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Reaction of the Silylene $PhC(NtBu)_2SitBu$ with 4,4'-Bis(dimethylamino)thiobenzophenone and Treatment of the Silylene $PhC(NtBu)_2SiC(SiMe_3)_3$ with 3,5-Di-*tert*-butyl-*o*benzoquinone

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Dedicated to Professor Vladimir Bregadze on the occasion of his 75th birthday

Keywords: Silylenes / Silicon / Heterocycles / Cycloaddition

The reaction of LSitBu [L = PhC(NtBu)₂] (1) with 4,4'-bis(dimethylamino)thiobenzophenone resulted in the [1+2]-cycloaddition product silathiacyclopropane 3, bearing a threemembered SiCS ring. The reaction of LSiC(SiMe₃)₃ (2) with 3,5-di-*tert*-butyl-o-benzoquinone leads to the [1+4]-cycload-

Introduction

The chemistry of stable singlet silvlenes has received considerable attention^[1] after the first report of the stable Nheterocyclic silvlene (NHSi) by West et al. in 1994.^[2] The presence of two non-bonding electrons in the HOMO and a vacant p orbital as the LUMO shows that silvlenes have the tendency to function both as Lewis acids as well as Lewis bases.^[3] Because of the presence of an ambiphilic character, many noteworthy reactivity studies with a variety of substrates have been documented.^[1,4-6] We reported on a facile method for the synthesis of heteroleptic silylenes^[7] by the metathesis reaction of alkali metal amide, phosphide, alkoxide, or organoalkyl reagent with amidinato ligand stabilized monochlorosilylene LSiCl $[L = PhC(NtBu)_2]$.^[7c,7d] Silvlenes are highly reactive species and provide an alternative route to inaccessible new organosilicon compounds, which are difficult to prepare by conventional methods. In general, three- and four-membered ring compounds with a heteroatom play a substantial role in the development of heterocyclic chemistry.^[8] The high degree of strain in the three-membered ring compounds results in various properties such as high reactivity in the ring cleavage and low elec-

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dition product 4. In 3 the silicon atom is five- and in 4 it is four-coordinate. Compounds 3 and 4 were characterized by spectroscopic and spectrometric techniques. The molecular structures of 1, 3, and 4 were unequivocally established by single-crystal X-ray structure analysis.

tron-donor ability for coordinating electron acceptors.^[8] The three-membered ring compounds containing a silicon atom are fascinating because of their high strain and novel bonding arrangement within the ring.^[9] In addition, threemembered rings with high coordinate silicon at the position adjacent to the heteroatom have attracted synthetic chemists as a result of their unique structure and reactivity.^[9] In the case of a thia-Brook rearrangement the transition state has been proposed as a three-membered ring compound possessing a five-coordinate silicon at the position adjacent to the sulfur atom.^[10] Ando et al. reported the first structurally characterized silathiacyclopropane.[11] This compound was obtained by the reaction of dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanethione. Later Brook et al. obtained the silathiacyclopropane by the reaction of silene with elemental sulfur.^[12] Recently we synthesized silathiacyclopropane from LSiCl $[L = PhC(NtBu)_2]$ with 4,4'-bis(dimethylamino)thiobenzophenone.^[13] In this manuscript, we report on the reaction of LSitBu (1) with 4,4'-bis(dimethylamino)thiobenzophenone, which resulted in the [1+2]-cycloaddition product silathiacyclopropane 3. The latter consists of a three-membered SiCS ring. The reaction of LSiC-(SiMe₃)₃ (2) with 3,5-di-tert-butyl-o-benzoquinone leads to the [1+4]-cycloaddition product 4, with a four-coordinate silicon atom. This is quite different from the five-coordinate silicon atom product formed by the reaction of LSiCl with 3.5-di-tert-butyl-o-benzoquinone, which we reported previously.^[14] We presume that the formation of a four-coordinate product 4 might be due to the presence of a bulkier $C(SiMe_3)_3$ group on the silicon atom.



Results and Discussion

Compounds $LSitBu [L = PhC(NtBu)_2]$ (1) and LSiC- $(SiMe_3)_3$ (2) were prepared as reported in the literature.^[7c] The molecular structure of 1 is shown in Figure 1. Compound 1 crystallizes in the monoclinic space group *Pbca*. The silicon atom is three coordinate and features a trigonal pyramidal geometry, with the lone pair of electrons residing on the apex. The coordination environment of the silicon is made up of two nitrogen atoms of the amidinato ligand and one tertiary carbon atom of the alkyl group. The Si(1)-C(20) bond length in 1 is 1.9571(10) Å. This is longer than that in compound [LSitBu(µ-O)]₂ [1.9209 (13) Å] reported in the literature.^[7c] The bond length between the chelating nitrogen atoms and the silicon are Sil-N1 1.8803(8) and Si1–N3 1.8937(8) Å, respectively. The bite angle N1–Si1– N3 is 69.10(3)°. The Si atom is shifted out of the plane defined by a N1-C1-N3 angle of 0.3012(0.0002) Å.



Figure 1. Molecular structure of 1. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N1–Si1 1.8803(8), N3–Si1 1.8937(8), C20–Si1 1.9571(10); N1–Si1–N3 69.10(3), N1–Si1–C20 102.37(4), N3–Si1–C20 102.44(4).

Equimolar amounts of LSitBu (1) and 4,4'-bis(dimethylamino)thiobenzophenone lead to the [1+2]-cycloaddition product 3 (Scheme 1). Compound 3 is soluble in benzene and toluene. It is stable both in the solid state as well as in solution for a long time without any decomposition under an inert gas atmosphere.



Scheme 1. Synthesis of compound 3.

The ²⁹Si NMR spectrum of **3** exhibits a single resonance at $\delta = -86.09$ ppm, which is shifted upfield compared with that of LSi*t*Bu ($\delta = 61.50$ ppm).^[7c] The protons of the *t*Bu groups attached to the nitrogen atoms of compound **3** show two resonances ($\delta = 1.10$ and 1.28 ppm) in the ¹H NMR spectrum. The protons of the Si*t*Bu group resonate at $\delta = 1.40$ ppm. The mass spectrum of compound **3** exhibits the molecular ion at m/z = 600.

The molecular structure of the [1+2]-cycloaddition product 3 was unequivocally established by single-crystal X-ray structural analysis. Compound 3 crystallizes in the monoclinic space group $P2_1/n$. The molecular structure is shown in Figure 2. The three-membered ring of 3 comprises a carbon, sulfur, and silicon atom. The silicon atom is five-coordinate, made up from two nitrogen atoms, a sulfur atom, and two carbon atoms. The structural index τ , which defines the extent of deviation from trigonal-bipyramidal to square-pyramidal geometry ($\tau = 1$ for perfect trigonal bipyramidal; $\tau = 0$ for perfect square-based pyramid), is 0.32.^[15] The N-Si-N bite angle at the silicon atom of the backbone amidinate ligand is 68.22(14)°, whereas in 1 it is 69.10(3)°. There is a slight variation of the Si-C20 bond length of 1.934(5) Å in 3 when compared with that of 1 [1.9571(10) Å]. The angles of the newly formed SSiC threemembered ring are S1-Si1-C4 [54.32(12)°], Si1-C4-S1 [71.03(14)°], and C4–S1–Si1 [54.64(13)°]. Correspondingly the bond lengths within the three-membered ring are Si1-S1 [2.2073(16) Å], S1–C4 [1.896(4) Å], and Si1–C4 [1.904(4) Å]. These values are comparable to those of the SSiC three-membered ring reported in the literature.^[11–13]



Figure 2. Molecular structure of **3**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N1–Si1 1.839(3), N3–Si1 2.001(3), C20–Si1 1.934(5), Si1–S1 2.2073(16), S1–C4 1.896(4), Si1–C4 1.904(4); N1–Si1–N3 68.22(14), S1–Si1–C4 54.32(12), Si1–C4–S1 71.03(14), C4–S1–Si1 54.64(13), N1–Si1–C20 110.19(18), N3–Si1–C20 100.96(18), N3–Si1–S1 149.30(12), N1–Si1–C4 130.10(18).

The reaction of equimolar amounts of LSiC(SiMe₃)₃ and 3,5-di-*tert*-butyl-o-benzoquinone afforded the [1+4]-cyclo-addition product **4** (Scheme 2). Compound **4** is soluble in common organic solvents. Like **3**, compound **4** is stable both in the solid state as well as in solution. Compound **4** exhibits a double resonance in its ²⁹Si NMR spectrum [$\delta = -0.96 \text{ C}(SiMe_3)_3$ and -16.98 (LSi) ppm]. The protons of the *t*Bu groups, which reside over the nitrogen atoms of compound **4**, display a single resonance at $\delta = 1.32$ ppm in the ¹H NMR spectrum. We surmise that the single resonance might be from the coordination of both nitrogen atoms, from the amidinato ligand, to the silicon center in solution.



The SiMe₃ protons resonate at $\delta = 0.58$ ppm. Further, compound **4** shows its molecular ion in the mass spectrum at m/z = 710.



Scheme 2. Synthesis of compound 4.

The [1+4]-cycloaddition product **4** was confirmed by single-crystal X-ray structural analysis. Compound **4** crystallizes in the triclinic space group $P\bar{1}$ and the molecular structure is depicted in Figure 3. The silicon atom is fourcoordinate, made up of one nitrogen atom, two oxygen atoms, and a carbon atom. The Si1–C20 bond length is 1.8842(17) Å.



Figure 3. Molecular structure of **4**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and methyl carbon atoms of the *t*Bu groups are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N1–Si1 1.7593(14), O4–Si1 1.6781(11), O5–Si1 1.6988(11), C20–Si1 1.8842(17); O4–Si1–O5 94.63(5), O4–Si1–N1 102.95(6), O5–Si1–N1 107.04(6), N1–Si1–C20 126.67(7), O4–Si1–C20 112.93(7), O5–Si1–C20 107.86(7).

The bond lengths of Si1–O4 and Si1–O5 are 1.6781(11) Å and 1.6988(11) Å, respectively. The bond length between the silicon and nitrogen atom of the amidinato ligand is 1.7593(14) Å, which is comparable to the Si–N bond length reported in the literature.^[16]

Conclusions

In summary we report on the reactivity of the monoalkyl-substituted silylene LSi*t*Bu with 4,4'-bis(dimethylamino)thiobenzophenone, which afforded the CSiS threemembered ring compound silathiacyclopropane **3** with a five-coordinate silicon atom. The reaction of LSiC-(SiMe₃)₃ with 3,5-di-*tert*-butyl-*o*-benzoquinone leads to the [1+4]-cycloaddition product **4** exhibiting a four-coordinate silicon atom.

Experimental Section

General: Syntheses were carried out under an inert atmosphere of dinitrogen in oven-dried glassware using standard Schlenk techniques. All other manipulations were accomplished in a dinitrogen filled glove box. Solvents were purified by a MBRAUN solvent purification system MB SPS-800. Compounds 1 and 2 were prepared as reported in the literature.^[7c] ¹H NMR and ²⁹Si NMR spectra were recorded with a Bruker Avance DPX 300 or a Bruker Avance DRX 500 spectrometer, using C₆D₆ as solvent. Chemical shifts, δ , are given relative to SiMe₄. EI-MS spectra were obtained using a Finnigan MAT 8230 spectrometer. Elemental analyses were performed at the Institut für Anorganische Chemie, University of Göttingen.

Synthesis of 3: Toluene (60 mL) was added to a Schlenk flask (100 mL) containing **1** (0.55 g, 1.74 mmol) and 4,4'-bis(dimethyl-amino)thiobenzophenone (0.49 g, 1.72 mmol). The reaction mixture was stirred at room temperature for 6 h. The solvent was reduced in vacuo (10 mL) and stored at -26 °C to obtain single crystals of **3** in 1 w. Yield: 0.82 g, 79%. C₃₆H₅₂N₄SSi (600.98): calcd. C 71.95, H 8.72, N 9.32; found C 71.87, H 8.66, N 9.31. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 1.10 (s, 9 H, *t*Bu), 1.28 (s, 9 H, *t*Bu), 1.40 [s, 9 H, Si(CH₃)₃], 6.33–6.35 (m, Ar*H*), 6.76–7.00 (m, Ar*H*), 7.90–7.92 (m, Ar*H*), 8.09–8.11 (m, Ar*H*) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): δ = -86.09 (LS*i*) ppm. EI–MS: *m/z* (%) = 600 [M⁺] (35), 568 [M⁺ – S] (100), 512 [M⁺ – 2N(CH₃)₂ – 2C(CH₃)₃] (15).

Synthesis of 4: Toluene (60 mL) was added to a Schlenk flask (100 mL) containing **2** (0.52 g, 1.06 mmol) and 3,5-di-*tert*-butyl-*o*-benzoquinone (0.29 g, 1.07 mmol). The reaction mixture was stirred at room temperature for 6 h. The solvent was reduced in vacuo (10 mL) and stored at 0 °C to obtain single crystals of **4** in 2 w. Yield: 0.58 g, 77%. C₃₉H₇₀N₂O₂Si₄ (711.33): calcd. C 65.85, H 9.92, N 3.94; found C 65.79, H 9.83, N 3.86. ¹H NMR (500 MHz, C₆D₆, 25 °C): $\delta = 0.58$ [s, 27 H, Si(CH₃)₃], 1.32 (s, 18 H, *t*Bu), 1.57 (s, 18 H, *t*Bu), 6.80–7.11 (m, Ar*H*) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): $\delta = -0.96$ [C(*Si*Me₃)₃], -16.98 (L*Si*) ppm. EI-MS: *m*/*z* (%) = 710 [M⁺] (35), 695 [M⁺ - CH₃] (30), 654 [M⁺ - C(CH₃)₃] (100), 639 [M⁺ - C(CH₃)₃ - CH₃] (70), 598 [M⁺ - 2C(CH₃)₃] (15), 583 [M⁺ - 2C(CH₃)₃ - CH₃] (50).

Crystal Structure Determination: Crystals were taken out of the mother liquor under an argon atmosphere using NVH oil. Diffraction data were collected at 100 K with a Bruker three-circle diffractometer equipped with a SMART 6000 CCD area detector and a Cu- K_{α} rotating anode. The data sets of **3** and **4** were collected to the edge of the Ewald sphere with high completeness and high multiplicity. Raw data were integrated with SAINT^[17] and an empirical absorption correction with SADABS^[18] was applied. The structures were solved by direct methods (SHELXS-97) and refined against F^2 by full-matrix least-squares methods using all data (SHELXL).^[19] SHELXLE^[20] was used as refinement GUI. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to ride on their parent atom with displacement parameters constrained to 1.2 or 1.5 of the U_{iso} of their parent atom. (Table 1).

CCDC-914774 (for 1), -914773 (for 3), and -914775 (for 4) contain 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.



	1	3	4
Empirical formula	$C_{19}H_{32}N_2Si$	C ₃₆ H ₅₂ N ₄ SSi	C ₃₉ H ₇₀ N ₂ O ₂ Si ₄
M_r [gmol ⁻¹]	316.56	600.97	711.33
Crystal system	orthorhombic	monoclinic	triclinic
Space group	Pbca	$P2_1/n$	ΡĪ
a [Å]	11.5227(2)	9.6497(3)	10.5289(3)
<i>b</i> [Å]	18.2842(4)	12.2223(4)	11.5585(3)
c [Å]	18.4286(4)	29.1719(11)	19.1660(5)
a [°]			77.4900(10)°
β [°]		90.894(2)	77.2730(10)
γ [°]			72.2970(10)
V [Å ³]	3882.60(14)	3440.2(2)	2139.14(10)
Ζ	8	4	2
$\rho_{\rm calcd.} [{\rm gcm^{-3}}]$	1.083	1.160	1.104
$\mu \text{ [mm^{-1}]}$	1.040	1.384	1.532
F (000)	1392	1304	780
Crystal size [mm]	$0.30 \times 0.20 \times 0.10$	$0.09 \times 0.07 \times 0.02$	$0.20 \times 0.20 \times 0.15$
θ Range for data collection	4.80 to 73.67°	3.03 to 66.58°	2.39 to 72.13°
Limiting indices	$-14 \le h \le 14;$	$-9 \le h \le 11;$	$-12 \le h \le 12;$
	$-22 \le k \le 22;$	$-13 \le k \le 11;$	$-14 \le k \le 14;$
	$-22 \le l \le 22$	$-30 \le l \le 31$	$-23 \le l \le 23$
Reflections collected	124304	44704	68660
Independent reflections	$3915 (R_{int} = 0.0296)$	5675 ($R_{int} = 0.1381$)	$8190 \ (R_{\rm int} = 0.0284)$
Completeness to θ	99.9% (<i>θ</i> = 73.67°)	$93.1\% (\theta = 66.58^{\circ})$	97.3% (<i>θ</i> = 72.13°)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3915/0/327	5675/360/392	8190/375/476
Goodness of fit on F^2	1.057	1.038	1.074
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0317, wR_2 = 0.0838$	$R_1 = 0.0740, wR_2 = 0.1400$	$R_1 = 0.0424, wR_2 = 0.1107$
R indices (all data)	$R_1 = 0.0317, wR_2 = 0.0838$	$R_1 = 0.1291, wR_2 = 0.1652$	$R_1 = 0.0432, wR_2 = 0.1142$
Largest diff. peak and hole $[e Å^{-3}]$	0.375 and -0.218	0.455 and -0.407	0.615 and -0.365

Table 1. Crystal and Structure Refinement Parameters for Complexes 1, 3, and 4.

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