CO_2 as an Oxygen Source for Polysiloxanes – Preparation, Crystal Structure and Thermal Decomposition of Two Novel Silylcarbamates

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Diaminosilanes $(CH_3)_2Si(NHR)_2$ **1a**, **b** are obtained from dichlorodimethylsilane and primary amines (R = *n*-hexyl, *iso*-propyl) in good yields. *Bis*-insertion of CO_2 into the Si–N bonds of the aminosilanes quantitatively gives the silylcarbamates $(CH_3)_2Si(OCONHR)_2$, **2a**, **b**. Oligo- and polydimethylsiloxanes **3a**, **b** as well as *N*,*N*′-substituted ureas $CO(NHR)_2$ **4a**, **b** are formed upon heating the silylcarbamates **2a**, **b** to ∼ 150 °C. The results of comprehensive NMR analyses of the aminosilanes, the two novel *bis*-silylcarbamates, the siloxanes and the ureas, and of single-crystal structure analyses of **2a** and **4b** are presented. In the crystal the *n*-hexyl silylcarbamate **2a** shows a similar molecular packing arrangement as the *iso*-propyl urea derivative **4b**.

Key words: Polysiloxane, Silylamine, CO_2 Insertion, Silylcarbamates, Crystal Structure

Introduction

CO_2 may be used as starting material for chemical syntheses, *e. g.* for the synthesis of $CO(NH_2)_2$, methanol, and several carbonates [1]. Hence, CO_2 is mainly used as a C1 source. One of the several methods known for the activation of CO_2 [2] is the insertion into a main group or transition metal nitrogen bond [3].

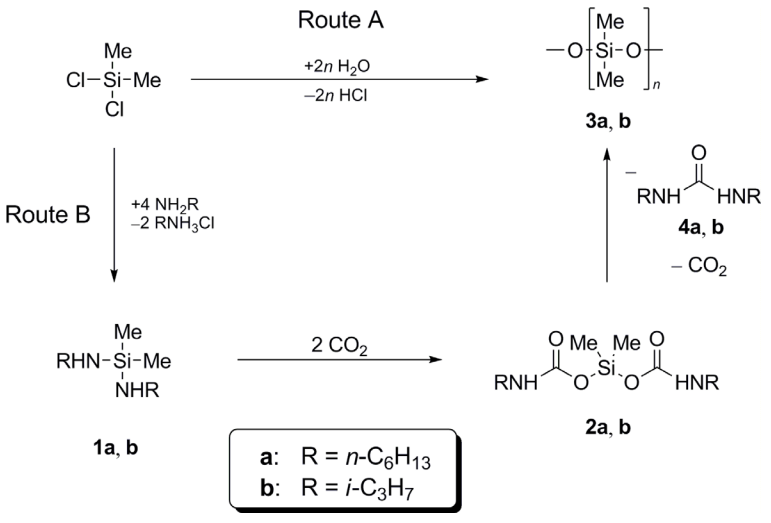
Regarding silicon, silylcarbamates are mainly formed upon mono-insertion of one CO_2 molecule into the Si–N bond of aminosilanes (or silylamines) of the type $R_3SiNR'_2$ (R = methyl, ethyl, R′ = alkyl, aryl). Few authors described the insertion of two CO_2 molecules into *bis*-aminosilanes [4 – 6]. Szalay *et al.* prepared trisilylesters of dicarbamic acids [7], while Belli Dell'Amico *et al.* described a homoleptic compound starting form $SiCl_4$, R_2NH and CO_2 [8]. Walther *et al.* inserted CO_2 into a Si–N bond in a nickel complex [9].

Besides, further methods for obtaining silylcarbamates have been reported. Sheludyakov *et al.* described various reactions of hexamethyldisilazane and amines or their salts with carbon dioxide [10]. Mironov *et al.* reported a transamination with primary or secondary amines [11, 12], while Birkofer and Sommer used chlorosilanes in the presence of a silver carbamate or an ammonium carbamate [13]. Knausz *et al.* prepared silylcarbamates by silylation of ammonium carbamate with trimethylchlorosilane including the reactions with anhydrides [14]. Breederveld [15], Mironov and other authors [16 – 18] reported the addition of carbon dioxide to silylated alkylamines. Recently Fuchter *et al.* used supercritical CO_2 for the synthesis of several *O*-silylcarbamates and studied their decomposition into various substituted ureas [19].

Most of these reports focus on the reactions of Me_3SiCl with primary and secondary amines, *e. g.* using the TMS substituent as directing group in organic synthesis [19]. In contrast, we report here the use of Me_2SiCl_2 and a primary amine as starting materials for the synthesis of diaminosilanes $Me_2Si(NHR)_2$. Subsequent quantitative *bis*-insertion of CO_2 yields the corresponding silylcarbamates $Me_2Si(OCONHR)_2$. Thermal treatment of these products at moderate temperatures generates *N*,*N*′-disubstituted ureas and polydimethylsiloxanes.

Results and Discussion

Scheme 1 shows the common route A for the synthesis of siloxanes as well as our new route B *via* the *bis*-insertion of CO_2 into the Si–N bonds of a diaminosilane $Me_2Si(NHR)_2$ [20]. The starting material for route B is also dichlorodimethylsilane, but it is first used for the preparation of aminosilanes. The resulting hydrogen chloride is captured in the hydrochloride



Scheme 1. The established route A and the new CO_2-based anhydrous route B to polysiloxanes.

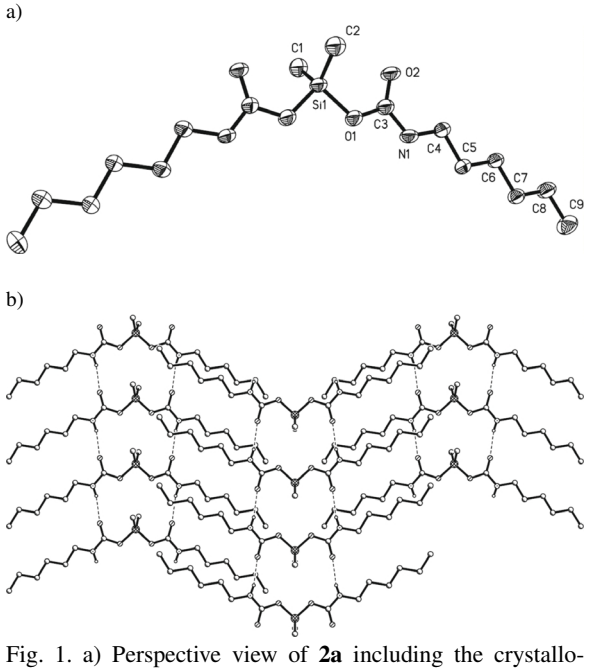


Fig. 1. a) Perspective view of **2a** including the crystallographic numbering of atoms. Displacement ellipsoids are at the 50 % probability level; hydrogen atoms are omitted; b) packing of molecules in crystals of **2a** as viewed along the crystallographic *c* axis. Broken lines represent N–H···O hydrogen bonds. All hydrogen atoms except those at N atoms are omitted for clarity.

of the corresponding amine. Hence, hydrogen chloride is removed before the formation of the siloxane *via* route B, whereas it is generated simultaneously with the siloxanes in the traditional route A. The 1,1-dimethyl-*N*,*N*′-diorganosilanediamines **1a**, **b** can be prepared as reported recently [21]. Addition of the respective amine to Me_2SiCl_2 in *n*-hexane at 20 °C yields the aminosilanes **1a** and **1b** in good yields as colorless liquids. The two hydrolysis-sensitive products show the expected ^{1}H, ^{13}C, ^{29}Si NMR data, *e. g.* chemical shifts of 1.7 (**1a**) and 1.6 ppm (**1b**) in the ^{29}Si NMR spectra.

Table 1. Crystal structure data for **2a** and **4b**.

Compound	**2a**	**4b**
Formula	$C_{16}H_{34}N_2O_4Si$	$C_7H_{16}N_2O$
M_r	346.54	144.22
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/m$	$P2_12_12$
a, Å	5.1096(6)	9.0336(11)
b, Å	25.053(3)	10.3401(12)
c, Å	7.6165(10)	4.6895(5)
β, deg	90.083(10)	90
V, Å^3	975.0(2)	438.04(9)
Z	2	2
F(000), e	380	160
D_{calcd}, g cm^{-3}	1.18	1.09
μ(MoK_α), cm^{-1}	0.1	0.1
Data collection temperature, K	200(2)	175(2)
θ range, deg	2.67 – 24.98	2.99 – 25.10
hkl range	−6/5, −26/29, ±9	±10, ±12, ±5
No. of coll. / unique refl.	4443 / 1694	4299 / 793
R_{int}	0.0931	0.0517
No. of refl. with $I \geq 2\sigma(I)$	1086	714
No. of refined parameters	117	53
$R1$ $(F)^a$ / $wR2$ $(F^2)^b$ (all data)	0.0601 / 0.1625	0.0335 / 0.0788
S (Goodness of fit on F^2)^c	0.988	1.084
Final $\Delta\rho_{max/min}$, e Å^{-3}	0.567 / −0.289	0.137 / −0.138
CCDC number	826981	826982

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Insertion of carbon dioxide was accomplished by bubbling dry CO_2 gas into a solution of the aminosilanes in dry THF at r. t. This exothermic reaction is quantitative and requires cooling if larger amounts of the silylcarbamate are prepared.

NMR spectroscopic analyses of the resulting di(*n*-hexylcarbamoyloxy)dimethylsilane (**2a**) and di(*iso*-propylcarbamoyloxy)dimethylsilane (**2b**) proved the insertion of two CO_2 molecules. ^{13}C NMR signals at 153.7 (**2a**) and 152.6 (**2b**) ppm are typical for carbonyl carbon atoms. A similar conclusion can be drawn from the small shift of the representative ^{13}C NMR resonance signals for the methyl silyl groups at −1.2 (**1a**) to −1.9 ppm (**2a**). The ^{29}Si NMR spectra show peak shifts from −8.9 (**1a**) to 1.7 ppm for **2a** and from −11.4 (**1b**) to 1.6 ppm for **2b**. Besides, the vibrational spectra clearly indicate that an insertion of CO_2 occurred, by showing typical carbonyl group vibrations at *ca.* 1670 cm^{-1}.

A single crystal of the carbamate **2a** was isolated and analyzed by X-ray diffraction. The carbamate **2a** crystallizes as colorless needles in the space group $P2_1/m$ with half a molecule in the asymmetric unit (Fig. 1, Table 1). All bond lengths and angles are within the expected ranges and prove the insertion of CO_2 into the Si–N bonds. The molecular packing is dominated by N–H···O hydrogen bonds generating molecular chains along the crystallographic *a* axis (Table 2).

The NMR and the X-ray diffraction data clearly prove the exhaustive insertion of two CO_2 molecules. This is surprising since it is in contrast to the observation of Fuchter *et al.* who reported the insertion of only one molecule of carbon dioxide using supercritical CO_2 and trialkylsilylamines [19]. The synthesis presented here occurs at r. t. with dry gaseous CO_2 leading to *bis*-inserted silylcarbamates.

The conversion of the carbamates **2a**, **b** to siloxanes **3a**, **b** and ureas **4a**, **b** can be achieved by heating the samples up to 150 °C. The ureas **4a**, **b** can be isolated *via* sublimation leading to single crystals of **4b**. The resulting urea **4b** was found to crystallize in the orthorhombic space group $P2_12_12$ with half a molecule in the asymmetric unit (Fig. 2). Again, all bond lengths and angles are within the expected ranges. As it was also observed for the carbamate **2a**, the crystal structure of **4b** is dominated by strong hydrogen bonds of the N–H···O type (Table 2) forming intermolecular chains along the crystallographic *c* axis.

Table 2. Hydrogen bond parameters in compounds **2a** and **4b**.

Atoms involved	Symmetry operation	Distance (Å) D···A	Distance (Å) H···A	Angle (deg)
2a N1–H1···O2	$x+1, y, z$	2.969(4)	2.16(6)	169(5)
4b N1–H1···O1	$x, y, z-1$	2.952(2)	2.17(2)	156(1)

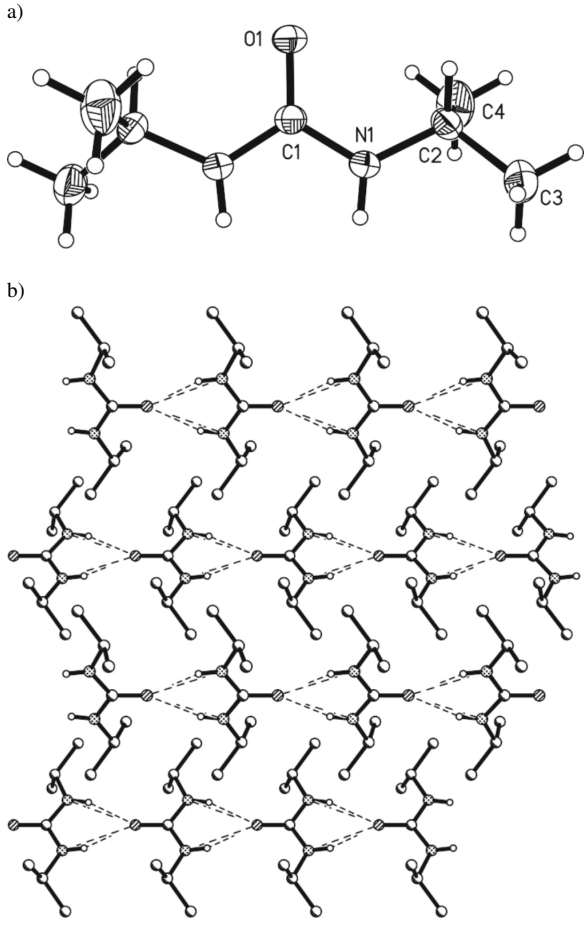


Fig. 2. a) Perspective view of **4b** including the numbering scheme of atoms. Displacement ellipsoids are at the 50 % probability level; b) packing of molecules in crystals of **4b** as viewed along the crystallographic *a* axis. Broken double lines represent N–H···O hydrogen bonds. All hydrogen atoms except those at N atoms are omitted for clarity.

Apart from the ureas **4a**, **b**, the thermal decomposition reaction of **2a**, **b** affords the siloxanes **3a**, **b**. As depicted in Fig. 3, the ^{29}Si NMR spectroscopic analyses show a signal at 21.6 ppm typical for siloxanes. Commercially available polydimethylsiloxanes (PDMS) with different molecular masses were measured for comparison and showed the same signals at 21.8 ppm. Further analyses of the color-

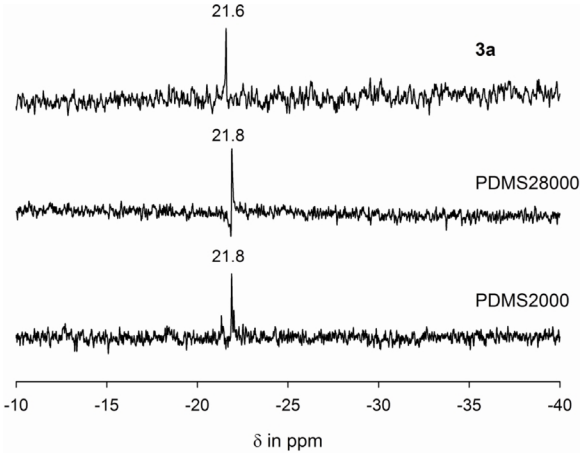


Fig. 3. ^{29}Si NMR spectra of **3a**, and of PDMS28000 and PDMS2000 for comparison.

less oils included FTIR, ^{1}H and ^{13}C NMR spectroscopy. All these data are in accordance with the PDMS composition. Attempts to determine the molecular mass distribution were not successful so far. A mass spectrometric study of the siloxane products is currently under way and will be published elsewhere. Future investigations will focus on asymmetric aminosilanes $Me_2Si(NHR)(NHR')$, on *tris*- and *tetrakis*-insertions into the corresponding tri- and tetraminosilanes, and on a thorough analysis of the molecular mass distribution of the oligo- and polysiloxanes.

Conclusion

Diaminosilanes of the type $(RHN)_2SiMe_2$, obtained from Me_2SiCl_2 and primary amines, were subjected to a double insertion of CO_2 at r. t. to afford the *bis*-(carbamates). The latter reaction is exothermic and proceeds quantitatively. In the thermolysis of these products at 150 °C one equivalent of CO_2, polydimethylsiloxanes and *N*,*N*′-disubstituted ureas are formed.

This reaction scheme has been exemplified using *n*-hexyl and *iso*-propyl amines. The diaminosilanes **1a**, **b**, both carbamates **2a**, **b**, the oligosiloxanes **3a**, **b** as well as the ureas **4a**, **b** were unambiguously identified by comprehensive NMR measurements.

The overall process is a novel route to polysiloxanes and *N*,*N*′-disubstituted ureas, and a contribution to the usage of CO_2 as a starting material for chemical syntheses.

Experimental Section

General

All syntheses and manipulations were performed in Schlenk-type glassware or in a glove box (MBraun, Germany, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). *Chemicals:* All solvents were purified and dried according to general procedures. Dichlorodimethylsilane (Sigma Aldrich), *iso*-propylamine (Sigma Aldrich) and *n*-hexylamine (Fluka) were used as received without further purification. Trimethylsiloxy-terminated polydimethylsiloxanes with a formula weight of 2000 g mol^{-1} (PDMS2000) and 28000 g mol^{-1} (PDMS28000) were obtained from ABCR. CO_2 was dried by bubbling it through concentrated sulfuric acid. *Instrumentation:* ^{1}H, ^{13}C and ^{29}Si NMR: Bruker Avance DPX 400; chemical shifts are given relative to $SiMe_4$. IR: Nicolet 380 FT-IR at r. t. using dried KBr pellets. Elemental analyses: elementar vario MICRO CUBE CHNS analyzer.

*Preparation of diaminodimethylsilanes **1a**, **b***

General procedure

To a solution of 20 g (0.15 mol) dichlorodimethylsilane in 300 mL *n*-hexane 0.7 mol of the respective amine was added dropwise at 20 °C. After standing at r. t. for one day, the resulting solid amine hydrochloride was separated *via* suction filtration. The solvent was removed from the filtrate under reduced pressure, and the raw product was distilled. Details for the individual compounds are given below.

***1a*:** *n*-hexylamine (70.8 g) was reacted according to the general procedure described above. Yield: 32.6 g (72 %). – ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -8.9$ ppm. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.29$ (s, 6H, $SiCH_3$), 0.82 (s, 2H, NH), 1.23 (t, $J_{HH} = 6.6$ Hz, 6H, CH_3), 1.63 (m, 16H, CH_2), 3.05 (m, 4H, NCH_2) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -1.2$, 14.2, 23.2, 27.1, 32.3, 35.4, 41.5 ppm. – $C_{14}H_{34}N_2Si$ (258.52): calcd. C 65.04, H 13.26, N 10.84; found C 65.06, H 13.86, N 12.21.

***1b*:** *iso*-propylamine (41.4 g) was reacted according to the general procedure described above. Yield: 25.3 g (83 %). – ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -11.4$ ppm. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.01$ (s, 6H, $SiCH_3$), 0.45 (s, 2H, NH), 1.04 (m, 6H, CH_3), 3.1 (m, 2H, CH) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.4$, 27.9, 42.3 ppm.

*Preparation of di(carbamoyloxy)dimethylsilanes **2a**, **b***

General procedure

Into a solution of the corresponding silylamine **1a**, **b** (0.05 mol) in 50 mL THF gaseous CO_2 (dried over sulfuric acid) is blown *via* a gas inlet. The exothermic reaction takes place at r. t. (CAUTION: larger amounts require cooling of the solution!). Removing the solvent at reduced pres-

sure yields the carbamate quantitatively (17.3 g, 100 %). Further purification of the product is not necessary.

***2a*:** Compound **1a** (12.9 g) was reacted according to the general procedure and gave **2a** as a colorless solid. Yield: 17.3 g (100 %). – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = 1.7 ppm. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.72 (s, 6H, $SiCH_3$), 1.30 (m, 6H, CH_3), 1.68 (m, 16H, CH_2), 3.17 (m, 4H, NCH_2) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.9, 13.3, 22.1, 26.0, 29.3, 31.1, 40.5, 153.7 ppm. – IR (KBr): ν = 3327 (m, ν NH); 2961, 2929 (m, ν CH); 1670 (str, ν CO); 1261 (str, ν $SiCH_3$) cm^{-1}. – $C_{16}H_{34}N_2O_4Si$ (346.54): calcd. C 55.45, H 9.89, N 8.08; found C 54.88, H 10.00, N 8.12.

***2b*:** Compound **1b** (8.7 g) was reacted according to the general procedure and gave **2b** as a colorless solid. Yield: 13.1 g (100 %). – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = 1.6 ppm. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.01 (s, 6H, $SiCH_3$), 0.67 (s, 2H, NH), 1.01 (m, 6H, CH_3), 2.9 (m, 2H, CH) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.1, 21.7, 42.1, 152.6 ppm. – $C_{10}H_{22}N_2O_4Si$ (262.38): calcd. C 45.78, H 8.45, N 10.68; found C 44.1, H 8.4, N 9.8.

*Preparation of siloxanes **3a, b** and ureas **4a, b***

General procedure

The carbamates were heated in a flask equipped with a reflux condenser to 150 °C and kept for half an hour. The urea derivatives **4a**, **b** were collected by sublimation out of the reaction mixture and analyzed. Siloxanes **3a**, **b** were found in the sublimation residue. At higher temperatures volatile oligosiloxanes started to evaporate as well.

***3a*:** Compound **2a** (17.3 g) was reacted according to the general procedure to give **3a** as a colorless oil. – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = −21.6 ppm. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, $SiCH_3$) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.2 ppm. Small amounts of the corresponding urea **4a** were also detected indicating an incomplete separation of products.

***3b*:** Compound **2b** (13.1 g) was reacted according to the general procedure to give **3b** as a colorless oil. – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = −21.5 ppm. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, $SiCH_3$) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.0 ppm. Small amounts of the corresponding urea **4b** were also detected indicating an incomplete separation of products.

***4a*:** Compound **2a** (17.3 g) was reacted according to the general procedure to give **4a** as a colorless solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (m, 6H, CH_3), 1.19 (m, 16H, CH_2), 3.05 (m, 4H, NCH_2), 4.59(s, 2H, NH) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.8, 26.8, 30.4, 31.7, 40.8 ppm.

***4b*:** Compound **2b** (13.1 g) was reacted according to the general procedure to give **4b** as a colorless solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (d, J_{HH} = 5.8 Hz, 12H, CH_3), 3.85 (m, 2H, CH), 4.1 (s, 2H, NH) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5, 42.1, 157.4 ppm.

PDMS2000: – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = 21.8 ppm.

PDMS28000: – ^{29}Si NMR (79 MHz, $CDCl_3$): δ = 21.8 ppm.

X-Ray structure determinations

Crystals suitable for X-ray crystallography of **2a** were grown from tetrahydrofuran, and of **4b** *via* sublimation. Data collection was performed on a Stoe IPDS-2T diffractometer (image plate) equipped with a low-temperature device (Cobra, Oxford Cryosystems, **2a**: 200(2) and **4b**: 175(2) K) with graphite-monochromatized MoK_α radiation (λ = 0.71073 A) using ω and ϕ scans. Reflections were corrected for background, Lorentz and polarization effects. Preliminary structure models were derived by application of Direct Methods (SHELXS-97 [22]), and the structures were refined by full-matrix least-squares calculations based on F^2 for all reflections using SHELXL-97 [22]. With the exception of H1 in the structure of **2a** and of H1N in the structure of **4b**, all hydrogen atoms were included in the models in calculated positions and were refined as constrained to the bonded atoms. The crystal of **2a** was measured as a twin with two domains in the ratio of 60 : 40. In **2a** the methyl groups at C1 and C2 show a disorder. The crystal data and parameters pertinent to data collection and structure refinement of **2a** are summarized in Table 1.

CCDC 826981 (**2a**) and 826982 (**4b**) 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.

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