Bis[bis(trimethylsilyl)amino]silylene, an Unstable Divalent Silicon Compound

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The divalent germanium and tin compounds [(Me₃Si)₂N]₂Ge and [(Me₃Si)₂N]₂Sn were prepared by Lappert and co-workers almost 30 years ago and are classic examples of stable germylenes and stannylenes.[1,2] It is, therefore, somewhat surprising that the corresponding silicon compound has never been reported. The explanation for this lack is now apparent, for we find that [(Me₃Si)₂N]₂Si: (**1**), although stable at low temperatures in solution, undergoes rapid decomposition above ~0 °C.

Compound **1** was prepared starting from hexamethyldisilazane and dichlorosilane, as shown in Scheme 1. The intermediate silane **2** was converted to the dibromo compound **3**, which was reduced with potassium graphite (KC₈) to give **1**. When a solution of **3** in THF was stirred with KC₈ at −78 °C, a bright orange-red color developed in solution. The color disappeared within minutes at room temperature, but it persisted for more than 12 h at −20 °C. Addition of methanol or phenol to the orange-red solution discharged the color and produced trapping products, identified as [(Me₃Si)₂N]₂Si-(H)OCH₃ and [(Me₃Si)₂N]₂Si(H)OC₆H₅, in good yield.[3] These are the expected products from the reaction of silylene **1** with the alcohols (Scheme 1).[4,5]

**Scheme 1.** Synthesis and Reactions of Silylene **1**
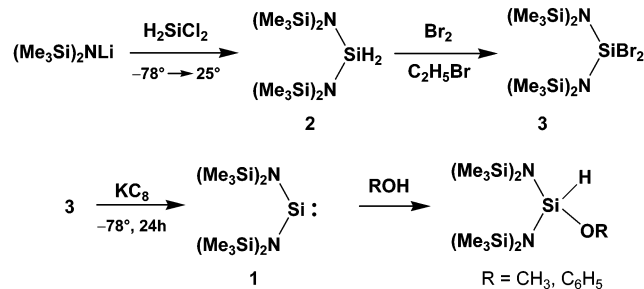
We determined the NMR spectrum of the product in THF−C₆D₆ solution at −20 °C. In the ²⁹Si spectrum, it exhibited two resonances: one at −0.30 ppm attributable to the Me₃Si silicons, and a strongly deshielded reasonance at +223.9 ppm which we assign to the silylene silicon. It is interesting to compare this resonance with the chemical shifts for the stable silylenes **4**−**7** (Chart 1).[6−9] In dialkylene **7**, which is stabilized only by steric hindrance, the silicon resonance lies at +567 ppm.[9] The five-membered ring diaminosilylenes **4**−**6** have silicon chemical shifts from +78 to +119 ppm. In these cyclic silylenes, the nitrogen lone pairs are parallel to the vacant p orbital on silicon, so that efficient π-overlap can take place, greatly reducing the deshielding. The resonance for **1** lies between these two extremes.[10]

The geometry of silylene **1** was calculated using B3LYP3/6-31G(d) (Figure 1),[11] and chemical shifts were estimated from a

Chart 1 ²⁹Si NMR Chemical Shifts for Stable Silylenes[6−9]

δ = 78 ppm   δ = 119 ppm   δ = 97 ppm   δ = 567 ppm
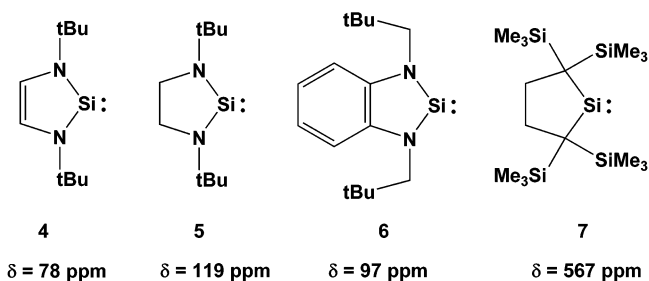
GIAO/B3LYP calculation.[12] The chemical shift for the silylene silicon in **1** was calculated to be +247.8 ppm, about 24 ppm higher than the measured value. DFT-based methods such as GIAO/B3LYP calculations are known to overestimate paramagnetic contributions to the chemical shielding, predicting overly deshielded chemical shifts in silylenes which have usually small HOMO−LUMO separations. For these molecules, MP2 based methods give more reliable results.[6b,13] The size of **1** prevents, however, the use of this more accurate method.
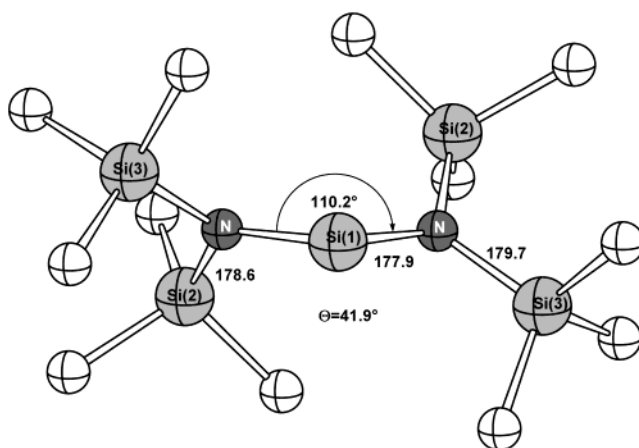
Figure 1. Calculated structure of **1** (B3LYP/6-31G(d)). Bond lengths are in picometers; hydrogens are omitted for clarity.

Model calculations for simple bisaminosilylene (H₂N)₂Si:, summarized in Figure 2, show that the ²⁹Si chemical shift strongly depends on the twist angle Θ between the H₂N and the N₂Si planes. For a planar diaminosilylene (Θ = 0°), δ²⁹Si around 100 ppm was predicted, while for the perpendicular diaminosilylene (Θ = 90°), a strong low field shift of the resonance to around 400 ppm was expected. This general trend was predicted by both the density functional based method and the MP2 based method, although the difference between the methods was larger for the perpendicular diaminosilylenes than for the planar silylenes.

From these calculations, it appears that Θ is the major factor determining δ²⁹Si in aminosilylenes. The correlation correction to

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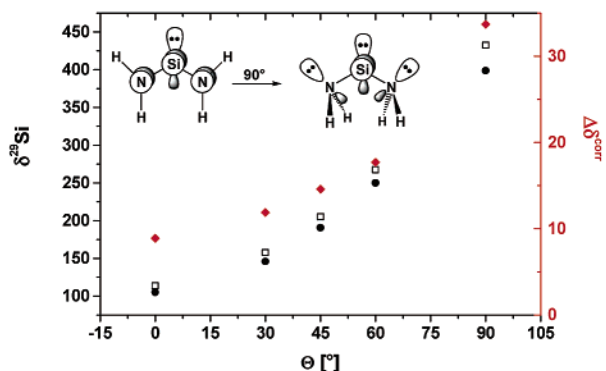[†] Hannam University.
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Figure 2. Angular dependence of calculated δ^{29}Si (● GIAO/MP2, □ GIAO/B3LYP, left) and of $\Delta\delta^{corr} = \delta^{29}$Si (GIAO/B3LYP) $- \delta^{29}$Si (GIAO/MP2) in diaminosilylene (◆, right).

the chemical shift, $\Delta\delta^{corr}$, which can be applied to correct the DFT calculated NMR chemical shift was also a function of Θ. For [(Me$_3$-Si)$_2$N]$_2$Si: with a calculated Θ of 42°, $\Delta\delta^{corr} \approx -15$ ppm, resulting in a predicted chemical shift of 233 ppm for the silylene, in quite reasonable agreement with the experimental data. Unlike the quasi-stable silylene (^{i}Pr$_2$N)$_2$Si reported by Kira et al., **1** does not appear to dimerize in solution.[14,15] This is in agreement with theoretical calculations, which indicate that dimerization of **1** is prevented by steric interactions between Me$_3$Si groups.[16,17]

Quantum mechanical calculations suggest that **1** is thermodynamically less stable than [(Me$_3$Si)$_2$N]$_2$Ge: and [(Me$_3$Si)$_2$N]$_2$Sn: by 17.3 and 31.0 kcal mol^{-1}, respectively.[18] This provides a rationalization for the observed thermal instability of **1**, and it is in agreement with the increased stability of low valent states of the heavier group 14 elements.[19]

Initial examination of the decomposition products from **1** suggests that they are complex. The decomposition, and additional reactions of the silylene, will be the objects of further study. It remains to be seen if **1**, like the corresponding Ge and Sn compounds, can serve as a source for other divalent substances.[20]

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Gynane, M. S. J.; Harris, D. H. G.; Lappert, M. F.: Power, P. P.; Riviere, P.; Riviere-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.
(2) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895.
(3) Experimental details for the synthesis of **1**, **2**, and **3** are given in the Supporting Information. Compound **2**: yield 73%, ^{1}H NMR (CDCl$_3$) δ 0.198 (s, SiCH_3, 36H), 4.792 (s, SiH, 2H); ^{13}C NMR (CDCl$_3$) δ 4.204; ^{29}Si NMR (C$_6$D$_6$) δ −42.3 (N$_2$SiH_2), 3.2 (Me$_3$SiN). Compound **3**: white crystals, mp 157−8 °C, yield 44%, ^{1}H NMR (CDCl$_3$) δ 0.406 (s, SiCH_3, 36H); ^{13}C NMR (CDCl$_3$) δ 5.695; ^{29}Si NMR (C$_6$D$_6$) δ −53.5 (N$_2$SiBr$_2$), 5.1 (Me$_3$SiN). [(Me$_3$Si)$_2$N]$_2$Si(H)OCH$_3$: pale yellow oil, 74%, ^{1}H NMR (C$_6$D$_6$) δ 0.299 (Si−CH$_3$), 3.271 (s, 3H, Si−OCH$_3$), 4.902 (s, 1H, Si−

H); ^{13}C NMR (C$_6$D$_6$) δ 7.40 (Si−CH$_3$, J_{C-H} = 119 Hz), 51.98 (Si−OCH$_3$, J_{C-H} = 142 Hz); ^{29}Si NMR (C$_6$D$_6$) δ 3.0 (Me$_3$SiN), −36.3 (N$_2$Si(H)-OCH$_3$, J_{Si-H} = 246 Hz); IR 2142 cm^{-1} (Si−H). [(Me$_3$Si)$_2$N]$_2$Si(H)OC$_6$H$_5$: colorless oil, 61%, ^{1}H NMR (C$_6$D$_6$) δ ∼0.2 (Si−CH$_3$); 5.396 (s, 1H, Si−H); 7.16−7.06 (m, OC$_6$H$_5$); ^{13}C NMR (C$_6$D$_6$) δ 4.95 (Si−CH$_3$), 126.7, 121.7, 114.7 (Si−OC$_6$H$_5$); ^{29}Si NMR (C$_6$D$_6$) δ 2.7 (Me$_3$SiN); −44.3 (N$_2$Si(H)OC$_6$H$_5$, J_{Si-H} = 253 Hz); IR 2142 cm^{-1} (Si−H).
(4) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*, 2nd ed.; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 1998; Vol. 2, Chapter 43, pp 2463−2568.
(5) Schmedake, T. A.; Haaf, M.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704.
(6) (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (b) West, R.; Buffy, J. J.; Haaf, M.; Müller, T.; Gehrhus, B.; Lappert, M. F.; Apeloig, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1639.
(7) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785.
(8) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931.
(9) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722.
(10) ^{13}C NMR for **1** (C$_6$D$_6$, −20 °C) δ 6.93 (Si−CH$_3$, $^1J_{C-H}$ = 118 Hz).
(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 94 and 98*, revisions A.3−A.9; Gaussian, Inc.: Pittsburgh, PA, 1995 and 1999.
(12) GIAO/B3LYP: A 6-311G(3d,p) (Si); 6-311G(d,p) (C, N, H) basis set was used. Relative chemical shifts versus calculated TMS σ(Si) = 323.5. δ^{29}Si: 247.8 (Si1), 4.6 (Si3), −4.7 (Si2). δ^{13}C: 6.2, 5.3. (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (e) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (f) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.
(13) GIAO/MP2: A 6-311G(3d,p) basis set was used. Relative chemical shifts versus calculated TMS σ(Si) = 364.3. (a) Gauss, J. *Chem. Phys.* **1993**, *99*, 3629. (b) Ottoson, C.-H.; Cremer, D. *Organometallics* **1996**, *15*, 5495. (c) For a short review, see: Webb, G. A. In *Encyclopedia of NMR Spectroscopy*; Grant, D., Webb, G. A., Eds.; Wiley: New York, 1996; p 4316.
(14) Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955.
(15) Takahashi, M.; Tsutsui, S.; Sakamoto, K.; Kira, M.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **2001**, *123*, 347.
(16) Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **2002**, *124*, 3457.
(17) To examine the possibility of complexation between the solvent THF and the silylene, the system Me$_2$O/[(Me$_3$Si)$_2$N]$_2$Si: was checked computationally. The result was that dimethyl ether is only very weakly coordinated to the silylene by ca. 2.1 kcal mol^{-1} (at B3LYP/6-31G(d)). Even when an additional contribution of ca. 2 kcal mol^{-1} from dispersion forces is allowed for, this number is too low to be chemically significant at −20 °C. Thus, it seems that we observe under our experimental conditions the free silylene.
(18) Calculated using the isodesmic equation: **1** + H$_2$E[N(SiMe$_3$)$_2$]$_2$ → **1**H$_2$ + :E[N(SiMe$_3$)$_2$]$_2$, E = Ge, Sn; at B3LYP/6-311+G(2d,p)(C, N, H), SDD-(Si, Ge, Sn)//B3LYP/6-31G(d)(C, H, N), SDD(Si, Ge, Sn).
(19) Interestingly, substitution with two N(SiMe$_3$)$_2$ groups stabilizes H$_2$Ge: and H$_2$Sn: to a similar extent as H$_2$Si; that is, the divalent compounds [(Me$_3$Si)$_2$N]$_2$E: are more stable than H$_2$E: by 25.9, 26.6, and 23.4 kcal mol^{-1} for E = Si, Ge, Sn, respectively.
(20) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

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