

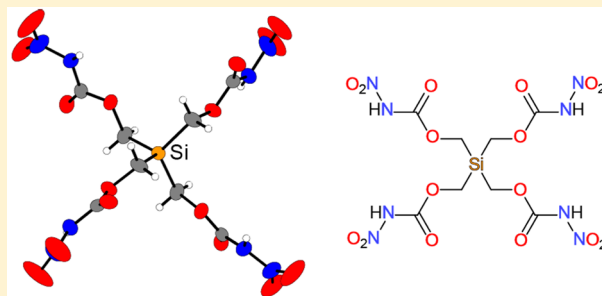
Energetic Sila-Nitrocarbamates: Silicon Analogues of Neo-Pentane Derivatives

Quirin J. Axthammer, Thomas M. Klapötke,* Burkhard Krumm, and Thomas Reith

Energetic Materials Research, Department of Chemistry, Ludwig-Maximilian University, Munich Butenandtstrasse 5-13 (D), D-81377 Munich, Germany

Supporting Information

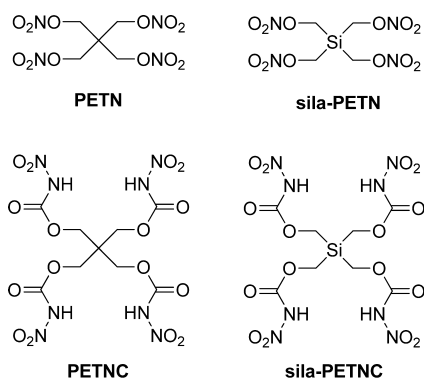
ABSTRACT: Four silanes based on the neo-pentane skeleton $\text{Me}_{4-x}\text{Si}(\text{CH}_2\text{R})_x$ containing carbamate groups ($x = 1-4$, $\text{R} = \text{OC}(\text{O})\text{NH}_2$) have been prepared via the corresponding alcohols $\text{Me}_{4-x}\text{Si}(\text{CH}_2\text{OH})_x$ starting from the chlorosilanes $\text{Me}_{4-x}\text{SiCl}_x$. Subsequent nitration leads to the corresponding primary nitrocarbamates ($\text{R} = \text{OC}(\text{O})\text{NHNO}_2$), examined for the purpose as potential energetic materials, including the silicon analogue of pentaerythritol tetranitrocarbamate (sila-PETNC) and a siloxane based nitrocarbamate side-product. All compounds were thoroughly characterized by spectroscopic methods including X-ray diffraction. Thermal stabilities and sensitivities toward impact and friction were examined, as well as detonation values by calculating energies of formation using the EXPLO5 V6.02 software.



INTRODUCTION

Recently, the class of primary nitrocarbamate compounds was examined as potential energetic materials as well as ligands for metal complexes.¹ Among them, the neo-pentane derivative pentaerythritol tetranitrocarbamate (PETNC, Scheme 1) was

Scheme 1. Structures of PETN, PETNC, and Their Silicon Analogues



synthesized by a two-step synthesis starting from pentaerythritol.^{1b} The reaction with the useful reagent chlorosulfonyl isocyanate (CSI) allowed easy access to the tetracarbamate of pentaerythritol, which upon further nitration forms PETNC. In comparison with the well-known and widely used explosive pentaerythritol tetranitrate (PETN), the nitrocarbamate PETNC shows an increased thermal stability as well as lower sensitivities against friction and impact.^{1b,2}

The compound tetrakis(nitratomethyl)silane (sila-PETN), the silicon derivative of PETN, was investigated in 2007.³ This

highly sensitive material was shown to exhibit a higher heat of explosion, based on the highly exothermic reaction forming silicon dioxide.⁴ Unfortunately, the extraordinarily high sensitivity of sila-PETN inhibits full characterization and further applications.³ In accordance, the synthesis and study of minor substituted silicon based neo-pentane nitrates feature much higher sensitivities than their corresponding carbon analogues and, as a consequence, exhibit better handling compared to sila-PETN.⁵ Furthermore, the first structural studies of silicon containing nitrate esters were established.

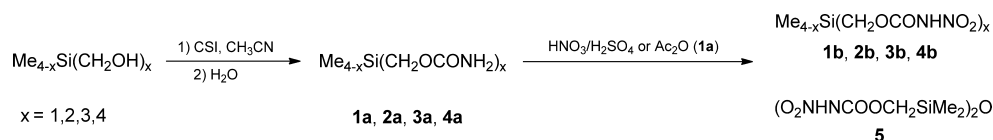
One of the points of interest for us in this study is if a hereto unknown sila-PETNC compound would outperform the carbon derivative PETNC and, furthermore, would be less sensitive than the sila-PETN. Apart from this, the stabilization with nitrocarbamates compared to nitrate esters of silicon compounds should be examined and discussed. Therefore, in addition to sila-PETNC, the minor substituted sila-neo-pentane derivatives containing nitrocarbamate moieties as shown in Scheme 2 were synthesized and examined, including their stability and sensitivities regarding friction and impact.

RESULTS AND DISCUSSION

Synthesis. The alcohol precursor compounds $\text{Me}_{4-x}\text{Si}(\text{CH}_2\text{OH})_x$ were synthesized from the corresponding chlorosilanes $\text{Me}_{4-x}\text{SiCl}_x$ according to literature procedures.^{5,6} The first step is the conversion into the chloromethylsilanes $\text{Me}_{4-x}\text{Si}(\text{CH}_2\text{Cl})_x$ by treatment with *n*-butyl lithium and bromochloromethane at -78°C in THF/hexanes. During these studies a modified and simplified synthesis procedure is

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Scheme 2. Syntheses of Silicon Containing Carbamates (1a–4a) and Nitrocarbamates (1b–4b and 5)



developed for the important precursor tetrakis(chloromethyl)silane, $\text{Si}(\text{CH}_2\text{Cl})_4$, avoiding the use of time-consuming column chromatography (described in detail in the [Experimental Section](#)). The chloromethylsilanes were converted into the acetoxymethylsilanes $\text{Me}_{4-x}\text{Si}(\text{CH}_2\text{OCOCH}_3)_x$ with sodium acetate in refluxing dimethylformamide. With an acid catalyzed methanolysis using acetyl chloride, the final conversion into the alcohols $\text{Me}_{4-x}\text{Si}(\text{CH}_2\text{OH})_x$ was achieved.

The reaction of the alcohols with equivalent amounts of the reagent chlorosulfonyl isocyanate (CSI) and subsequent hydrolysis yielded the corresponding carbamates $\text{Me}_{4-x}\text{Si}(\text{CH}_2\text{OCONH}_2)_x$ **1a** ($x = 1$ (**1a**), 2 (**2a**), 3 (**3a**), and 4 (**4a**)). In comparison to other carbamate functionalizing routes, the usage of CSI has several advantages in the synthesis toward primary carbamates, for instance, fast reaction times, high yields, and prevention of multiaddition.^{1b} The carbamates **1a** and **2a** were previously synthesized via the chloroformate–ammonia route, a multistep strategy with lower yields, but characterized only by melting points and elemental analyses.⁷ The nitrocarbamates **2b**, **3b**, and **4b** were obtained by treatment of the carbamates (**2a–4a**) with anhydrous nitric acid and concentrated sulfuric acid, followed by an aqueous workup ([Scheme 2](#)).

The synthesis of the trimethylsilylmethyl nitrocarbamate **1b** was successful by a slightly modified protocol via the nitration of **1a** using a less oxidizing mixture, anhydrous nitric acid and acetic anhydride. With application of mixed acid as above with **1a**, the reaction follows a different pathway by oxidative abstraction of a methyl group, and the formation of the disiloxane **5** was observed and also could be isolated ([Scheme 2](#)). All carbamates and nitrocarbamates are colorless solids, which are purified by recrystallization or precipitation. In the case of tetrakis(carbamoylmethyl)silane (**4a**) and tetrakis(nitrocarbamoylmethyl)silane (**4b**), pure products precipitate in good yields from the standard reaction workup. The yields of the other nitrocarbamates are rather low, possibly due to the harsh nitration conditions, resulting partially in cleavage of the carbamate molecules.

NMR and Vibrational Spectroscopy. In the ^1H NMR spectra of the carbamates **1a–4a** and nitrocarbamates **1b–4b**, with increasing number of carbamate/nitrocarbamate moieties per silicon atom, a slight low field shift of the NH_2/NH , CH_2 , and CH_3 signals is observed. The ^1H NMR resonances of the nitrated compounds **1b–4b** are in general shifted toward lower field in comparison with the corresponding carbamates, most significantly observed with the NH_2/NH resonance. The nitration of the carbamate nitrogen NH_2 causes a strong acidification and deshielding of the nitramino NH proton from 6.34–6.45 ppm to 13.2–13.4 ppm with additional broadening of the resonance.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, both the CH_2 and CH_3 signals are shifted to lower field for every additional carbamate/nitrocarbamate unit connected to the silicon center and are rather unaffected upon nitration. The opposite occurs for the carbonyl resonance, which is almost independent from the substitution pattern, but is strongly influenced by nitration. The

carbonyl resonance observed in the region 157.7–158.1 ppm for the carbamates **1a–4a** shifts to high field around 150.4–150.7 ppm for the nitrocarbamates **1b–4b**. The ^{13}C NMR resonances of sila-PETNC (**4b**) [150.7 (CO) and 55.6 (CH_2), acetone- D_6], when compared to those of the carbon analogue PETNC [148.9 (CO) and 64.3 (CH_2), $\text{DMSO}-\text{D}_6$],^{1b} show a significant difference for the CH_2 resonance, because of the adjacent silicon or carbon, resulting in a high field shift in the case of silicon. The ^{15}N NMR resonances of sila-PETNC (**4b**) with -45.3 (NO_2) and -190.4 (NH , br) are in the similar region as detected for the carbon analogue PETNC. Also, similar as found for PETNC,^{1b} coupling of the nitramine nitrogen with the acidic hydrogen is not observed, due to rapid exchange with the solvent deuterium. The ^{29}Si NMR resonance is strongly dependent on the number of carbamate moieties, respectively, nitrocarbamate units. Each additional unit attached to the sila-neo-pentane skeleton leads to a high field shift of the ^{29}Si NMR resonance, ranging from -0.4 to -15.5 ppm for the carbamates **1a–4a** and 0.4 to -9.8 ppm for the nitrocarbamates **1b–4b** ([Figure 1](#)).

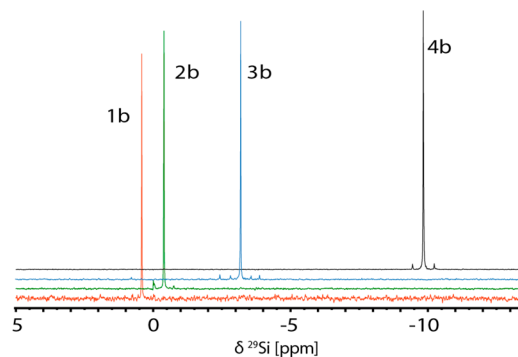


Figure 1. Influence of the substitution pattern to the ^{29}Si NMR resonance for the nitrocarbamates **1b**, **2b**, **3b**, and **4b** (in acetone- D_6).

The $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ NMR spectra of the nitrocarbamate containing a siloxane unit **5** are obviously very similar to those of nitrocarbamate **1b**, except the integral ratios in the ^1H NMR spectra. However, a major difference is detected in the ^{29}Si NMR resonances, due to the presence of an oxygen atom bound to silicon. Therefore, due to the deshielding effect of the electron withdrawing oxygen, the resonance of **5** is low field shifted to 3.5 ppm, compared to that of **1b** at 0.6 ppm.

In the vibrational spectra (IR and Raman) the N–H stretching vibrations for the carbamates **1a–4a** and nitrocarbamates **1b–4b** and **5** are found at $3450\text{--}3200\text{ cm}^{-1}$. The carbonyl $\text{C}=\text{O}$ stretching vibration of the carbamates **1a–4a** is detected in the region of $1703\text{--}1665\text{ cm}^{-1}$. Upon nitration, this vibration is shifted to higher wavenumbers at $1773\text{--}1735\text{ cm}^{-1}$ for the nitrocarbamates **1b–4b** and **5**. Additionally, the nitrocarbamates show the symmetrical and asymmetrical stretching vibrations of the nitro group, typically located at $1623\text{--}1604\text{ cm}^{-1}$ and $1336\text{--}1291\text{ cm}^{-1}$. The disiloxane unit in

5 shows a strong signal at 1076 cm^{-1} typical for the Si–O stretching vibration.⁸

Single-Crystal Structure Analysis. *Carbamate Structures.* Single crystals suitable for X-ray diffraction measurements of compounds **2a**, **3a**, and **4a** were obtained at ambient temperature from toluene, dioxane, and water, respectively. The carbamates **2a** (Figure 2), **3a** (Figure 3), and **4a** (Figure 4) show similar features regarding the symmetry around silicon.

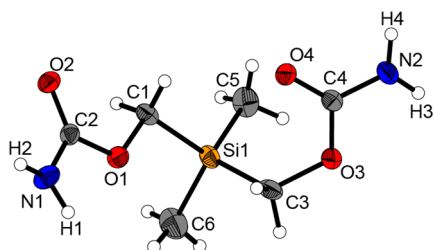


Figure 2. X-ray molecular structure of bis(carbamoylmethyl)dimethylsilane (**2a**). Selected atom distances [Å] and bond angles [deg]: Si1–C6 1.862(4), Si1–C5 1.867(4), Si1–C1 1.879(3), Si1–C3 1.893(3), O2–C2 1.225(3), O1–C2 1.347(3), O1–C1 1.467(4), N1–C2 1.346(4), N1–H2 0.94(4), N1–H1 0.89(3); C1–O1–C2–O2 2.3(4), C1–O1–C2–N1 179.6(2), C2–O1–C1–Si1 176.9(2).

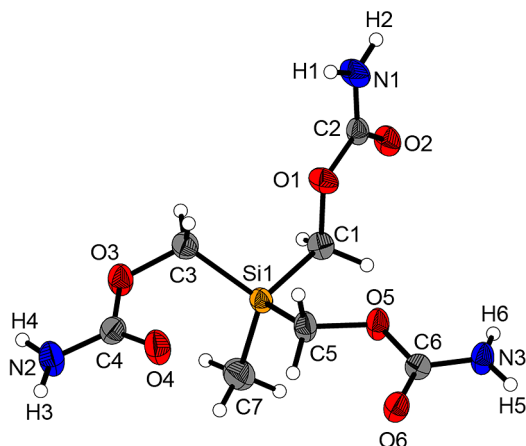


Figure 3. X-ray molecular structure of tris(carbamoylmethyl)methylsilane (**3a**) (dioxane solvate omitted). Selected atom distances [Å] and bond angles [deg]: Si–C7 1.854(2), Si–C1 1.879(2), Si–C5 1.883(2), Si–C3 1.884(2), O1–C2 1.351(2), O1–C1 1.450(2), O2–C2 1.221(2), N1–C2 1.324(3), N1–H2 0.83(2), N1–H1 0.86(2); C1–O1–C2–O2–3.6(3), C1–O1–C2–N1 177.58(17).

The silicon atom in the center of compounds **2a–4a** is surrounded by the methyl and methylene carbon units in an almost perfect tetrahedral sphere. The atom distances Si–C are in the range 1.854–1.893 Å; the C–Si–C bond angles with 102.70 – 115.68° differ only slightly from the ideal tetrahedral angle of 109.47° .

The carbamate units show a quite good planarity in all three compounds (**2a–4a**). The strongest misalignment is represented by the torsion angles C–O–C–N and C–O–C–O, and amounts are always less than 10° . The planarity can be interpreted as a delocalized π -system, which was confirmed regarding the quite short atom distances.^{1b} In all three compounds (**2a–4a**), the atom distance of the bridging oxygen atom and the carbonyl carbon is shortened to a distance between 1.347 and 1.357 Å. This implicates a substantial double bond character in between a C–O double bond (1.20

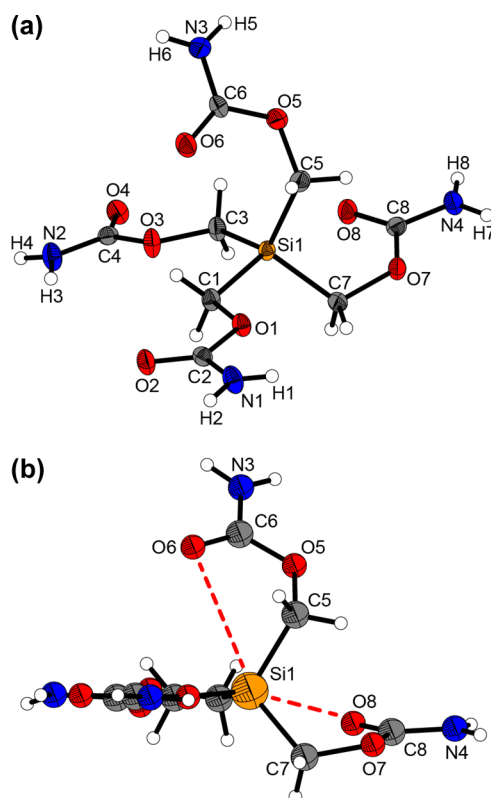


Figure 4. (a) X-ray molecular structure of tetrakis(carbamoylmethyl)silane (**4a**). Selected atom distances [Å] and bond angles [deg]: Si1–C1 1.890(2), O1–C2 1.357(2), O1–C1 1.456(2), O2–C2 1.225(2), N1–C2 1.324(2), N1–H1 0.84(2), N1–H2 0.92(2); C2–O1–C1–Si1 175.0(1), C3–Si1–C1–O1 176.7(1), C1–O1–C2–O2–1.5(2), C1–O1–C2–N1 178.4(1), C4–O3–C3–Si1 175.4(1), C1–Si1–C3–O3 14.2(1), C1–Si1–C7–O7 151.9(1), C3–Si1–C7–O7 94.6(1), C1–Si1–C5–O5 108.0(1), C3–Si1–C5–O5 8.9(1), C3–O3–C4–O4 7.5(2), C3–O3–C4–N2 173.8(1). (b) X-ray molecular structure of tetrakis(carbamoylmethyl)silane (**4a**). Red dotted lines represent attractive interactions between Si1...O6 (3.24 Å) and Si1...O8 (2.86 Å).

Å) and a single bond (1.43 Å). In accordance, the carbonyl C=O double bond is slightly enlarged to 1.225–1.221 Å. More so, the distance of the C–N bond value is 1.324–1.346 Å. Considering a standard C–N single bond with 1.47 Å, this indicates a strong double bond character. The free electron pair of the amino nitrogen seems to be delocalized all over the carbamate system, thus stabilizing it and favoring a planar conformation.

Surprisingly, all carbamate structures **2a–4a** show a noticeable short distance between the silicon atom in the center of the molecule and at least one carbonyl oxygen atom of the carbamate moieties.⁹ The compound tetrakis(carbamoylmethyl)silane (**4a**) shares this feature with two carbamate arms, ending up with a pseudo-hexavalent coordination shown in Figure 4. This conformation enforces an elongation of the Si–C–O bond angle (Table 1). Furthermore, the torsion angle Si–C–O–C of those two substitutes differs significantly, in sharp contrast with the two remaining carbamate arms developing one plane with the silicon center.

The carbamate moieties also define the majority of intra- and intermolecular interactions in compounds **2a–4a**. Especially, the hydrogen bonds between the amino hydrogens and

Table 1. Selected Bond Angles [deg], Torsion Angles [deg], and Atom Distances [Å] of Tetrakis(carbamoylmethyl)silane (**4a**)

	Si1–C1–O1–C2	Si1–C3–O3–C4	Si–C5–O5–C6	Si1–C7–O7–C8
bond angle Si–C–O	111.8	107.1	116.8	115.7
torsion angle Si–C–O–C	–5.0	4.6	74.0	–58.2
$d(\text{Si}\cdots\text{O})$	O2: 4.52	O4: 4.58	O6: 3.24	O8: 2.86

neighboring carbonyl oxygens are very strong. Consequently, the carbamate moieties attract each other and develop a layered structure of the molecules at the macromolecular view level.

Nitrocarbamate Structures. The crystal structures of nitrocarbamoylmethyltrimethylsilane (**1b**) and bis(nitrocarbamoylmethyl) dimethylsilane (**2b**) (Figures 5 and 6) display similar features as their previously discussed carbamate analogues **2a** and **3a** in regards to the almost identical Si–C atom distances and C–Si–C bond angles.

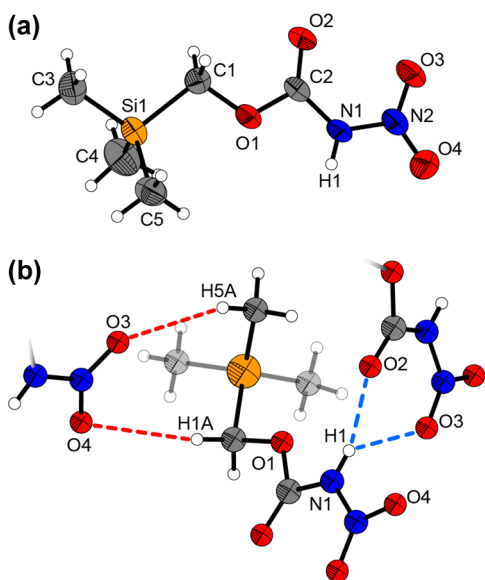


Figure 5. (a) X-ray molecular structure of nitrocarbamoylmethyltrimethylsilane (**1b**). Selected atom distances [Å] and bond angles [deg]: Si–C3 1.849(3), Si–C5 1.852(3), Si–C4 1.859(3), Si–C1 1.887(3), O1–C2 1.327(3), O1–C1 1.465(3), O2–C2 1.193(2), O4–N2 1.206(3), N2–O3 1.210(2), N2–N1 1.361(3), C2–N1 1.376(3), N1–H1 0.80(2), C3–Si–C5 111.37(13), C3–Si–C4 112.02(14), C5–Si–C4 111.49(14), C3–Si–C1 106.28(12), C5–Si–C1 108.36(13), C4–Si–C1 107.01(14); C1–O1–C2–O2 6.3(4), C1–O1–C2–N1 173.1(2), O4–N2–N1–C2 177.0(3), O3–N2–N1–C2 3.0(4), O2–C2–N1–N2 6.6(4), O1–C2–N1–N2 174.0(2), O4–N2–N1–H1 5.5(20), O3–N2–N1–H1 174.4(20). (b) Classical (blue dotted lines) and improper (red dotted lines) hydrogen bonds in **1b**.

The planarity of the nitrocarbamate moiety in compound **1b** is comparable to the planar carbamate structures in **2a–4a**. The N-hydrogen atom is part of strong classical hydrogen bonds to neighbored carbonyl and nitro functions. Additionally, multiple improper hydrogen bonds with carbon as hydrogen donor can be observed as shown in Figure 5. Overall, the nitrocarbamate functions align to each other and develop a layer-like structure.

The nitro groups of the bisnitrocarbamate **2b** are substantially out of plane, resulting in torsion angles C–N–N–O of 12.1°, 18.3°, and 20.5°. In comparison with the corresponding carbamate **2a**, the atom distances O–C and C=O are shortened upon nitration (from average 1.23 Å in the carbamate to 1.19 Å in the nitrocarbamate), while the

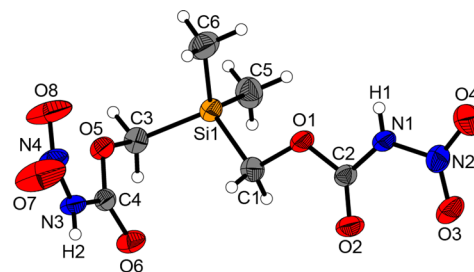


Figure 6. X-ray molecular structure of bis(nitrocarbamoylmethyl) dimethylsilane (**2b**). Selected atom distances [Å] and bond angles [deg]: Si–C5 1.851(2), Si–C1 1.883(2), O1–C2 1.318(2), O1–C1 1.462(2), O2–C2 1.188(2), O3–N2 1.205(2), N1–N2 1.371(2), N1–C2 1.383(2), N1–H1 0.77(2), O4–N2 1.211(2); C2–N1–N2–O3–12.1(3), C2–N1–N2–O4 167.0(2), C1–O1–C2–O2 4.9(3), C1–O1–C2–N1–174.2(2), N2–N1–C2–O2 7.5(3), N2–N1–C2–O1 173.4 (2).

distance C–N is enlarged (from 1.35 Å in **2a** to 1.38 Å in **2b**). The nitro groups in both structures (**1b** and **2b**) are located in *cis*-position with respect to the carbonyl group.

The sila-PETNC (**4b**) (Figure 7) crystallizes in the same tetragonal space group $P4_2/c$ as the carbon analogue PETNC.^{1b}

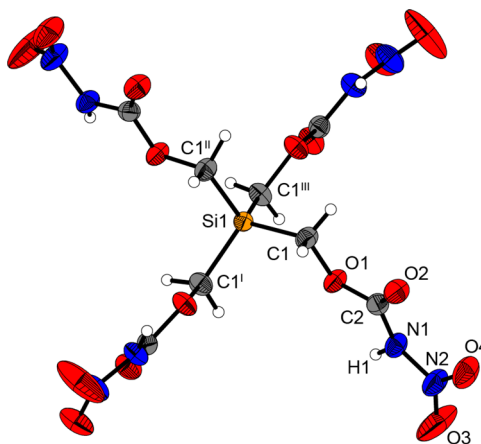


Figure 7. X-ray molecular structure of sila-PETNC (**4b**). Selected atom distances [Å] and bond angles [deg]: Si–C1 1.868(2), O1–C2 1.337(3), O1–C1 1.461(3), O2–C2 1.191(3), O3–N2 1.204(4), O4–N2 1.198(3), N1–N2 1.368(3), N1–C2 1.387(3), N1–H3 0.84(3); C1–O1–C2–O2 4.6(3), C1–O1–C2–N1 176.6(2), N2–N1–C2–O2 9.4(4), N2–N1–C2–O1 171.8(2), C2–N1–N2–O4 21.4(4), C2–N1–N2–O3 162.0(2), C2–O1–C1–Si1 170.7(1).

The unit cell contains two molecules, while the asymmetric unit is only represented by one-fourth of the molecule, induced by the 4-fold rotoinversion axis and two glide planes through the central silicon atom. The four nitrocarbamate units are involved in several strong classical hydrogen bonds, with the N–H linking to oxygen of a neighboring carbonyl and nitro functions. The strong intermolecular forces of sila-PETNC lead to a layer-like structure, comparable to the nitrocarbamates **1b** and **2b** and identical to the structure of PETNC.^{1b} The density of sila-

PETNC (1.70 g cm^{-3}) is lower than that of PETNC (1.77 g cm^{-3}), which can be explained by intramolecular reasons. The major difference in both structures is the atom distance between the center atoms and their surrounding methylene groups. In PETNC, the atom distance of the centering carbon to its closest neighbor amounts to 1.533 \AA , whereas the atom distance in sila-PETNC with $\text{Si1-C1} = 1.868 \text{ \AA}$ is much larger.^{1b}

The structure of the siloxane **5** consisted of one and a half asymmetric units; the structure shown in Figure 8 represents

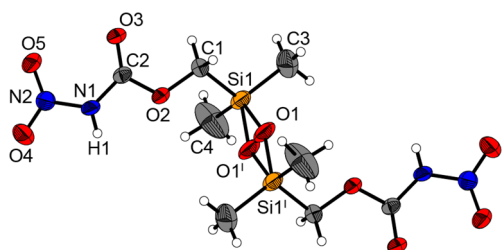


Figure 8. X-ray molecular structure of 1,3-bis(nitrocarbamoymethyl)-1,1,3,3-tetramethyldisiloxane (**5**). Selected atom distances [\AA] and bond angles [$^\circ$]: C1–O2 1.466(3), C1–Si1 1.867(3), C2–O3 1.190(2), C2–O2 1.318(2), C2–N1 1.388(3), C4–Si1 1.827(4), C3–Si1 1.837(3), N1–N2 1.377(3), N1–H3 0.81(2), N2–O4 1.213(2), N2–O5 1.216(2), O1–Si1¹ 1.613(4), O1–Si1 1.694(4); Si1¹–O1–Si1 147.6(2); O3–C2–N1–N2 14.9(4), O2–C2–N1–N2 165.5(2), C2–N1–N2–O4 169.5(2), C2–N1–N2–O5 11.8(3), N1–C2–O2–C1 178.46(18), Si1–C1–O2–C2 151.27(16).

the symmetrical unit created with the inversion center. The inversion center is located in between both silicon atoms Si1 and Si1¹; therefore, the bridging oxygen position gets split into O1 and O1¹ and is occupied half each. The atom distances Si1–O1 and Si1–O1¹ differ with 1.61 and 1.70 \AA , respectively, and lie between a Si–O single (1.77 \AA) and double (1.54 \AA) bond. Another characteristic is the obtuse angle Si1–O1–Si1¹ = 147.6° , which is in the range of other disiloxane structures of disilylether (144.1°), hexafluorodisiloxane (156°), and hexakis-(chloromethyl) disiloxane (161.9°).¹⁰

In comparison with the monosubstituted nitrocarbamate **1b**, the nitrocarbamate units of the disiloxane **5** deviate significantly from planarity, as is the case for the bisnitrocarbamate **2b**. Both nitrocarbamate units are located in antiperiplanar fashion to each other to avoid sterical hindrance.

Energetic Properties. The physical and energetic properties of the nitrocarbamates **1b–4b** and **5** were determined and are summarized in Table 2. Their thermal stabilities were measured with a differential scanning calorimetry (DSC) at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. The melting points increase with the number of nitrocarbamate groups from **1b** to **3b**, whereas sila-PETNC (**4b**) decomposes without melting. All nitrocarbamates are at least thermally stable up to $142 \text{ }^\circ\text{C}$ (onset temperature) with sila-PETNC having the highest decomposition point of $170 \text{ }^\circ\text{C}$. The sensitivities against friction and impact were evaluated according to BAM standards.¹¹ Both molecules with a single nitrocarbamate moiety per silicon atom, **1b** and **5**, can be classified as less sensitive against both friction and impact (FS = 360 N and IS = 35 J). One more nitrocarbamate attached to the silicon center in **2b** with an IS of 3 J can already be considered very sensitive toward impact, while being sensitive toward friction (192 N), but here always large-sized crystals (compared to the other nitrocarbamates) could be considered for measurements. Further nitrocarbamate groups in **3b** (FS = 240 N and IS = 5 J) and **4b** (FS = 240 N and IS = 3 J) somewhat surprisingly do not further enhance the sensitivity.

A very important property for energetic materials is their density, as it directly affects multiple performance parameters, such as detonation velocity and detonation pressure.¹¹ The density of the compounds **1b**, **2b**, and **4b** increases with the number of nitrocarbamate moieties attached to the silicon center up to 1.67 g cm^{-3} . As expected, sila-PETNC (**4b**) shows the highest detonation velocity and the highest detonation pressure.

Again, somewhat unexpected, dinitrocarbamate **2b** has the highest heat of explosion of all in this study that measured nitrocarbamates. The high amounts of gaseous product per mass of compounds **1b** and **2b** are based on the incomplete

Table 2. Physical and Energetic Properties of Nitrocarbamates **1b–4b** and **5**

	1b	2b	3b	4b	5
formula	$\text{SiC}_5\text{H}_{12}\text{N}_2\text{O}_4$	$\text{SiC}_6\text{H}_{12}\text{N}_4\text{O}_8$	$\text{SiC}_7\text{H}_{12}\text{N}_6\text{O}_{12}$	$\text{SiC}_8\text{H}_{12}\text{N}_8\text{O}_{16}$	$\text{Si}_2\text{C}_8\text{H}_{18}\text{N}_4\text{O}_9$
FW/g mol ⁻¹	192.25	296.27	400.29	504.31	370.42
IS ^a /J	35	3	5	3	35
FS ^b /N	360	192	240	240	360
N/%	14.57	18.91	20.99	22.22	15.13
Ω_{CO_2} ^c /%	-116.5	-64.8	-40.0	-25.4	-86.6
Ω_{CO} ^c /%	-74.9	-32.4	-12.0	0	-51.8
T_{melt} / $^\circ\text{C}$	50	100	133		68
T_{dec} / $^\circ\text{C}$	155	142	138	170	150
$\rho/\text{g cm}^{-3}$ (RT)	1.191	1.494	1.55 ^f	1.669	1.370
$\Delta_f H_m^{\text{od}}$ /kJ mol ⁻¹	-655.4	-900.5	-1134.7	-1364.0	-1585.8
$\Delta_f U^{\text{od}}$ /kJ kg ⁻¹	-3286.7	-2934.8	-2738.6	-2613.7	-4170.6
$\Delta_{\text{Ex}} Q^{\text{oe}}$ /kJ kg ⁻¹	-4359	-4729	-4654	-4671	-3628
p_{CJ} ^e /kbar	81	142	170	207	92
V_{det} ^e /m s ⁻¹	5393	6302	6698	7147	5438
V_0 ^e /L kg ⁻¹	707	691	702	669	631

^aImpact sensitivity. ^bFriction sensitivity. ^cOxygen balance assuming formation of CO and CO₂. ^dEnergy and enthalpy of formation calculated by the CBS-4 M method using Gaussian 09.¹² ^ePredicted heat of explosion, detonation pressure, detonation velocity, and volume of gaseous products calculated by using the EXPLO5 (Version 6.02) program package.¹³ ^fPredicted density.

Table 3. Physical and Energetic Properties (Conditions/Parameters as Table 2) of PETN, PETNC, Sila-PETN, and Sila-PETNC (4b)^{1b,2,3}

	PETN	PETNC	sil-PETN	sil-PETNC
formula	C ₅ H ₈ N ₄ O ₁₂	C ₉ H ₁₂ N ₈ O ₁₆	C ₄ H ₈ N ₄ O ₁₂ Si	C ₈ H ₁₂ N ₈ O ₁₆ Si
IS/J	3–4	8		3
FS/N	60–80	360		240
N/%	17.7	23.0	16.9	22.2
Ω _{CO₂} /%	+15.2	+3.3	+9.6	0
Ω _{CO} /%	–10.1	–26.2	–9.6	–25.4
T _{dec} /°C	165	196		170
T _{melt} /°C	143			
ρ/g cm ^{–3} (RT)	1.78	1.76		1.64
Δ _f H _m ^o /kJ mol ^{–1}	–561	–1311	–1568	–2240
Δ _{ex} U ^o /kJ kg ^{–1}	–5980	–4034		–4671
p _{CJ} /kbar	319	248		207
V _{det} /m s ^{–1}	8405	7742		7147
V ₀ /L kg ^{–1}	743	727		695

detonation reaction forced by the large negative oxygen balance of those compounds.

The physical and energetic properties of sila-PETNC (4b) were compared to the related materials (Scheme 1 and Table 3) as indicated in the Introduction. Concerning the sensitivities, sila-PETNC exhibits an impact sensitivity of 3 J and a friction sensitivity of 240 N, and therefore is expectedly much less sensitive compared to the nitrate ester sila-PETN (IS < 1 J, FS < 10 N). As expected from the empirical knowledge given from PETN and sila-PETN, the values for sila-PETNC are lower in regard to its carbon analogue PETNC and match roughly with the nitrate ester PETN. Considering the thermal stability, the carbon nitrocarbamate PETNC is more stable than sila-PETNC, which is again in the range of PETN (196 °C, 170 and 165 °C respectively).^{1b,2}

The heat of explosion of sila-PETNC is considerably higher compared to PETNC, which is explained with the very high molar heat of formation of silicon dioxide.¹⁴ Nevertheless, with regard to energetic parameters such as detonation velocity, detonation pressure, and amount of produced gas per mass, PETNC excels compared to its silicon analogue. The density of PETNC is remarkably higher than the density of sila-PETNC, which might be the main reason for this. Since both compounds crystallize in the identical tetragonal space group *P4₂1c*, the difference is found to be intramolecular as explained in the structure discussion. Apart from the density, the formation of silicon dioxide leads to a lower amount of gaseous products per mass. Silicon dioxide is a solid compound, and the molar mass of sila-PETNC exceeds that of PETNC, resulting in lower molar equivalents per mass. Furthermore, the formation of SiO₂, in contrast to CO₂, does not show a similar equilibrium with a gaseous mono-oxide (i.e., CO), but is converted quantitatively, which affects the oxygen balance Ω_{CO} negatively.¹¹

As an extension for the numbering system of Scheme 2, the compound with *x* = 0, i.e., tetramethylsilane, was considered also in this study in comparison to the carbon analogue neo-pentane. Using the well-known data from the literature for the enthalpies of formation for tetramethylsilane, SiMe₄, Δ_fH_m^o(SiMe₄(liq)) = –313.6 kJ mol^{–1}, and neo-pentane, CMe₄, Δ_fH_m^o(CMe₄(liq)) = –190.3 kJ mol^{–1},¹⁵ and the approximate densities for the liquid states of 0.65 g cm^{–3} (SiMe₄) and 0.6 g cm^{–3} (CMe₄), the enthalpies of combustion for both compounds using liquid oxygen as the oxidizer and an

oxygen balance of Ω = 0% were calculated,¹³ under the following conditions: chamber pressure = 70 bar, atmospheric pressure = 1 bar, isobaric combustion, and equilibrium expansion. As to be expected, the heat of combustion for SiMe₄ (Δ_{comb}H^o = –5469 kJ kg^{–1}, F:O ratio = 0.255:0.745) is slightly lower than that of neo-pentane (Δ_{comb}H^o = –5899 kJ kg^{–1}, F:O ratio = 0.22:0.78), due the higher atomic mass of silicon compared to carbon. On the other hand, for the heats of explosion of sila-PETNC and PETNC, the value of the silicon compound is more exothermic due to the higher enthalpy of formation in the absence of additional oxygen in the detonation process.

CONCLUSIONS

Several new silicon-centered carbamates and nitrocarbamates of the types Me_{4–x}Si(CH₂OCONH₂)_x and Me_{4–x}Si(CH₂OC(O)NHNO₂)_x (*x* = 1–4) and a siloxane based nitrocarbamate were synthesized and characterized in this study. The multistep synthesis starts from commercially available methyl chlorosilanes and silicon tetrachloride via the corresponding chloromethyl silanes, acetates, and sila-alcohols. Treatment with chlorosulfonyl isocyanate resulted in the formation of the sila-carbamates, which were nitrated to give the corresponding sila-nitrocarbamates. The new product class was examined in several aspects such as spectroscopic data, sensitivity, and structural behavior. Energetic materials combining silicon with the nitrocarbamate unit are substantially less sensitive compared to silicon nitrates or azides and stand out with high heats of explosion.

With the synthesis of sila-PETNC, a manageable silicon based energetic material was designed, which was compared to the related sila-PETN, PETN, and PETNC. It shows an extraordinary higher stability against outer stimuli compared to sila-PETN, and at the same time is superior to PETNC in terms of heat of explosion. Nevertheless, sila-PETNC is inferior to its carbon analogue PETNC and especially PETN in regards of detonation pressure, detonation velocity, and amounts of gaseous products.

EXPERIMENTAL SECTION

General. Solvents were dried and purified with standard methods. Trimethylsilyl methanol, bis(chloromethyl) dimethylsilane, trichloromethylsilane, silicon tetrachloride, and chlorosulfonyl isocyanate were commercially available and used without further purification. Raman

spectra were recorded in glass tube with a Bruker MultiRAM FT-Raman spectrometer with a Klaasstech DENICAFC LC-3/40 laser (Nd:YAG, 1064 nm, up to 1000 mW) in the range 4000–400 cm^{-1} . Relative intensity is given in percent. IR spectra were recorded with a PerkinElmer Spectrum BX-FTIR spectrometer coupled with a Smiths ATR DuraSample IRII device. Measurements were recorded in the range 4000–650 cm^{-1} . All Raman and IR spectra were measured at ambient temperature. NMR spectra were recorded with JEOL Eclipse and Bruker TR 400 MHz spectrometers at 25 °C. Chemical shifts were determined in relation to external standards Me_4Si (^1H , 399.8 MHz), (^{13}C , 100.5 MHz), (^{29}Si , 79.4 MHz), and MeNO_2 (^{14}N , 28.9 MHz; ^{15}N , 40.6 MHz). Mass spectrometric data were determined with a JEOL MStation JMS 700 spectrometer (DEI+, FAB–). Elemental analyses (CHN) were obtained with a Vario EL elemental analyzer.

The sensitivity data were acquired by measurements with a BAM drophammer and a BAM friction tester.¹¹ Melting and decomposition points were determined by differential scanning calorimetry (DSC) using a PerkinElmer Pyris6 DSC at a heating rate of 5 °C min^{-1} . Measurements were performed in closed aluminum containers against empty containers up to 400 °C via nitrogen flows.

The crystal structure data were obtained using an Oxford Xcalibur CCD diffractometer with a KappaCCD detector at low temperature (173 K, 123 K). Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was delivered by a Spellman generator (voltage 50 kV, current 40 mA). Data collection and reduction were performed using the CRYSTALIS CCD¹⁶ and CRYSTALIS RED¹⁷ software, respectively. The structures were solved by SIR92/SIR97¹⁸ (direct methods) and refined using the SHELX-97¹⁹ software, both implemented in the program package WinGX22.²⁰ Finally, all structures were checked using the PLATON software.²¹ Structures displayed with ORTEP plots are drawn with thermal ellipsoids at 50% probability level. Crystal data and refinement parameters are summarized in Table S1 (Supporting Information).

The theoretical calculations were achieved by using the Gaussian 09 program package¹² and were visualized by using GaussView 5.08.²² Optimizations and frequency analyses were performed at the B3LYP level of theory (Becke's B3 three parameter hybrid functional) by using the LYP correlation functional) with a cc-pVDZ basis set. After correction of the optimized structures with zero-point vibrational energies, the enthalpies and free energies were calculated on the CBS-4 M (complete basis set) level of theory.²³ The detonation parameters were obtained by using the EXPLO5 (V6.02) program package.^{13,24}

Caution! The higher substituted silicon containing nitrocarbamates (**2b**, **3b**, **4b**) are energetic materials and show sensitivities in the range of primary explosives! They should be handled with caution during synthesis or manipulation, and additional protective equipment (leather jacket, face shield, ear protection, Kevlar gloves) is strongly recommended.

Carbamoylmethyl Trimethylsilane (1a). To an ice-cooled solution of trimethylsilyl methanol (1.04 g, 10 mmol) in dry acetonitrile (20 mL) was added chlorosulfonyl isocyanate CSI (1.56 g, 11 mmol) slowly under dry nitrogen atmosphere. After 5 min at 0 °C, the ice bath was removed, and the colorless solution was stirred for another hour at ambient temperature. The reaction was cooled again with an ice-bath, water (10 mL) was added carefully, and the stirring was continued for 10 min at 0 °C. The organic solvent was removed in vacuo, and colorless oil precipitated out of the aqueous phase. After 24 h at 4 °C, the oily residue crystallized, and the colorless solid was collected by filtration. Recrystallization in boiling hexane yielded the pure product **1a** as colorless needles (1.45 g, 98%).

^1H NMR (CDCl_3): $\delta = 4.65$ (br, 2H, NH_2), 3.73 (s, 2H, $^2\text{J}(\text{H}, ^{29}\text{Si}) = 3.5 \text{ Hz}$, CH_2), 0.07 (s, 9H, $^2\text{J}(\text{H}, ^{29}\text{Si}) = 6.8 \text{ Hz}$, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 158.3$ (CO), 58.6 (CH_2), -3.1 ($^1\text{J}(\text{C}, ^{29}\text{Si}) = 52.5 \text{ Hz}$, CH_3). ^{15}N NMR (CDCl_3): $\delta = -310.5$ (NH_2). ^{29}Si NMR (CDCl_3): $\delta = 0.3$. Raman (800 mW): 2961 (40), 2902 (100), 1691 (8), 1440 (2), 1418 (9), 1114 (5), 1074 (10), 907 (10), 703 (10), 604 (77), 510 (5), 317 (12) cm^{-1} . IR: 3439 (w), 3330 (w), 3266 (w), 3209 (w), 2957 (w), 2905 (w), 1741 (w), 1687 (s), 1608 (m), 1436 (w), 1375 (s), 1265 (w), 1250 (m), 1219 (w), 1121 (w), 1061 (s), 904 (w), 841 (s), 785 (m), 719 (w), 701 (w) cm^{-1} . MS (DEI+) [m/z]: 147 [$\text{M} + \text{H}$] $^+$. $\text{C}_5\text{H}_{13}\text{NO}_2\text{Si}$ (147.25 g mol^{-1}): C 40.78, H 8.90, N 9.51. Found: C 40.73, H 8.90, N 9.51. Mp: 67 °C.

Nitrocarbamoylmethyl Trimethylsilane (1b). Acetic anhydride (10 mL) was slowly mixed with anhydrous nitric acid (>99.5%, 1 mL) at 0 °C and stirred for 1 h at that temperature. Carbamoylmethyl-trimethylsilane (**1a**, 294.5 mg, 2 mmol) was added in small portions, and the suspension was stirred for another 2 h at 0 °C. The clear solution was then poured onto ice/water (200 mL) with heavy stirring. The aqueous solution was extracted three times with ethyl acetate (3 \times 50 mL), and the combined organic phases were washed with water (2 \times 100 mL) and brine (80 mL). The organic phase was dried over magnesium sulfate, and the solvent was finally removed under reduced pressure. The oily, yellowish crude product was crystallized in boiling hexane, and 46 mg (12%) of **1b** was obtained as fine, colorless needles.

^1H NMR (CDCl_3): $\delta = 10.02$ (br, 1H, NH), 3.98 (s, 2H, $^2\text{J}(\text{H}, ^{29}\text{Si}) = 3.4 \text{ Hz}$, CH_2), 0.12 (s, 9H, $^2\text{J}(\text{H}, ^{29}\text{Si}) = 6.8 \text{ Hz}$, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 149.1$ (CO), 61.9 ($^1\text{J}(\text{C}, ^{29}\text{Si}) = 53.3 \text{ Hz}$, CH_2), -3.1 ($^1\text{J}(\text{C}, ^{29}\text{Si}) = 52.6 \text{ Hz}$, CH_3). ^{15}N NMR (CDCl_3): $\delta = -48.8$ (NO_2), -190.0 (NH , $^1\text{J}(\text{N}, \text{H}) = 98.1 \text{ Hz}$). ^{29}Si NMR (CDCl_3): $\delta = 0.6$; 0.4 (acetone- D_6). Raman (800 mW): 2963 (41), 2903 (100), 1747 (22), 1615 (8), 1431 (12), 1336 (29), 1283 (13), 1221 (6), 1013 (58), 859 (8), 703 (19), 604 (92), 424 (6), 318 (6), 277 (10), 235 (11) cm^{-1} . IR: 3232 (vs), 3132 (w), 3021 (w), 2960 (w), 2899 (vw), 1770 (w), 1743 (m), 1716 (w), 1612 (s), 1562 (w), 1523 (w), 1447 (m), 1429 (m), 1332 (m), 1283 (m), 1250 (m), 1220 (w), 1176 (s), 1101 (m), 1010 (w), 1001 (w), 935 (m), 842 (vs), 757 (m), 742 (s), 700 (m), 601 (m) cm^{-1} . MS (DEI+) [m/z]: 177.0 [$\text{M} - \text{CH}_3$] $^+$, 147.0 [$\text{C}_5\text{H}_{13}\text{NO}_2\text{Si}$] $^+$. $\text{C}_5\text{H}_{12}\text{N}_2\text{O}_4\text{Si}$ (192.25 g mol^{-1}): C 31.24, H 6.29, N 14.57. Found: C 31.31, H 6.22, N 14.69. Mp: 50 °C. Dec point: 155 °C. Sensitivities (BAM): impact 35 J; friction 360 N (grain size <100 μm).

Bis(carbamoylmethyl) Dimethylsilane (2a). To an ice-cooled solution of bis(hydroxymethyl) dimethylsilane (1.40 g, 11.6 mmol) in dry acetonitrile (30 mL) was added chlorosulfonyl isocyanate CSI (1.77 g, 12.5 mmol) slowly under dry nitrogen atmosphere. After 5 min at 0 °C, the ice bath was removed, and the colorless solution was stirred for another hour at ambient temperature. The reaction was cooled again with an ice-bath, water (10 mL) was added carefully, and the stirring was continued for 10 min at 0 °C. The organic solvent was removed in vacuo, and the aqueous residue started to tarnish. The aqueous phase was extracted with ethyl acetate (3 \times 50 mL), and the combined organic phases were washed with water (50 mL) and brine (50 mL). The organic solution was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The solid white product could be further purified by recrystallization in boiling toluene, yielding 0.9 g (38%) of **2a** as colorless plates. The yield can likely be improved by further concentrating the mother liquor.

^1H NMR (CDCl_3): $\delta = 4.64$ (br, 4H, NH_2), 3.84 (s, 4H, $^2\text{J}(\text{H}, ^{29}\text{Si}) = 3.4 \text{ Hz}$, CH_2), 0.16 (s, 6H, $^2\text{J}(\text{H}, ^{29}\text{Si}) = 7.0 \text{ Hz}$, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 158.0$ (CO), 56.2 ($^1\text{J}(\text{C}, ^{29}\text{Si}) = 58.2 \text{ Hz}$, CH_2), -5.9 ($^1\text{J}(\text{C}, ^{29}\text{Si}) = 53.1 \text{ Hz}$, CH_3). ^{14}N NMR (CDCl_3): $\delta = -152$ (NH_2). ^{29}Si NMR (CDCl_3): $\delta = -1.2$. Raman (800 mW): 2973 (51), 2935 (26), 2911 (100), 1665 (17), 1440 (18), 1418 (3), 1262 (9), 1218 (18), 1110 (5), 1088 (9), 1067 (19), 899 (33), 704 (6), 679 (12), 657 (8), 600 (65), 510 (11), 364 (5), 314 (6), 272 (11), 239 (6), 219 (14), 187 (3), 143 (5), 110 (52), 96 (19) cm^{-1} . IR: 3444 (w), 3407 (w), 3290 (w), 3212 (w), 2954 (vw), 2935 (vw), 2914 (vw), 1947 (vw), 1733 (w), 1686 (vs), 1627 (m), 1598 (w), 1430 (m), 1389 (s), 1367 (s), 1283 (w), 1257 (m), 1244 (m), 1217 (w), 1109 (m), 1085 (w), 1053 (vs), 986 (w), 898 (m), 846 (s), 811 (m), 786 (m), 773 (m), 727 (w), 702 (w), 677 (w), 656 (vw) cm^{-1} . MS (DEI+) [m/z]: 206.1 [M] $^+$, 191.1 [$\text{C}_6\text{H}_{13}\text{NO}_4\text{Si}$] $^+$, 132.1 [$\text{C}_5\text{H}_{13}\text{NO}_2\text{Si}$] $^+$. $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_4\text{Si}$ (206.27 g mol^{-1}): C 34.94, H 6.84, N 13.58. Found: C 34.98, H 6.89, N 13.38. Mp: 95 °C.

Bis(nitrocarbamoylmethyl) Dimethylsilane (2b). Anhydrous nitric acid (>99.5%, 3 mL) was slowly dropped into concentrated sulfuric acid (3 mL) at 0 °C. With strong stirring, bis-(carbamoylmethyl) dimethylsilane (**2a**, 309 mg, 1.5 mmol) was added in small portions, and the suspension was stirred for 1 h at 0 °C. The clear solution was then poured onto ice/water (200 mL) with heavy stirring. The aqueous solution was extracted three times with ethyl acetate (3 \times 50 mL), and the combined organic phases were

washed with water (2 × 100 mL) and brine (80 mL). The organic phase was dried over magnesium sulfate, and the solvent was finally removed under reduced pressure. The yellow, oily crude product was recrystallized in dichloromethane, and **2b** was obtained as chunky, colorless crystals (93 mg, 21%).

¹H NMR (DMSO-*D*₆): δ = 3.98 (s, 4H, CH₂), 0.16 (s, 6H, ²J (H,²⁹Si) = 7.0 Hz, CH₃). ¹³C{¹H} NMR (DMSO-*D*₆): δ = 150.0 (CO), 57.4 (¹J (C,²⁹Si) = 57.4 Hz, CH₂), -6.2 (¹J (C,²⁹Si) = 53.9 Hz, CH₃). ¹⁵N NMR (DMSO-*D*₆): δ = -41.7 (NO₂), -185.7 (NH). ²⁹Si NMR (DMSO-*D*₆): δ = -0.6; -0.4 (acetone-*D*₆). Raman (800 mW): 2970 (29), 2944 (39), 2905 (74), 1735 (38), 1623 (24), 1423 (19), 1382 (36), 1332 (13), 1006 (51), 897 (38), 750 (12), 707 (10), 677 (12), 604 (100), 464 (43), 416 (12), 309 (12), 230 (29) cm⁻¹. IR: 3224 (w), 3171 (w), 3124 (w), 3011 (w), 2819 (vw), 1764 (m), 1726 (s), 1615 (s), 1604 (s), 1554 (w), 1513 (vw), 1446 (m), 1415 (m), 1377 (m), 1321 (m), 1284 (s), 1264 (m), 1240 (s), 1223 (s), 1193 (vs), 1094 (w), 1069 (m), 1002 (s), 937 (m), 894 (m), 859 (m), 834 (s), 811 (m), 758 (m), 742 (m), 719 (w), 674 (vw) cm⁻¹. MS (DEI+) [*m/z*]: 295.3 [M]⁺, 147.2 [C₅H₁₁O₃Si]⁺. C₆H₁₂N₄O₈Si (296.27 g mol⁻¹): C 24.32, H 4.08, N 18.91. Found: C 24.24, H 4.36, N 19.06. Mp: 100 °C. Dec point: 142 °C. Sensitivities (BAM): impact 3 J; friction 192 N (grain size 100–500 μm).

Tris(carbamoylmethyl) Methylsilane (3a). To an ice-cooled solution of tris(hydroxymethyl)methylsilane (1.00 g, 7.3 mmol) in dry acetonitrile (50 mL) was added chlorosulfonyl isocyanate CSI (3.54 g, 25.0 mmol) slowly under dry nitrogen atmosphere. After 5 min at 0 °C, the ice bath was removed, and the colorless solution was stirred for another hour at ambient temperature. The reaction was cooled again with an ice-bath. Water (15 mL) was added carefully, and the stirring was continued for 10 min at 0 °C. The organic solvent was removed in vacuo. The aqueous phase was extracted with ethyl acetate (3 × 50 mL), and the combined organic phases were washed with water (50 mL) and brine (50 mL). The organic solution was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was obtained as colorless oil, which started to crystallize after a short period of time. The recrystallization in a mixture of dichloromethane and dioxane (50:50) yielded 520 mg (27%) of **3a** as colorless crystals.

¹H NMR (DMSO-*D*₆): δ = 6.45 (br, 6H, NH₂), 3.68 (s, 6H, ²J (H,²⁹Si) = 3.4 Hz, CH₂), 0.10 (s, 3H, ²J (H,²⁹Si) = 6.9 Hz, CH₃). ¹³C{¹H} NMR (DMSO-*D*₆): δ = 157.9 (CO), 53.7 (CH₂), -7.6 (CH₃). ²⁹Si NMR (DMSO-*D*₆): δ = -5.5. Raman (800 mW): 3261 (3), 3200 (9), 2973 (19), 2954 (3), 2945 (20), 2910 (100), 2861 (8), 1695 (20), 1633 (6), 1633 (6), 1444 (26), 1306 (12), 1265 (8), 1217 (14), 1121 (20), 1083 (10), 1071 (6), 1015 (9), 904 (40), 835 (30), 768 (5), 711 (10), 647 (4), 610 (41), 537 (6), 501 (19), 367 (12), 341 (3), 317 (9), 278 (7), 237 (3), 209 (6) cm⁻¹. IR: 3420 (m), 3332 (m), 3269 (m), 3207 (m), 2943 (vw), 2907 (w), 1779 (w), 1701 (vs), 1615 (s), 1429 (m), 1279 (m), 1246 (m), 1215 (m), 1121 (m), 1063 (vs), 903 (m), 840 (vs), 801 (m), 784 (s), 776 (s), 748 (m), 711 (m), 651 (m), 609 (m) cm⁻¹. MS (DEI+) [*m/z*]: 250.2 [C₇H₁₄N₂O₆Si]⁺, 191.2 [C₅H₁₁N₂O₄Si]⁺. C₇H₁₅N₃O₆Si (265.30 g mol⁻¹): C 31.69, H 5.70, N 15.84. found: C 31.80, H 5.65, N 15.60. Mp: 108 °C.

Tris(nitrocarbamoylmethyl) Methylsilane (3b). Anhydrous nitric acid (>99.5%, 1 mL) was slowly dropped into concentrated sulfuric acid (1 mL) at 0 °C. With strong stirring, tris(carbamoylmethyl) methylsilane (**3a**, 195 mg, 0.73 mmol) was added in small portions, and the suspension was stirred for 1 h at 0 °C. The clear solution was then poured onto ice/water (200 mL) with heavy stirring. The aqueous solution was extracted ice-cold three times with ethyl acetate (3 × 50 mL), and the combined organic phases were washed with water (2 × 100 mL) and brine (80 mL). The organic phase was dried over magnesium sulfate, and the solvent was finally removed under reduced pressure. The resulting colorless solid was dissolved in acetonitrile (1 mL), and large amounts of chloroform (50 mL) were added, resulting in precipitation of a colorless solid containing solvent molecules. The filtrated solid was again dissolved in acetonitrile, and the solvent was evaporated with time. After being dried under high vacuum, **3b** was obtained as colorless white solid (50 mg, 17%).

¹H NMR (acetone-*D*₆): δ = 13.31 (br, 3H, NH), 4.21 (s, 6H, ²J (H,²⁹Si) = 3.5 Hz, CH₂), 0.35 (s, 3H, ²J (H,²⁹Si) = 7.3 Hz, CH₃). ¹³C{¹H} NMR (acetone-*D*₆): δ = 150.4 (CO), 56.4 (¹J (C,²⁹Si) = 60.2 Hz, CH₂), -8.8 (¹J (C,²⁹Si) = 56.0 Hz, CH₃). ¹⁴N NMR (acetone-*D*₆): δ = -45 (NO₂); ²⁹Si NMR (acetone-*D*₆): δ = -3.2. Raman (800 mW): 3180 (6), 2975 (19), 2941 (54), 2910 (13), 1761 (36), 1612 (20), 1433 (18), 1333 (42), 1298 (22), 1234 (10), 1012 (100), 823 (6), 758 (8), 632 (17), 465 (20), 432 (7) cm⁻¹. IR: 3232 (w), 3172 (w), 3028 (vw), 2773 (vw), 1757 (m), 1609 (s), 1445 (m), 1422 (m), 1322 (m), 1286 (m), 1260 (w), 1233 (m), 1201 (m), 1163 (vs), 1091 (m), 1009 (m), 999 (m), 935 (m), 863 (m), 822 (m), 788 (m), 742 (m) cm⁻¹. MS (FAB-) [*m/z*]: 399.3 [M-H]⁻. C₇H₁₂N₆O₁₂Si (400.29 g mol⁻¹): C 21.00, H 3.02, N 20.99; C 21.01, H 3.08, N 20.69. Mp: 133 °C. Dec. point: 138 °C. Sensitivities (BAM): impact 5 J; friction 240 N (grain size <100 μm).

Modified Synthesis for Tetrakis(chloromethyl)silane Si-(CH₂Cl)₄. Into a stirred mixture consisting of tetrachlorosilane (11.5 g, 67.7 mmol), bromochloromethane (52.4 g, 405 mmol), and THF (150 mL) was added a pre-cooled *n*-butyl lithium solution in *n*-hexane (113 mL, 2.5 M, 283 mmol of *n*-BuLi) within 4 h. The mixture and also the *n*-butyl lithium solution were cooled to -78 °C with an ethanol/dry ice cooling. After the addition was complete, the reaction mixture was stirred at -78 °C for a further 5 h and then warmed to 20 °C overnight. The mixture was concentrated under reduced pressure, and the resulting precipitate was removed by filtration and washed with *n*-hexane. This procedure was repeated one more time to remove most of the THF, and the concentrated solution was cooled in the refrigerator overnight. A colorless crystalline crude product precipitates, and is filtered off and washed with *n*-hexane to yield crude tetrakis(chloromethyl)silane. Recrystallization from small amounts of boiling *n*-hexane yielded 3.95 g (26%) of the pure Si(CH₂Cl)₄ as fine colorless needles.

Tetrakis(carbamoylmethyl)silane (4a). To an ice-cooled solution of tetrakis(hydroxymethyl) silane (0.17 g, 1.1 mmol) in dry acetonitrile (15 mL) was added chlorosulfonyl isocyanate CSI (0.68 g, 4.8 mmol) slowly under dry nitrogen atmosphere. After 5 min at 0 °C, the ice bath was removed, and the colorless solution was stirred for another hour at ambient temperature. The reaction was cooled again with an ice-bath. Water (7 mL) was added carefully, and the stirring was continued for 10 min at ambient temperature. The organic solvent was removed in vacuo, and ice was added to the aqueous phase. With the help of ultrasound, **4a** precipitated out of the cold solution as colorless, pure solid (252 mg, 70%).

¹H NMR (DMSO-*D*₆): δ = 6.45 (s, 8H, NH₂), 3.70 (s, 8H, CH₂). ¹³C{¹H} NMR (DMSO-*D*₆): δ = 158.1 (CO), 53.4 (¹J (C,²⁹Si) = 64.5 Hz, CH₂). ²⁹Si NMR (DMSO-*D*₆): δ = -15.5. Raman (800 mW): 3331 (12), 3284 (2), 2969 (65), 2940 (100), 2860 (7), 1703 (49), 1593 (10), 1446 (55), 1271 (20), 1235 (19), 1120 (29), 1076 (22), 908 (76), 753 (25), 650 (6), 616 (20), 515 (8), 231 (21) cm⁻¹. IR: 3435 (m), 3334 (w), 3199 (vw), 2933 (vw), 1691 (s), 1592 (m), 1435 (w), 1376 (vs), 1269 (w), 1227 (w), 1120 (w), 1060 (vs), 895 (m), 837 (vw), 816 (m), 780 (s), 674 (vw) cm⁻¹. MS (DEI+) [*m/z*]: 250.2 [C₆H₁₂N₃O₆Si]⁺. C₈H₁₆N₄O₈Si (324.32 g mol⁻¹): C 29.63, H 4.97, N 17.28. Found: C 29.34, H 4.96, N 17.05. Mp: 138 °C.

Tetrakis(nitrocarbamoylmethyl)silane (Sila-PETNC, 4b). A 0.19 g (0.6 mmol) portion of tetrakis(carbamoylmethyl) silane (**4a**) was solved in concentrated sulfuric acid (2 mL) in small portions at 0 °C. With strong stirring, anhydrous acid (>99.5%, 2 mL) was added dropwise with caution to the clear solution. After 1 h at 0 °C, the solution was poured onto ice/water (150 mL) with heavy stirring, and a colorless precipitate formed. After filtering the colorless solid and washing with cold water, sila-PETNC was obtained as pure product (240 mg, 79%).

¹H NMR (acetone-*D*₆): δ = 13.40 (br, 4H, NH), 4.31 (s, 8H, ²J (H,²⁹Si) = 3.5 Hz, CH₂). ¹³C{¹H} NMR (acetone-*D*₆): δ = 150.7 (CO), 55.6 (¹J (C,²⁹Si) = 62.3 Hz, CH₂). ¹⁵N NMR (acetone-*D*₆): δ = -45.3 (NO₂), -190.4 (NH, br). ²⁹Si NMR (acetone-*D*₆): δ = -9.8. Raman (800 mW): 3178 (5), 2968 (17), 2935 (43), 2844 (3), 1773 (36), 1609 (15), 1433 (15), 1335 (41), 1302 (22), 1228 (13), 1180 (6), 1099 (3), 1014 (100), 952 (4), 853 (3), 822 (9), 748 (5), 489 (2),

646 (10), 469 (20), 432 (9) cm^{-1} . IR: 3236 (w), 3174 (m), 3024 (w), 2934 (vw), 2774 (vw), 1775 (m), 1607 (s), 1445 (m), 1423 (m), 1323 (m), 1291 (s), 1233 (m), 1180 (vs), 1165 (vs), 1014 (m), 1000 (m), 948 (m), 820 (m), 794 (m), 760 (m), 743 (s), 718 (m), 644 (s) cm^{-1} . MS (FAB⁻) [m/z]: 503.3 [$M - H$]⁻. $\text{C}_8\text{H}_{12}\text{N}_8\text{O}_{16}\text{Si}$ (504.31 g mol^{-1}): C 19.05, H 2.40, N 22.22. Found C 18.94, H 2.56, N 21.93. Dec point: 170 °C. Sensitivities (BAM): impact 3 J; friction 240 N (grain size <100 μm).

1,3-Bis(nitrocarbamoylmethyl)-1,1,3,3-tetramethyldisiloxane (5). Anhydrous nitric acid (>99.5%, 1 mL) was slowly dropped into concentrated sulfuric acid (1 mL) at 0 °C. With strong stirring, carbamoylmethyltrimethylsilane (**1a**, 147 mg, 1.0 mmol) was added in small portions, and the suspension was stirred for 1 h at 0 °C. The clear solution was then poured onto ice/water (200 mL) with heavy stirring. The aqueous solution was extracted ice-cold three times with ethyl acetate (3 × 50 mL), and the combined organic phases were washed with water (3 × 30 mL) and brine (30 mL). The organic phase was dried over magnesium sulfate, and the solvent was finally removed under reduced pressure. The crude, yellow gum was recrystallized from boiling toluene, and the disiloxane **5** was obtained as fine colorless needles (85 mg, 46%).

¹H NMR (CDCl_3): δ = 10.58 (br, 2H, NH), 3.96 (s, 4H, CH_2), 0.20 (s, 12H, ²J (H, ²⁹Si) = 6.8 Hz, CH_3). ¹³C{¹H} NMR (CDCl_3): δ = 149.3 (CO), 61.2 (¹J (C, ²⁹Si) = 63.9 Hz, CH_2), -1.2 (¹J (C, ²⁹Si) = 62.4 Hz, CH_3). ¹⁵N NMR (CDCl_3): δ = -48.2 (NO_2), -190.1 (NH, ¹J (N, H) = 97.5 Hz). ²⁹Si NMR (CDCl_3): δ = 3.5. Raman (800 mW): 2967 (53), 2933 (30), 2901 (100), 1748 (37), 1620 (10), 1451 (4), 1429 (17), 1415 (4), 1332 (44), 1282 (18), 1230 (8), 1011 (99), 756 (8), 667 (19), 522 (24), 459 (33), 427 (7), 324 (5), 294 (21), 205 (1) cm^{-1} . IR: 3236 (vw), 3154 (w), 3033 (w), 2961 (vw), 2933 (vw), 2771 (vw), 1747 (s), 1606 (s), 1554 (vw), 1449 (m), 1330 (m), 1280 (m), 1261 (m), 1228 (m), 1172 (vs), 1076 (vs), 1009 (m), 937 (m), 846 (m), 798 (vs), 753 (m), 714 (m) cm^{-1} . MS (DEI⁺) [m/z]: 281.2 [$\text{C}_8\text{H}_{21}\text{N}_2\text{O}_3\text{Si}_2$]⁺, 135.1 [$\text{C}_4\text{H}_{11}\text{O}_3\text{Si}$]⁺. $\text{C}_8\text{H}_{20}\text{N}_4\text{O}_9\text{Si}_2$ (370.42 g mol^{-1}): C 25.94, H 4.90, N 15.13. Found: C 26.03, H 4.88, N 15.04. Mp: 68 °C. Dec point: 150 °C. Sensitivities (BAM): impact 35 J; friction 360 N (grain size <100 μm).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00602.

Further crystallographic and calculation details (PDF)
X-ray crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: tmk@cup.uni-muenchen.de.

Notes

The authors declare no competing financial interest.

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DEDICATION

This paper is dedicated to Professor Karl O. Christe, our friend and colleague and an outstanding chemist, on the occasion of his 80th birthday.

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