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1,2-Disilanediyl Bis(triflate), $F_3CSO_3{-}SiH_2SiH_2{-}O_3SCF_3$, as the Key Intermediate for a Facile Preparation of Open-Chain and Cyclic 1,1- and 1,2-Diaminodisilanes

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Convenient high-yield syntheses for several open-chain and cyclic diaminodisilanes with fully hydrogenated Si−Si linkages are reported. The key intermediate for the preparation of the title compounds, 1,2-bis(((trifluoromethyl)sulfonyl)oxy)disilane (**1**), reacts with 2 equiv of diethylamine to afford a mixture of the isomers $Et_2NSiH_2SiH_2NEt_2$ (**2a**) and $(Et_2N)_2SiHSiH_3$ (**2a′**). Isopropylamine and **1** give $^iPr_2NSiH_2SiH_2N^iPr_2$ (**2b**) exclusively. Treatment of **1** with 1 equiv of a primary alkylamine affords 2,3,5,6-tetrasilapiperazines [$RNSiH_2SiH_2RNSiH_2SiH_2$; R = ^{i}Pr (**3a**), ^{t}Bu (**3b**), Bzl (**3c**)] comprising two $SiH_2{-}SiH_2$ linkages. 1,3-Bifunctional bis(isopropylamino)silanes [$(^iPrNH)_2SiR_2$; R = Me, Ph] were found to react with **1** to give trisilaimidazolidines [$(^iPrN)SiR_2(^iPrN)SiH_2SiH_2$; R = Me (**4a**), Ph (**4b**)] again comprising the $N{-}SiH_2{-}SiH_2{-}N$ unit. The crystal structures of *N*,*N*′-diisopropyl-2,2-diphenyl-2,4,5-trisilaimidazolidine (**4b**) and *N*,*N*′-di-*tert*-butyl-2,3,5,6-tetrasilapiperazine (**3b**) were determined in X-ray diffraction studies; the five-membered ring of **4b** is nearly planar with all nitrogen atoms in a planar configuration. The six-membered ring of **3b** has a twist conformation, but again with the two nitrogen atoms in a planar configuration. Surprisingly, the treatment of **1** with 1,4-bifunctional *N*,*N*′-dialkylethylenediamines [$(RNHCH_2{-})_2$; R = ^{i}Pr, ^{t}Bu] does not give the analogous six-membered-ring compounds but leads selectively to the isomeric five-membered heterocycles [$(CH_2NR)_2SiHSiH_3$; R = ^{i}Pr (**5a**), ^{t}Bu (**5b**)], which are the products of a Si → Si hydrogen shift rearrangement.

Introduction

Amino*disilanes* and amino*polysilanes*[1−7] are poorly investigated classes of silicon compounds as compared to the extensively studied silylamines bearing the simple H_3Si substituent.[1,8−10] However, owing to their unique thermal and photochemical properties, aminodisilanes are promising single-source precursors for the vapor deposition of silicon nitride thin films for high-performance electronic devices.[1,11−13] The low Si−Si bond energy and the intense UV absorption of Si−Si−N linkages, in particular, are the most important pertinent characteristics of amino-substituted di- and polysilanes,[14,15] and previous investigations have shown consistently that these prerequisites give rise to specific degradation mechanisms.[1]

Reactions of native or substituted di- or polysilanes with simple amines were found to lead to extensive Si−Si cleavage induced by the high basicity of the alkylamines.[16,17] This left the preparation of aminodisilanes as a synthetic challenge for several years, and it was only recently that we succeeded in the synthesis of the first fully hydrogenated 1,1- and 1,2-diaminodisilanes.[1] 1,1-Bis(diethylamino)disilane and 1,2-bis(diisopropylamino)disilane (BIPADS) were obtained by hydrogenation of the corresponding *symmetrical* chloro compounds and shown to be excellent single-source precursors for silicon nitride.

In an effort to open other routes to these promising materials and to widen the scope of potential precursors, we have now explored the applicability of a new precursor already employed successfully for the synthesis of other $X{-}SiH_2SiH_2{-}X$ compounds.[18] This concept is based on 1,2-disilanediyl bis(triflate), generated from the corresponding diaryldisilanes through protodearylation using trifluoromethanesulfonic (triflic) acid.[18,19] The bis(triflate) should also be suitable for generating cyclic disilanes which are expected to show further improved deposition characteristics as compared to open-chain species, owing to their higher volatility and compact structure. Cyclic diaminodisilanes could not be obtained in acceptable yields by the hydrogenation of halogen precursors due to Si−Si cleavage.[20]

1,2-Bis(((trifluoromethyl)sulfonyl)oxy)disilane (**1**) was first prepared from 1,2-di*phenyl*disilane and triflic acid.[19] Because the protodearylation reaction depends strongly on the electron

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density of the aryl groups, we turned now to 1,2-di-*p*-tolyldisilane,[18] which allows work under even milder conditions.

Experimental Section

General Procedures. All experiments were routinely carried out under an atmosphere of dry, pure nitrogen. Solvents were appropriately dried, distilled, and saturated with nitrogen prior to use; glassware was oven-dried and filled with nitrogen. NMR spectra were obtained on a JEOL JNM-GX 400 spectrometer using dry degassed C_6D_6 as the solvent. ^{15}N NMR spectra were referenced externally to aniline at δ -333.6 ppm. Infrared spectra were recorded on a Perkin-Elmer FT-IR 577 spectrometer. GLC-MS analyses were performed on an HP 5890/II gas-liquid chromatography system with a mass-selective detector HP 5971 A (EI, 70 eV). Mass spectra were registered on a Varian MAT 112 S instrument. UV spectra were recorded on a Perkin-Elmer UV/vis Lambda 2 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Technical University of Munich. The nitrogen contents were generally too low owing to the formation of silicon nitride in the combustion. Bis(isopropylamino)dimethylsilane and bis(isopropylamino)diphenylsilane were prepared by treatment of dimethyldichlorosilane and diphenyldichlorosilane, respectively, with isopropylamine according to standard procedures.[21] Other reagents were commercially available or prepared by following literature procedures.[18,22]

1,2-Bis(((trifluoromethyl)sulfonyl)oxy)disilane (1). A solution of 1,2-di-*p*-tolyldisilane (1.5 g/2.0 g, 6.2 mmol/8.2 mmol) in toluene (50 mL/65 mL) is cooled to −25 °C and treated with triflic acid (1.86 g/2.48 g, 12.4 mmol/16.5 mmol) with stirring. Stirring is continued for 1 h at −10 °C. The resulting solution is used in all further experiments. ^{1}H NMR (toluene-d_8, −15 °C): δ 4.47 (s, J(Si,H) = 272 Hz, SiH_2). ^{29}Si NMR (DEPT, v.s.): $\delta = -28.2$ (tm, J(Si,H) = 272 Hz).

1,2- and 1,1-Bis(diethylamino)disilane (2a, 2a′). A freshly prepared solution of **1** [from 1.5 g (6.2 mmol) of 1,2-di(*p*-tolyldisilane] in toluene (50 mL) is treated with a mixture of 0.90 g (12.4 mmol) of diethylamine and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. The reaction mixture is allowed to warm to 20 °C, the oily triethylammonium triflate is separated from the mixture, and the solvent is removed in a vacuum. Hexane is added to precipitate all remaining ammonium salts, which are filtered off. The filtrate is fractionally distilled in a vacuum to give a colorless liquid (**2a**, yield 0.50 g, 40%); bp 23 °C/0.05 Torr. The byproduct, 1,1-bis(diethylamino)disilane (**2a′**, 6%, derived from NMR analysis), can readily be isolated (bp 23 °C/0.2 Torr). **2a**: MS (EI, 70 eV) m/z = 204 (M^+); IR (liquid, 25 °C) 2137.0 cm^{-1} (vs, $\nu(SiH_2)$), 2061.7 cm^{-1} (s, $\nu(SiH_2)$); ^{1}H NMR (C_6D_6, 25 °C) δ 0.96 (t, J(H,H) = 6.7 Hz, 12H, Me), 2.76 (q, J(H,H) = 6.7 Hz, 8H, CH_2), 4.83 (s, J(Si,H) = 190.4 Hz, 4H, SiH_2); ^{13}C{^{1}H} NMR (v.s.) δ 15.4 (s, Me), 44.6 (s, CH_2); ^{29}Si NMR (DEPT, v.s.) δ −42.5 (ttquin, J(Si,H) = 190.4, 13.9, and 4.6 Hz, respectively, SiH_2); ^{15}N NMR (DEPT, v.s.) δ −376.7 (s). Anal. Found: C, 46.29; H, 11.43; N, 12.67. Calcd for $C_8H_{24}N_2Si_2$ (M_r = 204.47): C, 46.99; H, 11.83; N, 13.70. 1,1-Bis(diethylamino)disilane, **2a′**: ^{1}H NMR (C_6D_6, 25 °C) δ 0.96 (t, J(H,H) = 7.3 Hz, 12H, Me), 2.85 (q, J(H,H) = 7.3 Hz, 8H, CH_2), 3.38 (d, J(H,H) = 2.4, J(Si,H) = 183.7 Hz, 3H, SiH_3), 5.11 (q, J(H,H) = 2.4, J(Si,H) = 210.6 Hz, 1H, SiH); ^{13}C{^{1}H} NMR (v.s.): δ 15.7 (s, Me), 41.5 (s, CH_2); ^{29}Si NMR (DEPT, v.s.) δ −106.1 (qd, J(Si,H) = 183.7 and 21.1 Hz, respectively, SiH_3), −19.1 (dm, J(Si,H) = 210.6 Hz, SiH).

1,2-Bis(diisopropylamino)disilane (2b). As described for **2a**, a solution of **1** [from 2.0 g (8.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (65 mL) is treated with a mixture of 1.67 g (16.5 mmol) of diisopropylamine and 1.67 g (16.5 mmol) of triethylamine at −50 °C with stirring. After separation of the triethylammonium triflate precipitate from the mixture, the solvent is removed from the filtrate and the residue is fractionally distilled in a vacuum to give a colorless liquid (**2b**, yield 1.52 g, 71%); bp 68 °C/0.05 Torr. MS (EI, 70 eV): m/z = 260 (M^+). ^{1}H NMR (C_6D_6, 25 °C): δ 1.05 (d, J(H,H) = 6.7 Hz, 24H, Me), 3.01 (sept, J(H,H) = 6.7 Hz, 4H, CH), 4.87 (s, J(Si,H) = 188.6 Hz, 4H, SiH_2). ^{13}C{^{1}H} NMR (v.s.): δ 24.0 (s, Me), 48.5 (s, CH). ^{29}Si NMR (DEPT, v.s.): δ −54.3 (ttt, J(Si,H) = 188.6, 14.5, and 5.8 Hz, respectively, SiH_2).

***N,N′*-Diisopropyl-2,3,5,6-tetrasilapiperazine (3a).** A freshly prepared solution of **1** [from 1.5 g (6.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (50 mL) is treated with a mixture of 0.37 g (6.2 mmol) of isopropylamine and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. The reaction mixture is allowed to warm to 20 °C, the oily triethylammonium triflate is separated from the mixture, and the solvent is removed from the filtrate. Hexane is added to precipitate all remaining ammonium salts. The filtrate is fractionally distilled in a vacuum to give a colorless liquid (**3a**, yield 0.44 g, 61%); bp 43−44 °C/0.05 Torr. MS (EI, 70 eV): m/z = 234 (M^+). UV (hexane, 25 °C): λ_{max} = 213 nm; λ = 251 nm (broad). IR (liquid, 25 °C): 2099.0 cm^{-1} (vs, $\nu(SiH_2)$). ^{1}H NMR (C_6D_6, 25 °C): δ 1.07 (d, J(H,H) = 6.7 Hz, 12H, Me), 3.09 (sept, J(H,H) = 6.7 Hz, 2H, CH), 4.83 (s, J(Si,H) = 198.4 Hz, 8H, SiH_2). ^{13}C{^{1}H} NMR (v.s.): δ 23.2 (s, Me), 53.3 (s, CH). ^{29}Si NMR (DEPT, v.s.): δ −47.4 (tm, J(Si,H) = 198.4 Hz, SiH_2). ^{15}N NMR (DEPT, v.s.): δ −384.8 (s). Anal. Found: C, 30.57; H, 9.15; N, 10.92. Calcd for $C_6H_{22}N_2Si_4$ (M_r = 234.60): C, 30.72; H, 9.45; N, 11.94.

***N,N′*-Di-*tert*-butyl-2,3,5,6-tetrasilapiperazine (3b).** As described for **3a**, a solution of **1** [from 1.5 g (6.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (50 mL) is treated with a mixture of 0.45 g (6.2 mmol) of *tert*-butylamine and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. The triethylammonium triflate precipitate is separated from the mixture, and the solvent is removed from the filtrate. Hexane is added to precipitate all remaining ammonium salts. The filtrate is fractionally distilled in a vacuum to give a colorless liquid (**3b**, yield 0.54 g, 67%); bp 55 °C/0.05 Torr; mp 2 °C. MS (EI, 70 eV, GC-coupled): m/z = 262 (M^+). UV (hexane, 25 °C): λ_{max} = 215 nm; λ = 251 nm (broad). IR (liquid, 25 °C): 2102.0 cm^{-1} (vs, $\nu(SiH_2)$). ^{1}H NMR (C_6D_6, 25 °C): δ 1.22 (s, 18H, Me), 5.01 (s, J(Si,H) = 197.8 Hz, 8H, SiH_2). ^{13}C{^{1}H} NMR (v.s.): δ 30.6 (s, Me), 53.1 (s, C). ^{29}Si NMR (DEPT, v.s.): δ −48.1 (ttm, J(Si,H) = 197.8 and 10.1 Hz, respectively, SiH_2). ^{15}N NMR (DEPT, v.s.): δ −377.2 (s). Anal. Found: C, 36.44; H, 9.91; N, 10.22. Calcd for $C_8H_{26}N_2Si_4$ (M_r = 262.65): C, 36.58; H, 9.98; N, 10.67.

***N,N′*-Dibenzyl-2,3,5,6-tetrasilapiperazine (3c).** As described for **3a**, a solution of **1** [from 1.5 g (6.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (50 mL) is treated with a mixture of 0.66 g (6.2 mmol) of benzylamine and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. The triethylammonium triflate precipitate is separated from the mixture, and the solvent is removed from the filtrate. Hexane is added to precipitate all remaining ammonium salts. The filtrate is fractionally distilled in a vacuum to give an oily colorless liquid (**3c**, yield 0.51 g, 50%); bp 124 °C/0.05 Torr. MS (EI, 70 eV, GC-coupled): m/z = 330 (M^+). IR (liquid, 25 °C): 2128.9 cm^{-1} (vs, $\nu(SiH_2)$). ^{1}H NMR (C_6D_6, 25 °C): δ 3.91 (s, 4H, CH_2), 4.73 (s, J(Si,H) = 201.3 Hz, 8H, SiH_2), 7.15 (m, 10H, H_{ar}). ^{13}C{^{1}H} NMR (v.s.): δ 58.2 (s, CH_2), 127.6 (s, C_4), 127.9 (s, $C_{2/6}$), 128.7 (s, $C_{3/5}$), 139.7 (s, C_1). ^{29}Si NMR (DEPT, v.s.): δ −38.7 (tm, J(Si,H) = 201.3 Hz, SiH_2). ^{15}N NMR (DEPT, v.s.): δ −398.2 (s). Anal. Found: C, 50.33; H, 6.85; N, 8.05. Calcd for $C_{14}H_{22}N_2Si_4$ (M_r = 330.69): C, 50.85; H, 6.71; N, 8.47.

***N,N′*-Diisopropyl-2,2-dimethyl-2,4,5-trisilaimidazolidine (4a).** A freshly prepared solution of **1** [from 1.5 g (6.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (50 mL) is treated with a mixture of 1.08 g (6.2 mmol) of bis(isopropylamino)dimethylsilane and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. The reaction mixture is allowed to warm to 20 °C, the oily triethylammonium triflate is separated from the mixture, and the solvent is removed in a vacuum. Hexane is added to precipitate all remaining ammonium salts. The filtrate is fractionally distilled in a vacuum to give a colorless liquid (**4a**, yield 0.75 g, 52%); bp 38−39 °C/0.05 Torr. MS (EI, 70 eV): m/z = 232 (M^+). IR (liquid, 25 °C): 2107.7 cm^{-1} (vs, $\nu(SiH_2)$). ^{1}H NMR (C_6D_6, 25 °C): δ −0.01 (s, 6H, MeSi), 1.10 (d, J(H,H) = 6.1 Hz, 12H, Me), 3.00 (sept, J(H,H) = 6.1 Hz, 2H, CH), 4.67 (s, J(Si,H) = 200.9 Hz, 4H, SiH_2). ^{13}C{^{1}H} NMR (v.s.): δ 0.0 (s, MeSi), 24.5 (s, Me), 44.8 (s, CH). ^{29}Si NMR (DEPT, v.s.): δ −63.7 (ttd, J(Si,H) = 200.9, 10.5, and 8.2 Hz, respectively, SiH_2), 4.8 (m, SiMe). ^{15}N

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NMR (DEPT, v.s.): δ −357.1 (s). Anal. Found: C, 40.54; H, 10.43; N, 11.11. Calcd for $C_8H_{24}N_2Si_3$ (M_r = 232.55): C, 41.32; H, 10.40; N, 12.05.

***N,N′*-Diisopropyl-2,2-diphenyl-2,4,5-trisilaimidazolidine (4b).** As described for **4a**, a solution of **1** [from 1.5 g (6.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (50 mL) is treated with a mixture of 1.85 g (6.2 mmol) of bis(isopropylamino)diphenylsilane and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. The triethylammonium triflate precipitate is separated from the mixture, and the solvent is removed from the filtrate. After addition of hexane, the precipitate of all remaining ammonium salts is filtered off and the filtrate is fractionally distilled in a vacuum. The colorless liquid product (**4b**, yield 1.23 g, 56%) is collected at bp 130 °C/0.05 Torr. It solidifies in the receiver; mp 123 °C. MS (EI, 70 eV, GC-coupled): m/z = 356 (M^+). IR (CCl_4, 25 °C): 2115.3 cm^{-1} (vs, $\nu(SiH_2)$). ^1H NMR (C_6D_6, 25 °C): δ 0.90 (d, J(H,H) = 6.1 Hz, 12H, Me), 3.16 (sept, J(H,H) = 6.1 Hz, 2H, CH), 4.85 (s, J(Si,H) = 202.9 Hz, 4H, SiH_2), 7.22 (m, 6H, $H_{3/4/5}$), 7.73 (m, 4H, $H_{2/6}$). $^{13}C\{^1H\}$ NMR (v.s.): δ 23.7 (s, Me), 44.9 (s, CH), 128.1 (s, $C_{3/5}$), 130.0 (s, C_4), 135.8 (s, $C_{2/6}$), 136.0 (s, C_1). ^{29}Si NMR (DEPT, v.s.): δ −62.1 (ttd, J(Si,H) = 202.9, 10.5, and 8.1 Hz, respectively, SiH_2), −13.2 (m, SiPh). ^{15}N NMR (DEPT, v.s.): δ −360.0 (s). Anal. Found: C, 60.51; H, 8.06; N, 7.60. Calcd for $C_{18}H_{28}N_2Si_3$ (M_r = 356.69): C, 60.61; H, 7.91; N, 7.85.

***N,N′*-Diisopropyl-2-silyl-2-silaimidazolidine (5a).** A freshly prepared solution of **1** [from 2.0 g (8.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (65 mL) is treated with a mixture of 1.19 g (8.2 mmol) of *N,N′*-diisopropylethylenediamine and 1.67 g (16.5 mmol) of triethylamine at −50 °C with stirring. The mixture is then allowed to warm to 20 °C. The oily triethylammonium triflate precipitate is separated from the mixture, and the solvent is removed in a vacuum. Addition of hexane leads to precipitation of all remaining ammonium salts. After filtration, the filtrate is fractionally distilled in a vacuum to give a colorless liquid (**5a**, yield 1.02 g, 61%); bp 39 °C/0.05 Torr. MS (EI, 70 eV): m/z = 202 (M^+). IR (liquid, 25 °C): 2128.1 cm^{-1} (vs, $\nu(SiH_3)$), 2063.7 cm^{-1} (s, ν(SiH)). ^1H NMR (C_6D_6, 25 °C): δ 1.05 (d, J(H,H) = 6.4 Hz, 6H, Me), 1.08 (d, J(H,H) = 6.4 Hz, 6H, Me), 2.79 (m, AA′BB′, 4H, CH_2), 2.96 (sept, J(H,H) = 6.4 Hz, 2H, CH), 3.24 (d, J(H,H) = 2.1 Hz, J(Si,H) = 183.2 Hz, 3H, SiH_3), 5.58 (q, J(H,H) = 2.1 Hz, J(Si,H) = 210.6 Hz, 1H, SiH). $^{13}C\{^1H\}$ NMR (v.s.): δ 23.1 (s, Me), 23.5 (s, Me), 47.6 (s, CH_2), 48.7 (s, CH). ^{29}Si NMR (DEPT, v.s.): δ −101.4 (qdm, J(Si,H) = 183.2 and 45.2 Hz, SiH_3), −22.2 (dm, J(Si,H) = 210.6 Hz, SiH). ^{15}N NMR (DEPT, v.s.): δ −356.4 (s). Anal. Found: C, 47.67; H, 10.96; N, 14.24. Calcd for $C_8H_{22}N_2Si_2$ (M_r = 202.45): C, 47.46; H, 10.95; N, 13.84.

***N,N′*-Di-*tert*-butyl-2-silyl-2-silaimidazolidine (5b).** As described for **5a**, a solution of **1** [from 1.5 g (6.2 mmol) of 1,2-di-*p*-tolyldisilane] in toluene (50 mL) is treated with a mixture of 1.07 g (6.2 mmol) of *N,N′*-di-*tert*-butylethylenediamine and 1.25 g (12.4 mmol) of triethylamine at −50 °C with stirring. The triethylammonium triflate is separated from the mixture, and the solvent is removed in a vacuum. After addition of hexane, the precipitate of the remaining ammonium salts is filtered off and the filtrate is fractionally distilled in a vacuum to give a colorless liquid (**5b**, yield 0.67 g, 47%); bp 46−47 °C/0.05 Torr. MS (EI, 70 eV): m/z = 230 (M^+). UV (hexane, 25 °C): λ_{max} = 216 nm; λ = 239 nm (broad). IR (liquid, 25 °C): 2143.3 cm^{-1} (vs, $\nu(SiH_3)$), 2075.0 cm^{-1} (s, ν(SiH)). ^1H NMR (C_6D_6, 25 °C): δ 1.16 (s, 18H, Me), 2.85 (m, AA′BB′, 4H, CH_2), 3.45 (d, J(H,H) = 1.8 Hz, J(Si,H) = 181.4 Hz, 3H, SiH_3), 5.76 (q, J(H,H) = 1.8 Hz, J(Si,H) = 213.6 Hz, 1H, SiH). $^{13}C\{^1H\}$ NMR (v.s.): δ 29.5 (s, Me), 44.3 (s, CH_2), 51.0 (s, C). ^{29}Si NMR (DEPT, v.s.): δ −97.5 (qdm, J(Si,H) = 181.4 and 44.7 Hz, SiH_3), −26.2 (dm, J(Si,H) = 213.6 Hz, SiH). ^{15}N NMR (DEPT, v.s.): δ −348.9 (s, J(SiN) = 19.0 Hz). Anal. Found: C, 52.21; H, 11.25; N, 12.06. Calcd for $C_{10}H_{26}N_2Si_2$ (M_r = 230.50): C, 52.11; H, 11.37; N, 12.15.

X-ray Crystallography. Suitable crystals of **3b** and **4b** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for both compounds. Diffraction intensities were corrected for Lp but not for absorption effects. The thermal motion of all non-hydrogen atoms was treated anisotropically. All phenyl, methyl, and methylene hydrogen atoms were found and refined isotropically (**4b**) or were placed in idealized calculated positions and allowed to ride on their corresponding carbon atom with $U_{iso(fix)} = 1.5U_{eq}(C)$ (**3b**). The Si−*H* atoms in both compounds were located and refined isotropically. One of the *tert*-butyl groups in **3b** was disordered and refined in split positions with site occupation factors of 60/40. Further information on crystal data, data collection, and structure solution and refinement is summarized in Table 1. Important interatomic distances and angles are summarized in the corresponding figure captions.

Table 1. Crystal Data and Data Collection and Structure Refinement details for **4b** and **3b**

	4b	**3b**
	Crystal Data	
formula	$C_{18}H_{28}N_2Si_3$	$C_8H_{28}N_2Si_4$
M_r	356.69	262.67
crystal system	monoclinic	triclinic
space group	$I2/a$	$P\bar{1}$
a (Å)	15.439(1)	7.210(1)
b (Å)	8.754(1)	10.219(1)
c (Å)	15.762(2)	11.945(1)
α (deg)	90	107.24(1)
β (deg)	107.17(1)	104.00(1)
γ (deg)	90	90.86(1)
V (Å^3)	2035.3(4)	812.0(2)
ρ_{calc} (g cm^{-3})	1.164	1.074
Z	4	2
F(000) (e)	768	288
μ(Mo Kα) (cm^{-1})	2.35	3.24
	Data Collection	
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73
T (°C)	−68	−68
scan mode	$\omega-\theta$	$\omega-\theta$
hkl ranges	$-18 \rightarrow +18, -10 \rightarrow 0, -19 \rightarrow +19$	$\pm 11, \pm 11, +15$
$((\sin\theta)/\lambda)_{max}$ (Å^{-1})	0.62	0.62
no. of measd reflns	3344	6528
no. of unique reflns	1954	3473
no. of obsd reflns	1952	3460
$I \geq$	$2\sigma_I$	$2\sigma_I$
abs cor	none	none
	Refinement	
no. of refined params	161	188
no. of H atoms (found/calcd)	28/0	8/18
R1[a]	0.0302	0.0397
wR2[b]	0.0865	0.1188
(shift/error)$_{max}$	<0.001	<0.001
ρ_{fin} (e Å^{-3}): max/min	+0.289/−0.419	+0.528/−0.425

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0539 (**4b**), 0.0852 (**3b**); b = 1.26 (**4b**), 0.30 (**3b**).

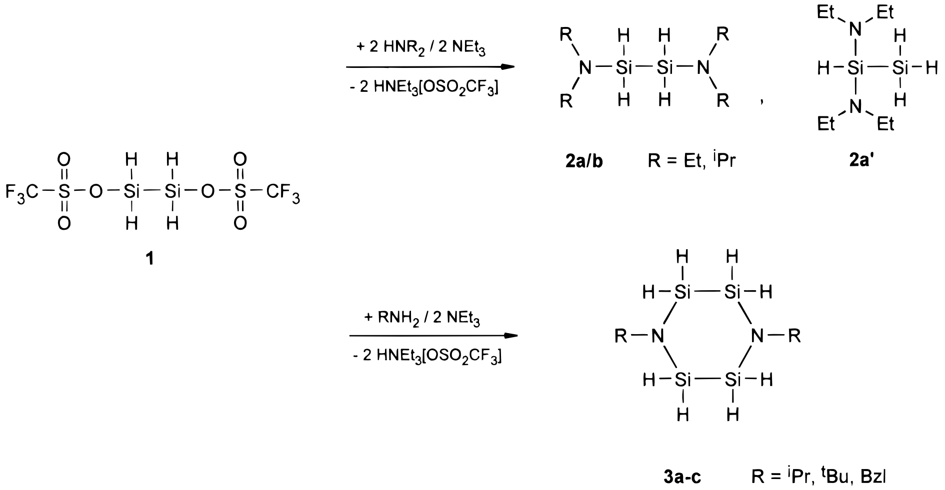
Results and Discussion

1,2-Diphenyl- and -di-*p*-tolyldisilane are readily available through Wurtz coupling of the corresponding arylchlorosilanes.[18,22] The partial or complete dearylation of these disilanes using stoichiometric quantities of trifluoromethanesulfonic ("triflic") acid is also an established regioselective, high-yield process, and on the basis of these two steps, the 1,2-bis(triflate) (**1**) is a convenient precursor for a variety of substituted disilanes.[18,19]

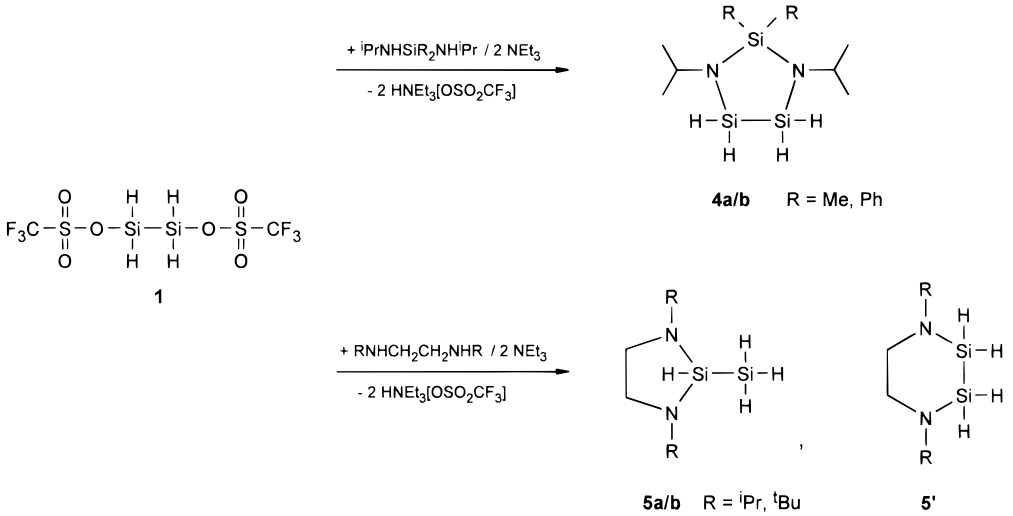
1,2- and 1,1-Bis(dialkylamino)disilanes. Treatment of compound **1** with 2 equiv of diethylamine in the presence of triethylamine (as an auxiliary base) gives a mixture of two products even under very mild conditions. The expected 1,2-diaminodisilane (**2a**) is always accompanied by small amounts of the 1,1-isomer (**2a′**), which is obviously generated in a Si → Si hydrogen shift reaction (Scheme 1).

By employment of a secondary amine with bulkier substituents, such as diisopropylamine, this rearrangement can be

Scheme 1



Scheme 2



suppressed completely, and only the 1,2-isomer (**2b**) is isolated in high yield. In the present context, the ethyl and isopropyl homologues were the preferred synthetic targets, because their disposition for β-elimination of olefines in thermal, photochemical, or high-energy decomposition processes (plasma, discharge) should secure a minimum carbon content in the thin-film products, as already proven for compound **2b**.[1] For the dimethylamino compounds, this was not to be expected.

Compounds **2** are colorless, volatile liquids, which do not inflame in air. They can be purified by distillation and identified by mass spectrometry and NMR spectroscopy (Experimental Section).

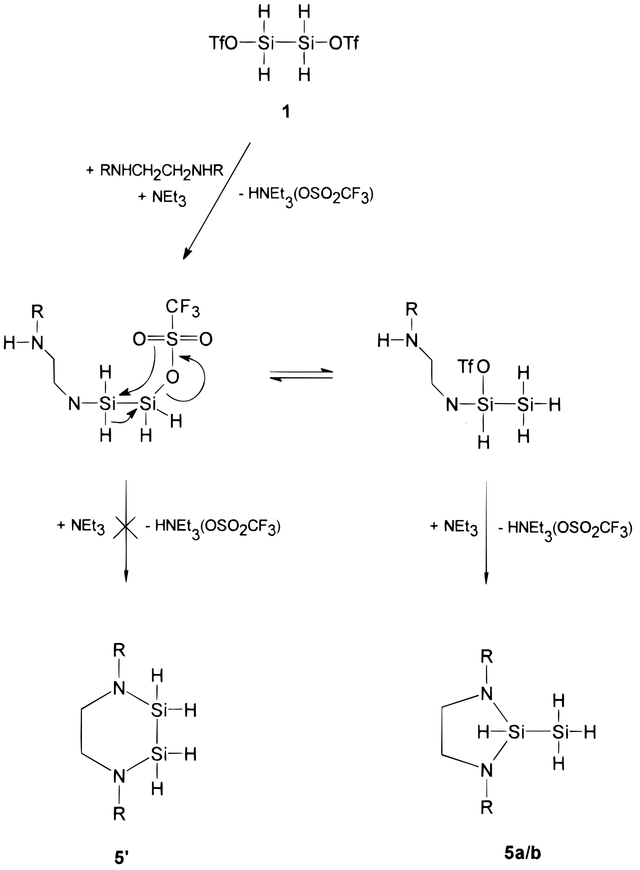
Cyclic 1,2-Diaminodisilanes. In an attempt to prepare cyclic analogues of the 1,2-diaminodisilanes, cyclization reactions of the 1,2-substituted disilane **1** with primary amines were carried out which were expected to give 2,3,5,6-tetrasilapiperazines through the condensation of 1,2-bis(alkylamino)disilane intermediates with a second equivalent of the 1,2-bis(triflate) **1** (Scheme 1). The six-membered heterocyclic compounds **3a**−**c** comprising two SiH_2-SiH_2 units could indeed be obtained in very high yields. Apparently, ring formation is kinetically preferred over the competitive polymerization reactions under the chosen reaction conditions. The benzyl homologue **3c** was expected to be a crystalline product amenable to structural investigations, but it solidified only as an amorphous glass. The *tert*-butyl derivative **3b** was then chosen for low-temperature crystallization experiments (see below).

At room temperature the tetrasilapiperazines **3a**−**c** are colorless liquids not spontaneously inflamable in air. Spectroscopic investigations of the heterocycles **3a**−**c** have unambiguously confirmed that two disilane units SiH_2-SiH_2 are incorporated unchanged into the cyclic systems (Experimental Section).

In an attempt to obtain related five-membered silacycles, two *1,3-difunctional* bis(isopropylamino)diorganosilanes were used for cyclization reactions with the 1,2-difunctional disilane **1** (Scheme 2). The reactions were found to proceed smoothly and give good yields of the expected heterocyclic species (**4a**,**b**). $Me_2Si(NH^iPr)_2$ was tested as the cyclization component because it is the smallest homologue available of the bis(isopropylamino)silane series, and $Ph_2Si(NH^iPr)_2$ was introduced since it was expected to give a crystalline product amenable to structural studies. The trisilaimidazolidine **4a** was obtained as a distillable liquid, and compound **4b** could indeed be crystallized and its structure determined (below). The spectroscopic investigation of both compounds provided evidence for the incorporation of the disilane unit SiH_2-SiH_2 into the cyclic system (Experimental Section).

Cyclic 1,1-Diaminodisilanes. Reactions of the 1,2-difunctional disilane **1** with *1,4-difunctional* diamines to give six-membered rings comprising the SiH_2-SiH_2 unit were carried out with *N*,*N*′-diisopropyl- and -di-*tert*-butylethylenediamine (Scheme 2). Surprisingly, both reactions led again to five-membered-ring compounds, however, with an exocyclic SiH_3 group attached to the silicon atom of the silaimidazolidine

Scheme 3



system. Hence this cyclization reaction involves a Si → Si hydride shift and affords a 1,1-diamination of the disilane. The composition and structure of compounds **5a**,**b** are easily confirmed by analytical and spectroscopic data.

In Scheme 3 a mechanism is proposed which is consistent with the observations of all experiments carried out with compound **1**. In the present case, it is to be assumed that compounds **5** are the kinetic products, which should differ very little in energy from the six-membered-ring isomers (**5′**). The preference for five-membered over six-membered rings with two silicon atoms will clearly also depend on substituent effects, and bulky groups like isopropyl and *tert*-butyl are likely to favor the smaller heterocycle.

Molecular Structures. The five-membered heterocycle **4b** crystallizes in the monoclinic space group *I*2/*a* with four formula units in the unit cell. The molecules have a crystallographically imposed 2-fold axis (point group C_2, Figure 1). The heterocycle is slightly twisted out of a complete planarity (Figure 2), with one of the silicon atoms above and one below the NSiN′ plane. The two nitrogen atoms are in a planar configuration with sums of angles at exactly 360°. The $H_2Si{-}SiH_2$ bond length of 2.326(1) Å is an important reference value for Si−Si bonds in five-membered rings, where these silicon atoms have no substituents other than hydrogen. The isopropyl and phenyl groups show no anomalies, and there are no unusual packing phenomena.

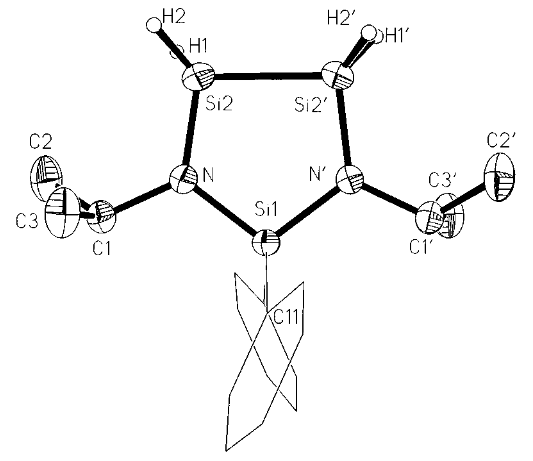


Figure 1. Molecular structure of compound **4b** with atomic numbering (ORTEP; 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Si2−Si2′ 2.326(1), Si2−N 1.720(1), Si1−N 1.729(1), N−C1 1.488(2), Si1−C11 1.873(1), Si2−H1 1.46(2), Si2−H2 1.36(2); Si2′−Si2−N 96.74(4), H1−Si2−H2 103.1(13), N−Si2−H1 114.3(9), N−Si2−H2 114.5(10), Si2′−Si2−H1 114.3(8), Si2′−Si2−H2 114.5(10), Si2−N−Si1 119.51(6), Si2−N−C1 122.95(9), Si1−N−C1 117.54(9), N−Si1−N′ 105.64(8), N−Si1−C11 109.70(5), N−Si1−C11′ 111.16(5).

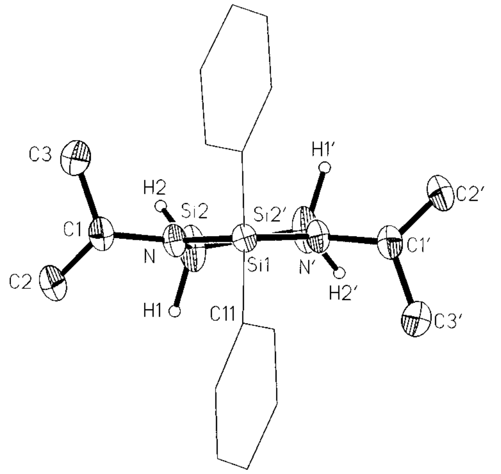


Figure 2. Molecular structure of compound **4b** showing the slightly twisted five-membered heterocycle.

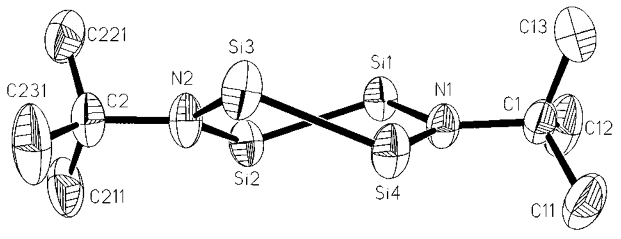


Figure 3. Molecular structure of compound **3b** with atomic numbering (ORTEP; 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Si1−N1 1.726(1), N1−Si4 1.734(1), Si4−Si3 2.334(1), Si3−N2 1.729(2), N2−Si2 1.724(2), Si2−Si1 2.337(1), N1−C1 1.502(2), N2−C2 1.503(2), Si1−H11 1.30(2), Si1−H12 1.45(3), Si2−H21 1.35(3), Si2−H22 1.39(3), Si3−H31 1.39(3), Si3−H32 1.32(4), Si4−H41 1.35(3), Si4−H42 1.33(3); Si1−N1−Si4 117.35(8), Si1−N1−C1 123.01(11), Si4−N1−C1 119.23(11), Si2−N2−Si3 116.69(8), Si2−N2−C2 120.88(12), Si3−N2−C2 122.36(12).

The six-membered heterocycle **3b** crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The molecules have no crystallographically imposed symmetry. The heterocycle has a twist configuration (approaching closely the symmetry requirements of point group C_{2v} if the *tert*-butyl substituents are neglected; Figure 3). The two nitrogen atoms are in a virtually planar configuration with sums of angles at 359.59° (for N1) and at 359.93° (for N2). The two independent $H_2Si{-}SiH_2$ distances are equal within the limit of standard deviations [2.337(1) and 2.334(1) Å for Si1−Si2 and Si3−Si4, respectively and only slightly longer than in the five-membered heterocycle **4b** (see above).

One of the two *tert*-butyl groups is disordered. The positions of its atoms in the two conformations could be accounted for

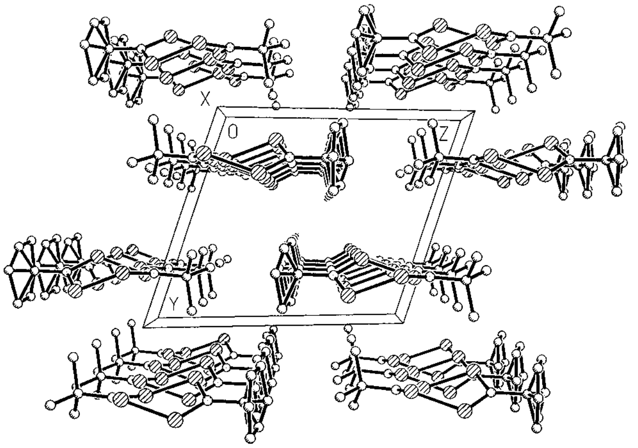


Figure 4. Packing of compound **3b** in the cell, showing the different environments of the *tert*-butyl groups. The rigid *tert*-butyl groups are surrounded by heterocycles, while the disordered groups are arranged in layers of *tert*-butyl groups.

by a split model. Only one of these is shown in Figure 3. The disorder probably results from the two different positions of the *tert*-butyl groups in the lattice. It is obvious from Figure 4 that the rigid *tert*-butyl groups are surrounded by heterocycles, while the disordered groups are arranged in layers of *tert*-butyl groups, which represent a more flexible environment. It is interesting to compare the structure of compound **3b** with the geometries of two isoelectronic *sulfur−nitrogen heterocycles*, where the SiH_2 groups are replaced by sulfur atoms.[23] These $S_4N_2R_2$ heterocycles have pronounced chair conformations with the substituents in axial positions at nonplanar nitrogen atoms (R = ethyl, benzyl). The S−S bonds (average 2.037 Å) are much shorter than the Si−Si bonds in the silicon analogues. It thus appears that shorter bonds (S versus Si) and lone pairs of electrons instead of hydrogen substituents (S versus SiH_2) give rise to pyramidalization at nitrogen and to much more pronounced folding of the heterocycles.

Conclusions

The results of the above experiments show that 1,2-disilanediyl bis(triflate) is a key intermediate for the preparation of small silicon−nitrogen heterocycles with fully hydrogenated silicon atoms. Five-membered and six-membered rings are the preferred ring sizes, and ring contraction with Si → Si hydrogen shifts may be encountered in the synthesis. The heterocycles show flat, flexible twist conformations with the nitrogen atoms in a planar configuration.

The molecules are stable, volatile, nonspontaneously inflammable liquids which are promising single-source precursors for surface-coating and thin-film technology. Their low carbon content and the absence of direct Si−C bonding in the precursors should allow deposition of largely carbon-free silicon nitride under particularly mild conditions, as already demonstrated for the less volatile open-chain analogues like $(^iPr)_2N-SiH_2SiH_2-N(^iPr)_2$ in some of our earlier studies.[1]

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Supporting Information Available: Tables of crystal data, structure refinement details, all atomic fractional coordinates, thermal parameters, and interatomic distances and angles and a fully labeled ORTEP diagram for **4b** (6 pages). Ordering information is given on any current masthead page.

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