Supplementary Information

An Access to Base-Stabilized Three-Membered

Silicon Heterocycles

Ramachandran Azhakar, Herbert W. Roesky,* Rajendra S. Ghadwal,* Julian J. Holstein and

Birger Dittrich*

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077

Göttingen, Germany

AUTHOR EMAIL ADDRESS *hroesky@gwdg.de*,

rghadwal@uni-goettingen.de,

bdittri@gwdg.de

Experimental Section

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 MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. LSitBu[S1] (**1**) was prepared as reported in the literature. ^{1}H and ^{29}Si NMR spectra were recorded with a Bruker Avance DPX 200, Bruker Avance DPX 300 or a Bruker Avance DRX 500 spectrometer, using C_6D_6 as a solvent. Chemical shifts δ are given relative to SiMe$_4$. EI–MS spectra were obtained using a Finnigan MAT 8230 spectrometer. Elemental analyses were performed at the Institut für Anorganische Chemie, Universität Göttingen.

Synthesis of 1: Toluene (30 mL) was added to a 100 mL Schlenk flask containing LSitBu (**1**) (0.54 g, 1.70 mmol) at room temperture. To this solution PhN=NPh (0.31 g, 1.70 mmol) was added. The reaction mixture was stirred for 6 h. Then the reaction mixture was filtered and the solvent was removed *in vacuo* to obtain **1**. (0.70 g, 82%). Elemental analysis (%) calcd for $C_{31}H_{42}N_4Si$ (498.78): C, 74.65; H, 8.49; N, 11.23. Found: C, 74.62; H, 8.45; N, 11.07. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 0.98 (s, 9H, C(CH_3)$_3$), 1.23 (s, 9H, C(CH_3)$_3$), 1.31 (s, 9H, SiC(CH_3)$_3$), 6.56–7.56 (m, 15 H, Ar) ppm. ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): δ –99.6 ppm. EI–MS: *m/z* 498 [M$^+$].

Synthesis of 2: Toluene (30 mL) was added to a 100 mL Schlenk flask containing LSitBu (**1**) (0.55 g, 1.74 mmol) at room temperture. To this solution PhN=CHPh (0.32 g, 1.74 mmol) was added. The reaction mixture was stirred for 6 h. Then it was filtered and the solvent was removed *in vacuo* to obtain **2**. (0.68 g, 79%). Elemental analysis (%) calcd for $C_{32}H_{43}N_3Si$ (497.79): C, 77.21; H, 8.71; N, 8.44. Found: C, 77.22; H, 8.68; N, 8.35. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.76 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$), 1.35 (s, 9H, SiC(CH_3)$_3$), 3.81 (s,

1H, C*H*Ph), 6.67–7.51 (m, 15 H, Ar) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ –104.6 ppm. EI–MS: *m/z* 497 [M^+].

Synthesis of 3: Toluene (30 mL) was added to a 100 mL Schlenk flask containing LSi*t*Bu (**1**) (0.46 g, 1.46 mmol) at room temperature. To this solution PhC≡CPh (0.25 g, 1.47 mmol) was added. The reaction mixture was stirred for 6 h and it was filtered. The solvent was removed *in vacuo* to obtain **3**. (0.58 g, 81%). Elemental analysis (%) calcd for $C_{32}H_{42}N_2Si$ (494.79): C, 80.11; H, 8.56; N, 5.66. Found: C, 80.06; H, 8.51; N, 5.59. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 1.09 (s, 18H, C(CH_3)$_3$), 1.50 (s, 9H, SiC(CH_3)$_3$), 6.86–7.53 (m, 15 H, Ar) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ –117.8 ppm. EI–MS: *m/z* 494 [M^+].

Crystal Structure Determination. Suitable single crystals for X-ray structural analysis of **1**, **2** and **3** were obtained by keeping their corresponding toluene solutions at –27 °C and the crystals were taken out of the mother liquor under argon atmosphere using NVH oil. The diffraction data were collected at 100 K on a Bruker three circle diffractometer equipped with a SMART 6000 CCD area detector and a CuKα rotating anode. Due to good crystal quality all three datasets were collected to the edge of the Ewald sphere with high completeness and high multiplicity. The raw data were integrated with SAINT[S2] and an empirical absorption correction with SADABS[S3] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-97).[S4] SHELXLE[S5] was used as refinement GUI. All non-hydrogen-atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined freely with isotropic displacement parameters. Highest residual density peaks in all three structures remain on the bond between the Silicium atom and the *t*Bu Carbon atom. Structure refinement using Hirshfeld atom partitioning to model the molecular electron density distribution in the crystal[S6] will be reported in a forthcoming paper.

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Table S1. Crystal and Structure Refinement parameters for compounds **1**, **2** and **3**.

Parameters	1	2	3
Empirical formula	$C_{31} H_{42} N_4$ Si	$C_{32} H_{43} N_3$ Si	$C_{33} H_{42} N_2$ Si
Formula Weight	498.78	497.78	494.78
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	$a = 9.4054(2)$ Å	$a = 9.5628(3)$ Å	$a = 9.6994(2)$ Å
	$b = 11.5657(2)$ Å	$b = 11.2764(3)$ Å	$b = 10.1424(2)$ Å
	$c = 13.8190(3)$ Å	$c = 14.1642(4)$ Å	$c = 16.2348(3)$ Å
	$\alpha = 95.018(1)°$	$\alpha = 92.785(2)°$	$\alpha = 95.111(1)°$
	$\beta = 107.767(1)°$	$\beta = 109.510(2)°$	$\beta = 100.321(1)°$
	$\gamma = 90.790(1)°$	$\gamma = 92.265(2)°$	$\gamma = 111.630(1)°$
Volume, Z	1424.75(5) Å^3, 2	1435.46(7) Å^3, 2	1439.45(5) Å^3, 2
Density (Calculated)	1.163 g/cm^3	1.152 mg/m^3	1.142 mg/m^3
Absorption coefficient	0.909 mm^{-1}	0.891 mm^{-1}	0.877 mm^{-1}
F (000)	540	540	536
Crystal size [mm^3]	0.20 x 0.10 x 0.05	0.20 x 0.10 x 0.05	0.50 x 0.50 x 0.50
θ range for data collection	3.4 to 73.7°	3.3 to 73.6 °	2.8 to 73.4°

Limiting indices	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-16 \leq l \leq 17$	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$	$-12 \leq h \leq 11$, $-12 \leq k \leq 12$, $-20 \leq l \leq 20$
Reflections collected	34207	49601	50192
Independent reflections	5549 ($R_{int} = 0.041$)	5607 ($R_{int} = 0.036$)	5634 ($R_{int} = 0.027$)
Completeness to θ	96.1% ($\theta = 73.7°$)	97.2% ($\theta = 73.6°$)	97.1% ($\theta = 73.4°$)
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	5549 / 0 / 493	5607 / 0 / 497	5634/ 0 / 493
Goodness - of - fit on F^2	1.12	1.02	1.08
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0380$, $wR2 = 0.0939$	$R1 = 0.0361$, $wR2 = 0.0952$	$R1 = 0.0358$, $wR2 = 0.1066$
R indices (all data)	$R1 = 0.477$, $wR2 = 0.1194$	$R1 = 0.0404$, $wR2 = 0.0990$	$R1 = 0.0382$, $wR2 = 0.1278$
Largest diff. peak and hole	0.45 and -0.39 eÅ^{-3}	0.48 and -0.25 eÅ^{-3}	0.44 and -0.46 eÅ^{-3}

References

S1. R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf and D. Stalke, *Chem. Commun.*, 2012, **48**, 4561–4563.

S2. SAINT, Bruker AXS Inc., Madison, Wisconsin (USA) 2000.

S3. G. M. Sheldrick, SADABS, Universität Göttingen, Germany, 2008.

S4. G. M. Sheldrick, *Crystallogr.Sect. A*, 2008, **64**, 112–122.

S5. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.*, 2011, **44**, 1281–1284.

S6 D. Jayatilaka, B. Dittrich. *Acta Cryst. A* 2008, **64**, 383–393.