

Disilanes with Pentacoordinate Si Atoms by Carbon Dioxide Insertion into Aminodisilanes: Syntheses, Molecular Structures, and Dynamic Behavior

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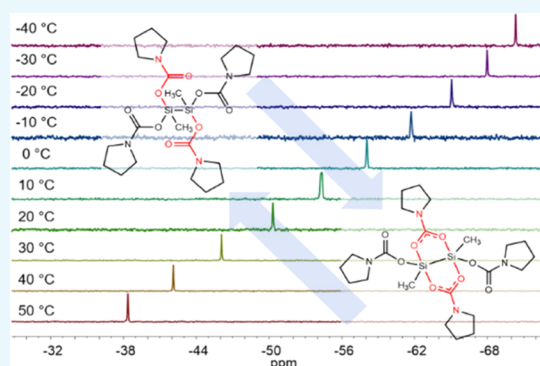


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ABSTRACT: The insertion of carbon dioxide into the Si–N bonds of aminodisilanes ((RR′N)_nMe_{3–n}Si)₂ affords carbamoyloxydisilanes ((RR′NC(O)O)_nMe_{3–n}Si)₂. Some of the obtained insertion products feature pentacoordinate silicon atoms in the solid state and in solution, with two carbamoyloxy moieties bridging the Si–Si bond. The aminodisilanes and their insertion products were extensively analyzed, including single-crystal X-ray structure analyses. The temperature dependence of the higher coordination was investigated using variable temperature NMR experiments.



INTRODUCTION

Silicon hypercoordination, i.e., the capability of silicon to extend its coordination number beyond 4, has gathered researchers' interest for numerous decades, and new challenges and aspects of research still evolve in this field.¹ As electronegative substituents (such as halides) foster silicon hypercoordination, and higher coordination numbers provoke weakening, activation, and even cleavage of various Si–X bonds, hypercoordination of methyloligosilanes with the retention of Si–Si bonds exerts particular appeal. The literature offers some examples of crystallographically confirmed oligosilanes (with highly electronegative substituents) with one or more hexacoordinate Si atoms, such as I,² II,³ III,⁴ and IV⁵ (Chart 1). Bridging ligands between adjacent hexacoordinate Si atoms (as in III and IV) may contribute to the retention of the Si–Si bond. Formation of compound V from disilane MeCl₂Si–SiMe(PhN(CH₂)₂NPh) demonstrates the ease at which a disilane's Si–Si bond may undergo scission upon one Si atom's hexacoordination,⁶ whereas an analogous compound with pentacoordinate Si atom (VI) is feasible.⁷ Oligosilanes with more than one pentacoordinate Si atom, e.g., VII and VIII, have been reported by El-Sayed et al.⁸ and Kano et al.,⁹ respectively. In the latter case, the ligand (carboxylate) buttresses the Si–Si bond, and the formation of O–Si–O axes may foster silicon pentacoordination. In the case of compound VIII, silicon pentacoordination was also achieved by subtle ligand tuning, i.e., a sterically demanding carboxylate was required, whereas the use of benzoate would result in an analogous compound with tetracoordinate Si atoms. Further examples of oligosilanes with isolated¹⁰ and neighboring¹¹

hypercoordinate Si atoms have been reported but will not be discussed here because bridging ligands and analogues of carboxylates will determine the focus of this paper. Carbamates may exhibit enhanced donor qualities, as their O atoms' electron density may be enhanced through conjugation with the amide N lone pair. In previous studies, we have shown that silicon carbamates (i.e., carbamoyloxysilanes) can be accessed in a convenient manner by the insertion of CO₂ into Si–N bonds of aminosilanes.¹² In the following, we have applied this strategy to aminodisilanes to provide convenient access to carbamoyloxy-substituted disilanes.

RESULTS AND DISCUSSION

Syntheses. The aminodisilanes were obtained from chlorodisilanes upon reaction with the respective amines, as shown in Scheme 1. An overview of the starting materials used and compounds aimed at is given in Table 1. Excess amine had to be used as it served as both a substituent and a sacrificial base. For the dichlorotetramethyl- and the tetrachlorodimethyl-disilane used, complete substitution of all chlorine atoms by amino groups proceeded in a clean manner along this amine-supported route for all three amines used (i.e., n-

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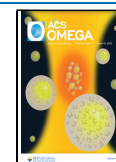
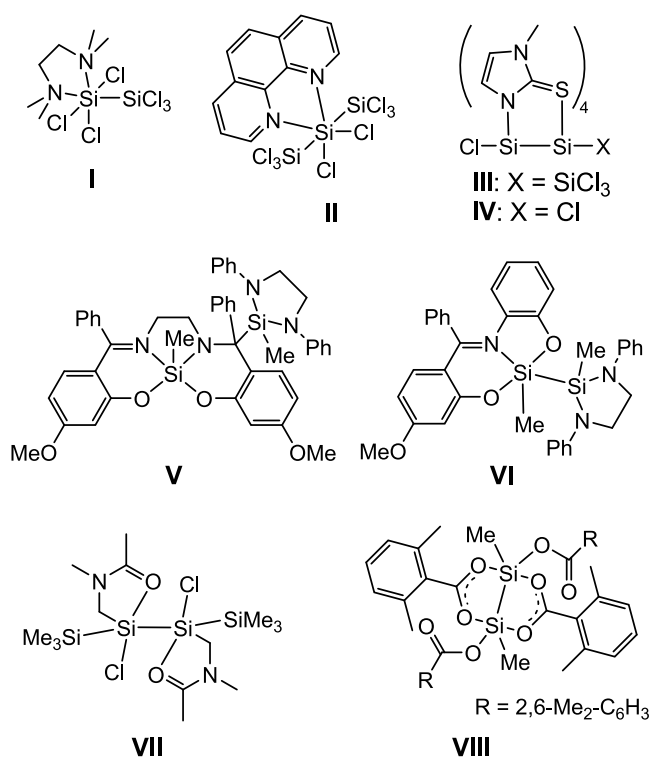


Chart 1. Examples of Crystallographically Confirmed Oligosilanes with One or More Higher Coordinate Silicon Atom(s)



Scheme 1. Generic Route from Chlorosilanes toward Carbamoyloxydisilanes

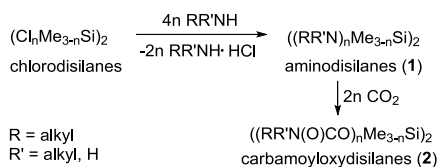


Table 1. Overview of the Aminodisilanes (1) and Their CO₂ Insertion Products (2) Discussed within This Work^a

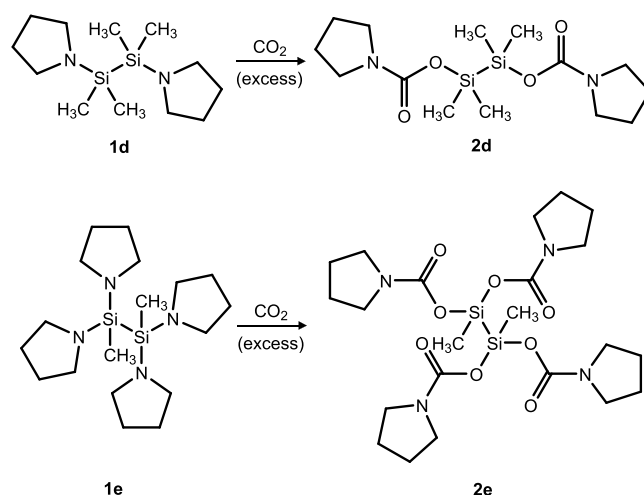
	ⁿ Pr	Pyrr.	Pip.
Cl ₂ Me ₃ Si ₂	1a/2a	1d/2d	1g/2g
Cl ₄ Me ₂ Si ₂	1b/2b	1e/2e	1h/2h
Cl ₆ Si ₂	1c/2c	1f/(2f)	(1i, 2i)

^aCrystallographically characterized compounds are underlined. The syntheses of the products in parentheses were unsuccessful via the route used here.

propylamine, pyrrolidine, and piperidine) with exception of **1h**. In the case of hexachlorodisilane, complete substitution was successful for *n*-propylamine and, with rather poor yield, pyrrolidine. The product of the latter reaction, **1f**, afforded crystals suitable for single-crystal X-ray diffraction analysis. The results are contained in the [Supporting Information](#). The steric demand of piperidine hampered full substitution under these conditions, and a disilane with one remaining Si–Cl bond was obtained instead.

The products (**2**) obtained through the reaction of the aminodisilanes (**1**) and carbon dioxide are shown in bold style in [Table 1](#). CO₂ insertion (as shown for the pyrrolidine-1-silanes **1d** and **1e** as representative examples; [Scheme 2](#))

Scheme 2. Examples of Formation of Carbamoyloxydisilanes through CO₂ Insertion into Aminodisilanes



proceeded in a straightforward fashion for all di- and tetraaminodisilanes under investigation. Whereas CO₂ insertion worked as well for hexaaminodisilane **1c**, the sterically more encumbered Si–N bonds of **1f** resisted CO₂ insertion even at a CO₂ pressure of 8 bar. Whereas the aminodisilanes are liquids at room temperature (except **1f**), the carbamoyloxydisilanes obtained are solids, which allowed for their ²⁹Si NMR spectroscopic investigation in the solid state and single-crystal X-ray structure analysis of most of them.

Molecular Structures. The carbamoyloxydisilanes **2d** and **2g**, which feature tetramethyldisilane cores, and **2b**, **2e**, and **2h**, which feature dimethyldisilane cores, formed crystals suitable for X-ray diffraction analysis ([Figures 1 and 2](#) and [Tables SI 2 and SI 4](#)). Interestingly, the Si atoms in **2d** are essentially tetracoordinate, whereas **2g** exhibits silicon pentacoordination in an almost trigonal–bipyramidal fashion with the O–Si–O axis and equatorial Si–Si and Si–C bonds. This configuration is achieved by the bridging coordination mode adopted by the carbamoyloxy groups. The coordination mode in **2d** is related to the tetracoordinate Si atoms in a carboxylate (2,6-Me₂C₆H₃-COO)-substituted tetramethyldisilane reported by Kano et al.,⁹ i.e., an approaching of the carbamoyloxy group toward a bridging coordination mode. To the best of our knowledge, compound **2g** represents the first crystallographically confirmed tetraalkyldisilane with two pentacoordinate Si atoms.¹³ Comparison of **2d** and **2g** allows for the conclusion that upon silicon pentacoordination by bridging carbamoyloxy groups the equatorial Si–C bonds get activated more pronounced (bond lengthening by 0.022 Å) than the Si–Si bonds (lengthening by 0.013 Å), which is speaking for the Si–Si bond-stabilizing effect of the bridging ligands.

Concluding from the coordination mode encountered with **2g**, carbamoyloxy groups may serve as better lone pair donors toward silicon than common carboxylates, and subtle differences between pyrrolidine and piperidine backbone appear to make a final cut. In general, the enhanced donor strength of carbamoyloxy groups can be explained by the π -electron donation from the amine N atom, thus supporting a zwitterionic resonance form with enhanced anionic features (enhanced basicity) of the O donor atoms ([Scheme 3](#)). This π -donation from the N atom should become more favorable, the closer the N atom can adopt idealized sp² hybridization, i.e.,

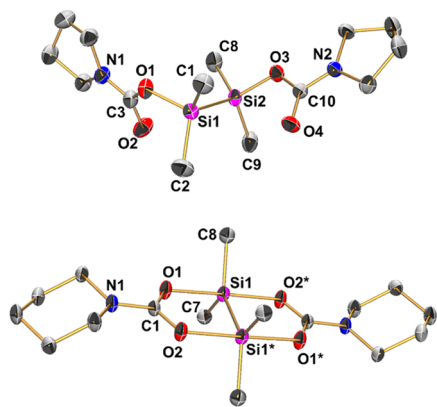


Figure 1. Molecular structures of **2d** (top) and **2g** (bottom) in their crystal structures. Ellipsoids are shown at the 50% probability level, selected atoms are labeled, and hydrogen atoms are omitted for clarity. The molecule of **2g** is located on a crystallographically imposed center of inversion. Symmetry equivalent atomic labels are asterisked. Selected bond lengths and interatomic separations [Å] and angles [deg] for **2d**: Si1–Si2 2.3337(5), Si1–O1 1.7066(11), Si1–C1 1.8579(16), Si1–C2 1.8558(18), Si1...O2 2.8574(12), Si1...O4 3.2367(12), Si2–O3 1.7051(11), Si2–C8 1.8569(16), Si2–C9 1.8577(18), Si2...O2 3.3072(14), Si2...O4 2.8334(11), O1–C3 1.3493(18), O2–C3 1.2218(19), N1–C3 1.330(2), O3–C10 1.3455(16), O4–C10 1.2296(17), N2–C10 1.3306(18), C1–Si1–C2 109.42(8), C8–Si2–C9 110.18(8); for **2g**: Si1–Si1* 2.3464(6), Si1–O1 1.9380(9), Si1–O2* 1.9435(9), Si1–C7 1.8796(12), Si1–C8 1.8781(12), O1–C1 1.2824(13), O2–C1 1.2788(13), N1–1.3451(14), O1–Si1–O2* 177.02(3), Si1*–Si1–C7 122.59(4), Si1*–Si1–C8 123.98(4), C7–Si1–C8 113.43(5).

the closer the C–N–C angle can approach 120°. Thus, with C–N–C angles of 115.27(9)° in the N-heterocyclic moieties, piperidinyl in **2g** may support this zwitterionic resonance form much better than pyrrolidinyl in **2d**, which exhibits the corresponding C–N–C angles of 112.70(13)° and 112.81(12)°.

In the crystal structures of compounds **2b**·THF, **2e**·2CHCl₃, and **2h**·2CHCl₃, the Si atoms are pentacoordinate in a highly distorted trigonal–bipyramidal fashion with the O–Si–O-axis and equatorial Si–Si, Si–O, and Si–C bonds (Figure 2). Whereas the axial O–Si–O angle is almost linear (wider than 175°), the equatorial angles exhibit pronounced deviations from 120°, with very narrow O–Si–C angle (ca. 105°) and rather wide Si–Si–C angle (up to 134°). This deformation is caused by the capping of the face trans-disposed to the equatorial Si–O bond (thus widening the Si–Si–C angle) by the dangling carbonyl O atom of the adjacent Si atom's equatorial carbamoyloxy group, i.e., [5 + 1] coordination. The O...Si interatomic separations range between 3.10 and 3.38 Å. In this regard, the molecules shown in Figure 2 are conformationally related to the disilane VIII,⁹ which exhibits the same deformation of the trigonal–bipyramidal Si coordination sphere by [5 + 1] coordination (remote coordination with an O...Si interatomic separation of 3.18 Å).

Tetra- and Pentacoordination, Solid-State, and Solution ²⁹Si NMR Spectroscopic Studies. As proven by X-ray crystallography, carbamoyloxydisilanes **2g**, **2b**, **2e**, and **2h** exhibit pentacoordinate silicon atoms in the solid state. For the compounds **2g** (pentacoordinate Si) and the related compounds **2a** and **2d** (tetracoordinate Si), all of which feature the Me₂SiSiMe₂ core, an upfield shift of the ²⁹Si NMR signal of **2g** by ca. 60 ppm clearly underlines the enhanced Si

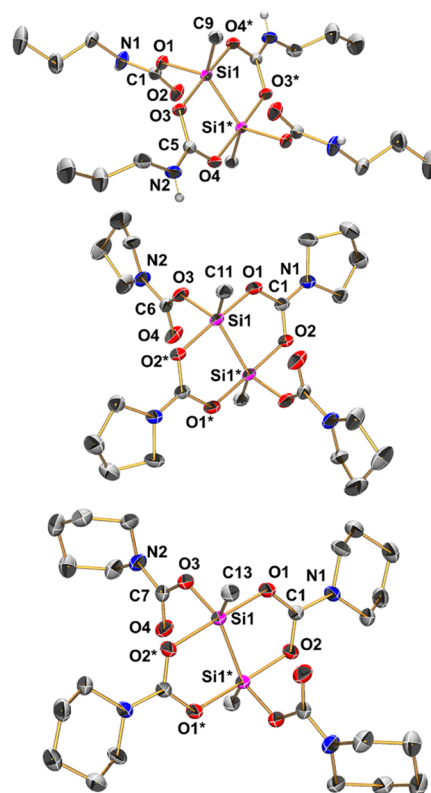
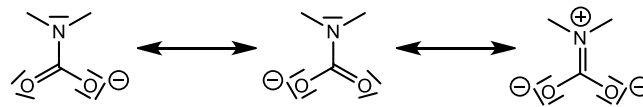


Figure 2. Molecular structures of (from top) **2b**, **2e**, and **2h** in the crystal structures of **2b**·THF, **2e**·2CHCl₃, and **2h**·2CHCl₃. Ellipsoids are shown at the 50% probability level, selected atoms are labeled, and hydrogen atoms, solvent molecules, and minor disorder position of the pyrrolidine ring at N2 in **2e** are omitted for clarity. In all cases, the molecules are located on a crystallographically imposed center of inversion. Symmetry equivalent atomic labels are asterisked. In cases of **2b** and **2e**, the asymmetric unit features two independent half-molecules (of similar conformation), and only one of them is depicted as a representative example in each case. Selected bond lengths and interatomic separations [Å] and angles [deg] for **2b**: Si1–Si1* 2.3346(6), Si1–O1 1.7201(9), Si1–O3 1.8636(9), Si1–O4* 1.9092(9), Si1–C9 1.8647(13), Si1*...O2 3.1013(10), O3–Si1–O4* 177.53(4), Si1*–Si1–O1 119.66(4), Si1*–Si1–C9 134.42(5), O1–Si1–C9 105.88(5); **2e**: Si1–Si1* 2.3466(7), Si1–O1 1.8781(12), Si1–O2* 1.8881(11), Si1–O3 1.6977(10), Si1–C11 1.8547(15), Si1*...O4 3.3750(12), O1–Si1–O2* 175.68(5), Si1*–Si1–O3 124.65(4), Si1*–Si1–C11 130.78(5), O3–Si1–C11 104.57(6); **2h**: Si1–Si1* 2.3454(7), Si1–O1 1.8916(11), Si1–O2* 1.8920(11), Si1–O3 1.7043(11), Si1–C13 1.8622(16), Si1*...O4 3.2730(12), O1–Si1–O2* 175.65(5), Si1*–Si1–O3 124.36(5), Si1*–Si1–C13 131.28(6), O3–Si1–C13 104.35(6).

Scheme 3. Resonance Structures of Carbamates



coordination number in **2g**. (Table 2 gives an overview of the ²⁹Si NMR shifts of the compounds under investigation in this paper.) Furthermore, the switch from tetra- to pentacoordination is accompanied by the noticeable widening of the span Ω of the chemical shift anisotropy (CSA), as shown in Figure 3 for the magic angle spinning (MAS) spectra of **2d** and **2g**, which visualize the CSA by the different spectral widths, in which the spinning side bands appear. Detailed

Table 2. ^{29}Si NMR Shifts δ of Aminodisilanes **1a–h** and Carbamoyloxydisilanes **2a–h** in Solution (Solvent CDCl_3) and as a Solid (Average Isotropic Shift δ_{iso} in the Case of Multiple Crystallographically Independent Si Sites), the Shift Difference $\Delta\delta(2 - 1)$ between the Insertion Products and Their Respective Aminodisilanes, and the Shift Differences $\Delta\delta(\text{Solid} - \text{soln})$ between the Carbamoyloxydisilanes in Solution and in the Solid State

1	$\delta(1)$	2	$\delta(2)$ (soln)	$\delta_{\text{iso}}(2)$ (solid)	$\Delta\delta(2)$ (solid – soln)	$\Delta\delta(2 - 1)$
1a	–8.9	2a	13.1	7.2	–5.9	21.1
1b	–18.2	2b	–39.7	–74.7	–35.2	–21.5
1c	–32.1	2c		–115.2		
1d	–7.6	2d	12.3	13.5	1.2	19.9
1e	–17.5	2e	–29.4	–74.4	–46.0	–11.9
1f	–34.7					
1g	–5.9	2g	12.6	–51.8	–64.4	18.5
1h	–12.0	2h	–25.8			–13.8

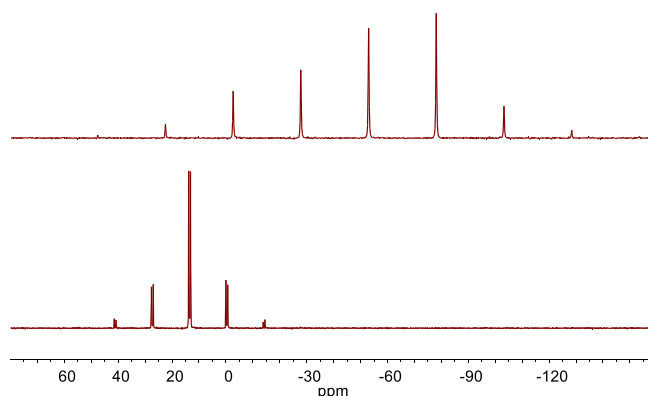


Figure 3. ^{29}Si MAS NMR spectra of **2d** (bottom, $\delta_{\text{iso}} = 13.2$ and 13.8 for the two crystallographically independent Si sites) and **2g** (top, $\delta_{\text{iso}} = -51.8$) at MAS frequencies of 1.1 and 2.0 kHz, respectively.

parameters of the CSA tensors extracted from the spinning side band spectra, i.e., principal values of the CSA tensors δ_{11} , δ_{22} , and δ_{33} ; span Ω and skew κ according to the Herzfeld–Berger notation,¹⁴ are summarized in the Supporting Information in Table SI 1. In accord, the spinning side bands of the MAS spectra of **2b**, **2c**, **2e**, and **2h** reveal a wide span of the CSA tensor for the upfield shifted signals, which is characteristic for pentacoordinated Si atoms compared to the tetrahedral or octahedral coordinated silicon. As a representative example, the MAS spectrum of **2e** is given in Figure 4.

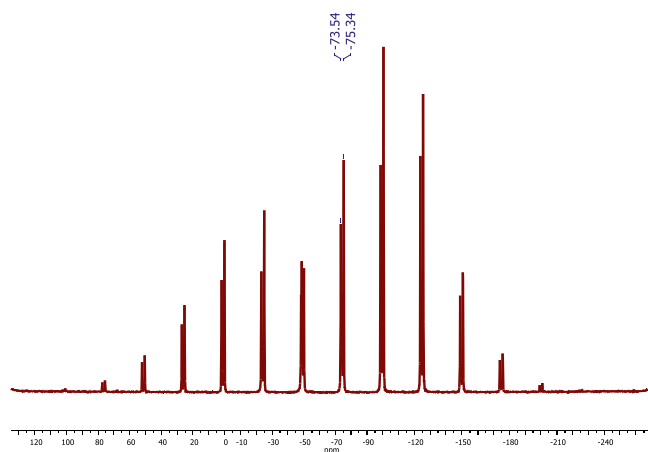
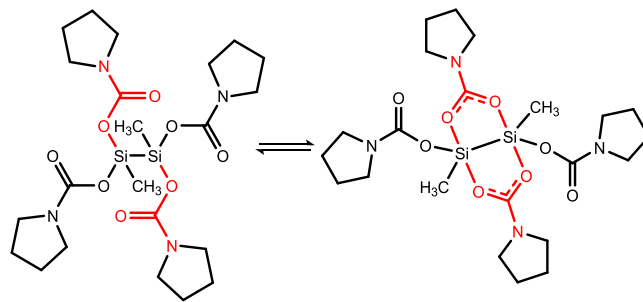


Figure 4. ^{29}Si MAS NMR spectrum of **2e** at a MAS frequency of 2.0 kHz.

The phenomenon of a rather wide span of the ^{29}Si CSA tensor of pentacoordinate Si compounds has already been reported in the literature, and the negative skew for various Si compounds with almost trigonal–bipyramidal coordination spheres and axial positioning of the highly electronegative donor atoms has been attributed to two principal directions of pronounced shielding in the equatorial plane (δ_{22} and δ_{33}), whereas δ_{11} points along the axis of the coordination polyhedron, which is significantly less shielded.¹⁵

In solution, the higher coordination at the silicon atom (if present in the solid state) is retained in part only, and the coordination equilibrium (as shown in Scheme 4 for **2e** as a

Scheme 4. Equilibrium of Silicon Tetra- and Pentacoordination in Solution for Compound **2e** as a Representative Example



representative example) depends heavily on the amine residue used. Disilanes with related substituent patterns should produce ^{29}Si signals at similar chemical shifts. In fact, for compounds **1**, the ^{29}Si chemical shifts of groups of silanes with $\text{C}_2\text{NSiSiNC}_2$ (**1a**, **1d**, **1g**), $\text{CN}_2\text{SiSiN}_2\text{C}$ (**1b**, **1e**, **1h**), and N_3SiSiN_3 patterns (**1c**, **1f**) cover rather narrow ranges. The same is true for the solid-state ^{29}Si NMR isotropic shifts of compounds **2** with related substitution patterns, i.e., $\text{C}_2\text{OSiSiOC}_2$ with tetracoordinate Si (**2a**, **2d**) and $\text{CO}_3\text{SiSiO}_3\text{C}$ with pentacoordinate Si (**2b**, **2e**). In the CDCl_3 solution, however, only the carbamoyloxydisilanes with $\text{Me}_2\text{SiSiMe}_2$ core (**2a**, **2d**, **2g**) exhibit ^{29}Si NMR signals in a very narrow range, which is very similar to the ^{29}Si NMR shift observed for the tetracoordinate silicon compound **2d** in the solid state and for the carboxylate $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{-COO})\text{-Me}_2\text{Si}]_2$ ($\delta^{29}\text{Si}$ in CDCl_3 solution: 13.4 ppm⁹). The ^{29}Si NMR shifts of CDCl_3 solutions of the carbamoyloxydisilanes with MeSiSiMe core (**2b**, **2e**, **2h**), however, span a range of ca. 14 ppm, and they are located in between the chemical shifts observed for the solids (ca. -74 ppm) and for carboxylates

with MeSiSiMe core (e.g., $\delta^{29}\text{Si}$ of compound **VIII** in CDCl_3 solution: -20.7 ppm⁹). As the polar C–H bond of chloroform has solvating effects on Lewis bases (e.g., on chloride ions¹⁶ or N atoms of oxinato ligands¹⁷) and may thus compete with the Lewis acidic Si site and thus obstruct coordination of the Lewis base to Si, chloroform is likely to hinder carbamate coordination at Si. Hence, solvents devoid of C–H donation should support silicon hypercoordination. For compound **2e**, this was probed with tetrahydrofuran (THF)- d_8 as an NMR solvent, and indeed a clear upfield shift of the ^{29}Si signal (at 25 °C -29.4 ppm in CDCl_3 solution, -48.1 ppm in THF- d_8 ; Figure SI 33) confirms this hypothesis.

Variable Temperature NMR Studies. In addition to solvent dependence, the coordination equilibrium shown in Scheme 4 is highly temperature-dependent and was thus explored using variable temperature ^{29}Si NMR spectroscopy (for compound **2e** in THF- d_8 in a temperature range from -40 to 50 °C). As shown in Figure 5, the ^{29}Si NMR signal is shifted

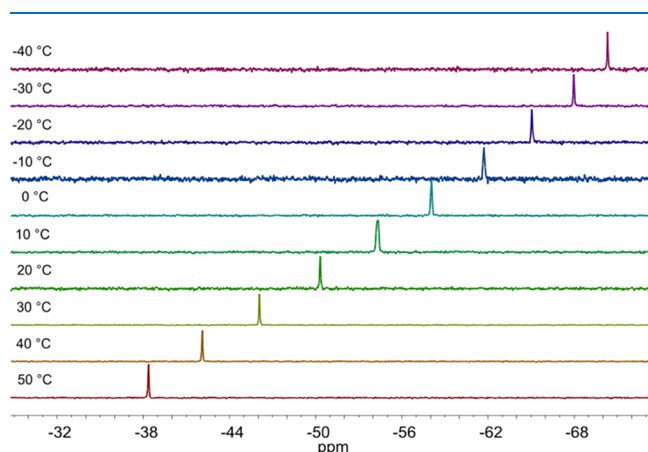


Figure 5. ^{29}Si NMR chemical shifts of **2e** (solution in THF- d_8) in a temperature range from -40 to 50 °C.

upfield (thus reflecting enhanced silicon higher coordination) with decreasing temperature. In detail, in the investigated temperature range, the ^{29}Si NMR signal of **2e** shifts from -38.4 ppm at 50 °C to -70.2 ppm at -40 °C. Within this temperature range (limited by the experimental setup and the boiling point of the solvent used), the ^{29}Si NMR shift change $\Delta\delta$ did not approach a plateau. For the upper temperature range (associated with silicon tetracoordination), we would expect approaching a ^{29}Si NMR shift around -20 ppm, characteristic of tetracarboxylatodimethyldisilanes, and for the lower temperatures, we would expect approaching a chemical shift close to the shift encountered in the NMR spectra of the solid (around -75 ppm). Therefore, for assessing the temperature-dependent equilibrium fractions of tetra- and pentacoordinate Si (to derive the thermodynamic characteristics of this equilibrium), the chemical shifts of -20 and -74.4 ppm (the latter taken from solid-state measurements) for tetra- and pentacoordinate Si, respectively, were used as starting values, and the former was altered (to -18 ppm) to achieve a better linear fit of the van't Hoff plot ($\ln(K)$ vs $1/T$) (see Figure SI 57), resulting in $R^2 = 0.9996$. This analysis indicates a reaction enthalpy of ΔH -21 kJ mol⁻¹ and a decrease in entropy of ΔS -70 J mol⁻¹ K⁻¹ associated with the transition from silicon tetra- to pentacoordination in this system. In this regard, the coordination equilibrium of this carbamoyloxydisilane system exhibits thermodynamic features similar to those

of oxinato silicon complexes,¹⁷ for two of which ΔH , ΔS sets of -23.5 kJ mol⁻¹, -85.8 J mol⁻¹ K⁻¹ and of -9.0 kJ mol⁻¹, -55.7 J mol⁻¹ K⁻¹ had been determined. Interestingly, these equilibria exhibit some common structural features: for achieving silicon pentacoordination, a five-membered ring is formed, and the initially dangling ligand arm experiences loss of two rotational degrees of freedom (about the Si–O and O–C bonds in both these disilanes and the oxinato silanes). Loss of a greater number of rotational degrees of freedom upon silicon higher coordination would be associated with greater loss in entropy, as shown for an enamine–imine system (loss of rotational degrees of freedom about the Si–O, C–C–C bond and, in part, about a C=N bond, ΔS -116.7 J mol⁻¹ K⁻¹).¹⁸

CONCLUSIONS

Aminodisilanes were shown to undergo CO_2 insertion into the Si–N bonds, sterics permitting. Thus, hexa(pyrrolidine-1-yl)disilane failed to react with CO_2 even upon pressurizing to 8 bar. Successful CO_2 insertion (with the formation of carbamoyloxydisilanes) gave, in most cases, access to compounds with pentacoordinate silicon atoms in the solid state. Solvent- and temperature-dependent NMR studies reveal that this silicon hypercoordination is, in part, retained in solution within a dynamic equilibrium. Furthermore, carbamoyloxy groups were shown to foster this kind of disilane hypercoordination with respect to simple carboxylates and allowed for the first crystallographic characterization of a tetraalkyldisilane with two pentacoordinate Si atoms. The bracing effect of the bridging carbamoyloxy ligands stabilizes the Si–Si bond as the latter exhibited a surprisingly low response to the increase of silicon coordination number.

EXPERIMENTAL SECTION

General Methods and Instrumentation. All syntheses and manipulations were performed in Schlenk-type glassware. All solvents were purified and dried according to general procedures. Commercially available chemicals were used in p.a. quality as obtained from the suppliers. Raman spectra were recorded in the range 100 – 3500 cm⁻¹ at room temperature using an RFS 100/S instrument (Bruker Optik) with a Nd-YAG-laser and a nitrogen-cooled NIR germanium detector. Standard ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Nanobay 400 or an AVIII 500 spectrometer (Bruker Biospin GmbH, Rheinstetten/Karlsruhe) at 293 K. Chemical shifts are reported relative to tetramethylsilane (0 ppm for ^1H , ^{13}C , ^{29}Si), and spectra were referenced to tetramethylsilane in most cases. For ^1H and/or ^{13}C spectra with signals of disilane Si–Me groups in very close proximity to the SiMe₄ signal, solvent signals (^1H : residual CHCl_3 , ^{13}C : CDCl_3) were engaged for referencing. ^{29}Si solid-state NMR measurements were carried out at 79.51 MHz on a Bruker AVANCE HD 400 MHz WB spectrometer using 7 mm ZrO_2 rotors and a DVT CP/MAS probe. A contact time of 5 ms was applied for CP/MAS measurements, and experiment recycle delays were 5–30 s depending on the substituents at silicon. Tppm15 decoupling was applied. The chemical shift was referenced using the high-field signal of the Q⁴-groups in Q₈M₈ (octakis-(trimethylsilyloxy)silsesquioxane: -109 ppm with respect to TMS = 0 ppm). Principal components of the CSA tensor were extracted using the DMFIT program (version 20200306)¹⁹ or the SOLA module in Topspin. Atmospheric pressure chemical

ionization mass spectroscopy (under a stream of dry nitrogen) was performed using an Advion expression CMS L. Determination of boiling points was performed with an apparatus reported by Herbig and Kroke.²⁰ C/H/N elemental analyses were carried out using a Heraeus CHN Rapid analyzer. For single-crystal X-ray structure determination, a crystal of the appropriate size was selected under inert oil and mounted on a glass capillary, which was coated with silicone grease. Data sets were collected on an IPDS-2(T) diffractometer (STOE, Darmstadt, Germany) using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Intensities were measured by ω scans using the diffractometer software X-Area.²¹ Numerical absorption corrections were applied by modeling the crystal surfaces based upon the intensities of symmetry equivalent reflections (X-Shape as implemented in X-Area). The structures were solved using SHELXS or SHELXT, and all non-hydrogen atoms were anisotropically refined against F^2 in full-matrix least-squares cycles (SHELXL 2014/7).²² C-bound hydrogen atoms were (isotropically) included in the refinement in geometrically idealized positions (riding model). N-bound H atoms were located as residual electron density peaks and were refined isotropically without restraints. Further details of the structure determinations are given in the [Supporting Information](#). CCDC 2112133 (**2b**-THF), 2112134 (**1f**, modification 1), 2112135 (**1f**, modification 2), 2112136 (**2e**-2CHCl₃), 2112137 (**2d**), 2112138 (**2h**-2CHCl₃), and 2112139 (**2g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure A. With stirring and under cooling with a water bath, the respective amine was added dropwise to a solution of the respective chlorodisilane in *n*-hexane. Stirring at room temperature for 1 day gave the respective solid amine hydrochloride as a precipitate. Removal of the hydrochloride by filtration and washing with *n*-hexane (3 \times 20 mL) followed by removal of the solvent from the combined filtrate and washings under reduced pressure yielded the aminodisilanes as colorless liquids.

General Procedure B. Gaseous carbon dioxide (purity 5.3) was added via a gas inlet to a cold (-78 °C) solution of the respective aminodisilane in THF (50 mL). Thereafter, the reaction mixture was allowed to attain room temperature. Removal of the solvent under reduced pressure yielded the carbamoyloxydisilanes as solids of sufficient purity.

General Procedure C. A solution of the respective aminodisilane and 30 mL THF was placed in an autoclave. The solution was stirred overnight at ambient temperature and a carbon dioxide pressure of 8 bar. Removal of the solvent under reduced pressure yielded the carbamoyloxydisilanes as solids of sufficient purity.

Synthesis of Aminodisilanes 1a–h. **Preparation of Di(*n*-propylamino)tetramethyldisilane, Me₂(NHC₃H₇)₂Si₂(NHC₃H₇)₂Me₂ (**1a**).** General procedure A using 5.10 g (27.2 mmol) of 1,2-dichlorotetramethyldisilane and 7.10 g (120 mmol) of *n*-propylamine in *n*-hexane (400 mL) gave **1a** (5.56 g, 23.9 mmol, 88%) as a colorless liquid: bp 228 °C. ²⁹Si NMR (99 MHz, CDCl₃): $\delta = -8.9$ ppm. ¹³C NMR (126 MHz, CDCl₃): $\delta = 44.8$ (NH-CH₂-CH₂-CH₃), 28.0 (NH-CH₂-CH₂-CH₃), 11.4 (NH-CH₂-CH₂-CH₃), -0.5 (Si-CH₃) ppm. ¹H NMR (500 MHz, CDCl₃): $\delta = 2.62$ (4H, NH-CH₂-CH₂-CH₃, t, ³J_{H-H} = 7.0 Hz), 1.34 (4H, NH-CH₂-CH₂-CH₃, sx), 0.81 (6H, NH-CH₂-

CH₂-CH₃, t, ³J_{H-H} = 7.4 Hz), 0.28 (2H, N-H, s), 0.05 (12H, Si-CH₃, s) ppm. Raman (298 K, glass capillary): $\nu = 3402$ (vw, ν N-H); 2974, 2893 (vs, ν C-H); 1447 (w, δ Si-CH₃); 1402 (vw); 1241 (vw); 1105 (vw); 888 (vw); 863 (vw); 756 (vw); 677 (vw); 654 (w); 410 (vw); 184 (w); 101 (vw) cm⁻¹. Elemental analysis for C₁₀H₂₈N₂Si₂ (232.52): calc. C 51.7%; H 12.1%; N 12.1%; found C 50.7%; H 11.9%; N = 11.6%. APCI-MS: m/z 233.046 (M⁺).

Preparation of Tetra(*n*-propylamino)dimethyldisilane, Me(NHC₃H₇)₂Si₂(NHC₃H₇)₂Me (1b**).** General procedure A using 6.15 g (27.0 mmol) of 1,1,2,2-tetrachlorodimethyldisilane and *n*-propylamine (15.45 g, 261 mmol) gave **1b** (7.15 g, 22.4 mmol, 83%) as a colorless liquid: bp 257 °C. ²⁹Si NMR (79 MHz, CDCl₃): $\delta = -18.1$ ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 43.7$ (NH-CH₂), 27.9 (NH-CH₂-CH₂), 11.4 (NH-CH₂-CH₂-CH₃), -1.4 (Si-CH₃) ppm. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.66$ (8H, NH-CH₂, t, ³J_{H-H} = 7.4 Hz), 1.34 (8H, NH-CH₂-CH₂, sx), 0.81 (12H, NH-CH₂-CH₂-CH₃, t, ³J_{H-H} = 7.4 Hz), 0.71 (4H; N-H, s), 0.00 (6H, Si-CH₃, s) ppm. Raman (298 K, glass capillary): $\nu = 3401$ (vw, ν N-H); 2959, 2933, 2894, 2875, 2860 (vs, ν C-H); 2733 (vw); 2662 (vw); 1446 (w, δ Si-CH₃); 1404 (vw); 1300 (vw); 1230 (vw); 1100 (vw); 1029 (vw); 888 (vw); 862 (vw); 806 (vw); 680 (vw); 507 (vw); 378 (vw); 171 (w) cm⁻¹. Elemental analysis for C₁₄H₃₈N₄Si₂ (318.66): calc. C 52.8%; H 12.0%; N 17.6%; found C 51.7%; H 11.1%; N = 16.1%. APCI-MS: m/z 319.202 (M⁺).

Preparation of Hexa(*n*-propylamino)disilane, (NHC₃H₇)₃Si₂(NHC₃H₇)₃ (1c**).** General procedure A using 5.31 g (19.8 mmol) of hexachlorodisilane and *n*-propylamine (18.98 g, 321 mmol) in 400 mL of *n*-hexane gave **1c** (6.51 g, 16.1 mmol, 81%) as a colorless liquid: bp 290 °C. ²⁹Si NMR (79 MHz, CDCl₃): $\delta = -32.0$ ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 43.1$ (NH-CH₂), 28.0 (NH-CH₂-CH₂), 11.5 (NH-CH₂-CH₂-CH₃) ppm. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.75$ (12H, NH-CH₂, t, ³J_{H-H} = 7.0 Hz), 1.40 (12H, NH-CH₂-CH₂, sx), 0.88 (18H, NH-CH₂-CH₂-CH₃, t, ³J_{H-H} = 7.4 Hz), 0.67 (6H, N-H, s(br)). Raman (298 K, glass capillary): $\nu = 3400$ (vw, ν N-H); 2961, 2932, 2874, 2859 (vs, ν C-H); 2659 (vw); 1447 (w, δ Si-CH₃); 1398 (vw); 1301 (vw); 1230 (vw); 1100 (vw); 1029 (vw); 888 (vw); 863 (vw); 721 (vw); 141 (vw) cm⁻¹. Elemental analysis for C₁₈H₄₈N₆Si₂ (404.79): calc. C 53.4%; H 11.9%; N 20.8%; found C 52.7%; H 11.2%; N 19.8%. APCI-MS: m/z 405.218 (M⁺).

Preparation of Di(pyrrolidin-1-yl)tetramethyldisilane, Me₂(NC₄H₈)Si₂(NC₄H₈)Me₂ (1d**).** General procedure A using 4.92 g (26.3 mmol) of 1,2-dichlorotetramethyldisilane and pyrrolidine (8.83 g, 124 mmol) in 400 mL of *n*-hexane gave **1d** (5.84 g, 22.8 mmol, 87%) as a colorless liquid: bp 266 °C. ²⁹Si NMR (99 MHz, CDCl₃): $\delta = -7.6$ ppm. ¹³C NMR (126 MHz, CDCl₃): $\delta = 47.7$ (N-(CH₂)₂), 26.9 (N-(CH₂)₂-(CH₂)₂), -1.1 (Si-CH₃) ppm. ¹H NMR (500 MHz, CDCl₃): $\delta = 2.92$ (8H, N-(CH₂)₂, m), 1.70 (8H, N-(CH₂)₂-(CH₂)₂, m), 0.16 (12H, Si-CH₃, s) ppm. Raman (298 K, glass capillary): $\nu = 2954$, 2893, 2824 (vs, ν C-H); 2688 (vw); 1486, 1446 (vw, ν Si-C); 1430 (vw); 1241 (vw); 1068 (vw); 1004 (vw); 908 (w); 757 (vw); 661 (w); 385 (w); 187 (w) cm⁻¹. Elemental analysis for C₁₂H₂₈N₂Si₂ (256.54): calc. C 56.2%; H 11.0%; N 10.9%; found C 56.6%; H 11.0%; N 11.0%. APCI-MS: m/z 257.086 (M⁺).

Preparation of Tetra(pyrrolidin-1-yl)dimethyldisilane, Me(NC₄H₈)₂Si₂(NC₄H₈)₂Me (1e**).** General procedure A using 4.94 g

(21.7 mmol) of 1,1,2,2-tetrachlorodimethyldisilane and pyrrolidine (13.70 g, 193 mmol) in 400 mL of *n*-hexane gave **1e** (6.89 g, 18.8 mmol, 87%) as a colorless liquid: bp 298 °C. ²⁹Si NMR (99 MHz, CDCl₃): δ = -17.5 ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 47.2 (N-(CH₂)₂), 27.0 (N-(CH₂)₂-(CH₂)₂), -1.0 (Si-CH₃) ppm. ¹H NMR (500 MHz, CDCl₃): δ = 2.97 (16H, N-(CH₂)₂, m), 1.65 (16H, N-(CH₂)₂-(CH₂)₂, m), 0.17 (6H, Si-CH₃, s) ppm. Raman (298 K, glass capillary): ν = 2956, 2895, 2868, 2822 (s, ν C-H); 2684 (vw); 2631 (vw); 1486, 1445 (vw, ν Si-C); 1320 (vw); 1237 (vw); 1067 (vw); 1005 (vw); 908 (w); 690 (vw); 402 (vw); 207 (vw) cm⁻¹. Elemental analysis for C₁₈H₃₈N₄Si₂ (366.70): calc. C 59.1%; H 10.5%; N 15.3%; found C 56.2%; H 10.0%; N 16.0%. APCI-MS: *m/z* 367.195 (M⁺).

Preparation of Hexa(pyrrolidin-1-yl)disilane, (NC₄H₈)₃Si₂(NC₄H₈)₃ (1f). General procedure A using 5.12 g (19.0 mmol) of hexachlorodisilane and pyrrolidine (17.45 g, 245 mmol) in 400 mL of *n*-hexane gave a colorless high viscous liquid. The liquid was diluted with 3 mL of CHCl₃ and afforded, after storage for 2 weeks at room temperature, colorless crystals of **1f** (1.02 g, 2.1 mmol, 12%) in a red residual solution: mp > 300 °C. ²⁹Si NMR (99 MHz, CDCl₃): δ = -34.7 ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 46.3 (N-(CH₂)₂), 26.9 (N-(CH₂)₂-(CH₂)₂) ppm. ¹H NMR (500 MHz, CDCl₃): δ = 2.98 (32H, N-(CH₂)₂, m), 1.64 (32H, N-(CH₂)₂-(CH₂)₂, m) ppm. Raman (298 K, glass capillary): ν = 2955, 2904, 2866, 2809 (s, ν C-H); 2681 (vw); 2627 (vw); 2569 (vw); 1486, 1456, 1444 (vw, ν Si-C); 1344 (vw); 1318 (vw); 1236 (vw); 1073 (vw); 1006 (vw); 906 (w); 750 (vw); 277 (w); 203 (w) cm⁻¹. Elemental analysis for C₂₄H₄₈N₆Si₂ (476.86): calc. C 60.5%; H 10.2%; N 17.6%; found C 59.2%; H 10.5%; N 16.8%. APCI-MS: *m/z* 477.223 (M⁺).

Preparation of Di(piperidin-1-yl)tetramethyldisilane, Me₂(NC₅H₁₀)Si₂(NC₅H₁₀)Me₂ (1g). General procedure A using 5.04 g (26.9 mmol) of 1,2-dichlorotetramethyldisilane and piperidine (9.99 g, 117 mmol) in 400 mL of *n*-hexane gave **1g** (5.89 g, 20.7 mmol, 77%) as a colorless liquid: bp 300 °C. ²⁹Si NMR (100 MHz, CDCl₃): δ = -5.9 ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 47.7 (N-(CH₂)₂), 28.2 (N-(CH₂)₂-(CH₂)₂), 25.8 (N-(CH₂)₂-(CH₂)₂-CH₂), -0.7 (Si-CH₃) ppm. ¹H NMR (500 MHz, CDCl₃): δ = 2.80 (8H, N-(CH₂)₂, m), 1.54 (4H, N-(CH₂)₂-(CH₂)₂-CH₂, m), 1.39 (8H, N-(CH₂)₂-(CH₂)₂, m), 0.10 (12H, Si-CH₃, s) ppm. Raman (298 K, glass capillary): ν = 2954, 2893, 2824 (s, ν C-H); 2688 (vw); 2668 (vw); 1486 (vw); 1447 (w, ν Si-C); 1403 (vw); 1241 (vw); 1068 (w); 1004 (vw); 909 (w); 757 (vw); 661 (w); 385 (vw); 186 (w) cm⁻¹. Elemental analysis for C₂₄H₄₈Si₂N₆ (284.59): calc. C 59.1%; H 11.3%; N 9.8%; found C 57.0%; H 11.0%; N 9.6%. 285.120 (M⁺).

Preparation of Tetra(piperidin-1-yl)dimethyldisilane, Me-(NC₅H₁₀)₂Si₂(NC₅H₁₀)₂Me (1h). General procedure A using 4.00 g (17.5 mmol) of 1,1,2,2-tetrachlorodimethyldisilane and piperidine (7.94 g, 93.2 mmol) gave chlorotri(piperidin-1-yl)dimethyldisilane. Piperidine lithium salt, prepared from 0.91 g (10.7 mmol) of piperidine and *n*-butyllithium (0.70 g, 10.8 mmol; as a solution in cyclohexane, ω = 20%), was then added to the chlorotri(piperidin-1-yl)dimethyldisilane to give **1h** (2.37 g, 5.6 mmol, 32%) as a colorless liquid. NMR spectroscopy confirmed the identity of **1h**. This crude product (purity > 90%; Figures SI 44–46) was used for insertion reaction with CO₂ without further purification. ²⁹Si NMR (100 MHz, CDCl₃): δ = -12.0 ppm. ¹³C NMR (126 MHz, CDCl₃):

δ = 47.0 (N-(CH₂)₂), 28.2 (N-(CH₂)₂-(CH₂)₂), 26.0 (N-(CH₂)₂-(CH₂)₂-CH₂), -0.6 (Si-CH₃) ppm. ¹H NMR (500 MHz, CDCl₃): δ = 2.53 (16H, N-(CH₂)₂, m), 1.52 (8H, N-(CH₂)₂-(CH₂)₂-CH₂, m); 1.35 (16H, N-(CH₂)₂-(CH₂)₂, m), 0.05 (6H, Si-CH₃, s) ppm.

Synthesis of Carbamoyloxydisilanes 2a–h. Preparation of Di(*n*-propylcarbamoyloxy)tetramethyldisilane Me₂(OCONHC₃H₇)Si₂(OCONHC₃H₇)Me₂ (2a). General procedure C using 4.43 g (19.1 mmol) of **1a** in 50 mL THF gave **2a** (4.90 g, 15.3 mmol, 80%) as a colorless solid. ²⁹Si NMR (79 MHz, CDCl₃): δ = 13.0 ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 156.7 (C=O), 42.9 (NH-CH₂), 23.2 (NH-CH₂-CH₂), 11.2 (NH-CH₂-CH₂-CH₃), -1.5 (Si-CH₃) ppm. ¹H NMR (400 MHz, CDCl₃): δ = 5.12–4.93 (2H, N-H, s(br)), 3.01 (4H, NH-CH₂, m), 1.42 (4H, NH-CH₂-CH₂, m), 0.83 (6H, NH-CH₂-CH₂-CH₃, t, ³J_{H-H} = 7.4 Hz) 0.28 (12H, Si-CH₃, s) ppm. Raman (298 K, glass capillary): ν = 3423 (vw, ν N-H); 2982, 2963, 2942, 2884, 2862 (vs, C-H); 1662 (m ν C=O); 1461 (w, δ Si-CH₃); 1414 (vw); 1335 (vw); 1324 (vw); 1298 (vw); 1160 (vw); 1141 (vw); 1116 (vw); 1054 (vw); 1013 (vw); 988 (vw); 842 (vw); 762 (vw); 516 (vw); 421 (vw); 180 (vw); 162 (vw) cm⁻¹. Elemental analysis for C₁₄H₂₈N₂O₄Si₂ (344.56): calc. C 45.0%; H 8.8%; N 8.7%; found C 45.0%; H 9.1%; N 8.0%.

Preparation of Tetra(*n*-propylcarbamoyloxy)-dimethyldisilane Me(OCONHC₃H₇)₂Si₂(OCONHC₃H₇)₂Me (2b). General procedure B using 6.03 g (18.9 mmol) of **1b** in 50 mL THF gave **2b** (7.14 g, 14.4 mmol, 76%) as a colorless solid. ²⁹Si NMR (79 MHz, THF-*d*₈): δ = -43.4 ppm. ¹³C NMR (100 MHz, THF-*d*₈): δ = 157.7 (C=O), 43.4 (NH-CH₂), 24.0 (NH-CH₂-CH₂), 11.6 (NH-CH₂-CH₂-CH₃), 0.0 (Si-CH₃) ppm. ¹H NMR (400 MHz, THF-*d*₈): δ = 6.36 (4H, N-H, s(br)), 2.98 (8H, NH-CH₂, m), 1.45 (8H, NH-CH₂-CH₂, m), 0.88 (12H, NH-CH₂-CH₂-CH₃, t, ³J_{H-H} = 7.4 Hz), 0.37 (6H (superimposed with TMS), Si-CH₃, s) ppm. Raman (298 K, glass capillary): ν = 3382 (vw, ν N-H); 2962, 2948, 2924, 2918, 2865, 2843 (vs, C-H); 1653 (m ν C=O); 1445 (w, δ Si-CH₃); 1432 (vw); 1330 (vw); 1308 (vw); 1273 (vw); 1144 (vw); 1122 (vw); 1115 (vw); 1030 (vw); 1012 (vw); 965 (vw); 823 (vw); 787 (vw); 729 (vw); 591 (vw); 404 (vw); 169 (vw); 146 (vw) cm⁻¹. Elemental analysis for C₁₈H₃₈N₄O₈Si₂ (494.69): calc. C 43.7%; H 7.7%; N 11.3%; found C 44.2%; H 8.0%; N 10.1%.

Preparation of Hexa(*n*-propylcarbamoyloxy)disilane (OCONHC₃H₇)₃Si₂(OCONHC₃H₇)₃ (2c). General procedure C using 6.51 g (16.1 mmol) of **1c** in 50 mL THF gave **2c** (9.80 g, 14.7 mmol, 91%) as a colorless solid. ²⁹Si MAS NMR (1.25 kHz): δ_{iso} = 113.9, 115.2, 116.2 ppm (Figure SI 18). Raman (298 K, glass capillary): ν = 3326 (vw, ν N-H); 2988, 2964, 2943, 2932, 2881, 2867 (vs, C-H); 1662 (m ν C=O); 1466 (w, δ Si-CH₃); 1415 (vw); 1353 (vw); 1324 (vw); 1292 (vw); 1161 (vw); 1140 (vw); 1132 (vw); 1062 (vw); 1021 (vw); 991 (vw); 847 (vw); 708 (vw); 641 (vw); 516 (vw); 425 (vw); 188 (vw); 111 (vw) cm⁻¹. Elemental analysis for C₂₄H₄₈N₆O₁₂Si₂ (668.85): calc. C 43.1%; H 7.2%; N 12.6%; found C 42.6%; H 7.9%; N 13.2%.

Preparation of Di(pyrrolidin-1-ylcarboxylato)-tetramethyldisilane Me₂(OCONC₄H₈)Si₂(OCONC₄H₈)Me₂ (2d). General procedure B using 4.48 g (17.5 mmol) of **1d** in 100 mL THF gave **2d** (5.30 g, 15.4 mmol, 88%) as a colorless solid. ²⁹Si NMR (79 MHz, CDCl₃): δ = 12.3 ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 155.1 (C=O), 46.0 (N-

(CH_2)₂, 25.3 (N-(CH_2)₂-(CH_2)₂), -1.5 (Si- CH_3) ppm. ¹H NMR (400 MHz, CDCl_3): δ = 3.34 (8H, N-(CH_2)₂, m), 1.86 (8H, (N-(CH_2)₂-(CH_2)₂), m), 0.37 (12H, Si- CH_3 , s) ppm. Raman (298 K, glass capillary): ν = 2972, 2934, 2898 (vs, ν C-H); 2794 (vw); 2672 (vw); 2616 (vw); 1647 (vw ν C=O); 1495, 1452 (vw, ν Si-C); 1342 (vw); 1249 (vw); 1226 (vw); 1104 (vw); 1029 (vw); 970 (vw); 915 (w); 865 (vw); 819 (vw); 774 (vw); 750 (vw); 679 (w); 522 (vw); 439 (vw); 263 (vw); 276 (vw); 253 (w); 218 (vw); 196 (w); 124 (vw) cm^{-1} . Elemental analysis for $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}_4\text{Si}_2$ (344.56): calc. C 48.8%; H 8.2%; N 8.1%; found C 48.8%; H 8.7%; N 8.2%.

Preparation of Tetra(pyrrolidin-1-ylcarboxylato)-dimethyldisilane $\text{Me}(\text{OCONC}_4\text{H}_8)_2\text{Si}_2(\text{OCONC}_4\text{H}_8)_2\text{Me}$ (**2e**). General procedure C using 5.87 g (16.0 mmol) of **1e** in 50 mL THF gave **2e** (7.29 g, 13.4 mmol, 84%) as a colorless solid. ²⁹Si NMR (79 MHz, CDCl_3): δ = -29.4 ppm. ¹³C NMR (100 MHz, CDCl_3): δ = 154.7 ($\text{C}=\text{O}$), 46.0 (N-(CH_2)₂), 25.4 (N-(CH_2)₂-(CH_2)₂), -0.4 (Si- CH_3) ppm. ¹H NMR (400 MHz, CDCl_3): δ = 3.36 (16H, N-(CH_2)₂, m), 1.84 (16H, N-(CH_2)₂-(CH_2)₂, m), 0.58 (6H, Si- CH_3 , s) ppm. Raman (298 K, glass capillary): ν = 2972, 2934, 2898 (vs, ν C-H); 2794 (vw); 2672 (vw); 2616 (vw); 1647 (vw ν C=O); 1495, 1452 (vw, ν Si-C); 1342 (vw); 1249 (vw); 1226 (vw); 1104 (vw); 1029 (vw); 970 (vw); 915 (w); 865 (vw); 819 (vw); 774 (vw); 750 (vw); 679 (w); 522 (vw); 439 (vw); 263 (vw); 276 (vw); 253 (w); 218 (vw); 196 (w); 124 (vw) cm^{-1} . Elemental analysis for $\text{C}_{22}\text{H}_{38}\text{N}_4\text{O}_8\text{Si}_2$ (542.74): calc. C 48.7%; H 7.1%; N 10.3%; found C 48.2%; H 7.0%; N 11.0%.

Preparation of Di(piperidin-1-ylcarboxylato)-tetramethyldisilane, $\text{Me}_2(\text{OCONC}_5\text{H}_{10})_2\text{Si}_2(\text{OCONC}_5\text{H}_{10})_2\text{Me}_2$ (**2g**). General procedure C using 4.03 g (14.2 mmol) of **1g** in 50 mL THF gave **2g** (4.24 g, 11.4 mmol, 80%) as a colorless solid. ²⁹Si NMR (79 MHz, CDCl_3): δ = 12.6 ppm. ¹³C NMR (100 MHz, CDCl_3): δ = 155.6 ($\text{C}=\text{O}$), 45.0 (N-(CH_2)₂), 25.8 (N-(CH_2)₂-(CH_2)₂), 24.4 (N-(CH_2)₂-(CH_2)₂- CH_2), -1.5 (Si- CH_3) ppm. ¹H NMR (400 MHz, CDCl_3): δ = 3.31 (8H, N-(CH_2)₂, m), 1.51–1.42 (12H, N-(CH_2)₂-(CH_2)₂- CH_2 , m) 0.27 (12H, Si- CH_3 , s) ppm. Raman (298 K, glass capillary): ν = 3030, 3000, 2959, 2926, 2908, 2864 (vs, ν C-H); 2680 (vw); 1567 (vw, ν C=O), 1450, 1433 (w, ν Si-C); 1356 (vw); 1282 (vw); 1263 (vw); 1244 (vw); 1166 (w); 1101 (w); 1028 (vw); 992 (vw); 847 (vw); 814 (vw); 773 (vw); 687 (w); 657 (vw); 538 (vw); 417 (vw); 194 (vw); 101 (w) cm^{-1} . Elemental analysis for $\text{C}_{16}\text{H}_{32}\text{SiO}_4\text{N}_2$ (372.61): calc. C 51.6%; H 8.7%; N 7.5%; found C 50.8%; H 8.7%; N 7.0%.

Preparation of Tetra(piperidin-1-ylcarboxylato)-dimethyldisilane, $\text{Me}(\text{OCONC}_5\text{H}_{10})_2\text{Si}_2(\text{OCONC}_5\text{H}_{10})_2\text{Me}$ (**2h**). General procedure C: a solution of **1h** (2.10 g, 4.97 mmol) in 50 mL THF was stirred at room temperature for 72 h in an autoclave with a CO_2 pressure of 8 bar to afford, upon workup, a yellowish-colored resin. This was dissolved in CHCl_3 (ca. 4 mL) and stored at room temperature. After 2 weeks of storage at room temperature, some crystalline needles of **2h** had formed (ca. 100 mg). ²⁹Si NMR (99 MHz, CDCl_3): δ = -25.5 ppm. ¹³C NMR (126 MHz, CDCl_3): δ = 155.1 ($\text{C}=\text{O}$), 45.1 (N-(CH_2)₂), -25.8 (N-(CH_2)₂-(CH_2)₂), 24.5 (N-(CH_2)₂-(CH_2)₂- CH_2), -0.6 (Si- CH_3) ppm. ¹H NMR (500 MHz, CDCl_3): δ = 3.39 (16H, N-(CH_2)₂, m), 1.55–1.49 (24H, N-(CH_2)₂-(CH_2)₂- CH_2 , m), 0.55 (6H, Si- CH_3 , s) ppm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06868>.

¹H, ¹³C, ²⁹Si solution NMR, and ²⁹Si MAS NMR spectra; APCi mass spectra; selected data of the single-crystal X-ray diffraction analyses; and a van't Hoff plot ($\ln(K)$ vs $1/T$) derived from the VT NMR analysis of compound **2e** (PDF)
Crystallographic data (CIF)

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Notes

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