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Insertion of phenyl isocyanate into mono- and diaminosilanes

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Abstract: The aminosilanes $Me_nSi(NRR')_{4-n}$ (n=2,3) with NRR′ = ethylamino (NHEt), *n*-propylamino (NH^{n}Pr), *sec*-butylamino (NH^{s}Bu), *n*-octylamino (NH^{n}Oct), *n*-dodecylamino (NH^{n}Dodec), allylamino (NHAll), *tert*-butylamino (NH^{t}Bu), diethylamino (NEt_2), and anilino (NHPh) were synthesized and their reactions with phenyl isocyanate were studied. In all cases of these silanes Me_3SiNRR' and $Me_2Si(NRR')_2$ formal insertion of the –NCO group into their Si–N bonds was observed, i.e. formation of products with Si–N (rather than Si–O) bonds was found. In some cases, the products could be crystallized and their molecular structures have been elucidated with single-crystal X-ray diffraction analyses.

Keywords: amines; insertion; silanes; silicon-nitrogen bond; silylated urea.

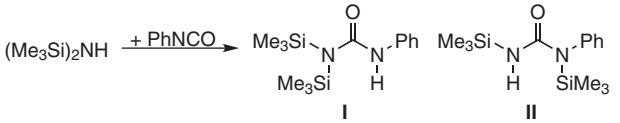
Dedicated to: Professor Dietrich Gudat on the occasion of his 60th birthday.

1 Introduction

Aminoorganosilanes have been frequently studied during the past decades [1–17] and often they have been utilized as substrates for further transformations, for example as reagents [18–31] or precursors for the generation of silicon nitride [32–36]. Various applications are claimed for the products resulting from the insertion of isocyanates and isothiocyantes into the Si–N bond(s) of aminosilanes, e.g. material science associated applications are reported such as modification and generation of polymers or ceramics. For instance, *N*-phenyl substituted polyureas can be modified with bis[(*N*,*N*′-diphenylureylene)methyl]silane moieties resulting in an efficient photodegradable polymer. Bond cleavage in the polymer occurs only by UV light [37] while by contrast the silicon-free polyurea is degraded by visible light as well [37]. Ureidosilanes are utilized as precursors for the synthesis of silarylen-siloxane polymers and carborane-siloxane polymers [38]. The silazane based derivatives are polymer precursors for silicon carbide nitride and silicon nitride ceramics [36]. Such ceramics exhibit high thermal, mechanical and electrical stability and are utilized in high temperature applications [39, 40]. This list of different applications serves as motivation for the search for further potential fields of application of silylated urea derivatives and also justifies the need to explore such organosilicon compounds in terms of bonding situations and the development of selective synthetic routes to this class of compounds. A convenient route toward silylated urea or urea analogs is the insertion of heterocumulenes into the Si–N bond of aminosilanes. For example, we reported the insertion of carbon dioxide (1) [28–31].

$$Me_nSi(NHR)_{4-n} \xrightarrow{+(4-n)CO_2} Me_nSi(OCONHR)_{4-n} \quad (1)$$

A related type of reaction, to yield silylated urea compounds, is the reaction of aminosilanes with isocyanates. So far, the literature offers contradictory statements about the constitution of silylated ureas (*N*- vs. *O*-silylation) and also about the reaction pathway [41–51]. Early investigations of these reactions were done by Fink, e.g. he describes the reaction of hexamethyldisilazane with phenyl isocyanate in a ratio of 1:1 (2). In this particular case it is not clear whether an insertion reaction takes place either into the nitrogen-hydrogen (**I**) or the silicon-nitrogen bond (**II**), a question which arises for all aminosilanes with the structural feature Si–NHR.



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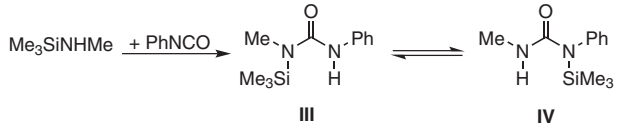
Analysis of the product indicates insertion into the silicon-nitrogen bond (i.e. formation of compound **II**), but this may as well be the result of initial formation of compound **I** followed by rearrangement of H vs. $SiMe_3$ [41, 42]. Klebe et al. describe the NMR spectroscopic investigation of an equilibrium of two possible isomers in dependence of the solvent used. They carried out the reaction of (methylamino)trimethylsilane with phenyl isocyanate (3) in deuterated chloroform as a hydrogen bond donor (equilibrium shifts to **IV**) and in dimethyl sulfoxide as a hydrogen bond acceptor (equilibrium shifts to **III**) [43]. The equilibrium can be achieved via intramolecular proton trimethylsilyl exchange or alternatively by intermolecular exchange via bis-silylated and non-silylated intermediates.



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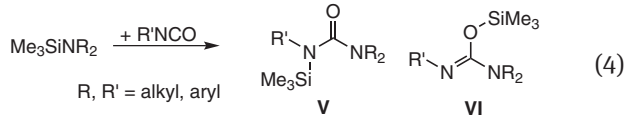
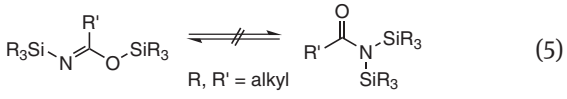
In lack of a nitrogen-hydrogen bond, reactions of aminosilanes with tertiary nitrogen atoms and isocyanates yield silylated urea compounds. Even in these "less ambiguous" systems one question arises: does this reaction (4) afford an *N*-silylated (**V**) or an *O*-silylated (**VI**) urea derivative? [43]



(4)

Based on the spectroscopic analysis of bis(trimethylsilyl) ureas formation of *N*-trimethylsilyl substituted urea (**V**) is favored. These spectra reveal no splitting of the trimethylsilyl group signals in the ^1H NMR spectra of several bis(trimethylsilyl) substituted ureas, thus being indicative that no slow exchange of the trimethylsilyl groups takes place on the NMR timescale (5).



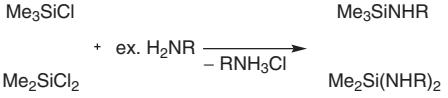
(5)

Further detailed information on this topic can be found in the review of Kraushaar et al. [30] and the literature cited therein. To address the question about the conformation of the products formed by reaction of aminosilanes and phenylisocyanate, we synthesized and characterized a greater library of silylated urea derivatives.

2 Results and discussion

2.1 Synthesis of aminosilanes by reaction of chlorosilanes and amines

To investigate the influence of the type of aminosilane on the course of the insertion reaction of phenyl isocyanate, a variety of amines was used for the synthesis of the aminosilanes: ethyl-, *n*-propyl-, *n*-octyl-, *n*-dodecyl-, allyl-, *sec*-butyl- and *tert*-butylamine as primary amines, diethylamine as an acyclic secondary amine and aniline to represent the class of aryl amines. Chlorotrimethylsilane and dichlorodimethylsilane were used as silane starting materials. The aminosilanes were prepared by base-supported aminolysis of the Si–Cl bond in hexane or diethyl ether as solvent, the amine itself (alternatively trimethylamine) serving as the supporting base (6).



(6)

The numbering of the aminosilanes and their PhNCO insertion products as well as their ^{29}Si NMR shifts are listed in Table 1.

All synthesized aminosilanes are colorless distillable liquids, except the di(anilino)dimethylsilane, which is a colorless solid at room temperature. The crystal structure of this solid has been reported in the literature [52]. As we obtained a crystal structure determination of better quality, we include our structure of this compound in the Supporting Information. Also we obtained crystals suitable for X-ray diffraction of the aniline solvate of

Table 1: ^{29}Si NMR shifts of the aminosilanes and their PhNCO insertion products under investigation.

Aminosilane	Compound	$\delta^{29}Si$ (ppm)	Number of insertion product	$\delta^{29}Si$ (ppm)
Me_3SiNH^nPr	**1**	3.3	**13**	8.2
Me_3SiNH^sBu	**2**	1.1	**14**	10.1
Me_3SiNEt_2	**3***	3.9	**15***	12.4
$Me_3SiNHPh$	**4**	2.4	**16**	10.3
$Me_2Si(NHEt)_2$	**5***	−9.5	**17**	−3.9
$Me_2Si(NH^nPr)_2$	**6***	−9.1	**18**	−3.9
$Me_2Si(NH^nOct)_2$	**7***	−9.3	**19***	−4.0
$Me_2Si(NH^nDodec)_2$	**8***	−9.4	**20**	−4.0
$Me_2Si(NHAll)_2$	**9**	−6.9	**21**	−3.4
$Me_2Si(NH^tBu)_2$	**10**	−16.7	**22**	−3.6
$Me_2Si(NEt_2)_2$	**11***	−5.4	**23**	−3.3
$Me_2Si(NHPh)_2$	**12***	−10.6	**24**	−1.8

Asterisked compounds have been published earlier.

compound **12**. Its crystal structure data can be found in the Supporting Information as well.

2.2 Synthesis of ureaylsilane by reaction of aminosilanes with phenyl isocyanate

For the insertion reaction the aminosilane was placed in a Schlenk flask together with chloroform (amylene stabilized) or *n*-pentane as a solvent. The mixture was cooled with dry ice/isopropanol, and with stirring the phenyl isocyanate was added dropwise through a syringe. After vacuum evaporation of the solvent the products were obtained as white solids. For the insertion of phenyl isocyanate into aminosilanes derived from primary amines we observed the expected insertion products (formal single insertion into the Si–N bond). In case of the reactions of diethylaminosilanes, single and double insertions were observed, depending on the stoichiometric ratio of the starting materials. The molecular structure of the product of double insertion of phenyl isocyanate into **3** has been published [49]. Interestingly, the enhanced reactivity of phenyl isocyanate (in comparison to other heterocumulenes, like carbon dioxide) allowed for the insertion into sterically more demanding silanes. In previous work it was shown that amines with sterically hindered residues, like *sec*-butyl or *tert*-butyl and also aromatic amines, did not afford insertion products of carbon dioxide [31].

In all insertion reactions into dimethyldiaminosilanes, except those with bis(diethylamino)dimethylsilane and dianilinodimethylsilane, a well-defined product was obtained.

From the reactions of the aminosilanes **1**, **3**, **4**, **6**, **7**, **10**, **11**, and **12** with phenyl isocyanate crystalline products were obtained in crystal quality suitable for X-ray diffraction. In Figs. 1 and 2 the molecular structures of trimethyl-(1-phenyl-3-*n*-propylureayl)silane **13** and trimethyl-1,3-diphenylureaylsilane **16** are shown (Tables 2 and 3).

The comparison of the depicted molecular structures shows that in both cases one methyl group (of the trimethylsilyl group) and the adjacent phenyl ring are nearly in *cis* position. The deviation of the $C_{(Me)}$–Si–N–C_{ipso} angle from planarity is 8.15(16)° for **13** and 3.25(15)° for **16**. This particular methyl group (C13 in **13**, C7 in **16**) exhibits a somewhat longer Si–C bond, which may arise from a combination of contacts between the protons of the methyl group and the π electron system of the phenyl rings and the influence of the carbonyl oxygen atom O1 with the Si atom with Si···O separations of 2.86 Å for **13** and 2.81 Å for **16**.

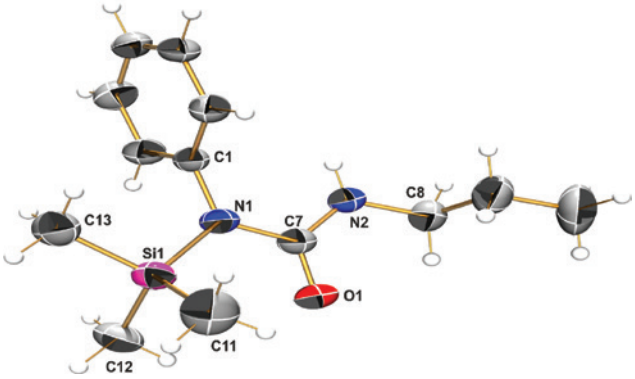


Fig. 1: Molecular structure of trimethyl-(1-phenyl-3-*n*-propylureayl) silane **13** in the crystal (displacement ellipsoids drawn at the 50% probability level).

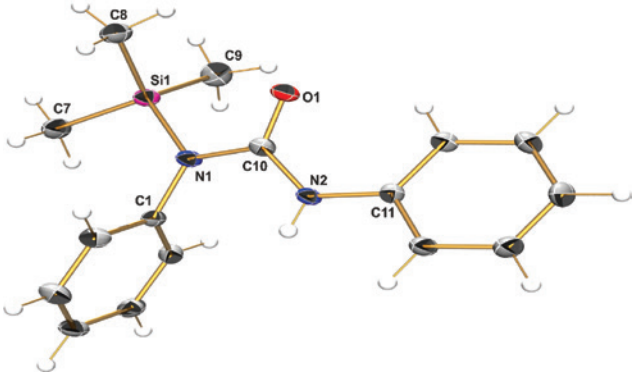


Fig. 2: Molecular structure of trimethyl-1,3-diphenylureaylsilane **16** in the crystal (displacement ellipsoids drawn at the 50% probability level).

Insertion products are obtained from the reactions of dimethyldi(*n*-propylamino)silane **6**, di(*tert*-butylamino) dimethylsilane **10** and bis(diethylamino)dimethylsilane **11** with two equivalents of phenyl isocyanate. The molecular structures of these products (**18**, **22** and **23**) were determined by single-crystal X-ray diffraction (Figs. 3–5; Tables 2–4). The comparison of these structures indicates that the bulky *tert*-butylamino (**22**) and diethylamino (**23**) groups induce a slight extension of the Si–N bonds. The phenyl rings of compounds **22** and **23** are arranged perpendicular to each other. The N–C–N bond angles of the urea framework vary between these compounds, and for **23** even within the same molecule (117.67(7)° and 117.78(7)° for **18**; 116.83(15)° and 116.77(14)° for **22**; 118.45(9)° and 121.20(9)° for **23**). The C–N–C bond angles of the diethylamino groups in **23** are also different in the same molecule (115.26(10) and 116.33(9)°). The variation of angles in the latter molecule can be explained by the steric repulsion between the

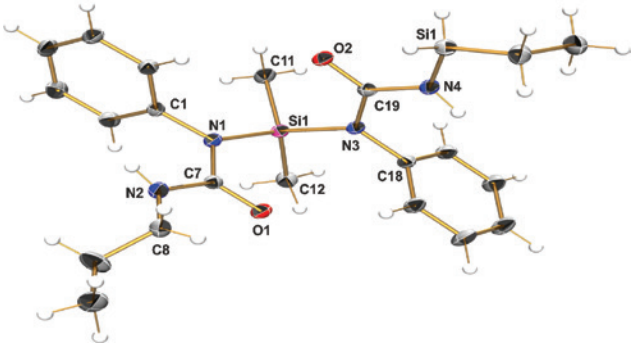


Fig. 3: Molecular structure of dimethyldi(1-phenyl-3-*n*-propylureayl) silane **18** in the crystal (displacement ellipsoids drawn at the 50% probability level).

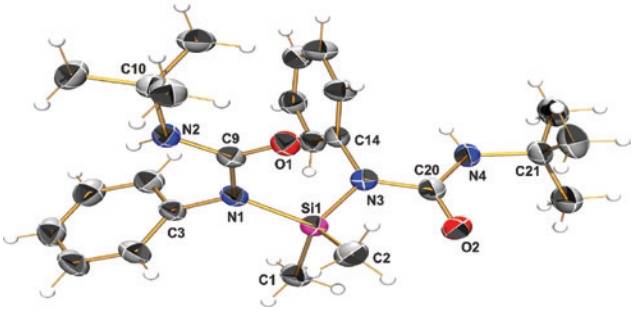


Fig. 4: Molecular structure of dimethyldi(1-phenyl-3-tert-butylureayl)silane **22** in the crystal (displacement ellipsoids drawn at the 50% probability level).

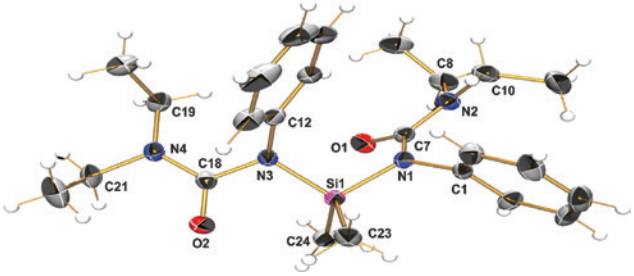


Fig. 5: Molecular structure of dimethyl-bis(1-phenyl-3,3′-diethylureayl)silane **23** in the crystal (displacement ellipsoids drawn at the 50% probability level).

diethylamino group and the phenyl rings and the attempt to achieve a favorable arrangement within the molecule but also in the packing of the molecules in the crystal. In compound **18** the carbonyl O atoms are *trans*-disposed to the Si–C bonds. In contrast, in **22** and **23** one carbonyl group is capping a tetrahedral face *trans* to an Si–C bond, the other a tetrahedral face *trans* to an Si–N bond, thus allowing a comparison of sets of chemically different Si–C and Si–N bonds in the latter two cases. As observed for **13** and **16**, the molecular structures of **22** and **23** also exhibit a longer Si–C and a longer Si–N bond *trans* to the capping carbonyl O atom (Si–C: 1.8581(18)/1.8473(19) Å and Si–N: 1.7708(14)/1.7682(15) Å for **22** and Si–C: 1.8537(12)/1.8483(11) Å and Si–N: 1.7754(9)/1.7714(9) Å for **23**). The intramolecular Si···O separations are similar to those found in **13** and **16**: 2.85 Å for **18**, 2.86 Å for **22** and 2.76 Å for **23**.

The reaction leading from **12** to **24** also involves the insertion of phenyl isocyanate into both Si–N bonds of **12**. The molecular structure of this product was determined by single-crystal X-ray diffraction (Fig. 6, Table 4). The molecule contains two urea units which are connected by the silicon atom Si1. Both urea units are planar (see least-squares planes in the Supporting Information). The phenyl ring beginning at C3 is nearly coplanar with the urea unit N1–C15(=O1)–N3 with a dihedral angle of 7.6(2)°. In contrast, the phenyl ring C16–C21 has a dihedral angle of 86.9(1)° with this urea unit. A similar situation is found at the urea unit N2–C22(=O2)–N4. The phenyl group beginning at C9 is nearly coplanar with this urea unit (6.0(1)°), the phenyl group beginning at C23 being rotated away with an dihedral angle of 78.4(1)°. The conformations of the phenyl groups can be explained with the overall geometry of the molecule: The phenyl groups which are localized close to the tetrahedral silicon atom (beginning at C16 and C23) are rotated away from the neighboring methyl groups C1 and C2. The phenyl groups which are located at the periphery of the molecule (beginning at C3 and C9) are able to adopt coplanar conformations in order to maximize conjugation with the urea units. This coplanarity leads also to intramolecular hydrogen contacts C8–H8···O1 and C14–H14···O2 (numeric values in the Supporting Information).

In all cases of this study it is obvious that silicon-nitrogen bonds are formed (rather than silicon-oxygen bonds) during the insertion reactions of phenyl isocyanate into the silicon-nitrogen bonds of mono- and diaminosilanes.

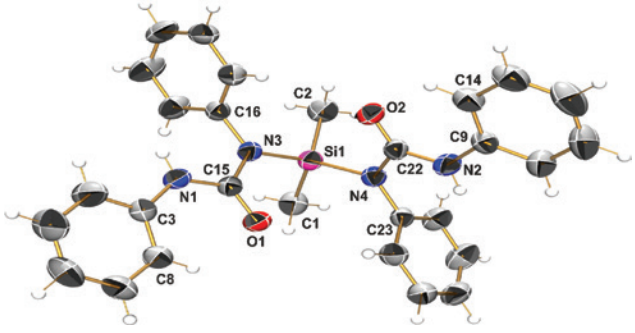


Fig. 6: Molecular structure of dimethyl-bis(1,3-diphenylureayl) silane **24** in the crystal (displacement ellipsoids drawn at the 50% probability level).

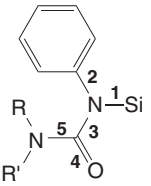


Fig. 7: Numbering of the bonds in the ureaylsilanes (Table 2).

To compare the structures, the bond lengths of the *N*-silylated urea moieties of the herein discussed compounds are collected in Table 2 (a bond numbering Scheme is shown in Fig. 7). The Si–N bonds cover a very narrow range (1.760(1)–1.779(1) Å), which can be attributed to the essentially identical Ph–N–C(=O) substitution pattern. There is no obvious influence of the $SiMe_3$ vs. $SiMe_2$ moiety

Table 2: Bond lengths 1–5 in the compounds **13**, **16**, **18**, **22**, **23** and **24**.

Compound	Bond 1 (Å)	Bond 2 (Å)	Bond 3 (Å)	Bond 4 (Å)	Bond 5 (Å)
13	1.7657(14)	1.4409(19)	1.382(2)	1.2394(18)	1.348(2)
16	1.7787(14)	1.440(2)	1.379(2)	1.2317(19)	1.367(2)
18	1.7598(7)/1.7609(8)	1.4352(10)/1.4393(10)	1.3855(10)/1.3811(10)	1.2346(7)/1.2357(10)	1.3573(11)/1.3531(11)
22	1.7682(15)/1.7708(14)	1.441(2)/1.445(2)	1.399(2)/1.388(2)	1.2315(19)/1.231(2)	1.360(2)/1.367(2)
23	1.7754(9)/1.7714(9)	1.4379(12)/1.4370(13)	1.3998(13)/1.4059(13)	1.2301(13)/1.2307(14)	1.3599(14)/1.3545(14)
24	1.771(2)/1.765(2)	1.446(3)*	1.384(3)*	1.218(3)/1.223(3)	1.377(3)/1.371(3)

The values with asterisks indicate that both bonds in this molecule have the same length.

Table 3: Crystal structure data for compounds **13**, **16** and **18**.

	13	**16**	**18**
Empirical formula	$C_{13}H_{22}N_2OSi$	$C_{16}H_{20}N_2OSi$	$C_{22}H_{32}N_4O_2Si$
M_r	250.41	284.43	412.60
T, K	200(2)	90(2)	93(2)
Crystal size, mm³	0.45×0.37×0.10	0.60×0.11×0.07	0.08×0.20×0.32
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	15.3500(5)	15.3708(13)	9.5545(2)
b, Å	10.1615(3)	10.4026(9)	10.0260(2)
c, Å	9.9036(3)	10.0438(9)	13.1263(3)
α, deg	90	90	67.876(1)
β, deg	96.161(1)	97.475(4)	78.265(1)
γ, deg	90	90	78.981(1)
V, Å³	1535.83(8)	1592.3(2)	1131.36(4)
Z	4	4	2
$D_{calcd.}$, g cm⁻³	1.08	1.19	1.21
$\mu(MoK_\alpha)$, mm⁻¹	0.1	0.1	0.1
$F(000)$, e	544	608	444
hkl range	$-18 \le h \le +18$	$-17 \le h \le +19$	$-15 \le h \le +15$
	$-12 \le k \le +9$	$-13 \le k \le +12$	$-16 \le k \le +16$
	$-12 \le l \le +11$	$-12 \le l \le +11$	$-20 \le l \le +21$
$((\sin\theta)/\lambda)_{max}$, Å⁻¹	0.62	0.64	0.81
θ_{max}, deg/% completeness	26/100	27/99.9	35/99.8
Refl. measured	12 661	13 371	48 916
Refl. unique/R_{int}	3027/0.0218	3478/0.0568	9946/0.0337
Param. refined	181	188	290
$R(F)/wR(F^2)$[a,b] ($I > 2\sigma(I)$)	0.0384/0.0982	0.0406/0.0926	0.0415/0.1141
$R(F)/wR(F^2)$[a,b] (all refls.)	0.0576/0.1054	0.0735/0.1013	0.0595/0.1209
GoF (F^2)[c]	1.040	1.054	1.056
$\Delta\rho_{fin}$ (max/min), e Å⁻³	0.25/−0.21	0.35/−0.28	0.58/−0.28

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; [c] GoF $= S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Table 4: Crystal structure data for compounds **22**, **23** and **24**.

	22	**23**	**24**
Empirical formula	$C_{24}H_{36}N_4O_2Si$	$C_{24}H_{36}N_4O_2Si$	$C_{28}H_{28}N_4O_2Si$
M_r	440.66	440.66	480.63
T, K	153(2)	160(2)	203(2)
Crystal size, mm³	0.45×0.42×0.40	0.50×0.40×0.12	0.40×0.40×0.30
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$C2/c$	$P\bar{1}$	$P2_12_12_1$
a, Å	27.4953(14)	9.6863(2)	9.9776(4)
b, Å	10.0196(5)	10.6711(2)	10.5468(5)
c, Å	19.2232(10)	12.8127(3)	24.3988(14)
α, deg	90	72.570(1)	90
β, deg	105.809(4)	80.854(1)	90
γ, deg	90	80.918(1)	90
V, Å³	5095.5(5)	1238.92(5)	2567.5(2)
Z	8	2	4
$D_{calcd.}$, g cm⁻³	1.15	1.18	1.24
$\mu(MoK_\alpha)$, mm⁻¹	0.1	0.1	0.1
$F(000)$, e	1904	476	1016
hkl range	$-34 \le h \le +34$	$-13 \le h \le +13$	$-12 \le h \le +12$
	$-12 \le k \le +12$	$-14 \le k \le +15$	$-13 \le k \le +12$
	$-24 \le l \le +24$	$-18 \le l \le +17$	$-30 \le l \le +28$
$((\sin\theta)/\lambda)_{max}$, Å⁻¹	0.60	0.70	0.60
θ_{max}, deg/% completeness	25/99.9	30/99.0	25/96.7
Refl. measured	35 511	19 845	13 831
Refl. unique	5467	7147	5319
R_{int}	0.0748	0.0213	0.0286
Param. refined	297	286	326
$R(F)/wR(F^2)$[a,b] ($I > 2\sigma(I)$)	0.0464/0.1072	0.0391/0.1020	0.0356/0.0809
$R(F)/wR(F^2)$[a,b] (all refls.)	0.0597/0.1199	0.0515/0.1071	0.0445/0.0867
Abs. structure param. x (Flack)	–	–	−0.05(6)
GoF (F^2)[c]	1.091	1.040	1.087
$\Delta\rho_{fin}$ (max/min), e Å⁻³	0.24/−0.38	0.40/−0.22	0.20/−0.18

[a,b,c]See definitions given in Table 3.

on the Si–N bond lengths in the herein studied compounds. The N–C(=O) bonds are systematically longer for the Ph,Si substituted N atom (range 1.379(2)–1.406(1) Å), whereas the N–C(=O) bonds to the R,R′ substituted N atom are noticeably shorter (range 1.348(2)–1.377(3) Å). The C=O bonds, although involved in long range coordination with different Si atoms ($SiMe_3$ and $SiMe_2$ groups, *trans* to Si–C and Si–N bonds), cover a very narrow range (1.218(3)–1.239(2) Å).

3 Conclusions

Insertion reactions of phenyl isocyanate into the silicon-nitrogen bonds of different aminosilanes were carried out. Different kinds of amines were used to synthesize aminosilanes, with ethyl-, *n*-propyl-, *n*-octyl-, *n*-dodecyl-, allyl-, *sec*-butyl- and *tert*-butylamine representing primary amines, diethylamine as an acyclic secondary amine, and aniline as an aromatic amine. The following types of aminosilanes were synthesized: $Me_nSi(NRR')_{4-n}$, with $n = 2$–3. Single-crystal X-ray diffraction analyses of the insertion products reveal the formal insertion of phenyl isocyanate into the silicon-nitrogen bonds of Me_3SiNRR' and $Me_2Si(NRR')_2$ (i.e. formation of a silicon-nitrogen bond). In all cases it is shown that there is a longer Si–C bond of the methyl group *trans*-disposed to a carbonyl oxygen atom.

4 Experimental section

4.1 General methods and reagents

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen by

using standard Schlenk or glovebox techniques (MBraun UNILab glovebox maintained at less than 0.1 ppm O_2 and less than 0.1 ppm H_2O) unless otherwise specified.

Chlorotrimethylsilane (Me_3SiCl; Sigma Aldrich, ≥99%), dichlorodimethylsilane (Me_2SiCl_2; Sigma Aldrich, ≥99.5%) were used as received. Triethylamine (Et_3N, Sigma Aldrich, ≥99%) was distilled from sodium/benzophenone. *n*-Propylamine ($C_3H_7NH_2$, Sigma Aldrich, ≥99%), *n*-octylamine ($C_8H_{17}NH_2$, Fluka, 98%), allylamine ($C_3H_5NH_2$, Sigma-Aldrich, 99%), *sec*-butylamine ($C_4H_9NH_2$, Sigma-Aldrich, 98%), *tert*-butylamine ($C_4H_9NH_2$, Sigma-Aldrich, 98%), diethylamine (Et_2NH, Sigma Aldrich, ≥99.5%) and deuterated chloroform ($CDCl_3$, ARMAR Chemicals, 99.8 atom%D) were freshly distilled from CaH_2. After the distillation of $CDCl_3$, 0.03% tetramethylsilane (Me_4Si, ABCR, 99.9%) was added. The aniline used was distilled three times, first from $SnCl_2 \cdot H_2O$, the second time over KOH and finally from CaH_2. Phenylisocyanate (C_5H_7NO, ACROS, ≥99%) was freshly distilled over P_4O_{10}. *n*-Pentane (C_5H_{12}, technical grade) was dried by passing the solvent through a molecular sieve column (3 Å, Sigma Aldrich). *n*-Hexane (C_6H_{14}, Overlack, technical grade) and diethyl ether ($C_4H_{10}O$, technical grade) were dried by a technical solvent dryer (MBraun SPS 800). Ethylamine ($C_2H_5NH_2$, Fluka, for Synthesis) and *n*-dodecylamine ($C_{12}H_{25}NH_2$, Sigma-Aldrich, 98%) were used as received.

General procedure for the synthesis of aminosilanes **1–12**

A) Four equivalents of low-boiling amines or two equivalents of high boiling amines and two equivalents of triethylamine were disolved in *n*-pentane and cooled to 273 K in an ice bath. Chlorotrimethylsilane (two equivalents) or dichlorodimethylsilane (one equivalent) was added dropwise with stirring. The mixture was allowed to attain room temperature and stirring was continued overnight. The hydrochloride residue was filtered off and washed with *n*-pentane. From the filtrate and washings volatiles were removed *in vacuo*.

B) Chlorotrimethylsilane or dichlorodimethylsilane was dissolved in a flask with dry diethyl ether at 195 K. With stirring the corresponding amine was added dropwise in large excess. The mixture was allowed to attain room temperature and stirring was continued overnight. Thereafter the volatiles were removed *in vacuo*, *n*-hexane was added to extract the product, and the hydrochloride precipitate was filtered off and washed with *n*-hexane. From the filtrate the *n*-hexane was removed *in vacuo*.

For the assignment of the signals in the NMR spectra the following labels were used (as shown in Fig. 8). For the phenyl ring of the isocyanate function the carbon atoms are indicated with *o* for *ortho*, *m* for *meta*, *p* for *para* and *i* for *ipso*.

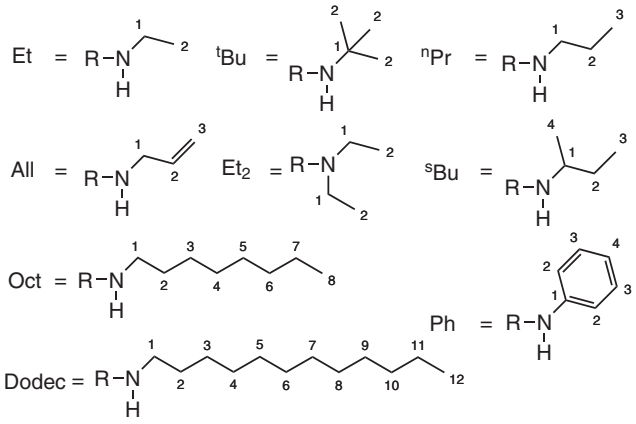


Fig. 8: Numbering of the amino residues.

Trimethyl(*n*-propylamino)silane 1: Was prepared by the general procedure **A**. Using 10.02 g (92.2 mmol) of trimethylchlorosilane and 10.90 g (184.4 mmol) of *n*-propylamine in 100 mL *n*-pentane (2×20 mL for washing after hydrochloride filtering) yielded a colorless liquid, 6.90 g (57%). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 0.00$ (9H, Me_3Si, s); 0.48 (1H, N–H, s(broad)); 0.85 (3H, H-3, q, $^3J_{H-H} = 7.3$ Hz); 1.37 (2H, H-2, sext, $^3J_{H-H} = 7.3$ Hz); 2.64 (2H, H-1, t, $^3J_{H-H} = 10.0$ Hz) ppm. – $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta = 0.1$ (Me_3Si); 11.4 (C-3); 27.9 (C-2); 44.1 (C-1) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): $\delta = 3.3$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3415$ (vw, ν N–H); 2961, 2949, 2933, 2916, 2864, 2841 (s, ν C–H); 1444 (w, δ Si CH_3); 1410 (w); 1403 (w); 1351 (vw); 1327 (vw); 1262 (m); 1141 (vw); 1128 (vw); 1106 (vw); 1060 (vw); 1011 (vw); 962 (vw); 941 (vw); 810 (vw); 802 (vw); 791 (vw); 728 (vw); 642 (vw); 113 (m) cm^{-1}. – Elemental analysis for $C_6H_{17}NSi$: Calcd. C 54.9, H 13.1, N 10.7; found C 55.4, H 13.4, N 11.2%.

(*sec*-Butylamino)trimethylsilane 2: Was prepared by the general procedure **A**. Using 5.00 g (46.0 mmol) of trimethylchlorosilane and 6.73 g (92.0 mmol) of *sec*-butylamine in 50 mL *n*-pentane (2×10 mL for washing after hydrochloride filtering) yielded a colorless liquid, 1.20 g (19%). B. p.: 125°C. – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = -0.06$ (9H, Me_3Si, s); 0.31 (1H, NH, s(broad)); 0.84 (3H, H-3, t, $^3J_{H-H} = 10.0$ Hz); 0.99 (3H, H-4, d, $^3J_{H-H} = 10.0$ Hz); 1.29 (2H, H-2, quint, $^3J_{H-H} = 10.0$ Hz); 2.74 (1H, H-1, t, $^3J_{H-H} = 10.0$ Hz) ppm. – $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta = -0.1$ (Me_3Si); 10.6 (C-3); 25.2 (C-4), 34.6 (C-2), 48.2 (C-1) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): $\delta = 1.1$ ppm.

– Raman (298 K, neat in glass capillary): ν = 3417 (vw, ν N–H); 2962, 2945, 2932, 2918, 2865, 2848 (s, ν C–H); 1445 (w, δ Si CH_3); 1412 (w); 1407 (w); 1355 (vw); 1323 (vw); 1265 (m); 1145 (vw); 1123 (vw); 1101 (vw); 1056 (vw); 1018 (vw); 965 (vw); 945 (vw); 815 (vw); 810 (vw); 798 (vw); 724 (vw); 645 (vw); 118 (m) cm^{-1}. – Elemental analysis for $C_7H_{19}NSi$: Calcd. C 57.9, H 13.2, N 9.6; found C 56.8, H 12.9, N 9.2%.

(Diethylamino)trimethylsilane 3: Was prepared by the general procedure **A**. Using 20.00 g (184 mmol) of trimethylchlorosilane and 26.90 g (368.0 mmol) of diethylamine in 250 mL *n*-pentane (2×40 mL for washing after hydrochloride filtering) yielded a colorless liquid, 17.2 g (64%). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 0.00 (9H, Me_3Si, s); 0.93 (6H, H-2, t, $^3J_{H–H}$ = 7.0 Hz); 2.6 (4H, H-1, q, $^3J_{H–H}$ = 7.0 Hz) ppm. – $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 298 K): δ = 0.1 (Me_3Si); 16.1 (C-2); 40.3 (C-1) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): δ = 4.0 ppm. – Raman spectroscopic data are published in literature [53].

Anilinotrimethylsilane 4: Was prepared by the general procedure **A**. Using 5.00 g (46.0 mmol) of trimethylchlorosilane and 8.60 g (92.0 mmol) of aniline in 100 mL *n*-pentane (2×20 mL for washing after hydrochloride filtering) yielded a colorless liquid, 6.60 g (87%). – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.58 (9H, Me_3Si, s); 3.67 (1H, N–H, s(broad)); 7.47–6.93 (5H, Ar-H, m) ppm. – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = 0.1 (Me_3Si); 116.1 (C-2); 117.5 (C-4); 129.3 (C-3); 147.4 (C-1) ppm. – ^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): δ = 2.7 ppm. – Raman spectroscopic data are published in literature [54].

Di(ethylamino)dimethylsilane 5: Was prepared by the general procedure **A**. DOI: 10.1021/om300313f [27].

Dimethyldi(*n*-propylamino)silane 6: Was prepared by the general procedure **A**. DOI: 10.1021/om300313f [27].

Dimethyldi(*n*-octylamino)silane 7: Was prepared by the general procedure **A**. DOI: 10.1021/om300313f [27].

Dimethyldi(*n*-dodecylamino)silane 8: Was prepared by the general procedure **A**. DOI: 10.1021/om300313f [27].

Dimethyldi(allylamino)silane 9: Was prepared by the general procedure **B**. Using 5.00 g (38.7 mmol) of dimethyldichlorosilane and 33.2 g (581 mmol) of allylamine in 150 mL diethyl ether. The extraction with 50 mL *n*-hexane yielded a colorless liquid, 4.10 g (62%). B. p.: 169°C. – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.02 (6H, Me_2Si, s); 0.66 (2H, N–H, s(broad)); 3.35 (4H, H-1, ddd, $^4J_{HB–H-1}$ = 1.6 Hz, $^4J_{HA–H-1}$ = 1.7 Hz, $^3J_{H-2–H-1}$ = 5.2 Hz); 4.94 (2H, H_B, ddt, $^4J_{HB–H-1}$ = 1.6 Hz, $^2J_{HA–HB}$ = 1.9 Hz, $^3J_{H-2–HB(cis)}$ = 10.1 Hz); 5.10 (2H, H_A, ddt, $^4J_{HA–H-1}$ = 1.7 Hz, $^2J_{HA–HB}$ = 1.9 Hz, $^3J_{H-2–HA(trans)}$ = 17.1 Hz); 5.88 (2H, H-2, ddt, $^3J_{H-2–H-1}$ = 5.2 Hz, $^3J_{H-2–H–B(cis)}$ = 10.1 Hz, $^3J_{H-2–HA(trans)}$ = 17.1 Hz). – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = –1.5 (Me_2Si); 45.3 (C-1); 113.9 (C-3); 142.5 (C-2) ppm. – ^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): δ = –6.9 ppm. – Raman (298 K, neat in glass capillary): ν = 3424 (vw, ν N–H); 3080 (s, ν C–H unsat.); 3006 (vs); 2980, 2957, 2900, 2850, 2826 (vs, ν C–H); 1640 (s); 1444 (w, δ Si–CH_3); 1418 (w); 1401 (w); 1288 (m); 1226 (vw); 1101 (vw); 1026 (vw); 994 (vw); 951 (vw); 914 (vw); 891 (vw), 839 (vw); 784 (vw); 683 (vw); 651 (w); 601 (w); 548 (vw); 402 (vw); 364 (vw); 219 (w); 191 (w); 125 (m) cm^{-1}. – Elemental analysis for $C_8H_{18}N_2Si$: Calcd. C 56.4, H 10.7, N 16.5; found C 55.9, H 9.5, N 15.8%.

Dimethyldi(*tert*-butylamino)silane 10: Was prepared by the general procedure **B**. Using 5.00 g (38.7 mmol) of dimethyldichlorosilane and 11.33 g (155 mmol) of *tert*-butylamine in 100 mL diethyl ether. The extraction with 50 mL *n*-hexane yielded a colorless liquid, 4.75 g (61%). B. p.: 245°C. – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 0.04 (6H, Me_2Si, s); 0.72 (2H, NH, s(broad)); 1.38 (18H, H-2, s) ppm. – $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 298 K): δ = –0.5 (Me_2Si); 34.4 (C-2); 51.4 (C-1) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): δ = –16.7 ppm. – Raman (298 K, neat in glass capillary): ν = 3389 (vw, ν N–H); 2960, 2932, 2904, 2704 (s, ν C–H); 1464 (w); 1446 (w, δ Si–CH_3); 1216 (vw); 1195 (vw); 1027 (m); 904 (vw); 795 (vw); 680 (vw); 638 (vw); 623 (vw); 499 (vw); 395 (vw); 368 (vw); 328 (vw); 227 (vw); 182 (vw); 133 (vw) cm^{-1}. – Elemental analysis for $C_{10}H_{26}N_2Si$: Calcd. C 59.3, H 12.9, N 13.8; found C 58.9, H 12.0, N 12.9%.

Bis(diethylamino)dimethylsilane 11: Was prepared by the general procedure **A**. DOI: 10.1021/om300313f [27].

Dianilinodimethylsilane 12: Was prepared by the general procedure **A**. Using 5.00 g (38.7 mmol) of dimethyldichlorosilane and 14.4 g (155 mmol) of aniline in 150 mL *n*-pentane (2×30 mL for washing after hydrochloride filtering) yielded a colorless solid, 7.10 g (55%). Standing at room temperature in *n*-hexane for several days afforded colorless crystals suitable for single-crystal X-ray diffraction. They were identified as $C_{14}H_{18}N_2Si$ (CCDC 1568242, Figure S1 in Supporting Information), in the same mixture there were other crystals suitable for X-ray diffraction, which were identified as the aniline solvate $C_{14}H_{18}N_2Si \cdot C_6H_7N$ (CCDC 1568240, Figure S2 in Supporting Information). – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.11 (6H, Me_2Si, s); 4.32 (2H, N–H, s); 7.86–7.55 (10H, Ar-H, m) ppm. – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = –0.16 (Me_2Si); 116.5 (C-2);

118.1 (C-4); 129.1 (C-3); 146.1 (C-1) ppm. – ^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = 10.4$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3374$ (vw, ν N–H); 3163, 3077, 3055, 3011 (s, ν C–H unsat.); 2965 (w), 2903 (s, ν C–H); 1601 (m, δ C=C); 1499 (vw); 1476 (vw); 1389 (vw); 1324 (vw); 1287 (w); 1262 (vw); 1239 (vw); 1179 (w); 1154 (w); 1077 (vw); 1033 (w); 998 (vs, $\delta_{inplane}$ C–H); 973 (vw); 957 (vw); 909 (vw); 886 (w); 834 (vw); 770 (vw); 749 (vw); 722 (vw); 695 (vw); 662 (w); 614 (w); 516 (vw); 489 (vw); 413 (vw); 388 (w); 304 (vw); 269 (w); 251 (vw); 234 (vw); 203 (w); 182 (w); 105 (vs) cm^{-1}.

General procedure for the synthesis of ureaylsilanes **13–24**

C) To a solution of the aminosilane in *n*-pentane, stirred at 273 K, the appropriate amount of phenylisocyanate was added dropwise through a syringe. The solution was stirred overnight at room temperature. Thereafter, volatiles were removed *in vacuo*.

D) To a solution of the aminosilane in chloroform, stirred at 195 K, the appropriate amount of phenylisocyanate was added dropwise through a syringe. The solution was stirred overnight at room temperature. Thereafter, volatiles were removed *in vacuo*.

Trimethyl-(1-phenyl-3-*n*-propylureayl)silane 13: Was prepared by the general procedure **D**. Using 1.00 g (4.6 mmol) of trimethyl(*n*-propylamino)silane **1** and 1.64 g (13.8 mmol) of phenyl isocyanate in 5 mL chloroform yielded a colorless solid, 1.70 g (89%). Standing at room temperature in *n*-pentane for several days yielded colorless crystals suitable for single-crystal X-ray diffraction. They were identified as $C_{13}H_{22}N_2OSi$ (CCDC 1568237). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 0.33$ (9H, Me_3Si, s); 0.94 (3H, H-3, q, $^3J_{H-H} = 7.3$ Hz); 1.53 (2H, H-2, sext, $^3J_{H-H} = 7.3$ Hz); 3.18 (2H, H-1, t, $^3J_{H-H} = 10.0$ Hz); 4.76 (1H, N-H, s(broad)); 7.27–7.58 (5H, Ar-H, m) ppm. – ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta = 0.4$ (Me_3Si); 11.1 (C-3); 22.5 (C-2); 41.9 (C-1); 127.1 (C-*o*); 129.4 (C-*m*); 129.6 (C-*p*); 141.1 (C-*i*); 159.6 (C=O) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): $\delta = 8.2$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3321$ (vw, ν N–H); 3189, 3072, 3068 (s, ν C–H unsat.); 2971, 2953, 2925, 2909 (s, ν C–H); 1642 (w); 1634 (m); 1596 (s); 1508 (s); 1446 (w, δ Si–CH_3); 1442 (w); 1440 (w); 1413 (w); 1353 (vw); 1251 (m); 1179 (vw); 1152 (vw); 1107 (vw); 1034 (vw); 1024 (s); 971 (vw); 966 (vw); 858 (vw); 810 (vw); 776 (vw); 731 (m); 698 (vw); 674 (vw); 668 (w); 622 (m); 511 (vw); 487 (vw); 452 (vw); 385 (vw); 368 (m); 282(vw); 266 (vw); 252 (vw); 211 (vw); 145 (vw); 110 (s) cm^{-1}.

(1-Phenyl-3-*sec*-butylureayl)trimethylsilane 14: Was prepared by the general procedure **D**. Used 0.30 g (2.1 mmol) of trimethyl(*sec*-butylamino)silane **2** and 0.25 g (2.1 mmol) of phenyl isocyanate in 5 mL chloroform yielded a colorless solid, 0.50 g (93%). – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 0.24$ (9H, Me_3Si, s); 0.88 (3H, H-3, t, $^3J_{H-H} = 8.0$Hz); 0.92 (3H, H-4, d, $^3J_{H-H} = 8.0$ Hz); 1.28 (2H, H-2, quint., $^3J_{H-H} = 8.0$ Hz); 3.42 (1H, H-1, sext., $^3J_{H-H} = 8.0$ Hz); 6.04 (1H, NH, s(broad)); 7.00–7.26 (5H, Ar-H, m) ppm. – ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = 0.4$ (Me_3Si); 14.1 (C-3); 22.6 (C-4); 34.4 (C-2); 53.2 (C-1); 124.8 (C-*o*); 125.8 (C-*m*); 129.6 (C-*p*); 133.8 (C-*i*); 157.1 (C=O) ppm. – ^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = 10.1$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3325$ (vw, ν N–H); 3181, 3075, 3063 (s, ν C–H unsat.); 2977, 2955, 2929, 2907 (s, ν C–H); 1648 (w); 1636 (m); 1594 (s); 1502 (s); 1450 (w, δ Si–CH_3); 1443 (w); 1441 (w); 1415 (w); 1357 (vw); 1259 (m); 1177 (vw); 1154 (vw); 1111 (vw); 1035 (vw); 1028 (s); 972 (vw); 969 (vw); 856 (vw); 813 (vw); 770 (vw); 733 (m); 696 (vw); 679 (vw); 662 (w); 625 (m); 518 (vw); 481 (vw); 454 (vw); 387 (vw); 360 (m); 286 (vw); 262 (vw); 258 (vw); 214 (vw); 160 (vw); 112 (s) cm^{-1}.

Trimethyl-(1-phenyl-3,3′-diethylureayl)silane 15: Was prepared by the general procedure **C**. DOI: 10.1002/ejic.200900784 [49].

Trimethyl-1,3-diphenylureaylsilane 16: Was prepared by the general procedure **C**. Using 1.00 g (6.1 mmol) of anilinotrimethylsilane **4** and 0.70 g (6.1 mmol) of phenyl isocyanate in 10 mL *n*-pentane yielded a colorless solid, 0.95 g (56%). Standing at room temperature in *n*-pentane for several days yielded colorless crystals suitable for single-crystal X-ray diffraction, which were identified as $C_{16}H_{20}N_2OSi$ (CCDC 1568241). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = -0.01$ (9H, $SiMe_3$, s); 3.17 (1H, N–H, s(broad)); 6.39–7.17 (10H, Ar-H, m) ppm. – ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta = 0.5$ ($SiMe_3$); 115.6; 119.0; 122.7; 128.4; 129.1; 129.7; 140.2; 147.0 (Ar-C); 156.6 (C=O) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): $\delta = 10.3$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3192$ (vw, ν N–H); 3123, 3079, 3063, 3052 (s, ν C–H unsat.); 2984 (w, ν C–H); 1700 (vw); 1646 (m); 1599 (vs); 1549 (vw); 1538 (vw); 1522 (vw); 1499 (vw); 1449 (w, δ Si–CH_3); 1308 (w); 1270 (w); 1249 (vw); 1235 (vw); 1175 (w); 1156 (w); 1135 (vw); 1112 (vw); 1087 (vw); 1052 (w); 1027 (w); 998 (s); 979 (vw); 965 (vw); 913 (w); 894 (w); 834 (vw); 791 (vw); 763 (w); 749 (vw); 701 (vw); 666 (vw); 641 (vw); 616 (w); 556 (vw); 529 (vw); 500 (vw); 413 (w); 385 (vw); 294 (w); 246 (vw); 176 (w); 118 (s); 101 (s) cm^{-1}.

Dimethyldi(1-phenyl-3-ethylureayl)silane 17: Was prepared by the general procedure **D**. Using 0.60 g (4.1 mmol) of di(ethylamino)dimethylsilane **5** and 0.98 g (8.2 mmol)

of phenyl isocyanate in 10 mL chloroform yielded a colorless solid, 0.88 g (56%). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = -0.01$ (6H, Me_2Si, s); 1.14 (6H, H-2, t, $^3J_{H-H} = 8.0$ Hz); 3.20 (4H, H-1, q, $^3J_{H-H} = 8.0$ Hz); 5.05 (2H, NH, s(broad)); 7.06–7.36 (10H, Ar-H, m) ppm. – ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta = 0.2$ (Me_2Si); 15.6 (C-2); 35.4 (C-1); 127.5 (C-*o*); 129.6 (C-*m*); 129.9 (C-*p*); 140.8 (C-*i*); 159.7 (C=O) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): $\delta = -3.9$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3345$ (vw, ν N–H); 3182, 3072, 3060, 3000 (s, ν C–H unsat.); 2978, 2958, 2929, 2903 (s, ν C–H); 1649 (w); 1634 (m); 1591 (s); 1501 (s); 1480 (w); 1454 (w, δ Si–CH_3); 1440 (w); 1405 (w); 1359 (vw); 1311 (vw); 1254 (m); 1171 (vw); 1159 (vw); 1101 (vw); 1078 (vw); 1026 (vw); 1005 (s); 972 (vw); 966 (vw); 887 (vw); 845 (vw); 812 (vw); 768 (vw); 738 (m); 697 (vw); 673 (vw); 662 (w); 620 (m); 536 (vw); 520 (vw); 480 (vw); 448 (vw); 380 (vw); 364 (m); 336 (vw); 286 (vw); 265 (vw); 257 (vw); 236 (vw); 215 (vw); 198 (vw); 172 (vw); 112 (s) cm^{-1}.

Dimethyldi(1-phenyl-3-*n*-propylureayl)silane 18: Was prepared by the general procedure **D**. Using 5.00 g (28.7 mmol) of di(*n*-propylamino)dimethylsilane **6** and 6.80 g (57.4 mmol) of phenyl isocyanate in 10 mL chloroform yielded a colorless solid, 7.90 g (68%). Standing at room temperature in chloroform for several days yielded colorless crystals suitable for single-crystal X-ray diffraction, which were identified as $C_{22}H_{32}N_4O_2Si$ (CCDC 1568236), also we obtained suitable crystals of the hydrolysis product the *N*-propyl-*N*-phenylurea (Figure S3 in Supporting Information), which were identified as $C_{10}H_{14}N_2O$ (CCDC 1568238). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 0.28$ (6H, Me_2Si, s); 0.77 (6H, H-3, t, $^3J_{H-H} = 8.0$ Hz); 1.35 (6H, H-2, t, $^3J_{H-H} = 8.0$ Hz); 3.07 (4H, H-1, q, $^3J_{H-H} = 8.0$ Hz); 4.15 (2H, NH, s(broad)); 7.18–7.38 (10H, Ar-H, m) ppm. – ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta = 0.8$ (Me_2Si); 11.4 (C-3); 23.7 (C-2); 42.1 (C-1); 127.3 (C-*o*); 129.5 (C-*m*); 130.2 (C-*p*); 140.8 (C-*i*); 159.5 (C=O) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): $\delta = -3.9$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3349$ (vw, ν N–H); 3178, 3072, 3064, 3025 (s, ν C–H unsat.); 2972, 2951, 2928, 2909 (s, ν C–H); 1641 (w); 1634 (m); 1592 (s); 1507 (s); 1481 (w); 1447 (w); 1442 (w, δ Si–CH_3); 1416 (w); 1348 (vw); 1327 (vw); 1254 (m); 1176 (vw); 1154 (vw); 1112 (vw); 1074 (vw); 1026 (vw); 1023 (s); 972 (vw); 965 (vw); 887 (vw); 846 (vw); 813 (vw); 764 (vw); 733 (m); 696 (vw); 673 (vw); 663 (w); 629 (m); 527 (vw); 526 (vw); 483 (vw); 456 (vw); 383 (vw); 354 (m); 348 (vw); 274 (vw); 268 (vw); 251 (vw); 243 (vw); 212 (vw); 172 (vw); 154 (vw); 102 (s) cm^{-1}.

Dimethyldi(1-phenyl-3-*n*-octylureayl)silane 19: Was prepared by the general procedure **D**. DOI: 10.1016/B978-0-12-420221-4.00004-4 [30].

Dimethyldi(1-phenyl-3-*n*-dodecylureayl)silane 20: Was prepared by the general procedure **D**. Using 1.00 g (2.3 mmol) of di(*n*-dodecylamino)dimethylsilane **8** and 0.56 g (4.7 mmol) of phenyl isocyanate in 20 mL chloroform yielded a colorless solid, 1.11 g (71%). – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = -0.01$ (6H, Me_2Si, s); 0.88 (6H, H-12, t, $^3J_{H-H} = 8.0$ Hz); 1.25 (40H, H-2 to H-11, m); 3.01 (4H, H-1, t, $^3J_{H-H} = 8.0$ Hz); 4.91 (2H, NH, s(broad)); 7.07–7.35 (10H, Ar-H, m) ppm. – ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = 0.2$ (Me_2Si); 14.3 (C-12); 22.8 (C-11); 26.9 (C-3); 29.4–30.2 (C-4 to C-9); 30.3 (C-2); 32.1 (C-10); 40.6 (C-1); 127.5 (C-*o*); 129.4 (C-*m*); 129.6 (C-*p*); 140.5 (C-*i*); 159.7 (C=O) ppm. – ^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = -4.0$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3352$ (vw, ν N–H); 3180, 3079, 3068, 3027 (s, ν C–H unsat.); 2976, 2955, 2924, 2907 (s, ν C–H); 1644 (w); 1631 (m); 1598 (s); 1505 (s); 1482 (w); 1449 (w); 1446 (w, δ Si–CH_3); 1413 (w); 1350 (vw); 1323 (vw); 1256 (m); 1179 (vw); 1152 (vw); 1115 (vw); 1078 (vw); 1021 (vw); 1024 (s); 977 (vw); 960 (vw); 881 (vw); 843 (vw); 815 (vw); 767 (vw); 739 (m); 692 (vw); 674 (vw); 666 (w); 628 (m); 530 (vw); 524 (vw); 488 (vw); 452 (vw); 386 (vw); 360 (m); 335 (vw); 280 (vw); 266 (vw); 252 (vw); 238 (vw); 214 (vw); 190 (vw); 177 (vw); 104 (s) cm^{-1}.

Dimethyldi(1-phenyl-3-allylureayl)silane 21: Was prepared by the general procedure **D**. Using 0.50 g (2.9 mmol) of di(allylamino)dimethylsilane **9** and 0.70 g (5.9 mmol) of phenyl isocyanate in 5 mL chloroform yielded a colorless solid, 1.10 g (94%). – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 0.33$ (6H, Me_2Si, s); 3.75 (4H, H-1, ddd, $^4J_{HB-H-1} = 1.4$ Hz, $^4J_{HA-H-1} = 1.5$ Hz, $^3J_{H-2-H-1} = 5.5$ Hz); 3.90 (2H, NH, s(broad)); 4.96 (2H, HB, ddt, $^4J_{HB-H-1} = 1.4$ Hz, $^2J_{HA-HB} = 1.7$ Hz, $^3J_{H-2-HB(cis)} = 10.5$ Hz); 4.99 (2H, HA, ddt, $^4J_{HA-H-1} = 1.5$ Hz, $^2J_{HA-HB} = 1.7$ Hz, $^3J_{H-2-HA(trans)} = 17.2$ Hz); 5.71 (2H, H-2, ddt, $^3J_{H-2-H-1} = 5.5$ Hz, $^3J_{H-2-H-B(cis)} = 10.5$ Hz, $^3J_{H-2-HA(trans)} = 17.2$ Hz); 7.22–7.45 (10H, Ar-H, m) ppm. – ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = 0.57$ (Me_2Si); 42.5 (C-1); 114.8 (C-3); 135.2 (C-2); 127.5 (C-*o*); 129.5 (C-*m*); 130.2 (C-*p*); 140.5 (C-*i*); 159.2 (C=O) ppm. – ^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = -3.4$ ppm. – Raman (298 K, neat in glass capillary): $\nu = 3373$ (vw, ν N–H); 3181, 3073, 3065, 3027 (s, ν C–H unsat.); 2979, 2952, 2924, 2906 (s, ν C–H); 1648 (w); 1630 (m); 1593 (s); 1506 (s); 1489 (w); 1442 (w); 1445 (w, δ Si–CH_3); 1418 (w); 1351 (vw); 1324 (vw); 1257 (m); 1170 (vw); 1154 (vw); 1118 (vw); 1072 (vw); 1026 (vw); 1020 (s); 975 (vw); 960 (vw); 886 (vw); 842 (vw); 818 (vw); 764 (vw); 732 (m); 690 (vw); 677 (vw); 664 (w); 621 (m); 538 (vw); 525 (vw); 482 (vw); 459 (vw); 386 (vw); 363 (m); 330 (vw); 288 (vw); 266 (vw); 254 (vw); 232 (vw); 210 (vw); 199 (vw); 178 (vw); 107 (s) cm^{-1}.

Dimethyldi(1-phenyl-3-*tert*-butylureayl)silane 22: Was prepared by the general procedure **D**. Using 1.00 g

(4.9 mmol) of di(*tert*-butylamino)dimethylsilane **10** and 1.17 g (9.9 mmol) of phenyl isocyanate in 10 mL chloroform yielded a colorless solid, 2.00 g (92%). Standing at room temperature in chloroform for several days yielded colorless crystals suitable for single-crystal X-ray diffraction. They were identified as $C_{24}H_{36}N_4O_2Si$ (CCDC 1567264). We also obtained suitable crystals of the hydrolysis product the *N*-*tert*-butyl-*N*-phenylurea (Figure S4 in Supporting Information), which were identified as $C_{11}H_{16}N_2O$ (CCDC 1567265). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 0.37 (6H, Me_2Si, s); 1.17 (18H, H-2, s); 4.08 (2H, NH, s(broad)); 6.93–7.33 (20H, Ar-H, m) ppm. – $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 298 K): δ = 1.5 (Me_2Si); 29.3 (C-2); 50.6 (C-1); 119.9 (C-*o*); 127.2 (C-*m*); 129.5 (C-*p*); 141.3 (C-*i*); 158.9 (C=O) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): δ = –3.6 ppm. – Raman (298 K, neat in glass capillary): ν = 3391 (vw, ν N–H); 3188, 3076, 3064, 3022 (s, ν C–H unsat.); 2970, 2957, 2924, 2901 (s, ν C–H); 1648 (w); 1635 (m); 1592 (s); 1509 (s); 1456 (w); 1443 (w, δ Si–CH_3); 1440 (w); 1416 (w); 1352 (vw); 1328 (vw); 1254 (m); 1170 (vw); 1155 (vw); 1110 (vw); 1074 (vw); 1028 (vw); 1022 (s); 976 (vw); 960 (vw); 883 (vw); 846 (vw); 819 (vw); 762 (vw); 735 (m); 698 (vw); 671 (vw); 664 (w); 627 (m); 530 (vw); 522 (vw); 484 (vw); 456 (vw); 388 (vw); 360 (m); 331 (vw); 283 (vw); 265 (vw); 257 (vw); 239 (vw); 219 (vw); 172 (vw); 164 (vw); 114 (s) cm^{-1}.

Dimethyl-bis(1-phenyl-3,3′-diethylureayl)silane 23: Was prepared by the general procedure **C**. Using 5.00 g (24.7 mmol) of bis(diethylamino)dimethylsilane **11** and 5.90 g (49.4 mmol) of phenyl isocyanate in 10 mL *n*-pentane yielded a colorless solid, 7.36 g (68%). Standing at room temperature in *n*-pentane for several days yielded colorless crystals suitable for single-crystal X-ray diffraction. They were identified as $C_{24}H_{36}N_4O_2Si$ (CCDC 1568239). – ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 0.00 (6H, $SiMe_2$, s); 0.80 (12H, H-2, t, $^3J_{H-H}$ = 7.0 Hz); 3.08 (8H, H-1, q, $^3J_{H-H}$ = 7.0 Hz); 7.03–7.04 (10 H, Ar-H, m) ppm. – $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 298 K): δ = 0.8 ($SiMe_2$); 12.7 (C-2); 42.1 (C-1); 119.1; 124.4; 127.3; 128.8; 128.9; 144.3 (Ar-C); 161.0 (C=O) ppm. – ^{29}Si NMR (99.4 MHz, $CDCl_3$, 298 K): δ = –2.5 ppm. – Raman (298 K, neat in glass capillary): ν = 3325 (vw, ν N–H); 3061, 3007 (s, ν C–H unsat.); 2967, 2934, 2911, 2876 (s, ν C–H); 2726 (vw); 1613 (w); 1592 (m, Amid I); 1478 (w); 1453 (w, Amid II); 1441 (w, δ Si–CH_3); 1422 (vw); 1312 (vw); 1276 (w, Amid III); 1264 (w); 1245 (w); 1171 (w); 1156 (w); 1081 (w); 1054 (w); 1029 (w); 1004 (s, $\delta_{inplane}$ C–H); 971 (w); 959 (vw); 934 (w); 743 (vw); 712 (w); 699 (w); 668 (w, ν Si–C); 618 (w); 537 (vw); 516 (vw); 454 (vw); 404 (vw); 356 (vw); 331 (w); 304 (vw); 250 (w); 217 (w); 178 (w); 101 (vs) cm^{-1}.

Dimethyl-bis(1,3-diphenylureayl)silane 24: Was prepared by the general procedure **C**. Using 1.80 g (7.3 mmol) of dianilinodimethylsilane **12** and 1.80 g (14.7 mmol) of phenyl isocyanate in 10 mL *n*-pentane. The product always appears in an undefined mixture, therefore no yield and melting point are specified. Standing at room temperature in chloroform for several days yielded colorless crystals suitable for single-crystal X-ray diffraction, which were identified as $C_{28}H_{28}N_4O_2Si$ (CCDC 1569611). – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = –0.35 (6H, Me_2Si, s); 5.83 (1H, NH, s(broad)); 6.6–7.1 (10H, Ar-H, m) ppm. – $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ = –0.2 (Me_2Si); 119–130 (C-*o*, C-*m*, C-*p*); 138–140 (C-*i*); 157.1 (C=O) ppm. – ^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): δ = –1.8 ppm. – Raman (298 K, neat in glass capillary): ν = 3443 (vw, ν N–H); 3063 (s), 3052 (m), 3005 (s, ν C–H unsat.); 2984, 2963, 2903 (s, ν C–H); 1648 (w); 1599 (vs); 1522 (vw); 1499 (vw); 1308 (w); 1270 (w); 1235 (vw); 1175 (w); 1156 (w); 1087 (vw); 1052 (w); 1027 (w); 998 (s); 913 (w); 894 (w); 834 (vw); 763 (vw); 751 (vw); 662 (vw); 641 (vw); 618 (w); 500 (vw); 413 (w); 294 (vw); 246 (w); 213 (vw); 178 (w); 101 (vs) cm^{-1}.

4.2 Analytical methods

4.2.1 NMR spectroscopy

^{1}H, ^{13}C and ^{29}Si NMR spectra were acquired at 500.0, 125.8 and 99.4 MHz, respectively, with a Bruker AVIII 500 MHz NMR spectrometer and also at 400.0, 100.6, 79.5 MHz, respectively, with an AVANCE DPX 400 NMR spectrometer. ^{1}H, ^{13}C and ^{29}Si NMR shifts are reported relative to $Si(CH_3)_4$ (δ_H = 0 ppm, δ_C = 0 ppm, δ_{Si} = 0 ppm) and were referenced to residual solvent resonances ($CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm). All spectra were obtained at 298 K. Data were processed by using the Bruker TopSpin 3.1 program or Mestrelab Research Mestrenova 8.1.

4.2.2 Raman

The Raman measurements were done at a Raman Spectrometer RFS 100/S from Bruker Optik with a Nd/YAG-Laser and a NIR Germanium detector. The wavenumbers are reported in cm^{-1}. The intensity of the bands are divided as follows: vw (very weak), w (weak), m (medium), s (strong), vs (very strong).

4.2.3 Elemental analyses

The analyses were performed in tin capsules with a Vario Micro cube from Elementar.

4.2.4 Boiling and melting points

We have developed a fast method to determine the boiling point of small samples under inert atmosphere using standard Schlenk technique. A measurement only takes about 15 min and the sample volume should be 0.05–0.2 mL. Boiling points up to 300°C can be measured with our low cost glassware apparatus by recording the temperature during heating until the boiling equilibrium is reached [55].

4.2.5 X-ray structure determinations

Single-crystal X-ray diffraction data were collected by using either an Bruker Nonius X8 APEX2 CCD diffractometer or a STOE IPDS-2T image plate diffractometer equipped with a low-temperature device using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å).

Software for data collection: X-Area, cell refinement: X-Area and data reduction: X-Red [56]. Preliminary structure models were derived by Direct Methods [57, 58] and the structures were refined by full-matrix least-squares calculations based on F^2 for all reflections using Shelxl [59–61]. *N*-bound hydrogen atoms were localized from difference Fourier maps and were refined without restraints. All other hydrogen atoms were included in the models in calculated positions and were refined as constrained to the bonding atoms. All further details regarding crystallographic results are reported in the Supporting Information available online.

CCDC 1568242 (**12**), 1568240 (aniline solvate of **12**), 1568237 (**13**), 1568241 (**16**), 1568236 (**18**), 1568238 (*N*-propyl-*N*-phenylurea), 1567264 (**22**), 1567265 (*N*-*tert*-butyl-*N*-phenylurea), 1568239 (**23**) and 1569611 (**24**) 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.

5 Supporting Information

Further structure data of compound **24** and the additional crystal structures of compound **12**, the aniline solvate of **12**, the hydrolysis product of **18** and **22** are given as Supporting Information available online (DOI: 10.1515/znb-2017-0149).

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