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Reaction of a Stable Silylene with Covalent Azides: A New Synthesis for Silaimines

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Compounds with double bonds to silicon were first described in 1981, when the use of bulky substituents on silicon allowed the isolation of compounds with stable Si=Si[1] and Si=C[2] double bonds. Research on these highly reactive compounds continues unabated and has led to compounds with stable double bonds Si=E where E = Ge,[3] N,[4] P,[5] and As[6] and S.[7]

The synthesis of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene (**1**, LSi:), a stable silylene,[8] opens new possibilities for the synthesis of doubly bonded silicon compounds.[9] We now report on the formation $LSi(THF){=}NC(Ph)_3$ (**4**), a stable silaimine, from LSi (**1**) and Ph_3CN_3.

Although a large number of stable germaimines has been obtained from germylenes and azides,[10] examples of stable silaimines are still rare. The first silaimines were obtained by N. Wiberg et al. in 1986 by thermal salt elimination and have been structurally characterized.[4]

The reaction of **1** with the covalent azides Me_3SiN_3 and Ph_3CN_3 resulted in rapid evolution of nitrogen. The temperatures needed for the reaction reflect the relative reactivity of **1** toward the two different azides (see Scheme 1).

Reaction of **1** with Ph_3CN_3 resulted in the clean formation of the silaketimine **4**, stabilized by a THF molecule coordinated to silicon.[11] Use of the less hindered trimethylsilyl azide did not result in formation of the analogous silaimine **2**. Instead, the silaimine is trapped by the addition of a second equivalent of azide resulting in the formation of **3**.[11] No formation of **2** could be detected by NMR (^1H, ^{13}C, ^{29}Si) of the crude reaction mixture.

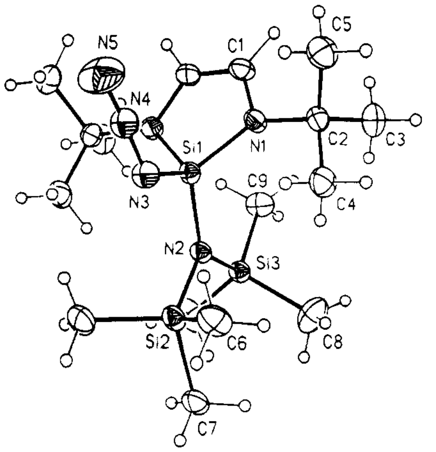
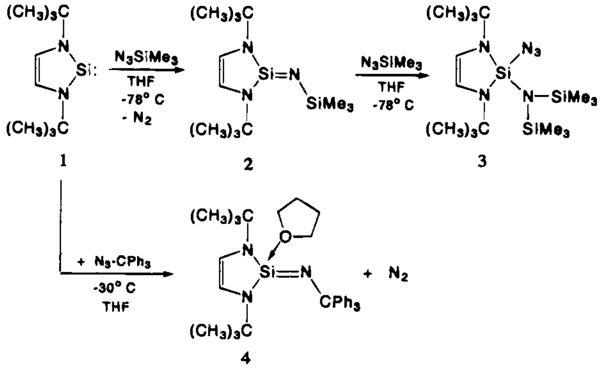


Figure 1. 1. Molecular structure of $({}^{t}BuNCH{=}CHN{}^{t}Bu)Si(N_3)N(SiMe_3)_2$ (**3**).[12] ORTEP view with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond distances (pm) and bond angles (deg) are as follows: Si(1)−N(1) 172.8(2), Si(1)−N(2) 170.4(3), Si(1)−N(3) 176.0(3), N(1)−C(1) 141.6(3), C(1)−C(1A) 133.0(5), N(1)−C(1) 141.6(3), N(2)−Si(2) 178.1(3), N(2)−Si(3) 177.2(3), N(3)−N(4) 121.9(5), N(4)−N(5) 112.8(5), N(1)−Si(1)−N(1A) 92.9(1), N(1)−Si(1)−N(2) 120.1(1), N(1)−Si(1)−N(3) 112.1(1), N(2)−Si(1)−N(3) 100.2(1), Si(2)−N(2)−Si(3) 118.9(2), Si(1)−N(2)−Si(3) 117.9(2), Si(1)−N(3)−N(4) 124.5(3), N(3)−N(4)−N(5) 174.8(4).

Scheme 1. Reaction of the Stable Silylene **1** with Covalent Azides



The structures of **3** and **4** were established by single-crystal X-ray crystallography.[12] In **3**, both N(1) and N(2) are in planar coordination; the azide and the bis(trimethylsilyl)amino group are coplanar with the plane of symmetry bisecting the five-membered ring. The *tert*-butyl groups are slightly tilted toward the azide group, out of the plane defined by the N_2Si ring fragment (torsion angle N(1a)−Si(1)−N(1)−C(2), −177.0(2)°), and the C_2N_2Si ring is slightly puckered (torsion angle N(1a)−Si(1)−N(1)−C(1) 2.0(2)°).

The short Si(1)−N(3) bond (159.9 pm) shows **4** to be a silaimine stabilized by the donor molecule THF. The Si=N distance is similar to that reported[4] for $Me_2Si(THF){=}NSi(tBu)_3$ (**6**, two crystallographically independent molecules, Si=N: 158.8(9)/157.4(10) pm). The Si−O distance, however, is significantly shortened in **4** (181.5(3) pm as compared to 188.8(8)/186.6(8) pm). This suggests that THF is more strongly coordinated in **4** than in **6** and could explain why we have been unable to obtain the donor-free silaimine **5** from **4**.

The two endocyclic nitrogen atoms in **4** are planar (the sum of the bond angles is 360°). The geometry of the five-membered C_2N_2Si ring is best described as an envelope conformation with the Si atom tilted off the C_2N_2 plane. Although Si(1) is clearly tetracoordinate, its coordination by the three nitrogen atoms is close to planar (the sum of the bond angles is 350°).

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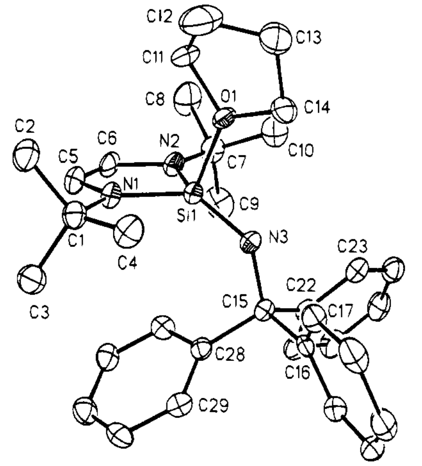

Figure 2. 2. Molecular structure of (^{t}BuNCH=CHN^{t}Bu)Si=NC(Ph$_3$)·(THF).[12] ORTEP view with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond distances (pm) and bond angles (deg) are as follows: Si(1)–N(1) 173.5(3), Si(1)–N(2) 173.6(3), Si(1)–N(3) 159.9(4), Si(1)–O(1) 181.5(3), N(3)–C(15) 144.4(6), C(5)–C(6) 133.4(6), C(5)–N(1) 140.0(5), C(6)–N(2) 141.0(5), N(1)–Si(1)–N(2) 91.8(2), Si(1)–N(3)–C(15) 134.6(2), O(1)–Si(1)–N(3) 98.2(1), O(1)–Si(1)–N(2) 100.4(2), O(1)–Si(1)–N(1) 103.5(2), C(1)–N(1)–Si(1) 131.3(2), C(5)–N(1)–Si(1) 109.5(3), C(5)–N(1)–C(1) 119.0(3).

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and further details on the crystallography of **3** and **4** (25 pages); listing of observed and calculated structure factors for **3** and **4** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) (a) Synthesis of **3**: A solution of 1.45 g of **1**[8] (7.4 mmol) dissolved in 60 mL of THF was cooled to −20 °C and 2 equiv of Me_3SiN_3 (14.8 mmol, 1.71 g, 1.96 mL) dissolved in 20 mL of THF was added over a period of 5 min. After stirring at room temperature for 24 h and removal of the solvent, the crude reaction product was sublimed at 80 °C / 0.1 Torr; 2.09 g of pure **3** (71%) was isolated as white needles. (b) Synthesis of **4**: A solution of 1.45 g of **1**[8] (7.4 mmol) dissolved in 60 mL of THF was cooled to −50 °C, and 1 equiv of Ph_3CN_3 (7.4 mmol, 2.51 g, Pfaltz & Bauer T32438) dissolved in 20 mL of THF was added (5 min). After stirring at room temperature for 24 h and removal of the solvent, the crude reaction product was dissolved in 120 mL of *n*-hexanes. Cooling to −10 °C gave 2.53 g of pure **4** (65%). (c) Selected spectroscopic data: NMR data (in ppm and Hz) were recorded at room temperature in C_6D_6 solution at 200 MHz (^{1}H), 126 MHz (^{13}C), and 99.3 MHz (^{29}Si), **3**: ^{1}H-NMR: δ 0.25 + 0.34 (18H, s, Si(CH_3)$_3$), 1.27 (18H, s, C(CH_3)$_3$), 5.67 (s, 2H). ^{13}C-NMR: 4.40 + 5.50 (Si(CH$_3$)$_3$), 31.3 (C(CH$_3$)$_3$), 51.9 (C(CH$_3$)$_3$); 112.0 (=CH). δ $_{29}$Si: −46.9 (s). MS (40 eV, positive ions): 398 (70) [M^{+}], 383 (10), 341 (22), 309 (55), 286 (30), 57 (100), 41 (64), 28 (38). IR (Nujol): 2139 s, 1307 m, 1226 s, 1224 m, 1154 w, 1113 m, 1094 m, 1054 w, 1019 m, 956 s, 879 s, 844 m, 803 m, 722 s, 566 m. **4**, δ ^{1}H: 1.05 (18H, s, C(CH_3)$_3$), 1.32 (4H, m, CH$_2$CH_2), 3.73 (4H, m, OCH_2), 5.70 (s, 2H, =CH), 6.95 (m, Ph), 7.25 (m, Ph), 7.76 (m, Ph). δ ^{13}C: 25.5 (t, ^1J = 132.8 Hz, CH$_2$$CH_2$), 31.1 (s ($CH_3$)$_3$), 51.1 ($C$(CH$_3$)$_3$), 69.5 (t, ^1J = 148.1 Hz, OCH$_2$), 110.1 (dd, ^1J = 177.7 Hz, ^2J = 7.2 Hz, =CH), 127.0, 128.8, 129.1, 130.0, 140.9, 155.6 (s, CPh$_3$). δ ^{29}Si: −66.6 (s).

(12) Crystal data. **3**, orthorhombic, space group *Pnma*, $a = 18.5253(14)$ Å, $b = 14.110(2)$ Å, $c = 8.9577(4)$ Å, $V = 2341.5(3)$ Å^3, $Z = 4$, $D_c = 1.131$ g cm^{-3}, $F(000) = 872$, total unique data 1652 ($R_i = 4.54\%$), number of observations [$(F) > 4\sigma(F)$] 1464, $R = 0.048$, $R_w = 0.069$; **4**, triclinic, space group $P\bar{1}$, $a = 10.899(2)$ Å, $b = 12.6348(13)$ Å, $c = 13.9071(13)$ Å, $\alpha = 87.327(13)°$, $\beta = 67.854(8)°$, $\gamma = 67.663(11)°$, $V = 1630.2(4)$ Å^3, $Z = 2$, $D_c = 1.159$ g cm^{-3}, $F(000) = 618$, total unique data 4248 ($R_i = 4.23\%$), number of observations [$(F) > 4\sigma(F)$] 3141, $R = 0.055$, $R_w = 0.072$.