

# Controlled Synthesis and Molecular Structures of Methoxy-, Amino-, and Chloro-Functionalized Disiloxane Building Blocks

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*Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday*

**Abstract.** Functionalized disiloxane units with defined structures are interesting molecular models for investigating the reactivity and chemoselectivity in transformations that are of interest in synthesis, surface chemistry, and materials science. (Mes)PhSi(OMe)<sub>2</sub> (**1**) (Mes = mesityl) and (Mes)PhSiCl<sub>2</sub> (**5**) were chosen as starting compounds for the controlled synthesis of methoxy-, amino-, and chloro-functionalized unsymmetric disiloxanes. Two synthesis routes towards

(Mes)PhSi(OMe)(OSiPh<sub>3</sub>) (**3**) were followed, one via the aminomethoxysilane (Mes)PhSi(OMe)(NC<sub>4</sub>H<sub>8</sub>) (**2**) and the other via the chlorodisiloxane (Mes)PhSiCl(OSiPh<sub>3</sub>) (**6**). The amino-substituted disiloxane (Mes)PhSi(NC<sub>4</sub>H<sub>8</sub>)(OSiPh<sub>3</sub>) (**4**) was obtained from the chloro derivative **6** with *N*-pyrrolidinylolithium, but the same reaction starting from compound **3** was not successful. All provided disiloxanes were structurally characterized by X-ray crystallography.

## Introduction

The siloxane bond (Si–O–Si) is a ubiquitous structural motif in nature and in our daily life.<sup>[1]</sup> It is the basis for silicate minerals,<sup>[2]</sup> used by marine organisms for building skeletons,<sup>[3]</sup> and has broad technical applications as inorganic-organic hybrid polymers (silicones) and in materials science.<sup>[4]</sup> Smaller siloxane units with defined structures are interesting molecular models for mimicking complex silicate materials in nature and in technical processes.<sup>[5]</sup>

The development of preparative methods for providing functionalized siloxane units is of great interest.<sup>[6]</sup> Organoalkoxy-siloxanes turned out to be important building blocks for the controlled construction of siloxane-based materials with precisely defined structures and functionalities, and some impressive contributions to their synthesis have been discovered recently.<sup>[7]</sup> Even an asymmetric approach to enantiomerically pure silicon-stereogenic alkoxy-siloxanes using aminomethoxysilanes, a synthetically valuable class of reagents,<sup>[8]</sup> has been reported previously.<sup>[9]</sup> The design of complex siloxane-based structures with a high degree of functionality generally requires an easy and targeted transformation of functional groups without attacking the siloxane framework.<sup>[10]</sup> In addition to alkoxy-silanes that are sometimes quite inert compounds, amino- and chlorosilanes play an important role as precursors for synthetic purposes.<sup>[11]</sup>

Functionalized disiloxanes in particular have interesting properties and are a valuable class of compounds because they represent the smallest structural segment of more complex siloxane networks and surfaces, and are therefore ideal candidates for model studies.<sup>[12]</sup> Unsymmetrically substituted functional disiloxanes are synthetically challenging. The introduction of a triphenylsilyl group enables the study of functional group reactivity on only one silicon atom. Another advantage of Ph<sub>3</sub>E units (E = group 14 element) is that the crystallization tendency of molecules, which are otherwise difficult to crystallize, can be increased significantly.<sup>[13]</sup> This allows studying the effects of functional groups directly attached to a silicon atom on structural parameters of the siloxane bond in the molecular crystalline material.

Herein, we set out to investigate synthetic paths towards the racemic triphenylsilyl-substituted methoxy-, amino-, and chloro-functionalized disiloxanes **3**, **4**, and **6** (Scheme 1), which are reactive building blocks for targeted further transformations depending on the chemical purpose. The molecular structures of all disiloxanes were elucidated by single-crystal X-ray diffraction analysis.

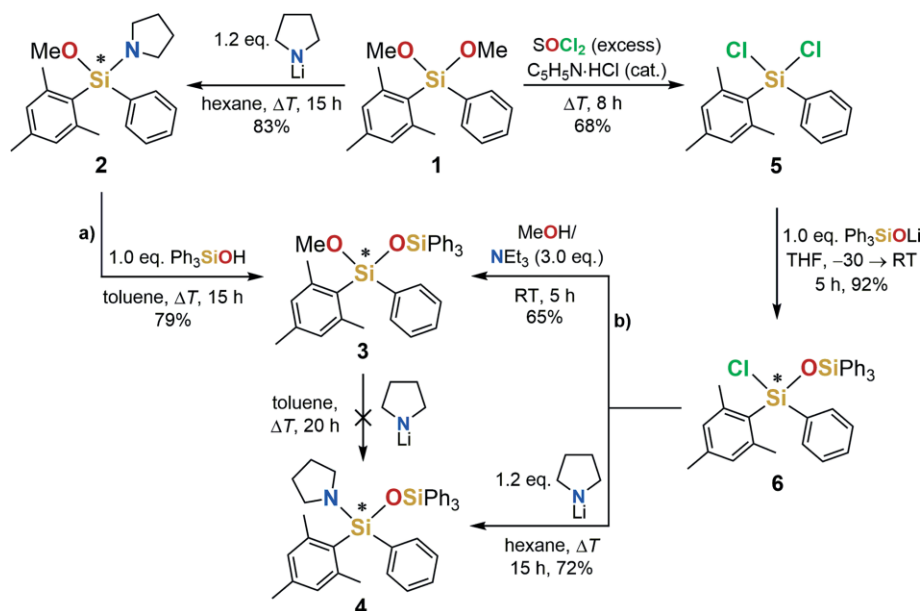
## Results and Discussion

Mesityl(dimethoxy)phenylsilane (**1**), synthesized from mesityltrimethoxysilane via methoxy/phenyl exchange, was chosen as suitable starting compound, since the steric requirement of the mesityl group guaranteed a high degree of chemoselectivity over several nucleophilic substitution steps (Scheme 1). In the first step, reaction of dimethoxysilane **1** with *N*-pyrrolidinylolithium in hexane at reflux resulted in the formation of the mixed-functionalized aminomethoxysilane **2** in 83% isolated yield. This type of reaction has been studied in detail and provides synthetically useful intermediates for subsequent chemoselective transformations because of the presence of two reac-

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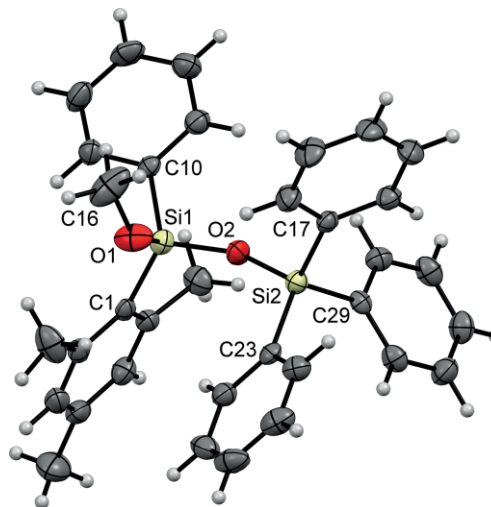


**Scheme 1.** Functionalization paths starting from mesityl(dimethoxy)phenylsilane (**1**) towards the racemic methoxy-, amino-, and chlorodisiloxanes **3**, **4**, and **6**.

tive functionalities within the same molecule that behave differently in chemical reactions with different nucleophiles.<sup>[8,9,14]</sup> When the reaction was carried out at room temperature, compound **2** was formed with a conversion of only 38% after 20 h. The reduced reactivity can be explained by the increased steric shielding by the mesityl group, since the same reaction under same conditions using dimethoxydiphenylsilane leads to full conversion.<sup>[8]</sup> Heating a solution of (Mes)PhSi(OMe)(NC<sub>4</sub>H<sub>8</sub>) (**2**) and triphenylsilanol in toluene at reflux for 15 h led to chemoselective substitution of the amino group and gave the methoxydisiloxane (Mes)PhSi(OMe)(OSiPh<sub>3</sub>) (**3**) in good yield (79%) (Path a, Scheme 1). However, no conversion was observed when performing the reaction at room temperature. This model reaction with a racemic and sterically demanding aminomethoxysilane provides important information that can be transferred to possible stereospecific reactions with optically enriched starting compounds, since it is known that the Si–N bond is stereospecifically cleaved when hydroxy-containing compounds attack a stereogenic silicon center.<sup>[9,15]</sup>

Compound **3** crystallized from a tetrahydrofuran solution layered with pentane at –30 °C in the monoclinic crystal system, space group *P2<sub>1</sub>/n*, as colorless blocks suitable for single-crystal X-ray diffraction analysis (Figure 1). The methoxy-substituted silicon atom in the mesitylmethoxydisiloxane **3** differs only marginally from an ideal tetrahedral coordination with angles ranging from 107.29(9)° [O(2)–Si(1)–C(10)] to 110.91(9)° [C(10)–Si(1)–C(1)]. The Si(1)–O(2)–Si(2) bond angle of 147.37(8)° is slightly smaller than the respective angle of the previously described methoxypentaphenyldisiloxane [150.72(9)°],<sup>[8]</sup> but differs significantly from the Si–O–Si angle in the naphthylmethoxydisiloxane [164.97(9)°].<sup>[9]</sup> These siloxane bond angles are in good agreement with the angles found in the molecular structures of Ph<sub>2</sub>Si(OH)(OSiPh<sub>3</sub>),

which range around two separate areas with extreme values of 145.1(2)° and 169.5(2)°,<sup>[16]</sup> whereas hexaphenyldisiloxane exhibits a linear Si–O–Si bond.<sup>[17]</sup>

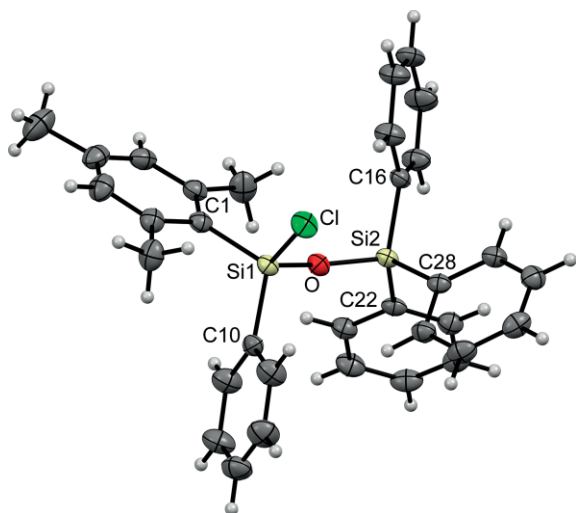


**Figure 1.** Molecular structure of compound **3** in the crystal. Selected bond lengths /Å and angles /°: C(1)–Si(1) 1.868(2), C(10)–Si(1) 1.851(2), C(16)–O(1) 1.383(2), C(17)–Si(2) 1.864(2), C(23)–Si(2) 1.858(2), C(29)–Si(2) 1.8572(19), O(1)–Si(1) 1.6148(13), O(2)–Si(1) 1.6218(13), O(2)–Si(2) 1.6247(13), C(16)–O(1)–Si(1) 131.11(14), Si(1)–O(2)–Si(2) 147.37(8), O(1)–Si(1)–O(2) 107.85(8), O(1)–Si(1)–C(10) 110.32(8), O(2)–Si(1)–C(10) 107.29(9), O(1)–Si(1)–C(1) 110.73(9), O(2)–Si(1)–C(1) 109.63(8), C(10)–Si(1)–C(1) 110.91(9).

The search for new reagents for mild surface modifications is a worthwhile goal.<sup>[18]</sup> In this context, aminosilanes can be regarded as an atom-economic class of silylation reagents and have a number of advantages over chlorosilanes and alkoxy-silanes in terms of surface functionalization; mild and additive-free reaction conditions, formation of easy-to-separate by-

products and slow surface reactions allow for controlled monofunctionalization.<sup>[19]</sup> We therefore attempted to convert methoxydisiloxane **3** to the *N*-pyrrolidinyl-substituted derivative (Mes)PhSi(NC<sub>4</sub>H<sub>8</sub>)(OSiPh<sub>3</sub>) (**4**) to provide access to another synthetically useful class of siloxane building blocks. However, direct substitution of the silicon-bound methoxy group by *N*-pyrrolidinyl lithium was unsuccessful even under toluene reflux over a period of 20 hours, presumably due to the increased steric bulkiness around the silicon atom. Based on this finding, we modified our approach to compound **4** and examined a synthetic route via chlorosilanes (Scheme 1), also starting from (Mes)PhSi(OMe)<sub>2</sub> (**1**). Compound **1** was readily chlorinated using excess thionyl chloride and catalytic amounts of pyridine hydrochloride and led to dichlorosilane **5** in 68% yield. The applicability of this reaction was impressively demonstrated by *Muzavarov* and *Rebrov* for the stepwise construction of organopolysiloxane dendrimers.<sup>[10]</sup> Next, the Si–O–Si backbone was built up by straightforward monosubstitution reaction of compound **5** with lithium triphenylsiloxide in tetrahydrofuran at room temperature, with the chlorodisiloxane **6** being formed in very good isolated yield (92%).

(Mes)PhSiCl(OSiPh<sub>3</sub>) (**6**) crystallized from a tetrahydrofuran solution layered with pentane at –30 °C in the triclinic crystal system, space group *P* $\bar{1}$ , as colorless blocks suitable for single-crystal X-ray diffraction analysis (Figure 2). The angles around the Si1 atom in the chlorodisiloxane **6** range from 106.76(5)° [O–Si(1)–Cl] to 114.25(7)° [C(1)–Si(1)–C(10)] and thus deviate more from the ideal tetrahedral angle than in the methoxy derivative. The Si(1)–O–Si(2) bond angle [153.60(8)°] is larger than in compound **3** as well as in compound **4** (see below). Also noticeable in disiloxane **6** is the significantly shorter O–Si(1) bond length of 1.6109(12) Å compared to the O–Si(2) bond [1.6390(12) Å]. These struc-

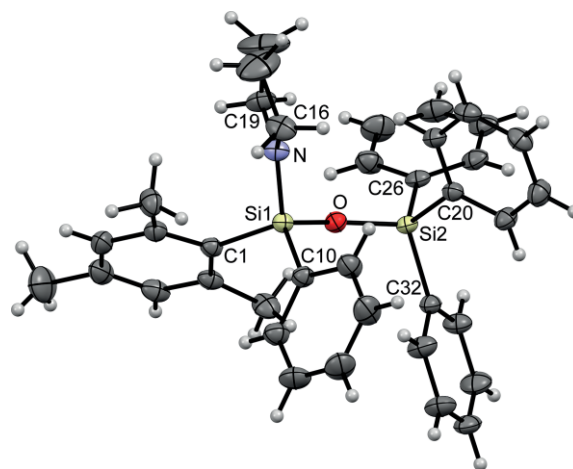


**Figure 2.** Molecular structure of compound **6** in the crystal. Selected bond lengths /Å and angles /°: C(1)–Si(1) 1.8677(17), C(10)–Si(1) 1.8726(16), C(16)–Si(2) 1.8638(16), C(22)–Si(2) 1.8669(16), C(28)–Si(2) 1.8646(16), Cl–Si(1) 2.0847(6), O–Si(1) 1.6109(12), O–Si(2) 1.6390(12), Si(1)–O–Si(2) 153.60(8), O–Si(1)–C(1) 112.31(7), O–Si(1)–C(10) 106.78(6), C(1)–Si(1)–C(10) 114.25(7), O–Si(1)–Cl 106.76(5), C(1)–Si(1)–Cl 108.09(5), C(10)–Si(1)–Cl 108.33(6).

tural parameters may indicate hyperconjugative delocalization of oxygen lone electron pairs into adjacent antibonding orbitals.<sup>[20]</sup> However, the Cl–Si(1) bond length [2.0847(6) Å] is in the typical range for triaryl- and alkyl/aryl-substituted chlorosilanes and shows no noticeable elongation in the crystalline molecular structure.<sup>[21]</sup> Instead, the C(10)–Si(1) bond of 1.8726(16) Å is remarkably longer than the respective bond in disiloxane **3** [1.851(2) Å].

Chlorodisiloxane **6** opens access to both the amino (**4**) and the methoxy derivative (**3**) (Scheme 1). Heating a solution of compound **6** with *N*-pyrrolidinyl lithium at hexane reflux gave chemoselectively (Mes)PhSi(NC<sub>4</sub>H<sub>8</sub>)(OSiPh<sub>3</sub>) (**4**) in 72% yield after 15 h, whereas methanolysis of **6** in the presence of triethylamine at room temperature smoothly led to methoxydisiloxane **3** in 65% yield (Path **b**, Scheme 1).

*N*-Pyrrolidinyl disiloxane **4** crystallized from hot hexane in the triclinic crystal system, space group *P* $\bar{1}$ , as colorless plates suitable for single-crystal X-ray diffraction analysis (Figure 3). The silicon atom Si1 of aminodisiloxane **4** shows a slightly distorted tetrahedral coordination ranging from 106.49(7)° [O–Si(1)–C(1)] to 111.89(7)° [N–Si(1)–C(10)], which is comparable to compounds **3** and **6**. The Si(2)–O–Si(1) bond angle of 148.62(8)° lies between the angles of the other two mesityl-disiloxanes. The almost ideal planar geometry around the nitrogen atom [sum of angles: 359.9(4)°] is possibly the result of a pronounced lone-pair electron density transfer from the nitrogen atom towards the N–Si bond, which leads to a short N–Si(1) bond length of 1.7127(14) Å.<sup>[22]</sup> This might also be the reason for a slight increase of the O–Si(1) bond length [1.6324(12) Å] compared with the respective bond in the molecular structures of disiloxanes **3** and **6**.



**Figure 3.** Molecular structure of compound **4** in the crystal. Selected bond lengths /Å and angles /°: C(1)–Si(1) 1.8864(17), C(10)–Si(1) 1.8657(17), C(20)–Si(2) 1.8699(17), C(26)–Si(2) 1.8692(17), C(32)–Si(2) 1.8661(16), N–Si(1) 1.7127(14), O–Si(1) 1.6324(12), O–Si(2) 1.6258(12), C(16)–N–C(19) 110.17(14), C(16)–N–Si(1) 129.80(12), C(19)–N–Si(1) 119.97(12), Si(2)–O–Si(1) 148.62(8), O–Si(1)–N 107.03(7), O–Si(1)–C(10) 109.70(7), N–Si(1)–C(10) 111.89(7), O–Si(1)–C(1) 106.49(7), N–Si(1)–C(1) 111.11(7), C(10)–Si(1)–C(1) 110.42(7).

## Conclusions

In summary, we presented the synthesis and molecular structures of three unsymmetrically substituted new disiloxanes equipped with Si–O (**3**), Si–N (**4**), and Si–Cl (**6**) functions, respectively. They are model systems to further investigate their suitability as building blocks for the targeted design of more complex functional siloxane frameworks. The reactivity and chemoselectivity studies on racemic precursors used in this work provide valuable information that are also of interest for future studies on stereospecific transformations using enantio-merically enriched functionalized silanes. Furthermore, crystallographic data for small disiloxane units in which only one silicon atom is bound to another heteroatom are scarce but interesting molecular models to study influences on structural parameters of the Si–O–Si backbone. The Si–O–Si bond angle can differ considerably when compared with related molecules, which results from the interplay between steric and electronic effects.

## Experimental Section

**General Remarks:** All experiments were performed in an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated at 140 °C prior to use. Diethyl ether, hexane, pentane, tetrahydrofuran, and toluene were dried and degassed with a MBraun SP800 solvent purification system. 2-Bromomesitylene (98%, Sigma–Aldrich), *n*-butyllithium (2.5 M solution in hexane, Sigma–Aldrich), phenyllithium (1.9 M solution in dibutyl ether, Sigma–Aldrich), pyrrolidine (99%, Sigma–Aldrich), tetramethoxysilane (98%, ABCR), trichlorophenylsilane (97%, Sigma–Aldrich), triphenylsilanol (98%, Sigma–Aldrich), triethylamine (Merck, 99%), pyridine hydrochloride (Merck, 98%), thionyl chloride (99%, Merck), and magnesium turnings (99%, Merck) were used without further purification. Mesityltrimethoxysilane was synthesized according to a published procedure.<sup>[23]</sup> Dichloromesitylphenylsilane (**5**) has been reported previously,<sup>[24]</sup> but was prepared according to a modified procedure; the new protocol is presented herein. [D<sub>6</sub>]benzene used for NMR spectroscopy was dried with Na/K amalgam. NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz) at 25 °C. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra are referenced to tetramethylsilane (SiMe<sub>4</sub>,  $\delta$  = 0.0 ppm) as external standard, with the deuterium signal of the solvent serving as internal lock and the residual solvent signal as an additional reference. <sup>29</sup>Si{<sup>1</sup>H} NMR spectra are referenced to SiMe<sub>4</sub> ( $\delta$  = 0.0 ppm) as external standard. For the assignment of the multiplicities the following abbreviations were used: s = singlet, m = multiplet. High resolution mass spectrometry was carried out on a Jeol AccuTOF GCX and an Agilent Q-TOF 6540 UHD spectrometer. Elemental analyses were performed on a Vario MICRO cube apparatus.

**X-ray Crystallography:** Single-crystal X-ray diffraction analysis of **3** was performed on an Oxford Diffraction CCD Xcalibur S diffractometer equipped with a Sapphire3 CCD detector at 173(2) K using graphite-monochromated Mo-*K*<sub>α</sub> radiation ( $\lambda$  = 0.71073 Å). Single-crystal X-ray diffraction analyses of **4** and **6** were performed on a GV50 diffractometer equipped with a TitanS2 CCD detector at 123(1) K using Cu-*K*<sub>α</sub> radiation ( $\lambda$  = 1.54184 Å). Data collection and reduction were performed using the CrysAlisPro software system (Version 1.171.33.55 for **3** and Version 1.171.40.66a for **4** and **6**).<sup>[25]</sup> The

crystal structure of **3** was solved with SHELXS-97 and the crystal structures of **4** and **6** were solved with SHELXT 2018/2 using Olex2.<sup>[26–29]</sup> All crystal structures were refined based on F<sup>2</sup> with the full-matrix least-squares method (SHELXL-2018/3)<sup>[27,30,31]</sup> using the SHELX program package as implemented in WinGX.<sup>[32]</sup> A multi-scan absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was employed. The non-hydrogen atoms were refined using anisotropic displacement parameters. All hydrogen atoms were placed in idealized geometric positions and each was assigned a fixed isotropic displacement parameter based on a riding-model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the methylene (CH<sub>2</sub>) and aromatic (CH) hydrogen atoms and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl (CH<sub>3</sub>) hydrogen atoms. The C–H distances constrained to 0.98 Å for the methyl groups, to 0.97 Å for the methylene groups, and to 0.95 Å (**3**) and 0.93 Å (**4**, **6**) for the aryl groups. Figure 1, Figure 2, and Figure 3 were created using Mercury 4.1.0.<sup>[33]</sup>

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1981219 (**3**), CCDC-1981220 (**6**), and CCDC-1981221 (**4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

**Crystal Data and Structure Refinement of 3:** Colorless blocks, 0.30 × 0.20 × 0.20 mm<sup>3</sup>, C<sub>34</sub>H<sub>34</sub>O<sub>2</sub>Si<sub>2</sub>, Mr = 530.79 g·mol<sup>-1</sup>, monoclinic, space group (Nr.) *P*2<sub>1</sub>/*n* (14), *a* = 7.8554(4) Å, *b* = 18.7946(12) Å, *c* = 19.8423(12) Å,  $\beta$  = 90.926(5)°, *V* = 2929.1(3) Å<sup>3</sup>, *Z* = 4,  $\rho$  = 1.204 g·cm<sup>-3</sup>,  $\mu$  = 0.150 mm<sup>-1</sup>. 21716 reflections collected with  $\theta$  in the range 2.322 – 24.997°, index ranges  $-9 \leq h \leq 9$ ,  $-21 \leq k \leq 22$ ,  $-23 \leq l \leq 23$ , 5164 independent reflections ( $R_{\text{int}} = 0.0564$ ), 347 parameters with 0 restraints gave final *R* indices  $R_1 = 0.0379$  and  $wR_2 = 0.0475$  [data with  $I > 2\sigma(I)$ ].  $R_1 = 0.0855$ ,  $wR_2 = 0.0496$  (all data), goodness-of-fit on  $F^2 = 1.000$ , largest electron density peak 0.223 e·Å<sup>-3</sup>, largest hole  $-0.267$  e·Å<sup>-3</sup>.

**Crystal Data and Structure Refinement of 4:** Colorless plates, 0.37 × 0.21 × 0.04 mm<sup>3</sup>, C<sub>37</sub>H<sub>39</sub>NOSi<sub>2</sub>, Mr = 569.87 g·mol<sup>-1</sup>, triclinic, space group (Nr.) *P* $\bar{1}$  (2), *a* = 9.5542(4) Å, *b* = 12.6193(5) Å, *c* = 14.6829(7) Å,  $\alpha$  = 103.043(4)°,  $\beta$  = 92.016(4)°,  $\gamma$  = 111.301(4)°, *V* = 1593.35(13) Å<sup>3</sup>, *Z* = 2,  $\rho$  = 1.188 g·cm<sup>-3</sup>,  $\mu$  = 1.226 mm<sup>-1</sup>. 10793 reflections collected with  $\theta$  in the range 3.889 – 74.077°, index ranges  $-8 \leq h \leq 11$ ,  $-15 \leq k \leq 13$ ,  $-18 \leq l \leq 17$ , 6164 independent reflections ( $R_{\text{int}} = 0.0305$ ), 373 parameters with 0 restraints gave final *R* indices  $R_1 = 0.0449$  and  $wR_2 = 0.1180$  [data with  $I > 2\sigma(I)$ ].  $R_1 = 0.0498$ ,  $wR_2 = 0.1225$  (all data), goodness-of-fit on  $F^2 = 1.027$ , largest electron density peak 0.797 e·Å<sup>-3</sup>, largest hole  $-0.553$  e·Å<sup>-3</sup>.

**Crystal Data and Structure Refinement of 6:** Colorless blocks, 0.19 × 0.18 × 0.09 mm<sup>3</sup>, C<sub>33</sub>H<sub>31</sub>ClOSi<sub>2</sub>, Mr = 535.21 g·mol<sup>-1</sup>, triclinic, space group (Nr.) *P* $\bar{1}$  (2), *a* = 9.34760(10) Å, *b* = 10.9306(2) Å, *c* = 14.8126(2) Å,  $\alpha$  = 104.5680(10)°,  $\beta$  = 96.9890(10)°,  $\gamma$  = 94.2340(10)°, *V* = 1445.31(4) Å<sup>3</sup>, *Z* = 2,  $\rho$  = 1.230 g·cm<sup>-3</sup>,  $\mu$  = 2.141 mm<sup>-1</sup>. 16989 reflections collected with  $\theta$  in the range 4.204 – 74.104°, index ranges  $-11 \leq h \leq 11$ ,  $-13 \leq k \leq 13$ ,  $-18 \leq l \leq 17$ , 5763 independent reflections ( $R_{\text{int}} = 0.0207$ ), 337 parameters with 0 restraints gave final *R* indices  $R_1 = 0.0381$  and  $wR_2 = 0.1093$  [data with  $I > 2\sigma(I)$ ].  $R_1 = 0.0394$ ,  $wR_2 = 0.1106$  (all data), goodness-of-fit on  $F^2 = 1.048$ , largest electron density peak 0.453 e·Å<sup>-3</sup>, largest hole  $-0.446$  e·Å<sup>-3</sup>.

**Synthesis of (Mes)PhSi(OMe)<sub>2</sub> (1):** Phenyllithium (14.3 mL of a 1.9 M solution in dibutyl ether, 27.0 mmol) was added dropwise to a solution of mesityltrimethoxysilane (6.49 g, 27.0 mmol) in pentane

(140 mL) at  $-68\text{ }^{\circ}\text{C}$  over a period of 20 minutes. The resulting light red suspension was then allowed to slowly warm up to room temperature and kept stirring for 15 h. The suspension was filtered through a fritted column layered with Celite® and the remaining solids washed with pentane ( $2 \times 20\text{ mL}$ ). All volatiles of the filtrate were removed in vacuo. The brownish oily residue was purified by Kugelrohr distillation ( $110\text{ }^{\circ}\text{C}$  oven temperature,  $1.3 \times 10^{-2}\text{ mbar}$ ) to give compound **2** (6.33 g, 22.1 mmol, 82%) as a colorless oil.  $^1\text{H NMR}$  (400.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.10$  [s, 3 H, Ar(*p*-CH<sub>3</sub>)], 2.56 [s, 6 H, Ar(*o*-CH<sub>3</sub>)], 3.40 (s, 6 H, OCH<sub>3</sub>), 6.71 (s, 2 H, *H*<sub>Ar</sub>), 7.16 (m, 3 H, *H*<sub>Ph</sub>), 7.74 (m, 2 H, *H*<sub>Ph</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 21.1$  [s, Ar(*p*-CH<sub>3</sub>)], 24.0 [s, Ar(*o*-CH<sub>3</sub>)], 49.8 (s, OCH<sub>3</sub>), 126.3 (s, *C*<sub>ipso</sub>(Ar)), 128.1 (s, *C*<sub>Ph</sub>), 129.6 (s, *C*<sub>meta</sub>(Ar)), 130.1 (s, *C*<sub>Ph</sub>), 134.6 (s, *C*<sub>Ph</sub>), 135.5 (s, *C*<sub>Ph</sub>), 140.1 (s, *C*<sub>para</sub>(Ar)), 146.2 (s, *C*<sub>ortho</sub>(Ar)).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -25.4$  (s) ppm. HRMS (EI+):  $\text{C}_{17}\text{H}_{22}\text{O}_2\text{Si}$  calcd. *m/z* for [M<sup>+</sup>] 286.13836; found 286.13762.  $\text{C}_{17}\text{H}_{22}\text{O}_2\text{Si}$ : calcd. C 71.30, H 7.74%; found C 71.43, H 7.66%.

**Synthesis of (Mes)PhSi(OMe)(NC<sub>4</sub>H<sub>9</sub>) (2):** *n*-Butyllithium (6.2 mL of a 2.5 M solution in hexane, 15.4 mmol) was added dropwise to a solution of pyrrolidine (1.09 g, 15.4 mmol) in hexane (80 mL) at  $-30\text{ }^{\circ}\text{C}$ . The resulting white suspension was then allowed to slowly warm up to room temperature and kept stirring for 1 h. The reaction mixture was transferred by means of a PTFE tube in one portion to a solution of **1** (3.68 g, 12.8 mmol) in hexane (40 mL) at ambient temperature. The resulting suspension was refluxed for 15 h. After cooling down to room temperature, the mixture was filtered through a fritted column layered with Celite® and the remaining solids washed with hexane ( $2 \times 20\text{ mL}$ ). All volatiles of the filtrate were removed in vacuo. The oily residue was purified by Kugelrohr distillation ( $110\text{ }^{\circ}\text{C}$  oven temperature,  $1.3 \times 10^{-3}\text{ mbar}$ ) to give compound **2** (3.45 g, 10.6 mmol, 83%) as a colorless oil.  $^1\text{H NMR}$  (400.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 1.56$  (m, 4 H, NCH<sub>2</sub>CH<sub>2</sub>), 2.15 [s, 3 H, Ar(*p*-CH<sub>3</sub>)], 2.49 [s, 6 H, Ar(*o*-CH<sub>3</sub>)], 3.00–3.10 (m, 4 H, NCH<sub>2</sub>CH<sub>2</sub>), 3.46 (s, 3 H, OCH<sub>3</sub>), 6.81 (s, 2 H, *H*<sub>Ar</sub>), 7.20 (m, 3 H, *H*<sub>Ph</sub>), 7.68 (m, 2 H, *H*<sub>Ph</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 21.1$  [s, Ar(*p*-CH<sub>3</sub>)], 24.2 [s, Ar(*o*-CH<sub>3</sub>)], 26.9 (s, NCH<sub>2</sub>CH<sub>2</sub>), 47.6 (s, NCH<sub>2</sub>CH<sub>2</sub>), 50.3 (s, OCH<sub>3</sub>), 128.1 (s, *C*<sub>Ph</sub>), 129.1 (s, *C*<sub>ipso</sub>(Ar)), 129.5 (s, *C*<sub>meta</sub>(Ar)), 129.6 (s, *C*<sub>Ph</sub>), 135.2 (s, *C*<sub>Ph</sub>), 137.4 (s, *C*<sub>Ph</sub>), 139.3 (s, *C*<sub>para</sub>(Ar)), 145.9 (s, *C*<sub>ortho</sub>(Ar)).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -23.2$  (s) ppm. HRMS (EI+):  $\text{C}_{20}\text{H}_{27}\text{NOSi}$  calcd. *m/z* for [M<sup>+</sup>] 325.18564; found 325.18350.  $\text{C}_{15}\text{H}_{25}\text{NOSi}$ : calcd. C 73.39, H 8.36, N 4.30%; found C 73.73, H 8.00, N 4.15%.

**Synthesis of (Mes)PhSi(OMe)(OSiPh<sub>3</sub>) (3):** **Procedure (a)** A mixture of compound **2** (1.78 g, 5.48 mmol) and triphenylsilanol (1.51 g, 5.48 mmol) in toluene (40 mL) was refluxed for 15 h. After cooling down to room temperature, all volatiles were removed in vacuo and the obtained residue was dissolved in the minimum volume of tetrahydrofuran. The clear colorless concentrated solution was layered with pentane and stored at  $-30\text{ }^{\circ}\text{C}$ . Within 5 days, colorless crystals of compound **3** suitable for single-crystal X-ray diffraction analysis were formed (2.29 g, 4.32 mmol, 79%). **Procedure (b):** A mixture of compound **6** (2.34 g, 4.37 mmol) and triethylamine (1.32 g, 13.1 mmol) in methanol (10 mL) was stirred for 5 h at room temperature yielding a pale beige suspension. Then, all volatiles were removed in vacuo and the oily residue washed with hexane (20 mL). The crude solid was suspended in diethyl ether (30 mL) and the formed triethylammonium chloride filtered off through a pad of Celite®. After the remaining solids had been washed again with diethyl ether ( $2 \times 10\text{ mL}$ ), the filtrates were collected and dried in vacuo. Compound **3** was obtained as a colorless solid (1.51 g, 2.84 mmol, 65%).  $^1\text{H NMR}$  (400.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.07$  [s, 3 H, Ar(*p*-CH<sub>3</sub>)], 2.48 [s, 6 H, Ar(*o*-CH<sub>3</sub>)], 3.27

(s, 3 H, OCH<sub>3</sub>), 6.71 (s, 2 H, *H*<sub>Ar</sub>), 7.09–7.15 (m, 12 H, *H*<sub>Ph</sub>), 7.70 (m, 2 H, *H*<sub>Ph</sub>), 7.76 (m, 6 H, *H*<sub>Ph</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 21.1$  [s, Ar(*p*-CH<sub>3</sub>)], 24.6 [s, Ar(*o*-CH<sub>3</sub>)], 50.2 (s, OCH<sub>3</sub>), 128.1 (s, *C*<sub>Ph</sub>), 128.2 (s, *C*<sub>Ph</sub>), 129.6 (s, *C*<sub>ipso</sub>(Ar)), 130.0 (s, *C*<sub>Ph</sub>), 130.1 (s, *C*<sub>meta</sub>(Ar)), 134.3 (s, *C*<sub>Ph</sub>), 135.7 (s, *C*<sub>Ph</sub>), 135.9 (s, *C*<sub>Ph</sub>), 136.8 (s, *C*<sub>Ph</sub>), 140.0 (s, *C*<sub>para</sub>(Ar)), 145.9 (s, *C*<sub>ortho</sub>(Ar)).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -33.3$  (s, SiOCH<sub>3</sub>),  $-18.1$  (s, SiPh<sub>3</sub>). HRMS (EI+):  $\text{C}_{34}\text{H}_{34}\text{O}_2\text{Si}_2$  calcd. *m/z* for [M<sup>+</sup>] 530.20918; found 530.21062.  $\text{C}_{34}\text{H}_{34}\text{O}_2\text{Si}_2$ : calcd. C 76.93, H 6.46%; found C 77.21, H 6.41%.

**Synthesis of (Mes)PhSiCl<sub>2</sub> (5):** Thionyl chloride (8.7 mL, 120 mmol) was added to a mixture of compound **1** (5.73 g, 20.0 mmol) and pyridine hydrochloride (240 mg, 2.0 mmol) at room temperature with stirring. The reaction mixture was refluxed for 8 h. After cooling down to room temperature, all volatiles were removed in vacuo. The yellow oily residue was purified by Kugelrohr distillation ( $110\text{ }^{\circ}\text{C}$  oven temperature,  $4.6 \times 10^{-2}\text{ mbar}$ ) to give compound **5** (4.01 g, 13.6 mmol, 68%) as a pale yellow oil.  $^1\text{H NMR}$  (400.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.00$  [s, 3 H, Ar(*p*-CH<sub>3</sub>)], 2.36 [s, 6 H, Ar(*o*-CH<sub>3</sub>)], 6.60 (s, 2 H, *H*<sub>Ar</sub>), 7.07 (m, 3 H, *H*<sub>Ph</sub>), 7.71 (m, 2 H, *H*<sub>Ph</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 20.7$  [s, Ar(*p*-CH<sub>3</sub>)], 24.9 [s, Ar(*o*-CH<sub>3</sub>)], 125.3 (s, *C*<sub>ipso</sub>(Ar)), 128.4 (s, *C*<sub>para</sub>(Ar)), 130.2 (s, *C*<sub>meta</sub>(Ar)), 130.9 (s, *C*<sub>Ph</sub>), 133.3 (s, *C*<sub>Ph</sub>), 136.7 (s, *C*<sub>Ph</sub>), 141.6 (s, *C*<sub>para</sub>(Ar)), 145.1 (s, *C*<sub>ortho</sub>(Ar)).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 4.7$  (s) ppm. HRMS (EI+):  $\text{C}_{15}\text{H}_{16}\text{SiCl}_2$  calcd. *m/z* for [M<sup>+</sup>] 294.03928; found 294.03938.  $\text{C}_{15}\text{H}_{16}\text{SiCl}_2$ : calcd. C 61.02, H 5.46%; found C 60.98, H 5.40%.

**Synthesis of (Mes)PhSiCl(OSiPh<sub>3</sub>) (6):** *n*-Butyllithium (4.0 mL of a 2.5 M solution in hexane, 10.0 mmol) was added dropwise to a solution of triphenylsilanol (2.76 g, 10.0 mmol) in tetrahydrofuran (20 mL) at  $-30\text{ }^{\circ}\text{C}$ . The clear colorless solution was then allowed to slowly warm up to room temperature and kept stirring for 1 h. A solution of compound **5** (2.95 g, 10.0 mmol) in tetrahydrofuran (10 mL) was added to the reaction mixture by means of a PTFE tube at  $-30\text{ }^{\circ}\text{C}$ . The resulting clear mixture was allowed to slowly warm up to room temperature and kept stirring for 5 h. Then, the mixture was concentrated to around 15 mL volume. Lithium chloride was precipitated by adding pentane (40 mL) to the concentrated solution under vigorous stirring. The mixture was stirred for 30 min, the solids left to sediment, and the mother liquor recovered by means of filtration through a PTFE tube. All volatiles of the filtrate were removed in vacuo yielding pure compound **6** as a pale beige solid (4.92 g, 9.2 mmol, 92%). Colorless crystals suitable for single-crystal X-ray diffraction analysis were obtained from a concentrated tetrahydrofuran solution layered with pentane at  $-30\text{ }^{\circ}\text{C}$  within one week.  $^1\text{H NMR}$  (400.13 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.00$  [s, 3 H, Ar(*p*-CH<sub>3</sub>)], 2.41 [s, 6 H, Ar(*o*-CH<sub>3</sub>)], 6.63 (s, 2 H, *H*<sub>Ar</sub>), 6.97 (m, 2 H, *H*<sub>Ph</sub>), 7.02 (m, 1 H, *H*<sub>Ph</sub>), 7.09 (m, 9 H, *H*<sub>Ph</sub>), 7.61 (m, 2 H, *H*<sub>Ph</sub>), 7.71 (m, 6 H, *H*<sub>Ph</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 21.0$  [s, Ar(*p*-CH<sub>3</sub>)], 25.1 [s, Ar(*o*-CH<sub>3</sub>)], 127.0 (s, *C*<sub>ipso</sub>(Ar)), 128.1 (s, *C*<sub>Ph</sub>), 128.2 (s, *C*<sub>Ph</sub>), 130.1 (s, *C*<sub>Ph</sub>), 130.3 (s, *C*<sub>meta</sub>(Ar)), 130.5 (s, *C*<sub>Ph</sub>), 133.7 (s, *C*<sub>Ph</sub>), 135.0 (s, *C*<sub>Ph</sub>), 135.8 (s, *C*<sub>Ph</sub>), 137.5 (s, *C*<sub>Ph</sub>), 141.0 (s, *C*<sub>para</sub>(Ar)), 145.6 (s, *C*<sub>ortho</sub>(Ar)).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -18.85$  (s),  $-16.4$  (s) ppm. HRMS (EI+):  $\text{C}_{33}\text{H}_{31}\text{ClOSi}_2$  calcd. *m/z* for [M<sup>+</sup>] 534.15965; found 534.16142.  $\text{C}_{33}\text{H}_{31}\text{ClOSi}_2$ : calcd. C 74.05, H 5.84%; found C 73.89, H 5.97%.

**Synthesis of (Mes)PhSi(NC<sub>4</sub>H<sub>9</sub>)(OSiPh<sub>3</sub>) (4):** *n*-Butyllithium (2.6 mL of a 2.5 M solution in hexane, 6.43 mmol) was added dropwise to a solution of pyrrolidine (457 mg, 6.43 mmol) in hexane (20 mL) at  $-30\text{ }^{\circ}\text{C}$ . The resulting white suspension was then allowed to slowly warm up to room temperature and kept stirring for 1 h. A solution of compound **6** (2.86 g, 5.35 mmol) in hexane (20 mL) was added to the reaction mixture by means of a PTFE tube at ambient temperature. The resulting suspension was refluxed for 15 h. After cooling down to

room temperature, the mixture was filtered through a fritted column layered with Celite® and the remaining solids washed with hexane (2 × 20 mL). The filtrate was concentrated to around 20 mL volume rendering a beige suspension. The mixture was then refluxed for a period of 30 min and the hot clear beige solution allowed to slowly cool down to room temperature yielding compound **4** as colorless crystals suitable for single-crystal X-ray diffraction analysis (2.19 g, 3.85 mmol, 72%). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 1.44 (m, 4 H, NCH<sub>2</sub>CH<sub>2</sub>), 2.10 [s, 3 H, Ar(*p*-CH<sub>3</sub>)], 2.42 8s, 6 H, Ar(*o*-CH<sub>3</sub>)], 2.95–3.05 (m, 4 H, NCH<sub>2</sub>CH<sub>2</sub>), 6.76 (s, 2 H, H<sub>Ar</sub>), 7.08–7.16 (m, 12 H, H<sub>Ph</sub>), 7.66 (m, 2 H, H<sub>Ph</sub>), 7.70 (m, 6 H, H<sub>Ph</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 21.0 [s, Ar(*p*-CH<sub>3</sub>)], 24.8 [s, Ar(*o*-CH<sub>3</sub>)], 26.9 (s, NCH<sub>2</sub>CH<sub>2</sub>), 47.6 (s, NCH<sub>2</sub>CH<sub>2</sub>), 127.9 (s, C<sub>Ph</sub>), 128.0 (s, C<sub>Ph</sub>), 129.6 (s, C<sub>Ph</sub>), 129.6 (s, C<sub>Ph</sub>), 129.7 (s, C<sub>Ph</sub>), 129.9 (s, C<sub>meta</sub>(Ar)), 134.9 (s, C<sub>Ph</sub>), 135.7 (s, C<sub>Ph</sub>), 136.5 (s, C<sub>Ph</sub>), 139.1 (s, C<sub>ipso</sub>(Ar)), 139.4 (s, C<sub>para</sub>(Ar)), 145.8 (s, C<sub>ortho</sub>(Ar)). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>): δ = -31.0 (s, SiN), -19.9 (s, SiPh<sub>3</sub>) ppm. HRMS (EI+): C<sub>37</sub>H<sub>39</sub>NOSi<sub>2</sub> calcd. *m/z* for [M<sup>+</sup>] 569.25647; found 569.25478. C<sub>37</sub>H<sub>39</sub>NOSi<sub>2</sub>: calcd. C 77.98, H 6.90, N 2.46%; found C 77.91, H 6.87, N 2.44%.

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## References

- [1] a) F. Liebau, *Structural Chemistry of Silicates: Structure, Bonding, and Classification*, Springer-Verlag, Berlin, Heidelberg, **1985**; b) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, John Wiley & Sons, New York, **2000**.
- [2] T. W. Swaddle, J. Salerno, P. A. Tregloan, *Chem. Soc. Rev.* **1994**, *23*, 319–325.
- [3] a) R. Tacke, *Angew. Chem. Int. Ed.* **1999**, *38*, 3015–3018; *Angew. Chem.* **1999**, *111*, 3197–3200; b) D. Volkmer, S. Tugulu, M. Fricke, T. Nielsen, *Angew. Chem. Int. Ed.* **2003**, *42*, 58–61; *Angew. Chem.* **2003**, *115*, 60–64; c) A. E. Voinescu, M. Kellermeier, B. Bartel, A. M. Carnerup, A.-K. Larsson, D. Touraud, W. Kunz, L. Kienle, A. Pfitzner, S. T. Hyde, *Cryst. Growth Des.* **2008**, *8*, 1515–1521.
- [4] a) H. A. Höpfe, F. Stadler, O. Oeckler, W. Schnick, *Angew. Chem. Int. Ed.* **2004**, *43*, 5540–5542; *Angew. Chem.* **2004**, *116*, 5656–5659; b) S. Ganachaud, S. Boileau, B. Boury (Eds.), *Silicon Based Polymers: Advances in Synthesis and Supramolecular Organization*, Springer, Netherlands, **2008**.
- [5] a) S. Spirk, M. Nieger, F. Belaj, R. Pietschnig, *Dalton Trans.* **2009**, 163–167; b) C. Däschlein, J. O. Bauer, C. Strohmman, *Angew. Chem. Int. Ed.* **2009**, *48*, 8074–8077; *Angew. Chem.* **2009**, *121*, 8218–8221; c) M. Janssen, J. Wiltig, C. Müller, D. Vogt, *Angew. Chem. Int. Ed.* **2010**, *49*, 7738–7741; *Angew. Chem.* **2010**, *122*, 7904–7907; d) N. Oguri, Y. Egawa, N. Takeda, M. Unno, *Angew. Chem. Int. Ed.* **2016**, *55*, 9336–9339; *Angew. Chem.* **2016**, *128*, 9482–9485; e) K. S. Lokare, N. Frank, B. Braun-Cula, I. Goikoetxea, J. Sauer, C. Limberg, *Angew. Chem. Int. Ed.* **2016**, *55*, 12325–12329; *Angew. Chem.* **2016**, *128*, 12513–12517; f) K. S. Lokare, P. Wittwer, B. Braun-Cula, N. Frank, S. Hoof, T. Braun, C. Limberg, *Z. Anorg. Allg. Chem.* **2017**, *643*, 1581–1588; g) J. O. Bauer, C. Strohmman, *Inorg. Chim. Acta* **2018**, *469*, 133–135; h) K. S. Lokare, B. Braun-Cula, C. Limberg, M. Jorewitz, J. T. Kelly, K. R. Asmis, S. Leach, C. Baldauf, I. Goikoetxea, J. Sauer, *Angew. Chem. Int. Ed.* **2019**, *58*, 902–906; *Angew. Chem.* **2019**, *131*, 912–917.
- [6] a) R. G. Jones, W. Ando, J. Chojnowski (Eds.), *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications*, Springer, Netherlands, **2000**; b) U. Schubert, N. Hüsing, *Synthesis of Inorganic Materials* (4th Ed.), Wiley-VCH, Weinheim, **2019**.
- [7] a) A. Shimojima, K. Kuroda, *Angew. Chem. Int. Ed.* **2003**, *42*, 4057–4060; *Angew. Chem.* **2003**, *115*, 4191–4194; b) A. Shimojima, Z. Liu, T. Ohsuna, O. Terasaki, K. Kuroda, *J. Am. Chem. Soc.* **2005**, *127*, 14108–14116; c) D. B. Thompson, M. A. Brook, *J. Am. Chem. Soc.* **2008**, *130*, 32–33; d) J. Suzuki, A. Shimojima, Y. Fujimoto, K. Kuroda, *Chem. Eur. J.* **2008**, *14*, 973–980; e) R. Wakabayashi, K. Kawahara, K. Kuroda, *Angew. Chem. Int. Ed.* **2010**, *49*, 5273–5277; *Angew. Chem.* **2010**, *122*, 5401–5405; f) K. Matsumoto, K. V. Sajna, Y. Satoh, K. Sato, S. Shimada, *Angew. Chem. Int. Ed.* **2017**, *56*, 3168–3171; *Angew. Chem.* **2017**, *129*, 3216–3219; g) M. Yoshikawa, Y. Tamura, R. Wakabayashi, M. Tamai, A. Shimojima, K. Kuroda, *Angew. Chem. Int. Ed.* **2017**, *56*, 13990–13994; *Angew. Chem.* **2017**, *129*, 14178–14182; h) J. Yu, Y. Liu, *Angew. Chem. Int. Ed.* **2017**, *56*, 8706–8710; *Angew. Chem.* **2017**, *129*, 8832–8836.
- [8] J. O. Bauer, C. Strohmman, *Chem. Commun.* **2012**, *48*, 7212–7214.
- [9] J. O. Bauer, C. Strohmman, *Angew. Chem. Int. Ed.* **2014**, *53*, 720–724; *Angew. Chem.* **2014**, *126*, 738–742.
- [10] A. M. Muzafarov, E. A. Rebrov, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4935–4948.
- [11] a) R. Fessenden, J. S. Fessenden, *Chem. Rev.* **1961**, *61*, 361–388; b) W. Uhlig, C. Tretner, *J. Organomet. Chem.* **1994**, *467*, 31–35; c) R. Wakabayashi, Y. Sugiura, T. Shibue, K. Kuroda, *Angew. Chem. Int. Ed.* **2011**, *50*, 10708–10711; *Angew. Chem.* **2011**, *123*, 10896–10899; d) P. Mizar, T. Wirth, *Angew. Chem. Int. Ed.* **2014**, *53*, 5993–5997; *Angew. Chem.* **2014**, *126*, 6103–6107.
- [12] a) P. D. Lickiss, S. A. Litster, A. D. Redhouse, C. J. Wisener, *J. Chem. Soc., Chem. Commun.* **1991**, 173–174; b) R. Pietschnig, K. Merz, *Organometallics* **2004**, *23*, 1373–1377; c) H. W. Peindy N'dongo, S. Clément, S. Richeter, F. Guyon, M. Knorr, P. le Gendre, J. O. Bauer, C. Strohmman, *J. Organomet. Chem.* **2013**, *724*, 262–270; d) N. Hurkes, C. Bruhn, F. Belaj, R. Pietschnig, *Organometallics* **2014**, *33*, 7299–7306; e) D. Čas, N. Hurkes, S. Spirk, F. Belaj, C. Bruhn, G. N. Rechberger, R. Pietschnig, *Dalton Trans.* **2015**, *44*, 12818–12823; f) K. M. Diemoz, J. E. Hein, S. O. Wilson, J. C. Fettinger, A. K. Franz, *J. Org. Chem.* **2017**, *82*, 6738–6747; g) K. M. Diemoz, S. O. Wilson, A. K. Franz, *Chem. Eur. J.* **2016**, *22*, 18349–18353; h) P. Roesch, U. Warzok, M. Enke, R. Meller, C. Schattenberg, C. A. Schalley, M. Kaupp, T. Braun, P. Wittwer, *Chem. Eur. J.* **2017**, *23*, 13964–13972.
- [13] a) J. O. Bauer, C. Strohmman, *Acta Crystallogr., Sect. E* **2010**, *66*, o461–o462; b) J. O. Bauer, *Main Group Met. Chem.* **2020**, *43*, 1–6.
- [14] M. R. Stober, K. W. Michael, J. L. Speier, *J. Org. Chem.* **1967**, *32*, 2740–2744.
- [15] a) L. H. Sommer, J. D. Citron, *J. Am. Chem. Soc.* **1967**, *89*, 5797–5801; b) D. Terunuma, K. Murakami, M. Kokubo, K. Senda, H. Nohira, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 789–794; c) D. Terunuma, K. Senda, M. Sanazawa, H. Nohira, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 924–927; d) M. Mewald, M. Oestreich, *Chem. Eur. J.* **2012**, *18*, 14079–14084.
- [16] a) A. C. Coelho, T. R. Amarante, J. Klinowski, I. S. Gonçalves, F. A. Almeida Paz, *Acta Crystallogr., Sect. E* **2008**, *64*, o237–o238; b) T. R. Amarante, A. C. Coelho, J. Klinowski, I. S. Gonçalves, F. A. Almeida Paz, *Acta Crystallogr., Sect. E* **2008**, *64*, o239.

- [17] a) C. Glidewell, D. C. Liles, *Acta Crystallogr., Sect. B* **1978**, *34*, 124–128; b) J. Percino, J. A. Pacheco, G. Soriano-Moro, M. Cerón, M. E. Castro, V. M. Chapela, J. Bonilla-Cruz, T. E. Lara-Ceniceros, M. Flores-Guerrero, E. Saldivar-Guerra, *RSC Adv.* **2015**, *5*, 79829–79844.
- [18] S. Spirk, H. M. Ehmman, R. Kargl, N. Hurkes, M. Reischl, J. Novak, R. Resel, M. Wu, R. Pietschnig, V. Ribitsch, *ACS Appl. Mater. Interfaces* **2010**, *2*, 2956–2962.
- [19] a) C. Zopilko, M. Widenmeyer, I. Nagl, F. Estler, R. Anwänder, G. Raudaschl-Sieber, O. Groeger, G. Engelhardt, *J. Am. Chem. Soc.* **2006**, *128*, 16266–16276; b) T. Deschner, Y. Liang, R. Anwänder, *J. Phys. Chem. C* **2010**, *114*, 22603–22609.
- [20] a) F. Weinhold, R. West, *Organometallics* **2011**, *30*, 5815–5824; b) F. Weinhold, R. West, *J. Am. Chem. Soc.* **2013**, *135*, 5762–5767.
- [21] a) S. K. Liew, S. M. I. Al-Rafia, J. T. Goettel, P. A. Lummis, S. M. McDonald, L. J. Miedema, M. J. Ferguson, R. McDonald, E. Rivard, *Inorg. Chem.* **2012**, *51*, 5471–5480; b) K. Reuter, R. G. M. Maas, A. Reuter, F. Kilgenstein, Y. Asfaha, C. von Hänisch, *Dalton Trans.* **2017**, *46*, 4530–4541; c) M. Marin-Luna, B. Pölloth, F. Zott, H. Zipse, *Chem. Sci.* **2018**, *9*, 6509–6515.
- [22] N. Kocher, C. Selinka, D. Leusser, D. Kost, I. Kalikhman, D. Stalke, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1777–1793.
- [23] R. Tamaki, S. Han, Y. Chujo, *Silicon Chem.* **2002**, *1*, 409–416.
- [24] J. Harloff, E. Popowski, H. Reinke, *J. Organomet. Chem.* **2007**, *692*, 1421–1441.
- [25] a) CrysAlisPro Software System, Oxford Diffraction Ltd., **2010**; b) CrysAlisPro Software System, Rigaku Oxford Diffraction, **2019**.
- [26] G. M. Sheldrick, *SHELXS-97*, Universität Göttingen, Göttingen (Germany), **1997**.
- [27] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
- [28] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8.
- [29] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [30] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.
- [31] G. M. Sheldrick, *SHELXL-2018*. Universität Göttingen, Göttingen (Germany), **2018**.
- [32] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849–854.
- [33] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* **2006**, *39*, 453–457.

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