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Article

Linear and Cyclic Polysilanes Containing the Bis(trimethylsilyl)amino Group: Synthesis, Reactions, and Spectroscopic Characterization

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The reaction of linear (Si_nCl_{2n+2}; $n = 3–5$) and cyclic (Si_5Cl_{10}) perchloropolysilanes with 1 or 2 equiv of $LiN(SiMe_3)_2$ results in the formation of the bis(trimethylsilyl)amino derivatives $(Me_3Si)_2NSi_3Cl_7$ (**1**), $(Me_3Si)_2NSi_4Cl_9$ (**2**), $(Me_3Si)_2N(SiCl_2)_nN(SiMe_3)_2$ ($n = 3$, **4**; $n = 4$, **5**; $n = 5$, **6**), *cyclo*-$(Me_3Si)_2NSi_5Cl_9$ (**7**), and *cyclo*-$[(Me_3Si)_2N]_2Si_5Cl_8$ (**8**). **1**–**8** easily can be hydrogenated with $LiAlH_4$ to give the corresponding amino and diamino polysilanyl hydrides. The monosubstituted and cyclic compounds **1**, **2**, **7,** and **8** additionally afford Si–Si bond scission products, which cannot be separated in all cases. Chloro- and dichloro derivatives of Si_3H_8, *n*-Si_4H_{10}, and *n*-Si_5H_{12} are obtained from the corresponding aminosilanes and dry HCl. All compounds were characterized by standard spectroscopic techniques. For Si–H derivatives the coupled ^{29}Si NMR spectra were analyzed to obtain an unequivocal structural proof.

Introduction

In contrast to the well-known class of (organylamino)-disilanes only a few amino derivatives of Si_2Cl_6 and Si_2H_6 have been prepared so far.[1] Amino groups can be easily attached to silicon by the reaction of halosilanes with ammonia, amines, or alkali metal amides using standard literature procedures.[2] Using this method aminochlorodisilanes $Si_2Cl_{6-n}(NR_2)_n$ can be made from Si_2Cl_6 with *n* depending mainly on the R groups attached to nitrogen. The corresponding hexakis(dialkylamino)disilanes, thus, are accessible from Si_2Cl_6 and $HNMe_2$ or $HNEt_2$,[1b,g] while Si_2Cl_6 and $LiN(SiMe_3)_2$ or $LiN(SiMe_2Ph)_2$ only afford the corresponding mono- or 1,2-bis(amino)chlorodisilanes, respectively.[3] In a recent study Roesky et al. reported on tetraaminodisilanes $R_2Si_2(NH_2)_4$ synthesized from tetrachlorodisilanes and ammonia.[4] In our laboratories we were able to demonstrate that $-NR_2$ groups can even be introduced into rather reactive oligosilane molecules, such as $H_3SiSiXHSiXHSiH_3$ or $XH_2SiSiH_2SiH_2SiH_2X$ ($X = Cl$, Br) under proper reaction conditions.[5]

Si−N bonds are rather stable against nucleophiles, hence allowing chemical reactions to be carried out at the Si center without affecting the $Si-NR_2$ moiety. The triflate group in $(Et_2N)_2MeSi-OTf$, for example, can be substituted by MeO^-, $LiSiPh_3$, or LiR (R = alkyl), while the Si−N bond remains intact.[6] The stability of Si−N linkages is even enhanced if more than one silicon atom is attached to nitrogen or bulky substituents such as *tert*-butyl or aryl groups are present. Consequently, tris(silylamines), silazanes, or cyclosilazanes are moderately stable toward hydrolysis and easily can be metalated with alkyl or aryl alkali metal compounds[7] or hydrogenated with $LiAlH_4$ without Si−N bond scission.[1e,3,4b] Despite the relative stability of Si−N bonds, they are readily cleaved by acids and various electrophiles, both organic and inorganic. The hydrogen halides or their acids, for instance,

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readily convert (triorganylamino)silanes to the appropriate halosilanes R_3SiX (X = F, Cl, Br),[8,9] which provides an excellent route for the removal of amino substituents from silicon substrates with concurrent formation of Si−halogen bonds.

The ease with which Si−N bonds can be made and broken together with the remarkable chemical stability of aminosilanes toward various nucleophiles provides an attractive basis for the synthesis of multifunctionalized polysilane derivatives. In a recent paper we reported on chlorodisilanes bearing $(R_3Si)_2N$ groups and their facile conversion to multifunctionalized disilanes by various selective substituent exchange reactions.[3] In continuation of these studies this contribution describes the synthesis, properties, and spectroscopic characterization of previously unknown $(Me_3Si)_2N$ derivatives of higher linear (Si_nCl_{2n+2}; $n = 3-5$) and cyclic (Si_5Cl_{10}) perchloropolysilanes.

Experimental Section

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried with sodium−potassium alloy and distilled under nitrogen prior to use. HCl 4.5, purchased from Messer Griessheim, and hexachlorodisilane, generously donated by Wacker Chemie, Burghausen, Germany, were used without further purification. $(Me_3Si)_2NLi$[10] and *cyclo*-Si_5Cl_{10}[11] were synthesized as previously reported. Si_3Cl_8, *n*-Si_4Cl_{10}, and *n*-Si_5Cl_{12} were made by the chlorodephenylation method[12] from Si_3Ph_8,[13] 1,4-$Cl_2Si_4Ph_8$,[14] and 1,5-$Cl_2Si_5Ph_{10}$,[15] respectively. ^1H (300.13 MHz), ^{29}Si (59.62 MHz), and ^{13}C (75.4 MHz) NMR spectra were recorded on a Bruker 300-MSL spectrometer in C_6D_6 solution versus external TMS. Mass spectra were run either on a HP 5971/A/5890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm poly(dimethylsiloxane)) or on a Kratos Profile mass spectrometer equipped with a solids probe inlet. Infrared spectra were obtained in Nujol mull on a Perkin-Elmer 883 spectrometer. Melting points were determined using a Buechi apparatus according to Dr. Tottoli and are noncorrected.

1-[Bis(trimethylsilyl)amino]heptachlorotrisilane (1). A 4.8 g (20 mmol) amount of $(Me_3Si)_2NLi{\cdot}Et_2O$ suspended in 40 mL of pentane was added dropwise to a solution of 7.3 g (20 mmol) of Si_3Cl_8 in 40 mL of pentane at −40 °C. The reaction mixture was allowed to warm to room temperature over a period of 30 min and stirred for additional 48 h. After filtration and removal of the solvent distillation of the liquid residue in a vacuum gave 9.2 g (94%) of pure white crystalline **1**.

Bp: 85 °C (0.01 mbar). ^{29}Si NMR (ext TMS, ppm): δ +9.76 (−*Si*Me_3), −0.03 (−*Si*Cl_3), −3.21 (−*Si*Cl_2−), −18.33 (−N*Si*Cl_2−). ^1H NMR (ext TMS, ppm): δ 0.27 (s, −$SiMe_3$). EI-MS (70 eV): *m/z* 493 (M^+). Anal. Calcd for $C_6H_{18}Cl_7NSi_5$ (M_r = 492.82): C, 14.64; H, 3.68; N, 2.84. Found: C, 14.62; H, 3.73; N, 2.86.

1-[Bis(trimethylsilyl)amino]nonachlorotetrasilane (2). The synthetic procedure is similar as described for **1**. A 4.8 g (20 mmol) amount of $(Me_3Si)_2NLi{\cdot}Et_2O$ and 9.3 g (20 mmol) of *n*-Si_4Cl_{10} gave a crude viscous oil, which easily can be crystallized by the addition of 20 mL of *n*-pentane and cooling to −80 °C. Yield: 11.5 g (97%) of white crystalline **2** (the product contains about 10% of **5** which could not be removed by repeated recrystallization).

^{29}Si NMR (ext TMS, ppm): δ +9.76 (−*Si*Me_3), −0.52 (−*Si*Cl_3), −1.57 (2Si, − *Si*Cl_2−), −18.19 (−N*Si*Cl_2−). ^1H NMR (ext TMS, ppm): δ 0.26 (s, −$SiMe_3$).

1,3-Bis[bis(trimethylsilyl)amino]hexachlorotrisilane (4). The synthetic procedure is similar as described for **1**. A 9.7 g (40 mmol) amount of $(Me_3Si)_2NLi{\cdot}Et_2O$ and 7.3 g (20 mmol) of Si_3Cl_8 gave a crude viscous oil, which easily can be crystallized by the addition of 20 mL of *n*-pentane and cooling to −80 °C. Yield: 11.5 g (94%) of white crystals.

Mp: 94−95 °C. ^{29}Si NMR (ext TMS, ppm): δ +9.11 (−*Si*Me_3), −0.84 (−*Si*Cl_2−), −14.86 (−N*Si*Cl_2−). ^1H NMR (ext TMS, ppm): δ 0.22 (s, CH_3). EI-MS (70 eV): *m/z* 617 (M^+). Anal. Calcd for $C_{12}H_{36}Cl_6N_2Si_7$ (M_r = 617.75): C, 23.33; H, 5.87; N, 4.53. Found: C, 23.40; H, 5.78; N, 4.52.

1,4-Bis[bis(trimethylsilyl)amino]octachlorotetrasilane (5). The synthetic procedure is similar as described for **1**. A 9.7 g (40 mmol) amount of $(Me_3Si)_2NLi{\cdot}Et_2O$ and 9.3 g (20 mmol) of *n*-Si_4Cl_{10} gave a highly viscous oil, which easily can be crystallized from pentane at −30 °C. Yield: 13.8 g (93%) of white crystals.

Mp: 119−120 °C. ^{29}Si NMR (ext TMS, ppm): δ +9.29 (−*Si*Me_3), +4.23 (−*Si*Cl_2), −16.25 (−N*Si*Cl_2−). ^1H NMR (ext TMS, ppm): δ 0.23 (s, CH_3). EI-MS (70 eV): *m/z* 717 (M^+). Anal. Calcd for $C_{12}H_{36}Cl_8N_2Si_8$ (M_r = 716.75): C, 20.11; H, 5.06; N, 3.91. Found: C, 20.27; H, 5.11; N, 3.90.

1,5-Bis[bis(trimethylsilyl)amino]decachloropentasilane (6). The synthetic procedure is similar as described for **1**. A 9.7 g (40 mmol) amount of $(Me_3Si)_2NLi{\cdot}Et_2O$ and 11.3 g (20 mmol) of *n*-Si_5Cl_{12} gave a highly viscous oil, which can be crystallized from pentane at −30 °C. Yield: 15.5 g (95%) of white crystals.

Mp: 126−128 °C. ^{29}Si NMR (ext TMS, ppm): δ +9.48 (−*Si*Me_3), +3.06 (−*Si*Cl_2), +0.89 (−*Si*Cl_2), −17.39 (−N*Si*Cl_2−). ^1H NMR (ext TMS, ppm): δ 0.23 (s, CH_3). EI-MS (70 eV): *m/z* 816 (M^+). Anal. Calcd for $C_{12}H_{36}Cl_{10}N_2Si_9$ (M_r = 815.73): C, 17.67; H, 4.45; N, 3.43. Found: C, 17.41; H, 4.42; N, 3.50.

[Bis(trimethylsilyl)amino]nonachlorocyclopentasilane (7). A 4.8 g (20 mmol) amount of $(Me_3Si)_2NLi{\cdot}Et_2O$ suspended in 150 mL of heptane was added dropwise to a solution of 9.9 g (20 mmol) of *cyclo*-Si_5Cl_{10} in 150 mL of heptane at −70 °C. Subsequently the reaction mixture was stirred at room temperature for 12 h. After filtration and removal of the solvent the resulting yellow solid is recrystallized from toluene at −80°C to give 9.9 g (80%) of white crystals.

Mp: 96−99 °C. ^{29}Si NMR (ext TMS, ppm): δ +10.42 (−*Si*Me_3), +3.44 (−*Si*Cl_2), +0.51 (−*Si*Cl_2), −19.95 (−N*Si*Cl−). ^1H NMR (ext TMS, ppm): δ 0.24 (s, CH_3). EI-MS (70 eV): *m/z* 619 (M^+). Anal. Calcd for $C_6H_{18}Cl_9NSi_7$ (M_r = 619.80): C, 11.62; H, 2.92; Si, 31.72. Found: C, 31.62; H, 3.08; Si, 31.62.

Bis[bis(trimethylsilyl)amino]octachlorocyclopentasilane (8). A 9.6 g (40 mmol) amount of $(Me_3Si)_2NLi{\cdot}Et_2O$ suspended in 40 mL of heptane was added dropwise to a solution of 9.9 g (20 mmol) of *cyclo*-Si_5Cl_{10} in 40 mL of heptane at −30 °C. Subsequently the reaction mixture was stirred at room temperature for 12 h and refluxed for additional 3 h. After filtration and removal of the

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Table 1. ^{29}Si Chemical Shifts δ (ppm) of Polysilanyl Hydrides (C_6D_6 Solution vs Ext TMS)

	δSi(1)	δSi(2)	δSi(3)	δSi(4)	δSi(5)	J(Si-H)
$(Me_3Si)_2NSiH_2SiH_2SiH_3$ **(9)** 1 2 3 4	+7.04	−46.59	−109.30	−102.39		$^1J(Si2) = 204.1(t)$; $^1J(Si3) = 185.2(t)$; $^2J(Si3) = 15.3(t), 4.6 (q)$; $^1J(Si4) = 196.3(q)$
$(Me_3Si)_2NSiH_2SiH_2SiH_2SiH_3$ **(10)** 1 2 3 4 5	+6.99	−46.55	−104.49	−114.84	−98.25	$^1J(Si2) = 202.8(t)$; $^1J(Si3) = 184.2(t)$; $^2J(Si3) = 11.2(t)$; $^1J(Si4) = 191.2(t)$; $^1J(Si5) = 197.4(q)$
$(Me_3Si)_2NSiH_2SiH_2SiH_2N(SiMe_3)_2$ **(11)** 1 2 3	+6.53	−47.74	−100.01			$^1J(Si2) = 200.5(t)$; $^1J(Si3) = 177.6(t)$; $^2J(Si3) = 21.5(p)$
$(Me_3Si)_2NSiH_2SiH_2SiH_2SiH_2N(SiMe_3)_2$ **(12)** 1 2 3	+6.73	−45.67	−107.14			$^1J(Si2) = 202.5(t)$; $^1J(Si3) = 191.4(t)$; $^2J(Si3) = 15.8(t)$
$(Me_3Si)_2NSiH_2SiH_2SiH_2(SiH_2)_2N(SiMe_3)_2$ **(13)** 1 2 3 4	+6.83	−46.14	−103.45	−113.24		$^1J(Si2) = 202.3(t)$; $^1J(Si3) = 185.1(t)$; $^2J(Si3) = 15.0(t)$; $^1J(Si4) = 186.8(t)$
$ClSiH_2SiH_2SiH_3$ **(16)** 2 3 4		−25.33	−108.16	102.96		$^1J(Si2) = 222.4(t)$; $^1J(Si3) = 198.0(t)$; $^2J(Si3) = 14.9(t)$; $^1J(Si4) = 201.3(q)$
$ClSiH_2SiH_2SiH_2SiH_3$ **(17)** 2 3 4 5		−25.99	−104.14	−115.40	−99.20	$^1J(Si2) = 224.3(t)$; $^1J(Si3) = 195.3(t)$; $^1J(Si4) = 196.0(t)$; $^1J(Si5) = 199.9(q)$
$ClSiH_2SiH_2SiH_2Cl$ **(18)** 2 3		−27.51	−101.12			$^1J(Si2) = 230.8(t)$; $^1J(Si3) = 197.7(t)$; $^2J(Si3) = 24.9(t)$
$ClSiH_2SiH_2SiH_2SiH_2Cl$ **(19)** 2 3		−25.35	−105.49			$^1J(Si2) = 227.3(t)$; $^1J(Si3) = 198.1(t)$; $^2J(Si3) = 23.2(t)$
$ClSiH_2SiH_2SiH_2SiH_2SiH_2Cl$ **(20)** 2 3 4		−25.02	−102.3	−112.52		$^1J(Si2) = 225.8(t)$; $^1J(Si3) = 196.5(t)$; $^2J(Si3) = 25.4(t)$; $^1J(Si4) = 199.0(t)$

solvent the resulting yellow solid is recrystallized from pentane at −80 °C to give 11.9 g (80%) of white crystals (mixture of cis- and trans-isomers).

Mp: 108−110 °C. ^{29}Si NMR (ext TMS, ppm): δ +10.02/+9.83 (−*Si*Me$_3$), +6.00/+5.91 (−*Si*Cl$_2$), +5.45 (2Si, −*Si*Cl$_2$), −16.97/−17.04 (−N*Si*Cl$_2$−). ^{1}H NMR (ext TMS, ppm): δ 0.22 (s, −CH$_3$). EI-MS (70 eV): *m*/*z* 744 (M$^+$). Anal. Calcd for $C_{12}H_{36}Cl_8N_2Si_9$ (M_r = 744.74): C, 19.35; H, 4.87; N, 3.76. Found: C, 19.41; H, 5.02; N, 3.81.

1-[Bis(trimethylsilyl)amino]trisilane (9). A 27 mL volume of a 1.8 M solution of lithium aluminum hydride (50 mmol) in diethyl ether was slowly added to 7.4 g (15 mmol) of **1** dissolved in 100 mL of a 1:2 mixture of diethyl ether and pentane at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for additional 12 h. After removal of the solvents in a vacuum 100 mL of pentane were added and the salts were filtered off. The resulting colorless liquid (3.5 g) containing **9** and residual lithium aluminum hydride was used for subsequent reactions without further purification. Attempts to isolate pure **9** by distillation or fractional condensation gave rise to the formation of $H_3SiSiH_2N(SiMe_3)_2$ and SiH_4 as byproducts. Addition of saturated aqueous NH_4Cl solution to a pentane solution of **9** at 0 °C to destroy $LiAlH_4$ affords considerable amounts of siloxanes.

Bp (dec): 56−58 °C (0.1 mbar). ^{1}H NMR (ext TMS, ppm): δ 0.18 (s, 18H, Si−CH$_3$), 3.23 (m, 2H, −SiH$_2$−), 3.39 (t, 3H, −SiH$_3$), 4.97 (t, 2H, −SiH$_2$−N). ^{29}Si NMR (ext TMS, ppm): Table 1. MS (70 eV): *m*/*z* 251 (M$^+$).

1-[Bis(trimethylsilyl)amino]tetrasilane (10). The synthetic procedure is similar as described for **9** except that the reaction time was extended to 72 h. A 37 mL volume of a 1.8 M solution of lithium aluminum hydride (67 mmol) and 8.9 g (15 mmol) of **2** (containing 10% of **5**) gave 4.0 g of a colorless liquid containing **10**, **13**, and residual lithium aluminum hydride. This mixture was used for subsequent reactions without further purification. Attempts to isolate pure **10** failed. Addition of saturated aqueous NH_4Cl solution to a pentane solution of the crude product at 0 °C to destroy $LiAlH_4$ affords considerable amounts of siloxanes, while distillation or fractional condensation of the crude material gave mixtures of chain scission products.

Bp (dec): 81−83 °C (0.1 mbar). ^{1}H NMR (ext TMS, ppm): δ 0.19 (s, 18H, Si−CH$_3$), 3.25 (m, 2H, −SiH$_2$−), 3.31 (m, 2H, −SiH$_2$−), 3.39 (t, 3H, −SiH$_3$), 4.99 (t, 2H, −SiH$_2$−N). ^{29}Si NMR (ext TMS, ppm): Table 1. MS (70 eV): *m*/*z* 281 (M$^+$).

1,3-Bis[bis(trimethylsilyl)amino]trisilane (11). A 25 mL volume of a 1.8 M solution of lithium aluminum hydride (45 mmol) in diethyl ether was slowly added to 9.2 g (15 mmol) of **4** dissolved in 100 mL of a 1:2 mixture of diethyl ether and pentane at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for additional 24 h. After removal of the solvents in a vacuum 100 mL of pentane were added and the salts were filtered off. Subsequently saturated aqueous NH_4Cl solution was added dropwise to the filtrate at 0 °C until gas evolution ceases to destroy excess lithium aluminum hydride. After separation the organic layer was dried with Na_2SO_4 and the solvent was stripped off again. Distillation of the resulting colorless liquid at reduced pressure afforded 2.5 g (40%) of pure **11**. Spectroscopic data for the product are consistent with those of the literature.[5]

Bp: 91−93 °C (0.1 mbar). ^{1}H NMR (ext TMS, ppm): δ 0.23 (s, 36H, Si−CH$_3$), 3.36 (m, 2H, −SiH$_2$−), 5.09 (t, 4H, −SiH$_2$−N). ^{29}Si NMR (ext TMS, ppm): Table 1. MS (70 eV): *m*/*z* 411 (M$^+$). Anal. Calcd for $C_{12}H_{42}N_2Si_7$ (M_r = 411.08): C, 35.06; H, 10.30; N, 6.81. Found: C, 34.95; H, 10.23; N, 6.73.

1,4-Bis[bis(trimethylsilyl)amino]tetrasilane (12). The synthetic procedure is similar as described for **11** except that the reaction time was extended to 72 h. A 33 mL volume of a 1.8 M solution of lithium aluminum hydride (60 mmol) in diethyl ether and 10.8 g (15 mmol) of **5** gave a viscous colorless liquid. After aqueous workup with saturated NH_4Cl solution and distillation at reduced pressure 2.6 g (40%) of pure **12** was obtained. Spectroscopic data for the product are consistent with those of the literature.[5]

Bp: 101−102 °C (0.1 mbar). ^{1}H NMR (ext TMS, ppm): δ 0.22 (s, 36H, Si−CH$_3$), 3.35 (m, 4H, −SiH$_2$−), 5.02 (m, 4H, −SiH$_2$−N). ^{29}Si NMR (ext TMS, ppm): Table 1. MS (70 eV): *m*/*z* 442 (M$^+$).

Anal. Calcd for $C_{12}H_{44}N_2Si_8$ (M_r = 441.18): C, 32.67; H, 10.05; N, 6.35. Found: C, 32.80; H, 9.94; N, 6.42.

1,5-Bis[bis(trimethylsilyl)amino]pentasilane (13). The synthetic procedure is similar to that described for **11**. A 41 mL volumr of a 1.8 M solution of lithium aluminum hydride (75 mmol) in diethyl ether and 12.2 g (15 mmol) of **6** gave a viscous colorless liquid. After aqueous workup with saturated NH_4Cl solution and distillation at reduced pressure 2.7 g (40%) of pure **13** was obtained.

Bp: 107−108 °C (0.06 mbar). ^{1}H NMR (ext TMS, ppm): δ 0.20 (s, 36H, Si−CH_3), 3.45 (m, 6H, −SiH_2−), 5.06 (m, 4H, −SiH_2−N). ^{29}Si NMR (ext TMS, ppm): Table 1. MS (70 eV): m/z 471 (M^+). Anal. Calcd for $C_6H_{28}N_2Si_9$ (M_r = 471.28): C, 30.58; H, 9.84; N, 5.94. Found: C, 30.48; H, 9.85; N, 5.87.

Chlorination of 9−13. Anhydrous HCl was slowly passed through 40 mL of a solution of 10 mmol of the corresponding aminosilane in pentane at −80 °C for 30 min. After filtration and removal of the solvent at 300 mbar and 0 °C pyrophoric liquid samples of $H_3SiSiH_2SiH_2Cl$ **(16)**, $H_3SiSiH_2SiH_2SiH_2Cl$ **(17)**, $ClH_2SiSiH_2SiH_2Cl$ **(18)**, $ClH_2SiSiH_2SiH_2SiH_2Cl$ **(19)**, or $ClH_2SiSiH_2SiH_2SiH_2SiH_2Cl$ **(20)**, respectively, are obtained containing up to 5% of lower chlorosilane byproducts which cannot be removed by fractional condensation or distillation. ^{29}Si NMR data are summarized in Table 1.

Results and Discussion

Reaction of $LiN(SiMe_3)_2$ with Si_3Cl_8, *n*-Si_4Cl_{10}, and *n*-Si_5Cl_{12}. The reaction of Si_3Cl_8 with 1 equiv of $LiN(SiMe_3)_2$ under mild conditions (−40 °C, heptane solution) leads to the formation of $(Me_3Si)_2NSi_3Cl_7$ (**1**) (eq 1), while the higher homologues *n*-Si_4Cl_{10} and *n*-Si_5Cl_{12} afford mixtures of the mono- and the α,ω-disubstituted products (eq 2), which clearly reflects the dominating influence of the steric bulk of the $(Me_3Si)_2N$ moiety on the course of the substitution reaction.

$$Cl_3SiSiCl_2SiCl_3 \xrightarrow[\text{heptane}, -40\ °C]{+LiN(SiMe_3)_2} \underset{\mathbf{1}}{Cl_3SiSiCl_2SiCl_2{\cdot}N(SiMe_3)_2} \qquad (1)$$

$$Cl(SiCl_2)_nCl \xrightarrow[\text{heptane}, -40\ °C]{+LiN(SiMe_3)_2}$$

$$Cl(SiCl_2)_n{\cdot}N(SiMe_3)_2 + \qquad (2)$$
$$\mathbf{2}\text{: } n = 4;\ 90\%$$
$$\mathbf{3}\text{: } n = 5;\ 70\%$$

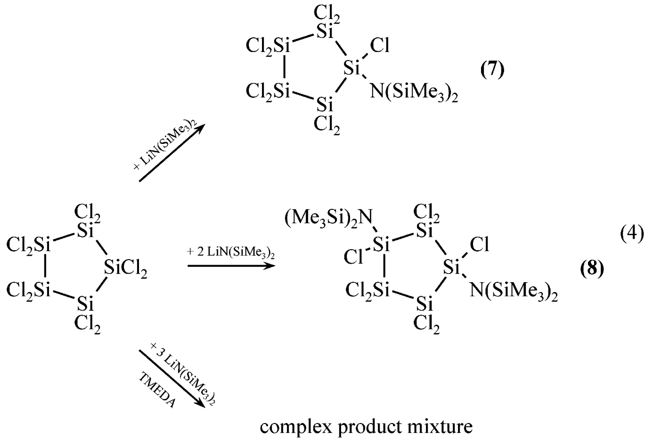
$$(Me_3Si)_2N\ (SiCl_2)_n{\cdot}N(SiMe_3)_2$$
$$\mathbf{5}\text{: } n = 4;\ 10\%$$
$$\mathbf{6}\text{: } n = 5;\ 30\%$$

Thus, replacement of chlorine is only observed at the terminal $SiCl_3$ groups while the internal $SiCl_2$ groups turned out to be completely inert under the conditions applied. In the case of **1**, moreover, the sterically demanding amino substituent attached to the α-silicon atom apparently retards the reactivity in the ω-position strongly enough to allow the selective formation of the monosubstituted product. The effect obviously diminishes with increasing chain length resulting in the formation of mixtures of the mono- and the α,ω-diamino derivatives in the attempted synthesis of **2** and **3**. The α,ω-diaminopolysilanes **4**−**6**, nevertheless, can be selectively made from the corresponding perchlorosilane precursor and 2 equiv of $LiN(TMS)_2$ (eq 3).

$$Cl(SiCl_2)_nCl \xrightarrow[\text{heptane, 25 °C}]{+2LiN(SiMe_3)_2} (Me_3Si)_2N(SiCl_2)_n{\cdot}N(SiMe_3)_2 \qquad (3)$$
$$\mathbf{4},\ n = 3;\ \mathbf{5},\ n = 4;\ \mathbf{6},\ n = 5$$

Attempts to attach more than two $(Me_3Si)_2N$ moieties to the oligosilane backbones also failed. The reaction of *n*-Si_5Cl_{12} with 3 equiv of $LiN(SiMe_3)_2$, for instance, only affords mixtures of **3**, **6**, and unreacted $LiN(SiMe_3)_2$ even under harsh conditions (refluxing THF or DME, prolonged reaction times, addition of TMEDA). ^{29}Si NMR additionally indicates the formation of increasing amounts of unidentified decomposition products arising from Si−Si bond scission and skeletal rearrangment reactions.

Reaction of $LiN(SiMe_3)_2$ with *cyclo*-Si_5Cl_{10}. In attempts to extend the current study to cyclic substrates, we chose to react decachlorocyclopentasilane (Si_5Cl_{10}) with $LiN(SiMe_3)_2$. The results are outlined in eq 4. Under mild conditions (−40 °C, heptane solution) the monosubstituted product **7** is formed from equimolar amounts of the reactants. A significant part of Si_5Cl_{10}, however, remains unreacted and subsequently has to be removed by recrystallization, what again reflects the comparably low reactivity of the $SiCl_2$ moiety versus $LiN(SiMe_3)_2$. A second $(SiMe_3)_2N$ group, nevertheless, can be attached to the cyclopentasilane ring, when more severe reaction conditions are applied. Thus, in refluxing heptane Si_5Cl_{10} reacts with 2 equiv of $LiN(SiMe_3)_2$ to give the disubstituted product **8**.



(4)

In the ^{29}Si NMR spectrum of **8** 7 resonance lines at +10.02/+9.83 (−*Si*Me_3), +6.00/+5.91 (−*Si*Cl_2), +5.45 (−*Si*Cl_2), and −16.97/−17.04 ppm (−N*Si*Cl_2−) appear, what is consistent with an isomeric mixture of *cis*- and *trans*-**8**. Substitution of two of the chlorines in Si_5Cl_{10} by $(Me_3Si)_2N$ groups produces three magnetically nonequivalent endocyclic silicon atoms. Since the amino substituents can be attached to the cyclopentasilane ring either cis or trans relative to each other, 8 individual ^{29}Si resonances are expected, two of which apparently superimpose in the experimental spectrum at +5.45 ppm. Although crystals of **8** suitable for X-ray crystallography could not be grown and ^{29}Si NMR cannot distinguish between 1,2- or 1,3-**8** it seems likely to assume the formation of the 1,3-isomer simply for steric reasons. The 1,2 substitution, furthermore, also could not be accomplished, when Si_5Cl_{10} was reacted with 3 or more equiv of $\text{LiN(SiMe}_3)_2$. In refluxing heptane, **8** is obtained as the only product again along with unreacted $\text{LiN(SiMe}_3)_2$, while harsh reaction conditions (refluxing THF or DME, prolonged reaction times, addition of TMEDA) give rise to the formation of unidentified complex product mixtures.

Compounds **1**−**8** are generally moisture sensitive solids due to the presence of Si−Cl bonds. The reactivity toward H_2O, however, is significantly affected by the bulky $(\text{Me}_3\text{Si})_2\text{N}$ groups. For example, compounds **1**−**3** are readily decomposed by atmospheric moisture, while **4**−**6** containing two $(\text{Me}_3\text{Si})_2\text{N}$ substituents can be handled in air for limited periods without detectable deterioration.

Hydride Reduction Reactions. It is noteworthy that hydride reduction of **1**−**6** with LiAlH_4 can only be successfully performed in a 2:1 mixture of pentane and ether, because the aminochloropolysilane starting materials turned out to be unstable in pure diethyl ether. Significantly prolonged reaction times are therefore necessary. The linear α,ω-bis[bis(trimethylsilyl)amino]polysilanes **11**−**13**, nevertheless, are easily accessible according to eq 5 without significant Si−Si or the Si−N bond scission and can be isolated after quenching of residual traces of LiAlH_4 with saturated NH_4Cl solution and subsequent distillation in a vacuum.

$$\textbf{4−6} \xrightarrow[\text{pentane/ether,2:1; 25 °C}]{+\text{LiAlH}_4} \underset{\textbf{11},\ n = 3;\ \textbf{12},\ n = 4;\ \textbf{13},\ n = 5}{(\text{Me}_3\text{Si})_2\text{N}(\text{SiH}_2)_n\text{N}(\text{SiMe}_3)_2} \qquad (5)$$

Hydride reduction of **1** proceeds less straightforward. Although the desired (bis(trimethylsilyl)amino)trisilane **9** is obtained nearly exclusively after the addition of LiAlH_4, the pure target molecule could not be isolated because of the relatively good leaving group character of the terminal $-\text{SiH}_3$ moiety. Distillation or fractional condensation of the crude material gives rise to the formation of $\text{H}_3\text{SiSiH}_2\text{N(SiMe}_3)_2$ and SiH_4 as byproducts very likely arising from scission of the terminal Si−Si bond by residual LiAlH_4 at elevated temperatures. Aqueous workup with saturated NH_4Cl solution to destroy excess LiAlH_4 prior to distillation affords considerable amounts of linear siloxanes. For the same reason the pure tetrasilane derivative **10** is not accessible by the hydride reduction of a mixture of **2** and **5** synthesized according to eq 2. Crude samples of **9** and **10**, however, can be used without further purification for subsequent reactions or spectroscopic characterization.

One could expect that hydride reduction of the cyclic compounds **7** and **8** affords the corresponding cyclosilanyl hydrides just as observed for their linear counterparts **4**−**6**. However, while the Si−N bond remains intact during hydride reduction, the Si−Si bonds within the cyclopentasilane ring do not (eq 6).

$$\textbf{7},\ \textbf{8} \xrightarrow[\text{pentane/ether, 2:1; 25 °C}]{+\text{LiAlH}_4} \underset{\textbf{14},\ n = 1;\ \textbf{15},\ n = 2}{cyclo\text{-Si}_5\text{H}_{10-n}[\text{N(SiMe}_3)_2]_n} + \text{ring scission products} \qquad (6)$$

GC/MS analysis of the product mixtures obtained after treatment of **7** and **8** with LiAlH_4 reveals the formation of considerable amounts of linear aminosilanes arising from ring cleavage reactions along with the desired products **14** and **15**, which could not be isolated by distillation or fractional condensation due to their limited thermal stability.

Rechlorination Reactions. The general sensitivity of aminosilanes under acidic conditions can be utilized to rechlorinate the Si−N bonds in **9**−**13**, which provides an easy access to chloro- and dichloro-containing trisilanes, tetrasilanes, and pentasilanes. Passing anhydrous HCl through pentane solutions of **9**−**13** at −80°C, thus, affords reasonably pure $\text{H}_3\text{SiSiH}_2\text{SiH}_2\text{Cl}$ **(16)**, $\text{H}_3\text{SiSiH}_2\text{SiH}_2\text{SiH}_2\text{Cl}$ **(17)**, $\text{ClH}_2\text{SiSiH}_2\text{SiH}_2\text{Cl}$ **(18)**, $\text{ClH}_2\text{SiSiH}_2\text{SiH}_2\text{SiH}_2\text{Cl}$ **(19)**, and $\text{ClH}_2\text{SiSiH}_2\text{SiH}_2\text{SiH}_2\text{SiH}_2\text{Cl}$ **(20)**, respectively (eq 7). In all cases the crude products contain variable amounts of lower chlorosilanes due to Si−Si bond rupture. Attempts to purify the desired compounds by distillation or fractional condensation only gave rise to the formation of increased amounts of chain scission products.

$$\textbf{9−13} \xrightarrow[\text{pentane/−80 °C}]{+\text{HCl}} \textbf{16−20} + \text{lower chlorosilanes} \qquad (7)$$

Characterization. All substances were characterized by standard spectroscopic techniques. The analytical data included in the Experimental Section are consistent with the proposed structures in all cases.

^{29}Si NMR parameters of the polysilanyl hydrides **9**−**13** and **16**−**20** are summarized in Table 1. Excellent agreement with literature data obtained for amino- and chloro-containing di-, tri-, and tetrasilanes is observed.[5,16] The $-\text{SiH}_2\text{NR}_2$ and $-\text{SiH}_2\text{Cl}$ resonances, respectively, exhibit the characteristic low-field shifts relative to the $-\text{SiH}_3$ and to the $-\text{SiH}_2-$ signals. Typical values for $^1J(^{29}\text{Si}-^1\text{H})$ are observed; the increased coupling constants within the $-\text{SiH}_2\text{NR}_2$ and $-\text{SiH}_2\text{Cl}$ groups are typical for silicon hydrides bearing electronegative substituents. Increasing carbon−proton coupling constants in the presence of electron-withdrawing substituents at the coupling carbon are also common in ^{13}C NMR spectroscopy.[17]

All compounds exhibit first-order coupled ^{29}Si NMR spectra; the spectrum of the trisilane derivative **9** is depicted in Figure 1 as representative example. The multiplet at +7.04 ppm is easily assigned to the $-\text{SiMe}_3$ groups. The resonance line of the $-\text{SiH}_3$ group centered at −102.39 ppm is split into a quartet due to $^1J(^{29}\text{Si}-^1\text{H})$ coupling, while the $-\text{SiH}_2$ resonances at −109.30 ($-\text{SiH}_2-$) and −46.59 ($-\text{SiH}_2\text{N}$) ppm appear as triplets. The individual resonance lines of the central $-\text{SiH}_2-$ Si(3) triplet exhibit additional hyperfine structures, which could not be resolved for Si(2) and Si(4). Therefore, each line of the Si(3) triplet in the spectrum of **9** appears as a triplet of quartets arising from long-range coupling to the protons of the adjacent $-\text{SiH}_2\text{NR}_2$

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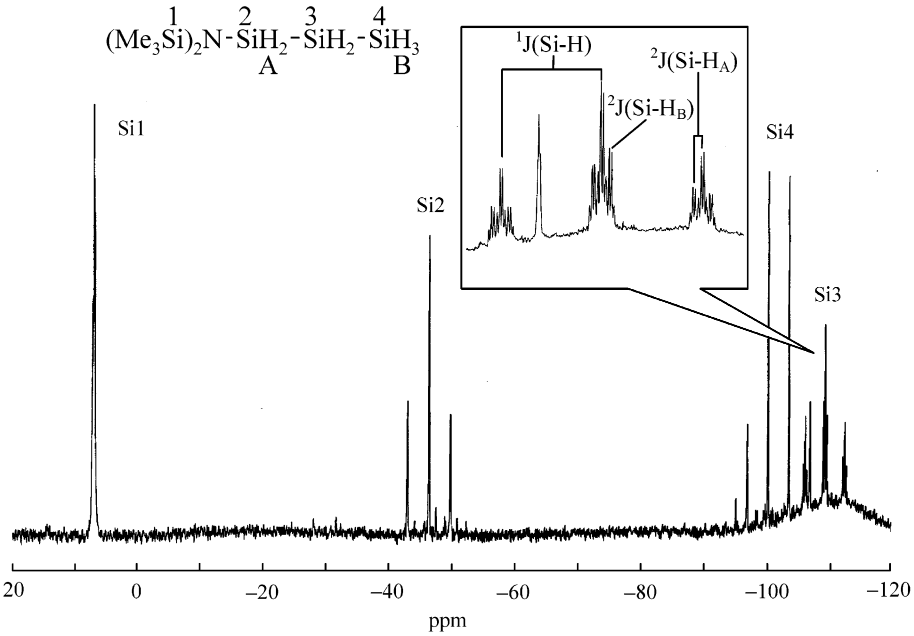

Figure 1. Coupled ^{29}Si NMR spectrum of crude **9** (C_6D_6 solution vs ext TMS).

($^2J_{Si(3)-HA}$ = 15.3 Hz) and $-SiH_3$ ($^2J_{Si(3)-HB}$ = 4.65 Hz) groups, respectively. In the spectrum of the symmetrical diamino derivative **11** each line of the Si(3) triplet is split into 5 signals ($^2J_{Si(3)-H}$ = 21.5 Hz) indicating coupling of the ^{29}Si nucleus to the 4 magnetically equivalent protons of the $-SiH_2NR_2$ groups.

Conclusions

The results obtained in this study clearly indicate that $LiN(SiMe_3)_2$ is a suitable reagent for the selective substitution of chlorine in linear and cyclic perchloropolysilanes. In linear substrates substitution occurs exclusively at the terminal $-SiCl_3$ groups due to the steric bulk of the $-N(SiMe_3)_2$ group. The α,*ω*-diamino derivatives $(Me_3Si)_2N(SiCl_2)_nN(SiMe_3)_2$ (n = 3−5), thus, are formed as the only products from the appropriate perchlorinated precursors and 2 equiv of $LiN(SiMe_3)_2$. When Si_3Cl_8 is reacted with an equimolar amount of $LiN(SiMe_3)_2$, the sterically demanding amino substituent attached to the α-Si atom retards the reactivity in the *ω* position strongly enough to allow the selective formation of the monosubstituted product $(Me_3Si)_2NSi_3Cl_7$. Expectedly, the effect diminishes with increasing chain length resulting in mono- and α,*ω* disubstitution in the attempted synthesis of the corresponding tetra- and pentasilanes. Starting from *cyclo*-Si_5Cl_{10} and $LiN(SiMe_3)_2$, the mono- and the diaminocyclopentasilanes can be obtained depending on the stoichiometric ratio of the reactants.

The resulting bis(trimethylsilyl)aminochloropolysilanes are valuable starting materials for the synthesis of multifunctional polysilane derivatives, because the $(Me_3Si)_2N$ group turned out to be remarkably stable against nucleophiles. Hydride reduction of the remaining Si−Cl bonds with $LiAlH_4$, for example, leads to previously unknown (bis(trimethylsilyl)amino)silicon hydrides, which again can be used for further derivatization. Additional studies concerning chemical transformations of (bis(trimethylsilyl)amino)chloropolysilanes are currently in progress.

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