

Synthesis and Reactivity of a Base-Free N-Heterocyclic Silanimine[†]

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Received June 9, 2010

Summary: Reaction of the N-heterocyclic silylene $(HCNDipp)_2$ -Si $(1, Dipp = 2,6-iPr_2C_6H_3)$ with the terphenyl azide ArN_3 ($Ar = 2,6-Mes_2C_6H_3$, $Mes = 2,4,6-Me_3C_6H_2$) in THF yielded the base-free silanimine $(HCNDipp)_2Si=NAr$ (2) with the almost linear Si=NC geometry in high yield. Reaction of 2 with sulfur and H_2O resulted in the 1,3-addition of S_2 to the C_2N_2Si ring and 1,2-addition of H_2O to the Si=N bond, respectively.

Since the first isolable silene and disilene were reported by Brook and West in 1981,¹ multiply bonded group 14 elemental species have been some of the main focuses in main-group chemistry.² Silanimines, doubly bonded silicon-nitrogen species, have attracted much attention as the heavy analogues of imines. The first silanimines were reported independently by Wiberg and Klingebiel in 1986.³ Although a fair number of stable silanimines have been isolated and structurally characterized, the majority of them are stabilized by the coordination of a Lewis base, such as THF, pyridine and other donors, ^{4,5,7a} to the silicon center, and stable donor-free silaimines with a three-coordinate silicon atom remain extremely rare in number. To the best of our knowledge, there are only two donor-free silanimines, namely Bu^t₂Si=N-SiBu^t₃ and $Bu_2^tSi=N-SiBu_2^tPh$, that have been structurally char-aterized.^{3b,5} The most interesting structural feature of the two compounds is their almost linear Si=N-Si angle. Subsequent

theoretical calculations on the model compound $H_2Si=NSiH_3$ predict a very similar geometry as a result of the electropositive silyl group on the nitrogen atom.⁶ However, there are no examples of base-free silanimines with a Si=N-C skeleton that have been isolated and structurally characterized for comparison. This situation may be largely related to the highly polarized Si-N double bond and limited synthetic approaches.

The successful isolation of stable N-heterocyclic silvlenes opens a new and facile way for the generation of doubly bonded silicon species. Thus, reactions of the stable silylenes A-E (Chart 1) toward various organic azides, such as Me₃SiN₃, Ph₃CN₃, PhN₃, p-MeC₆H₄-N₃, Ph₃SiN₃, and AdN₃ (Ad = adamantyl), have been investigated.⁷ There are four types of final products (Chart 2) that have been prepared through the silvlene-azide reactions, indicating that steric effects of both silvlenes and azides are the main factors for the control of reaction products. Notably, a stable silanimine with a THF molecule strongly coordinated to the silicon center was obtained and structurally characterized by employing the bulky azide Ph₃SiN₃ and the silylene A.^{7a} Herein, we report on the isolation and structural characterization of the base-free silanimine (HCNDipp)₂Si=NAr (2) prepared by the reaction of our recently reported N-aryl-substituted silvlene 1^8 with the bulky terphenyl azide 2,6-Ar₂C₆H₃N₃ $(Ar = 2,4,6-Me_3C_6H_2)$.⁹ Interestingly, the N-heterocycle of the silanimine undergoes a 1,3-cycloaddition reaction with sulfur to give a bicyclic donor-supported silanimine.

Treatment of **1** with 2,6-Ar₂C₆H₃N₃ in THF resulted in immediate and rapid evolution of nitrogen. The base-free silanimine **2** was obtained as yellow crystals in ca. 85% yield after workup. **2** has been fully characterized by ¹H, ¹³C, and ²⁹Si NMR and IR spectroscopy, elemental analysis, and an X-ray single-crystal analysis. The ²⁹Si resonance of **2** in CDCl₃ occurs at δ –49.0 ppm, slightly deshielded compared to that in the solvated silanimine (HCNBu¹)₂Si(THF)-NC(C₆H₅)₃ (δ –66.6 ppm)^{7a} because of the electron deficiency of the low-coordinate silicon atom of **2**.

Single crystals of **2** suitable for X-ray single-crystal analysis were obtained from *n*-hexane at -40 °C. The structure is shown in Figure 1 with selected bond parameters.¹⁰ The

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[†] Dedicated to Prof. Herbert W. Roesky on the occasion of his 75th birthday. *To whom correspondence should be addressed. E-mail: cmcui@ nankai.edu.cn.

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[Si] = N-heterocyclic silylene fragment

silicon atom in 2 is three-coordinated and adopts a trigonalplanar geometry (sum of the bond angles around the silicon 359.93(9)°). The Si1-N3 bond distance (1.5329(16) Å) is the shortest one observed so far compared to those in the structurally characterized free and base-stabilized silanimines (1.568–1.665 Å).^{3a,5} The most notable structural feature of 2 is the almost linear Si1-N3-C27 angle $(176.69(15)^{\circ})$. A similar linear Si-N-Si angle (177.8(2)°) was previously observed in the N-silvl-substituted silanimine Bu^t₂Si=NSi-Bu^t₃, which is in accord with ab initio calculations (6-31G* basis set) on $H_2Si=NSiH_3$ (175.6°). On the other hand, the same basis set calculations on H₂Si=NH predicted a bent Si-N-H geometry (126.6°), with the low linearization barrier of ca. 6.0 kcal/mol at MP4/6-31G*.6,11 Moreover, theoretical predictions on H₂Si=NMe with a 6-31G(d) basis set also indicated the bent Si-N-C geometry (132.6°).¹² We reasoned that the almost linear Si1-N3-C27 angle in 2 may result from the steric effects afforded by the Ar and Dipp groups as well as the crystal packing (some close intermolecular contacts among the aryl carbon atoms are present in the unit cell: 3.629, 3.730, 3.801 Å). The five-membered SiN_2C_2 ring is essentially planar (average deviation from the plane 0.0028 Å). The two endocyclic Si-N distances (Si1-N1 = 1.7040(16) Å; Si1-N2 = 1.6990(16) Å) are very close to the corresponding Si-N bond lengths in (HCNDipp)₂SiCl₂ (1.702Å).¹³ The N3–C27 bond length of 1.375(2) Å is shortened, probably due to the sp hybrid N3 atom.

Reaction of the silanimine 2 with elemental sulfur in toluene at 60 °C for 2 days lead to the degradation of S_8 to give the donor-supported silanimine 3 containing an S2 subunit in 88% yield (Scheme 1). 3 has been fully characterized by multinuclear NMR and IR spectroscopy, elemental analysis, and an X-ray single-crystal analysis. The ²⁹Si resonance of 3 in



Figure 1. Ortep drawing of 2 with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (A) and angles (deg): Si1-N1 = 1.7040(16), Si1-N2 =1.6990(16), Si1-N3 = 1.5329(16), N1-C13 = 1.413(2), N2-C14 = 1.413(2), N3-C27 = 1.375(2), C13-C14 = 1.323(3); N1-Si1-N2 = 93.23(8), N1-Si1-N3 = 133.50(9), N2-Si1-N3 = 133.20(9), C27-N3-Si1 = 176.69(15), C1-N1-C13 = 119.75(15),C13-N1-Si1 = 109.38(12), C14-N2-Si1 = 109.38(12), C1-N1-Si1 = 130.81(12), C15-N2-Si1 = 132.63(13).





CDCl₃ occurs at δ -72.9 ppm, which is shifted to high field compared to that for 2 but close to that for (HCNBu^t)₂Si-(THF)NC(C₆H₅)₃ (δ –66.6 ppm).^{7a} The ¹H NMR spectrum of 3 shows a single peak for the SiN₂C₂ ring protons (d_8 -toluene, CD₂Cl₂, and CDCl₃) at 298 K, and the ¹³C NMR spectrum for the ring carbon also exhibits only one broad singlet (105.1 ppm, CDCl₃), indicating its fluxional behavior due to the S_2 swinging between the two carbon atoms. The variable-temperature ¹H NMR spectra showed that the single peak broadened when the temperature was lowered to 233 K and disappeared as the temperature dropped to 193 K. The same phenomena were observed in the ¹³C NMR spectra at these temperatures. However, the single peak reappeared in both the ¹H and ¹³C NMR spectra when the temperature rose to 233 K. It is quite possible that the signals are too broad to be observed at low temperatures. The structure of **3** was finally confirmed by an X-ray single-crystal analysis.

Single crystals of 3 were obtained from *n*-hexane/THF at -40 °C.¹⁴ There are two independent molecules in the asymmetric unit, and only one of the molecules is shown in

⁽¹⁰⁾ The X-ray data were collected on a Rigaku Saturn CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 113 K. The structure was solved by direct methods (SHELXS-97)¹⁸ and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).¹⁹ Crystal data for $2:_{C_50}H_{61}N_3Si$, fw = by a riding model (SHELXL-97).¹⁹ Crystal data for **2**: $C_{50}H_{61}N_3Si$, fw = 732.11, monoclinic, space group $P_{2_1/c}$, a = 12.956(3)Å, b = 13.282(3)Å, c = 25.126(5)Å, $\beta = 90.31(3)^\circ$, V = 4323.6(15)Å³, Z = 4, $\rho_{calcd} = 1.125$ g cm⁻³, 24981 reflections measured, 7612 unique reflections ($R_{int} = 0.0323$), R1 = 0.0577 ($I > 2\sigma(I)$), wR2 = 0.1533 (all data). (11) Avakyan, V. G.; Sidorkin, V. F.; Belogolova, E. F.; Guselnikov,

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⁽¹⁴⁾ Crystal data for 3: $C_{103}H_{129}N_6S_4Si_2$, fw = 1635.54, triclinic, space group $P\bar{1}, a = 10.9167(19)$ Å, b = 19.022(3) Å, c = 23.425(3) Å, $\beta = 83.910(9)^\circ$, V = 4659.3(12) Å³, Z = 2, $\rho_{calcd} = 1.166$ g cm⁻³; 30.789 reflections measured, 17 892 unique reflections ($R_{int} = 0.0323$), R1 = $0.0558 (I > 2\sigma(I)), wR2 = 0.1470$ (all data).



Figure 2. Ortep drawing of one of the two independent molecules of **3** with 30% probability ellipsoids. Hydrogen atoms and solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for the molecule with the Si1 atom (selected parameters for the molecule with Si2 atom are also given for comparison): Si1–N1 = 1.892(2)/Si2–N4 = 1.892(2), Si1–N2 = 1.7448(18)/Si2–N5 = 1.7410(18), Si1–N3 = 1.5709(19)/Si2–N6 = <math>1.5866(19), Si1–S1 = 2.2183(8)/Si2–S3 = 2.2056(8), C27–N3 = 1.373(3)/C77–N6 = <math>1.381(3), C1-N1 = 1.309(3), C2-N2 = 1.398(3), C1-C2 = 1.473(3); N2–Si1–N3 = 121.94(10), N1–Si1–N3 = 124.57(9), N1–Si1–N2 = 87.05(9), N3–Si1–S1 = 124.77(7), N2–Si1–S1 = 97.29(7), N1–Si1–S1 = 91.56(6), C27–N3–Si1 = 157.28(16)/C77–N6–Si2 = 145.40(16).

Figure 2 with selected bond lengths and angles. The silicon atom is four-coordinate and is covalently coordinated to two nitrogen atoms and one sulfur atom, and the other coordination site is occupied by an imine nitrogen atom. Consequently, the Si=N double bond lengths (1.5709(19) and 1.5866(19) Å) in the two independent molecules of 3 are slightly lengthened compared to that found in 2(1.5329(16) Å). The central Si=N-C angles in the two molecules of 3(157.28)and 145.40°) are significantly contracted in comparison with that in 2 due to the four-coordinate silicon atoms in 3. In the SiN₂C₂ rings of 3, the two Si-N bonds in one molecule are significantly different (1.892(2) vs 1.7448(18) Å and 1.892(2) vs 1.740(18) Å in the two independent molecules); the longer bonds are consistent with a dative Si–N bond. Consequently, one C-N single bond (1.398(3)/1.410(3) Å) and one C-N double bond (1.309(3)/1.297(3) Å) are observed in the SiN₂C₂ ring. The bond distances of Si-S, S-S, and S-C in 3 are in good agreement with those reported in the literature.¹⁵

The mechanism for the formation of 3 is not clear at this stage. Due to the highly polarized Si-N bond, it is

quite possible that S_8 attacks the partially positive silicon center to result in the fragmentation of S_8 and formation of the electrophilic sulfur center Si-S-S^{δ +}, which could either be attacked by the C=C bond or the negatively charged nitrogen atom.¹⁶ Since the formation of the fivemembered ring in 3 is favorable, the reaction exclusively yielded 3.

The reaction of **2** with water resulted in the formation of the amino–silanol **4** via the 1,2-addition of H₂O to the Si=N double bond.^{3a,4c-4e,17} Compound **4** has been fully characterized by multiple nuclear NMR and IR spectroscopy and elemental analysis. The H₂O addition product **4** displays two single peaks at δ 2.46 and 3.96 ppm, indicating the formation of N–H and Si–OH bonds.

In conclusion, the first stable base-free silanimine, 2, with an almost linear Si=N-C skeleton has been prepared and structurally characterized. Reaction of 2 with elemental sulfur yielded the novel imine-supported silanimine 3. 2 is a new addition to the rare examples of well-defined base-free silanimines. The structural analysis of 2 alone with the known Bu^t₂Si=N-SiBu^t₃ disclosed that both the steric and electronic effects of the substituents on the unsaturated nitrogen atom are responsible for the central geometry of unsupported silanimines. Initial examinations of the reactivity of 2 demonstrated that either the five-membered heterocycle or the Si=N double bond may be involved in chemical reactions, as shown by the 1,3-addition of $S_{\rm 2}$ to the SiN₂C₂ ring and 1,2-addition of H₂O to the Si=N double bond. Further studies on the reactivity of 2 and theoretical calculations on 2 and the related systems are currently in progress.

Acknowledgment. We are grateful to the National Natural Science Foundation of China (Grant No. 20725205) and 111 plan for the support of this work.

Supporting Information Available: Text and figures giving experimental details for the synthesis and characterization of the compounds reported in this paper and representive VT NMR spectra of **3** and CIF files giving crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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