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# New silatranes possessing urea functionality: Synthesis, characterization and their structural aspects

Jugal Kishore Puri [c,*], Raghubir Singh [c], Varinder Kaur Chahal [a], Raj Pal Sharma [c], Jörg Wagler [b], Edwin Kroke [b]

[a] *Department of Chemistry, G.H.G. Khalsa College, Gurusar Sadhar, India*
[b] *Institut für Anorganische Chemie, Technische Universität Bergakademie, Freiberg 09596, Germany*
[c] *Department of Chemistry, Panjab University, Chandigarh 160 014, India*

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## ABSTRACT

The present work aims at the synthesis of various novel silatranes bearing substituted urea functionality. Nucleophilic addition of various amines (morpholine, aniline, ethylenediamine and 3-aminopropyltriethoxysilane) to 3-isocyanatopropyltriethoxysilane resulted in the four triethoxysilanes; N-[3-(triethoxysilyl)propyl]morpholine-4-carboxylic acid amide (**1**), 1-[3-(triethoxysilyl)propyl]-3-phenylurea (**2**), 1,2-bis{*N*′-[3-(triethoxysilyl)propyl]ureido}-ethane (**3**) and N-[3-(triethoxysilyl)propyl]-N′-[3-(triethoxysilyl)propyl]urea (**4**), respectively. In the presence of a base the resulting silanes undergo transesterification reaction with triethanolamine, thus forming the corresponding silatranes, N-(3-silatranylpropyl)morpholine-4-carboxylic acid amide (**5**), 1-(3-silatranylpropyl)-3-phenylurea (**6**), 1,2-Bis[*N*′-(3-silatranylpropyl)ureido]-ethane (**7**) and N-(3-silatranylpropyl)-N′-(3-silatranylpropyl)urea (**8**), respectively. Among these are four novel compounds (**5**–**8**), which were characterized by elemental analysis, IR, multinuclear ($^{1}$H, $^{13}$C and $^{29}$Si) NMR and mass spectroscopy. Structures of compounds **5** and **6** were deduced by X-ray crystallography. Single crystal X-ray studies revealed distorted trigonal bipyramidal coordination about Si in **5** and **6** with Si–N bond distance of 2.121(1) Å and 2.189(2) Å, respectively.

## 1. Introduction

Research on substituted ureas is a continuously growing field in chemistry due to the importance of urea functional group in a wide range of biological compounds such as enzyme inhibitors [1] and pseudopeptides [2]. Substituted ureas are widely applied in chemical industry, especially pesticides [3] and pharmaceuticals [4]. During the past decade, a considerable amount of academic- and industrial-based research has been carried out with the aim of developing new trialkoxysilanes with substituted urea moiety. Such silanes have been used to prepare new xerogels [5], hybrid materials [6–12] and functionalized mesoporous silicas [13]. Some sol–gel procedures for preparing xerogels containing arch fixed urea functional groups in the surface layer have also been reported [14]. Urea functional groups are efficient in recovery and separation of rare-earth metal ions [15], in preparation of membranes [16] and wear-resistant protective coatings on the surface of lenses made of organic polymers [17]. Urea based ligands can act as anion receptors due to their potential to bind transition metal ions with simultaneous formation of hydrogen bonds with anions. These are good candidates for metal chelation because in these bitopical ligands, urea group can act as hydrogen bond donor and/or acceptor [18].

A large number of silatranes with different groups present at axial position are known. Apparently, crystal structures of silatranes having urea-functionalized substituents in the axial position have not been reported yet. In previous studies, it was shown that urea moieties could also act as mono- or bidentate ligands in the coordination sphere of silicon [19–21]. We have now shown that urea-functionalized triethoxysilanes can be transformed into silatranes despite the presence of this potential competitor.

In continuation of our work on hypervalent silicon chemistry [22,23], we have devoted our considerable attention to the use of 3-isocyanatopropyltriethoxysilane as a precursor for the synthesis of some new silatranes. Herein, we synthesized a series of substituted triethoxysilanes (**1**–**4**) by reacting 3-isocyanatopropyltriethoxysilane with different amines (morpholine, aniline, ethylenediamine and 3-aminopropyltriethoxysilane), respectively. These were further reacted with triethanolamine in the presence of different catalysts to form corresponding silatranes (**5**–**8**). All the compounds were

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* Corresponding author. Tel.: +91 9814522681.
*E-mail address:* prof_jkpuri@yahoo.com (J.K. Puri).

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analyzed by using elemental analysis, IR, NMR and Mass spectrometry. Furthermore, the molecular structures of **5** and **6** were deduced by using X-ray crystallography. A detailed description of fragmentation pattern of silatranes **5**–**8** is also provided.

## 2. Results and discussion

### 2.1. Synthesis

A typical procedure for the synthesis of substituted ureas involves treatment of alkyl isocyanates with primary or secondary amines in organic solvent [24]. In the presence of transition metal catalysts, selenium [25] or sulfur [26] compounds, symmetrical, unsymmetrical and even cyclo-ureas can be prepared by reacting primary amines or ammonia with carbon monoxide.

It is known that carbofunctional organosilicon isocyanates readily react with amines or diamines in a highly exothermic manner. Therefore, to prepare trifunctional silanes containing a urea functional group > NC(=O)N<, reaction of primary and secondary amines with 3-isocyanatopropyltriethoxysilane has been carried out. It is known that 3-isocyanatopropylsilanes are more reactive than isocyanatomethylsilanes.

Herein, a known N-(3-(triethoxysilyl)propyl)morpholine-4-carboxylic acid amide (**1**) [27] was prepared by a new method, whereas the other triethoxysilanes (**2**–**4**) were synthesized according to a method published earlier (Scheme 1). The method of preparation is found to be advantageous because of high yields of desired products as well as no need of further purification [28,29].

In the present work, silatranes (**6**–**8**) were synthesized by transesterification reaction of the corresponding triethoxysilane with triethanolamine in the presence of KOH. By contrast, silatrane **5** was obtained in the presence of sodium ethoxide catalyst, as this reaction was not successful in the presence of KOH (Scheme 2). Therefore, a strong base was used to obtain the product. Silanes **3** and **4** contain two triethoxysilyl groups; therefore, the corresponding silatranes (**7** and **8**) contain two silatranyl moieties, whereas, **5** and **6** contain one silatranyl moiety. All of these compounds are very stable in air and highly soluble in common organic solvents.

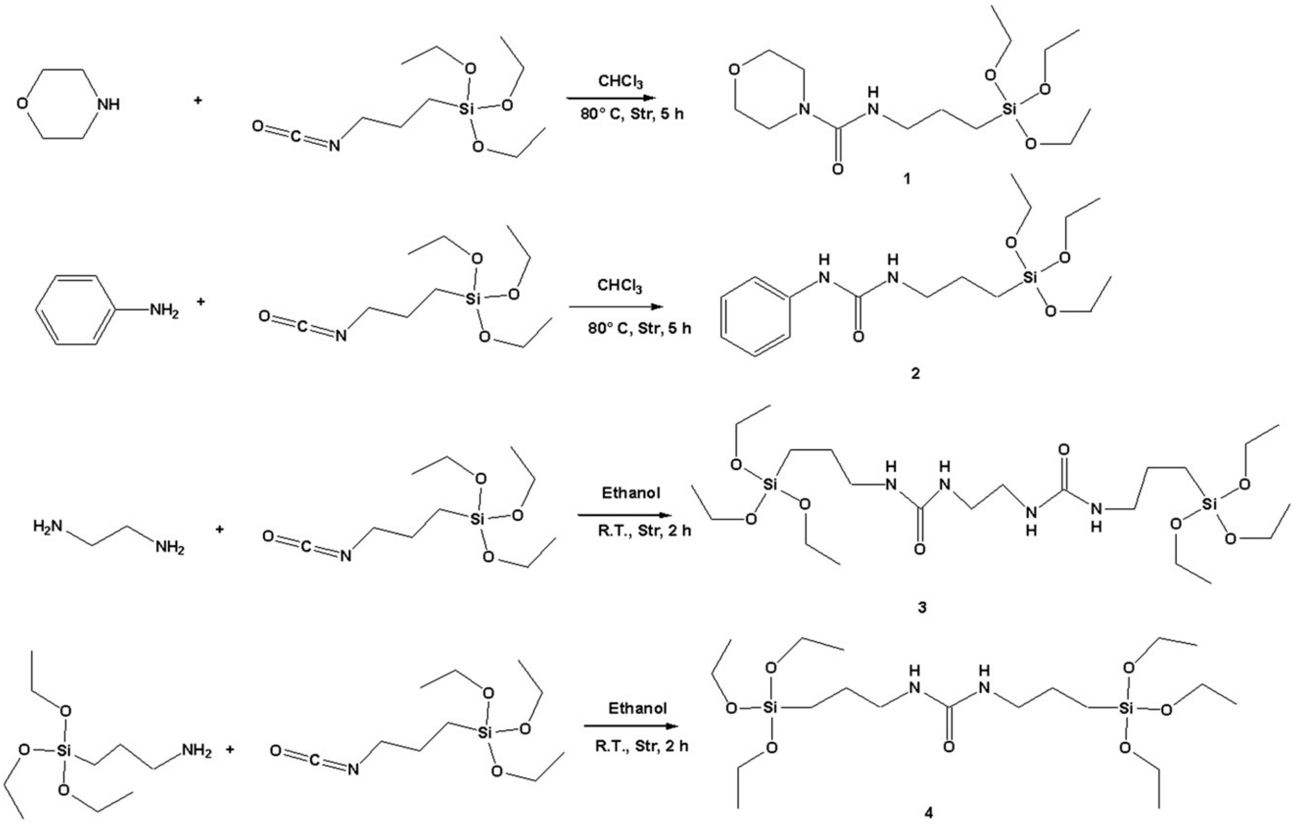
### 2.2. Spectroscopic studies

#### 2.2.1. IR spectroscopy

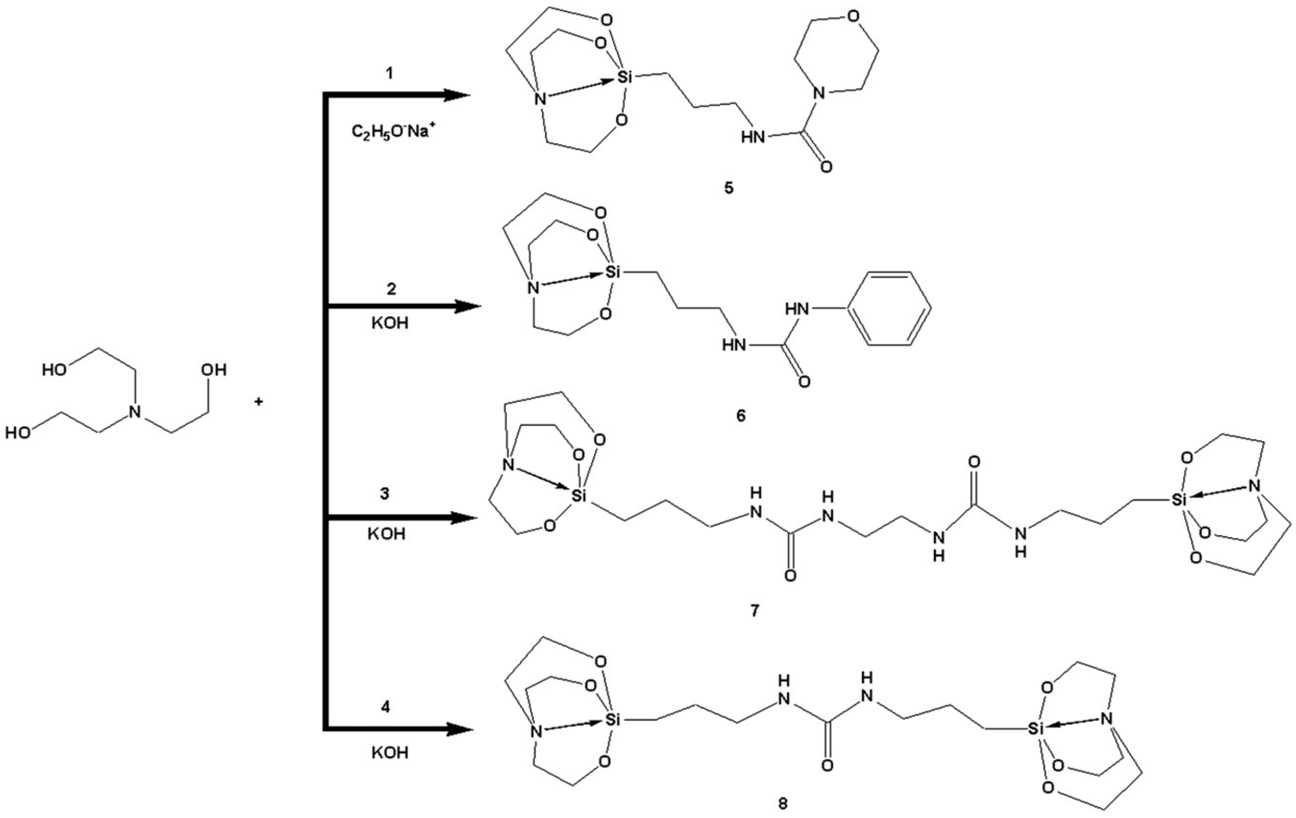
IR spectra exhibit absorption bands characteristic of both >NC(=O)N< and silatranyl moiety. These bands are assigned by comparing with the spectra of starting materials [29]. Bands observed in the region of 3400-3000 $cm^{-1}$ are assigned to asymmetric and symmetric NH stretching modes, whereas C–H stretching vibrations of methylene and methyl groups are observed in the region 3000–2800 $cm^{-1}$. The >C=O stretching vibrations are observed at 1650–1619 $cm^{-1}$, relatively low values, which are reasoned by C=O bond weakening due to the resonance involved in NHC(=O)NH moiety. Strong bands present in the regions 1550–1150 $cm^{-1}$ are assigned to asymmetric and symmetric deformations of NH and $CH_2$ group. Si–O stretching vibration is assigned to the bands present in 1100–1080 $cm^{-1}$ region. In addition, symmetric deformational vibration of the silatranyl skeleton with a predominant contribution from the Si–N bond is observed in the region 590–579 $cm^{-1}$. All bands observed for silatranyl moiety are consistent with previous literature reports [23].

#### 2.2.2. NMR spectroscopy

Multinuclear ($^1$H, $^{13}$C and $^{29}$Si) NMR spectra of **2**–**4** are consistent with the literature [28,29]. It is noteworthy that $^1$H NMR spectra of compounds **5**–**8** at room temperature are quite different



**Scheme 1.** Reaction pathway for the synthesis of triethoxysilanes (**1**–**4**).



**Scheme 2.** Reaction pathway for the synthesis of silatranes (**5**–**8**).

from their parent compounds with two intense triplets as the characteristic feature (due to protons of $OCH_2$, 3.75–3.78 ppm and $NCH_2$, 2.80–2.83 ppm of $Si(OCH_2CH_2)_3N$ moiety). Interestingly, rather than producing a triplet the $-CH_2NH$ proton resonances split up into a multiplet (region 2.66–2.87 ppm) due to their additional coupling with adjacent –NH proton, which is also validated by a triplet splitting of the –NH proton resonance. A triplet for $SiCH_2$ protons appears up field due to direct Si–C bond. In addition, a multiplet due to protons of $CCH_2C$ is also observed.

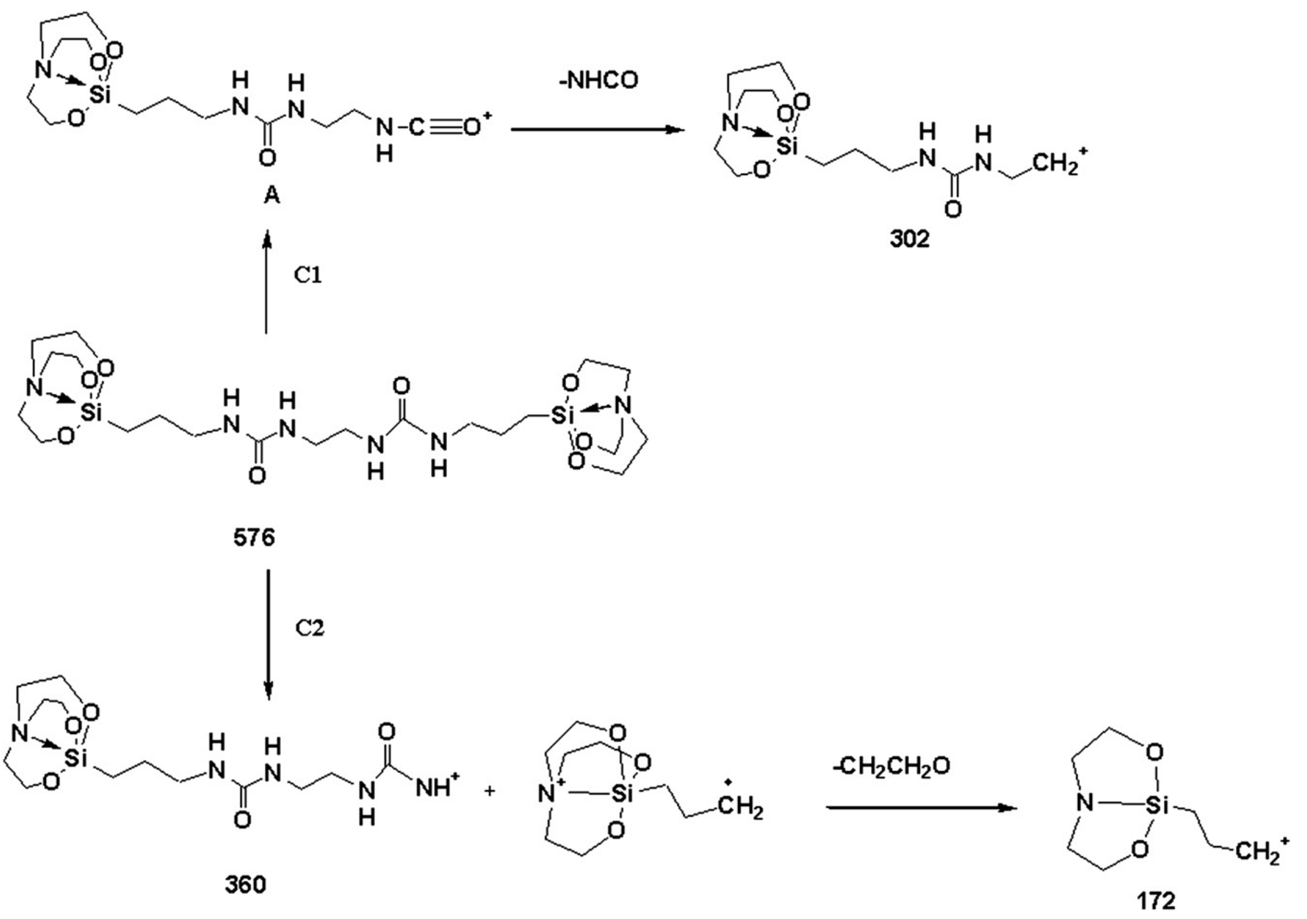
$^{13}C$ NMR spectra for all compounds are consistent with their structures. Compound **1** shows two peaks at 17.8 and 57.9 ppm due to $CH_3$ and $OCH_2$, respectively. In the $^{13}C$ NMR of silatranes **5**–**8**, peaks observed in region 57.6–58.0 and 51.0–55.4 are assigned to silatranyl $OCH_2$ and $NCH_2$, respectively. Most shielded carbon, i.e., $Si-CH_2$ is observed around 13.0 ppm, whereas the notably less shieled >C=O is observed in the region 156.0–158.7 ppm. Other peaks due to $CH_2CH_2NH$ are observed in the region 24.7–25.1 and 41.8–43.6 ppm, respectively. A peak due to $CH_2NH$ is shifted downfield due to presence of adjacent >C=O group. In compound **5**, two additional peaks due to $NCH_2$ and $OCH_2$ groups of morpholine ring are observed at 44.0 and 67.0 ppm, respectively. In compound **6**, aromatic carbons are also observed which show chemical shift in 120.7–139.2 ppm region. Compound **7** shows additional peaks due to $NCH_2CH_2N$ moiety, which are also shifted downfield as compared to silatranyl $NCH_2$.

$^{29}Si$ NMR spectra of the silatranes **5**–**8** exhibit the characteristic up field-shifted resonance at about −67 ppm, representative for alkyl-substituted silatranes [22,30,31].

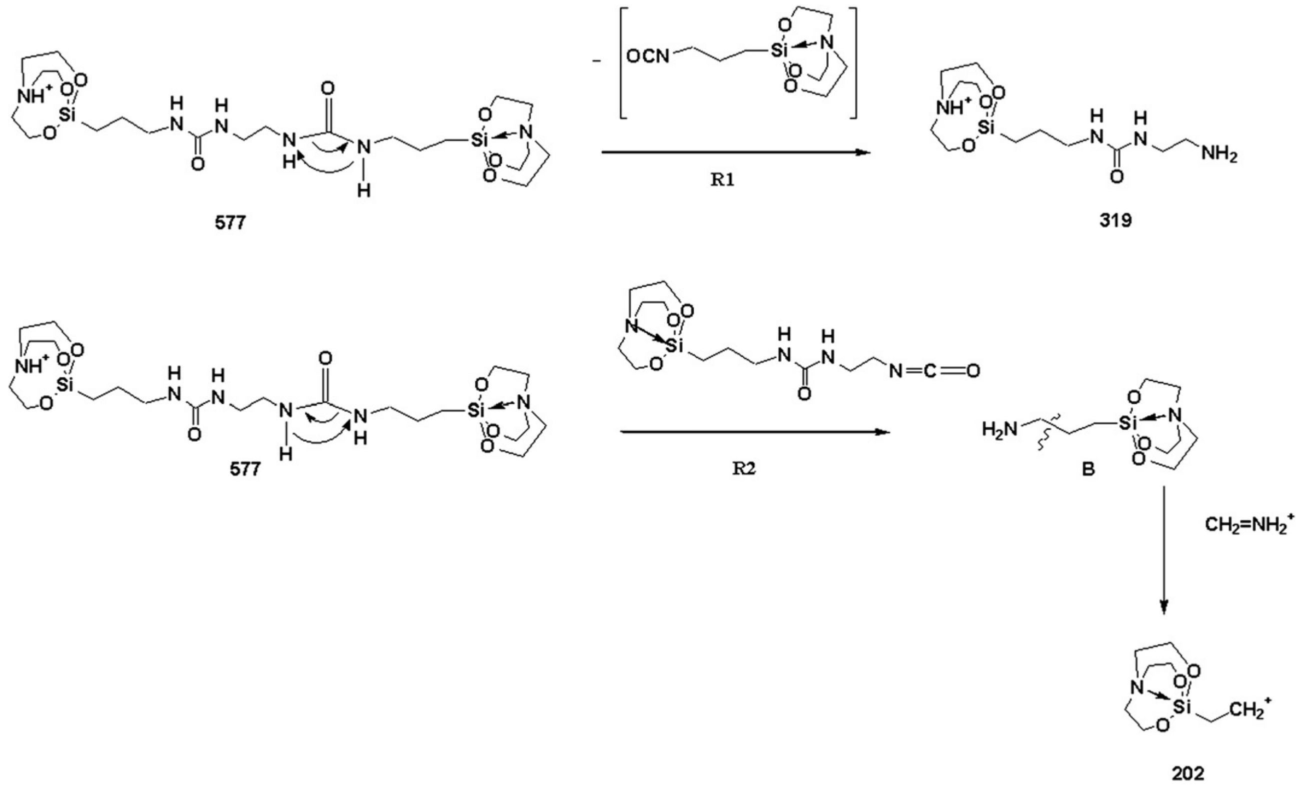
### 2.2.3. Mass spectroscopy

Mass spectra of all compounds show their respective molecular ion peaks with addition of H, Na and K, and their fragmentation pattern resemble with N-alkylamides. Compound **1** shows molecular ion peak as well as a peak at $m/z$ 289 due to loss of one of the ethoxy groups. In compound **6**, only molecular ion peaks, 374 (M + Na), 390 (M + K), along with an additional peak at 725 (2M + Na) are observed. Compound **7** may undergo $\alpha$ and $\beta$ cleavage, which is shown in Scheme 3. After $\alpha$ cleavage (C1), very weak fragment ion A may be formed, which eliminates NHCO to give a peak at $m/z$ 302. In case of $\beta$ cleavage (C2), two fragments may form, a fragment with $m/z$ 360 is observed and the other loses one arm $-OCH_2CH_2-$ of tricyclic silatranyl ring to form a new fragment with $m/z$ 172. The presence of covalent Si–N bond in this fragment is supported by literature [32]. The other main feature observed in the spectrum of **7** is $\alpha$ cleavage along with rearrangement of one hydrogen. Two simultaneous rearrangements, R1 and R2, are possible from both sides of >C=O group (Scheme 4). Rearrangement of H away from silatranyl part (R1) may lead to removal of 3-isocyanatopropylsilatrane with the subsequent formation of a fragment with $m/z$ 319. Whereas, rearrangement of H towards silatranyl part (R2) results in B, which undergoes further cleavage to form a fragment with $m/z$ 202.

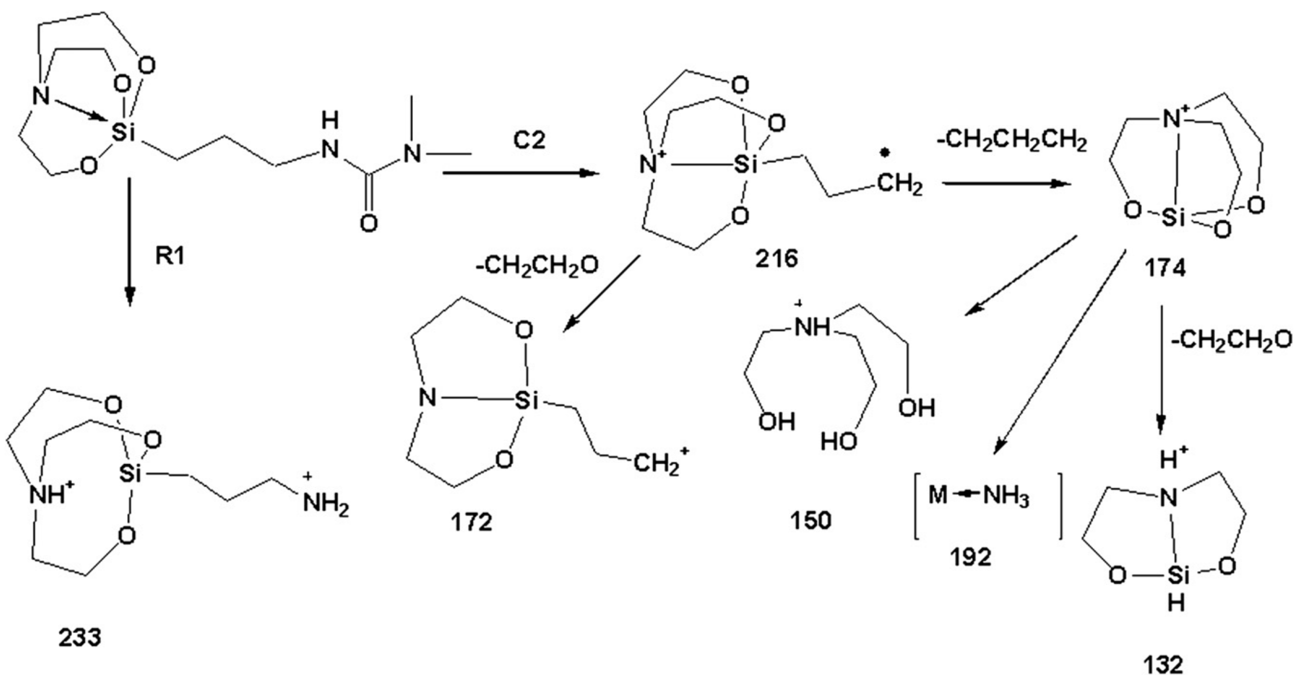
The fragmentation patterns of compounds **5** and **8** involve rearrangement R1, which results in aminopropylsilatranyl cation ($m/z = 233$). On the other hand, cleavage at $\beta$ (C2) gives rise to a fragment having $m/z$ 216, which in turn loses one of the $OCH_2CH_2-$ arm to form a bicyclic fragment with alkyl chain ($m/z = 172$). Homolytic cleavage of $Si-CH_2$ forms a silatranyl fragment with direct Si–N covalent bond (at $m/z = 174$), which is a general feature found in most of the silatranes. This fragment also loses one arm to form bicyclic moiety ($m/z = 132$). Along with a very intense peak due to protonated triethanolamine ($m/z = 150$), most abundant peak at $m/z = 192$ is also observed due to the formation of siltranyl adduct with $NH_4^+$, which is also a general feature of silatrane fragmentation (Scheme 5).



**Scheme 3.** Mass fragmentation pattern of compound **7** showing possible cleavages.



**Scheme 4.** Mass fragmentation pattern of **7** showing rearrangements and cleavages.



**Scheme 5.** Mass fragmentation pattern of compounds **5** and **8**.

### 2.3. X-ray crystallography

Colorless crystals suitable for X-ray analysis were grown from concentrated solutions of **5** and **6** in acetone. Single crystal X-ray diffraction study has shown that both compounds crystallize in a monoclinic crystal system (space group = $P2_1/c$). The ORTEP view of **5** and **6** with atomic labeling (thermal ellipsoids are drawn at 50% probability) is shown in Fig. 1 and Fig. 2, respectively. Details of X-ray data collection and structure refinement, and selected bond distances and angles of both compounds are listed in Table 1 and 2, respectively. These compounds possess usual silatrane skeleton containing Si atom in distorted trigonal bipyramidal geometry because of the coordination of tripodal triethanolamine ligand. The trianionic $N(CH_2CH_2O-)_3$ entities act as tetradentate ligands coordinating each to Si to form five membered rings, so that the transannular Si–N bond is formed. Due to this bond, Si achieves a coordination number of five with trigonal bipyramidal coordination sphere (which persists in solution, as indicated by $^{29}$Si NMR spectroscopy). The O atoms of the tetradentate ligand occupy equatorial positions and the N donor is present at apical site trans to the urea-functionalized alkyl chain.

The most noteworthy (because quite variable) parameter is the Si–N bond length, which is 2.121(1) Å and 2.188(2) Å for **5** and **6,** respectively. These Si–N bond distances are noticeably shorter than the sum of the van der Waals radii and indicate a weak bonding interaction between both atoms. Any effect of $-NHC(=O)NH$ group is not observed on the Si–N bond distance due to presence of intervening $-CH_2-CH_2-CH_2-$ alkyl chain. The bond angle N–Si–$C_{ax}$ is found to 178.85(4)° and 179.18(9)° for **5** and **6**, respectively.

The bond angles around Si atom can be discussed in terms of pentacoordination character i.e. percentage trigonal bipyramidal (% TBP). The pentacoordination character may be calculated from three apical-to-equatorial bond angles of three equatorial-to-equatorial bond angles. $\%TBP_{ax}$ and $\%TBP_{eq}$ for compound **5** are 67.6% and 89.7%, whereas for compound **6** are 65.4% and 87.5%, respectively as found according to the equations given below.

$$\%TBP_{ax} = 100\% \, [109.5^\circ - 1/3(\Sigma\theta_n)/109.5^\circ - 90.0^\circ)]$$

$$\%TBP_{eq} = 100\% \, [120.0^\circ - 1/3(\Sigma\varphi_n)/120.0^\circ - 109.5^\circ)]$$

Where $\theta_n$ is average of angles $O_{eq}-Si-C_{ax}$

Where $\varphi_n$ is average of angles $O_{eq}-Si-O_{eq}$

The O–Si–O bond angles can be discussed in terms of progress of transition from a tetrahedral Si-coordination sphere towards trigonal bipyramidal coordination (%TBP). According to the equation %TBP = 100% [(Σ O–Si–O angles)−(3 109.47°)/(3 120°)−(3

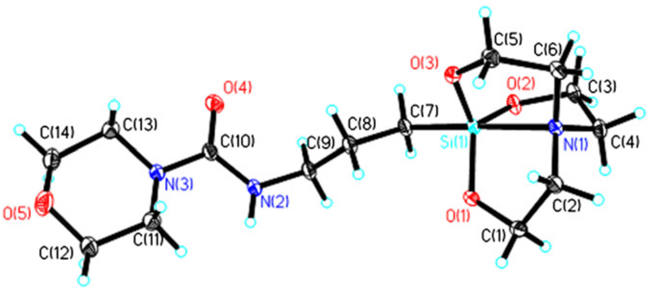


**Fig. 1.** ORTEP view of 5 (thermal ellipsoids drawn at 50% probability).

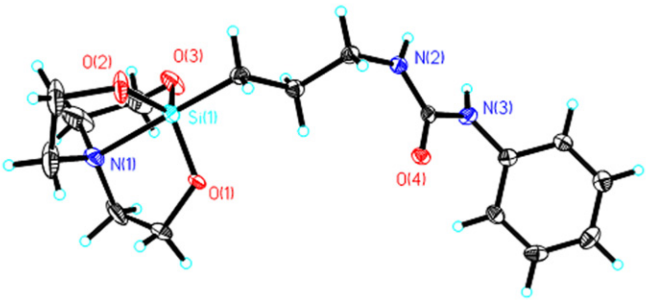


**Fig. 2.** ORTEP view of 6 (thermal ellipsoids drawn at 50% probability).

**Table 1**
X-ray crystal data and structure refinement of **5** and **6**.

| | Compound **5** | Compound **6** |
|---|---|---|
| Empirical formula | $C_{14}H_{27}N_3O_5Si$ | $C_{16}H_{25}N_3O_4Si$ |
| Formula weight | 345.48 | 351.48 |
| $T$ (K) | 150(2) | 150(2) |
| λ(Å) | 0.71073 | 0.71073 |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/c$ |
| Unit cell dimensions | | |
| $a$ (Å) | 6.6310(2) | 10.1758(8) |
| $b$ (Å) | 16.7435(5) | 7.4198(4) |
| $c$ (Å) | 15.1252(4) | 23.3010(16) |
| β (°) | 97.737(2) | 100.350(4) |
| $V$ (Å$^3$) | 1664.01(8) | 1730.7(2) |
| Z | 4 | 4 |
| $\rho_{calc}$(Mg/m$^3$) | 1.379 | 1.349 |
| $\mu_{MoK}\alpha$(mm$^{-1}$) | 0.170 | 0.161 |
| $F$(000) | 744 | 752 |
| Crystal size (mm) | 0.50 × 0.40 × 0.20 | 0.22 × 0.20 × 0.15 |
| Limiting indices | $-10 \le h \le 5$, $-26 \le k \le 26$, $-24 \le l \le 24$ | $-11 \le h \le 11$, $-8 \le k \le 8$, $-27 \le l \le 27$ |
| Reflections collected | 26439 | 13362 |
| Unique | 7323 [$R$(int) = 0.030] | 2873 [$R$(int) = 0.058] |
| θmax (°)/completeness (%) | 35.0/100 | 25.0/94.4 |
| Absorption correction | Semi-empirical from equivalents | None |
| Refinement method | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ |
| Data/restraints/parameters | 7323/0/212 | 2873/12/252 |
| GoF on $F^2$ | 1.072 | 1.049 |
| $R$ [$I > 2\sigma(I)$] | $R_1 = 0.0393$, $wR_2 = 0.1036$ | $R_1 = 0.0786$, $wR_2 = 0.2068$ |
| $R$(all data) | $R_1 = 0.0601$, $wR_2 = 0.1104$ | $R_1 = 0.0999$, $wR_2 = 0.2206$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.467 and −0.260 | 0.463 and −0.560 |

109.47°)] the N–Si bonds in **5** and **6** have flattened $O_3Si$ tetrahedral face towards an equatorial plane to an extent of %TBP = 88.7% and 87.0%, respectively.

## 3. Experimental

### 3.1. General details

#### 3.1.1. Synthesis

All the syntheses were carried out under a dry nitrogen atmosphere using vacuum glassline. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. 3-Aminopropyl(triethoxy)silane (Aldrich), 3-isocyanatopropyltriethoxysilane (Acros organics) and triethanolamine (Merck) were used as received from supplier. Ethylenediamine (Merck), aniline (Merck) and morpholine (Merck) was distilled by refluxing over KOH pellets under dry nitrogen atmosphere.

#### 3.1.2. Characterization

Infrared spectra were routinely obtained as thin films or Nujol mulls and KBr pellet on a Perkin–Elmer RX-I FT IR Spectrophotometer. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer. C, H and N analyses were obtained on a Perkin–Elmer Model 2400 CHN elemental analyzer and Si was estimated gravimetrically. The solution NMR spectra were recorded at 25 °C on a Jeol FT NMR (AL 300 M Hz) and Bruker Avance II FT NMR (AL 400 MHz) spectrometers ($^1$H, $^{13}$C) and a Bruker DPX 400 spectrometer ($^{29}$Si) using $CDCl_3$ as the solvent. Chemical shifts in ppm were determined relative to internal $CDCl_3$ and external tetramethylsilane (TMS).

#### 3.1.3. X-ray crystallography

Single-crystal X-ray structure analyses were carried out on a Bruker X8 APEX II CCD diffractometer using Mo Kα-radiation ($\lambda = 0.71073$ Å). Whereas for the small crystal of compound **6** with rather uniform dimensions (expected transmission ratio $T_{min}/T_{max} = 0.99$) redundant reflections were merged without absorption correction, a multi-scan absorption correction was applied to the data set of **5** (expected transmission ratio $T_{min}/T_{max} = 0.95$). The structures were solved by direct methods (SHELXS-97) and refined with full-matrix least-squares method (refinement of $F^2$ against all reflections with SHELXL-97) [33,34]. All non-hydrogen atoms were anisotropically refined, whereas C-bound H-atoms were refined isotropically in idealized positions (riding model). The N-bound H-atom in the structure of **5** was located as a residual electron density peak and refined isotropically without restraints, whereas in the structure of **6** the N-bound H-atoms were refined isotropically in idealized positions for sp$^2$ nitrogen.

The structure of compound **5** did not reveal any effects of disorder or twinning, thus the quality of the crystal allowed for data collection

**Table 2**
Selected bond lengths (Å) and angles (°) of **5** and **6**.

| Parameter | X-ray crystal data | |
|---|---|---|
| | **5** | **6** |
| N(1)–Si | 2.121 (1) | 2.189 (2) |
| C(7)–Si | 1.883 (1) | 1.877 (2) |
| C(9)–N(2) | 1.456 (1) | 1.448 (3) |
| C(10)–N(2) | 1.348 (1) | 1.340 (3) |
| O(1)–Si | 1.670 (1) | 1.651 (2) |
| O(2)–Si | 1.670 (1) | 1.654 (2) |
| O(3)–Si | 1.684 (1) | 1.662 (2) |
| C(10)–N(3) | 1.386 (1) | 1.375 (3) |
| C(10)–O(4) | 1.229 (1) | 1.246 (2) |
| C(11)–N(3) | 1.461 (1) | 1.395 (3) |
| C(7)–C(8) | 1.534 (1) | 1.530 (3) |
| C(8)–C(9) | 1.522 (1) | 1.530 (3) |
| O(1)–Si–O(2) | 119.87 (4) | 118.17 (15) |
| O(1)–Si–O(3) | 119.61 (4) | 118.06 (14) |
| O(2)–Si–O(3) | 116.95 (3) | 119.47 (16) |
| C(8)–C(7)–Si | 115.83 (7) | 113.97 (14) |
| C(9)–C(8)–C(7) | 111.90 (8) | 112.69 (17) |
| C(8)–C(9)–N(2) | 114.05 (8) | 113.64 (17) |
| N(2)–C(10)–N(3) | 117.17 (8) | 115.21 (19) |
| C(10)–N(2)–C(9) | 121.28 (8) | 123.35 (18) |
| C(10)–N(3)–C(11) | 113.48 (8) | 125.13 (18) |
| N(2)–C(10)–O(4) | 122.05 (8) | 122.60 (2) |
| N(3)–C(10)–O(4) | 120.75 (9) | 122.22 (19) |
| N(1)–Si(1)–C(7) | 178.85 (4) | 179.18 (9) |

at higher angle, whereas the crystal structure of **6** is disturbed by both disorder of the silatrane moiety (s.o.f. 0.731(5) and 0.269(5)) and twinning (BASF refined to 0.423(2)). Therefore, the data set for crystal of **6** (exhibiting significantly lower diffraction power) was collected up to $\theta = 25°$. A HKLF5 format data set was generated in WinGX upon identification of the twin law (1 0 0)(0 − 1 0)(−0.83 0 − 1), which corresponds to a 180° rotation about direct axis 1 0 0, using ROTAX as implemented in WinGX [35,36]. For twin refinement only separated and overlapping reflections were considered. Partly overlapping reflections, inclusion of which would have caused refinement of a lower BASF and therefore generated a worse structure model, were omitted (in the procedure, which generated the HKLF5 data file). Hence, only 94.4% of the data were used in the refinement for the sake of structure quality and better bond precision.

As to the disorder, the silatrane moiety of **6** is disordered by means of alternative directionalities of the propeller tilt of the $CH_2CH_2O$ groups. Thus, only 1 s.o.f. was refined, as the three $CH_2CH_2O$ groups would have to form an almost $C_3$ symmetric propeller for steric reasons, and refinement of **6** was restrained to same bond lengths (SADI instruction) for corresponding bonds of the two disordered parts. Thus, only bond lengths for the predominant part are reported, as the same values were obtained for the alternative part.

## *3.2. Synthesis of silanes*

### *3.2.1. N-(3-(triethoxysilyl)propyl)morpholine-4-carboxylic acid amide (**1**)*

Morpholine (1.05 g, 12.1 mmol) was dissolved in $CHCl_3$ and 3-isocyanatopropyltriethoxysilane (3 g, 12.1 mmol) was slowly added. The mixture was stirred and heated at 80 °C for 5 h. After cooling the contents, the solvent was evaporated under vacuum and a light yellow oil was obtained. Yield: (3.33 g, 82.0%). IR (KBr plates, Neat, $cm^{-1}$): 792 s ($\nu_s$ Si—O), 860 w ($\nu$ C—N), 913 m ($\nu_s$ $NC_3$), 957 m ($\nu$ C—C), 997 w ($\nu_{as}$ $NC_3$), 1080 vs ($\nu_{as}$ Si—O), 1108 vs ($\nu$ C—O), 1166 m ($\tau$ $CH_2O$), 1269 m ($\omega$ $CH_2O$), 1295 m ($\omega$ $CH_2N$), 1347 w, 1438 w ($\delta$ $CH_3C$), 1530 m ($\delta$ NH), 1640 vs ($\nu$ C=O), 2974 s, 2931 ($\nu_s$ $CH_2$), 3346 b ($\nu_s$ NH) ($\nu_{as}$ NH); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm); 0.44 (t, 2H, $SiCH_2$, $J = 8.40$ Hz), 1.04 (t, 9H, $CH_3$, $J = 6.90$ Hz), 1.44 (q, 2H, $CCH_2C$, $J = 8.40$ Hz), 3.04 (q, 2H, $CH_2NH$, $J = 12.60$ Hz), 3.17 (t, 4H, $NCH_2$), 3.47 (t, 4H, $OCH_2$), 3.63 (q, 6H, $OCH_2$, $J = 14.10$ Hz), 5.24 (t, 1H, NH); $^{13}C$ NMR (75.57 MHz, $CDCl_3$): $\delta$ 7.27 ($SiCH_2$), 17.78 ($CH_3$), 23.00 ($C\mathbf{C}H_2C$), 42.77 ($HNCH_2$), 44.34 ($CH_2N$), 57.86 ($OCH_2$), 66.85 $(OCH_2)_{morph}$, 157.60 (C=O); $^{29}Si$ NMR (79.5 MHz, $CDCl_3$): $\delta$ −45.18; MS: *m/z* (relative abundance: %, assignment): 289 (17.75, $M{-}OC_2H_5)^+$, 357 $(100, M + Na)^+$.

### *3.2.2. 1-(3-(triethoxysilyl)propyl)-3-phenylurea (**2**)*

Aniline (1.13 g, 12.1 mmol) was dissolved in $CHCl_3$ and 3-isocyanatopropyltriethoxysilane (3 g, 12.1 mmol) was slowly added. The mixture was stirred and heated at 80 °C for 5 h. After cooling the contents, the solvent was evaporated under vacuum and a light brown solid was obtained. Yield: (3.55 g, 86.0%). IR (KBr plates, Nujol, $cm^{-1}$): 726 s, 770 s ($\nu_s$ Si—O), 790 m, 862 w ($\nu$ C—N), 908 s ($\nu$ C—C), 931 m ($\nu$ C—C), 1023 s ($\nu_s$ $NC_3$), 1062 s ($\nu_{as}$ Si—O), 1104 vs, 1133 vs ($\nu$ C—O), 1180 m ($\tau$ $CH_2O$), 1260 m ($\omega$ $CH_2O$), 1316 m ($\omega$ $CH_2N$), 1390 w, 1443 w ($\delta$ $CH_3C$), 1538 m ($\delta$ NH), 1630 vs ($\nu$ C=O), 2735 s, 2942 ($\nu_s$ $CH_2$), 2972 vs ($\nu_{as}$ $CH_3$), 3039 w ($\nu_s$ NH), 3224 s, 3250 s ($\nu_{as}$ NH).

### *3.2.3. 1,2-bis{N′-[3-(triethoxysilyl)propyl]ureido}-ethane (**3**)*

A solution of ethylenediamine (0.24 g, 4 mmol) in 10 ml of ethanol was added dropwise with vigorous stirring to a solution of 3-isocyanatopropyltriethoxysilane (2 g, 8 mmol) in 20 ml of ethanol, cooled on an ice bath. The reaction mixture was stirred for 2 h. Stirring was stopped, and the mixture was allowed to stand at room temperature for 24 h. After that, the solvent was evaporated under vacuum and white solid separate out which was stored under nitrogen. (M.p. 140–143 °C, yield: (1.95 g, 89%). IR (KBr plates, Nujol, $cm^{-1}$): 730 s, 769 s ($\nu_s$ Si—O), 793 m, 890 w ($\nu$ C—N), 915 m ($\nu_s$ $NC_3$), 958 m ($\nu$ C—C), 1007 s br, ($\nu_{as}$ $NC_3$), 1079 vs ($\nu_{as}$ Si—O), 1102 vs ($\nu$ C—O), 1166 w ($\tau$ $CH_2O$), 1263 m br ($\omega$ $CH_2O$) ($\omega$ $CH_2N$), 1389 w, 1444 w ($\delta$ $CH_3C$), 1577 m ($\delta$ NH), 1624 vs ($\nu$ C=O), 2826 s, 2974 ($\nu_s$ $CH_2$), 3336 b ($\nu_s$ NH) ($\nu_{as}$ NH).

### *3.2.4. N-[3-(Triethoxysilyl)propyl]-N′-[3-(triethoxysilyl) propyl]urea (**4**)*

3-isocyanatopropyltriethoxysilane (1 g, 4 mmol) was dissolved in 10 ml of ethanol, and a solution of 3-aminopropyltriethoxysilane (0.95 g, 4 mmol) in 10 mL of ethanol, was added dropwise with vigorous stirring. An exothermic reaction occurred. After stirring for 2 h at room temperature, the contents were refluxed for 1 h. The solvent was evaporated under vacuum, which afforded a white solid. (M.p. 55 °C, yield: 1.59 g, 84%). IR (KBr plates, Nujol, $cm^{-1}$): 739 s, 782 s ($\nu_s$ Si—O), 813 m, 861 w ($\nu$ C—N), 915 m ($\nu_s$ $NC_3$), 957 m ($\nu$ C—C), 1015 s, 1058 s ($\nu_{as}$ $NC_3$), 1080 vs ($\nu_{as}$ Si—O), 1135 vs ($\nu$ C—O), 1166 m ($\tau$ $CH_2O$), 1255 m ($\omega$ $CH_2O$), 1317 m ($\omega$ $CH_2N$), 1390 w, 1419 w ($\delta$ $CH_3C$), 1576 m ($\delta$ NH), 1630 vs ($\nu$ C=O), 2926 s, 2974 ($\nu_s$ $CH_2$), 3346 b ($\nu_s$ NH) ($\nu_{as}$ NH).

## *3.3. Synthesis of silatranes*

### *3.3.1. N-(3-silatranylpropyl)morpholine-4-carboxylic acid amide (**5**)*

The compound was prepared by adding triethanolamine (0.45 g, 3.0 mmol) to **1** (1.0 g, 3.0 mmol) with simultaneous addition of catalytic amount of sodium ethoxide in benzene (50 mL). The contents were refluxed for 5 h in a flask fitted with Dean–Stark apparatus. The solvent was evaporated under vacuum and 10 mL of ether was added. The contents were stirred for 30 min and product was isolated as a white powder. Solid was filtered and dried under vacuum. (M.p. 175–177° C, yield 0.81 g, 78.0%). Anal. Calcd for $C_{14}H_{27}N_3O_5Si$: C, 48.67; H, 7.88; N, 12.16; Si, 8.13. Found: C, 48.01; H, 7.54; N, 11.89; Si, 8.02. IR (KBr pellet, $cm^{-1}$): 590 m $\nu$ (Si ← N), 717 s, 776 s ($\nu_s$ Si—O), 830 m, 863 w ($\nu$ C—N), 913 m ($\nu_s$ $NC_3$), 944 m ($\nu$ C—C), 992 w,1023 s, ($\nu_{as}$ $NC_3$), 1089 vs ($\nu_{as}$ Si—O), 1118 vs ($\nu$ C—O), 1181 m ($\tau$ $CH_2O$), 1257 m ($\omega$ $CH_2O$), 1304 m ($\omega$ $CH_2N$), 1355 w, 1458 w ($\delta$ $CH_3C$), 1538 m ($\delta$ NH), 1648 vs ($\nu$ C=O), 2888 s, 2931 ($\nu_s$ $CH_2$), 3360 b ($\nu_s$ NH) ($\nu_{as}$ NH); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm); 0.37 (t, 2H, $SiCH_2$, $J = 7.81$ Hz), 1.55 (m, 2H, $CCH_2C$, $J = 7.84$ Hz), 2.74 (t, 6H, $NCH_2$, $J = 5.82$ Hz), 3.16 (q, 2H, $CH_2NH$, $J = 11.94$ Hz), 3.25 (t, 4H, $CH_2N$), 3.60 (t, 4H, $OCH_2$), 3.69 (t, 6H, $OCH_2$, $J = 5.83$ Hz), 4.86 (t, 1H, NH); $^{13}C$ NMR (100.62 MHz, $CDCl_3$): $\delta$ 12.92 ($SiCH_2$), 24.65 ($C\mathbf{C}H_2C$), 43.39 ($CH_2NH$), 43.96 ($\mathbf{C}H_2N_{morph}$), 51.03 ($NCH_2$), 57.67 ($OCH_2$), 66.60 ($CH_2O_{morph}$), 158.08 (C=O); $^{29}Si$ NMR (79.5 MHz, $CDCl_3$): $\delta$ −66.8. MS: *m/z* (relative abundance: %, assignment): 132 (20), 150 (41), 172 (74), 174 (18), 192 (25), 216 (11), 233 (43), 346 $(100, M + H)^+$, 368 $(96, M + Na)^+$, 713 $(41, 2M + Na)^+$.

### *3.3.2. 1-(3-silatranylpropyl)-3-phenylurea (**6**)*

2.56 g (7.53 mmol) of **2** was dissolved in benzene and triethanolamine (1.12 g, 7.53 mmol) was added slowly to 100 mL flask equipped with Dean–Stark apparatus. A catalytic amount of KOH (0.2 g) was added to reaction mixture. The ethanol formed was removed azeotropically, and the white solid was filtered under vacuum. The solid was washed with ether (2 × 10 mL) and dried under vacuum. (M.p. 175° C, yield 0.83 g, 80%). Anal. Calcd. for $C_{16}H_{25}N_3O_4Si$: C, 54.68; H, 7.17; N, 11.96; Si, 7.99. Found: C, 53.98; H, 7.04; N, 11.23; Si, 7.11. IR (KBr pellet, $cm^{-1}$): 579 m $\nu$ (Si ← N), 723 s, 764 s ($\nu_s$ Si—O), 813 m, 876 w ($\nu$ C—N), 904 s ($\nu$ C—C), 933 m ($\nu$ C—C), 1012 s ($\nu_s$ $NC_3$), 1053 s ($\nu_{as}$ Si—O), 1100 vs, 1133 vs ($\nu$ C—O), 1178 m ($\tau$ $CH_2O$), 1276 m ($\omega$ $CH_2O$), 1311 m ($\omega$ $CH_2N$), 1360 w, 1442 w ($\delta$ $CH_3C$), 1555 m (δ NH), 1631 vs (ν C=O), 2874 s, 2922 ($\nu_s$ $CH_2$), 2971 vs ($\nu_{as}$ $CH_3$), 3037 w ($\nu_s$ NH), 3247 s, 3253 s ($\nu_{as}$ NH); $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm); 0.02 (t, 2H, $SiCH_2$, $J = 7.80$ Hz), 1.18 (m, 2H, $CCH_2C$, $J = 7.80$ Hz), 2.31 (t, 6H, $NCH_2$, $J = 5.70$ Hz), 2.77 (q, 2H, $CH_2NH$, $J = 12.6$ Hz), 3.26 (t, 6H, $OCH_2$, $J = 5.70$ Hz), 4.81 (t, 1H, $CH_2N\boldsymbol{H}$), 6.28 (s, 1H, NHC), 6.53–6.91 (m, 5H, aromatic ring); $^{13}C$ NMR (100.62 MHz, $CDCl_3$): δ 13.05 ($SiCH_2$), 25.09 ($C\boldsymbol{C}H_2C$), 43.19 ($\boldsymbol{C}H_2NH$), 50.95 ($NCH_2$), 57.59 ($OCH_2$), 120.66–139.21 (aromatic ring), 155.99 (C=O); $^{29}Si$ NMR (79.5 MHz, $CDCl_3$): δ −67.0. MS: *m/z* (relative abundance: %, assignment): 374 (100, M + Na)$^+$, 390 (5.8, M + K)$^+$, 725 (86, 2M + Na)$^+$.

### 3.3.3. *1,2-bis{N′-[3-silatranylpropyl]ureido}-ethane* (**7**)

A solution of **3** (1.0 g, 1.81 mmol) and triethanolamine (0.56 g, 3.75 mmol) in 50 mL benzene was heated to reflux. After addition of KOH (0.2 g), the ethanol formed was distilled off by using Dean–Stark apparatus. The white solid obtained was filtered, washed with ether (2 × 10 mL) and dried under vacuum. (M.p. 182–185° C, yield 0.73 g, 70%). Anal. Calcd. for $C_{22}H_{44}N_6O_8Si_2$: C, 45.81; H, 7.69; N, 14.57; Si, 9.74. Found: C, 44.97; H, 7.28; N, 14.33; Si, 9.12. IR (KBr pellet, cm$^{-1}$): 587 m ν (Si ← N), 720 s, 764 s ($\nu_s$ Si–O), 815 m, 878 w (ν C–N), 911 m ($\nu_s$ $NC_3$), 940 m (ν C–C), 1017 s br, ($\nu_{as}$ $NC_3$), 1099 vs ($\nu_{as}$ Si–O), 1123 vs (ν C–O), 1188 w (τ $CH_2O$), 1272 m br (ω $CH_2O$) (ω $CH_2N$), 1355 w, 1425 w (δ $CH_3C$), 1573 m (δ NH), 1623 vs (ν C=O), 2876 s, 2928 ($\nu_s$ $CH_2$), 3339 b ($\nu_s$ NH) ($\nu_{as}$ NH); $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm); 0.02 (t, 2H, $SiCH_2$, $J = 7.9$ Hz), 1.26 (m, 2H, $CCH_2C$, $J = 7.50$ Hz), 3.35 (m, 4H, $NCH_2CH_2N$), 2.71 (t, 6H, $NCH_2$, $J = 5.70$ Hz), 2.87 (q, 2H, $CH_2NH$, $J = 11.73$ Hz), 3.51 (t, 6H, $OCH_2$, $J = 5.7$ Hz), 5.69 (t, 1H, NH), 5.76 (t, 1H, NH); $^{13}C$ NMR (100.62 MHz, $CDCl_3$): δ 13.27 ($SiCH_2$), 25.00 ($C\boldsymbol{C}H_2C$), 41.81 ($\boldsymbol{C}H_2NH$), 48.69 ($N\boldsymbol{C}H_2\boldsymbol{C}H_2N$), 55.43 ($NCH_2$), 57.95 ($OCH_2$), 156.99 (C=O); $^{29}Si$ NMR (79.5 MHz, $CDCl_3$): δ −69.6. MS: *m/z* (relative abundance: %, assignment): 150 (100), 172 (10), 202 (7.4), 302 (10), 319 (11), 360 (12), 577 (31, M + H)$^+$, 599 (58, M + Na)$^+$.

### 3.3.4. *N-[3-silatranylpropyl]-N′-[3-silatranylpropyl]urea* (**8**)

A solution of **4** (1.58 g, 3.46 mmol) and triethanolamine (1.12 g, 7.52 mmol) in benzene (50 mL) was refluxed for 4 h in a flask fitted with Dean–Stark apparatus. A catalytic amount of KOH (0.2 g) was added. The precipitate was filtered off; solid was washed with ether and dried under vacuum. (M.p. 219–221° C, yield 1.08 g, 65%). Anal. Calcd for $C_{19}H_{38}N_4O_7Si_2$: C, 46.51; H, 7.81; N, 11.42; Si, 11.45. Found: C, 46.06; H, 7.07; N, 11.23; Si, 11.03. IR (KBr pellet, cm$^{-1}$): 584 m ν (Si ← N), 719 s, 762 s ($\nu_s$ Si–O), 811 m, 878 w (ν C–N), 910 m ($\nu_s$ $NC_3$), 940 m (ν C–C), 1016 s, 1053 s ($\nu_{as}$ $NC_3$), 1099 vs ($\nu_{as}$ Si–O), 1125 vs (ν C–O), 1194 m (τ $CH_2O$), 1277 m (ω $CH_2O$), 1312 m (ω $CH_2N$), 1354 w, 1415 w (δ $CH_3C$), 1573 m (δ NH), 1619 vs (ν C=O), 2874 s, 2926 ($\nu_s$ $CH_2$), 3336 b ($\nu_s$ NH) ($\nu_{as}$ NH); $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm); 0.02 (t, 2H, $SiCH_2$, $J = 8.10$ Hz), 1.17 (m, 2H, $CCH_2C$, $J = 8.10$ Hz), 2.38 (t, 6H, $NCH_2$, $J = 6.00$ Hz), 2.66 (q, 2H, $CH_2NH$, $J = 12.6$ Hz), 3.33 (t, 6H, $OCH_2$, $J = 6.00$ Hz), 4.16 (t, 1H, NH); $^{13}C$ NMR (100.62 MHz, $CDCl_3$): δ 13.01 ($SiCH_2$), 25.12 ($C\boldsymbol{C}H_2C$), 43.62 ($\boldsymbol{C}H_2NH$), 51.04 ($NCH_2$), 57.68 ($OCH_2$), 158.65 (C=O); $^{29}Si$ NMR (79.5 MHz, $CDCl_3$): δ −66.7. MS: *m/z* (relative abundance: %, assignment): 132 (9.2), 150 (25), 192 (5.2), 233 (5.4), 491 (100), 513 (92, M + Na)$^+$, 529 (21, M + K)$^+$.

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## Appendix A. Supplementary material

CCDC 782354 and 782353 contains the supplementary crystallographic data for **5** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.12.039.

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