CHEMISTRY OF
MATERIALS
Article

Chem. Mater. **2009,** *21,* 3941–3949 3941
DOI:10.1021/cm9006958

Cyclic Silylcarbodiimides as Precursors for Porous Si/C/N Materials: Formation, Structures, and Stabilities

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Received March 11, 2009. Revised Manuscript Received July 14, 2009

Exchange reactions of bis(trimethylsilyl)carbodiimide (BTSC) with diorganodichlorosilanes were investigated with the aim to synthesize substitution products of the types $R_2SiCl(NCNSiMe_3)$, $R_2Si(NCNSiMe_3)_2$, and $[R_2Si(NCN)]_n$ (R = Me, Ph, PhCH$_2$, and Vin), which can be used as precursors for Si/C/N materials with tuned pore structures. Extensive ^{29}Si NMR spectroscopic investigations indicated that complex product mixtures containing several of the mentioned compounds are formed, independent of the starting materials and reaction conditions. The relative stabilities of the cyclic silylcarbodiimides of ring sizes $4n$ with $n = 2-6$ were calculated with DFT methods and compared, also considering the respective isomeric cyanamides with rings containing $2n$ atoms. According to these quantum chemical studies, the cyclic tetramer $[Ph_2Si(NCN)]_4$ was predicted to be the most stable among the phenyl-substituted rings. It was experimentally synthesized via pyridine-catalyzed reactions of Ph_2SiCl_2 with BTSC, isolated as $[Ph_2Si(NCN)]_4\cdot(\text{dioxane})_2$ and structurally analyzed. In the course of attempts to selectively prepare oligosilylcarbodiimides from cyclosilazanes, high-quality crystals of hexaphenylcyclotrisilazane $[Ph_2Si\text{-}NH]_3$ were obtained and characterized by X-ray single crystal structure analysis.

1. Introduction

The NCN group, existing in the two tautomeric forms $\mathrm{-N{=}C{=}N-}$ (carbodiimide) and $\mathrm{>N-C{\equiv}N}$ (cyanamide), can be considered as a pseudochalcogenide,[1-4] due to its oxygen-like behavior in molecular compounds, oligomers, polymers, and ionic solids. In analogy to the well established concept of pseudohalogenides, this pseudochalcogenide concept was suggested already in 1970 by Köhler,[1a] based on the pseudoelement model and on the more than 80 year old Grimm's rule, also called hydride replacement law,[5] which was discussed in text books and further developed,[6] partly with respect to the isolobal concept.

For silyl carbodiimides, such as bis(trimethylsilyl)-carbodiimide, (BTSC) **1**, a further special analogy is evident, namely, a pseudowater concept: The electronegativity (EN) of the NCN group is very close to that of the oxygen atom (3.36 for NCN[7] versus 3.44 for oxygen[8]), and, on the other hand, the EN of the trimethylsilyl group[9] (2.25) resembles that of the hydrogen atoms[8] (2.20), resulting in striking similarities of BTSC and H_2O, symbolized in Figure 1.

One of the applications of this concept is the synthesis of silylcarbodiimide polymers in analogy to the well-known polysiloxanes, that is, linear and cyclic oligomers of the type $[R_2SiO]_n$. Thus, dichlorosilanes such as Me_2SiCl_2 were transformed into oligomers and polymers, which were used as precursors for Si/C/N ceramics.[10] Independent of the dichlorosilanes used as starting

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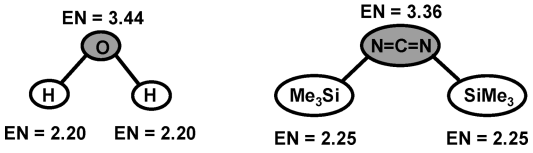
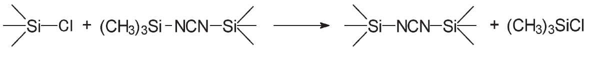


Figure 1. Schematic comparison of the water molecule with bis(trimethylsilyl)carbodiimide (BTSC, **1**).

materials, the general reaction can be described by the following equation:

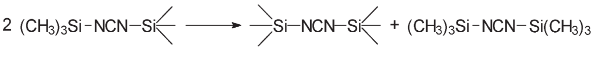
$$nR_2SiCl_2 + n(CH_3)_3Si—NCN—Si(CH_3)_3 \xrightarrow{\text{pyridine}} [R_2Si(NCN)]_n + 2n(CH_3)_3SiCl$$

Analogous reactions with trichlorosilanes yield cross-linked oligomers and polymers, typically in the form of gels (see below). These processes can involve two possible condensation steps, forming cyclic and linear silylcarbodiimides and chlorotrimethylsilane or BTSC as volatile molecular side products:



(a)

and

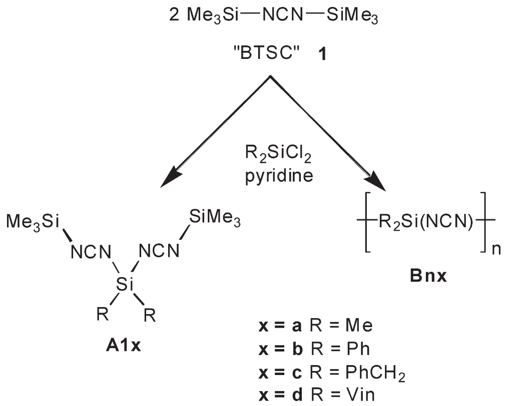


(b)

However, due to the fact that BTSC is present in the reaction mixtures as a starting material, it is difficult to prove that condensations of type (b) really take place. If they take place, it remains an open question how significant they can contribute to cross-linking under moderate temperatures. Thus, one of the original goals of the present study was to answer this question by synthesizing carbodiimidosilanes of the type $R_2Si(NCNSiMe_3)_2$. These compounds should allow a chlorine-free condensation reaction to yield linear and/or cyclic silylcarbodiimides.

Interestingly, it turned out that $SiCl_4$ and almost all trichlorosilanes form sols and gels very similar to the well-known oxide systems, which are usually obtained by hydrolysis of alkoxides.[11] The carbodiimide sol−gel systems show numerous analogies to the silica based gels. Among these parallels is the formation of monodisperse spherical particles similar to the so-called Stöber process,[12] the rheological behavior at the sol−gel transition,[13] the possibility to form amorphous microporous materials suitable for membrane fabrication,[14] and the formation mechanism of the polymeric network structure by substitution and condensation reactions.[4,15] Furthermore, the BTSC-based sol−gel process was expanded to B/C/N materials[16] and used for the synthesis of mesoporous organic−inorganic composite materials.[17]

Scheme 1



Only very few molecular silylcarbodiimides have been structurally analyzed. These include BTSC itself,[10,18] bis(triphenylsilyl)carbodiimide $Ph_3Si(NCN)SiPh_3$,[19] bis[tris(2-(diphenylmethylsilyl)ethyl)silyl]carbodiimide $[(Ph_2MeSiCH_2CH_2)_3Si]NCN[Si(CH_2CH_2SiMePh_2)_3]$,[20] and $[Me_2Si(NCN)]_4$.[10,21]

In this paper, we report on condensation and cross-linking reactions of BTSC with dichlorosilanes, focusing on the formation and size distribution of cyclic carbodiimide species. Reaction products were thoroughly analyzed by ^{29}Si NMR spectroscopy indicating the formation of different oligomers. These experimental results are accompanied and interpreted by DFT calculations on the stability of the cyclic carbodiimides of different ring sizes and their corresponding cyanamide tautomers, including also diphenyl-substituted derivatives and the influence of different solvents.

2. Results and Discussion

2.1. Exchange Reactions between BTSC and Diorganodichlorosilanes. As mentioned in the introduction, we planned to prepare silylcarbodiimides of the type $R_2Si(NCNSiMe_3)_2$ (type **A**, Scheme 1) as monomers for a controlled, chlorine-free synthesis of linear and cyclic silylcarbodimiides via condensations of the type shown in equation b. Similarly, monomers derived from trichlorosilanes, that is, silanes with the structure $RSi(NCNSiMe_3)_3$, would allow an analogous preparation of polymers as precursors for porous Si/C/N materials. A comprehensive literature search indicated that there are

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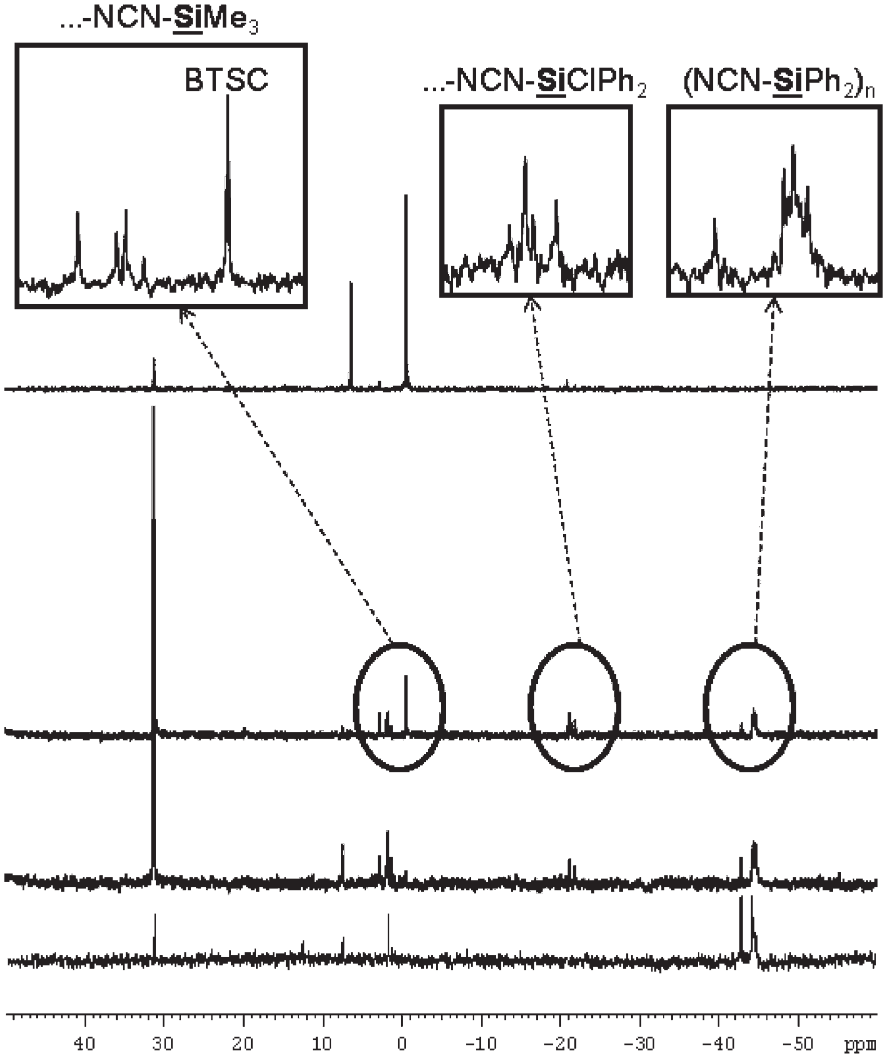


Figure 2. ^{29}Si NMR spectra of the mixture **Bnb**, i.e., pyridine catalyzed reactions of Ph_2SiCl_2 (at 6.2 ppm) with BTSC (at -0.8 ppm) in THF (from top to bottom: after 10 h, 20 h, 30 h at 60 °C and after intermediate removal of both the solvent and Me_3SiCl (at 30.9 ppm) and heating again for 10 h).

no silylcarbodiimides of the type $R_2Si(NCNSiMe_3)_2$ known.

In an initial attempt, the carbodiimide source BTSC **1** was reacted with a selection of diorganodichlorosilanes in a ratio of 2:1 to form monomers such as **A1** as shown in Scheme 1. These reactions were performed in tetrahydrofuran (THF) at 60 °C in the presence of pyridine as catalyst.

To monitor the progress of the exchange reactions between the trimethylsilyl groups of BTSC with the diorganodichlorosilanes, ^{29}Si NMR spectra of the reaction solutions were recorded in 10 h intervals of heating. In each case a signal at δ_{Si} 30.9 ppm indicated the formation of Me_3SiCl, and the intensity of the Me_3Si-NCN-$SiMe_3$ signal (at -0.8 ppm) decreased (Figure 2). Regarding $R_2\mathit{Si}$-groups the spectra exhibited both noticeably high-field shifted signals corresponding to $R_2\mathit{Si}(NCNR')_2$ environments ($R' = -SiMe_3, -SiR_2-NCN$ ..., $-SiR_2Cl$; for R = Me with at least four peaks between -20.7 and -22.6 ppm, for R = Ph with at least four peaks between -42.7 and -44.8 ppm, for R = $PhCH_2$ with at least four peaks between -29.6 and -33.1 ppm, and for R = Vin with at least three peaks between -46.0 and -48.3 ppm) and signals about midway between the former and the ^{29}Si NMR shift of the starting silane R_2SiCl_2, hence indicating the presence of $R_2\mathit{Si}Cl(NCNR')$ moieties. The intensity of the latter signals decreased during the course of the reaction (Figure 2).

In addition to a variety of products bearing $R_2Si(NCN\mathit{Si}Me_3)$ moieties (e.g., **A1x** and **A2x** in Scheme 2), indicated by ^{29}Si NMR signals at around 0 ppm, even more superimposed signals in the $R_2\mathit{Si}(NCNR')_2$ region are caused by the formation of oligomeric and polymeric products $[R_2Si(NCN)]_n$ (such as **B3x** and **B4x**). Since the reaction of BTSC with different diorganodichlorosilanes in the ratio 2:1 led to the formation of oligomeric products rather than selectively providing access to the aimed monomers **A1x**, the conversions were repeated with a large excess of BTSC. Unfortunately, similar complex reaction mixtures were obtained and the target monomers $R_2Si(NCNSiMe_3)_2$ could not be isolated.

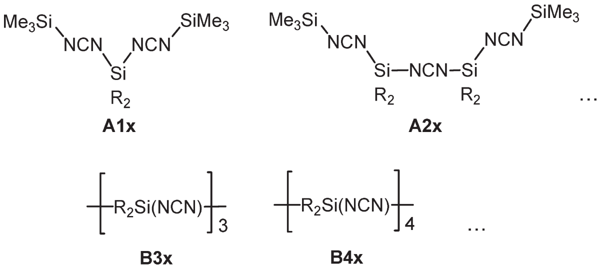
Further reactions were performed in the ratio 1:1 to deliberately synthesize oligomers **Bnx**. These reactions were also monitored ^{29}Si NMR spectroscopically in

Table 1. ^{29}Si NMR Shifts (δ_{Si} in ppm, THF Solution) Found after 20 h at 60 °C^{a}

mixture	R	δ ^{29}Si
Bna	Me	−20.9, −21.6, −22.5, −22.8, −23.4
Bnb	Ph	−42.9, −44.2, −44.4, −44.7
Bnc	$PhCH_2$	−29.8, −32.4, −32.8
Bnd	Vin	−46.6, −48.5

[a] The signals for BTSC (at −0.8 ppm), chlorotrimethylsilane (at 30.9 ppm), and the respective dichlorosilane are not included.

Scheme 2



intervals of 10 h. Instead of the straightforward formation of the aimed products **Bnx**, the spectra recorded after 20 h and after 30 h indicated a state of equilibrium between species such as Me_3SiCl (at 30.9 ppm), **Anx** (R′-NCN-*Si*Me_3 at ca. 0 ppm, R′-NCN-*Si*Ph_2-NCN-R′ at ca. −40 to −45 ppm), **Bnx** (at ca. −40 to −45 ppm), and compounds comprising R_2*Si*Cl(NCN-R′) moieties (at ca. −20 to −25 ppm). Upon removal of both the solvent and the Me_3SiCl formed under reduced pressure, followed by addition of THF and some drops of pyridine, the equilibrium was shifted further toward the chlorine free products such as **Bnx** (Figure 2). Table 1 shows the ^{29}Si NMR shifts of several mixtures **Bnx** depending on different diorganodichlorosilanes as starting materials.

Several attempts to separate and isolate certain linear and/or cyclic oligomers from the obtained mixtures using HPLC and various organic solvents and solvent mixtures as eluents were not successful so far. One of the problems encountered is the sensitivity of the silanes toward moisture, which makes it difficult to find an appropriate stationary phase (column material).

Although the ring size of the cyclic silylcarbodiimides formed may vary in a large range, the formation of both dimeric silyl carbodiimide rings $[R_2Si(NCN)]_2$ and cyanamide isomers $[R_2SiN(CN)]_n$ is very unlikely: By quantum chemical calculations the latter were shown to be distinctly less stable than the corresponding carbodiimides $[R_2Si{-}N{=}C{=}N]_n$, and the di- and trimeric carbodiimides are also significantly less stable than larger carbodiimide ring systems (see section 2.2). In addition, dimers $[R_2Si(NCN)]_2$ can be expected to exhibit remarkably downfield shifted ^{29}Si NMR signals, which, in contrast to the above-mentioned ^{29}Si NMR signals, have not been observed within the s/n limits of our NMR experiments.

2.2. Theoretical Estimation of Cyanamide and Carbodiimide Ring Stabilities. Along with the chain polymers, the reaction of BTSC with diorganodichlorosilanes may yield a variety of cyclic oligomers, the cyclotetramers $[R_2Si(NCN)]_4$ being only one out of many alternatives. Moreover, the possible tautomerization may lead to the formation of different carbodiimide and cyanamide derivatives. By comparing the theoretically calculated relative energies of a variety of model carbodiimide and cyanamide cyclic molecules, the thermodynamic preference of different product species upon cross-linking of the BTSC with diorganodichlorosilanes was estimated.

DFT calculations were performed for dimeric up to hexameric cyclic carbodiimides and for di-, tri-, and tetrameric cyclic cyanamides, symmetrically substituted with R = R′ = Ph, Vin or having two different substituents at the silicon atom (R = H, R′ = Me, Vin, NCNH) (Scheme 3).

To allow for comparison, the single point energies, calculated for the above model compounds, E_{oligomer}, have been divided by the number of the monomer units constituting the ring, N_{monomers}, and the calculated reference energy of the biradical fragment unit $RR'Si^{\bullet}(NCN)^{\bullet}$, E_{ref}, has been subtracted as a threshold energy, giving a reduced relative energy, $E_{\text{reduced}} = E_{\text{oligomer}}/N_{\text{monomers}} - R_{\text{ref}}$ (Figure 3).

The results revealed that (i) cyclodimers are thermodynamically less stable than larger rings for both carbodiimide and cyanamide rings, and (ii) carbodiimide rings are in general energetically more favorable than cyanamide rings. The lability of the dimeric ring is caused by the strong deviation of the N−Si−N angle from the tetrahedral one: The equilibrium angle for the tetrahedrally coordinated silicon atom corresponds to nearly 109°; in the dimeric ring systems this angle is reduced to 102°, compared to 107−110° for larger rings. The energy difference between tri-, tetra-, penta-, and hexameric rings in the case of the carbodiimides is quite small (< 1 kcal/mol), implying that from the thermodynamic point of view there is no significant preference for smaller or bigger rings or even chains (the latter being the limiting case of infinitely large rings). An exception is observed for the diphenyl-substituted derivatives. In this system a pronounced energetic minimum is found for the tetrameric ring molecule $[Ph_2Si(NCN)]_4$, as demonstrated in Figure 3.

The lability of the cyclic silylcyanamide compared to their silylcarbodiimide tautomers might be explained by the pronounced charge separation in the silylcyanamide molecule, as demonstrated for the monomer model molecule (Figure 4).

This charge separation is reduced in the silylcarbodiimide tautomer, due to back-bonding of the lone electron pair of nitrogen to the empty 3d-orbitals of silicon or to the vicinal σ^*-orbital of the silyl group. This kind of back-bonding is not possible in the alkylcarbodiimides, so that the latter is less stable in comparison with alkylcyanamides. The calculated electron localization functions (ELF)[22] for the model alkylcarbodiimide and silylcarbodiimide demonstrate the peculiarities of the electronic structure in the absence and in the presence of the

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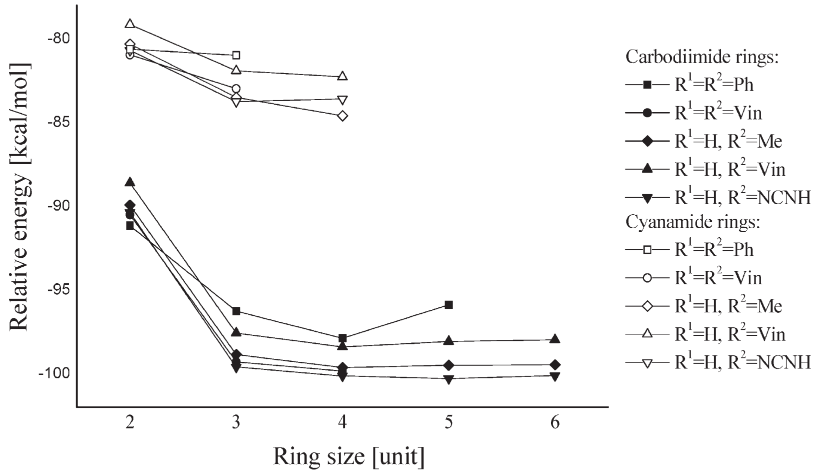
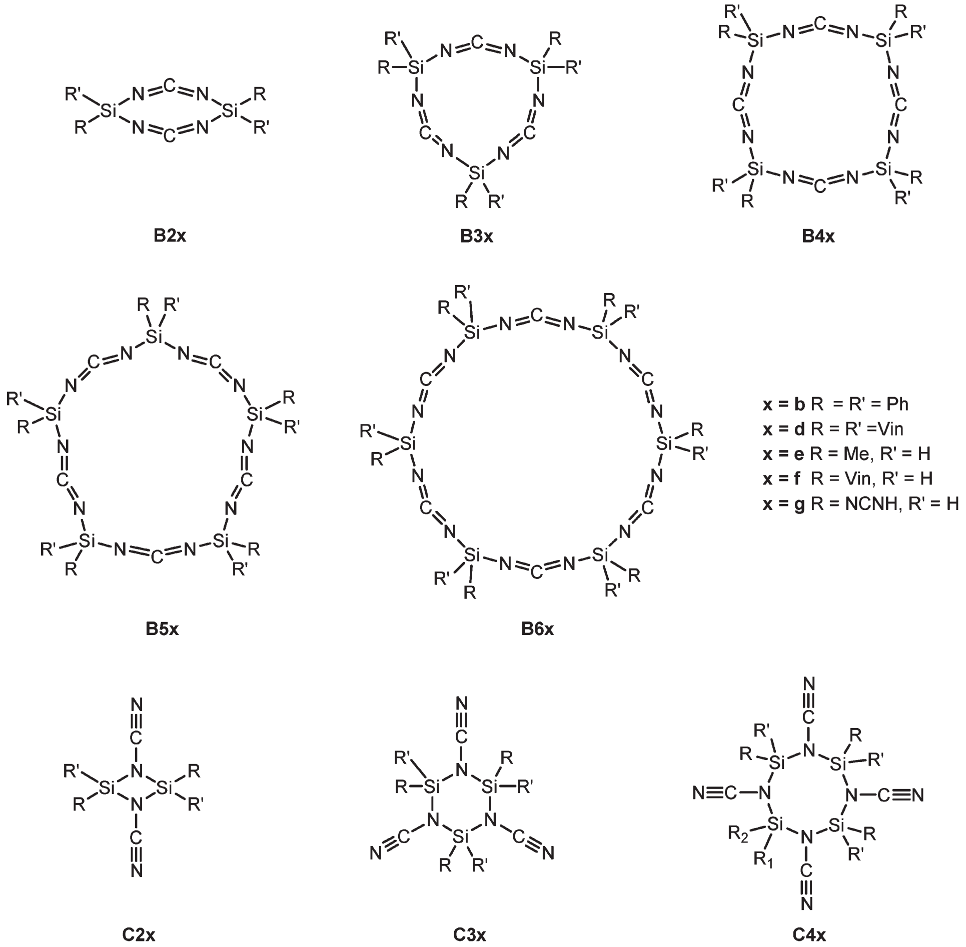


Figure 3. Comparison of calculated reduced relative energies of cyclic carbodiimides and cyanamides with various substitution patterns.

Scheme 3



back-bonding: in the alkylcarbodiimide the nitrogen atoms of the N=C=N structural unit are sp^2-hybridized (∠C—N=C is 130°), and the lone electron pair on nitrogen atom is situated in one of three sp^2-orbitals (Figure 5(a)); in silylcarbodiimide the nitrogen atoms of the N=C=N structural unit are predominantly sp-hybridized (∠Si—N=C is 160−175°) so that the lone electron pair on nitrogen atom is located in the p-orbital, whose electron density is notably localized between nitrogen and silicon atoms, participating in the Si—N bonding (Figure 5(b)).

BTSC has been calculated to be 16.18 kcal/mol more stable than the corresponding cyanamide. Our previously published results[23] on the tautomerism of carbodiimides and cyanamides are in good accordance with the present findings.

In the calculations presented above, the model molecules have been treated as noninteracting molecules in a

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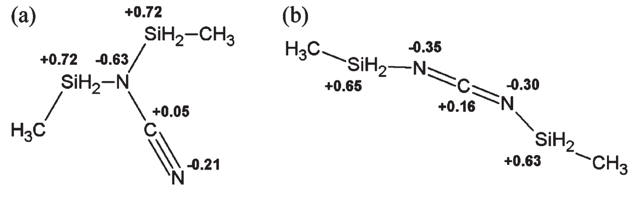


Figure 4. Model monomer molecules: (a) bis(methylsilyl)cyanamide and (b) bis(methylsilyl)carbodiimide with the calculated Mulliken charges indicated for the selected atoms.

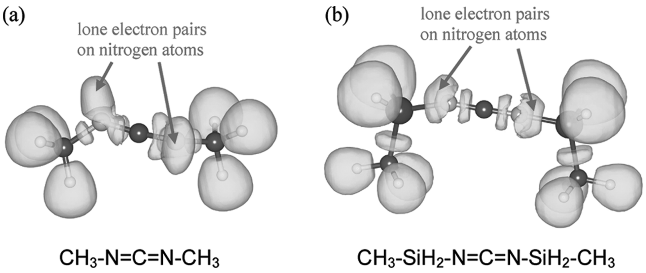


Figure 5. Isosurface (F = 0.8) of the calculated electron localization function for (a) dimethylcarbodiimide and (b) bis(methylsilyl)-carbodiimide.

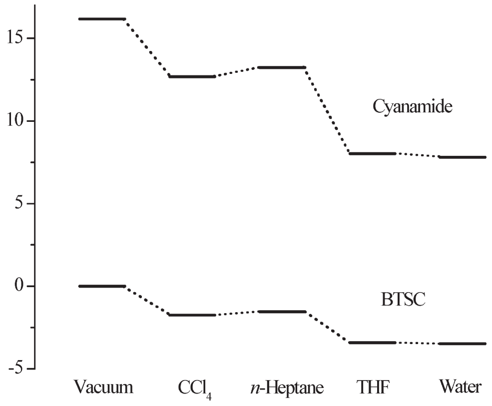


Figure 6. Relative energies of BTSC and cyanamide tautomer in vacuum and in different solvents.

vacuum. Taking into account the solvent effects should yield a remarkably different situation. To check if the cyanamide tautomers can be stabilized against carbodiimide in polar solvents, the single point energies of the solvated carbodiimide and cyanamide have been calculated using the polarizable continuum model (PCM) with tetrachlorocarbon, *n*-heptane, THF, and water as solvents, as shown in Figure 6. In this approximation, the solvent molecules are not treated explicitly, but only the shielding effect of the solvent on the electrostatic interaction between the partially charged groups of the investigated molecule is taken into account. In this hypothetical situation, compounds such as water may also be treated as a solvent, though the carbodiimides and their cyanamide tautomers would rather tend to hydrolysis under experimental conditions.

As expected, the shielding effect of the solvent generally reduces the total energy of both isomers, that is, of BTSC and of the corresponding cyanamide tautomer. As demonstrated in Figure 6, this stabilization effect is, however, much larger for bis(trimethylsilyl)cyanamide than for BTSC, especially in very polar solvents. Nevertheless, even in polar solvents the carbodiimide still remains thermodynamically more favorable than the corresponding cyanamide tautomer. The investigated solvation effects calculated via the PCM model follow the same trend in the stability changes as reported for organic carbodiimides and cyanamides.[12]

2.3. Molecular structure of the cyclo-tetramer [$Ph_2Si(NCN)]_4$. From the reaction mixture of diphenyldichlorosilane with BTSC, the dioxane solvate of the cyclo-tetramer $[Ph_2Si(NCN)]_4$ (**B4b**·(dioxane)$_2$) was isolated as a crystalline compound and analyzed by single crystal X-ray diffraction. The experimentally determined molecular structure was compared to that which was revealed by quantum mechanical calculations of the optimized geometry of **B4b**, as shown in Figure 7.

B4b·(dioxane)$_2$ crystallizes in the monoclinic system in space group *C*2/*c*. The carbodiimide units are, as expected, almost linear (angle N1−C1−N2, 174.3(2)°; N3−C2−N4, 174.1(2)°). The two crystallographically independent carbodiimide units exhibit cisoid conformation with respect to the torsion angle about the N1−N2 and N3−N4 axes (22.9(1) and 6.2(1)°, respectively). The carbodiimide nitrogen atoms N1, N2, N3, and N4 exhibit bond angles of 162.8(2), 148.4(2), 157.2(2), and 154.7(2)°, respectively. They indicate contributions of Si—N multiple bonding which result in bond angles between 120° and 180°, indicative of sp^2 and sp hybrid situations at the electronegative bonding partner. The Si—N—C angles of **B4b** fall within the range of Si−O−Si angles encountered with disiloxanes, hence supporting the pseudowater concept, that is, similar bonding properties of structurally related siloxanes. Even more similar are the structural characteristics of **B4b** to the other silyl-carbodiimides, which have been investigated by single crystal X-ray analyses. Table 2 gives a comparison of the experimental bond lengths and angles of different silyl-carbodiimides and their theoretically predicted values from the DFT calculations performed in this work.

The close electronic analogy between siloxanes and silylcarbodiimides is furthermore reflected in the ^{29}Si NMR spectroscopic properties of **B4b**, with a resonance at $\delta = -44.4$ ppm being similar to the ^{29}Si NMR signal of octaphenylcyclotetrasiloxane with $\delta = -43.0$ ppm (both in dioxane solution). In sharp contrast to the latter, **B4b** is very moisture sensitive and thus readily transformed into diphenylsilane diole ($\delta = -32.7$ ppm) in the presence of traces of water.

To prove the equilibrium between silylcarbodiimides and chlorosilanes in the course of the formation of compounds **Bnx**, a THF solution of the cyclotetramer **B4b** was treated with Me_3SiCl in the presence of pyridine, whereupon compounds such as $Me_3Si-NCN-SiMe_3$ and such bearing $Ph_2SiCl(NCNR')$ moieties had formed, as indicated by ^{29}Si NMR spectra which were similar to the intermediate ones in Figure 2. Owing to the coexistence of various unspecified species in the solution, a closer

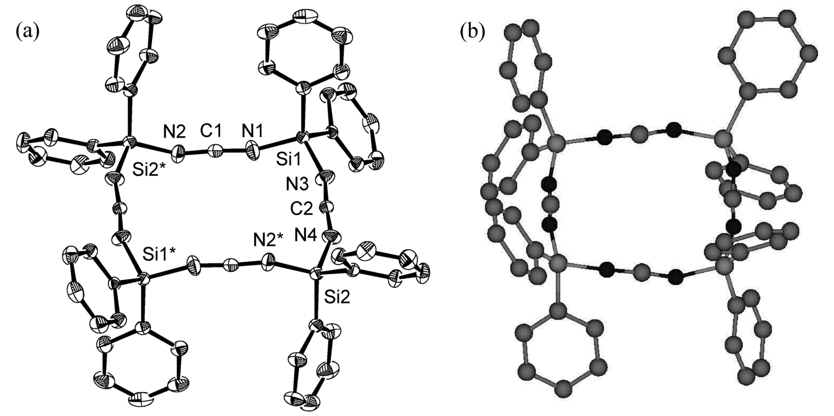


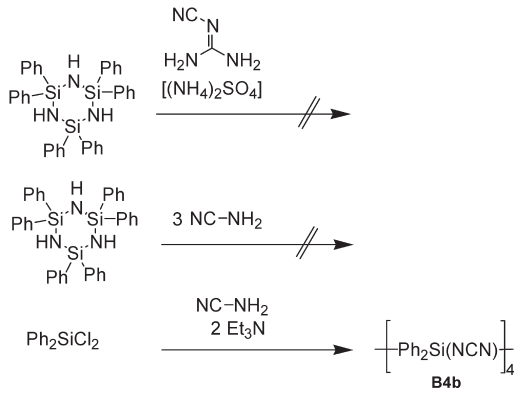
Figure 7. (a) Experimentally determined molecular structure of **B4b** in the crystal structure of **B4b**·(dioxane)$_2$ (thermal ellipsoids at the 30% probability level, hydrogen atoms and dioxane molecules omitted, selected atoms labeled). The asymmetric unit comprises one-half of the **B4b** cyclotetramer molecule and one dioxane molecule. Asterisks indicate symmetry-generated atomic positions. (b) Optimized molecular structure of **B4b** from DFT calculations (hydrogens omitted).

Table 2. Comparison of Selected Bond Lengths (pm) and Angles (deg) of B4b with the Corresponding Values for Silylcarbodiimides Reported in Literature and Calculated Theoretically

compound	Si−N	C−N	Si−N−C	N−C−N	literature
B4b exp.	174.1−174.3	118.4−120.0	148.4−162.8	174.1−174.3	this work
B4b theo.	172.4−172.8	121.7−122.4	156.8−162.5	176.7−176.8	this work
BTSC exp.	168−172	117−120	149−166	172.6−176.6	10
BTSC theo.	173.3	121.2	163.3−163.9	178.1	this work
$Ph_3Si(NCN)SiPh_3$	167−173	112−121	180	180	19
$[Me_2Si(NCN)]_4$ exp.	170−171	120−121	148−161	176−178	10, 21
$[Me_2Si(NCN)]_4$ theo.	171.5	119.1	165.0−165.2	177.9	this work
$R_3Si(NCN)SiR_3$[a]	172.5	121.3	148.4	180.0	20

[a] R = $Ph_2MeSiCH_2CH_2$.

Scheme 4



examination of the equilibrium (i.e., relative concentrations of distinct silylcarbodiimides) was not possible so far.

2.4. Alternative Synthesis Routes. The tetrameric compounds **B4b** and **B4a**[10] are the only cyclic silylcarbodiimides isolated so far. Hence, we tried to isolate oligomers of different ring size from an alternative route, considering the synthesis of compounds **Bnb** from different starting materials (Scheme 4).

In an initial attempt, which was related to the synthesis of BTSC from cyanoguanidine and hexamethyldisilazane,[24] cyanoguanidine was heated in *p*-xylene in the presence of hexaphenylcyclotrisilazane and the catalyst ammonium sulfate. Upon cooling to room temperature the starting material (hexaphenylcyclotrisilazane) crystallized from the solution, enabling the determination of its solid state structure by single crystal X-ray diffraction analysis for the first time (Figure 8).

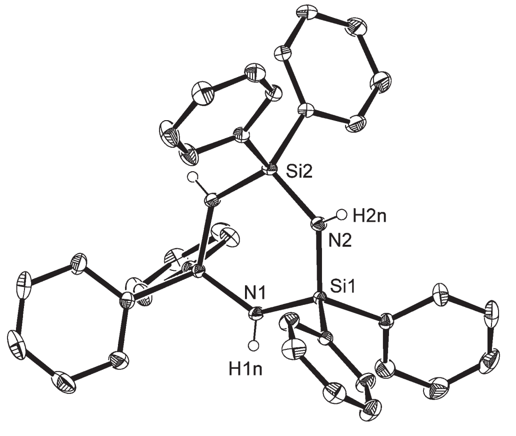


Figure 8. Molecular structure of hexaphenylcyclotrisilazane in the crystal structure (thermal ellipsoids at the 30% probability level, C-bound hydrogen atoms omitted, heteroatoms labeled). The asymmetric unit comprises one-half of the cyclotrimer molecule which is located on a crystallographically imposed twofold axis (through N1 and Si2). Selected bond lengths [Å] and angles [deg]: Si1−N1 1.716(1), Si1−N2 1.714(1), Si2−N2 1.715(1), N1−Si1−N2 107.1(1), N2−Si2−N2* 106.8(1), Si1−N1−Si1* 132.8(1), Si1−N2−Si2 133.1(1).

In a second attempt hexaphenylcyclotrisilazane was treated with the more reactive cyanamide (in THF solution). As

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(24) Rosenberg, S. D.; Walburn, J. J.; Ramsden, H. E. *J. Org. Chem.* **1957**, *22*, 1606.

for the first attempt, the cyclotrisilazane remained unaffected in solution (as indicated by ^{29}Si NMR spectroscopy). A third attempt proved successful, that is, the reaction of diphenyldichlorosilane with cyanamide in the presence of triethylamine as a sacrificial base. This alternative route led to the exclusive formation of chlorine free carbodiimides **Bnx**, whereas the conversion of BTSC with diphenyldichlorosilane led to an equilibrium between chloro- and carbodiimide-substituted silanes. In analogy to the initial synthesis of **B4b**, the cyclotetramer could also be crystallized from this reaction as a dioxane solvate (Figure 7). In contrast to the synthesis of **B4b** via BTSC, the reaction of diphenyldichlorosilane with cyanamide provided access to this cyclic carbodiimide in reasonable yield.

3. Conclusions

On the basis of previous studies on oligomeric and polymeric silylcarbodiimides, several attempts to isolate monomeric bis(trimethylsilylcarbodiimido)silanes of the type $R_2Si(NCNSiMe_3)_2$ were performed. Detailed NMR investigations of the products clearly indicate that complex reaction mixtures are generally obtained. Experiments aimed to prepare cyclic silylcarbodiimides of the type $[R_2Si(NCN)]_n$ gave similar results, that is, mixtures containing several linear and cyclic oligomers. These findings support the pseudowater concept described in the introduction, since hydrolysis of dichlorosilanes is also known to yield mixtures of linear and cyclic oligosiloxanes. DFT calculations were used to analyze the stability of cyclic carbodiimides of different ring sizes and their corresponding cyanamide tautomers, including also diphenyl-substituted derivatives and the influence of different solvents. The results indicate that the smallest possible rings $[R_2Si(NCN)]_2$ are energetically very unfavored, while the stability of the remaining rings with $n > 2$ among each other is similar. However, depending on the substituent of the silicon atom R significant differences were found. Interestingly, for R = phenyl, a pronounced energetic minimum is predicted in the case of $n = 4$ by the theoretical studies, which was also supported by two successful synthesis routes and structural characterization of this oligomer $[Ph_2Si(NCN)]_4$ via single crystal X-ray analysis.

4. Experimental and Calculations

4.1. Synthesis of Silylcarbodiimides and Related Compounds. Except for $(PhCH_2)_2SiCl_2$ all chemicals are commercially available. All manipulations were carried out under an atmosphere of dry argon using the Schlenk technique. THF and dioxane were distilled from sodium/benzophenone prior to use. Triethyl amine was distilled from calcium hydride and stored over a 3 Å molecular sieve. Pyridine was dried over a 3 Å molecular sieve.

Dibenzyldichlorosilane $(PhCH_2)_2SiCl_2$ was prepared from benzylmagnesiumchloride and tetrachlorosilane according to a literature method.[24] Bis(trimethylsilyl)carbodiimide (BTSC **1**) was synthesized by the reaction of hexamethyldisilazane (HMDS) with cyanoguanidine as described in the literature.[25] Spectroscopic data as well as boiling points agreed well with the literature data.

Hexaphenylcyclotrisilazane **2** was prepared according to a literature method.[26]

The mixtures **Bna**−**Bnd** were all prepared with the same procedure as follows: A solution of **1** (1.00 g; 5.36 mmol) in THF (15 mL) was stirred at room temperature, and both the diorganodichlorosilane (5.36 mmol) and pyridine (0.1 mL, 1.2 mmol) were added. The resulting clear solution was then stored at 60 °C for 10 h and cooled to room temperature, whereupon ^{29}Si NMR spectra were recorded. This procedure of storing the mixture at 60 °C, cooling to ambient temperature, and recording a ^{29}Si NMR spectrum was repeated several times. In the course of the reaction only very little amounts of pyridine hydrochloride precipitated, which were allowed to settle after completed conversion. The clear supernatant was separated by decantation, solvent and Me_3SiCl were removed in vacuo, and the resulting oil was dissolved in dioxane (different amounts depending on the mixture).

Preparation of **B4b**·(dioxane)$_2$ from BTSC occurred as follows: The above procedure applied to diphenyldichlorosilane followed by dissolution of the final oily product in 5 mL of dioxane and storage at room temperature afforded colorless needles of **B4b**·(dioxane)$_2$, which were filtered off and briefly dried in vacuo. Yield: 0.35 g (0.33 mmol, 25%).

Preparation of **B4b**·(dioxane)$_2$ from cyanamide occurred as follows: A solution of diphenyldichlorosilane (6.32 g, 25.0 mmol) and triethylamine (5.05 g, 50.0 mmol) in THF (120 mL) was cooled to 0 °C before a solution of cyanamide (1.05 g, 25.0 mmol) in THF (15 mL) was added dropwise while stirring. Immediatedly a white precipitate of triethylamine hydrochloride formed. After complete addition of the cyanamide the mixture was stirred at 50 °C for 1 h and stored at room temperature overnight. Then the hydrochloride precipitate was filtered off and washed with THF (30 mL). From the combined filtrate and washings the solvent was removed in vacuo and the oily residue was dissolved in dioxane (10 mL), whereupon **B4b**·(dioxane)$_2$ crystallized within 1 week. The solid product was separated by filtration, washed with dioxane (8 mL), and dried in vacuo. Yield: 2.9 g (2.7 mmol, 44%). ^{1}H NMR ($CDCl_3$): δ = 7.25−7.65 (mm, 40 H). ^{13}C NMR ($CDCl_3$): δ = 122.9 (N=C=N), 128.1 (o/m), 130.7 (p), 132.9 (i), 134.1 (o/m). ^{29}Si NMR ($CDCl_3$): δ = −45.1. C/H/N Analysis. Found (%): C, 67.24; H, 5.18; N, 10.52. Calcd for $C_{60}H_{56}N_8O_4Si_4$ (%): C, 67.63; H, 5.30; N, 10.52.

4.2. Single Crystal Structure Analyses. *Crystal Structure Analysis of* ***B4b***·*(dioxane)*$_2$. $C_{60}H_{56}N_8O_4Si_4$, CCDC-722666, T 220(2) K; monoclinic, $C2/c$; a 33.8685(13), b 8.6997(3), c 24.5163(10) Å, β 128.909(1)°; V 5621.0(4) Å^{-3}; Z 4; μ(Mo Kα) 0.160 mm^{-1}; θ_{max} 26°; 23703 reflections (5502 unique, R_{int} 0.0365), 362 parameters, GoF 1.057, R_1/wR_2 [$I > 2\sigma(I)$] 0.0455/0.1173, R_1/wR_2 (all data) 0.0730/0.1277, residual electron density (highest peak, deepest hole) 0.419, −0.311 e Å^{-3}.

Crystal Structure Analysis of Hexaphenylcyclotrisilazane. $C_{36}H_{33}N_3Si_3$, CCDC-722667, T 180(2) K; monoclinic, $C2/c$; a 17.9633(6), b 9.2284(3), c 18.8003(6) Å, β 94.242(1)°; V 3108.04(18) Å^{-3}; Z 4; μ(Mo Kα) 0.183 mm^{-1}; θ_{max} 30°; 24299 reflections (5433 unique, R_{int} 0.0265), 197 parameters, GoF 1.082, R_1/wR_2 [$I > 2\sigma(I)$] 0.0355/0.0965, R_1/wR_2 (all data)

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(25) (a) Vostokov, I. A.; Dergunov, Y. I.; Gordetsov, A. S. *Zh. Obshch. Khim.* **1977**, *47*, 1769. (b) Greiner, A. Dissertation, Technische Universität Darmstadt, Germany, 1997; Shaker Verlag: Aachen, 1998 (ISBN 3-8265-3247-3).

(26) Larsson, E.; Bjellerup, L. *J. Am. Chem. Soc.* **1953**, *75*, 995.

0.0482/0.1027, residual electron density (highest peak, deepest hole) 0.349, −0.190 e Å^{-3}.

4.3. Theoretical methods. The geometry optimizations and the single point energy calculations were performed with GAMESS-US[27] program in the framework of the density functional theory (DFT). The B3LYP hybrid exchange-correlation functional was used along with a 6-31G* Gaussian-type basis set for the geometry optimization and with a triple-ζ valence basis set with one additional polarization function on heavy atoms to perform single-point energy calculations. The transition states have been identified by searching for a stationary point of first order on the potential energy surface. To ensure the connection of the initial and final geometry the internal reaction coordinate path has been followed along the lowest frequency mode starting from the transition state found.

In case of phenyl substituted carbodiimides, the geometry optimizations were done with a Stevens−Basch−Krauss−Jasien−Cundari (SBKJC) basis set including the effective core potential (ECP) with one additional polarization function on heavy atoms along with the B3LYP hybrid exchange correlation functional.

Acknowledgment. The German research foundation (DFG, Bonn) is gratefully acknowledged for financial support (project numbers: KR1739/18-1 and WO 482/19-1).

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