Synthesis of Dendrimers with a N−Si−C Framework

Michael Veith* and Ralf Elsässer

Institut für Anorganische Chemie, Universität des Saarlandes, Postfach 151150,
66041 Saarbrücken, Germany

Ralph-Peter Krüger

Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87,
12205 Berlin, Germany

Received September 14, 1998

A novel family of air-stable dendrimers with a N−Si−C framework has been prepared up to the fourth generation. The divergent synthesis starts with the hydrosilylation of the trisilazane $N(SiMe_2vinyl)_3$ [0-G(vinyl)] by $HSiMe_2Cl$, which gives the three-directional core molecule $N(SiMe_2CH_2CH_2SiMe_2Cl)_3$ [0-G(Cl)]. A 1-to-2 branching achieved by reacting the core molecule [0-G(Cl)] with 3 equiv of $KN(SiMe_2vinyl)_2$ affords the first generation dendrimer [1-G(vinyl)]. By repeating the above two steps, the second [2-G(vinyl)], third [3-G(vinyl)], and fourth generation [4-G(vinyl)] can be obtained. The compounds have been characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, by elemental analysis, and up to the third generation by MALDI-TOF mass spectrometry. Gel permeation chromatography was used to prove the fourth generation [4-G(vinyl)].

Introduction

Dendrimer chemistry had been pure organic chemistry[1] until the end of the 1980s, when the first dendrimers containing heteroatoms such as phosphorus[2] or silicon[3−5] were published. The silicon-containing dendrimers that are described to date can be divided into three groups: (I) silicones with a $-(O-SiMe_nO_m)_x$ framework,[3] (II) carbosilanes in which the silicon atoms are connected by alkyl[4a−d] or alkeneyl[4e] chains such as $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, or $-CH{=}CH-$, and (III) polysilanes with an overall silicon skeleton bearing methyl substituents.[5a−d] Only very recently, a dendrimer with a framework of alternating Si and Ge atoms was published by Sekiguchi et al.[5e] The carbosilane dendrimers have attracted wide attention as a base for dendrimers that are peripherally functionalized with transition metal fragments[6] because the branches can easily be terminated with reactive groups, whereas their C−Si skeleton is chemically inert. We report here the divergent synthesis and spectroscopic characterization of a novel group of silicon-containing dendrimers possessing a $N(SiMe_2-)_3$ core and up to 45 trigonal planar $N(SiMe_2-)_3$ building blocks (fourth generation) that are connected by $-CH_2CH_2-$ chains. Thus, the molecules can be described as "inorganic", rigid, trigonal planar NSi_3- groups in a flexible "organic" matrix. The synthesis of the first two generations of these carbosilazane dendrimers has been reported by Son et al.,[7] while our work was in progress.

Results and Discussion

Synthesis of the Core Molecules. $KN(SiMe_2vinyl)_2$ is easily synthesized by adding the commercially available $HN(SiMe_2vinyl)_2$ to a suspension of KH in diethyl ether and stirring the reaction mixture at room temperature for several hours (eq 1). After filtration and removal of the solvent, the crude product is recrystallized as colorless crystals in high yields from a hexane/benzene mixture. The isolated compound is very sensitive toward air and moisture but can be handled and stored under nitrogen for long periods. Treatment of $KN(SiMe_2vinyl)_2$ with $Cl-SiMe_2vinyl$ in THF at room

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10.1021/om9807708 CCC: $18.00

temperature provides, after filtration and removal of solvent, $N(SiMe_2vinyl)_3$ [0-G(vinyl)] as a white, low-melting solid (eq 2). Hydrosilylation of $N(SiMe_2vinyl)_3$ with $H-SiMe_2Cl$ using the Karstedt catalyst[8] affords the three-directional core molecule $N(SiMe_2CH_2CH_2SiMe_2Cl)_3$ [0-G(Cl)] as a colorless, distillable liquid (eq 3).

$$HN(SiMe_2vinyl)_2 + KH \rightarrow KN(SiMe_2vinyl)_2 + H_2 \qquad (1)$$

$$KN(SiMe_2vinyl)_2 + Cl-SiMe_2vinyl \rightarrow N(SiMe_2vinyl)_3 + KCl \qquad (2)$$

$$N(SiMe_2vinyl)_3 + 3H-SiMe_2Cl \rightarrow N(SiMe_2CH_2CH_2SiMe_2Cl)_3 \qquad (3)$$

Divergent Dendrimer Growth. The branching unit of our dendrimer synthesis is $KN(SiMe_2vinyl)_2$, the synthesis of which is described above. The first generation dendrimer [1-G(vinyl)] is synthesized simply by adding a solution of 3 equiv of $KN(SiMe_2vinyl)_2$ to a solution of the core molecule [0-G(Cl)]. The reaction can be carried out in THF, diethyl ether, or toluene; however, THF is the most convenient solvent, as no heating of the reaction mixture is required. After filtration and evaporation of the solvent, the analytically pure product [1-G(vinyl)] is obtained as a colorless oil. Platinum-catalyzed hydrosilylation of the six double bonds of [1-G(vinyl)] with $H-Sime_2Cl$ affords the dendrimer [1-G(Cl)] with six $R-SiMe_2Cl$ groups to which the second layer of branching units can be connected using the same procedure that afforded [1-G(vinyl)]. By repeating these two steps, the third [3-G(vinyl)] and fourth generation [4-G(vinyl)] can be obtained (Scheme 1).

Several combinations of solvents and catalysts have been employed successfully in hydrosilylation reactions.[4] In our work, we followed the strategy employed by Seyferth et al.,[4d] who prepared the third and fourth generation of carbosilane dendrimers by adding $H-SiCl_3$ to vinylic double bonds using the Karstedt catalyst in Et_2O solution.

We found that these reaction conditions proved to be suitable for the addition of $HSiMe_2Cl$ to the $NSiMe_2$-vinyl group as well, and the procedure reliably affords not only the core molecule [0-G(Cl)] but also the first [1-G(Cl)], second [2-G(Cl)], and third [3-G(Cl)] generation as analytically pure oils of increasing viscosity. As observed in the ^1H, ^{13}C, and ^{29}Si NMR spectra of the products, β-addition occurs exclusively. In Figure 1, the ^{13}C NMR spectrum of the core [0-G(Cl)] is depicted exemplarily.

Both the branching step and the hydrosilylation are very straightforward reactions. All products are formed in quantitive yields; however, as losses occur when KCl is filtered off, the vinyl terminated dendrimers [1-G(vinyl)] to [4-G(vinyl)] are isolated in yields between 70 and 80%. The Cl-terminated dendrimers [1-G(Cl)] to [3-G(vinyl)] are isolated in yields between 85 and 95%.

The branching unit $KN(SiMe_2vinyl)_2$ can be replaced by other metalated disilazanes such as $LiN(SiMe_2phenyl)_2$[9] or by the well-known compound $LiN(SiMe_3)_2$, which can be reacted with [0-G(Cl)], [1-G(Cl)], and [2-G(Cl)] to yield the phenyl-substituted compound [1-G(phenyl)] (eq 4) and all methyl-substituted dendrimers [1-G(methyl)], [2-G(methyl)], and [3-G(methyl)] (eqs 5−7). [1-G(methyl)] and [2-G(methyl)] are obtained

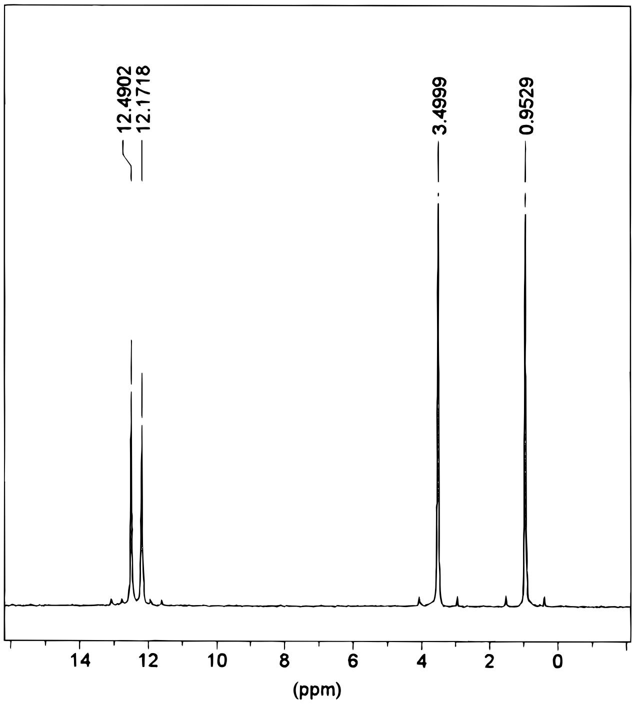

Figure 1. ^{13}C NMR of $N(SiMe_2CH_2CH_2SiMe_2Cl)_3$ [0-G(Cl)].

$$[0\text{-}G(Cl)] + 3LiN(SiMe_2phenyl)_2 \rightarrow [1\text{-}G(phenyl)] + 3LiCl \qquad (4)$$

$$[0\text{-}G(Cl)] + 3LiN(SiMe_3)_2 \rightarrow [1\text{-}G(methyl)] + 3LiCl \qquad (5)$$

$$[1\text{-}G(Cl)] + 6LiN(SiMe_3)_2 \rightarrow [2\text{-}G(methyl)] + 6LiCl \qquad (6)$$

$$[2\text{-}G(Cl)] + 12LiN(SiMe_3)_2 \rightarrow [3\text{-}G(methyl)] + 12LiCl \qquad (7)$$

as crystalline solids. Single crystals could be grown from an ethanol/benzene mixture, but X-ray structure determinations have been unsuccessful so far.

The $N(SiR_3)_3-$ group is known to be stable toward hydrolysis.[10] We confirmed this by adding H_2O to a solution of [1-G(vinyl)] in THF and stirring the mixture at room temperature. Even after 72 h, the ^1H and ^{13}C NMR spectra showed no formation of hydrolyzed product.

Characterization of the Dendrimers. All the dendrimers reported so far have been characterized by elemental analysis and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy.

Up to the second generation, all $-Si(CH_3)_2-$ groups can be detected in the ^1H or ^{13}C NMR spectra. In Figure 2, the ^1H NMR spectrum of the dendrimer [2-G(Cl)] is

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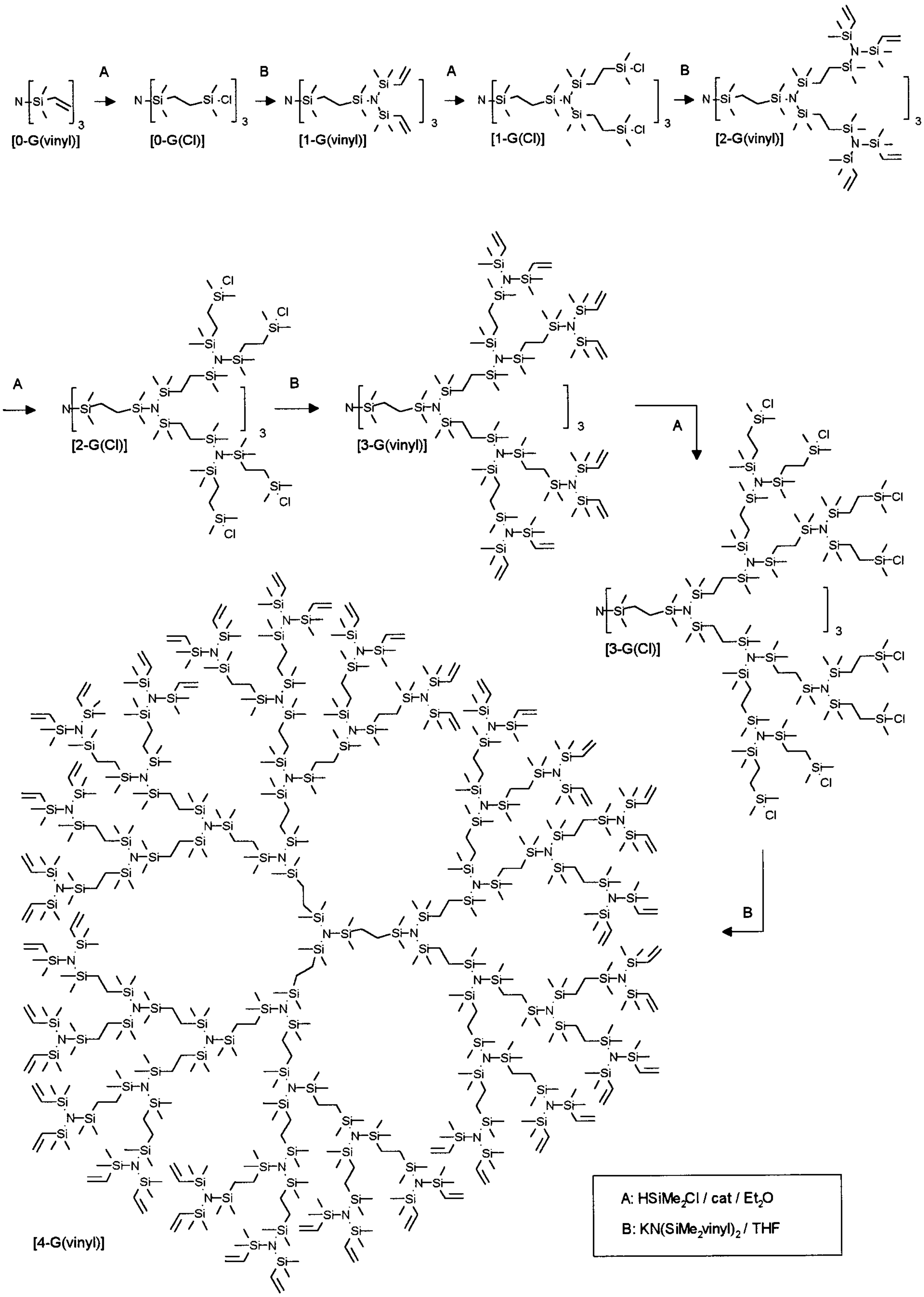
Scheme 1



depicted exemplarily. It can be seen that the three signals due to the inner, the middle, and the outer alkyl chain and the six signals due to the six different $-Si(CH_3)_2-$ groups appear as separated peaks (interior groups are shifted downfield). The ^1H NMR spectrum of [3-G(Cl)] is very similar to that of [2-G(Cl)].

Figures 3 and 4 show the ^{29}Si NMR spectra of the dendrimers [0-G(Cl)] to [3-G(Cl)] and [1-G(vinyl)] to

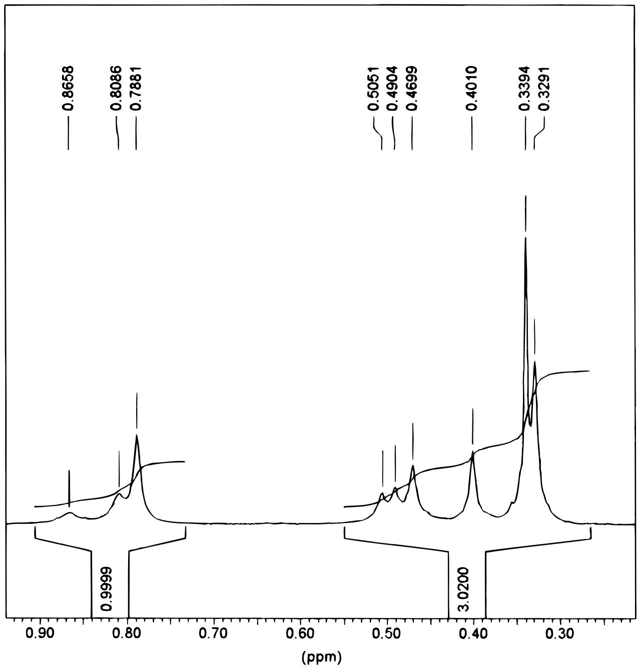


Figure 2. ^{1}H NMR of [2-G(Cl)].

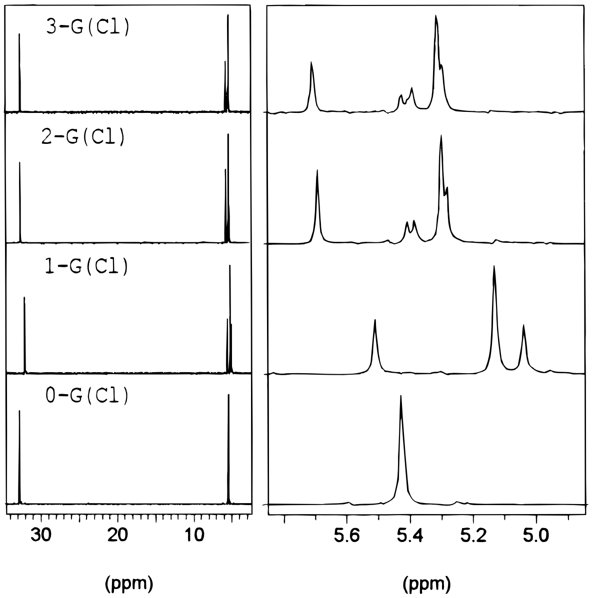


Figure 3. ^{29}Si spectra of [0-G(Cl)] to [3-G(Cl)].

[4-G(vinyl)]. In the spectra of [0-G(Cl)] to [2-G(Cl)] and [1-G(vinyl)] to [2-G(vinyl)] each silicon atom gives a clearly separated singlet, whereas the two inner silicon atoms in [3-G(Cl)] appear as a shoulder. In the spectrum of [3-G(vinyl)] and [4-G(vinyl)], one signal corresponding to an inner silicon (lowest generation) is overlapped by a signal due to a first generation silicon.

The air-stable dendrimers [1-G(vinyl)] to [4-G(vinyl)] and [1-G(methyl)] to [3-G(methyl)] have been studied by MALDI-TOF MS. The protonated molecular ions of all compounds with the exception of dendrimer [4-G(vinyl)] were observed. The spectra show no impurities and no signals due to imperfectly branched dendrimers that are encountered when the reactions employed in a divergent dendrimer synthesis have been incomplete. The compounds [1-G(vinyl)] to [4-G(vinyl)] have also been studied by gel permeation chromatography. As expected, the elution time of the four compounds increases from [4-G(vinyl)] to [1-G(vinyl)]. All four different generations could be assigned without doubt.

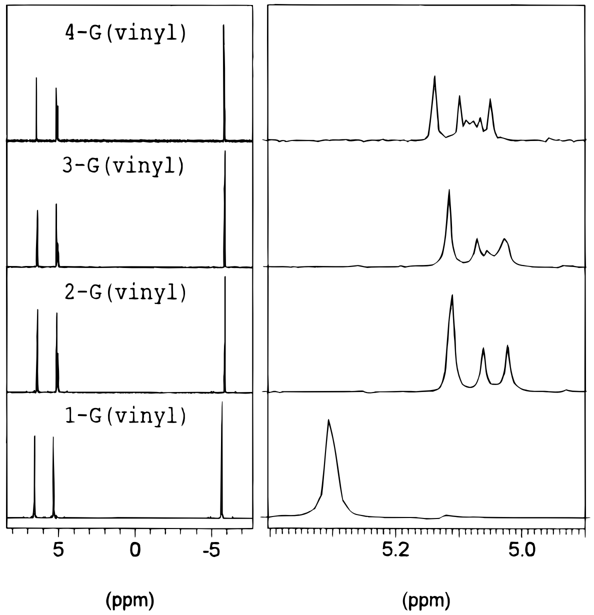


Figure 4. ^{29}Si spectra of [1-G(vinyl)] to [4-G(vinyl)].

Experimental Section

Preparation and handling of KN(SiMe$_2$vinyl)$_2$ and the compounds [0-G(Cl)] to [3-G(Cl)] were performed under rigorous exclusion of air and moisture in a nitrogen atmosphere. All solvents were dried with sodium-wire/benzophenone and distilled. The suspension of KH in mineral oil was obtained from Aldrich. Hexane was added to the suspension, and the KH was filtered off and washed with hexane several times until a fine powder was obtained. Cl−SiMe$_2$vinyl was purchased from Fluka and Cl−SiMe$_2$H from Aldrich. Both silanes were distilled before use. The Karstedt catalyst was obtained from Gelest, Inc., as a 2.1−2.4% solution in xylene. Melting points were determined by sealing samples of the compounds under an inert atmosphere inside melting point capillaries. Elemental analyses (C, H, N) were performed on a LECO CHN 900 elemental analyzer. The NMR (^{1}H, ^{13}C, and ^{29}Si) spectra were recorded on Bruker AC 200 and AM 400 spectrometers and referenced relative to TMS. Samples were run at room temperature using C$_6$D$_6$ as the lock solvent. The numbering of the atoms used for ^{1}H, ^{13}C, and ^{29}Si NMR is shown in Figure 5.

MALDI-TOF spectra were recorded with a Kratos Kompact MALDI III (Shimadzu Europe GmbH, Duisburg, Germany) using a nitrogen laser source ($\lambda = 337$ nm), a positive polarity, a reflectron mode, and 20 kV acceleration voltage. A 0.5 μL portion of the samples (1 mg/1 mL THF) and 0.5 μL of matrix solution (25 mg 2,4,6-trihydroxyacetophenone/1 mL THF) were mixed on a stainless steel sample slide, and the solvent was evaporated. Bovine insulin was used for calibration. The spectra were averaged over 122 laser shots and smoothed. Some MALDI spectras were conducted on a Reflex III (Bruker-Franzen Analytik GmbH, Bremen, Germany). The accelarating potential was 30 kV; the other experimental data were the same as described before. The molecules were detected as protonated species. Gel permeation chromatography was performed on a system with three columns (PS/DVD-Gel, P1 mix E, PSS 100 A, P1 50 A). THF at 1 mL/min was the eluent. A differential refractometer was used as detector.

Preparation of N-Potassium-1,1,3,3-tetramethyl-1,3-divinyldisilazane. A solution of 4.115 g (22.19 mmol) 1,1,3,3-

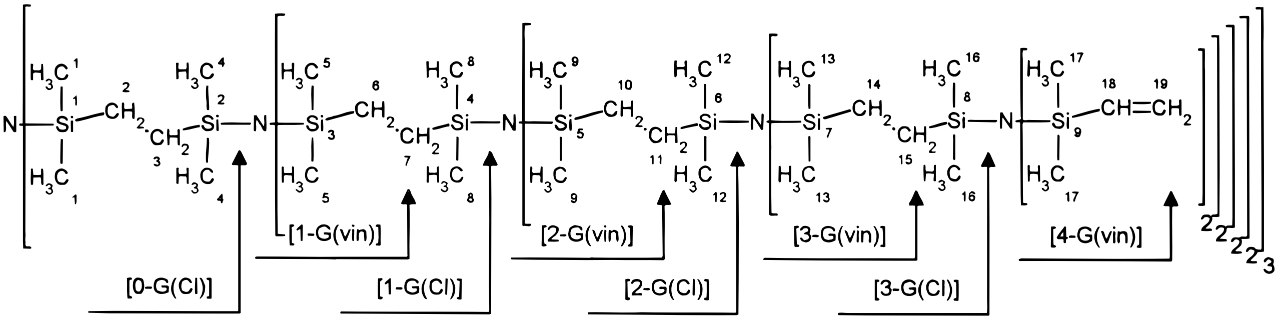


Figure 5. Numbering of the atoms for the ^{1}H, ^{13}C, and ^{29}Si spectra.

tetramethyl-1,3-divinyldisilazane in 5 mL of Et_2O was added slowly to a suspension of 0.960 g (24 mmol) KH in 20 mL of Et_2O, and the mixture was stirred overnight at room temperature. Unreacted KH was removed by filtration, and volatiles were evaporated in a vacuum. Recrystallization of the crude product from hexane/benzene (30:2, v/v) gave 3.665 g (74%) of $KN(SiMe_2vinyl)_2$ as colorless crystals.

Mp: 102–105 °C. ^{1}H NMR: δ 0.21 (s, 12 H, Si–CH_3), 6.35 (dd, $^3J_{cis}$ = 14.6 Hz, $^3J_{trans}$ = 20.0 Hz, 2 H, Si–CH=), 5.81, (dd, $^3J_{cis}$ = 14.6 Hz, ^2J = 4.6 Hz, 2 H, =CH_2), 5.61 (dd, ^2J = 4.6 Hz, $^3J_{trans}$ = 20.0 Hz, 2 H, =CH_2). ^{13}C NMR: δ 5.29 (Si–CH_3), 127.20 (=CH_2), 150.25 (Si–CH=). ^{29}Si NMR: δ −24.94. Anal. Calcd for $C_8H_{18}KNSi_2$: C, 42.99; H, 8.12; N, 6.27. Found: C, 42.71; H, 8.24; N, 6.23.

Preparation of Tris(dimethylvinylsilyl)amine [0-G(vinyl)]. A 2.5 mL (18.5 mmmol) sample of Cl–$SiMe_2$vinyl was slowly added to a solution of 3.200 g (14.34 mmol) of $KN(SiMe_2vinyl)_2$ in 20 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure (ca. 10 Torr), the residue was suspended in 20 mL of benzene, and KCl was filtered off. The benzene was evaporated and the residue was distilled at reduced pressure (70 °C, 10^{-2} Torr) to yield 2.79 g (72%) of [0-G(vinyl)] as a colorless liquid that solidified upon sitting.

Mp: 54–57 °C. ^{1}H NMR: δ 0.32 (s, 18 H, Si–CH_3), 6.32 (dd, $^3J_{cis}$ = 14.8 Hz, $^3J_{trans}$ = 20.1 Hz, 3 H, Si–CH=), 5.86, (dd, $^3J_{cis}$ = 14.7 Hz, ^2J = 3.7 Hz, 3 H, =CH_2), 5.67 (dd, ^2J = 3.7 Hz, $^3J_{trans}$ = 20.1 Hz, 3 H, =CH_2). ^{13}C NMR: δ 4.08 (Si–CH_3), 130.69 (=CH_2), 143.44 (Si–CH=). ^{29}Si NMR: δ −5.09. Anal. Calcd for $C_{12}H_{27}NSi_3$: C, 53.46; H, 10.09; N, 5.20. Found: C, 53.53; H, 10.26; N, 5.29.

Preparation of [0-G(Cl)]. A solution of 2.300 g (8.55 mmol) of [0-G(vinyl)] in 20 mL of Et_2O, 5 mL (45 mmol) of $HSiMe_2Cl$, and 5 drops of Karstedt catalyst solution was refluxed for 18 h. Volatiles were removed at reduced pressure and the remaining oil was distilled at reduced pressure (190 °C, 10^{-3} Torr) to give 4.415 g (93%) of [0-G(Cl)] as a clear, colorless liquid.

Bp: 190 °C/10^{-3} Torr. ^{1}H NMR: δ 0.24 (s, 18 H, H^1), 0.29 (s, 18 H, H^4), 0.73 (s, 12 H, H^2, H^3). ^{13}C NMR: δ 0.95 (C^4), 3.50 (C^1), 12.18 and 12.49 (C^2 and C^3). ^{29}Si NMR: δ 5.43 (Si^1), 32.75 (Si^2). Anal. Calcd for $C_{18}H_{48}Cl_3NSi_6$: C, 39.06; H, 8.74; N, 2.53. Found: C, 38.90; H, 8.92; N, 2.68.

Preparation of [1-G(vinyl)]. A solution of 3.086 g (13.8 mmol) of $KN(SiMe_2vinyl)_2$ in 30 mL of THF was added slowly to a solution of 2.547 g (4.60 mmol) of [0-G(Cl)] in 10 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 30 mL of benzene, and KCl was filtered off. The benzene was evoporated, leaving 3.5 g (76%) of [1-G(vinyl)] as a colorless oil.

^{1}H NMR: δ 0.34, 0.37 (s, 18 H, H^1 and H^4), δ 0.36 (s, 36 H, H^5), 0.74 (s, 12 H, H^2 and H^3), 6.36 (dd, $^3J_{cis}$ = 14.7 Hz, $^3J_{trans}$ = 20.1 Hz, 6 H, H^6), 5.90, (dd, $^3J_{cis}$ = 14.7 Hz, ^2J = 3.8 Hz, 6 H, =CH_2), 5.71 (dd, ^2J = 3.7 Hz, $^3J_{trans}$ = 20.1 Hz, 6 H, =CH_2). ^{13}C NMR: δ 3.47, 3.58 (C^1 and C^4), 4.32 (C^5), 13.84, 13.94 (C^2 and C^3), 130.70 (C^7), 143.6 (C^6). ^{29}Si NMR: δ −5.69 (Si^3), 5.30 (Si^1), 6.56 (Si^2). MS (MALDI-TOF): *m/z* 1002.4, calcd (MH^+) 1001.3. Anal. Calcd for $C_{42}H_{102}N_4Si_{12}$: C, 50.43; H, 10.28; N, 5.60. Found: C, 50.16; H, 10.25; N, 5.54.

Preparation of [1-G(methyl)]. A solution of 0.905 g (5.41 mmol) of $LiN(SiMe_3)_2$ in 10 mL of THF was added slowly to a solution of 0.998 g (1.80 mmol) of [0-G(Cl)] in 10 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 10 mL of hexane, and LiCl was filtered off. The hexane was evoporated, leaving a white solid that could be recrystallized from a mixture of ethanol and toluene to give 1.03 g (62%) of [1-G(methyl)] as a white solid.

Mp: 73–76 °C. ^{1}H NMR: δ 0.30 (s, 54 H, H^5), 0.33 and 0.38 (s, 18 H, H^1 and H^4), 0.74 (m, 12 H, H^2 and H^3).^{13}C NMR: δ 3.50 and 3.57 (C^1 and C^4), 5.89 (C^5), 13.79 and 13.99 (C^2 and C^3). ^{29}Si NMR: δ 2.57 (Si^3), 5.19 and 5.28 (Si^1 and Si^2). MS (MALDI-TOF): *m/z* 929.9, calcd (MH^+) 929.3. Anal. Calcd for $C_{36}H_{102}N_4Si_{12}$: C, 46.58; H, 11.08; N, 6.04. Found: C, 46.84; H, 11.02; N, 5.93.

Preparation of [1-G(phenyl)]. A solution of 0.745 g (2.56 mmol) of $LiN(SiMe_2phenyl)_2$ in 10 mL of THF was added slowly to a solution of 0.472 g (0.854 mmol) of [0-G(Cl)] in 5 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 10 mL of benzene, and LiCl was filtered off. The benzene was evoporated, leaving 0.81 g (73%) of [1-G(phenyl)] as a colorless oil.

^{1}H NMR: δ 0.25, 0.33 (s, 18 H, H^1 and H^4), δ 0.44 (s, 36 H, H^5), 0.74 (s, 12 H, H^2 and H^3). 7.15–7.20, 7.62–7.70 (m, 30 H, phenyl). ^{13}C NMR: δ 3.04, 3.57 (C^1 and C^4), 4.76 (C^5), 13.96, 14.10 (C^2 and C^3), 128.53, 129.03, 133.37, 143.79 (phenyl). ^{29}Si NMR: δ −2.64 (Si^3), 5.24 (Si^1), 7.50 (Si^2). Anal. Calcd for $C_{66}H_{114}N_4Si_{12}$: C, 60.95; H, 8,84; N, 4.31. Found: C, 60.84; H, 8.83; N, 4.31.

Preparation of [1-G(Cl)]. A solution of 2.64 g (2.64 mmol) of [1-G(vinyl)] in 20 mL of Et_2O, 3 mL (27 mmol) of $HSiMe_2Cl$, and 5 drops of Karstedt catalyst solution was refluxed for 24 h. Volatiles were evaporated, leaving 3.89 g (94%) of [1-G(Cl)] as a slightly brown oil.

^{1}H NMR: δ 0.31 and 0.32 (s, 36 H, H^5 and H^8), 0.38 and 0.44 (s, 18 H, H^4 and H^1), 0.77 (s, 24 H, H^7 and H^6), 0.78 (s, 12 H, H^2 and H^3). ^{13}C NMR: δ 1.03 (C^8), 3.59 and 3.79 (C^1 and C^4), 3.62 (C^5), 12.20 and 12.55 (C^6 and C^7), 14.18 (broad, C^2 and C^3). ^{29}Si NMR (Et_2O): δ 5.04 and 5.51 (Si^1 and Si^2), 5.13 (Si^3), 32.03 (Si^4). Anal. Calcd for $C_{54}H_{144}Cl_6N_4Si_{18}$: C, 41.36; H, 9.26; N, 3.57. Found: C, 41.22; H, 9.38; N, 3.65.

Preparation of [2-G(vinyl)]. A solution of 2.933 g (13.2 mmol) of $KN(SiMe_2vinyl)_2$ in 30 mL of THF was added slowly to a solution of 3.434 g (2.19 mmol) of [1-G(Cl)] in 10 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 30 mL of benzene, and KCl was filtered off. The benzene was evoporated, leaving a slightly yellow semi-solid that could be recrystallized from a mixture of ethanol and toluene to give 3.80 g (70%) of [2-G(vinyl)] as a white solid.

Mp: 47–50 °C. ^{1}H NMR: δ 0.35 and 0.38 (s, 36 H, H^5 and H^8), δ 0.36 (s, 72 H, H^9), δ 0.43 and 0.45 (s, 18 H, H^1 and H^4), 0.75 (s, 24 H, H^6 and H^7), 0.81 (s, 12 H, H^2 and H^3), 6.36 (dd, $^3J_{\text{cis}} = 14.7$ Hz, $^3J_{\text{trans}} = 20.0$ Hz, 12 H, H^{10}), 5.91, (dd, $^3J_{\text{cis}} = 14.7$ Hz, $^2J = 3.7$ Hz, 12 H, H^{11}), 5.72 (dd, $^2J = 3.7$ Hz, $^3J_{\text{trans}} = 20.0$ Hz, 12 H, H^{11}). ^{13}C NMR: δ 3.51 and 3.67 (C^5 and C^8), 3.71 and 3.81 (C^1 and C^4), 4.35 (C^9), 13.86 and 13.97 (C^6 and C^7), 14.24 (broad, C^2 and C^3), 130.72 (C^{11}), 143.6 (C^{10}). ^{29}Si NMR (Et$_2$O): δ −5.89 (Si^5), 5.02 and 5.06 (Si^1 and Si^2), 5.11 (Si^3), 6.38 (Si^4). MS (MALDI-TOF): *m/z* 2461.8, calcd (MH$^+$) 2462.8. Anal. Calcd for $C_{102}H_{252}N_{10}Si_{30}$: C, 49.77; H, 10.32; N, 5.69. Found: C, 49.80; H, 10.39; N, 5.64.

Preparation of [2-G(methyl)]. A solution of 0.434 g (2.60 mmol) of LiN(SiMe$_3$)$_2$ in 6 mL of THF was added slowly to a solution of 0.677 g (0.432 mmol) of [1-G(Cl)] in 4 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 10 mL of hexane, and LiCl was filtered off. The hexane was evoporated, leaving a white solid that could be recrystallized from a mixture of ethanol and toluene to give 0.61 g (60%) of a white solid.

Mp: 78−80 °C. ^{1}H NMR: δ 0.32 (s, 108 H, H^9), 0.37 and 0.44 (s, 36 H, H^5 and H^8), 0.48 and 0.51 (s, 18 H, H^1 and H^4), 0.78 (m, 24 H, H^6 and H^7), 0.87 (m, 12 H, H^2 and H^3).^{13}C NMR: δ 3.53 and 3.68 (C^5 and C^8), 3.73 and 3.84 (C^1 and C^4), 5.94 (C^9), 13.81 and 14.02 (C^6 and C^7), 14.25 (broad, C^2 and C^3). ^{29}Si NMR: δ 2.58 (Si^5), 5.21 and 5.33 (Si^3 and Si^4), 5.27 and 5.34 (Si^1 and Si^2). MS (MALDI-TOF): *m/z* 2318.6, calcd (MH$^+$) 2318.6. Anal. Calcd for $C_{90}H_{252}N_{10}Si_{30}$: C, 46.64; H, 10.96; N, 6.04. Found: C, 46.37; H, 10.79; N, 6.04.

Preparation of [2-G(Cl)]. A solution of 2.57 g (1.04 mmol) of [2-G(vinyl)] in 15 mL of Et$_2$O, 2 mL (18 mmol) of HSiMe$_2$Cl, and 4 drops of Karstedt catalyst solution was refluxed for 24 h. Volatiles were evaporated, leaving 3.44 g (92%) of [2-G(Cl)] as a brown oil.

^{1}H NMR: δ 0.33 and 0.34 (s, 72 H, H^9 and H^{12}), 0.40 and 0.47 (s, 36 H, H^5 and H^8), 0.49 and 0.51 (s, 18 H, H^1 and H^4) 0.79 (s, 48 H, H^{10} and H^{11}), 0.81 (s, 24 H, H^6 and H^7), 0.87 (s, 12 H, H^2 and H^3). ^{13}C NMR: δ 1.06 (C^{12}), 3.66 (C^9), 3.86 (C^5 or C^8), 12.25 and 12.60 (C^{10} and C^{11}), 14.23 (broad, C^2, C^3, C^6, and C^7). ^{29}Si NMR: δ 5.28 and 5.69 (Si^3 and Si^4), 5.30 (Si^5), 5.38 and 5.41 (Si^1 and Si^2), 32.65 (Si^6). Anal. Calcd for $C_{126}H_{336}Cl_{12}N_{10}Si_{42}$: C, 42.07; H, 9.41; N, 3.89. Found: C, 42.11; H, 9.47; N, 3.84.

Preparation of [3-G(vinyl)]. A solution of 1.825 g (8.17 mmol) of KN(SiMe$_2$vinyl)$_2$ in 15 mL of THF was added slowly to a solution of 2.448 g (0.681 mmol) of [2-G(Cl)] in 5 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 20 mL of benzene, and KCl was filtered off. The benzene was evoporated, leaving 3.01 g (82%) of [3-G(vinyl)] as a yellow oil.

^{1}H NMR: δ 0.37 and 0.41 (s, 72 H, H^9 and H^{12}), δ 0.39 (s, 144 H, H^{13}), δ 0.46 and 0.49 (s, 36 H, H^5 and H^8, the peaks corresponding to H^1 and H^4 are probably overlapped by the broad peak at 0.49), 0.78 (s, 48 H, H^{10} and H^{11}), 0.84 (s, 36 H, H^2, H^3, H^6, and H^7). 6.39 (dd, $^3J_{\text{cis}} = 14.7$ Hz, $^3J_{\text{trans}} = 20.1$ Hz, 24 H, H^{14}), 5.93, (dd, $^3J_{\text{cis}} = 14.7$ Hz, $^2J = 3.8$ Hz, 24 H, H^{15}), 5.72 (dd, $^2J = 3.8$ Hz, $^3J_{\text{trans}} = 20.1$ Hz, 24 H, H^{15}). ^{13}C NMR: δ 3.53 and 3.70 (C^9 and C^{12}), 3.75 and 3.86 (C^5 and C^8), 4.36 (C^{13}), 13.87 and 13.99 (C^{11} and C^{12}), 14.26 (broad, C^2, C^3, C^6, and C^7), 130.73 (C^{14}), 143.6 (C^{15}). ^{29}Si NMR (Et$_2$O): δ −5.89 (Si^7), 5.02 and 5.07 (Si^3 and Si^4), 5.05 (Si^1 or Si^2, the other peak is probably overlapped by the broad peak at 5.02), 5.11 (Si^5), 6.38 (Si^6). MS (MALDI-TOF): *m/z* 5386.3, calcd (MH$^+$) 5385.6. Anal. Calcd for $C_{222}H_{552}N_{22}Si_{66}$: C, 49.52; H, 10.33; N, 5.72. Found: C, 49.27; H, 10.36; N, 5.62.

Preparation of [3-G(methyl)]. A solution of 0.234 g (1.40 mmol) of LiN(SiMe$_3$)$_2$ in 6 mL of THF was added slowly to a solution of 0.420 g (0.117 mmol) of [2-G(Cl)] in 4 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 10 mL of hexane, and LiCl was filtered off. The hexane was evoporated, leaving 0.480 g (80%) of [3-G(methyl)] as a colorless oil.

^{1}H NMR: δ 0.33 (s, 216 H, H^{13}), 0.37 and 0.43 (s, 72 H, H^9 and H^{12}), 0.47 and 0.51 (s, 36 H, H5 and H8, the peaks corresponding to H^1 and H^4 are probably buried in the broad peak at 0.51), 0.78 (m, 48 H, H^{10} and H^{11}), 0.86 (m, 24 H, H^6 and H^7), 0.88 (shoulder, 12 H, H^2 and H^3).^{13}C NMR: δ 3.56 and 3.69 (C^9 and C^{12}), 3.76 and 3.88 (C^5 and C^8) 5.96 (C^{13}), 13.81 and 14.02 (C^{10} and C^{11}), 14.26 (broad, C^2, C^3, C^6, and C^7). ^{29}Si NMR: δ 2.59 (Si^7), 5.22 and 5.34 (Si^5 and Si^6), 5.29 and 5.37 (Si^3 and Si^4). MS (MALDI-TOF): *m/z* 5099.4, calcd (MH$^+$) 5097.4. Anal. Calcd for $C_{198}H_{552}N_{22}Si_{66}$: C, 46.66; H, 10.92; N, 6.05. Found: C, 46.57; H, 11.02; N, 6.26.

Preparation of [3-G(Cl)]. A solution of 2.26 g (0.42 mmol) of [3-G(vinyl)] in 10 mL of Et$_2$O, 2 mL (18 mmol) of HSiMe$_2$Cl, and 4 drops of Karstedt catalyst solution was refluxed for 24 h. Volatiles were evaporated, leaving 3.06 g (95%) of [3-G(Cl)] as a brown oil.

^{1}H NMR: δ 0.34 and 0.35 (s, 144 H, H^{13} and H^{16}), 0.41 and 0.47 (s, 72 H, H^9 and H^{12}), 0.50 and 0.51 (s, 36 H, H^5 and H^8) 0.79 (s, 96 H, H^{14} and H^{15}), 0.81 (shoulder, 48 H, H^{10} and H^{11}), 0.87 (s, 36 H, H^2, H^3, H^6, and H^7). ^{13}C NMR: δ 1.06 (C^{16}), 3.66 (C^{13}), 3.86 (C^9 or C^{12}), 12.22 and 12.56 (C^{14} and C^{15}), 14.20 (broad, C^2, C^3, C^6, C^7, C^{10}, and C^{11}). ^{29}Si NMR: δ 5.29 and 5.71 (Si^5 and Si^6), 5.31 (Si^7), 5.39 and 5.42 (Si^3 and Si^4), 5.40 (shoulder, Si^1 and Si^2), 32.61 (Si^8). Anal. Calcd for $C_{270}H_{720}Cl_{24}N_{22}Si_{90}$: C, 42.36; H, 9.48; N, 4.03. Found: C, 42.69; H, 9.38; N, 4.20.

Preparation of [4-G(vinyl)]. A solution of 0.917 g (4.10 mmol) of KN(SiMe$_2$vinyl)$_2$ in 5 mL of THF was added slowly to a solution of 1.309 g (0.171 mmol) of [3-G(Cl)] in 5 mL of THF, and the mixture was stirred overnight at room temperature. Volatiles were removed at reduced pressure, the residue was suspended in 10 mL of benzene, and KCl was filtered off. The benzene was evoporated, leaving 1.43 g (74%) of [4-G(vinyl)] as a colorless oil.

^{1}H NMR (toluene): δ 0.39 and 0.44 (s, 144 H, H^{13} and H^{16}), δ 0.41 (s, 288 H, H^{17}), δ 0.48 and 0.51 (s, 72 H, H^9 and H,^{12} the peaks corresponding to H^1, H^4, H^5, and H^8 are probably buried in the broad peak at 0.51), 0.79 (s, 96 H, H^{14} and H^{15}), 0.86 (s, 48 H, H^{10} and H^{11}), 0.87 (shoulder, 36 H, H^2, H^3, H^6, and H^7), 6.40 (dd, $^3J_{\text{cis}} = 14.7$ Hz, $^3J_{\text{trans}} = 20.8$ Hz, 48 H, H^{18}), 5.96, (dd, $^3J_{\text{cis}} = 14.7$ Hz, $^2J = 3.8$ Hz, 48 H, H^{19}), 5.76 (dd, $^2J = 3.8$ Hz, $^3J_{\text{trans}} = 20.8$ Hz, 48 H, H^{19}). ^{13}C NMR (toluene): δ 3.57 and 3.75 (C^{13} and C^{16}), 3.81 and 3.94 (C^9 and C^{12}), 4.39 (C^{17}), 13.92 and 14.03 (C^{14} and C^{15}), 14.31 (broad, C^2, C^3, C^6, C^7, C^{10}, and C^{11}), 130.76 (C^{18}), 143.7 (C^{19}). ^{29}Si NMR (Et$_2$O): δ −5.87 (Si^9), 5.05 and 5.10 (Si^5 and Si^6), 5.07 and 5.09 (Si^3 and Si^4), 5.08 (Si^1 or Si^2), 5.14 (Si^7), 6.40 (Si^8). Anal. Calcd for $C_{462}H_{1152}N_{46}Si_{138}$: C, 49.41; H, 10.34; N, 5.74. Found: C, 49.35; H, 10.38; N, 5.66.

Acknowledgment. We thank Dr. Ch. Mathur for reading the manuscript and the DFG (Schwerpunktprogramm "Spezifische Phänomene in der Siliciumchemie") for financial support.

OM9807708