

Electronic Supplementary Information for:

Twice Silicon-Induced C-H Activation and Tautomerisation of a β -
Diketiminato Ligand and Formation of New Types of
N-Heterocyclic Silanes

Yun Xiong, Shenglai Yao and Matthias Driess*

Technische Universität Berlin, Institute of Chemistry: Metalorganics and Inorganic Materials, Sekr. C2, Strasse
des 17. Juni 135, D-10623 Berlin, Germany. Fax: +49(0)30-314-29732 Tel: +49(0)30-314-29731;

E-mail: matthias.driess@tu-berlin.de;

General Considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material $L^{\text{Me}}\text{H}$ ($L^{\text{Me}} = \text{HC}[\text{C}(\text{Me})\text{-NR}]_2\text{H}$, $\text{R} = 2, 6\text{-Me}_2\text{C}_6\text{H}_3$)¹ was prepared according to literature procedure. SiBr_4 , MeLi (1.6 M in diethyl ether) were purchased from ACROS and used as received. The NMR spectra were recorded

on Bruker Spectrometers AS 200 and AV 400 with residual solvent signals as internal reference (^1H and $^{13}\text{C}\{^1\text{H}\}$) or with an external reference (SiMe_4 for ^{29}Si). Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; mult = multiplet; br = broad.

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of Compounds **2**, **3** and **5** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined on F^2 with the SHELX-97² software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 705079 (**2**), 705080 (**3**) and 705081 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Compound 2, 3 and 4:

Methyl lithium (27.00 mL, 43.20 mmol, 1.6 mol/L in diethyl ether) was dropped into a solution of $\text{L}^{\text{Me}}\text{H}$ (13.24 g, 43.20 mmol) in diethyl ether (200 mL) at -20°C with stirring. After the addition the reaction mixture was allowed to warm to room temperature and stirred further for 4 hours. The resulting solution was then cooled to -40°C and silicon tetrabromide (5.38 mL, 43.20 mmol,) were added with stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. The proton NMR spectrum of the solution showed that there were two products (**2** and **3**). The volatile components were removed *in vacuo*. The residue was first extracted with n-hexane (300 mL, in portions), then with toluene (300 mL, in portions) and finally with dichloromethane (200 mL). Concentration of the n-hexane extract (to about 100 mL) and cooling to -20°C for 2 days led to the isolation of colourless crystals of **2** (8.08 g, 16.42 mmol, 38%). Concentration of the toluene extract (to about 50 mL) and cooling to -20°C for 2 days led to the isolation of colourless crystals of **3** (2.95 g, 3.89 mmol, 9%). Evaporation of the dichloromethane extract gave a white solid of **4** (3.51 g, 9.07 mmol, 21%).

For compound 2:

Mp: 137 °C (decomp.). ^1H NMR (200.13 MHz, C_6D_6 , 298K): δ 1.40 (s, 3 H, NCMe), 2.11 (s, 6 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 2.31 (s, 6 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 4.25 (d, 1 H, $^4J_{\text{HH}} = 2.7\text{Hz}$, $\alpha\text{-CH}$), 4.47 (s, 1 H, NH), 4.76 (d, ^1H , $^4J_{\text{HH}} = 2.7\text{Hz}$, $\gamma\text{-CH}$), 6.91-7.02 (m, br, 6 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6 , 298K): δ 18.2 – 22.6 (Me), 78.12($\alpha\text{-C}$), 100.4 ($\gamma\text{-C}$), 125.6-155.2 (NCMe , NCCH_2 , 2,6- $\text{Me}_2\text{C}_6\text{H}_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, C_6D_6 , 298K): δ -31.4 (s). IR (KBr, cm^{-1}): 426 (w), 524 (w), 731 (w), 766 (s), 969 (m), 1041 (s), 1094 (s), 1196 (s), 1298 (s), 1341 (m), 1381 (s), 1442 (s), 1472 (s), 1531 (s), 1559 (s), 1597 (s), 2655 (w), 2845 (s), 2969 (s), 3145(s). EI-MS: m/z (%): 492.3(5, $[\text{M}]^+$), 476.9 (6, $[\text{M-Me}]^+$), 371.8 (7, $[\text{M-NHR}]^+$, $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$), 306.2 (35, $[\text{M-SiBr}_2]^+$), 291.1 (30.0, $[\text{M-SiBr}_2\text{-Me}]^+$), 187.1(100, $[\text{HSiBr}_2]^+$). Elemental analysis (%) calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{SiBr}_2$: C, 51.23; H, 4.91; N, 5.69. Found: C, 50.82; H, 4.70; N, 5.44.

For compound 3:

Mp: 140 °C (decomp.). ^1H NMR (200.13 MHz, C_6D_6 , 298K): δ 1.36 (s, 3 H, NCMe), 2.21 (s, 6 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 2.28 (s, 6 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 5.22 (d, 1 H, $^4J_{\text{HH}}=3.0\text{Hz}$, $\alpha\text{-CH}$), 5.96 (d, 1H, $^4J_{\text{HH}}=3.0\text{Hz}$, $\gamma\text{-CH}$), 6.81-6.90 (m, br, 6 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6 , 298K): δ 19.3 – 22.7 (Me), 92.7 ($\alpha\text{-C}$), 101.1 ($\gamma\text{-C}$), 128.6-153.7 (NCMe , NCCH_2 , 2,6- $\text{Me}_2\text{C}_6\text{H}_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, C_6D_6 , 298K): δ -31.2 (s, SiBr_2), -66.1 (s, SiBr_3). IR (KBr, cm^{-1}): 443 (w), 525 (w), 732 (w), 765 (s), 962 (m), 1041 (s), 1094 (s), 1165 (s), 1197 (s), 1298 (s), 1341 (w), 1381 (s), 1443 (s), 1472 (s), 1540 (s), 1558 (s), 1597 (s), 2655 (w), 2845 (s), 2968 (s), 3140 (s). EI-MS: m/z (%): 759.6(55, $[\text{M}]^+$), 744.6 (21, $[\text{M-Me}]^+$), 679.7 (35, $[\text{M-Br}]^+$), 491.9 (14, $[\text{M-SiBr}_3]^+$), 477.0(13, $[\text{M-SiBr}_3\text{-Me}]^+$), 371.7(13, $[\text{M-SiBr}_3\text{-NHR}]^+$, $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$). Elemental analysis (%) calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{Si}_2\text{Br}_5$: C, 33.23; H, 3.05; N, 3.69. Found: C, 33.05; H, 3.21; N, 3.70.

For compound 4:

^1H NMR (200.13 MHz, C_6D_6 , 298K): δ 1.89 (s, 12 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 2.61 (s, 6 H, NCMe), 4.10 (s, 1 H, $\gamma\text{-CH}$), 6.72-6.98 (m, br, 6 H, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$), 11.45 (s, 2H, NH); EI-MS: m/z (%): 307.1 (9, $[\text{M-Br}]^+$), 187.1 (100, $[\text{M-NC}_6\text{H}_3\text{Me}_2]^+$).

Compound 5: Methyl lithium (23.65 mL, 37.85 mmol, 1.6 mol/L in diethyl ether) was dropped into a solution of $\text{L}^{\text{Me}}\text{H}$ (11.60 g, 37.85 mmol) in diethyl ether (200 mL) at -20°C

with stirring. After the addition the reaction mixture was allowed to warm to room temperature and stirred further for 4 hours. The resulting solution was then cooled to $-40\text{ }^{\circ}\text{C}$ and tetramethylethylenediamine (17 mL) and silicon tetrabromide (7.70 mL, 37.85 mmol) were added with stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. The volatile components were removed *in vacuo* and the residue extracted with n-hexane (500 mL, in portions). Concentration (to about 100 mL) and subsequent cooling to -20°C for 12 hours led to the isolation of colourless crystals of **5** (11.74 g, 23.84 mmol, 63%). Mp: $128\text{ }^{\circ}\text{C}$ (decomp.). ^1H NMR (200.13 MHz, C_6D_6 , 298K): δ 1.32 (s, 3 H, NCMe), 2.39 (s, 6 H, 2,6-Me₂C₆H₃), 2.49 (s, 6 H, 2,6-Me₂C₆H₃), 3.56 (s, 1 H, NCCH₂), 3.97 (s, 1 H, NCCH₂), 5.36 (s, 1 H, γ -CH), 6.87-7.14 (m, br, 6 H, 2,6-Me₂C₆H₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6 , 298K): δ 20.1, 20.2, 21.2 (NCMe, 2,6-Me₂C₆H₃), 87.5 (NCCH₂), 105.9 (γ -C), 129.2-144.7 (NCMe, NCCH₂, 2,6-Me₂C₆H₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, C_6D_6 , 298K): δ -55.1 (s). IR (KBr, cm^{-1}): 414 (w), 452 (w), 475 (w), 500 (w), 533 (w), 561 (w), 613 (w), 655 (w), 780 (s), 846 (w), 873 (w), 958 (m), 977 (s), 998 (s), 1039 (s), 1097 (m), 1183 (s), 1204 (m), 1233 (s), 1262 (m), 1327 (s), 1364 (s), 1437 (s), 1471 (s), 1558 (s), 1591 (m), 2458 (m), 2586 (s), 2630 (s), 3038 (s). EI-MS: m/z (%): 492.8 (7, $[\text{M}]^+$), 491.8 (20, $[\text{M}-\text{H}]^+$), 476.9 (100, $[\text{M}-\text{Me}]^+$). Elemental analysis (%) calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{SiBr}_2$: C, 51.23; H, 4.91; N, 5.69. Found: C, 51.08; H, 4.96; N, 5.99.

Reference

¹ Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514-1516.

² G. M. Sheldrick, *SHELX-97 Program for Crystal Structure Determination*, Universität Göttingen (Germany) **1997**.