2, Si1, Si2) are drawn at 50% probability level. H atoms (except those at C30) are omitted for clarity. Selected distances (pm): Si1−O1 157.9(3), Si1−O2 162.9(2), Si2−O2 162.6(2), Si1−N1 176.8(2), Si1−N2 178.3(2), Si2−N3 173.5(2), Si2−N4 174.6(2), N1−C2 137.1(3), N2−C4 136.3(3), N3−C31 140.3(3), N4−C33 139.9(3), C1−C2 147.4(3), C2−C3 138.4(4), C3−C4 139.6(3), C4−C5 147.6(3), C30−C31 142.4(4), C31−C32 139.2(4), C32−C33 139.5(4), C33−C34 145.7(3).

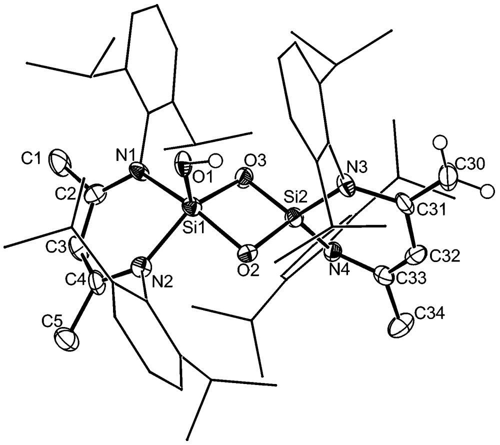


Figure 2. Molecular structure of **4**. Thermal ellipsoids (C1−C5, C30−C34, N1−N4, O1−O3 , Si1, Si2) are drawn at 50% probability level. H atoms (except those at O1 and C30) are omitted for clarity. Selected interatomic distances (pm) and angles (deg): Si1−O1 163.3(3), Si1−O2 174.0(3), Si1−O3 174.5(3), Si1−N2 185.9(4), Si1−N1 189.6(4), Si2−O2 162.5(3), Si2−O3 162.5(3), Si2−N4 170.2(4), Si2−N3 172.0(3), Si1−Si2 246.8(2); Si2−O2−Si1 94.3(2), Si2−O3−Si1 94.1(2).

observed in **1** (165.6(1) and 163.2(1) pm).[6] In line with that, the Si1−O2−Si2 angle of 140.5(1)° is similar to values observed for disiloxanes. As expected, the C−C and N−C distances in the C_3N_2-Si rings as well as the excocyclic C−C bond lengths exhibit significant differences owing to the varying π-systems in the backbone of the two distinct chelate ligands, L and L′. It is noteworthy that the steric congestion of the β-diketiminato ligand L in **2** is sufficient of preventing dimerization of the Si=O moiety in solution at ambient temperature. Thus we examined whether the corresponding stable dioxasilirane (cyclosilaperoxide) **4′** could be synthesized by dioxygenation of the divalent silicon atom in **2** with dry dioxygen. In fact, brownish solutions of the silylene **1** in toluene react readily with molecular oxygen at −78 °C to give clear yellow solutions of a sole product. However, the conversion furnishes solely the isomeric 2,4-dioxa-1,3-disiletane **4** which has been isolated in 76% yield (Scheme 2).

To our knowledge, compound **4** represents a unique type of cyclodisiloxane which results by a remarkably clean dioxygenation process of a stable silylene with O_2. Although the mechanism is still unknown, we assume the formation of **4′** and **4″** as reactive intermediates (Scheme 2) in accord with results from related experiments where transient silylenes and O_2 have been converted under gas-phase conditions[9] and in cryogenic argon matrices below −250 °C.[5] The composition and constitution of **4** have been supported by EI-MS (M = 940 au), correct combustion analysis, IR, and NMR spectroscopy. According to an X-ray diffraction analysis, **4** consists of two almost planar six-membered C_3N_2Si-rings which are perpendicular to each other and linked by two Si1−O−Si2 bridges (Figure 2). Additionally, the Si1 atom bears a terminal OH group which leads to a planar, four-membered Si_2O_2-cycle with, at the same time, tetracoordinate and neutral pentacoordinate silicon centers.

Expectedly, the Si−O and the Si−N distances of the pentacoordinate Si1 atom are longer than those of the Si2 atom owing to the higher coordination number. Likewise, the Si1−Si2 distance of 246.8(2) pm is significantly larger than that in related organocyclodisiloxanes of the type $(R_2SiO)_2$.[10]

Supporting Information Available: Experimental details for the synthesis and spectroscopic data of **2**, **3**, and **4** (PDF) and crystallographic data for **2** and **4** (CIF), respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) X = group 13 elements: (a) Nakata, N.; Sekiguchi, A. *J. Am. Chem. Soc.* **2006**, *128*, 422. X = group 14 elements: (b) West, R. *Polyhedron* **2002**, *21*, 467. (c) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348. (d) Tokitoh, N.; Okazaki, R. *Adv. Organomet. Chem.* **2001**, *47*, 121. X = group 15 elements: (e) Driess, M. *Adv. Organomet. Chem.* **1996**, *39*, 193. (f) Driess, M.; Block, S.; Brym, M.; Gamer, M. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2293−2296. (g) Hemme, I.; Klingebiel, U. *Adv. Organomet. Chem.* **1996**, *39*, 159. X = group 16 elements: (h) Arya, R.; Boyer, J.; Carré, F.; Corriu, R.; Lanneau, G.; Lappasset, J; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016−1018. (i) Suzuki, H.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578. (j) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625. (k) Iwamoto, T.; Sato, K.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 16914.

(2) Apeloig, Y. Theoretical aspects of organosilicon compounds. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, Chapter 2, p 57 and references cited therein. (b) Kapp, J.; Remko, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 5745. (c) Gordon, M. S.; George, C. *J. Am. Chem. Soc.* **1984**, *106*, 609. (d) Kimura, M.; Nagase, S. *Chem. Lett.* **2001**, 1098.

(3) Becerra, R.; Bowes, S.-J.; Ogden, J. S.; Cannady, J. P.; Adamovic, I.; Gordon, M. S.; Almond, M. J.; Walsh, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2900 and cited references therein.

(4) Selected papers: (a) Khabashesku, V. N.; Kerzina, Z. A.; Kudin, K. N.; Nefedov, O. M. *J. Organomet. Chem.* **1998**, *566*, 45. (b) Maier, G.; Meudt, A.; Jung, J.; Pacl, H. Matrix isolation studies of silicon compounds. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1998; Vol. 2, Chapter 2, p 1143 and references cited therein. (c) Schnöckel, H. *Z. Anorg. Allg. Chem.* **1980**, *460*, 37. (d) Whithnall, R.; Andrew, L. *J. Am. Chem. Soc.* **1985**, *107*, 2567. (e) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6167.

(5) Patyk, A.; Sander, W.; Gauss, J.; Cremer, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 898 (see also ref 3 and ref 4b).

(6) Yao, S.; Brym, M.; van Wüllen, C.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, published online Apr, 13, 2007, http://dx.doi.org/10.1002/anie.200700398.

(7) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628.

(8) (a) Vidovic, D.; Moore, J. A.; Jones, J. N.; Cowley, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 4566. (b) Nuculei, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Walfort, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4294.

(9) Nagase, S.; Kudo, T.; Akasaka, T.; Ando, W. *Chem. Phys. Lett.* **1989**, *163*, 23 (see also ref 3).

(10) (a) Sohn, H.; Tan, R. P.; Powell, D. R.; West, R. *Organometallics* **1994**, *13*, 1390. (b) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 9300.

JA072425S