Synthesis of a Lewis Base Stabilized Dimer of N-Substituted Hydrosila Hydrazene and a Silaaziridine

Sankaranarayana Pillai Sarish,† Anukul Jana,† Herbert W. Roesky,*† Prinson P. Samuel,† Carlos E. Abad Andrade,‡ Birger Dittrich,‡ and Carola Schulzke§

†Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany, and §School of Chemistry, Trinity College Dublin, Dublin 2, Ireland

Received November 12, 2010

The dehydrohalogenation of a silicon(IV)-substituted diphenyl hydrazene derivative leads to a dimer of a N-substituted hydrosila hydrazene, which consists of a four-membered Si₂N₂ core and a hydrogen attached to each of the silicon atoms instead of giving a substituted hydrosilaneimine. The compound is obviously formed by dimerization of hydrosilaneimine. Moreover there are no straightforward synthetic methods known for the synthesis of silaaziridine. The preparation of such species would be of special importance for the development of a new field of silicon chemistry. The reaction of chlorosilylene, LSiCl, and PhCH=NPh resulted in a base-stabilized silaaziridine. All compounds were characterized by NMR spectroscopy, mass spectrometry, microanalysis, and X-ray structural analysis.

Introduction

The stable allotropes of the lighter p block elements such as nitrogen and oxygen possess triple and double bonds, respectively. Nitrogen has a ubiquitous nature to form double as well as triple bonds with carbon. Silicon, the congener of carbon, forms silane imine complexes,1 which constitute a vital area of research in the last two decades. The stable allotropes of the lighter p block elements such as nitrogen and oxygen possess triple and double bonds, respectively. Nitrogen has a ubiquitous nature to form such as nitrogen and oxygen possess triple and double bonds, respectively. Nitrogen has a ubiquitous nature to form double as well as triple bonds with carbon. Silicon, the congener of carbon, forms silane imine complexes,1 which constitute a vital area of research in the last two decades.

Moreover examples of silaaziridines, which are elusive and have been characterized only in an argon matrix.4,5 However, this method lacks generality. Moreover, silaaziridines have been proposed as reactive intermediates in thermal and photochemical silylene transfer reactions to imines, although the strained three-membered ring compounds were not isolated, and instead rearranged products were obtained.7–9 In 2007 Woerpel et al. reported the synthesis of silaaziridine by applying silver triflate catalyzed silylene transfer from silacyclop propane to imines.10 The aziridines are used as precursors for the synthesis of N-containing heterocyclic compounds, which are important for producing drugs11 and natural products.12 Stable silaaziridine could be an alternative precursor for the synthesis of N,Si-containing heterocyclic compounds. Subsequently a facile synthesis of stable hydrosilaneimines and silaaziridines would be a real challenge for the synthetic chemist. Recently we were successful in isolating the previously reported stable chlorosilylene LSiCl (1) (L = Ph(C(N(Bu))13 in high yield using LiN(SiMe3)2 as a dehydrohalogenating agent,14 which helped to carry out its versatile reactivities. Among them, one is the convenient synthesis of monosilaepoxide, which was formed by the reaction of 1 with ketones.15 The successful stabilization of monosila oxirane by the benzamidinato ligand prompted us to probe the reaction of 1 with the >C=NR precursor. The question arises whether it will afford [1+2] cycloaddition compounds or oxidative addition products.

*To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

Article

Herein, we report on the synthesis of a stable base-stabilized Si₂N₂ core [LSi(H)-N-N=CP₂]₂ (L = PhC(NtBu)₂) (3) from the reaction of LSiCl(H)N-H=CP₂ (2) with 1,3-bis(tert-butyl)dimidazol-2-ylidene under HCl elimination. Here it is worth mentioning that compound 2 is obtained from the unprecedented oxidative addition of one of the N–H bonds of diphenyl hydrazone (Ph₂C=NH₂) to the silicon(II) center of the base-stabilized chlorosilylene, LSiCl (1). Furthermore an efficient method is outlined for the synthesis of stable silaaziridine 4 by the reaction of 1 with N-benzylideneaniline (PhCH=NHPh).

Results and Discussion

The reaction of chlorosilylene, LSiCl (1), with diphenyl hydrazine in toluene leads to the silicon(IV)-substituted diphenyl hydrazine derivative LSiCl(H)N-H=CP₂ (2) (Scheme 1). The reaction proceeds via the oxidative addition of one of the N–H bonds to the silicon(II) center. A similar reaction was observed when ammonia was reacted with the silylene L’Si (L’ = CH₂(CH₃)(CMe)(2,6-Pr₂C₆H₃)(N₂)). In contrast to the present results, when L’Si was reacted with diphenyl hydrazine, there was exclusive formation of the [1+4] cycloaddition product. The different reactivity is mainly due to the difference in coordination numbers around the silicon atom of the two silylenes.

The formation of compound 2 was confirmed by elemental analysis, multinuclear NMR spectroscopy, and EI mass spectrometry. The ¹H NMR spectrum of 2 shows resonances at 6 6.48 and 6.62 ppm for the Si–H and N–H proton, respectively, and both exhibit doublets with the same coupling constant (³J = 3 Hz). The ²⁹Si NMR spectrum exhibits a doublet of doublets at δ -99.82 ppm (³J²⁹Si-¹H = 299.45 Hz, ²J²⁹Si-¹H = 10.78 Hz). Furthermore the solid-state structure of compound 2 was confirmed by single-crystal X-ray structural analysis.

Single crystals of 2 were obtained from a hot saturated n-hexane solution at room temperature after one day. Compound 2 crystallizes in the triclinic space group P刑警, with one monomer in the asymmetric unit as illustrated in Figure 1. Surprisingly, 2 is monomeric in the solid state, and what is even more striking, the NH group is not involved in any kind of hydrogen bonding. Compound 2 is stable in the solid state as well as in solution for a longer period of time without any decomposition under an inert atmosphere. The coordination polyhedron around the silicon atom features a distorted tetragonal-pyramidal geometry. The silicon is attached to two nitrogen atoms from the backbone of the chelating ligand, the chloroatom from the hydrazine moiety, the Cl atom, and a hydrogen atom. The N1–N2 bond length is 1.364(3) Å, which is indicative of a N–N single bond. A noteworthy feature of compound 2 is the Si(H)NH moiety (Si1–N1 1.722(3) Å). The Si–N1 bond length can be compared with the slightly shorter Si–N bond lengths than that in RSi(NH₂)₃ (R = 2,4,6-Pr₂C₆H₃) av 1.709(7) Å, ²R = 2,6-Pr₂C₆H₃-NSiMe₃ av 1.709(2) Å, and R = 2,4,6-tBuC₆H₃O av 1.692(6) Å.

Compound 2 exhibits a Si–H as well as a N–H bond, which both are potential proton donors for the elimination of HCl. This would occur from either the 1,1 or 1,2 position while adding a proton scavenger (such as amine, N-heterocyclic carbene). In the case of 1,1 HCl elimination there would be the formation of LSiN(H)=CP₂, while 1,2 HCl elimination would lead to the substituted hydrosilane derivative LSi(H)=NSiMe₃. In the literature there are protocols on both the formation of silylene compounds by

N11 the hydrosilaneimine derivative LSi(H)$_d$ with Si$_1$ slightly disordered THF molecule. The 1H NMR spectrum of LSiCl$_2$ was characterized by multinuclear spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The 1H NMR spectrum of 3 exhibits a singlet resonance ($\delta$ 4.86 ppm) that can be assigned to the Si–H proton, accompanied by two 29Si satellite resonances. The 29Si NMR spectrum shows a doublet resonance ($\delta$ –96.65 ppm) with a coupling constant of $J$(29Si–H) = 286.18 Hz. Suitable crystals for X-ray structural analysis were obtained from a saturated THF solution of 3 after storing this solution overnight at room temperature. The coordination polyhedron around the silicon atom comprises two nitrogen atoms from the supporting ligand, one hydrogen atom, and two nitrogen atoms of the hydrazone moiety, featuring a distorted trigonal-bipyramidal geometry. The axial positions are occupied by two nitrogen atoms. The axial substituents include an angle of 80.34° with the silicon atom. The distorted trigonal-bipyramidal architecture includes different Si–N bond distances for axial and equatorial substituents. The Si–N bond lengths in the equatorial positions (Si1–N1 1.752 Å and Si1–N21 1.831 Å) are shorter than that in the axial positions (Si1–N1 2.028 Å). In summary, compound 3 represents a stable crystalline compound with three four-membered rings that are connected through silicon atoms, and it exhibits at each silicon center a terminal-bound hydrogen atom.

After the successful synthesis of an N-substituted hydrosilane hydrazone, we turned our attention to the synthesis of silaaziridine. From the retrosynthetic point of view, the silaaziridines can be prepared by reacting either silene with nitrene or, alternatively, silaamine with carbene, or imine with silylene. The preparation of stable silene24–26 and silaamine1–3 is limited, although nowadays there are numerous reports on stable silylenes.27,28 For developing a new route to stable silaaziridines we employed the reaction of stable silylenes with imines. Finally it is noteworthy that in all the known silaaziridines the silicon atom binds to either carbon or silicon. So far no compounds are available where heteroatoms are attached to silicon.

The addition of N-benzylideneneiline (PhCH=NH) to a solution of 1 in toluene leads to compound 4 (Scheme 1). The colorless solution was evaporated, and the residue extracted with hot n-hexane to yield colorless crystals of 4 in 88% yield. The exact mechanism for the formation of 4 is unknown, but both mechanistic pathways can be envisioned. Either an electrophilic attack of 1 could occur at the imine nitrogen of N-benzylideneneiline to give a silyl ylide, or alternatively, a nucleophilic attack of 1 to the imine carbon of N-benzylideneneiline might be possible to result in a charge-separated species. Both pathways can lead to compound 4 after successive ring closure. Compound 4 is well soluble in benzene, toluene, THF, and diethyl ether and shows no decomposition on exposure to dry air. 4 was characterized by 1H and 29Si NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis.

The 1H NMR spectrum of 4 exhibits a singlet resonance ($\delta$ 4.07 ppm) that can be assigned to the C–H proton of the three-membered silaaziridine ring. The 29Si NMR spectrum exhibits a singlet resonance ($\delta$ –131.35 ppm) consistent with a neutral pentacoordinate silicon.26 Single crystals of 4 were obtained from a saturated hot n-hexane solution after one day. Compound 4 crystallizes in the triclinic space group $P\bar{1}$, with two molecules in the asymmetric unit. Interestingly, the
techniques or inside a MBraun MB 150-GI glovebox maintained at or below 1 ppm of O₂ and H₂O. All solvents were distilled from Na₂O₂benzenephene prior to use. The starting material 1 was prepared using a literature procedure. Other chemicals were purchased and used as received. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Bruker Avance DRX instrument and referenced to the deuterated solvent in the case of the ¹H and ¹³C NMR and SiMe₄ for the ²⁹Si NMR spectra. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. El-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

Synthesis of 2. A solution of Ph₂C=CHCl (0.19 g, 1 mmol) in toluene (10 mL) was added to a toluene solution (35 mL) of 1 (0.29 g, 1 mmol) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 12 h at this temperature. After that all volatiles were removed under vacuum. The residue was dissolved in n-hexane (45 mL), and the solution was warmed and filtered over a Celite pad. The resulting solution was kept overnight at room temperature to afford colorless crystals of 2. Yield: 0.39 g, 80%. Mp: 138−140 °C. ¹H NMR (500 MHz, C₆D₆): δ 7.85−7.84, 7.18−6.84 (m, 15H, C₆H₅); 6.62 (d, 1H, NH); 6.48 (d, 1H, SiH); 1.15 (s, 18H, C(CH₃)₃) ppm. ¹³C NMR (125 MHz, C₆D₆): δ 172.08, 147.08, 140.00, 134.78, 129.87, 129.67, 129.63, 128.84, 128.69, 128.31, 127.72, 127.01, 54.68, 31.67 ppm. ²⁹Si NMR (99.35 MHz, C₆D₆): δ −99.82 ppm (d, J = 10.79 Hz). El-MS (70 eV) m/z (%): 453(100%) [M − 2H − Cl]²⁻, 409(10%) [M−H]⁺. Anal. Calcld for C₂₈H₃₅ClN₄Si: C, 71.48; H, 7.49; N, 9.08.

Synthesis of 3. A solution of 1,3-bis(tert-butyl)imidazol-2-ylidenec (0.18 g, 1 mmol) in THF (20 mL) was added to a THF solution (30 mL) of 2 (0.49 g, 1 mmol) at −78 °C. The reaction mixture was allowed to warm gradually to room temperature and stirred overnight. After that all volatiles were removed under vacuum. The residue was dissolved in n-hexane (40 mL), and the solution was warmed and filtered over a Celite pad. Single crystals of 3 suitable for X-ray structural analysis were obtained by storing the solution overnight at room temperature. Yield: 0.38 g, 85%. Mp: 299−301 °C. ¹H NMR (300 MHz, C₆D₆): δ 7.44−7.09 (m, 30H, C₆H₅); 4.86 (s, 2H, SiH); 1.06 (s, 36H, C(CH₃)₃) ppm. ¹³C NMR (75.47 MHz, C₆D₆): δ 169.81, 143.46, 142.30, 137.11, 132.60, 130.50, 130.17, 128.81, 128.25, 128.12, 127.95, 126.99, 54.58, 32.01 (br) ppm. ²⁹Si NMR (59.63 MHz, C₆D₆): δ −96.65 ppm (d, J = 286.18 Hz). El-MS (70 eV) m/z (%): 728.4 (100) [M⁺−N=C(Ph₂)₂]; 908.55 (55%) [M⁺−2H], 454.2 (30) [M/2]⁺. Anal. Calcld for C₅₆H₆₈N₈Si₂: C, 73.96; H, 7.54; N, 12.32. Found: C, 73.12; H, 8.07; N, 12.12.

Synthesis of 4. A solution of PhCH=CHCl (0.18 g, 1 mmol) in toluene (10 mL) was added to a toluene solution (35 mL) of 1 (0.29 g, 1 mmol) at −30 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for an additional 1 h at the same temperature. After that all volatiles were removed under vacuum. The residue was dissolved in n-hexane (40 mL), and the solution was warmed and filtered over a Celite pad. The resulting solution was stored overnight at room temperature to afford colorless crystals of 4. Yield: 0.42 g, 88%. Mp: 117 °C. ¹H NMR (500 MHz, C₆D₆): δ 7.54−6.62 (m, 15H, C₆H₅); 4.07 (s, 1H, CH); 1.15 (s, 9H, C(CH₃)₃) ppm. ¹³C NMR (125 MHz, C₆D₆): δ 174.16, 159.97, 150.66, 145.71, 131.26, 131.22, 130.15, 129.34, 129.22, 129.11, 128.81, 128.75, 128.24, 126.02, 124.89, 124.22, 121.27, 118.36, 117.79, 54.65, 54.29, 53.28, 31.80, 30.47 ppm. ²⁹Si NMR (125 MHz, C₆D₆): δ −131.35 ppm. El-MS (70 eV) m/z (%): 475 (100%) [M⁺]. Anal. Calcld for C₃₉H₄₆C₄N₄Si: C, 76.73; H, 7.20; N, 8.83. Found: C, 71.45; H, 7.49; N, 9.08.

X-ray Crystal Structure Determination. Suitable crystals of 2 and 4 were mounted on a glass fiber, and data was collected on

an IPDS II Stoe image-plate diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) at 133(2) K. The data for 3 were collected from a shock-cooled crystal at 100(2) K on a Bruker SMART 6000 diffractometer equipped with a rotating anode and INCOATEC mirror optics. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F² (SHELXL-97). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically at calculated positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp³-carbon atoms and 1.2 times for all other carbon atoms. Hydrogen atoms bound to nitrogen, silicon and the chiral carbon atoms of 4 were located and refined freely; for the latter only, unlike their location Uiso was refined as being dependent on the pivot atoms.

Disordered moieties were refined using bond length restraints, rigid bond restraints, similarity restraints, and ADP restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge crystallographic data center. Copies of the data can be obtained free of charge from the Cambridge crystallographic data center via www.ccdc.cam.ac.uk/data_request/cif.

**Compound 2:** Space group: P1; a = 8.2690(17) Å, b = 9.7193(19) Å, c = 17.875(4) Å; α = 101.04(3)°, β = 102.46(3)°, γ = 96.72(3)°, R1 = 0.0647 for [I > 2σ(I)], wR2 (all data) = 0.1500 (CCDC number for 2: 778977).

**Compound 3:** Space group: P2₁/n; a = 12.7543(3) Å, b = 18.2098(4) Å, c = 13.9106(3) Å; α = 90.0°, β = 113.1287(7)°, γ = 90.0°, R1 = 0.0367 for [I > 2σ(I)], wR2 (all data) = 0.0960 (CCDC number for 3: 781161).

**Compound 4:** Space group: P1; a = 11.161(2) Å, b = 15.987(3) Å, c = 16.576(3) Å; α = 89.93(3)°, β = 83.27(3)°, γ = 71.19(6)°, R1 = 0.0873 for [I > 2σ(I)], wR2 (all data) = 0.1633 (CCDC number for 4: 776751).

**Acknowledgment.** Support by the Deutsche Forschungsgemeinschaft is highly acknowledged.

**Supporting Information Available:** X-ray data for 2, 3, and 4 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.