

Supplementary Information

A Début for Base Stabilized Monoalkylsilylenes

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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. LSiCl^{S1} (**1**) and $\text{KC}(\text{SiMe}_3)_3^{\text{S2}}$ were prepared as reported in the literature. ^1H and ^{29}Si NMR spectra were recorded with a 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 $\text{LSi}i\text{Bu}$ (2**)** Toluene (60 mL) was added to a 100 mL Schlenk flask containing LSiCl (0.41 g, 1.39 mmol) at room temperature. To this solution $\text{Li}i\text{Bu}$ (1.7 M in pentane, 0.85 mL, 1.45 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**. (0.40 g, 91%). Elemental analysis (%) calcd for $\text{C}_{19}\text{H}_{32}\text{N}_2\text{Si}$ (316.56): C, 72.09; H, 10.19; N, 8.85. Found: C, 72.02; H, 10.25; N, 8.67. ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 1.11 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.30 (s, 9H, $\text{SiC}(\text{CH}_3)_3$), 6.88–7.08 (m, 5 H, C_6H_5) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.36 MHz, C_6D_6 , 25 °C): δ 61.5 ppm. EI-MS: m/z 316 [M^+].

Synthesis of $\text{LSi}[\text{C}(\text{SiMe}_3)_3]$ (3**)** Toluene (60 mL) was added to a 100 mL Schlenk flask containing LSiCl (0.31 g, 1.05 mmol) and $\text{KC}(\text{SiMe}_3)_3$ (0.29 g, 1.07 mmol) at room temperature. The reaction mixture was stirred for 6 h. Then it was filtered and the solvent was removed *in vacuo* to obtain **3**. (0.46 g, 88%). Elemental analysis (%) calcd for $\text{C}_{25}\text{H}_{50}\text{N}_2\text{Si}_4$ (491.02): C, 61.15; H, 10.26; N, 5.71. Found: C, 61.06; H, 10.01; N, 5.56. ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 0.57 (s, 27H, $\text{SiC}[\text{Si}(\text{CH}_3)_3]$), 1.23 (s, 18H, $\text{C}(\text{CH}_3)_3$), 6.83–7.21 (m,

5 H, C₆H₅) ppm. ²⁹Si{¹H} NMR (59.63 MHz, C₆D₆, 25 °C): δ 72.7 SiC[Si(CH₃)₃], -0.4 SiC[Si(CH₃)₃] ppm. EI-MS: *m/z* 490 [M⁺].

Synthesis of [LSi^{*i*}Bu(μ-O)]₂ (4) Toluene (60 mL) was added to a 100 mL Schlenk flask containing **2** (0.31 g, 0.98 mmol). To this solution, dry N₂O was passed through for 10 min. Then the solution was reduced *in vacuo* to about 30 mL and stored at -32 °C in a freezer for 3 days to obtain colorless single crystals of **4**. (0.22 g, 73%). Elemental analysis (%) calcd for C₃₈H₆₄N₄O₂Si₂ (665.11): C, 68.62; H, 9.70; N, 8.42. Found: C, 68.42; H, 9.50; N, 8.32. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 1.35 (s, 36H, C(CH₃)₃), 1.68 (s, 18H, SiC(CH₃)₃), 6.88–7.08 (m, 5 H, C₆H₅) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): δ -74.3 ppm. EI-MS: *m/z* 665 [M⁺].

Crystal Structure Determination. Suitable single crystals for X-ray structural analysis of **3** and **4** were obtained by slow evaporation of their corresponding toluene solutions and the crystals were mounted at low temperature in an inert oil under argon atmosphere by applying the X-Temp2 device.^{S3} The diffraction data were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Ag microsource with INCOATEC Quazar mirror optics (λ = 0.5608 Å).^{S4} The data were integrated with SAINT^{S5} and an empirical absorption correction with SADABS^{S6} 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).^{S7} All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*_{iso} values constrained to 1.5 *U*_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

Table S1. Crystal and Structure Refinement parameters for compounds **3** and **4**.

Parameters	3	4
Empirical formula	C ₂₅ H ₅₀ N ₂ Si ₄	C ₃₈ H ₆₄ N ₄ O ₂ Si ₂
Formula Weight	491.03	665.11
Crystal system	monoclinic	triclinic
Space group	<i>P2₁/n</i>	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 14.7600(10) Å <i>b</i> = 12.02020(10) Å <i>c</i> = 17.706(2) Å β = 112.04(2)°	<i>a</i> = 9.878(3) Å <i>b</i> = 10.371(4) Å <i>c</i> = 11.472(5) Å α = 110.480(10) β = 94.95(2) γ = 116.21(2)
Volume, <i>Z</i>	2955.8(5) Å ³ , 4	946.3(6) Å ³ , 1
Density (calcd)	1.103 g/cm ³	1.167 g/cm ³
Absorption coefficient	0.216 mm ⁻¹	0.131 mm ⁻¹
<i>F</i> (000)	1080	364
Crystal size/mm	0.20 x 0.20 x 0.20	0.50 x 0.50 x 0.30
θ range for data collection	1.54 to 27.11°	1.98 to 28.35°
Limiting indices	-18 ≤ <i>h</i> ≤ 18; -15 ≤ <i>k</i> ≤ 15; 22 ≤ <i>l</i> ≤ 22	-13 ≤ <i>h</i> ≤ 13; -13 ≤ <i>k</i> ≤ 13; -15 ≤ <i>l</i> ≤ 15
Reflections collected	50349	27594
Independent reflections	6530 (<i>R</i> _{int} = 0.0277)	4682 (<i>R</i> _{int} = 0.0284)
Completeness to θ	99.9% (θ = 27.11°)	99.5% (θ = 28.35°)
Refinement method	Full- matrix least - squares on <i>F</i> ²	Full- matrix least - squares on <i>F</i> ²
Data/restraints/ parameters	6530 / 0 / 295	4682 / 0 / 217
Goodness - of - fit on <i>F</i> ²	1.046	1.060
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0278, <i>wR</i> 2 = 0.0715	<i>R</i> 1 = 0.0327, <i>wR</i> 2 = 0.0909
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0325, <i>wR</i> 2 = 0.0740	<i>R</i> 1 = 0.0339, <i>wR</i> 2 = 0.0918
Largest diff. peak and hole	0.354 and -0.200 eÅ ⁻³	0.450 and -0.216 eÅ ⁻³

References

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