

## **An Isolable NHC Supported Silanone**

Yun Xiong, Shenglai Yao, Matthias Driess \*

*Institute of Chemistry: Metalorganics and Inorganic Materials, Technische Universität Berlin, Strasse  
des 17. Juni 135, Sekr. C2, D-10623 Berlin, Germany*

## ***Supporting Information***

## Experimental Section

### 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  $\text{LSi}:(\mathbf{1})^1$   $\{\text{L} = \text{CH}[(\text{C}=\text{CH}_2)\text{CMe}][\text{N}(\text{Ar})]_2\}$ ,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\}$  and 1,3,4,5-tetramethylimidazol-2-ylidene  $^2$  were prepared according to literature procedures.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , NMR spectra were recorded on Bruker ARX200 and AV 400 Spectrometers.

**Single-Crystal X-ray Structure Determinations:** Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold  $\text{N}_2$  flow. The data of compounds **2** and **3** 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-97  $^3$  software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

**Compound 2:** 1,3,4,5-tetramethylimidazol-2-ylidene (0.22g, 1.77 mmol) in toluene (10mL) was added to a solution of silylene **1** (0.79 g, 1.77 mmol) in toluene (10 mL) at  $-60^\circ\text{C}$ . After 30 min the reaction was completed and the solution was concentrated to about 5 mL and cooled at  $-20^\circ\text{C}$ . The product **2** crystallized as yellow crystals (0.87 g, 1.52 mmol, 86 %). M.p.  $127^\circ\text{C}$  (decomp.);  $^1\text{H}$  NMR (200.13 MHz,  $[\text{D}_6]\text{benzene}$ ,  $25^\circ\text{C}$ ):  $\delta = 0.36$  (d,  $^3J(\text{H,H}) = 7.0 \text{ Hz}$ , 6 H;  $\text{CHMe}_2$ ), 1.06 (s, 3 H;  $\text{C}_2\text{Me}_2$ ), 1.12 (d,  $^3J(\text{H,H}) = 7.0 \text{ Hz}$ , 3 H;  $\text{CHMe}_2$ ), 1.41 (s, 3 H,  $\text{C}_2\text{Me}_2$ ), 1.45 (d,  $^3J(\text{H,H}) = 7.0 \text{ Hz}$ , 3 H;  $\text{CHMe}_2$ ), 1.49 (d,  $^3J(\text{H,H}) = 7.0 \text{ Hz}$ , 3 H;  $\text{CHMe}_2$ ), 1.61-1.63 ( $3 \times \text{d}$ ,  $^3J(\text{H,H}) = 7.0 \text{ Hz}$ , 9 H;  $\text{CHMe}_2$ ), 1.65 (s, 3 H;  $\text{NCMe}$ ), 2.93 (m, 2 H;  $\text{CHMe}_2$ ), 3.16 (s, 3 H;  $\text{NMe}$ ), 3.29 (s, 1 H;  $\text{NCCH}_2$ ), 3.79 (s, 3 H,  $\text{NMe}$ ), 3.96 (s, 1 H;  $\text{NCCH}_2$ ), 4.27 (m, 2 H;  $\text{CHMe}_2$ ), 5.50 (s, 1 H;  $\gamma\text{-CH}$ ), 7.04 – 7.40 ppm (m, br, 6 H; 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.61 MHz,  $[\text{D}_6]\text{benzene}$ ,  $25^\circ\text{C}$ ):  $\delta = 7.8, 7.9$  ( $\text{C}_2\text{Me}_2$ ), 23.5, 23.9, 24.2, 24.3, 24.8, 24.9, 25.8, 26.0, 26.1, 27.5, 28.1, 29.2, 29.4 ( $\text{NCMe}$ ,  $\text{CHMe}_2$ ), 32.5, 34.2 ( $\text{NMe}$ ), 81.2 ( $\text{NCCH}_2$ ), 103.4 ( $\gamma\text{-C}$ ), 123.1, 123.6, 124.7, 124.8, 125.1, 125.4, 126.1, 126.4, 143.3, 144.0, 144.3, 147.7, 148.4, 148.7, 149.3, 151.5 ( $\text{NCMe}$ ,  $\text{NCCH}_2$ , 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ ,  $\text{C}_2\text{Me}_2$ ), 169.4 ppm ( $\text{SiC}$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $[\text{D}_6]\text{benzene}$ ,  $25^\circ\text{C}$ ):  $\delta = -12.0$  ppm (s); EI-MS:  $m/z$  (%): 568.42 (12  $[\text{M}^+]$ ), 553.38 (21  $[\text{M-Me}]^+$ ), 525.32 (18  $[\text{M-}i\text{Pr}]^+$ ), 418.35 (43  $[\text{L}]^+$ ), 403.32 (100  $[\text{L-Me}]^+$ ). Elemental analysis calcd (%) for  $\text{C}_{36}\text{H}_{52}\text{N}_4\text{Si}$ : C 76.0, H 9.2, N

9.9, found: C 76.4, H 9.4, N 9.8. IR (KBr,  $\text{cm}^{-1}$ ): 420 (W), 464 (W), 490 (w), 738 (w), 759 (m), 787 (w), 804 (m), 851 (w), 880 (w), 930 (w), 983 (w), 1045 (m), 1058 (m), 1078 (m), 1105 (m), 1136 (w), 1177 (w), 1197 (w), 1210 (w), 1254 (m), 1357 (m), 1382 (s), 1440 (s), 1466 (s), 1551 (m), 1624 (s), 2052 (w), 2867 (m), 2927 (m), 2963 (s), 3055 (w), 3105 (w).

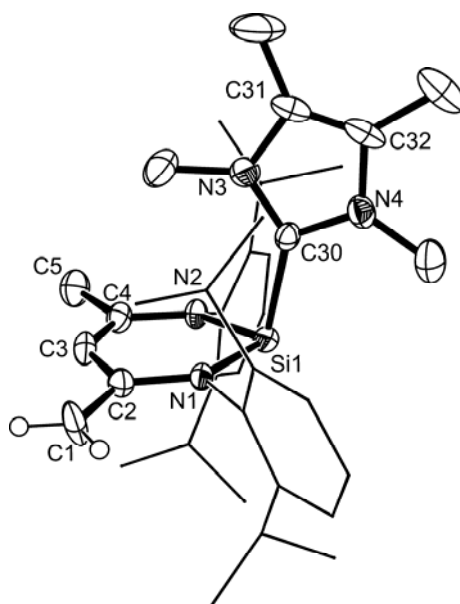
**Compound 3:** A solution of **2** (0.45 g, 0.79 mmol) in toluene (20 ml) was cooled to  $-78^{\circ}\text{C}$ . The  $\text{N}_2$  atmosphere in the flask was exchanged to  $\text{N}_2\text{O}$ . In the course of stirring and warming to room temperature a colorless precipitate formed. Volatiles were removed in *vacuo* and the residue was washed with hexane to afford compound **3** as a white powder (0.43 g, 0.74 mmol, 94 %). X-ray diffraction-quality crystals were obtained by recrystallization from toluene/dichloromethane (v/v: 5:1) at  $-20^{\circ}\text{C}$ . M.p.  $239\text{--}241^{\circ}\text{C}$ .  $^1\text{H}$  NMR (200.13 MHz,  $[\text{D}_2]$ dichloromethane,  $25^{\circ}\text{C}$ ):  $\delta$  = 0.32 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3 H;  $\text{CHMe}_2$ ), 0.42 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3 H;  $\text{CHMe}_2$ ), 1.09 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3 H;  $\text{CHMe}_2$ ), 1.11 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3 H;  $\text{CHMe}_2$ ), 1.17 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3 H;  $\text{CHMe}_2$ ), 1.22 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 9 H;  $\text{CHMe}_2$ ), 1.34 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3 H;  $\text{CHMe}_2$ ), 1.37 (d,  $^3J(\text{H,H})$  = 6.9 Hz, 3 H;  $\text{CHMe}_2$ ), 1.50 (s, 3 H;  $\text{NCMe}$ ), 2.06 (s, 3 H,  $\text{C}_2\text{Me}_2$ ), 2.26 (s, 3 H;  $\text{C}_2\text{Me}_2$ ), 2.62 (sept,  $^3J(\text{H,H})$  = 6.9 Hz, 1 H;  $\text{CHMe}_2$ ), 2.71 (sept,  $^3J(\text{H,H})$  = 6.9 Hz, 1 H;  $\text{CHMe}_2$ ), 2.80 (s, 1 H;  $\text{NCCH}_2$ ), 3.59 (s, 1 H;  $\text{NCCH}_2$ ), 3.81 (sept,  $^3J(\text{H,H})$  = 6.9 Hz, 1 H;  $\text{CHMe}_2$ ), 3.83 (sept,  $^3J(\text{H,H})$  = 6.9 Hz, 1 H;  $\text{CHMe}_2$ ), 3.99 (s, 3 H;  $\text{NMe}$ ), 4.17 (s, 3 H,  $\text{NMe}$ ), 5.532 (s, 1 H;  $\gamma\text{-CH}$ ), 6.95 – 7.25 ppm (m, br, 6 H; 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.61 MHz,  $[\text{D}_2]$ dichloromethane,  $25^{\circ}\text{C}$ ):  $\delta$  = 8.9, 9.0 ( $\text{C}_2\text{Me}_2$ ), 22.6 – 29.1 ( $\text{NCMe}$ ,  $\text{CHMe}_2$ ), 34.20, 34.22 ( $\text{NMe}$ ), 84.3 ( $\text{NCCH}_2$ ), 103.5 ( $\gamma\text{-C}$ ), 123.4 – 154.7 ( $\text{NCMe}$ ,  $\text{NCCH}_2$ , 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ ,  $\text{C}_2\text{Me}_2$ ,  $\text{SiC}$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $[\text{D}_6]$ benzene,  $25^{\circ}\text{C}$ ):  $\delta$  =  $-74.2$  ppm (s); EI-MS:  $m/z$  (%): 584.39 (12,  $[\text{M}]^+$ ), 569.39 (29,  $[\text{M-Me}]^+$ ), 541.34 (100,  $[\text{M-}^i\text{Pr}]^+$ ). Elemental analysis (%): calcd for  $\text{C}_{36}\text{H}_{52}\text{N}_4\text{SiO}$ : C, 73.9; H, 9.0; N, 9.6. Found C, 74.4; H, 9.3; N, 9.4. IR (KBr,  $\text{cm}^{-1}$ ): 407 (W), 462 (m), 475 (m), 490 (m), 510 (w), 540 (w), 564 (m), 584 (w), 600 (w), 737 (w), 760 (m), 805 (m), 851 (m), 911 (w), 923 (m), 938 (w), 980 (w), 1046 (m), 1057 (m), 1134 (s), 1178 (m), 1195 (m), 1252 (m), 1309 (m), 1355 (s), 1380 (s), 1407 (w), 1442 (m), 1466 (m), 1523 (w), 1583 (w), 1639 (s), 2866 (m), 2927 (m), 2966 (s), 3056 (w), 3109 (w).

### Crystallographic data for **2**

Empirical formula

$\text{C}_{36}\text{H}_{52}\text{N}_4\text{Si}$

Formula weight	568.91	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 12.5248(7) Å	$\alpha = 90^\circ$ .
	b = 16.5902(7) Å	$\beta = 105.545(5)^\circ$ .
	c = 17.3318(8) Å	$\gamma = 90^\circ$ .
Volume	3469.6(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.089 Mg/m <sup>3</sup>	
Absorption coefficient	0.096 mm <sup>-1</sup>	
F(000)	1240	
Crystal size	0.06 x 0.05 x 0.04 mm <sup>3</sup>	
Theta range for data collection	2.98 to 25.00°.	
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	
Reflections collected	24365	
Independent reflections	6086 [R(int) = 0.1483]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6086 / 18 / 383	
Goodness-of-fit on F <sup>2</sup>	0.936	
Final R indices [I > 2σ(I)]	R1 = 0.0699, wR2 = 0.0700	
R indices (all data)	R1 = 0.1972, wR2 = 0.0939	
Largest diff. peak and hole	0.216 and -0.185 e.Å <sup>-3</sup>	



**Figure 1.** Molecular structure of compound **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except for those at C1) are omitted for clarity.

Table 1. Selected interatomic distances and angles of compound **2**

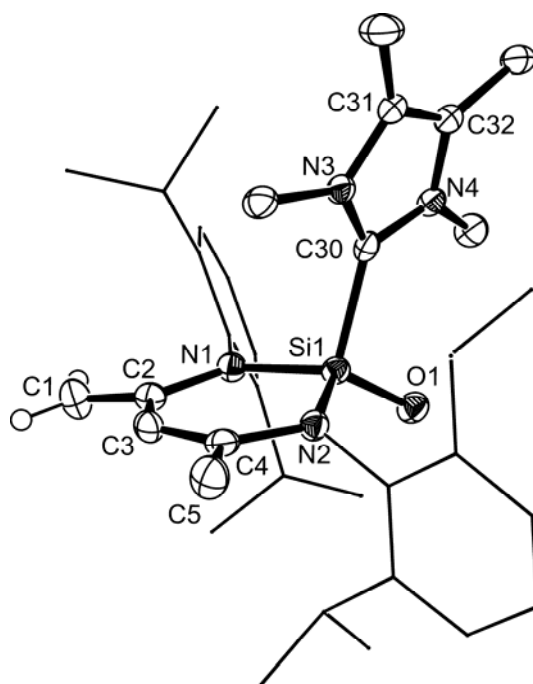
Interatomic distances (pm)		Angles(°)	
Si1-N2	1.802(3)	N2-Si1-N1	97.7(1)
Si1-N1	1.805(3)	N2-Si1-C30	100.4(1)
Si1-C30	2.016(3)	N1-Si1-C30	97.8(1)
N1-C2	1.392(3)	C2-N1-Si1	128.4(2)
N2-C4	1.401(4)	C4-N2-Si1	125.5(2)
N3-C30	1.358(4)	C30-N3-C31	111.8(3)
N3-C31	1.389(4)	C30-N4-C32	111.9(3)
N4-C30	1.359(3)	N1-C2-C3	118.1(3)
N4-C32	1.385(4)	C4-C3-C2	127.7(3)
C1-C2	1.383(4)	C3-C4-N2	122.0(3)
C2-C3	1.427(4)	N3-C30-N4	102.9(3)
C3-C4	1.376(4)	N3-C30-Si1	134.6(3)
C4-C5	1.470(4)	N4-C30-Si1	121.7(3)
C31-C32	1.329(4)	C32-C31-N3	106.6(3)
		C31-C32-N4	106.8(3)

### Crystallographic data for **3**

Empirical formula

C<sub>46.50</sub> H<sub>64</sub> N<sub>4</sub> O Si

Formula weight	723.11	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.6511(9) Å	$\alpha = 90^\circ$ .
	b = 15.6914(4) Å	$\beta = 114.280(2)^\circ$ .
	c = 24.5387(8) Å	$\gamma = 90^\circ$ .
Volume	8652.2(5) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.110 Mg/m <sup>3</sup>	
Absorption coefficient	0.092 mm <sup>-1</sup>	
F(000)	3144	
Crystal size	0.48 x 0.42 x 0.31 mm <sup>3</sup>	
Theta range for data collection	3.08 to 25.00°.	
Index ranges	-28 ≤ h ≤ 29, -17 ≤ k ≤ 18, -29 ≤ l ≤ 29	
Reflections collected	25696	
Independent reflections	7611 [R(int) = 0.0303]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.82001	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7611 / 185 / 551	
Goodness-of-fit on F <sup>2</sup>	1.041	
Final R indices [I > 2σ(I)]	R1 = 0.0490, wR2 = 0.1170	
R indices (all data)	R1 = 0.0760, wR2 = 0.1271	
Largest diff. peak and hole	0.521 and -0.399 e.Å <sup>-3</sup>	



**Figure 2.** Molecular structure of compound **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except those at C1) are omitted for clarity.

Table 2 Selected interatomic distances and angles of compound **3**

Interatomic distances (pm)		Angles (°)	
Si1-O1	1.541(2)	O1-Si1-N1	118.81(8)
Si1-N1	1.745(2)	O1-Si1-N2	115.21(8)
Si1-N2	1.750(2)	N1-Si1-N2	102.42(8)
Si1-C30	1.930(2)	O1-Si1-C30	106.09(8)
N1-C2	1.412(3)	N1-Si1-C30	105.61(9)
N2-C4	1.411(2)	N2-Si1-C30	108.00(9)
N3-C30	1.354(3)	C2-N1-Si1	125.8(2)
N3-C31	1.386(3)	C6-N1-Si1	117.1(1)
N4-C30	1.357(3)	C4-N2-Si1	122.8(2)
N4-C32	1.381(3)	N1-C2-C3	117.1(2)
C1-C2	1.355(3)	C4-C3-C2	128.5(2)
C2-C3	1.451(3)	C3-C4-N2	122.0(2)
C3-C4	1.347(3)	N3-C30-N4	104.5(2)
C31-C32	1.351(3)		

## References

<sup>1</sup> Driess, M.; Yao, S.; Brym, M.; van Wüllen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628.

<sup>2</sup> Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

<sup>3</sup> G. M. Sheldrick, *SHELX-97 Program for Crystal Structure Determination*, Universität Göttingen (Germany) **1997**.