Frauke Schödel, Michael Bolte and Hans-Wolfram Lerner*

Crystal structure and thermal decomposition of the Silanimine tBu₂Si=N-Si(tBu)₃·thf

Abstract: The thf-complexed silanimine tBu₃Si=N-Si(tBu)₂·thf (1(thf)); monoclinic, space group C2/c was prepared by the reaction of 1 equivalent of tBu₃SiClN₃ with 1 equivalent of Na[Si(tBu)₃] in Bu₂O and subsequent addition of thf. By heating a benzene solution over a period of 11 d –140 °C, 1(thf) slowly released the thf donor to form the uncomplexed silanimine 1. However, under these conditions the silanimine 1 is unstable and is thermolized uncomplexed silanimine. However, under these conditions the silanimine 1 is unstable and is thermolized uncomplexed silanimine. However, under these conditions the silanimine 1 is unstable and is thermolized uncomplexed silanimine.

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However, when this reaction was carried out in thf instead of Bu₂O as solvent, the sodium amide tBu₃SiCl⋅NNa–Si(tBu)₃ was formed rather than the silanimine 1 [21]. In this context, it should also be noted that the 2:1 reaction of tBu₃ClSiN₃ with Na[Si(tBu)₃] [19, 20] yielded the [3+2] cycloadduct of tBu₃ClSiN₃ with 1 [22, 23].

Recently, we have reported that the tBu-substituted, donor-free silanimines 1 and tBu₃Si=N-SiPhHtBu₃ [24] are thermolabile compounds that already decompose in benzene at r.t. [25]. In the course of their thermolysis, b-H elimination takes place to form isobutene. The purpose of the work described in this paper is to examine the thermal and chemical behavior of the thf-complexed silanimine 1(thf) and to make a comparison with the reactivity of its methyl-substituted congeners Me₂Si=N–Si(tBu)₂·thf (2(thf)). Additionally, an X-ray crystal structure determination of the thf-complexed silanimine 1(thf) was performed to compare its structural parameters with those of the parent silanimine 1.

1 Introduction

In the past few decades, the reactivity of unsaturated silicon compounds has been extensively studied. In this period, several examples of stable compounds with Si=N double bonds (silanimines) have been synthesized and structurally characterized [1–18]. Ab-initio calculations have shown that the parent silanimine H₂Si=N–SiH₂ possesses an almost linear Si=N–Si skeleton with a short Si=N double bond and a short Si=N single bond [11]. Additionally, these calculations have revealed a negative charge of 1.71 on the N center of H₂Si=N–SiH₂. It is interesting to note that the molecular structure of the first characterized silanimine tBu₂Si=N–Si(tBu) (1) [1], which bears bulky tBu groups features nearly the same Si=N–Si skeleton as that calculated for H₂Si=N–SiH₂. Apparently, only electronic effects, namely the difference in electronegativity between Si and N, determine the molecular structure of this type of silanimines.

In 1986, Wiberg and co-workers reported the first synthesis of 1 by the reaction of 1 equivalent of the silyl azide tBu₂SiClN₃ with 1 equivalent of the silanides Na[Si(tBu)₃] [19, 20] in the weakly polar solvent Bu₂O (Scheme 1) [1]. However, when this reaction was carried out in thf instead of Bu₂O, the sodium amide tBu₃SiCl⋅NNa–Si(tBu)₃ was formed rather than the silanimine 1 [21]. In this context, it should also be noted that the 2:1 reaction of tBu₃ClSiN₃ with Na[Si(tBu)₃] [19, 20] yielded the [3+2] cycloadduct of tBu₃ClSiN₃ with 1 [22, 23].

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2 Results and Discussion

Following the approach of Wiberg et al. [1], we first prepared the donor-free silanimine 1 by the reaction of tBu₂SiClN₃ with Na[Si(tBu)₃] [19, 20] in the weakly polar solvent Bu₂O. Subsequent treatment of a benzene solution of 1 with thf quantitatively gave the thf-complexed silanimine 1(thf) (Scheme 1). By storing a saturated benzene solution for 1 week at r.t. single crystals of a new polymorph of 1(thf) were obtained. This polymorph crystallized in the monoclinic space group C2/c.

To assess the stability of 1(thf), we conducted a series of thermolysis experiments. When a benzene solution of
Scheme 1 Synthesis of the silanimine \( \text{tBu}_2\text{Si}=\text{N}\text{–SiBu}_3 \) (1). (i) \(-\text{N}_2, -\text{NaCl, in Bu}_2\text{O}, -78 \, ^\circ\text{C}\). (ii) + thf.

Scheme 2 Decomposition of the thf-complexed silanimines \( \text{R}_2\text{Si}=\text{N}\text{–SiBu}_3 \), \( \text{thf} \) (i) (thf), \( \text{R} = \text{tBu}_2 \); (ii) (thf), \( \text{R} = \text{Me} \). (i) \(-\text{BuHSiN}\text{–SiBu}_3\), in benzene, 11 d at 140 \, ^\circ\text{C}. (ii) \(-\text{H}, \text{C}=\text{CH}_2\), in benzene, 19 h at 110 \, ^\circ\text{C}.

The thf-complexed silanimine 1(thf) (Fig. 1) crystallizes together with a half molecule benzene in the asymmetric unit. The selected bond lengths and angles are listed in the caption of Fig. 1.

(Continued)
Si=N = 1.574(10), 1.588(9) Å. As depicted in Table 1, the N–Si single bonds in the parent silanimine 1 and in the silanimine adducts 1(thf) and 2(thf), however, are remarkably shorter than those found in related supersilylated nitrogen compounds.

While the chemical behavior of the thf-supported silanimines 1(thf) resembles that of the corresponding donor-free silanimine 1 (e.g., ene reaction with acetone or insertion reaction with water as trapping agent [26]), the use of the thermally stable thf-complex 1(thf) instead of the parent silanimine 1 appears to be particularly advantageous for preparative chemistry.

3 Experimental section

The solvents thf, pentane, benzene, and C₆D₆ were stirred over sodium/benzophenone and distilled prior to use. 1 [1] and 2(thf) [1] were prepared according to the published procedures. All other starting materials were purchased from commercial sources and used without further purification. The NMR spectra were recorded on Bruker AM 250, DPX 250, Avance 400, and Avance 500 spectrometers. NMR chemical shifts are reported in ppm. Abbreviations d = doublet; dd = doublet of doublets. For quantitative separation, the dried filtrate was redissolved and separated by HPLC (Reprosil-pur C18-AQ, flow rate: 3 mL min⁻¹, two solvent system (MeOH-TBME 2: 1, λ = 254 nm; Sykam Refractive Index Monitor RI2000)) with isocratic elution.

3.1 tBu₂Si=N–SitBu₂ · thf (1(thf))

The thf-complexed silanimine 1(thf) was prepared by a modified literature-known procedure [26]. To a benzene (5 mL) solution of 1 (0.37 g; 1.03 mmol) thf (0.5 mL) was added. X-ray-quality crystals of 1(thf) were grown from a concentrated benzene solution after one week at r. t. 1(thf): M. p. 143 °C. – ¹H NMR (250.1 MHz; C₆D₆ Me₃Si): δ = 1.11 (CH₃), 1.17 (SitBu₂), 1.46 (SitBu₂), 3.94 ppm (OCH₂). – ¹C NMR (62.9 MHz; C₆D₆; Me₃Si): δ = 24.3 (CH₃), 24.9 (CMe₂), 25.6 (CMe₃), 30.5 (CMe₃), 32.3 (CMe₃), 73.5 ppm (OCH₂). – ²⁹Si NMR (49.7 MHz; C₆D₆; Me₃Si): δ = 1.1 (SitBu₂), –14.7 ppm (SiMe₂).

3.2 Thermolysis of 1(thf)

1(thf) (0.05 g, 0.12 mmol) was dissolved in C₆D₆ (0.6 mL). The solution was heated in a sealed NMR tube to 140 °C for 11 d. The NMR spectra of the solution revealed that 3 [25], the ene reaction product of 1 with isobutene, was formed in 60 % yield.

3.3 Thermolysis of 2(thf)

2(thf) (0.02 g, 0.05 mmol) was dissolved in C₆D₆ (0.6 mL). The solution was heated in a sealed NMR tube to 110 °C for 19 h. The NMR spectra of the solution revealed that the silanimine dimer 4 [21] was formed in 51 % and the vinyl ether 5 in 49 % yield. The vinyl ether 5 was separated by HPLC (Reprosil-pur C18-AQ, flow rate: 3 mL min⁻¹, two solvent system (MeOH-TBME 2: 1, τ = 19 min). 5: – ¹H NMR (250.1 MHz; C₆D₆ Me₃Si): δ = 0.22 (SiMe₂), 1.13 (SitBu₂), 4.18 (d, J = 5.86 Hz; H;c= (cis)), 4.63 (d, J = 13.7 Hz; H;c= (trans)), 6.48 ppm (dd, δ = 1.2 (SiMe₂), 6.8 ppm (SitBu₂);

3.4 Crystal structure determination

Data of 1(thf) were collected on a Stoe IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoKα radiation (λ = 0.71073 Å) and were scaled using the frame scaling procedure in the X-Area program system [27]. The structure was solved by Direct Methods using the program SHELXLX [28] and refined against F² with full-matrix least-squares techniques using the program SHELXL-97 [29].

The C atoms of the thf ligand are disordered over two positions with a site occupation factor of 0.635(9) for the major occupied site. The benzene molecule is disordered over two positions with a site occupation factor of 0.68(1) for the major occupied site. The disordered atoms were refined isotropically. Details of the crystal structure analysis are summarized in Table 2.

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<th>Si=N</th>
<th>N–Si/BU₄</th>
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<tr>
<td>1 [1]</td>
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<td>1.695(3)</td>
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<tr>
<td>1(thf)</td>
<td>1.6025(16)</td>
<td>1.6714(16)</td>
</tr>
<tr>
<td>2(thf)</td>
<td>1.574(10)</td>
<td>1.588(9)/161.0(6)/161.5(6)</td>
</tr>
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</table>

Two crystallographically independent molecules.
Table 2 Crystallographic data of 1(thf).

<table>
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<th>Property</th>
<th>Value</th>
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<tr>
<td>∆ρmax (max/min), e Å⁻³</td>
<td>0.37/–0.28</td>
</tr>
</tbody>
</table>

*R(F) = Σ|F_{o}||-|F_{e}||/Σ|F_{o}|; \ wR(F) = (Σw(F_{o}²−F_{e}²)²)/Σw(F_{o}²)²)^{1/2};
\ w = [σ²(F_{o})+(P²+bP)]⁻¹, where P = (Max(F_{o}², 0)+2F_{e}²)/3;
\ GoF = (Σw(F_{o}²−F_{e}²)²/|n_{obs}−n_{param}|)¹/².

CCDC 1009965 (1(thf)) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[27] X-Area, Stoe & Cie GmbH, Darmstadt (Germany) 2002.