Inorganic Solid-State Chemistry with Main Group Element Carbodiimides

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Organosilicon carbodiimides have been successfully applied as single-source precursor compounds for the synthesis of novel ternary Si-, C-, and N-containing solid phases. Their thermally induced decomposition gives either amorphous silicon carbonitrides or polycrystalline silicon nitride and silicon carbide mixtures, materials that are presently of technological interest for their exceptional hardness, strength, toughness, and high temperature resistance even in corrosive environments. This review is concerned with the synthesis, characterization, and thermal stability of element carbodiimides. The main part of this paper is focused on polymeric silicon-based carbodiimides obtained by the reaction of chloro(organo)silanes with bis(trimethylsilyl)carbodiimide. In the case of $RSiCl_3$, novel poly(silylcarbodiimide) gels are formed. Starting from silicon tetrachloride, new crystalline SiCN phases (namely, SiC_2N_4 and Si_2CN_4), have been isolated. Their crystal structures as well as their thermal behavior in the range between room temperature and 1600 °C are discussed. Moreover, preliminary results on the synthesis of germanium- and boron-containing carbodiimides are reported. It is also shown that carbon-based carbodiimides can be obtained by the reaction of cyanuric halides with bis(trimethylsilyl)carbodiimide. These materials are investigated as precursors for the synthesis of new carbon nitrides with high hardness.

Contents

1. Introduction

Main group element carbodiimides such as the recently discovered solid silicon dicarbodiimide, $Si(N{=}C{=}N)_2$, are currently being investigated as suitable precursor compounds for the synthesis of carbide/nitride-based ceramics.[1,2] Many of the element carbide and nitride materials have attracted much attention in the past decades for structural and electronic applications.[3] In addition to the well-known binary phases SiC and Si_3N_4, silicon dicarbodiimide with the stoichiometry SiC_2N_4 now represents the first crystalline ternary Si−C−N phase. These findings clearly indicate the high potential of element carbodiimides for the synthesis of advanced non-oxide materials.

Molecular silylcarbodiimides, namely disilylcarbodiimide ($H_3Si{-}N{=}C{=}N{-}SiH_3$) and bis(trimethylsilyl)carbodiimide, $(CH_3)_3Si{-}N{=}C{=}N{-}Si(CH_3)_3$, have been known since the work of Ebsworth and Mays,[4] Pump and Wannagat,[5] and Birkhofer et al.[6] in the early 1960s. Since then, a great variety of monomeric and polymeric silylcarbodiimides have been prepared and characterized. It has been found that organosilylcarbodiimides can be applied, for example, as stabilizer for polyurethane and poly(vinylchloride), for high-temperature and radiation-resistant dyes and sealing materials, as well as for the synthesis of organic cyanamides, carbodiimides, and heterocycles.[7,8]

It should be noted that Köhler and Kotte[9] synthesized the first phosphorus-containing carbodiimide, namely triphenylphosphonio cyanamide (Ph_3PNCN).[9] The molecular structure of Ph_3PNCN was then elucidated by Kaiser et al.[10] Köhler and Jäger et al. also intensively investigated solid carbodiimide-modified phosphates $[PO_{4-n}(NCN)_n]^{3-}$, where $n = 1{-}3$;[11−14] sulfites $[SO(NCN)_2]^{2-}$; sulfates $[PO_{4-n}(NCN)_n]^{2-}$, where $n = 1{-}2$;

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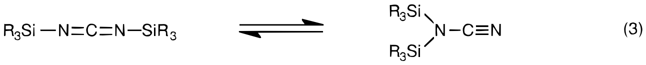
sulfonates $[RSO_2NCN]^-$, where R = Et, Ph, naphtyl;[15] as well as nitrites $[NO_{2-n}(NCN)_n]^-$, where $n = 1-2$.[16] The synthesis of sodium cyanamido phosphates and sulfates was achieved by the following reactions:[11,15]

$$P_4O_{10} + 6\ Na_2[NCN] \rightarrow 2\ Na_3[PO_3(NCN)] + 2\ Na_3[PO_2(NCN)_2] \quad (1)$$

$$SO_2(NHCN)_2 + 2\ NaOH \rightarrow Na_2[SO_2(NCN)_2] + 2\ H_2O \quad (2)$$

In the beginning, the preparation of disilylcarbodiimides was directed to monomeric and symmetrical molecules of the general form $R^1R^2R^3Si{-}N{=}C{=}N{-}SiR^1R^2R^3$, with R^1, R^2, R^3 = H−, CH_3, C_2H_5−, C_6H_5−, Cl−, F−, etc. This early work was summarized in a comprehensive review article published by Gordetsov et al. in 1982.[17]

Silyl-substituted carbodiimides can be distilled up to 250 °C without polymerization. Disilylcarbodiimides cannot be transformed to the isomeric disilylcyanamide structure, whereas this is a common feature of organocarbodiimides:[17]



It seems that the equilibrium of this isomerization reaction is far on the side of the carbodiimide form. However, there has been a report on the synthesis of stable bis(trimethylsilyl)cyanamide, but no spectroscopic characterization has been published.[18] Asymmetrical disilylcarbodiimides, $R_3Si{-}NCN{-}SiR'_3$, generally are thermally unstable and readily rearrange to give mixtures with the symmetrical ones upon distillation.[17] Alkylsilylcarbodiimides, $R{-}NCN{-}SiR'_3$, can simply be prepared by reactions of alkylsilylamines with Cl−CN.[19] Pure products are isolated by distillation, but upon standing at room temperature, a mixture with the corresponding cyanamide is formed. Again, by distillation of this mixture, the equilibrium is shifted back to the pure carbodiimide. The same behavior was observed for asymmetrically substituted silyl-, germyl-, and stannylcarbodiimides of the type $R_3E{-}NCN{-}E'R'_3$.[17]

One of the first methods developed for the synthesis of silylcarbodiimides was the reaction of disilvercyanamide, Ag_2NCN, with triorganochlorosilanes

$$Ag_2NCN + 2\ R_3SiCl \rightarrow R_3Si{-}N{=}C{=}N{-}SiR_3 + 2\ AgCl \quad (4)$$

Disilylcarbodiimides can also be obtained by the reaction of Cl_2CO, CO_2, $Si(NCO)_4$, $(NCS)_2$, XCN (X = Cl, Br), or R_3SiNCY (Y = O, S) with sodium(bistrimethylsilyl)amide, $(R_3Si)_2NNa$.[17] The reaction product has to be separated by filtration and distillation from the corresponding sodium salt formed as a byproduct. The direct silylation of cyanamide or its dimer, cyanoguanidine, gives disilylcarbodiimides

$$2\ R_3SiCl + H_2N{-}CN + 2\ Pyr \xrightarrow[-Pyr\cdot HCl]{} R_3Si{-}N{=}C{=}N{-}SiR_3 \quad (5)$$

In this case, stoichiometric amounts of triethylamine or pyridine have to be added to separate the side-product HCl.[20] The most convenient route to form molecular organosilylcarbodiimides in high yields is the transamination of cyanamide with hexaorganodisilazanes as published by Vostokov et al. in 1977:[21]

$$H_2NCN + (R_3Si)_2NH \rightarrow R_3Si{-}N{=}C{=}N{-}SiR_3 + NH_3 \quad (6)$$

It was found by Drake et al.,[22] Reischmann et al.,[23] and several other authors[17] that bis(trimethylsily)carbodiimide ($R_3Si{-}N{=}C{=}N{-}SiR_3$, with R = CH_3) itself is a very efficient starting material for the synthesis of other element carbodiimides. Thus, organoelement halides as well as pure element halides can be reacted with bis(trimethylsily)carbodiimide to form novel carbodiimides:[1,17,23−29]

$$(CH_3)_3Si{-}N{=}C{=}N{-}Si(CH_3)_3 + EX_n \rightarrow (CH_3)_3Si{-}N{=}C{=}N{-}EX_{n-1} + (CH_3)_3SiX \quad (7)$$

X = F, Cl
E = Al, Ga, B, Ge, Si, Sn, Sb, Ta, Mo, or W

The driving force of reaction 7 is the formation of stable $(CH_3)_3SiX$, which can be easily separated from the formed element carbodiimide by distillation.

The first polymeric silylcarbodiimides were found by Pump and Rochow.[30] The synthesis is based on the reaction of diorganochlorosilanes with disilvercyanamide. Klebe and Murray[31] reported the synthesis of several polysilylcarbodiimides obtained by the reaction of chlorosilanes with bis(trimethylsily)carbodiimide.[31] Very recently, the first cyclic oligomers of dimesitylgermylcarbodiimides $[Mes_2Ge{-}N{=}C{=}N]_n$ with $n = 3$ and 4, have been synthesized from dichlorodimesitylgermane and cyanamide.[32]

Polymeric element carbodiimides are, on the one hand, novel inorganic polymers that have not been studied in detail so far. On the other hand, these compounds can be used as single-source precursors for the pyrolytic synthesis of ternary element carbonitride (ECN) ceramics, as was shown for E = Si by Kienzle et al. in 1993.[33] For this reason, in the course of our work on the development of novel inorganic polymers suitable for the polymer-to-ceramic transformation process, we thoroughly investigated the synthesis and properties of polymeric silicon carbodiimides. Therefore, this review is mainly focused on silylcarbodiimides but also summarizes first results obtained with boron-, carbon-, and germanium-containing carbodiimides. Their thermal stability in terms of decomposition and ceramization is discussed.

Finally it should be noted that according to a systematic nomenclature, carbodiimides should be denoted as 1,3-diazapropadienes. This denotation is important for searches in databases like CAS Registry.

2. Silicon Carbodiimides

2.1. Molecular $(R_3Si)_2NCN$. The most relevant synthesis methods and applications of molecular (mon-

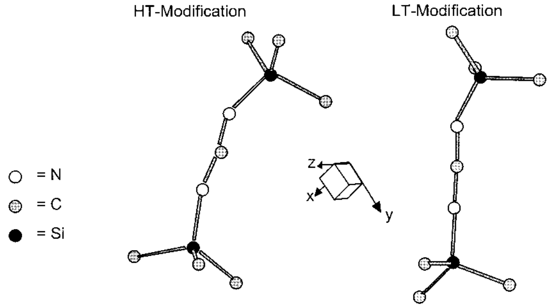


Figure 1. Molecular structures of the low- and high-temperature phase of bis(trimethylsilyl)carbodiimide determined by single-crystal X-ray diffraction. The most important difference between both configurations is the dihedral angle. For the high-temperature form, 10° was found, and for the low-temperature form, 114° was found. This value is far from the 90° expected for a hetero allene.

omeric) disilylcarbodiimides have already been described in the Introduction. Here we will focus on the most used silylcarbodiimide, bis(trimethylsilyl)carbodiimide. This compound can be prepared by many different ways.[17] Only the following three routes give high yields, are easy to perform, and can therefore be recommended:

(1) The reaction of cyanamide with chlorotrimethylsilane produces bis(trimethylsilyl)carbodiimide according to equation 5.[5,34–36] The bases pyridine or triethylamine are used to shift the equilibrium to the right side and to separate the hydrochloric acid from the reaction mixture. The observed yields vary from 52 to 81 wt %.

(2) The chlorotrimethylsilane in the former reaction can be replaced by hexamethyldisilazane as shown in reaction eq 6.[21] The main advantage of this method is that no filtration step is necessary. Also, almost quantitative yields can be achieved.

(3) From an economic point of view, the most efficient way to synthesize bis(trimethylsilyl)carbodiimide is the reaction of hexamethyldisilazane with cyanoguanidine, the dimer of cyanamide:[21,35]

$$2\ [(CH_3)_3Si]_2NH + H_2NC(NH)NHCN \rightarrow 2\ (CH_3)_3Si{-}NCN{-}Si(CH_3)_3 + 2\ NH_3 \quad (8)$$

As a side-product, tris[(trimethylsilyl)amino]-*s*-triazine is formed, but yields up to 80 wt % are still obtained. The fact that no solvent has to be used and that cynoguanidine is much cheaper than cyanamide makes this route most attractive. Bis(trimethylsilyl)carbodiimide is a colorless liquid at room temperature that boils at 164 °C and 1 bar and melts at −42 °C. Its structure has been examined by vibrational spectroscopy[22,37] and electron diffraction.[38] Two slightly different solid-state structures at −125 °C and −170 °C have been determined by single-crystal X-ray diffraction (XRD; Figure 1).[20,34]

The phase transition between these two structures occurs at −142 °C. In both modifications C−N bond lengths of ~118 pm (which is between a typical CN double and CN triple bond) and Si−N−C angles >120° (149−166°) are detected. This result indicates a deviation of a pure sp^2-hybridization for the N atoms towards a sp-hybridization. Similar to other silylcarbodiimides, N−C−N angles of 173° and 177° are found. The rotation of the silyl groups around the N(C)N-axis shows only small energy barriers (see also Section 7). For a pure cumulene system, a torsion angle between the silyl substituents of 90° would be expected. In the high-temperature modification, the angle is only 10°, whereas 114° was found for the low-temperature form.

These structural features of the disilylcarbodiimide unit in molecular bis(trimethylsilyl)carbodiimide are most likely also present in polymeric and oligomeric disilylcabodiimides. Accordingly, no rearrangements to cyanamides and NCN angles of 170−180° with a flexible *Z*-shaped conformation for the Si−NCN−Si chain are expected (see also Section 7).

Bis(trimethylsilyl)carbodiimide is an excellent starting material for the synthesis of silyl- and other element-carbodiimides. Examples will be discussed in the following sections.

2.2. Dialkylsilylcarbodiimides $[R_2Si{-}NCN{-}]_n$. The first syntheses of dialkylsilylcarbodiimides date back to 1963. Pump and Rochow[30] used disilvercyanamide suspended in ether or benzene and dialkyldichlorosilanes to obtain polymeric silylcarbodiimides

$$R^1R^2SiCl_2 + Ag_2NCN \rightarrow [R^1R^2Si{-}NCN{-}]_n + 2\ AgCl \quad (9)$$

$$R^1 = -CH_3, -C_6H_5, -OC_2H_5$$
$$R^2 = -CH_3, -CH{=}CH_2, -C_6H_5, -OC_2H_5$$

Depending on the substituents, the yields varied between 77 and 96 wt %. Values of 6.4 to 8.4 for *n* were determined by cryoscopic molecular mass techniques. In 1967, Klebe and Murray[31] used bis(trimethylsilyl)carbodiimide instead of the silver salt to synthesize polydialkylsilylcarbodiimides. In an exchange reaction, the trimethylsilyl groups are replaced by the dialkylchorosilane

$$n(C_6H_5)_2SiCl_2 + n(CH_3)_3Si{-}N{=}C{=}N{-}Si(CH_3)_3 \rightarrow [(C_6H_5)_2Si{-}N{=}C{=}N{-}]_n + 2n(CH_3)_3SiCl \quad (10)$$

A common feature of the poly(diorganylsilyl)carbodiimides is their excellent thermal stability. Even at temperatures up to 350 °C, no decomposition was measured in a vacuum. Moreover, these polymers showed high stability towards electron radiation. Another method to synthesize carbodiimide polymers was mentioned by Gordetsov et al. in 1982. They described transamination reactions between polysilazanes and cyanoguanidine:[17]

$$[R_1R_2Si{-}NH{-}]_n + n/2\ [H_2NCN]_2 \rightarrow [R_1R_2Si{-}NCN{-}]_n + n\ NH_3 \quad (11)$$

However, no details about the starting materials and the products have been published.

In the beginning of the 1990s we started the first work with respect to the use of polymeric dialkylsilylcarbodiimides as precursors for ceramics.[33] According to reaction eq 12, dichlorosilanes and cyanamide in tetrahydrofuran (THF) as a solvent and in the presence of

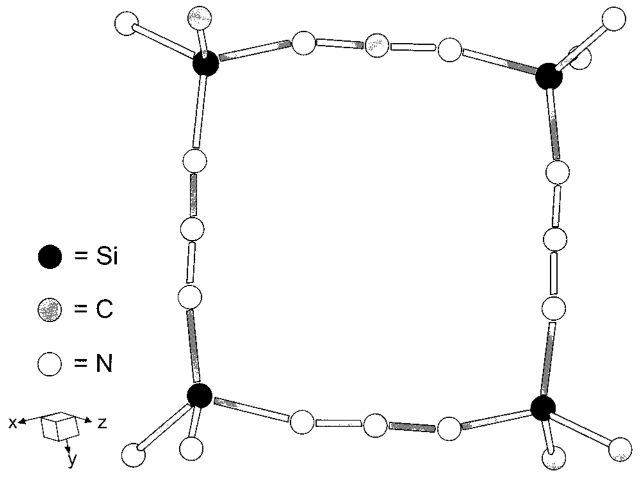


Figure 2. Molecular structure of $[(H_3C)_2SiNCN]_4$ determined by single-crystal X-ray diffraction.

pyridine form polymers or cyclic oligomers.[34,39]

$$n(CH_3)RSiCl_2 + nH_2NCN + 2n\ Py \rightarrow [(CH_3)RSi{-}NCN{-}]_n + 2n\ Py{\cdot}HCl \quad (12)$$

$$R = -CH_3, -CH{=}CH_2, -H \qquad Py = pyridine$$

Each reaction mixture contains different cyclic oligomers as has been shown by nuclear magnetic resonance (NMR), infrared (IR), and mass spectroscopy. In the case of dichlorodimethylsilane, the first cyclic silylcarbodiimide compound was isolated.[20,33] A single-crystal structure revealed a nearly planar 16-membered $[(CH_3)_2Si{-}NCN{-}]_4$ ring. The molecule can be described as a square with dimethylsilyl groups at the vertices connected by almost linear carbodiimide units (Figure 2). Again, structural features (i.e., bond length and angles) similar to bis(trimethylsilyl)carbodiimide and typical for disilylcarbodiimides were analyzed. In addition to the tetramer, oligomers with $n = 2-7$ were detected by mass spectroscopic investigations.

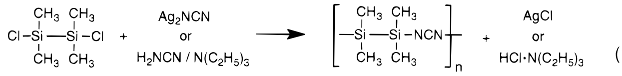
In contrast to the reaction of dichlorodimethyl- and dichloromethylvinylsilane, the reaction of dichloromethylsilane with cyanamide results in a highly cross-linked polymer. It was postulated that this is caused by hydrosilylation reactions between the carbodiimide and Si—H groups.[34] Similar polymers have been synthesized by solvent- and salt-free reactions of dichlorosilanes with bis(trimethylsilyl)carbodiimide.[40] Gels were obtained in the case of dichloromethylsilane, but no hints on cross-linking by inter- or intramolecular hydrosilylation were found.

Dichloromethylsilane has also been used by Seyferth et al.[41] to synthesize polysilylcarbodiimides. Disilvercyanamide or cyanamide together with triethylamine were used as carbodiimide sources. The mean molecular masses, 1813 and 2277, respectively, were used to derive mean chain lengths n, of 21.6 and 27.2, respectively, for the idealized linear polymeric products $[CH_3HSi{-}NCN{-}]_n$. Pyrolysis of the dialkylsilylcabodiimides at 1000 °C in argon produces ceramic materials in the ternary system Si—C—N.[33,34,39] The ceramic yield of the products strongly depends on the substituents attached to the silicon atoms. Low yields of 28 wt % are found for the dimethyl-substituted silylcarbodiimide. In contrast, the precursors containing Si—H or vinyl groups gave much higher ceramic yields of 70 and 64 wt %, respectively. This result is caused by cross-linking mechanisms during pyrolysis that are not possible for the dimethyl-substituted derivative (see also Section 2.6).

The silylcarbodiimide polymers described in this paragraph have not only been transformed to Si/C/N ceramics but have also been modified to obtain quaternary Si/B/C/N polymers and the corresponding boron-containing ceramics (see Section 5).

2.3. Silicon Carbodiimides from Disilanes, Disiloxanes, and Related Compounds.

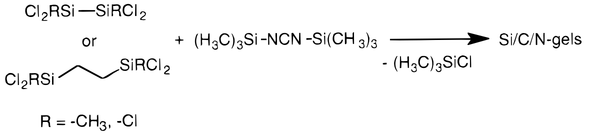
Disilanes and disiloxanes have been used by Razuvaev et al.[7] to prepare disilylcarbodiimide polymers according to reaction eq 13. The reaction is complete after 30−50 min in ether or ether/benzene at 20 °C. Colorless viscous liquids were isolated in 80% yield.



$$Cl{-}Si(CH_3)_2{-}Si(CH_3)_2{-}Cl + Ag_2NCN \text{ or } H_2NCN/N(C_2H_5)_3 \longrightarrow [{-}Si(CH_3)_2{-}Si(CH_3)_2{-}NCN{-}]_n + AgCl \text{ or } HCl{\cdot}N(C_2H_5)_3 \quad (13)$$

Cryoscopic determination of molecular masses showed values for the degree of polymerization n varying from 7.4 to 9.5, which is similar to the results for the polymers derived from dichlorosilanes (see Section 2.2).

The new sol−gel approach to carbodiimide-containing gels as described in Section 2.4 is not limited to monosilanes $RSiCl_3$. Various disilanes and chlorosilyl-substituted compounds produced non-oxidic transparent gels. We successfully prepared the polymeric networks by the stoichiometric pyridine-catalyzed reactions of bis(trimethylsilyl)carbodiimide with hexachlorodisilane, 1,2-bis(trichlorosilyl)ethane, 1,2-bis(dichloromethylsilyl)ethane, and tetrachloro-1,2-dimethyldisilane (eq 14).[40,42]



(14)

Gelation time, shrinkage, yield and pyrolysis behavior changed with the structure of the chlorosilane used as a starting material. In all these polymers the presence of the carbodiimide group was proofed by IR spectroscopy.[40,42]

2.4. Poly(methylsilsesquicarbodiimide), $[RSi(NCN)_{1,5}]_n$.

Recently, we reported on the formation of a non-oxidic gel by the reaction of methyltrichlorosilane with bis(trimethylsilyl)carbodiimide.[43,44] The conventional sol−gel technique is widely used for the preparation of oxidic glasses and ceramics. The variety of technological applications reflects the important position of the sol−gel process in applied inorganic chemistry.[45] Only a few approaches for the synthesis of non-oxidic gels are known. Narula et al.[46] described the formation of oxygen-free boron/nitrogen-containing gels by oligomerization reactions of substituted borazines with silylamine cross-linking groups.[46] Subsequent pyrolysis produced boron nitride ceramics.[47] In 1988, Seibold and Rüssel[48] described a route to aluminum nitride ceramics using a polyaminoalane precursor. Results from Bocarsly et al.[49] based on cyanogels derived from $K_3Fe(CN)_6$ or K_2PdCl_4 in aqueous solutions show that the non-oxidic

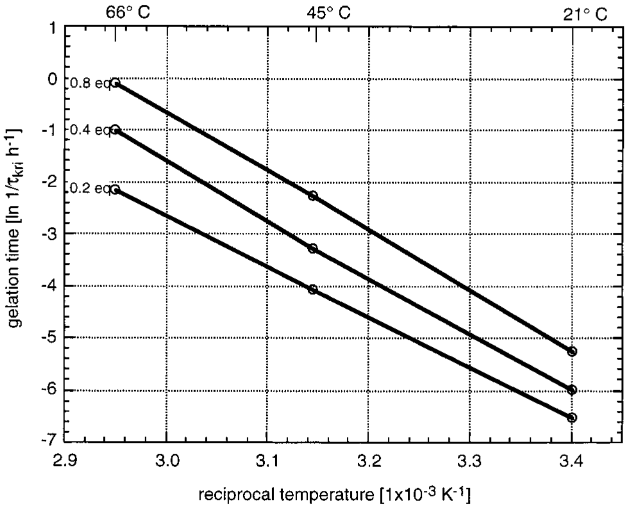


Figure 3. Arrhenius plot for the synthesis of poly(methylsilylcarbodiimide) gels. The reciprocal gelation time τ is described in relation to the reciprocal temperature.

sol–gel chemistry is not limited to main group element systems. Guiton et al.[50] reviews the organo metal chemistry with the sol–gel processing of metal sulfides using an Et_2Zn precursor. Gacoin et al.[51] recently found a sol–gel transition for CdS colloids. This brief overview shows that the sol–gel process is being extended to other types of materials, such as nitrides and sulfides. The formation of a non-oxidic carbodiimide-containing gel was first observed by reacting stoichiometric amounts of trimethylchlorosilane with bis(trimethylsilyl)carbodiimide (eq 15).

$$n\,\mathrm{MeSiCl_3} + 1.5\,n\,\mathrm{Me_3Si{-}N{=}C{=}N{-}SiMe_3} \xrightarrow{\{\text{Pyridin}\}} \underbrace{[\mathrm{MeSi(NCN)_{1.5}}]_n + 3n\mathrm{Me_3SiCl}}_{\text{Gel}} \qquad (15)$$

The reaction is performed without solvents and is catalyzed by pyridine. The gelation time can be controlled by varying the amount of the catalyst and by changing the reaction temperature. By determination of a rate constant for reaction eq 15 that is dependent on the reciprocal temperature (Arrhenius plot, Figure 3), the reaction time until gelation can be predicted. Each of the three lines in Figure 3 represents a fixed pyridine content. The slopes of 0.8, 0.4, and 0.2 eq (equivalents of pyridine with respect to the silane) have nearly the same value.

The synthesis of poly(methylsilylcarbodiimide) or more generally the reaction sequence for production of silylcarbodiimide polymers is closely related to that of chlorosilanes, R_xSiCl_{4-x} (R = H, alkyl or aryl; $x = 0$, 1, or 2), with water-forming silica gels, silicones, or organically modified silicon oxides denoted as ORMOSILs.[52] In the novel sol–gel process, bis(trimethylsilyl)carbodiimide adopts the role of H_2O applied in the conventional oxidic sol–gel route as indicated in Figure 4. The first reaction step involves the substitution of the silicon-bonded chlorine atoms by hydroxyl groups in the oxidic sol–gel path while chlorine is replaced by the silylcarbodiimide unit in the non-oxidic counterpart. Subsequent polycondensation results in the formation of polymeric gels. Finally, calcination and/or pyrolysis of the gels up to 1000–1200 °C in Ar or N_2 yields silicon oxycarbide ($Si_xO_yC_z$) glasses[53,54] and silicon carbonitride ($Si_xC_yN_z$) ceramics, respectively.

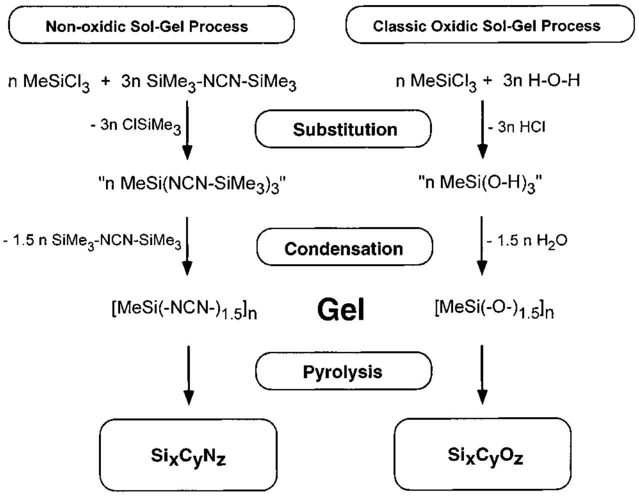


Figure 4. Comparison of the non-oxidic sol–gel process (left) with the aqueous counterpart (right) and the final products obtained after pyrolysis of the dried gels.

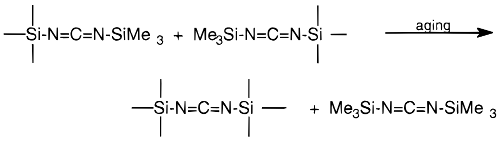
Table 1. Relative Length and Volume Shrinkages ($\Delta L/L$ and $\Delta V/V$) During Aging and Drying of the $[MeSi(NCN)_{1.5}]_n$ Gel

dimensions	gel as prepared	aged gel[a]	xerogel[b]
$\Delta L/L$ [%]	0	37	44
$\Delta V/V$ [%]	0	75	82

[a] Aging conditions: 30 d at 45 °C; pyridine content, 0.6 eq. [b] Drying conditions: evaporation of the liquid phase at 50 °C/1 bar for 24 h.

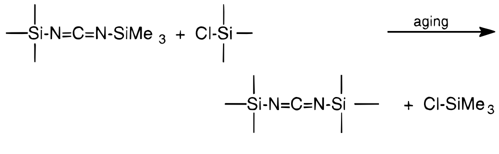
During the sol–gel transition, the poly(methylsilsesquicarbodiimide) system shows a similar behavior as the classic oxidic gels. The as-prepared gels are highly transparent. After an aging period of ~5 days at 45 °C, the gel becomes cloudy without change in gel volume. Further annealing at 45 °C induces irreversible shrinkage. Careful evaporation of the liquid fraction, mainly Me_3SiCl, provides a transparent xerogel. The corresponding length and volume shrinkage values of the $[MeSi(NCN)_{1.5}]_n$ gel are summarized in Table 1.

The rate of gel shrinkage is mainly determined by two parameters: increased pyridine content (0.0–1.5 eq) and prolonged annealing (20–45 °C) accelerate the aging and consequently enhance the degree of cross-linking of the gel network. During tempering at 45 °C, the gel remains completely X-ray amorphous. Infrared spectroscopic investigations also revealed that polycondensation (eq 16) and substitution (eq 17) continue after gelation:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}N{=}C{=}N{-}SiMe_3} + \mathrm{Me_3Si{-}N{=}C{=}N{-}}\overset{|}{\underset{|}{\mathrm{Si}}}- \xrightarrow{\text{aging}} -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}N{=}C{=}N{-}}\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{Me_3Si{-}N{=}C{=}N{-}SiMe_3} \qquad (16)$$

Crosslinking by substitution reactions



$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}N{=}C{=}N{-}SiMe_3} + \mathrm{Cl{-}}\overset{|}{\underset{|}{\mathrm{Si}}}- \xrightarrow{\text{aging}} -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}N{=}C{=}N{-}}\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{Cl{-}SiMe_3} \qquad (17)$$

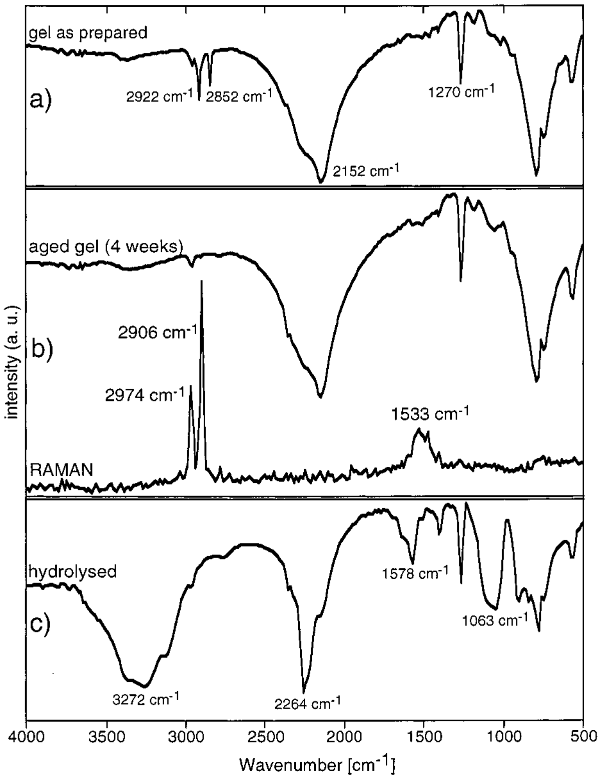
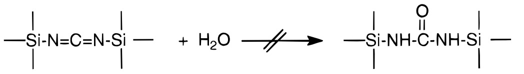
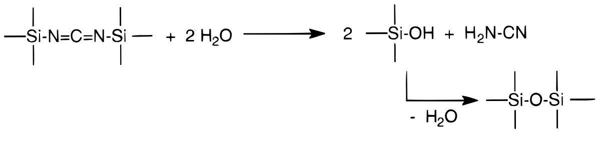


Figure 5. (a) FT-IR spectrum of the $[MeSi(NCN)_{1.5}]_n$ gel, as synthesized; (b) FT-IR and Raman spectra of an aged $[MeSi(NCN)_{1.5}]_n$ gel; (c) FT-IR spectrum of hydrolyzed $[MeSi(NCN)_{1.5}]$ (exposed to air for 10 s).

In the Fourier transform (FT)-IR spectra of the as-synthesized and dried gel, absorption bands at $\nu = 2850-2930$ cm^{-1} can be assigned to C—H bonds of $Si(CH_3)_3$ end groups (ν_s $(CH_3) = 2922$ cm^{-1} and ν_{as} $(CH_3) = 2852$ cm^{-1}). In contrast, after aging for 30 days, the relative intensity of the characteristic C—H vibration bands of $Si(CH_3)_3$ cannot be detected whereas the rest of the spectrum corresponds to that of the starting material (Figure 5). The presence of the carbodiimide group in the aged gel is supported by FT-IR (ν_{as}(N=C=N) = 2152 cm^{-1}) and Raman (ν_s(N=C=N) = 1533 cm^{-1}) spectroscopy. Furthermore, the vibrations of $Si-CH_3$ bonds at $\nu = 1270$ cm^{-1} can also be analyzed in the FT-IR spectrum in both samples (Figure 5).

The poly(methylsilsesquicarbodiimide) xerogel is very sensitive to moisture. According to Pump and Wannagat,[55] hydrolysis of silylcarbodiimides proceeds by attack of H_2O at the silicon atom forming silanol groups and cyanamide. Subsequent condensation of the silanol species gives Si—O—Si bonds (eq 19). This behavior is in contrast to that of organic diimides that react with H_2O to give urea derivatives (eq 18).

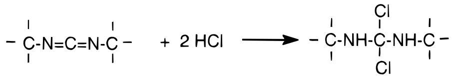

$$-\mathrm{Si{-}N{=}C{=}N{-}Si}- + H_2O \not\longrightarrow -\mathrm{Si{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}Si}- \qquad (18)$$

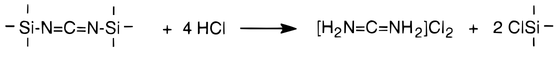

$$-\mathrm{Si{-}N{=}C{=}N{-}Si}- + 2\,H_2O \longrightarrow 2\ -\mathrm{Si{-}OH} + H_2N{-}CN \qquad (19)$$
$$\xrightarrow{-\,H_2O} -\mathrm{Si{-}O{-}Si}-$$

The vibrational spectra, especially the band located at 1063 cm^{-1} (Si—O stretching vibration), unambiguously illustrate the postulated hydrolysis mechanism.

In addition, the shift of the asymmetric carbodiimide vibration band (ν_{as} (N=C=N)) from 2152 cm^{-1} to the typical cyanamide absorption frequency (ν (C≡N)) at 2264 cm^{-1} and the broad signals of the SiO—H and N—H stretching vibrations at 3272 cm^{-1} also support the suggested reaction path.

The carbodiimide polymers are also sensitive to acids like HCl.[55] Organic and inorganic carbodiimides show different reaction mechanisms.


$$-\mathrm{C{-}N{=}C{=}N{-}C}- + 2\,HCl \longrightarrow -\mathrm{C{-}NH{-}\overset{Cl}{\underset{Cl}{C}}{-}NH{-}C}- \qquad (20)$$


$$-\mathrm{Si{-}N{=}C{=}N{-}Si}- + 4\,HCl \longrightarrow [H_2N{=}C{=}NH_2]Cl_2 + 2\,\mathrm{ClSi}- \qquad (21)$$

In the case of organic molecules, the hydrogen chloride reacts with the carbodiimide group to form a secondary amine according to reaction eq 20. It was postulated that the inorganic carbodiimides are protonated by the acid to form a salt by cleavage of the Si—N bonds according to reaction eq 21.[55] Chorosilanes hydrolyze in air forming HCl and siloxanes. Therefore, all synthesis approaches for silylcarbodiimide polymers involving the formation of HCl (see e.g. eq 12) must be carried out in an inert atmosphere to prevent the decomposition of the polymer.

2.5. Silicondicarbodiimide SiC_2N_4. The synthesis of highly crosslinked silylcarbodiimides from trichlorosilanes or tetrachlorosilane is not possible starting from the chlorosilane, cyanamide, and a base, because the resulting solid mixture of the polysilylcarbodiimide and the hydrochloride salt cannot be separated easily. Reacting bis(trimethylsilyl)carbodiimide with the corresponding chlorosilanes gives the desired silylcarbodiimide and trimethylchlorosilane as a byproduct, which can be easily distilled off. Bis(trimethylsilyl)carbodiimide is therefore a suitable reactant to introduce the carbodiimide group into highly crosslinked polymeric silylcarbodiimides.

To prepare silicondicarbodiimide, $Si(NCN)_2$ silicontetrachloride was mixed with bis(trimethylsilyl)carbodiimide in organic solvents like toluene or THF in the presence of pyridine as a catalyst.[1] The reaction (eq 22) can be considered as an oxygen-free sol−gel process resulting in an amorphous, colorless solid gel sensitive towards moisture (see also Section 2.4).

$$n\mathrm{SiCl_4} + 2n(\mathrm{CH_3})_3\mathrm{Si{-}N{=}C{=}N{-}Si}(\mathrm{CH_3})_3 \rightarrow [\mathrm{Si(N{=}C{=}N)_2}]_n + 4n(\mathrm{CH_3})_3\mathrm{SiCl} \qquad (22)$$

According to this process, the morphology of the resulting solid can be influenced by changing the synthesis parameters. Depending on the amount of solvent, the amount of catalyst, the reaction temperature, and stirring rate, silicondicarbodiimide is formed as a fine-grained powder or as a bulk xerogel.

A mixture of pyridine-free reactants yields a solid gel after 8 months, whereas an amount of 0.3 mol pyridine per 1 mol bis(trimethylsilyl)carbodiimide results in the immediate formation of a colorless suspension. ^{29}Si NMR spectroscopy of the reaction mixture showed the formation of $Cl_3Si(NCN)$ sites ($\delta = -44.7$ ppm) as the main product in pyridine-free mixtures after 3 days, in addition to $(CH_3)_3SiCl$ sites ($\delta = 30.2$ ppm) as the byproduct and residual $SiCl_4$ ($\delta = -18.9$ ppm). In

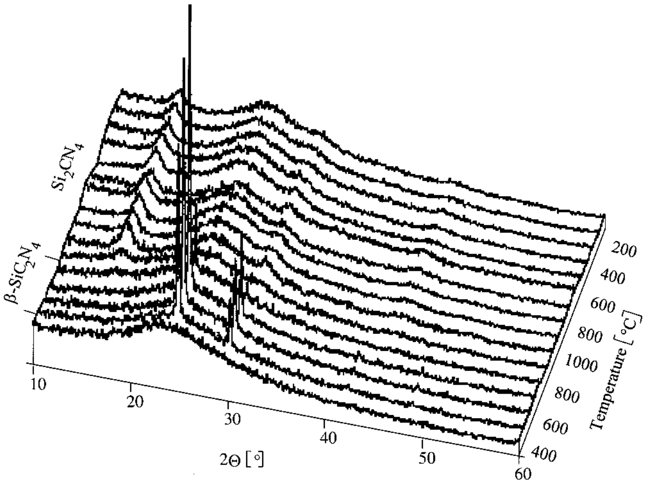


Figure 6. Formation of silicon (carbodiimide)nitride, Si_2CN_4, by pyrolysis of silicon dicarbodiimide, SiC_2N_4, examined by in situ X-ray diffraction (CoKα radiation).[1]

pyridine-containing reactions, different intermediate products can be detected after 3 days. The ^{29}Si NMR spectrum exhibits silicon sites that can be assigned to the presence of $(CH_3)_3SiCl$ ($\delta = 30.2$ ppm), $SiCl_4$ ($\delta = -19.3$ ppm), $Cl_3Si(NCN)$ sites ($\delta = -45.3$ ppm), $Cl_2Si(NCN)_2$ sites ($\delta = -69.3$ ppm) and $ClSi(NCN)_3$ sites ($\delta = -91.6$ ppm). The $Si(NCN)_4$ sites cannot be detected in the solution NMR spectrum, indicating the formation of solid silicondicarbodiimide $[Si(N{=}C{=}N)_2]_n$.

According to FT-IR measurements, the isolated silicondicarbodiimide contained residual trimethylsilyl end groups (Si—CH_3 band at $v = 1258$ cm^{-1}). To reduce the amount of end groups, the reaction product has to be calcined at 350 °C in a vacuum. Further rising of the temperature to 700 °C leads to crystallization of β-silicondicarbodiimide. The crystallization process was investigated in situ by powder X-ray diffraction (PXRD) at temperatures up to 1000 °C.[1]

As shown in Figure 6, the initial crystallization starts at 400 °C with the formation of β-silicondicarbodiimide, which is stable to 800 °C. Once β-SiC_2N_4 has crystallized, it undergoes a reversible phase transformation to α-SiC_2N_4, which has been shown by differential thermal analysis (DTA) experiments to take place at 150−155 °C (Figure 7). However, the crystal structure of α-SiC_2N_4 has not yet been determined.

Crystal Structure of β-Silicondicarbodiimide. The crystal structure of β-SiC_2N_4 was derived from PXRD data.[1] The measurements were performed in situ in the temperature range 250−650 °C. Within the accuracy of the measurements, no thermal expansion of β-SiC_2N_4 could be detected. The PXRD diffractogram shows only five lines: two intensive and sharp lines at low 2Θ values and three small lines in the higher 2Θ range. The structure determination by Rietveld refinement led to a cubic structure in the space group *Pn*3*m* (no. 224), which displays the topology of the anti-cuprite structure. The structure can be considered as two independent, interpenetrating networks[56] of the high cristobalite-type (SiO_2), with carbodiimide groups replacing the oxygen atoms. In this structure, the SiN_4 tetrahedra are interconnected by *sp*-hybridized carbon atoms as depicted in Figure 8.

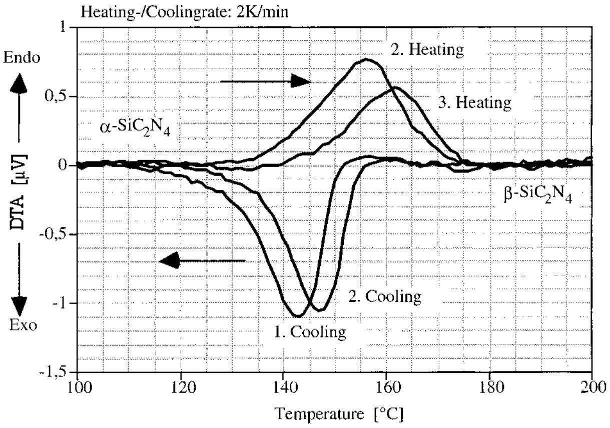


Figure 7. DTA examination of the reversible phase transition between α- and β-SiC_2N_4. The first heating cycle is applied to crystallize the amorphous SiC_2N_4 at $T > 400$ °C. It is obvious that the phase transition temperature increases from the second to the third heating cycle. This result is attributed to a reduced number of structural defects. The phase transition of all following heating cycles occurs at the same temperature as observed for the third cycle. The hysteresis effect is associated with the relatively high heating rate of 2 K/min.[35]

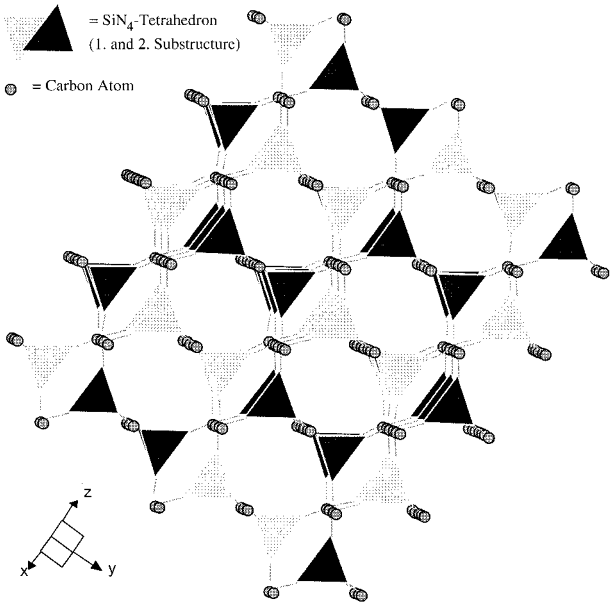


Figure 8. Solid-state structure of β-SiC_2N_4 determined from XRD using the Rietveld refinement method.[1,35]

The PXRD diffractogram shows an extreme decrease in intensity of the reflexes with decreasing *d*-value. This decrease leads to root mean square (rms) amplitudes of ~50 pm for all atoms, indicating a considerable static disorder.[1] The average structure, with symmetry-enforced Si—N—C bond angles of 180°, results in very short calculated interatomic distances for Si—N of 158 pm and for N—C of 110 pm. For the real Si—N—C, bond angles are known to be $<180°$ and the interatomic distances are certainly not shortened as much as calculated for this structure. The given atom positions can be considered as projections of the true positions and distances onto the space diagonal of the unit cell. The comparatively narrow line profiles of the PXRD diffractogram show that long-range order is preserved. Calculating the Si—N—C bond angle by taking the expected interatomic distances (Si—N $\approx$ 170 pm, N—C

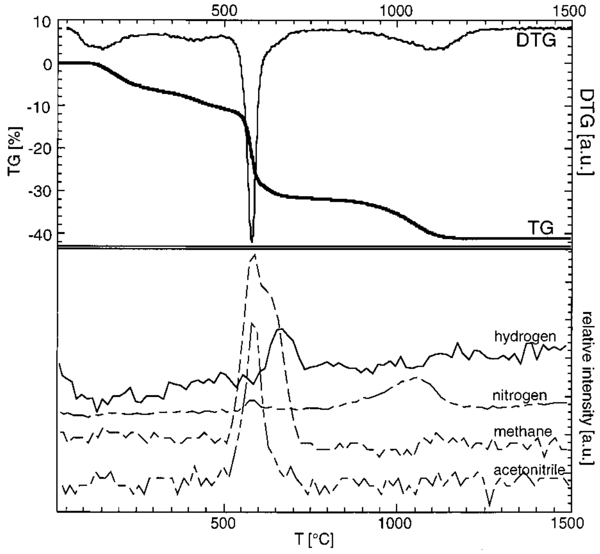


Figure 9. TGA of $[(H_3C)Si(NCN)_{1.5}]_n$ and the temperature-dependent evolution of the volatile gas species analyzed by in situ mass spectrometry.

≈ 120 pm) and bending the N=C=N group out of the space diagonal of the unit cell gives an Si—N—C bond angle of ~135° after neglecting possible dihedral angles.

2.6. Thermal Stability of Silylcarbodiimides. (a) $[R_2Si{-}N{=}C{=}N{-}]_n$. The synthesis of oligomeric cyclic silylcarbodiimides ($[RR'Si{-}N{=}C{=}N{-}]_n$, with R = CH_3 and R′ = H, CH_3, and $H_2C{=}CH$) and the structural characterization of the dimethylsilyl-substituted carbodiimide (with $n = 4$) initiated a systematic study of silylcarbodiimides produced from $R_{4-x}SiCl_x$, with $2 \leq x \leq 4$. Our particular interest is devoted to the thermally induced conversion of poly(silylcarbodiimides) to ceramics in the ternary Si—C—N system. The pyrolysis of $[(CH_3)RSi{-}N{=}C{=}N{-}]_n$ at 1050 °C in Ar gives amorphous silicon carbonitride ceramics with up to 70 wt % yield for R = H or $HC{=}CH_2$. The molar compositions have been analyzed to $Si_{1.0}C_{1.1}N_{1.4}$ (R = H), $Si_{1.0}C_{1.8}N_{1.2}$ (R = CH_3), and $Si_{1.0}C_{2.0}N_{1.1}$ (R = $HC{=}CH_2$). It is evident that for R = H, the composition is close to $Si_3C_3N_4$ and is, therefore, located on the C—Si_3N_4 tie line in the ternary SiCN phase diagram.[34] Thermodynamically, a solid-state reaction to form stoichiometric SiC is expected at enhanced temperatures ($T > 1400$ °C) according to the following reaction equation

$$Si_3C_3N_4 \rightarrow 3\ SiC + 2\ N_2 \qquad (23)$$

All other compositions give SiC/C mixtures upon crystallization at $T > 1500$ °C.

(b) $[RSi(N{=}C{=}N)_{1.5}]_n$. The thermal decomposition of poly(methylsilsesquicarbodiimide) up to 1450 °C gives a total ceramic yield of 60 wt %.[42] Analysis of the weight change versus temperature by thermal analysis coupled with mass spectrometry [thermogravimetric analysis (TGA)/MS] shows three distinguished steps characterized by weight loss (Figure 9). In the first step between room temperature and 550 °C, the mass change is due to evaporation of residual $(CH_3)_3SiCl$. The ceramization reaction proceeds at $T = 570{-}650$ °C with a loss of H_2, CH_4, and acetonitrile (CH_3CN), which are identified unambiguously by simultaneous MS (Figure 9). Finally, nitrogen is evolved exclusively between 850 and 1100 °C. The thermally induced polymer-to-ceramic conversion also coincides with the results from the FT-IR studies of $[RSi(N{=}C{=}N)_{1.5}]_n$ annealed between 200 and 1200 °C. Above 600 °C, the Si—CH_3 vibration at 1270 cm^{-1} decreases with increasing temperature, whereas the relative intensity of the asymmetric N=C=N absorption band declines after annealing between 800 and 1200 °C. X-ray diffraction studies of heat-treated $[RSi(N{=}C{=}N)_{1.5}]_n$ show no indications of the formation of crystalline phases. The material remains amorphous up to 1400 °C. ^{29}Si and ^{13}C solid-state NMR investigations give clear evidence that the decomposition of $[RSi(N{=}C{=}N)_{1.5}]_n$ at $T \geq 1200$ °C results in a mixture of amorphous silicon nitride and carbon. The chemical bulk analysis reveals a composition of 1 mol Si_3N_4 and 3 mol C, which in turn results in stoichiometric SiC at $T > 1500$ °C and 0.1 MPa Ar according to reaction eq 23.

(c) $[Si(N{=}C{=}N)_2]_n$. Silicondicarbodiimide, SiC_2N_4, decomposes at 940−1000 °C to yield colorless nanocrystalline silicon(carbodiimide)nitride, Si_2CN_4. Cyanogen and nitrogen are formed as gaseous side-products (eq 24). The solid-phase decomposition of SiC_2N_4 to Si_2CN_4 was analyzed by simultaneous TGA. A weight loss of ~40% above 900 °C coincides with two exothermal peaks in the DTA, which are attributed to the formation of cyanogen (C_2N_2) and nitrogen as well as to the crystallization of Si_2CN_4, respectively. The gaseous byproducts, cyanogen and nitrogen, have been detected in situ with a mass spectrometer linked to the TGA/DTA furnace. Accordingly, the following reaction equation can be derived

$$4\ SiC_2N_4 \rightarrow 2\ Si_2CN_4 + N_2 + 3\ C_2N_2 \qquad (24)$$

At temperatures >1000 °C, the reaction product Si_2CN_4 gradually decomposes to form amorphous silicon carbonitride. According to solid-state NMR studies, the SiCN material disintegrates to give amorphous carbon embedded in an amorphous silicon nitride matrix. Between 1500 and 1600 °C, crystallization of the thermodynamically stable binary phases, namely α-Si_3N_4 and α-SiC, is analyzed.

(d) Crystal Structure of Silicon(carbodiimide)nitride Si_2CN_4. In contrast to silicondicarbodiimide (SiC_2N_4), silicon(carbodiimide)nitride (Si_2CN_4) is relatively stable in air. The PXRD diffractogram displays broad lines of different shape and half-width. The formation of nanocrystals, indicated by this broadening of the X-ray reflections, was confirmed by transmission electron microscopy (TEM, Figure 10). Si_2CN_4 has a plate-like shape with a thickness of 4 to 10 nm and a lateral extension of 20 to 70 nm. The crystal structure was determined from PXRD data. Silicon(carbodiimide)nitride crystallizes in the space group *Aba*2, with a structure similar to that of silicon oxynitride (Si_2N_2O).[57]

Figure 11a shows the topology of the crystal structure of Si_2CN_4, consisting of layers of condensed SiN_4 tetrahedra, with apical N atoms belonging to the carbodiimide groups that link the SiN layers along the *b* axis. The interlayer distance is 0.679 nm, which is in accordance with the concentration of scattering density in planes with distances of ~0.7 nm in the TEM micrographs (Figure 11b).

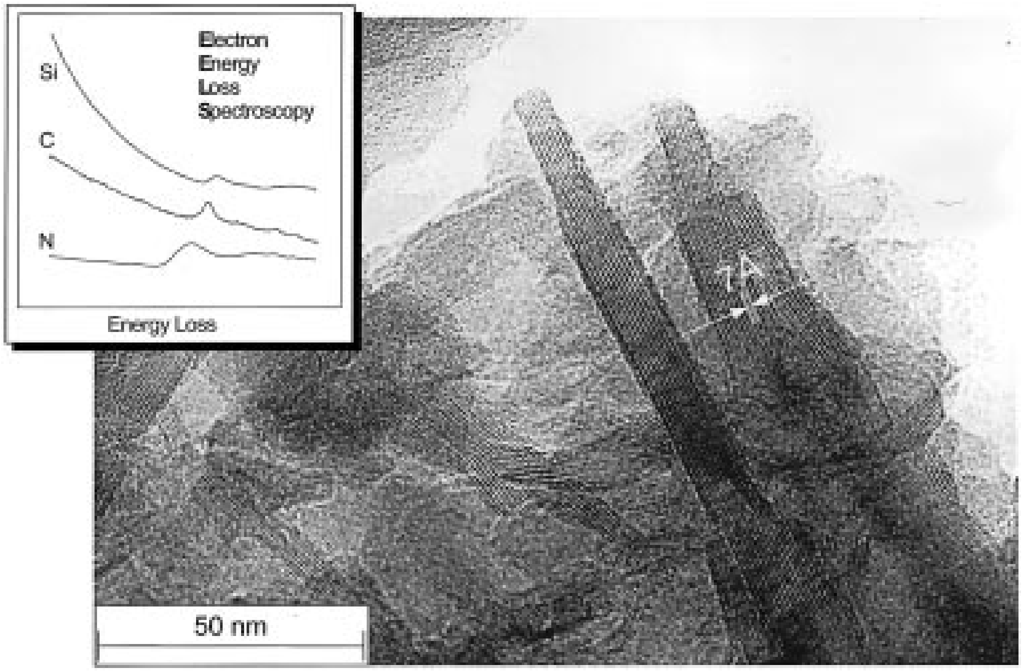


Figure 10. High-resolution TEM of nanocrystalline Si_2CN_4 obtained at 960 °C from SiC_2N_4. The EELS investigation of the crystals proves the presence of silicon, carbon, and nitrogen.

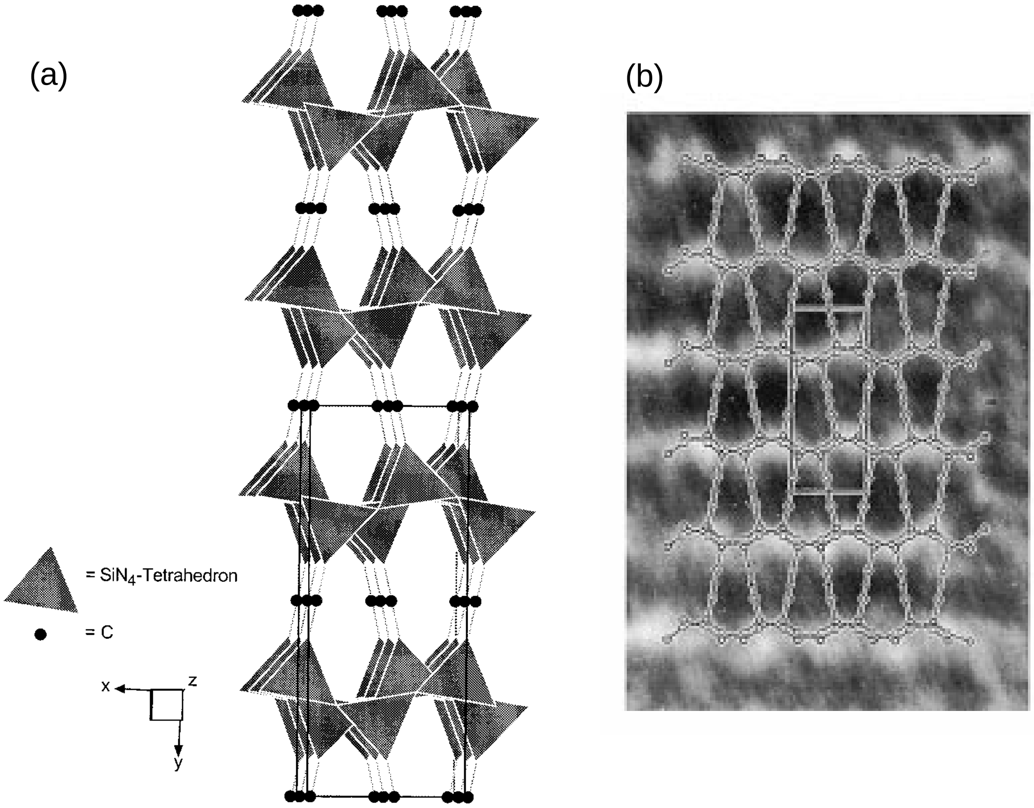


Figure 11. (a) Solid-state structure of Si_2CN_4. The view along the *z* axis shows layers consisting of SiN_4 tetrahedra. The layers are interconnected by the carbon atoms of the carbodiimide groups. (b) Superposition of the Si_2CN_4 structure with the high-resolution TEM micrograph indicating the high electron density (white areas) stemming from the SiN_4 layers.

(e) Decomposition Mechanism of Elementcarbodiimides. The thermal decomposition of group 14 elementcarbodiimides $E(N{=}C{=}N)_2$, with E = C, Si, or Ge, reveals significant similarities. Silicondicarbodiimide, $Si(NCN)_2$, decomposes at 960 °C under evolution of cyanogen and nitrogen to form Si_2CN_4 (vide supra and Figure 12).

Amorphous germaniumdicarbodiimide is thermally less stable. It decomposes above 720 °C with the loss N_2 and C_2N_2 (see Section 3 and Figure 12). Similarly "cyanurcarbodiimide" (E = C), formed by the reaction of cyanuric fluoride and bis(trimethylsilyl)carbodiimide, produces cyanogen and nitrogen at temperatures of ~650 °C (see Section 4 and Figure 12). A probable

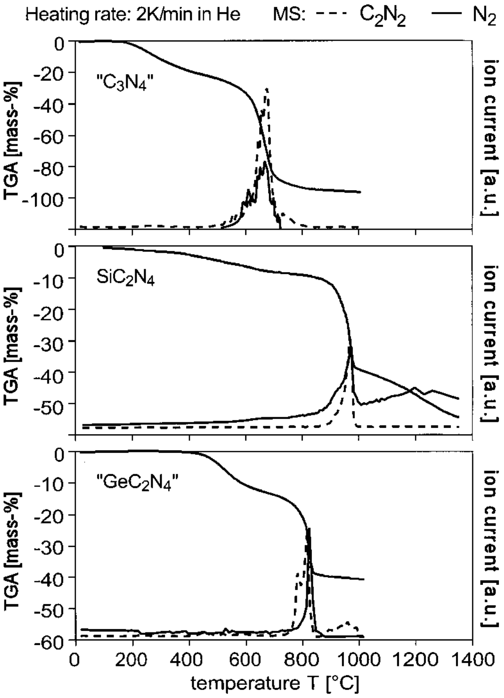
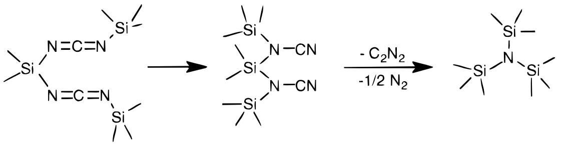


Figure 12. Comparison of the TGA curves of group 14 element carbodiimides. The outgassing species cyanogen (C_2N_2) and nitrogen as detected by in situ mass spectrometry are also shown versus temperature.

decomposition mechanism explaining the evolution of cyanogen is discussed in terms of the cleavage of C—N bonds of cyanamide units that are most likely present in "cyanurcarbodiimide" and germaniumdicarbodiimide. In the case of E = Si, the isomeric cyanamide structure might be formed intermediately by rearrangement during pyrolysis of disilylcarbodiimides, as depicted in reaction eq 25.



(25)

An additional decomposition mechanism has to be considered for the pyrolysis of polysilsesquicarbodiimides $[RSi(NCN)_{1.5}]_n$ (vide supra).[42] For R = methyl and R = phenyl, the formation of acetonitrile and benzonitrile were detected at ~560 °C. This temperature range is where the main decomposition reaction of poly(silsesquicarbodiimide)s proceeds. A 1,3-migration of the methyl or phenyl substituent from the silicon to the carbon atom of the carbodiimide group has to be taken into account.[42] This mechanism does not exclude an intermediate carbodiimide–cyanamide rearrangement.

2.7. Physical Properties of Polysilylcarbodiimides. *(a) Vibrational Spectroscopy.* FT-IR spectra of polysilylcarbodiimides reveal essentially three characteristic vibrational bands. In particular, the spectra of $[Si(N{=}C{=}N)_2]_n$ indicate that silicon is exclusively coordinated to carbodiimide groups. The very intense and broad band of the asymmetric vibration of the carbodiimide unit (ν_{as} N=C=N) can be found at $\nu = 2173\ cm^{-1}$. The likewise strong band of the deformation vibration δ N=C=N is located at $\nu = 795\ cm^{-1}$, and a band of medium intensity can be determined for the Si—N vibrations (ν Si—NCN) at $\nu = 578\ cm^{-1}$.

Vibrational spectroscopy is particularly useful to distinguish between a carbodiimide and a cyanamide configuration. Although the asymmetric N=C=N vibration is found at wavenumbers similar to those of the C≡N bonding (cyanamide modification), the linear N=C=N group has approximately $D_{\infty h}$ symmetry, which allows only the asymmetric vibrational band to occur in the IR spectra. For the cyanamide modification with lower C_{2v} symmetry, the symmetric vibration band of the N—C≡N group is also expected with a strong band at $\nu = 1550-1560\ cm^{-1}$. On the one hand, the absence of this band in the IR spectra is strong evidence for the carbodiimide configuration rather than for the cyanamide structure. On the other hand, the symmetric vibration of the carbodiimide unit at $\sim 1550\ cm^{-1}$ is allowed in Raman spectroscopy. Accordingly, the combination of FT-IR and Raman spectroscopy is a powerful tool to elucidate the structure of carbodiimide and cyanamide compounds. The FT-IR spectra of silicon(carbodiimide)nitride, Si_2CN_4, which is formed by decomposition of SiC_2N_4 (see Section 2.6) show the characteristic bands of the silylcarbodiimides.[1] In this case, additional vibration bands can be detected for the Si—N bonds of the SiN planes at $\nu = 946\ cm^{-1}$, $\nu = 901\ cm^{-1}$, and $\nu = 509\ cm^{-1}$.

(b) NMR-Spectroscopy. In the ^{29}Si magic-angle spin (MAS) NMR spectroscopy, the resonance signals of polysilylcarbodiimides are characterized by chemical shifts to unusual high field compared with other Si—N compounds, such as polysilazanes or silicon nitride, Si_3N_4. This finding is explained in accordance to the pseudoelement concept[58] in which the NCN group is considered to be a pseudochalcogen with a group electronegativity similar to that of oxygen.[59] Therefore, silicon carbodiimides strongly reflect similarities to the corresponding silicon oxide compounds with regard to their chemical reactivity and physical properties.

For silicondicarbodiimide with Si coordinated to four [N=C=N] units, one resonance signal can be found in the ^{29}Si MAS NMR spectrum at $\delta = -104$ ppm. This chemical shift is comparable to that of SiO_2 ($\delta = -110$ ppm) but far from that of SiN_4 sites (β-Si_3N_4: $\delta = -48.7$ ppm[60]). Moreover, investigation of the ^{29}Si NMR chemical shift of silicon carbodiimides with different Si coordination, $Si(NCN)_x(CH_3)_{4-x}$ sites with $4 \geq x \geq 0$, reveal a remarkable accordance with that of the corresponding silicon oxides containing $SiO_x(CH_3)_{4-x}$ sites (Figure 13).

The structure of silicon(carbodiimide)nitride is comprised of $SiN_3(NCN)$ sites exclusively. The ^{29}Si MAS NMR spectrum exhibits only one signal, with a chemical shift $\delta = -67$ ppm, which is close to that of SiN_3O sites in silicon oxynitride (Si_2N_2O: $\delta = -62$ ppm).

(c) X-ray Absorption Near Edge Spectroscopy (XANES). XANES allows one to elucidate the coordination sphere of the investigated nucleus. XANES spectra must be carefully referenced to compounds with well-known structure and chemical composition. Each atom or atom group bonded to the investigated nucleus generates a characteristic resonance signal in the spectrum. XANES enables one to identify the type of atoms or groups

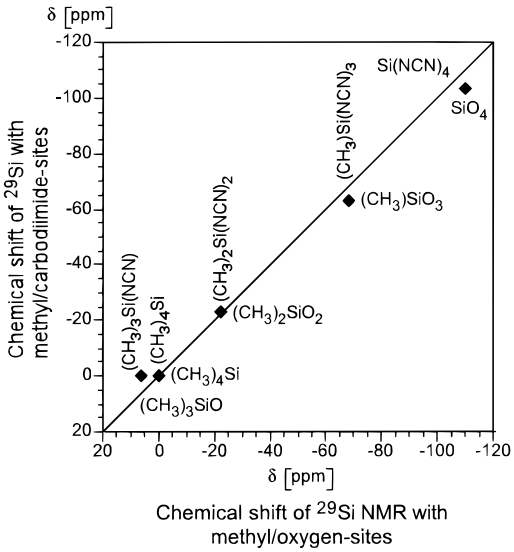


Figure 13. Comparison of the ^{29}Si NMR chemical shifts for $Si(CH_3)_x(NCN)_{4-x}$ environments with the corresponding $Si(CH_3)_x(O)_{4-x}$ environments. It is obvious that almost the same values are found for each $Si(CH_3)_x(X)_{4-x}$ coordination. Equivalent diagrams can be drawn for $Si(N)_x(NCN)_{4-x}$ and $Si(N)_x(O)_{4-x}$ sites, as well as for $Si(Cl)_x(NCN)_{4-x}$ and $Si(Cl)_x(O)_{4-x}$ sites.

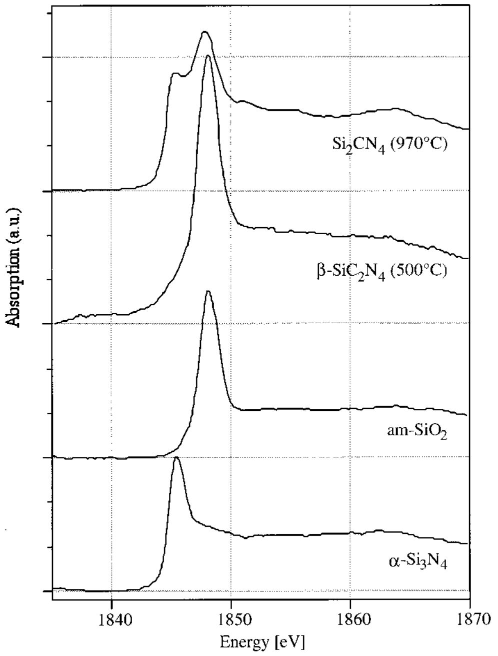


Figure 14. XANES at the Si—K edge of the novel Si—C—N phases Si_2CN_4 and β-SiC_2N_4. The comparison with amorphous SiO_2 and α-Si_3N_4 shows that the carbodiimide group gives rise to the same absorption energy as oxygen bonded to silicon.

coordinating the nucleus, whereas with NMR spectroscopy, one can distinguish different sites but not single neighbors of a nucleus. Silicondicarbodiimide, consisting exclusively of $Si(NCN)_4$ sites, shows a characteristic resonance (white line at 1848.0 eV) that is similar to that of oxygen (SiO_2; white line at 1848.05 eV) in the XANES spectrum at the Si—K edge.[61] Again the pseudochalcogenic character of the carbodiimide group leads to results that are in accordance with oxygen-containing compounds (Figure 14).

In the XANES Si—K edge spectrum, the Si_2N_2O-analogous silicon(carbodiimide)nitride, $Si_2N_2(NCN)$ (see Section 2.6) shows two main resonances at 1845.2 eV (white line) and at 1847.8 eV, indicating the presence of Si—N bonds (α-Si_3N_4: white line at 1845.45 eV) and Si—NCN bonds.

3. Germaniumdicarbodiimide

The synthesis of germaniumdicarbodiimide GeC_2N_4 is performed in an analogous manner to the synthesis of silicondicarbodiimide (eq 27).[35]

$$n\mathrm{GeCl_4} + 2n\,(\mathrm{CH_3})_3\mathrm{Si{-}N{=}C{=}N{-}Si(CH_3)_3} \rightarrow [\mathrm{Ge(N{=}C{=}N)_2}]_n + 4n(\mathrm{CH_3})_3\mathrm{SiCl} \quad (27)$$

To enforce this reaction, the byproduct trimethylchlorosilane has to be distilled off. A colorless solid remains. Calcination of this solid under reduced pressure at 350 °C removes most of the trimethylsilyl end groups. The FT-IR spectrum of the solid product implies not only the presence of carbodiimide units, but the formation of the cyanamide structure has also to be taken into account. TGA of GeC_2N_4 shows a decomposition reaction at temperatures >720 °C (Figure 12). Mass spectroscopy was used to detect the evolution of cyanogen and nitrogen. In contrast to SiC_2N_4, no crystallization was analyzed by in situ XRD measurements. After the decomposition reaction, the formation of crystalline germanium was detected. Recently, cyclic oligomers of dimesitylgermyl carbodiimides were synthesized by reactions between dimesityldichlorogermane and either cyanamide in the presence of triethylamine or lithium cyanamide.[32] X-ray analyses of the trimer and the tetramer show unstrained tetrahedral germanium atoms linked by carbodiimide units. This result is rather close to the molecular structure of $[(H_3C)_2SiNCN]_4$ already described (see also Section 2.2).

4. Carbon(IV)-Carbodiimides and Boron-Containing Carbodiimides

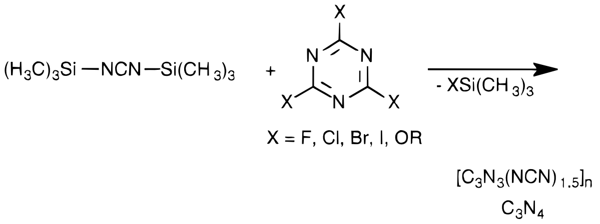
Solids containing only carbon and nitrogen, that is to say compounds in the binary CN_x system, and ternary BC_xN_y compounds are interesting materials.[62−64] Several theoretical examinations show, that *sp*^{3}-hybridyzed carbon(IV)nitrides with a stoichiometriy of C_3N_4 are ultrahard and have diamond-like properties.[65−67] Furthermore, these materials are of great interest for their electronic, optical, and mechanical properties, like large tunable band gaps or a negative Poisson ratio. Similar characteristics are predicted for B/C/N phases. Three-dimensional *sp*^{3}-networks should have properties intermediate to *c*-BN, and diamond, layered, hexagonal *sp*^{2}-structures correspond to *h*-BN and graphite.

A new and promising method for the synthesis of (B)/C/N polymers is the carbodiimidolysis of boron and carbon halides. These polymers can be used as precursors for ceramic (B)/C/N materials, including *sp*^{3}-hybridized C_3N_4 phases and graphitic or diamond-like $B_xC_yN_z$ materials.

Three-dimensional carbon nitride structures analogous to that of β-SiC_2N_4, as described in Section 2, can be designed with the stoichiometry C_3N_4 if the Si atoms are replaced by carbon. Reactions of CX_4 (X = halogen) instead of $SiCl_4$ with bis(trimthylsilyl)carbodiimide can produce a polymeric network with C_3N_4 stoichiometry

$$\underset{X = F, Cl, Br, I, OR}{(CH_3)_3Si{-}N{=}C{=}N{-}Si(CH_3)_3 + CX_4} \xrightarrow[-XSi(CH_3)_3]{} \underset{C_3N_4}{[C(NCN)_2]_n} \quad (28)$$

In the case of CBr_4, bromine is not completely substituted.[35,68] Another approach to obtain a three-dimensional carbon(IV)nitride is to replace the hydrogen atoms in hexamethylenetetramine by carbodiimide bridges. However, to our knowledge no attempts have been made to synthesize this structure. Furthermore, a carbodiimide-containing C_3N_4 network can be considered to be obtained by the polymerization of the hypothetical dicyanocarbodiimide NC−NCN−CN. Because dicyanocarbodiimide is not known and most likely very difficult to synthesize,[69,70] we have produced these materials by reaction of cyanuric halides with bis(trimethylsilyl)carbodiimide, as shown in reaction eq 29[71]



(29)

This reaction was examined using cyanurfluoride and cyanurchloride, different solvents, and several different reaction conditions. Depending on the temperature, reaction time, and presence of a catalyst, yellow, green, brown, or black powders are formed. The elemental composition varies from close to C_3N_4 to strongly contaminated with halogen and/or silicon and hydrogen. IR, Raman, and electron spectroscopy for chemical analysis (ESCA) examinations indicate that the carbodiimide group most likely rearranges during the reaction to form cyanamide units.

B/C/N-containing materials have generated considerable interest recently due to their potential application as a semiconducting material. In addition, most ultrahard materials can be found in the B/C/N system.[62−64] Thus, candidates for future hard materials are expected to be found in this system.

The first reactions of bis(trimethylsilyl)carbodiimide with boron-containing dialkylboron halides R_2BX (with R = phenyl, butyl, methyl, $-N(CH_3)_2$; and X = halogen) were performed by Schroen.[72] The preparation of $Bu_2BN{=}C{=}NBBu_2$ results in an insoluble yellow flaky polymer. ^{11}B NMR displays two signals at −52.5 and −31 ppm. The IR spectrum is dominated by bands at 2200 and 1650 cm^{-1}, suggesting the presence of a carbodiimide group. Likewise, the carbodiimide group can be found in the reaction products of bis(trimethylsilyl)carbodiimide with $ClB(NMe_2)_2$ and Ph_2BBr. However, the carbodiimide group is not preserved in the reaction of bis(trimethylsilyl)carbodiimide with Me_2BBr.

Einholz and co-workers[73,74] continued Schroen's research on borylated carbodiimides. Reactions of bis(trimethylsilyl)carbodiimide with boron trihalides are described in a patent.[75] A boron-containing carbodiimide has been synthesized in our laboratory by the reaction of bis(trimethylsilyl)carbodiimide with boron trichloride. Taking into account the reaction of bis(trimethylsilyl)carbodiimide with $SiCl_4$, we expected the formation of boroncarbodiimide $[B(NCN)_{1.5}]_n$ with a B_2O_3 analogous structure

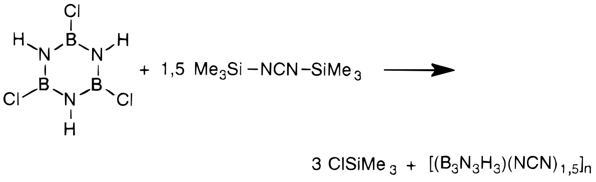
$$BCl_3 + 1.5\ Me_3Si{-}N{=}C{=}N{-}Si\ Me_3 \rightarrow [B(N{=}C{=}N)_{1.5}]_n + 3\ Me_3SiCl \quad (30)$$

A fine, yellow powder was obtained as the reaction product after distillation of CH_3SiCl. The presence of the carbodiimide group was analyzed by FT-IR and Raman spectroscopy. However, the vibrational spectra also suggest that the carbodiimide groups are partially replaced by cyanamide groups. Solid-state ^{11}B NMR investigations revealed three signals at −4.5, 11, and 18.5 ppm. A chemical analysis gave a composition of $Si_{1.00}B_{1.05}N_{3.95}C_{5.96}H_{9.04}$, with chlorine below the detection limit. Thus, chlorine can be completely replaced by use of excess bis(trimethylsilyl)carbodiimide, but at the expense of an increased silicon content. The following reaction is postulated using the results of the chemical analysis

$$BCl_3 + 3Me_3Si{-}N{=}C{=}N{-}SiMe_3 \rightarrow B(CN)_2(N{=}C{=}N)SiMe_3 + 3\ Me_3SiCl + N_2 + Me_3Si{-}SiMe_3 \quad (31)$$

The formation of hexamethyldisilane has been detected by in situ MS in the temperature range between 100 and 400 °C.

A similar approach to the aforementioned synthesis of carbon nitrides by the reaction of bis(trimethylsilyl)carbodiimide with cyanurhalides was also applied to the preparation of B/C/N polymers.[71] Borazine trichloride, $B_3N_3H_3Cl_3$, reacts with bis(trimthylsilyl)carbodiimide to form precipitates or gels analogous to the Si/C/N gels formed with trichlorosilanes (see Section 2.3)



(32)

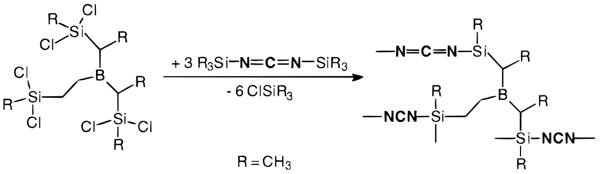
The reaction proceeds with or without a solvent at temperatures from 20 to 80 °C. The IR spectra indicate that the carbodiimide groups are still present. Elemental analyses show that only minor amounts of chlorine and silicon contaminations are left in the reaction product.

Currently we are examining the reactions described in this paragraph with respect to use the solid element carbodiimides as precursors for the synthesis of novel ceramic materials. It is expected that depending on the composition and structure of the obtained products, interesting mechanical, thermal, and electronic properties like ultra-high hardness, high-temperature stability, or semiconduction can be obtained.

5. Boron-Containing Polysilylcarbodiimides

Boron-containing silicon carbonitrides are candidate materials with excellent high-temperature properties, as reported by Riedel et al.[76] Based on hydroboration reactions of vinylsilanes and subsequent ammonolysis, the intermediately formed silyl-substituted borane was transformed into Si/B/C/N polymers. The obtained boron-containing polyorganosilazanes exhibit an extremely high temperature resistance towards decomposition between 1000 and 2000 °C. However, molecular starting materials are required for the production of homogenous and thermally stable ceramics.[77]

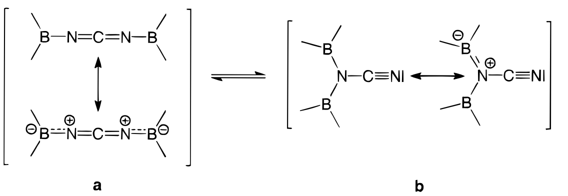
Basically, the production of boron-modified polysilylcarbodiimides can be accomplished by subsequent treatment of polysilylcarbodiimides with reactive boron compounds.[33,34,41] Another route to produce Si/B/C/N polymers was published by Bill and Aldinger.[78,79] In this study, the polymerization of tris[(dichloromethylsilyl)ethyl]borane with bis(trimethylsilyl)carbodiimide, as depicted by reaction eq 33 was investigated. In the absence of any solvent or catalyst, a colorless gel is formed that is analogous to the non-oxidic sol−gel process described in Section 2.3.



(33)

Usually, the polycondensation of the single-source precursors already described was accomplished by reactions with ammonia or amines like methylamine. Polymers prepared by this method are always formed together with an enormous amount of ammonium salt. The separation of the byproduct from the soluble polyorganoborosilazane reduces the total yields. Exchange of amines by bis(trimethylsilyl)carbodiimide excludes the formation of ammonium salts, and volatile chlorotrimethylsilane is produced instead. The concurrent generation of a three-dimensional covalent network and a liquid results in the formation of a non-oxidic polymeric gel. The sol−gel transition (i.e., gelation time and viscosity) is controlled by the reaction temperature and by the use of solvents.

Reactions of chlorosilyl-substituted chloroboranes with bis(trimethylsilyl)carbodiimides produces novel Si/B/C/N polymers[80] containing B−N bonds. As depicted in eq 34, depending on the substituents on the boron and silicon atoms, the carbodiimide or the cyanamide structure can be formed[74] (see also Section 4).



(34)

In the course of our work we synthesized new single-source precursors by hydroboration of vinylsilanes with chloroboranes followed by reaction with hexamethyldisilazane (eq 35). In this case, hexamethyldisilazane reacts at the boron atom to form B−N bonds at low temperatures. No reaction was detected at the silicon atoms under these conditions. The boron coordination was changed from BC_3 (eq 33) to BNC_2 (eq 35).[81] Subsequent reaction of the diborylamine with bis(trimethylsilyl)carbodiimide gave polymeric gels with the carbodiimide unit as the former interconnecting network (eq 36).

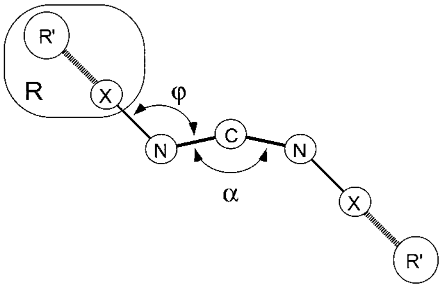
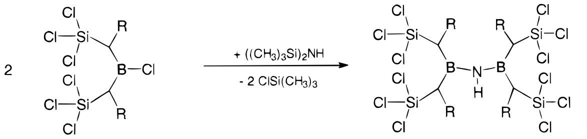
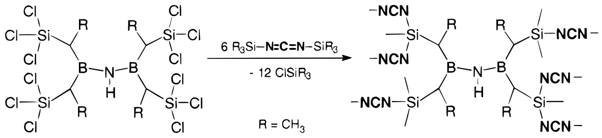


Figure 15. The general structure of symmetrically substituted carbodiimides, with R = XR′. X is the element bonding to the nitrogen atom, φ is the X−N−C angle, and α is the N−C−N angle.



(35)



(36)

The obtained novel polyborosilylcarbodiimides are presently being studied with respect to their application as precursors for ultra-high-temperature-resistant carbonitrides.

6. Theoretical Studies of the Geometrical Structure and the Electronic Properties of Carbodiimides

General Remarks. Early semiempirical molecular orbital calculations on carbodiimide and some of its symmetrically substituted derivatives were carried out by Gordon and Fischer[82] and by Williams and Damrauer.[83,84] The investigations concentrated on the bond angle φ at the nitrogen of the carbodiimide group (see Figure 15) as well as on the dihedral angle τ between the two planes R−N=C and C=N−R. Analogy to the isoelectronic allene would lead to $\tau = 90°$, and indeed τ is calculated to be ~90° for all carbodiimides, indicating that the R−N=C and C=N−R planes are perpendicular to each other. The bond angle φ varies from 110° to 180°, depending on the substituent. Moreover, the calculated value of φ for carbodiimide shows a large variation, depending on the level of theory applied.[85] The C=N bond length in carbodiimides is ~1.22 Å, which is intermediate between characteristic CN double- and CN triple-bond lengths.

The molecular orbitals of the carbodiimide molecule are published in the book of Jorgensen and Salem,[86] and are based on small basis set ab initio calculations. Both highest occupied molecular orbitals (HOMO and HOMO-1) correspond to "nitrogen lone-pair" electrons and show only very small coefficients on the central carbon. The lowest unfilled molecular orbital (LUMO), in contrast, is substantially localized on the central carbon atom. In general, there is a similarity between the molecular

Table 2. Results of DFT Calculations for Symmetrically Substituted Carbodiimide Molecules[91] [a]

X	R	$d_{C=N}$	α_{NCN}	$\varphi_{C=N-X}$	$\tau_{XNC..CNX}$	ΔE
H	H	1.227	169.3	120.0	87.2	70
Cl	Cl	1.236	166.8	116.5	89.2	
N	NH_2	1.237	169.1	122.0	98.1	
C	CH_3	1.226	170.1	128.4	90.1	55
C	$C(CH_3)_3$	1.228	170.2	128.0	90.7	
C	CN	1.213	168.4	143.3	82.8	
C	C_6H_5	1.225	170.0	132.5	89.0	38
C	$C_3N_3F_2$	1.220	174.3	132.2	87.5	27
Si	SiH_3	1.213	176.5	157.6	89.8	2
Si	$Si(CH_3)_3$	1.216	177.5	153.2	99.8	1
Si	$Si(NH_2)_3$	1.216	175.9	149.1	90.4	
Ge	GeH_3	1.224	173.6	133.9	96.9	16
Ge	$Ge(CH_3)_3$	1.226	174.0	134.9	99.3	
B	BH_2	1.209	180	180		0
B	$B(CH_3)_2$	1.209	180	180		0

[a] X is the atom bonded to the nitrogen of the carbodiimide, R is the whole substituent, $d_{C=N}$ (in Å) is the C=N bond length, α_{NCN} and $\varphi_{C=N-X}$ (in degrees) are internal parameter as given in Figure 15, $\tau_{XNC..CNX}$ (in degrees) is the dihedral angle between the two planes XNC and CNX, ΔE (in kJ/mol) is the difference in energy between the ground state and the structure with a linear X—NCN—X fragment.

orbitals of other heterocumulenes O=C=O, $H_2C=C=O$, $H_2C=N^+=N^-$, as well as allene $H_2C=C=CH_2$, and those of carbodiimide.

A frequent motivation for calculations of carbodiimide is curiosity concerning the relative stability to its isomers. Hart[87] was the first to explore the energy hypersphere using ab initio methods. He was followed by Moffat,[88] Thomson and Glidewell,[89] as well as Guimon et al.[90] Although it is experimentally evident that cyanamide (H_2N—CN) is the thermodynamically stable isomer at ambient temperature and pressures, it is striking that in the series of computational studies, the difference in total energy between carbodiimide and its tautomeric cyanamide decreases as the theoretical method applied improves.[90] Density functional studies even favor the carbodiimide structure over the cyanamide structure by 12 kJ/mol.[91]

The N=C=N angle α is also of interest. According to XRD data, the carbodiimide group is not linear; α can be as low as 166° for aliphatic- and aromatic-substituted carbodiimides[92] and 172.6° in silylated carbodiimides.[20] To explain this “unexpected” trend by the influence of packing factors in the solid state is not sufficient. Nearly all carbodiimides investigated exhibit this anomaly, as first mentioned by Thomson and Glidewell[89] in their ab initio study. All later investigators confirmed this trend for carbodiimide. However, the energy difference between the computed minimum and a structure with a linear NCN fragment is very small (4 kJ/mol[93]).

Elementorganic Carbodiimides. The only published calculations on a silylated carbodiimide molecule (disilylcarbodiimide), as well as boron, beryllium, and lithium derivatives, can be found in Pasinski et al.[94] In comparison with alkyl and aryl carbodiimides, which generally have a high barrier to linearity of the X—NCN—X fragment, these investigators found a very low barrier for disilylcarbodiimide, which is consistent with the low frequency for the deformation. The beryllium and the boron derivative were calculated to be linear.

Recent density functional calculations on a large variety of symmetrically substituted carbodiimides,[91] summarized in Table 2, agree with these results. In the simple borylated carbodiimides, diborylcarbodiimide and bis(dimethylboryl)carbodiimide, the linear arrangement is energetically favored. Silylated and germylated carbodiimides are still bent at the nitrogen, but with an order of magnitude smaller energy, disfavoring the ‘ideal’ linear arrangement ($\varphi = 180°$ and $\alpha = 180°$). Figure 16 displays the variation of the total energy with bond angle φ for bis(trimethylsilyl)carbodiimide.[95] This result reveals that this molecule is quite easy to bend. Therefore, it should be easy for reagents to approach this functional group. Moreover, the flexibility of the bond angle φ is very similar to the flexibility of the Si—O—Si angle in corresponding oxy compounds.

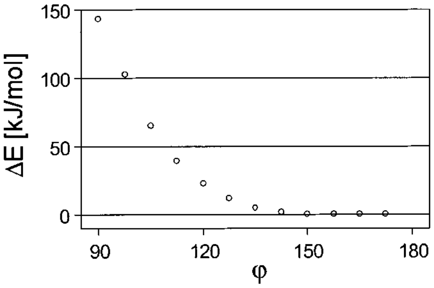


Figure 16. Variation of the energy with bond angle φ for bis(trimethylsilyl)carbodiimide.[95]

Extended Carbodiimide Structures. Calculations on extended carbodiimide structures have been published for the compounds silicon dicarbodiimide, SiC_2N_4, and silicon(carbodiimide)nitride, Si_2CN_4.[61] From the calculated cohesive energy it was established that the latter compound is a thermodynamically stable phase. The elastic properties of the compound were calculated to be highly anisotropic, a consequence of the layered structure.

For SiC_2N_4 it is still not clear if this phase is stable only for kinetic reasons. An interesting task is to determine the structure of both low- and high-temperature phases, α- and β-SiC_2N_4, respectively. The structure suggested for β-SiC_2N_4 resembles that of high-cristobalite SiO_2, and a comparison is therefore obvious.[95] However, the energy differences between several optimized structural arrangements, keeping the bonding topology fixed while changing angles and space group choices, are by more than an order of magnitude smaller than in the corresponding SiO_2 system.[96] Because of the flexibility of the bond angle φ, the material is expected to be very soft. The calculated bulk modulus B_0 is <30 GPa, the value of B_0 for cristobalite SiO_2, which in turn is a tenth of that of silicon nitride and a third of that of silicon. The demonstrated flexibility of φ and the tiny energy differences between several structural arrangements may also explain the difficulties in determining the structure of the low-temperature phase α-SiC_2N_4.

Hypothetical extended carbodiimide structures can also be constructed for germanium in analogy to the silicon dicarbodiimide. For boron, other trivalent main group elements, trivalent building blocks (such as the triazine molecule), or the three-connected net of B_2O_3 can be used to construct a carbodiimide derivative or even interpenetrating nets of these derivatives.[91]

7. Conclusion

Organic carbodiimides are well investigated and are applied in the field of organic synthesis, but inorganic element carbodiimides are rarely studied. Moreover, only few solid carbodiimides, mainly based on phosphorous and silicon, have been reported so far. However, the latest research results concerning the successful synthesis of the stoichiometric crystalline phases $Si(N{=}C{=}N)_2{\equiv}SiC_2N_4$ and $Si_2N_2(N{=}C{=}N){\equiv}Si_2CN_4$ indicate the great potential to form novel ternary solid-phase ECN. Due to the pseudochalcogene character of the $[N{=}C{=}N]^{2-}$ anion, the element carbodiimides reveal pronounced structural analogy to the well-known oxygen counterparts like SiO_2 and Si_2N_2O. The element carbodiimides are formed under mild conditions with or without organic solvents by the reaction of element halides with bis(trimethylsilyl)carbodiimide and subsequent annealing of the reaction product at $T < 1000$ °C. The annealing temperature is limited by the decomposition of the carbodiimide unit and strongly depends on the element E. Thus, the element carbodiimides $E(N{=}C{=}N)_2$, with E = C, Si, and Ge, disintegrate at $T > 600$, 970, and 800 °C, respectively, by the loss of cyanogen and nitrogen as analyzed by TGA/MS. In the case of E = silicon, the decomposition of $Si(N{=}C{=}N)_2$ in Ar starts at 970 °C, providing $Si_2N_2(N{=}C{=}N)$. The latter phase gives off nitrogen at higher temperatures and forms amorphous silicon carbonitride (SiCN). At $T > 1400$ °C, the resulting SiCN crystallizes to a mixture of α-Si_3N_4 and α-SiC, which is in accordance with thermodynamic considerations. Therefore, the element carbodiimides can be considered as single-source precursors for the formation of carbide- and nitride-based ceramics. In the course of our work, the synthesis of titanium- or zirconium-based carbodiimides is presently being explored.

The reaction of chlorosilanes R_xSiCl_{4-x} ($0 \leq x \leq 1$) with bis(trimethylsilyl)carbodiimide can be controlled to form nonaqueous sol–gel systems. The systematic investigation of this novel sol–gel process as well as its transformation to non-oxidic gels containing elements other than silicon is of great fundamental and technological relevance.

The pseudochalcogene anion $[N{=}C{=}N]^{2-}$ can be considered to be utilized to form silicate analogous carbodiimides. Therefore, our future research activities will be focused on the synthesis of corresponding silicates in which oxygen is substituted by the carbodiimide unit.

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References

(1) Riedel, R.; Greiner, A.; Miehe, G.; Dressler, W.; Fuess, H.; Bill, J.; Aldinger, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 603; *Angew. Chem.* **1997**, *106*, 657.
(2) Dressler, W.; Riedel, R. *Int. J. Refractory Metals Hard Mater.* **1997**, *15*, 13.
(3) Weimar, A. W. *Carbide, Nitride and Boride Materials Synthesis and Processing*; Chapman & Hall: London, 1997.
(4) Ebsworth, A. V.; Mays, M. J. *J. Chem. Soc.* **1961**, 4879.
(5) Pump, J.; Wannagat, U. *Angew. Chem.* **1962**, *74*, 117.
(6) Birkofer, L.; Ritter, A.; Richter, P. *Tetrahedron Let.* **1962**, *5*, 195.
(7) Razuvaev, G. A.; Gordetsov, A. S.; Kozina, A. P.; Brevnova, T. N.; Semenov, V. V.; Skobeleva, S. E.; Boxer, N. A.; Dergunov, Y. I. *J. Organomet. Chem.* **1987**, *327*, 303.
(8) Gorbatenko, V. I.; Gertsyuk, M. N.; Samarai, L. I.; *Zh. Org. Khim.* **1977**, *13*, 899.
(9) Köhler, H.; Kotte, B. *Z. Chem.* **1973**, *13*, 350.
(10) Kaiser, J.; Hartung, H.; Richter, R. *Z. Anorg. Allg. Chem.* **1980**, *469*, 188.
(11) Köhler, H. *Pure Appl. Chem.* **1980**, *52*, 879.
(12) Jäger, L.; Köhler, H. *Nova Acta Leopoldina, N.F.* **1985**, *59*, 259.
(13) Kolbe, A.; Glanz, D.; Köhler, H. *Z. Anorg. Allg. Chem.* **1988**, *561*, 99.
(14) Jäger, L.; Köhler, H. *Sulfur Rep.* **1992**, *12*, 159.
(15) Jäger, L.; Freude, B.; Skirl, R.; Schubert, K.; Köhler, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 711.
(16) Jäger, L.; Schädler, H. -D.; Grobe, U.; Köhler, H. *Z. Anorg. Allg. Chem.* **1992**, *617*, 123.
(17) Gordetsov, A. S.; Kozyukov, V. P.; Votokov, I. A.; Sheludyakova, S. V.; Dergunov, Y. I.; Mironov, V. F. *Uspekhi Khim.* **1982**, *51*, 848; *Russian Chem. Rev.* **1982**, *51*, 485.
(18) Banister, A. J.; Clegg, W.; Gorrell, I. B.; Hauptman, Z. V.; Small, R. W. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1611.
(19) Ruppert, I. *Angew. Chem.* **1977**, *89*, 336.
(20) Obermeyer, A.; Kienzle, A.; Weidlein, J.; Riedel, R.; Simon, A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1357.
(21) Vostokov, I. A.; Dergunov, Y. I.; Gordetsov, A. S. *Zh. Obshch. Khim.* **1977**, *47*, 1769.
(22) Drake, J. E.; Hemmings, R. T; Henderson, H. E. *J. Chem. Soc. (Dalton)* **1976**, 366.
(23) Reischmann, R.; Hausen, H. -D.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 123.
(24) Appel, R.; Montenahr, M. *Z. Naturforsch.* **1975**, *30B*, 847.
(25) Haag, P.; Lechler, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 112.
(26) Drake, J. E.; Glavincevski, B. M.; Henderson, H. E. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 7.
(27) Moscony, J. J.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.* **1965**, *14*, 307.
(28) Rajca, G.; Schwarz, W.; Weidlein, J. *Z. Naturforsch.* **1984**, *39B*, 1219.
(29) Rajca, G.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1986**, *538*, 36.
(30) Pump, J.; Rochow, E. G. *Z. Anorg. Allg. Chem.* **1964**, *330*, 101.
(31) Klebe, J. F.; Murray, J. G. U.S. Patent 3,352,799, 1967.
(32) Dahrouch, M.; Riviere-Baudet, M.; Satge, J.; Mauzac, M.; Cardin, C. J.; Thorpe, J. M. *Organometallics* **1998**, *17*, 623.
(33) Kienzle, A.; Obermeyer, A.; Riedel, R.; Aldinger, F.; Simon, A. *Chem. Ber.* **1993**, *126*, 2569.
(34) Kienzle, A. Dissertation (in German), Universität Stuttgart, Germany, 1994.
(35) Greiner, A. Dissertation (in German), Technische Universität Darmstadt, Germany, 1997; Shaker Verlag: Aachen, 1998; ISBN 3-8265-3247-3.
(36) Pump, J.; Wannagat, U. *Liebigs Ann. Chem.* **1962**, *652*, 21.
(37) Reischmann, R. Diploma Thesis, Universität Stuttgart, Germany, 1986.
(38) Hammel, A.; Volden, H. V.; Haaland, A.; Weidlein, J.; Reischmann, R. *J. Organomet. Chem.* **1991**, *408*, 35.
(39) Kienzle, A.; Wurm, K.; Bill, J.; Aldinger, F.; Riedel, R. In *Organosilicon Chemistry II - From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996; p 725.
(40) Kroke, E.; Gabriel, A.; Kim, D. S.; Riedel, R. in *Organosilicon Chemistry IV - From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, in press.
(41) Seyferth, D.; Strohmann, C.; Dando, N. R.; Perrotta, A. J.; Gardner, J. P. *Met. Res. Soc. Symp. Proc.* **1994**, *327*, 191.
(42) Gabriel, A. Dissertation (in German), Technische Universität Darmstadt, Germany, 1998.
(43) Gabriel, A. O.; Riedel, R. *Angew. Chem.* **1997**, *109*, 371; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 384.
(44) Gabriel, A. O.; Riedel, R.; Storck, S.; Maier, W. F. *Appl. Organomet. Chem.* **1997**, *11*, 833.

(45) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic: San Diego, CA, 1990.
(46) Narula, C. K.; Paine, R. T.; Schaeffer, R. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 383.
(47) Narula, C. K.; Schaeffer, R.; Datye, A.; Paine, R. T. *Inorg. Chem.* **1989**, *28*, 4053.
(48) Seibold, M.; Rüssel, C. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 477.
(49) Pfennig, B. W.; Bocarsly, A. B.; Prud'homme, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 2661.
(50) Guiton, T. A.; Czekaj, C. L.; Pantano, C. G. *J. Non-Cryst. Solids* **1990**, *121*, 7.
(51) Gacoin, T.; Malier, L.; Boilot, J. -P. *Chem. Mater.* **1997**, *9*, 1502; *J. Mater. Chem.* **1997**, *7*(6), 859.
(52) Schmidt, H.; Seiferling, B. *Mater. Res. Soc. Symp. Proc.* **1986**, 739.
(53) Renlund, G. M.; Prochazka, S.; Doremus, R. H. *J. Mater. Res.* **1991**, *6*, 2716.
(54) Renlund, G. M.; Prochazka, S.; Doremus, R. H. *J. Mater. Res.* **1991**, *6*, 2723.
(55) Pump, J.; Wannagat, U. *Justus Liebigs Ann. Chem.* **1962**, *652*, 21.
(56) Zawarotko, M. J. *Chem. Soc. Rev.* **1994**, 283.
(57) Sjoeberg, J.; Helgesson, G.; Idrestedt, I. *Acta Crystallogr., Sect. C* **1991**, 2438.
(58) Koehler, H.; Grobe, U. *Wiss. Z. Univ. Halle* **1990**, *39*, 3.
(59) Schädler, H. -D; Jäger, L.; Senf, I. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1115.
(60) Carduner, K. R.; Blackwell, C. S.; Hammond, W. B.; Reidinger, F.; Hatfield, G. R. *J. Am. Chem. Soc.* **1990**, *112*, 4676.
(61) Kroll, P. Dissertation (in German), Technische Universität Darmstadt, Germany, 1996; Shaker Verlag: Aachen, 1998; ISBN 3-8265-3001-2.
(62) Riedel, R. *Adv. Mater.* **1992**, *4*, 759.
(63) Kawaguchi, M. *Adv. Mater.* **1997**, *9*, 615.
(64) Riedel, R. *Adv. Mater.* **1994**, *6*, 549.
(65) Liu, A. Y.; Cohen, M. L. *Science* **1989**, *245*, 841.
(66) Liu, A. Y.; Cohen, M. L. *Phys. Rev. B* **1990**, *41*, 10727.
(67) Teter, D. M. *MRS Bull.* **1998**, 22.
(68) Kroke, E., unpublished results.
(69) McCarty, C. G.; Parkinson, J. E.; Wieland, D. M. *J. Org. Chem.* **1970**, *35*, 2067.
(70) Williams, D. R.; Damrauer, R. *Theoret. Chim. Acta (Berl.)* **1971**, *23*, 195.
(71) Riedel, R.; Kroke, E.; Greiner, A. German Patent, DE 197 06 028.5, 1997.
(72) Schroen, R. Dissertation, Marburg/Lahn, Germany, 1969.
(73) Einholz, W. Dissertation, Universität Stuttgart, Germany, 1980.
(74) Einholz, W.; Haubold, W. *Z. Naturforsch.* **1986**, *41b*, 1367.
(75) Riedel, R.; Aldinger, F.; Bill, J.; Kienzle, A. German Patent DE-OS 44 30 817.5, 1994.
(76) Riedel, R.; Kienzle, A.; Dressler, W.; Ruwisch, L.; Bill, J.; Aldinger, F. *Nature* **1996**, *382*, 796.
(77) Baldus, H. -P.; Jansen, M. *Angew. Chem.* **1997**, *109*, 338.
(78) Bill, J.; Aldinger, F. *Z. Metallkd.* **1996**, *87*, 827.
(79) Weinmann, M.; Haug, R.; Bill, J.; Aldinger, F.; Schuhmacher, J.; Müller, K. *J. Organomet. Chem.* **1997**, *541*, 345.
(80) Ruwisch, L.; Riedel, R., *to be published*.
(81) Riedel, R.; Ruwisch, L.; Eiling, A. German Patent, DE 197 13 767.9, 1997.
(82) Gordon, M. S.; Fischer, H. *J. Am. Chem. Soc.* **1968**, *90*, 2471.
(83) Williams, D. R.; Damrauer, R. *J. Chem. Soc. D (Chem. Comm.)* **1969**, 1380.
(84) Williams, D. R.; Damrauer, R. *Theoret. Chim. Acta* **1971**, *23*, 195.
(85) Nguyen, M. T.; Riggs, N. V.; Radom, L.; Winnewisser, M.; Winnewisser, B. P.; Birk, M. *Chem. Phys.* **1988**, *122*, 305.
(86) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic: New York, 1973; p 128.
(87) Hart, B. T. *J. Aust. Chem.* **1973**, *26*, 461−476, 477.
(88) Moffat, J. B. *J. Mol. Struct. (Theochem.)* **1979**, *52*, 275.
(89) Thomson, C.; Glidewell, C. *J. Comp. Chem.* **1983**, *4*, 1.
(90) Guimon, C.; Khayar, S.; Gracian, F.; Begtrup, M.; Pfister-Guillouzo, G. *Chem. Phys.* **1989**, *138*, 157.
(91) Kroll, P.; Hoffmann, R., unpublished results.
(92) Irgartigen, H.; Jäger, H. U. *Acta Crystallogr., Sect. B* **1978**, *34*, 3262.
(93) Nguyen, M. T.; Ha, T. -K. *J. Chem. Soc., Perkin Trans. II* **1983**, 1297.
(94) Pasinski, T.; Veszpremi,T.; Feher, M. *J. Mol. Struct. (Theochem.)* **1995**, *331*, 289.
(95) Kroll, P.; Riedel, R.; Hoffmann, R., to be published.
(96) Liu, F.; Garofalini, S. H.; King-Smith, D.; Vanderbilt, D. *Phys. Rev. B* **1994**, *49*, 12528.

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