J|A|C|S
COMMUNICATIONS

An Isolable NHC-Supported Silanone

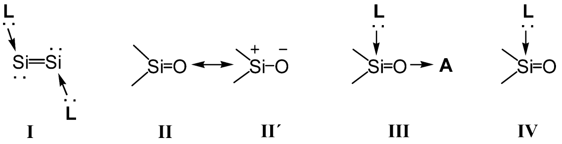
Yun Xiong, Shenglai Yao, and Matthias Driess*

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

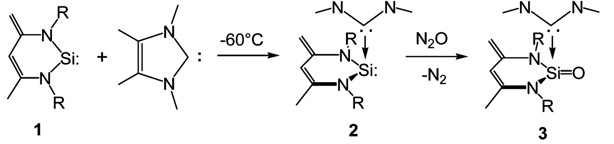
Received April 22, 2009; E-mail: matthias.driess@tu-berlin.de

Nowadays, low-valent silicon compounds with multiple bonds to silicon and other main-group elements are no longer laboratory curiosities but indispensable building blocks in contemporary organosilicon chemistry and silicon-assisted organic synthesis.[1] To date, numerous stable compounds featuring Si═X double bonds (X = group 13 to 16 element)[2] have been synthesized and structurally characterized since the seminal work by West et al.,[3] who reported on the first isolable disilene (>Si═Si<) in 1981. Even stable compounds with Si≡Si triple bonds have been reported recently.[4] Remarkably, Robinson and co-workers described the isolable N-heterocyclic carbene (NHC)-supported :Si═Si: compound **I** (L: = NHC) with silicon in the formal oxidation state 0 (Chart 1).[5] In spite of the tremendous successes mentioned above, the isolation of silanones ($R_2Si{=}O$) **II** that are stable at room temperature has remained elusive. This is presumably due to the difficulty of taming the pronounced polarity of the ylide-like Si═O double bond (**II** ↔ **II′** in Chart 1) and hence preventing silanones from undergoing oligomerization.[6] Taking advantage of the donor−acceptor (D−A) stabilization concept, we have already shown that a stable silaformamide−borane complex of type **III** (L: = N donor; A = BAr_3)[7] is accessible by addition of the corresponding water−borane adduct to the ylide-like silylene LSi: **1**.[8] More recently, we reported the isolation of a silanoic silylester[9] featuring a chelated nitrogen donor-supported Si═O double bond of type **IV** by facile oxygenation of a siloxysilylene[6] with N_2O. Inspired by the intriguing synthesis of **I**,[5] we probed the suitability of an NHC ligand to stabilize a Si═O double bond of type **IV** by employing the stable silylene **1**.[8a] Here we describe the synthesis of the NHC−silylene adduct **2** containing a highly nucleophilic Si(II) site, which undergoes remarkably facile oxygenation with N_2O to yield the first isolable NHC-supported silanone **3** (Scheme 1).

Chart 1



Scheme 1. Synthesis of the NHC−Silylene Adduct **2** and the Carbene-Stabilized Silicon Compound **3**



Treatment of **1** with an equimolar amount of 1,3,4,5-tetramethylimidazol-2-ylidene[10] in toluene at −60 °C led to quantitative formation of the corresponding NHC−silylene adduct **2** (for ^1H, ^{29}Si, and ^{13}C NMR data, see the Supporting Information). Subsequent workup of the resulting solution afforded **2** as yellow crystals in 86% yield. The composition of **2** was determined by multinuclear NMR and IR spectroscopies, elemental analysis, and EI-MS (M = 568 amu). The molecular structure of **2** was established by X-ray analysis (Figure 1). The Si(II) atom is bonded to the two nitrogen atoms of the C_3N_2 chelating ligand and the carbon(II) atom of the NHC ligand.

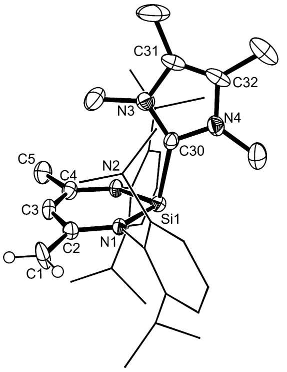


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms (except those at C1) have been omitted for clarity. Selected distances (Å): Si1−N2, 1.802(3); Si1−N1, 1.805(3); Si1−C30, 2.016(3); N1−C2, 1.392(3); N2−C4, 1.401(4); N3−C30, 1.358(4); N3−C31, 1.389(4); N4−C30, 1.359(3); N4−C32, 1.385(4); C1−C2, 1.383(4); C2−C3, 1.427(4); C3−C4, 1.376(4); C4−C5, 1.470(4); C31−C32, 1.329(4). Selected angles (deg): N2−Si1−N1, 97.7(1); N2−Si1−C30, 100.4(1); N1−Si1−C30, 97.8(1).

As expected, the ^{29}Si NMR spectrum of **2** exhibits a significant shielding for the donor-supported silicon(II) nucleus in comparison to the situation observed in **1** ($\delta = -12.0$ ppm vs 88.4 ppm for **1**).

The sum of the bond angles around the Si(II) atom amounts to 295.9°, indicating that the Si−N and Si−C σ bonds have large 3p character at silicon. The six-membered C_3N_2Si ring in **2** is almost planar and features two significantly longer Si−N distances in comparison to those in **1** (1.802 and 1.805(3) Å vs 1.734 and 1.735(1) Å in **1**).[8a] As expected, the five-membered C_3N_2 ring of the NHC donor remains almost planar. The Si1(silylene)−C30(carbene) distance of 2.016(3) Å is significantly longer than the typical Si−C single-bond length in organosilanes (1.86 Å). However, the Si−C distance in **2** is much shorter than that observed in a related NHC−silylene adduct reported by Lappert et al. [2.162(5) Å],[11] indicating a stronger D−A interaction in **2**. Apparently, the stronger acceptor character of the silylene ligand in **2** implies a larger nucleophilicity of the Si(II) site than in **1**. Thus, it can be expected that **2** is more reactive toward oxygenation

10.1021/ja9031049 CCC: $40.75

reagents compared with its precursor **1**.[8a] While no reaction occurred between silylene **1**[8a] and N_2O even after several days at room temperature, exposure of a yellow solution of **2** in toluene to N_2O at −60 °C led to gradual decoloration and formation of a colorless precipitate. Recrystallization of the latter in a toluene/dichloromethane solution at −20 °C furnished colorless blocks of the desired NHC-supported silanone **3** in 94% yield. The compound **3** is only sparingly soluble in hydrocarbons and diethyl ether but very soluble in tetrahydrofuran and dichloromethane. It is stable both in the solid state and in solution under exclusion of moisture. **3** was fully characterized by multinuclear NMR spectroscopy, elemental analysis, and EI-MS ($M = 584$ amu). While the ^{1}H NMR spectrum shows a resonance pattern similar to that of its preccusor **2** with slightly different chemical shifts, the ^{29}Si NMR spectrum exhibits a remarkable shift for the ^{29}Si nucleus in **3** ($\delta = -74.2$ ppm vs −12.0 ppm for **2**). However, the ^{29}Si chemical shift is close to that observed for a related silanoic silylester (−85.1 and −85.8 ppm).[9] The molecular structure of **3** was established by single-crystal X-ray diffraction analysis (Figure 2).

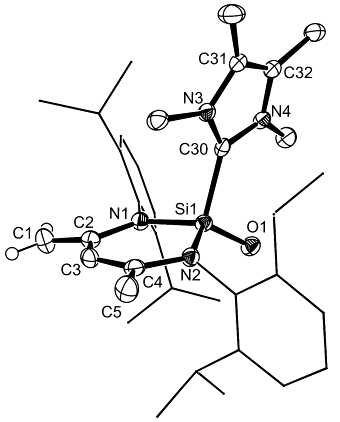


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms (except those at C1) have been omitted for clarity. Selected interatomic distances (Å): Si1−O1, 1.541(2); Si1−N1, 1.745(2); Si1−N2, 1.750(2); Si1−C30, 1.930(2); N1−C2, 1.412(3); N2−C4, 1.411(2); N3−C30, 1.354(3); N3−C31, 1.386(3); N4−C30, 1.357(3); N4−C32, 1.381(3); C1−C2, 1.355(3); C2−C3, 1.451(3); C3−C4, 1.347(3); C31−C32, 1.351(3). Selected angles (deg): O1−Si1−N1, 118.81(8); O1−Si1−N2, 115.21(8); N1−Si1−N2, 102.42(8); O1−Si1−C30, 106.09(8); N1−Si1−C30, 105.61(9); N2−Si1−C30, 108.00(9).

The conformation of the C−N−Si skeleton in **3** is similar to that of **2**, with a slightly puckered six-membered C_3N_2Si ring. However, the vertex of the silicon atom in **3** is occupied by an oxygen atom, leading to distorted tetrahedral coordination of the silicon atom. The structure of **3** is most notable for its remarkably short Si1−O1 distance of 1.541(2) Å. The latter is even shorter than the related values in a silaformamide−borane complex [1.552(2) Å][7] and a silanoic silylester [1.579(3) Å] with tetracoordinate silicon,[9] indicating a stronger silicon−oxygen interaction in **3**. Unexpectedly, both Si−N distances [1.745(2) and 1.750(2) Å] in **3** are significantly shorter than the related values observed in **2** [1.802 and 1.805(3) Å], despite the increased coordination number of the silicon atom in **3**. In addition, the Si1−C30 distance of 1.930(2) Å is shorter than that in **2** [2.016(3) Å]. Interestingly, the latter Si−C value is close to that observed in the NHC-supported :Si═Si: compound **I** [1.927(2) Å].[5] The shortening of the Si−N and Si−C distances in **3** suggests the presence of an ylide-like resonance stabilization of the Si═O double bond that involves a (carbene)$^+$−Si−O$^-$ resonance-betaine structure. Moreover, compound **3** represents a unique isolable silanone complex of type **IV** in which the Si═O double bond is largely stabilized by an NHC carbon lone-pair donor. Because of the coordination of the NHC ligand to the silicon atom, the hypothetical $N_2Si{=}O$ moiety in **3** loses its planarity. Thus, the metric and electronic features of the Si═O double bond in **3** are similar to those in isoelectronic, donor-supported silaimines ($L{\rightarrow}R_2Si{=}NR'$).[2g]

In summary, we have prepared the new NHC−silylene adduct **2** containing a highly nucleophilic Si(II) atom, which undergoes remarkably facile oxygenation with N_2O to give the unique isolable silanone complex **3** featuring a Si═O double bond. The highly nucleophilic Si═O moiety in the NHC-supported silanone **3** is a promising donor for the synthesis of unique Si═O→metal complexes. Related investigations are in progress.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. This work is dedicated to Professor Joachim Sauer on the occasion of his 60th birthday.

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

References

(1) (a) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 17, pp 1015−1142. (b) *Advances in Organometallic Chemistry*, Vol. 39; West, R., Stone, F. G. A., Eds.; Academic Press: San Diego, 1996. (c) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

(2) Selected examples: 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. (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. (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.

(3) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(4) (a) Wiberg, N.; Vasisht, K. S.; Fischer, G.; Meyer, P. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823. (b) Sekiguchi, A.; Kinjyo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755. (c) Sasamori, T.; Hironaka, K.; Sugiyama, Y.; Takagi, N.; Nagase, S.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *J. Am. Chem. Soc.* **2008**, *130*, 13856.

(5) (a) Wang, Y.; Xie, Y.; Wei, Y.; King, R. B.; Schaefer, H. F., III.; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069. (b) Dyker, C. A.; Bertrand, G. *Science* **2008**, *321*, 1050.

(6) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, Chapter 2, p 57 and references 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.

(7) Yao, S.; Brym, M.; van Wüllen, C.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4159.

(8) (a) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628. (b) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6730.

(9) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *J. Am. Chem. Soc.* **2007**, *129*, 7268.

(10) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

(11) Boesveld, W. B.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Schleyer, P. v. R. *Chem. Commun.* **1999**, 755.

JA9031049