Heteroatom Chemistry
Volume 10, Number 7, 1999

Synthesis of Aminotri- and Aminotetrasilanes by Cross-Coupling of Aminochlorosilanes with Chlorotrimethylsilane

Joachim Heinicke,[1] Steffen Mantey,[1] Anca Oprea,[1]
Markus K. Kindermann,[1] and Peter G. Jones[2]

[1]*Institut für Chemie und Biochemie, Ernst-Moritz-Arndt-Universität Greifswald, Soldmannstr. 16, D-17487 Greifswald, Germany.*

[2]*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig*[c] Postfach 3329, D-38023 Braunschweig, Germany.

Received 15 June 1999

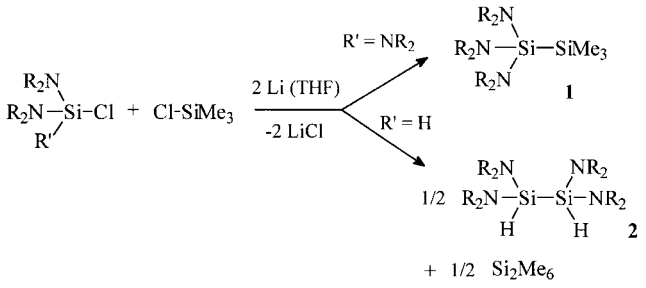
ABSTRACT: *We studied the reductive coupling of aminochlorosilanes and chlorotrimethylsilane by lithium in tetrahydrofuran. Cross-coupling was observed in the case of diaminodichlorosilanes* **7** *or aminotrichlorosilanes* **8** *and allows a direct access to 2,2-diamino-hexamethyltrisilanes* **9** *and amino(tristrimethylsilyl)silanes* **10**. *$Me_2Si(iPr_2N)Cl$* **3** *reacts instead preferentially to the symmetric diaminodisilane* **6**. *Bulkier diamino(chloro)methylsilanes* **5** *did not undergo the coupling reaction. The cross-coupled aminodi-, -tri- and tetrasilanes are useful starting compounds for other functionally substituted oligosilanes, as was shown by reaction of* **9** *with HX (X = Cl, Br, I) to* **11** *and the synthesis of the heterocyclic trisilanes* **9d** *and* **9f** *using* **11a**. *The molecular structure of $[(iPr_2N)_2SiH]_2$* **2a** *is discussed. NMR data including $^1J_{SiSi}$ coupling constants are given.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 605–614, 1999

Correspondence to: Joachim Heinicke. Fax: (internat) +49-3834-864319; E-mail: heinicke@mail.uni-greifswald.de.
Contract Grant Sponsor: Deutsche Forschungsgemeinschaft.
Grant Sponsor: Fond der Chemischen Industrie.
Dedicated to Prof. Dr. Alfred Schmidpeter on the occasion of his 70th birthday.
 CCC 1042-7163/99/070605-10

INTRODUCTION

Functionally substituted di- and oligosilanes are valuable building blocks for the synthesis of heterocycles or acyclic compounds containing Si-Si bonds, and also for the preparation of new silicon polymers or materials. They have usually been prepared by reductive coupling of suitable chlorosilanes containing phenyl or other aryl groups with lithium in tetrahydrofuran (THF) or with sodium in toluene [1] and subsequent cleavage of some or all of the aromatic substituents with gaseous $HCl/AlCl_3$ [2–4], or much more easily by triflic acid [5,6]. A convenient new method is the direct reductive coupling of chlorosilanes containing diethylamino groups, which can be replaced in the resulting Si-Si- compounds under very mild conditions by various HX reagents such as hydrogen halides or ROH [7–11]. The formation of aminosubstituted phenylsilyllithium species from the respective chlorosilanes and lithium in THF and their subsequent coupling with chlorosilanes was first reported by Tamao et al. [7] in 1992. The reductive coupling of amino(chloro)methylsilanes to symmetrical disilanes without detection of silyllithium intermediates followed in 1993 [8]. Unno et al. showed that this procedure can also be applied to the synthesis of bulkier 1,2-diorganotetrakis(diethylamino)disilanes [9]. The first exam-

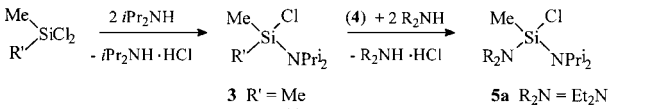
ples of reductive cross-couplings of methyl(diethylamino)chlorosilanes and of aminochlorosilanes with methylchlorosilanes by lithium in THF were recently described by Tamao et al. [10] and by Mantey and Helnicke [11], respectively. We observed that chlorotris(diorganoamino)silanes and $ClSiMe_3$ react with lithium to give cross-coupling products **1**, whereas the less bulky SiH-functional chlorotris(diorganoamino)silanes and $ClSiMe_3$ were reduced to give symmetrical disilanes **2** and Si_2Me_6 (Equation 1). The aim of this study is to extend the scope of cross-couplings of aminochlorosilanes and $ClSiMe_3$ with lithium and to explore limits of this reaction. Finally, we present examples of the application of aminotrisilanes for the access to other trisilanes.



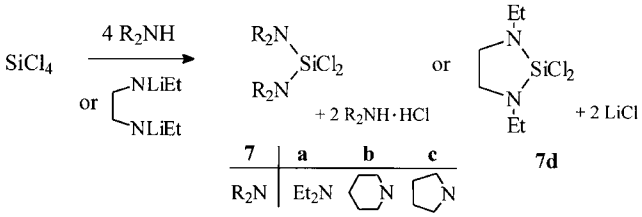
RESULTS AND DISCUSSION

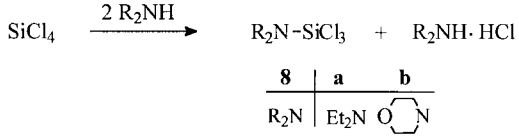
Syntheses

$Me_2Si(NEt_2)Cl$ and $MeSi(NEt_2)_2Cl$ react with lithium to give only the symmetrical disilanes [8], whereas bulkier aminochlorodisilanes $RMe(Et_2N)Si-SiMe(NEt_2)Cl$ (R = Me, NEt_2) undergo cross-coupling with $ClSiMe_3$ or $Me_2Si(NEt_2)Cl$ by action of lithium [10]. Therefore it seemed reasonable to attempt reductive cross-coupling of methyl and dimethyl(amino)chlorosilanes with $ClSiMe_3$ by use of more bulky diorganylamino derivatives. Diisopropylamino- and mixed diamino(chloro)methylsilanes **3–5** were prepared according to Equation 2. The introduction of the second amino group into **4** succeeded under forcing conditions.

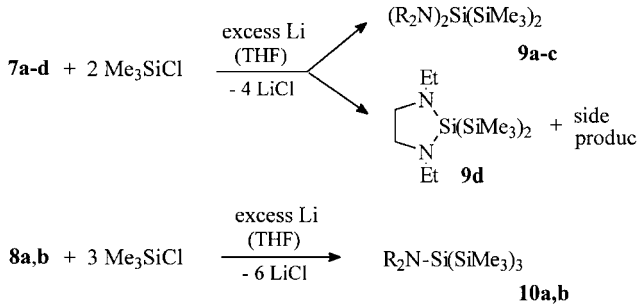


Attempts to cross-couple the sterically less demanding **3** with excess chlorotrimethylsilane by lithium in THF furnished instead the symmetric disilane $[Me_2Si(NiPr_2)]_2$ **6**, similarly to yielding **2** from $(R_2N)_2SiHCl$ (Equation 1), whereas the bulkier bis(diisopropylamino)derivatives **5** failed to give disilanes in analogous treatment. The low reactivity of the monochlorosilanes, enforced by the steric congestion of the diisopropylamino beside another amino group, seems to hinder both unsymmetrical and symmetrical couplings. Therefore, the investigation was redirected to more reactive diaminodichlorosilanes **7a–d** and aminotrichlorosilanes **8a,b**, which were obtained according to Equation 3 from silicon tetrachloride and the respective amines or amides.

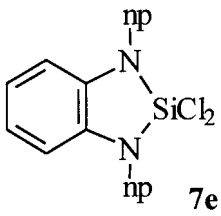




The reaction of mixtures of **7a–c** and chlorotrimethylsilane with lithium in THF proceeded slowly but furnished the 2,2-diamino-hexamethyltrisilanes **9a–c** in moderate yields (Equation 4). To achieve complete conversion of **7a–c**, a large excess of chlorotrimethylsilane was used, and the excess was added in portions over several days. This was necessary because unreacted **7a–c** and partly converted compounds $R_2NSi(Cl)SiMe_3$ cannot easily be separated from the corresponding products. For **9a**, which was synthesized repeatedly, we observed increasing reaction times and decreasing yields with increasing scale of the preparation. The higher yield (70%) in a small scale procedure [10] is in accordance with this observation. Attempts to accelerate the reaction by use of 4,4′-di(*tert*-butyl)diphenyl as an electron-transfer catalyst were not successful; many side products were formed. Similarly, refluxing the mixture produced low yields and large amounts of impurities. The reaction of the aminotrichlorosilanes **8a** or **8b**, excess chlorotrimethylsilane, and lithium in THF was faster and opened a direct access to aminotris(trimethylsilyl)silanes **10a** or **10b**. Especially in the case of the morpholino compounds, the coupling was accompanied by formation of small amounts of dismutation products, $(R_2N)_2Si(SiMe_3)_2$ **9** and $Si(SiMe_3)_4$, which cannot be separated from **10** by sublimation. Because repeated sublimation did not change the molar ratio of products and side products, the dismutation must occur at the chlorosilane stage.



Reaction of the cyclic diaminodichlorosilane **7d** and excess chlorotrimethylsilane with lithium in THF afforded a mixture of the expected **9d** and another *N,N′*-diethylethylenediamine derivative but no unreacted **7d**, thus indicating partial attack at the Si-N bonds of the ring during reduction. The cyclic diaminodichlorosilane **7e** (structure 1) and chlorotrimethylsilane reacted with lithium but failed to give the respective cyclic diaminotrisilane.



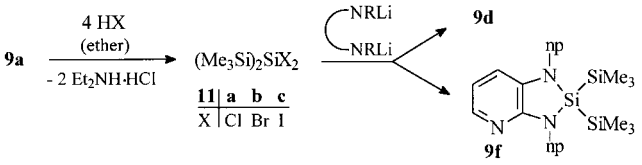
7e

The cleavage of arylamino-Si bonds by this metal seems to be easier than that of dialkylamino-Si bonds, although the complete reduction without Si-N bond rupture would give a much more stable, cyclodelocalized diaminosilylene. The latter was formed by reduction with potassium [12]. The unfavorable results in the silyl coupling of the cyclic diaminodichlorosilanes may be associated with the smaller N-Si-N angles within the five-membered rings.

The aminooligosilanes **9a–c** and **10a,b** are stable compounds with relatively high boiling or sublimation points. In the EI mass spectra (70 eV), they usually exhibit molar mass peaks with small or moderate intensity. Abundant peaks derive from silyl cations $Si(NR_2)_n(SiMe_3)^+_{3-n}$ (n = 1, 2), which form by loss of Me_3Si radicals or from radical cations $SiH(NR_2)_n(SiMe_3)^+_{3-n}$ (n = 1, 2), which result from cleavage of Me_2SiCH_2. Further fragmentation to $R_2NSiHSiMe_3^+$ (**9a–c**) or $SiH(SiMe_3)_2^+$ (**10b**) by loss of R_2N also gives rise to abundant peaks. The intensity of diaminosilylene cations in the fragmentation pattern of $\mathbf{9}^+$ is relatively low except in the case of $\mathbf{9a}^+$, in which it forms the base peak. A special feature of the decay of $\mathbf{10b}^+$ is the very abundant cation at m/z = 233 (99.9%), which may be caused by loss of C_2H_4 from morphSiH$(SiMe_3)_2^+$ (m/z = 261 (100%) and formation of a relatively stable 2,2-bis(trimethylsilyl)-1,3,2-oxazasilolidine cation.

Some Applications

As mentioned above, the aminooligosilanes are useful building blocks for the synthesis of other functional oligosilanes. They can easily be converted into the halogen derivatives **11**, earlier obtained by chlorination [13] or by cleavage of phenyl groups with HX/AlX_3 [14–16], or into alkoxy derivatives. Thus, **9a** or **9b** reacted with excess HCl in ether at low temperature (0–5°C) to form the respective 2,2-dichloro-1,1,1,3,3,3-hexamethyltrisilane **11a** with good yield. Uncontrolled, insufficient direct introduction of gaseous HCl may partly produce the monosubstitution product $Et_2N(Cl)Si(SiMe_3)_2$ **12a** observed in NMR spectra. During rectification of such a mixture, **12a** underwent partial dismutation to **11a** and the starting material **9a** as shown spectroscopically. The analogous 2,2-dibromo- and the extremely sensitive solid 2,2-diiodo-trisilanes **11b** and **11c** were prepared by introducing the gaseous hydrogen halides into the ethereal solution of **9a**. The reactive dihalotrisilanes **11** can be used, for example, in the synthesis of heterocycles. Although dilithiated *N,N′*-dineopentyl-*o*-phenylendiamine, -2,3-diaminonaphthalene, or -3,4-diaminopyridine failed to give cyclosubstitutions with **11a**, the ring closure succeeded with *N,N′*-dineopentyl-pyridine-2,3-diamide and furnished the dihydro-1,3,2-diazasilolo[4,5-b]pyridine **9f** in 47% yield (Equation 5). The saturated five-membered diaminotrisilane **9d** could also be prepared in this way.



Because trisilanes were found to form silylenes on irradiation by UV (254 nm) in matrix [17], **9d** and **9f** may be regarded as potential precursors for cyclic diaminosilylenes. The product expected from **9f** was obtained from the corresponding dichloride by reduction with potassium [18] and may serve as a reference.

Structural Aspects

The reductive coupling depends on electronic and steric factors. The rate of the reaction, as seen qualitatively from the very different times necessary for conversion of the starting materials, increases from

mono-, to di-, to trichloroaminosilanes. Bulky chlorotriaminosilanes or chlorobis(diisopropylamino)silanes have a lower tendency to undergo coupling reactions. If they react, they prefer cross-couplings, in contrast to less strained SiH- or methyl-substituted chlorodiaminosilanes, which yield symmetrical tetra(amino)disilanes **2** or **6**, respectively, also in the case of diisopropyl groups. From **2a** ($R_2N = iPr_2N$) [11], we have isolated crystals, which allow a closer structural characterization (Figure 1, Table 2). The Si-Si bond distance is somewhat longer than in Si_2Me_6 [2.34(10) Å], $Me_3SiSiPh_3$ [2.355(1) Å] [19,20], or $Si_2(NMe_2)_6$ [2.369(1) Å] [21], comparable to that in the tetrakis(diethylamino)disilane 1,2-$Ph_2Si_2(NEt_2)_4$ [2.391(6) Å] [22], but shorter than in bulkier tetrakis(diethylamino)disilanes 1,2-$tBu_2Si_2(NEt_2)_4$ (2.4769(9) Å) and 1,2-$tHex_2Si_2(NEt_2)_4$ [2.4769(9) Å] [9], in Si_2Ph_6 [2.519(4) Å] and in Si_2tBu_6 (2.697 Å) [19,20]. The Si-N bond lengths are slightly longer than in usual aminosilanes (1.715 Å) [23] and in $Si_2(NMe_2)_6$ [1.716(2) Å] but shorter than in $tBu_2Si_2(NEt_2)_4$ [1.743(1)–1.748(1) Å] and 1,2-$tHex_2Si_2(NEt_2)_4$ [1.747(4)–1.751(4) Å]. The N-Si-N bond angles are markedly larger than tetrahedral, whereas those in bulky organo-substituted tetraaminodisilanes $tBu_2Si_2(NEt_2)_4$ [105.25(6)°] and 1,2-$tHex_2Si_2(NEt_2)_4$ [105.3(2)–106.1(2)°] are smaller. Another particular feature, which is related to the large differences in size between the hydrogen and the isopropyl substituents in **2a**, is the very large difference of the Si-Si-N angles at Si(2) (21.3°), which was observed in neither of the other aminodisilanes. In $tBu_2Si_2(NEt_2)_4$ and 1,2-$tHex_2Si_2(NEt_2)_4$, the differences were ca. 7°; in $Ph_2Si_2(NEt_2)_4$, they were below 1.5°. The asymmetry of the molecule serves to moderate the steric congestion exerted by the diisopropylamino groups. The latter are arranged *gauche* to each other [dihedral angles N1-Si1-Si2-N3, 137.9(1); N2-Si1-Si2-N4, 43.7(1)] forcing the hydrogen atoms to positions nearly *trans* to each other [H-Si1-Si2-H 83.6(15)]. As typical for aminosilanes [20], the geometry around all nitrogen atoms is nearly planar (mean deviation from best planes: C4-N1-C1-Si1, 0.03 Å; C10-N2-C7-Si1 $<$ 0.01 Å; C19-N3-C13-Si2, 0.02 Å; C22-N4-C16-Si2, 0.02 Å).

^{29}Si NMR Spectra

The successive substitution of amino groups of **9a** by chlorine causes downfield shifts for both silicon atoms, Si^A and Si^B. The one-bond couplings $^1J_{SiSi}$ and

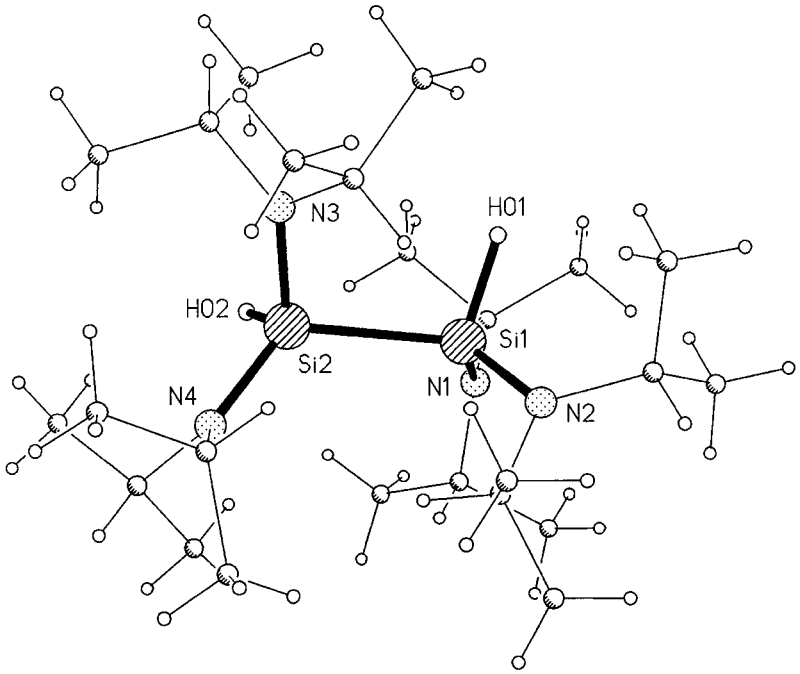


FIGURE 1 Selected bond lengths (Å) and angles (°) of **2a:** Si1-Si2 2.3899(10), Si1-N1 1.726(2), Si1-N2 and Si2-N4 1.732(2), Si2-N3 1.730(2), N-C 1.464(4)-1.487(4); N1-Si1-N2 116.20(11), N3-Si2-N4 114.67(11), N1-Si1-Si2 110.79(8), N2-Si1-Si2 114.77(8), N3-Si2-Si1 102.58(8), N4-Si2-Si1 123.96(8), C1-N1-Si1 124.30(18), C4-N1-Si1 120.38(18), C7-N2-Si1 123.11(19), C10-N2-Si1 120.35(17), C13-N3-Si2 123.34(18), C19-N3-Si2 120.49(18), C16-N4-Si2 125.2(2), C22-N4-Si2 120.22(19), C-N-C 114.3(2)-116.5(2).

$^1J_{SiC}$ reveal different trends; the former decrease, and the latter increase, as summarized in Table 1. Further interesting trends are seen by comparison of the three dihalogenotrisilanes **11a–c**. As shown for various substituted silanes, the ^{29}Si resonances present a parabolic dependence on the sum of the electronegativity (Σ_χ) of the substituents [24]. Below Σ_χ = 10.7, the chemical shifts $\delta(^{29}Si)$ increase with Σ_χ; above this value they decrease with increasing Σ_χ [25]. For **11a–c**, the sum is below the critical value, thus $\delta(^{29}Si)$ of Si^A increases with the electronegativity of the halogen. For Si^B, which is not directly connected with the halogen atoms, there is seemingly no effect. The one-bond coupling constants $^1J_{SiSi}$ and, to a limited degree, $^1J_{Si(A)C}$, reveal a linear correlation with the electronegativities of the halogens (Figure 2) as is also observed for disilanes [26]. The increase of $^1J_{SiSi}$ with Σ_χ may be attributed to a growing s-character of the Si-Si bond [27]. According to Bent's rule, the s-character is enhanced in the bond between the most electronegative atoms by the most electron-withdrawing substituents [28].

TABLE 1 ^{29}Si Chemical Shifts and Coupling Constants of Selected Trisilanes $R^1R^2Si_A(Si_BMe_3)_2$

Compd.	δ Si_A	δ Si_B	$^1J_{SiSi}$[Hz]	$^1J_{SiC}$[Hz]
9a	−3.2	−22.8	92.0	42.7
9b	−4.5	−22.0	90.3	42.5
9c	−16.2	−21.6	91.5	42.8
9d	5.4	−21.9	n.m.	n.m.
9f	23.6	−20.8	74	43.7
10a	−28.8	−16.5	65.8	43.0
10b	−27.5	−15.6	64.8	43.7
11a	34.4	−11.3	75.9	47.7
11b	22.6	−10.2	69.4	48.1
11c	−28.5	−10.7	62.4	48.5
12a	10.8	−17.0	89.0	46.3
$Si(SiMe_3)_4$ (cf.[30])	−135.4	−9.9	52.6	44.5

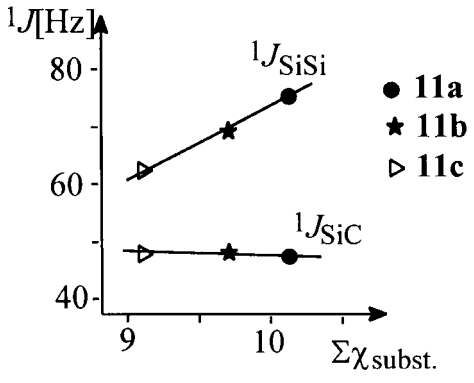


FIGURE 2 Correlation of $^1J_{SiSi}$ and $^1J_{SiC}$ with the sum of electronegativities of substituents at Si^A. According to the Pauling scale $\Sigma_{\chi subst.}$ for **11a–c** is 10.12, 9.72, and 9.12, respectively.

EXPERIMENTAL

Materials and Spectroscopy

All reactions were performed in carefully heat- and vacuum-dried Schlenk glassware using freshly distilled ketyl-dried solvents and, except for the preparation of aminochlorosilanes, a high-purity argon atmosphere. Amines were dried over KOH and distilled, and commercial chlorosilanes were recondensed in vacuo before use. Lithium was suspended in hot paraffin, washed with dry heptane and pentane, and stored under argon. The NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 59.6 MHz (^{29}Si). Unless noted otherwise, $CDCl_3$ was used as a solvent and as a reference for ^{1}H and ^{13}C NMR (δ = 7.27 and 77.0, respectively). ^{29}Si NMR data are referred to external tetramethylsilane (15% vol in

TABLE 2 Crystal Data and Structure Refinement

Empirical Formula	$C_{24}H_{58}N_4Si_2$
Formula Weight	458.92
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	$P2_1/n$
Unit Cell Dimensions	a = 11.331(2) Å α = 90° b = 16.240(3) Å β = 102.06(2)° c = 17.022(3) Å γ = 90°
Volume	3063.1(9) Å^3
Z	4
Density (calculated)	0.995 Mg/m^3
Absorption Coefficient	0.132 mm^{-1}
F(000)	1032
Crystal Size	0.60 × 0.40 × 0.25 mm^3
Theta Range for Data Collection	3.01–25°
Index Ranges	$-13 \le h \le 13$, $-19 \le k \le 7$, $-20 \le l \le 0$
Reflections Collected	8082
Independent Reflections	5388 [R(int) = 0.0215]
Completeness to Theta = 25.00°	99.8%
Absorption Correction	None
Refinement Method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	5388/1/295
Goodness-of-Fit on F^2	1.048
Final R Indices [I > 2sigma(I)]	R1 = 0.0577, wR2 = 0.1539
R Indices (all data)	R1 = 0.0816, wR2 = 0.1647
Largest Diff. Peak and Hole	1.401 and −0.277 e.Å^{-3}

$CDCl_3$). Chromium acetylacetonate was added in measurements of ^{29}Si-^{29}Si and ^{29}Si-^{13}C coupling constants via the satellites (sat.). Mass spectra were registered using a single-focusing sector-field mass spectrometer AMD40 (Intectra). CHN analyses were determined in the microanalytical laboratory of the institute on an analyzer CHNS-932 (LECO). Hydrolyzable halogen was titrated potentiometrically with n/10 $AgNO_3$. Melting points were measured under argon in glass capillaries and are uncorrected. The synthesis of *N,N′*-dineopentyl-2,3-diaminopyridine was recently described [18]. Procedures for the preparation of the known compounds **7a, 8a** [29], and **9a** [10] were modified. ^1H, ^{13}C, and ^{29}Si NMR data are given.

Aminochlorosilanes

Chloro(*diisopropylamino*)*dimethylsilane* (**3**). A solution of diisopropylamine (78.4 g, 0.78 mol) in ether (200 mL) was added dropwise with stirring to a solution of dichlorodimethylsilane (50.0 g, 0.39 mol) in ether (300 mL) and allowed to stir overnight at room temperature. The precipitate was removed by filtration and washed three times with ether (each 400 mL). After evaporation of ether, the residue was distilled affording 50.4 g (67%) of colorless liquid **3**, b.p. 78°C/18 Torr. ^1H NMR: δ = 0.54 (s, 6H, $SiCH_3$), 1.15 (d, J = 6.8 Hz, 12H, CH_3), 3.36 (hept, J = 6.8 Hz, 2H, NCH). ^{13}C NMR: δ = 4.9 ($SiCH_3$), 23.8 (CH_3), 45.5 (NCH). ^{29}Si NMR: δ = 9.3. Anal. calcd. for $C_8H_{20}ClNSi$ (193.79): Cl, 18.29. Found: Cl, 18.25.

Dichloro(*diisopropylamino*)*methylsilane* (**4**). Diisopropylamine (67.7 g, 0.67 mol), dissolved in toluene (300 mL), was added dropwise with stirring to a solution of methyltrichlorosilane (50.0 g, 0.33 mol) in toluene (300 mL). The mixture was refluxed for 3 hours, the hydrochloride was removed by filtration and washed with toluene. Fractional distillation gave 43.9 g (61%) of colorless liquid **4** with b.p. 56°C/50 Torr. ^1H NMR: δ = 0.90 (s, 3H, $SiCH_3$), 1.20 (d, J = 6.8 Hz, 12H, CH_3), 3.50 (hept, J = 6.8 Hz, 2H, NCH). ^{13}C NMR: δ = 7.94 ($SiCH_3$), 23.5 (CH_3), 45.6 (NCH). ^{29}Si NMR: δ = −4.1. GC–MS (EI 70eV): *m/z* (%) = 213 [M^+], 198 [M-CH_3^+], 178 [M-Cl^+], 156 [M-$NC_3H_7^+$], 100 [$N(C_3H_7)_2^+$]. Anal. calcd. for $C_7H_{17}Cl_2NSi$ (214.21): Cl, 33.10. Found: Cl, 32.30.

Chloro(*diethylamino*)(*diisopropylamino*)*methylsilane* (**5a**). Diethylamine (26.4 g, 0.36 mol) was dissolved in toluene (300 mL) and added to a solution of **4** (38.5 g, 0.18 mol) in toluene (300 mL). Because no reaction occurred at room temperature, the mixture was refluxed for 4 hours. On cooling, the precipitate was removed and carefully washed with toluene (3 × 200 mL). The solvent of the filtrate was stripped off in vacuo, and the residue was distilled to give 32.4 g (72%) liquid **5a** with b.p. 60°C/0.3 Torr. ^1H NMR: δ = 0.49 (s, 3H, $SiCH_3$), 1.05 (t, J = 7.1 Hz, 6H, CH_3), 1.39 (d, J = 6.8 Hz, 12H, $CHMe_2$), 2.94 and 2.944 (2 q, J = 7.1 Hz, 4H, NCH_2), 3.40 (hept, J = 6.8 Hz, 2H, NCH). ^{13}C NMR: δ = 7.9 ($SiCH_3$), 14.9 (CH_3), 23.7 and 23.8 (CMe_2), 38.9 (NCH_2), 44.7 (NCH). ^{29}Si NMR: δ = −12.3. GC–MS (EI 70eV): *m/z* (%) = 250 [M^+], 235 [M-CH_3^+], 207 [M-$C_3H_7^+$]; 150 [M-$N(C_3H_7)_2^+$]; 100 [$N(C_3H_7)_2^+$]. Anal. calcd. for $C_{11}H_{27}ClN_2Si$ (250.89): C, 52.66; H, 10.85; Cl, 14.13. Found: C, 52.15; H, 10.94; Cl, 13.98.

Chloro(*diisopropylamino*)(*piperidino*)*methylsilane* (**5b**). Analogously to the preparation of **5a**, piperidine (33.0 g, 0.39 mol) and **4** (41.3 g, 0.19 mol) in toluene (each 300 mL) were converted to 32.4 g (64%) of **5b**, b.p. 77–78°C/0.3 Torr. ^1H NMR: δ = 0.47 (s, 3H, $SiCH_3$), 1.14 (d, J = 6.8 Hz, 12H, CH_3), 1.41–1.47 (m, 4H, β-CH_2), 1.55–1.61 (m, 2H, γ-CH_2), 2.88–2.98 (m, 4H, α-CH_2), 3.35 (hept, J = 6.8 Hz, 2H, NCH). ^{13}C NMR: δ = 3.64 ($SiCH_3$), 23.7 and 23.8 ($CHMe_2$), 25.4 (γ-CH_2), 27.3 (β-CH_2), 44.7 (NCH), 45.9 (α-CH_2). ^{29}Si NMR: δ = −13.7. GC–MS (EI 70eV): *m/z* (%) = 262 [M^+], 247 [M-CH_3^+], 219 [M-$C_3H_7^+$], 162 [M-$N(C_3H_7)_2^+$]. Anal. calcd. for $C_{12}H_{27}N_2SiCl$ (262.90): Cl, 13.48. Found: Cl, 13.05.

Dichlorobis(*diethylamino*)*silane* (**7a**). A solution of diethylamine (209 mL, 2.02 mol) in ether (150 mL) was added dropwise with stirring to an ethereal (500 mL) solution of $SiCl_4$ (57.4 mL, 0.45 mol). The mixture was allowed to stir overnight at room temperature. The precipitate was removed by filtration and washed with ether. After evaporation of ether, the residue was distilled to give 84.1 g (76%) of colorless liquid **7a**, b.p. 71°C/3 Torr. ^1H NMR: δ = 1.08 (t, J = 7.1 Hz, 12H, CH_3), 3.01 (q, J = 7.1 Hz, 8H, CH_2). ^{13}C NMR: δ = 14.5 (CH_3), 39.2 (CH_2). ^{29}Si NMR: δ = −31.1. Anal. calcd. for $C_8H_{20}Cl_2N_2Si$ (243.25): C, 39.50; H, 8.29; N, 11.52; Cl, 29.15. Found: C, 40.60; H, 9.08; N, 11.33; Cl, 29.32.

Dichlorobis(*piperidino*)*silane* (**7b**). Reaction of $SiCl_4$ (61.0 g, 0.36 mol) with piperidine (122.2 g, 1.44 mol) in ether and work-up analogously to the above procedure furnished 40.6 g (42%) of **7b** with b.p. 73°C/0.01 Torr. ^1H NMR: δ = 1.44–1.52 (m, 8H, β-CH_2), 1.57–1.63 (m, 4H, γ-CH_2), 3.03 ("t", J = 5.3 Hz, 8H, α-CH_2). ^{13}C NMR: δ = 25.0 (γ-CH_2), 26.8 (β-CH_2), 45.7 (α-CH_2). ^{29}Si NMR: δ = −34.2. Anal. calcd. for $C_{10}H_{20}Cl_2N_2Si$ (267.27): Cl, 26.53. Found: Cl, 25.85.

Dichlorobis(pyrrolidino)silane (**7c**). Reaction of $SiCl_4$ (32.7 g, 0.19 mol) with pyrrolidine (57.0 g, 0.80 mol) in ether and work-up as described for **7a** afforded 24.7 g (54%) of **7c** with b.p. 70°C/0.01 Torr. ^{1}H NMR: δ = 1.74–1.85 (m, 8H, β-CH_2), 3.13 ("t", J = 5.3 Hz, 8H, α-CH_2). ^{13}C NMR: δ = 26.6 (β-CH_2), 46.4 (α-CH_2). ^{29}Si NMR: δ = −34.2. MS (EI 70eV): m/z (%) = 238 (4) [M^+], 168 (17) [M-$NC_4H_8^+$], 70 (99) [$NC_4H_8^+$], 43(100). Anal. calcd. for $C_8H_{16}Cl_2N_2Si$ (239.22): Cl, 29.64. Found: Cl, 29.00.

2,2-Dichloro-1,3-diethyl-1,3,2-diazasilolidine (**7d**). 4.1 g (35 mmol) of *N,N′*-diethyl-ethylenediamine, dissolved in ether (100 mL), was dilithiated at −60°C with *n*-BuLi (44 mL 1.6N in hexane, 70 mmol). The yellow solution was allowed to warm to room temperature, which yielded some colorless amide precipitate. Subsequently, $SiCl_4$ (6.0 g, 35 mmol) was added at −40°C, and the resulting mixture was stirred overnight at room temperature. After removal of the precipitation and of the solvent, 3.8 g (50%) of a colorless liquid was distilled at 52°C/2 Torr. ^{1}H NMR: δ = 1.19 (t, J = 7.2 Hz, 6H, CH_3), 2.94 (q, J = 7.2 Hz, 4H, NCH_2), 3.11 (s, 4H, 4-H, 5-H). ^{13}C NMR: δ = 14.5 (CH_3), 40.8 (NCH_2), 46.4 (4-CH_2, 5-CH_2). ^{29}Si NMR: δ = −28.9. Anal. calcd. for $C_6H_{14}Cl_2N_2Si$ (213.18): Cl, 33.26. Found: Cl, 33.63.

Trichloro(diethylamino)silane (**8a**). Two equivalents of diethylamine (51.7 g, 0.71 mol) were added dropwise to a solution of $SiCl_4$ (60.0 g, 0.35 mol) in ether (200 mL). Stirring was continued overnight. The mixture was then filtered, the precipitate was washed with ether, and the solvent was removed from the filtrate. Distillation gave 47.5 g (65%) of colorless liquid **8a**, b.p. 35–38°C/10 Torr. ^{1}H NMR: δ = 1.14 (t, J = 7 Hz, 6H, CH_3), 3.12 (q, J = 7 Hz, 4H, CH_2). ^{13}C NMR: δ = 14.7 (CH_3), 40.0 (CH_2). ^{29}Si NMR: δ = −27.7. Anal. calcd. for $C_4H_{10}Cl_3NSi$ (206.57): Cl, 51.49. Found: Cl, 49.93.

Trichloro(morpholino)silane (**8b**). Two equivalents of morpholine (29.4 g, 0.337 mol) were reacted dropwise with $SiCl_4$ (30.0 g, 0.177 mol) in ethereal solution. Work-up as mentioned previously furnished 15.5 g (42%) colorless liquid **8b**, b.p. 46–49°C/1 Torr. ^{1}H NMR: δ = 3.19 (t, J = 4.7 Hz, 4H, NCH_2), 3.66 (t, J = 4.7 Hz, 4H, OCH_2). ^{13}C NMR: δ = 44.6 (NCH_2), 67.1 (OCH_2). $_{29}$Si NMR: δ = −28.4. Anal. calcd. for $C_4H_8Cl_3NOSi$ (220.56): Cl, 48.24. Found: Cl, 49.51.

Si-Si Coupling Reactions

1,2-Bis(diisopropylamino)-1,1,2,2-tetramethyldisilane (**6**). Compound **3** (40.9 g, 0.211 mol) and chlorotrimethylsilane (26.0 mL, 0.205 mol) were added to a suspension of lithium (4.0 g, 0.576 mol) in THF (300 mL). After stirring for three weeks at room temperature, THF and unreacted $ClSiMe_3$ were evaporated in vacuo, hexane (100 mL) was added, and insoluble solids were filtered off. The solvent of the filtrate was evaporated, and the residue was distilled in vacuo yielding 7.8 g (24%) of colorless liquid **6** with b.p. 130–135°C/0.5 Torr. ^{1}H NMR: δ = 0.23 (s, 12H, $SiCH_3$), 1.08 (d, J = 6.7 Hz, 24H, CH_3), 3.27 (hept, J = 6.7 Hz, 4H, NCH). ^{13}C NMR: δ = 2.7 ($SiCH_3$), 24.7 (CH_3), 46.9 (NCH). MS (EI, 70 eV): m/z (%) = 317 (15) [$M+1^+$], 316 (43) [M^+], 301 (2) [M-15$^+$], 216 (18), 215 (15), 200 (15), 159 (42), 158 (100) [M/2$^+$], 116 (56), 73 (54), 59 (82), 43 (45). Anal. calcd. for $C_{16}H_{40}N_2Si_2$ (316.52): C, 60.71; H, 12.74; N, 8.85. Found: C, 59.34; H, 12.30; N, 8.59.

2,2-Bis(diethylamino)-1,1,1,3,3,3-hexamethyltrisilane (**9a**). Chlorotrimethylsilane (10.0 mL, 0.08 mol) was added rapidly to a suspension of lithium (4.6 g, 0.66 mol) in THF (100 mL). Then, a solution of **7a** (20.5 mL, 0.085 mol) and $ClSiMe_3$ (22.0 mL, 0.17 mol) in THF (150 mL) was added dropwise over 5 hours at room temperature. Stirring continued for 3 days at room temperature. Another portion of $ClSiMe_3$ (12.0 ml, 0.09 mol) was then added, and the mixture was stirred for a further 7 days. Then, the solvent was removed in vacuo, and the residue was treated with hexane (100 mL). Insoluble material was removed by filtration, hexane was evaporated, and the residue was distilled to give 11.3 g (42%) of colorless **9a** with b.p. 86–90°C/10^{-2} Torr, solidifying below 20–25°C. ^{1}H NMR δ = 0.14 (s, sat. $^2J_{SiH}$ = 9 Hz, $^3J_{SiH}$ = 6 Hz, 18H, $SiCH_3$), 1.03 (t, J = 7 Hz, 12H, CCH_3), 2.93 (q, ^3J = 7 Hz, 8H, NCH_2). ^{13}C NMR δ = 0.5 ($SiCH_3$), 15.1 (CH_3), 40.9 (NCH_2). ^{29}Si NMR δ = −3.2 (sat., $^1J_{SiSi}$ = 92.0 Hz, $^2J_{SiC}$ = 6 Hz, SiN_2), −22.9 (sat., $^1J_{SiSi}$ = 92.0 Hz, $^1J_{SiC}$ = 42.7 Hz, $SiMe_3$). MS (EI, 70 eV): m/z (%) = 318 (7) [M+], 245 (86) [M-$SiMe_3^+$], 232 (12), 174 (79) [$Et_2NSi(H)SiMe_3^+$], 172 (100) [M-2$SiMe_3^+$], 144 (8), 130 (13), 103 (15), 100 (17) [M-2$SiMe_3$-NEt_2^+], 73 (29) [$SiMe_3^+$]. Anal. calcd. for $C_{14}H_{38}N_2Si_3$ (318.72): C, 52.76; H, 12.02; N, 8.79. Found: C, 52.01; H, 11.36; N, 8.65.

2,2-Bis(piperidino)-1,1,1,3,3,3-hexamethyltrisilane (**9b**). Compound **7b** (30.0 g, 0.11 mol) and chlorotrimethylsilane (28.3 mL, 0.22 mol) were added to lithium (2.5 g, 0.36 mol) suspended in THF (300 mL), and the mixture was worked-up as described for **9a.** Distillation furnished 9.6 g (25%) of viscous liquid **9b**, b.p. 120°C/0.03 Torr. ^{1}H NMR: δ = 0.13 (s, 18H, $SiCH_3$), 1.38–1.45 (m, 8H, β-CH_2), 1.54–1.61 (m, 4H, γ-CH_2), 2.91 ("t", J = 5.2 Hz, 8H, α-CH_2).

^{13}C NMR: δ = 0.3 ($SiCH_3$), 25.7 (γ-CH_2), 28.0 (β-CH_2), 48.4 (α-CH_2). ^{29}Si NMR: δ = −22.0 (sat., $^1J_{SiSi}$ = 90.3 Hz, SiN_2), −4.5 (sat., $^1J_{SiSi}$ = 90.3 Hz, $^1J_{SiC}$ = 42.5, $SiCH_3$). GC–MS (EI 70eV): *m/z* (%) = 271 (23), 270 (87) [M + 1-$SiMe_3^+$], 197 (7), 196 (13) [M-2$SiMe_3^+$], 187 (20), 186 (100) [pipSi(H)$SiMe_3^+$], 185 (10), 156 (25), 84 (25) [pip$^+$], 73 (88) [$SiMe_3^+$]. Anal. calcd. for $C_{16}H_{38}N_2Si_3$ (342.75): C, 56.07; H, 11.17; N, 8.17. Found: C, 55.50; H, 11.00; N, 8.47.

2,2-Bis(pyrrolidino)-1,1,1,3,3,3-hexamethyltrisilane (**9c**). Compound **7c** (21.4 g, 89.5 mmol) and chlorotrimethylsilane (25.6 mL, 0.20 mol) were added to lithium (3.1 g, 0.45 mol) suspended in THF (300 mL) and worked-up as described for **9a**, which afforded 12.3 g (44%) of colorless solid **9c**, b.p. 120°C/0.3 Torr, m.p. 64°C. ^{1}H NMR: δ = 0.16 (s, 18H, $SiCH_3$), 1.66–1.74 (m, 8H, β-CH_2), 2.97–3.04 (m, 8H, α-CH_2). ^{13}C NMR: δ = 0.45 ($SiCH_3$), 26.8 (β-CH_2), 49.1 (α-CH_2). ^{29}Si NMR: δ = −16.2 (sat., $^1J_{SiSi}$ = 91.5 Hz, SiN_2), −21.6 (sat., $^1J_{SiSi}$ = 91.5 Hz, $^1J_{SiC}$ = 42.8, $SiCH_3$). MS (EI 70eV): *m/z* (%) = 314 (14) [M$^+$], 299 (3) [M-CH_3^+], 244 (10) [M-$NC_4H_8^+$], 241 (84) [M-$SiMe_3^+$], 174 (9) [M-2$NC_4H_8^+$], 172 (100) [$(C_4H_8N)SiHSiMe_3^+$], 171 (4), 168 (2) [M-2$SiMe_3^+$]. Anal. calcd. for $C_{14}H_{34}N_2Si_3$ (314.69): C, 53.43; H, 10.89; N, 8.90. Found: C, 53.54; H, 11.39; N, 8.51.

1,3-Diethyl-2,2-bis(trimethylsilyl)-1,3,2-diazasilolidine (**9d**). Compound **7d** (2.8 g, 13.1 mmol), lithium suspension (0.6 g, 86.5 mmol), and chlorotrimethylsilane (3.4 mL, 26.8 mmol) were reacted and worked-up as described for **9a.** Fractional distillation furnished 1.8 g of a colorless liquid with b.p. 53°C/0.3 Torr containing a small amount of a solid, which was removed by filtration to leave 1.3 g of a liquid. NMR-spectra indicated a mixture of **9d** (cf. following section), another *N,N′*-diethylethylenediamine derivative (ca. 55:45 mol%), and a small amount of trimethylsilyl compounds but no residual **7d.**

Diethylaminotris(trimethylsilyl)silane (**10a**). A mixture of **8a** (11.1 g, 53.7 mmol) and chlorotrimethylsilane (27.3 mL, 215 mmol) was added rapidly to a suspension of lithium (3.4 g, 490 mmol) in THF (250 mL). The initially exothermic reaction was kept at room temperature by use of a water bath. After stirring for 3 days the solvent was replaced by hexane, insoluble components were removed by filtration, and hexane was evaporated in vacuo. Sublimation at 150°C (bath)/0.01 Torr afforded 13.1 g (76%) of colorless solid **10a,** slightly contaminated (<5%) by $(Et_2N)_2Si(SiMe_3)_2$ and $Si(SiMe_3)_4$. ^{1}H NMR: δ = 0.19 (s, 27H, $SiCH_3$), 0.98 (t, J = 7.0 Hz, 6H, CH_3), 2.84 (q, J = 7.0 Hz, 4H, NCH_2). ^{13}C NMR: δ = 0.5 ($SiCH_3$), 15.2 (CH_3), 44.5 (NCH_2). ^{29}Si NMR: δ = −28.8 (sat., $^1J_{SiSi}$ = 65.8 Hz, SiN), −16.5 (sat., $^1J_{SiSi}$ = 65.8 Hz, $^1J_{SiC}$ = 43.2, $SiCH_3$). MS (EI 70eV): *m/z* (%) = 319 (18) [M$^+$], 304 (7) [M-CH_3^+], 247 (29) [M-NEt_2^+], 246 (100) [M-$SiMe_3^+$], 174 (5) [M-$SiMe_3$-NEt_2^+], 173 (9) [M-2$SiMe_3^+$], 73 (39) [$SiMe_3^+$].

Morpholinotris(trimethylsilyl)silane (**10b**). A mixture of **8b** (9.2 g, 41.7 mmol) and chlorotrimethylsilane (21.2 mL, 167 mmol) was added rapidly to a suspension of lithium (2.65 g, 382 mmol) in THF (200 mL). The mixture was stirred for 3 days at room temperature and worked-up as described for **10a**. Sublimation at 160°C (bath)/0.01 Torr furnished 10.4 g of colorless solid **10b**, contaminated by $morph_2Si(SiMe_3)_2$ and $Si(SiMe_3)_4$ (molar ratio ca.: 74:10:16%). ^{1}H NMR: δ = 0.19 (s, 27H, $SiCH_3$), 2.82 (t, J = 4.6 Hz, 4H, NCH_2), 3.54 (t, J = 4.6 Hz, 4H, OCH_2). ^{13}C NMR: δ = 1.3 ($SiCH_3$), 51.0 (NCH_2), 68.4 (OCH_2). ^{29}Si NMR: δ = −27.5 (sat., $^1J_{SiSi}$ = 64.8 Hz, SiN), −15.6 (sat., $^1J_{SiSi}$ = 64.8 Hz, $^1J_{SiC}$ = 43.7, $SiCH_3$). MS (EI 70eV): *m/z* (%) = 333 (38) [M$^+$], 320 (24), 318 (17) [M-$CH3_3^+$], 274 (15), 261 (100) [M-$SiMe_3^+$], 247 (5) [M-morph$^+$], 233 (99.9) [M-$SiMe_3$-$C_2H_4^+$], 175 (51) [M-$SiMe_3$-morph$^+$], 173 (24), 73 (99) [$SiMe_3^+$], 70 (86) [morph$^+$]. Calcd. for $C_{13}H_{35}NOSi_4$ (333.77). $morph_2Si(SiMe_3)_2$. ^{1}H NMR: δ = 0.26 (s, $SiCH_3$), 2.96 (t, J = 4.6 Hz, NCH_2), 3.57 (t, J = 4.6 Hz, OCH_2). ^{13}C NMR: δ = 0.1 ($SiCH_3$), 47.5 (NCH_2), 68.5 (OCH_2). ^{29}Si NMR: δ = −2.3 (SiN_2), −21.7 ($SiCH_3$). $Si(SiMe_3)_4$. ^{1}H NMR: δ = 0.20 (s, $SiCH_3$). ^{13}C NMR: δ = 2.6 ($SiCH_3$). ^{29}Si NMR (cf. [30]): δ = −135.4 (Si), −9.9 (sat., $^1J_{SiSi}$ = 52.6 Hz, $^1J_{SiC}$ = 44.5, $SiCH_3$).

Reactions of Aminooligosilanes

2,2-Dichloro-1,1,1,3,3,3-hexamethyltrisilane (**11a**). 100 mL of 0.9 M ethereal HCl solution (90 mmol) was added dropwise within 1 hour to a cold (0–5°C) solution of **9a** (4.85 g, 15.2 mmol) in ether (100 mL). The hydrochloride was separated and washed with ether, the solvent was removed in vacuo, and the residue was distilled to give 2.3 g (62%) colorless liquid of b.p. 74°C/5 Torr. In an analogous conversion of **9b** (6.8 g, 19.8 mmol), the yield was 2.5 g (51%). ^{1}H NMR: δ = 0.27 (s, $^2J_{SiH}$ = 6.7 Hz, $^3J_{SiH}$ = 4.3 Hz, CH3). ^{13}C NMR: δ = −3.0 (sat. $^1J_{SiC}$ = 47.5 Hz, CH_3). ^{29}Si NMR: δ = 34.4 (sat. $^1J_{SiSi}$ = 75.9 Hz, $SiCl_2$), −11.3 (sat. $^1J_{SiSi}$ = 75.9 Hz, $^1J_{SiC}$ = 47.7 Hz, $SiMe_3$). IR (cap.): $\bar{\nu}_{Si\text{-}Cl}$ = 514; $\bar{\nu}_{SiMe3}$ = 1249, 842 cm^{-1}.

2,2-Dibromo-1,1,1,3,3,3-hexamethyltrisilane

(**11b**). Dry gaseous HBr was introduced into a cold (0–5°C) ethereal solution (200 mL) of **9a** (6.0 g, 18.8 mmol), and the product was worked-up as described for **11a** to give 3.4 g (54%) of colorless, fuming liquid with b.p. 64°C/1 Torr. ^{1}H NMR: δ = 0.30 (s, sat. $^2J_{SiH}$ = 6.8 Hz, $^3J_{SiH}$ = 4.6 Hz, CH_3). ^{13}C NMR: δ = −2.7 (sat. $^1J_{SiC}$ = 48 Hz, CH_3). ^{29}Si NMR: δ = 22.6 (sat. $^1J_{SiSi}$ = 69.5 Hz, $^2J_{SiC}$ = 8.3 Hz, $SiBr_2$), −10.2 (sat. $^1J_{SiSi}$ = 69.5 Hz, $^1J_{SiC}$ = 48.1 Hz, $SiMe_3$). IR (cap.): $\bar{\nu}_{Si\text{-}Br}$ = 425; $\bar{\nu}_{SiMe3}$ = 1249, 842 cm^{-1}.

2,2-Diiodo-1,1,1,3,3,3-hexamethyltrisilane (**11c**). Dry gaseous HI was introduced into a cold (0–5°C) ethereal solution (250 mL) of **9a** (4.0 g, 12.6 mmol). The hydroiodide precipitate was removed by filtration and washed twice with cold ether (each 10 mL). Ether was evaporated in vacuo, and the residue was distilled to give 2.95 g (55%) of colorless solid with b.p. 78°C/0.005 Torr and m.p. 64–65°C. **11c** is highly reactive and must be stored cool and dark. $CDCl_3$ is attacked rapidly. ^{1}H NMR (C_6D_6): δ = 0.20 (s, sat. $^2J_{SiH}$ = 6.7 Hz, $^3J_{SiH}$ = 4.7 Hz, CH_3). ^{13}C NMR (C_6D_6): δ = −1.8 (sat. $^1J_{SiC}$ = 48.4 Hz, $^2J_{SiC}$ = 7.9 Hz, CH_3). ^{29}Si NMR (C_6D_6: δ = −28.5 (sat. $^1J_{SiSi}$ = 62.4 Hz, $^2J_{SiC}$ = 7.8 Hz, SiI_2), −10.7 (sat. $^1J_{SiSi}$ = 62.4 Hz, $^1J_{SiC}$ = 48.5 Hz, $SiMe_3$). Anal. calcd. for $C_6H_{18}I_2Si_3$ (428.27): C, 16.83; H, 4.24. Found: C, 17.29; H, 4.29.

2,2-Bis(*trimethylsilyl*)*-1,3-dineopentyl-2,3-dihydro-1H-1,3,2-diazasilolo[4,5-b]pyridine* (**9f**). A solution of *n*-butyllithium in *n*-hexane (8.3 mL 1,6 M, 13.2 mmol) was added dropwise at 5 to 10°C to *N,N′*-dineopentyl-2,3-diaminopyridine (1.65 g, 6.6 mmol) dissolved in benzene (40 mL). After 1 hour, a solution of **11a** (1.62 g, 6.6 mmol) in benzene (2 mL) was added, and the mixture was refluxed for 8 hours. LiCl was filtered off, and the solvent was removed in vacuo. Distillation of the residue afforded 1.3 g (47%) of pale yellow viscous oil, b.p. 125–130°C/0.005 Torr, which crystallized within a few hours, m.p. 62–65°C. ^{1}H NMR: δ = 0.20 (s, 18H, $SiCH_3$), 1.02 (s, 9H, CH_3), 1.04 (s, 9H, CH_3), 2.96 (s, 2H, 1-NCH_2), 3.24 (s, 2H, 3-NCH_2), 6.37 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H6), 6.58 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H7), 7.37 (dd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H5). ^{1}H NMR (C_6D_6): δ = 0.18 (s, sat. $^2J_{SiH}$ = 6.4 Hz, $^3J_{SiH} \approx$ 2.5 Hz, 18H, $SiCH_3$), 0.90 (s, 9H, CH_3), 1.18 (s, 9H, CH_3), 2.89 (s, 2H, 1-NCH_2), 3.50 (s, 2H, 3-NCH_2), 6.47 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H6), 6.57 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H7), 7.80 (dd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H5). ^{13}C NMR: δ = 0.4 ($SiCH_3$), 29.3 (CH_3), 33.8 (CMe_3), 34.5 (CMe_3), 53.3 (1-NCH_2), 56.4 (3-NCH_2), 111.5 (CH), 112.0 (CH), 133.7 (CH5), 138.1 (C_q7a), 155.3 (C_q3a). ^{29}Si NMR: δ = 23.6 (sat. $^1J_{SiSi}$ = 74 Hz, SiN_3), −20.8 (sat. $^1J_{SiSi}$ = 74 Hz, $^1J_{SiC}$ = 43.7 Hz, $SiMe_3$). MS (EI 70 eV): *m/z* (%) = 421 (9) [M$^+$], 370 (26), 348 (70) [M-$SiMe_3^+$], 275 (6) [M-2$SiMe_3^+$], 249 (15), 192 (58), 134 (15), 122 (20), 73 (100) [$SiMe_3^+$], 57 (13) [Bu^+], 43 (35). Anal. calcd. for $C_{21}H_{43}N_3Si_3$ (421.85): C, 59.79; H, 10.27; N, 9.96. Found: C, 59.08; H, 10.24; N, 9.96.

1,3-Diethyl-2,2-bis(*trimethylsilyl*)*-1,3,2-diazasilolidine* (**9d**). N,N′-Diethylethylenediamine (2.6 ml, 18.1 mmol) was dissolved in ether (100 mL) and dilithiated at −60°C with a hexane solution of *n*-butyllithium (23 mL 1,6 N, 36.8 mmol). After 1 hour at room temperature, the suspension was cooled to −50°C, and a solution of **7a** (4.42 g, 18.0 mmol) in a small amount of ether was added. The mixture was stirred overnight at room temperature, the precipitate was filtered off, and the solvent was removed in vacuo. Twofold distillation furnished 0.9 g (17%) of slightly contaminated **7d** with b.p. 64°C/0.1 Torr. ^{1}H NMR: δ = 0.12 (s, 6H, $SiCH_3$), 1.07 (t, J = 7.1 Hz, 6H, CH_3), 2.84 (q, J = 7.1 Hz, 4H, NCH_2), 2.94 (s, 4H, 4-CH_2, 5-CH_2). ^{13}C NMR: δ = −0.8 ($SiCH_3$), 16.0 (CH_3), 42.8 (NCH_2), 50.1 (4-CH_2, 5-CH_2). ^{29}Si NMR: δ = 5.4 (SiN_2), −21.9 ($SiMe_3$). MS (EI 70 eV): *m/z* (%) = 288 (43) [M+], 273 (15) [M-Me$^+$], 263 (14), 231 (35), 215 (100) [M-$SiMe_3^+$], 157 (28), 142 (7) [M-2$SiMe_3^+$], 141 (37), 73 (99) [$SiMe_3^+$]. $C_{12}H_{32}N_2Si_3$ (288.66).

X-ray Structure Analysis of **2a**. *Table 2*

Data Collection and Reduction. A colorless plate 0.60 × 0.40 × 0.25 mm^3 was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4). Using ω scans, 8082 intensities were collected in the theta range of 3.01 to 25° (index ranges $-13 \le h \le 13$, $-19 \le k \le 7$, $-20 \le 1 \le 0$), of which 5388 were independent (R_{int} 0.0215). No absorption correction was made.

Structure Solution and Refinement. The structure was solved with direct methods and refined anisotropically on F^2 using the program SHELXL-93 (G.M. Sheldrick, University of Göttingen). Methyls were used as rigid groups, and Si-H was freely refined but with bond distances restrained to be equal. The final R indices were R_1 = [I > 2 sigma(I)] 0.0577, wR2 (for all data) = 0.1647. Two difference peaks of ca. 1.4 e/ Å^3 probably correspond to silicon atoms of an alternative molecular orientation, but in the absence of other peaks, no disorder refinement was attempted.

Complete crystallographic data (except structure

factors) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-(125401):

ACKNOWLEDGMENTS

We thank B. Witt for numerous NMR, Dr. A. Müller for MS measurements.

REFERENCES

[1] Gilman, H.; Shiina, H.; Aoki, D.; Gaj, B. G.; Wittenberg, D.; Brennan, T. J. J Organomet Chem 1968, 13, 323.
[2] Kumada, M.; Ishikawa, M.; Maeda, S. J Organomet Chem 1964, 2, 478.
[3] (a) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. Tetrahedron Lett 1996, 5493; (b) Kumada, M.; Watanabe, T.; Sakurai, H. J Organomet Chem 1967, 7, C15.
[4] Tamao, K.; Kumada, M. J Organomet Chem 1971, 30, 329 and 339.
[5] Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Götz, A.; Hergott, H. H.; Hofmann, K.; Kober, W.; Krägeloh, K.; Oesterle, T.; Stepan, W.; West, W.; Simchen, G. Synthesis 1, 1982.
[6] Uhlig, W. Chem Ber 1996, 129, 733 and ref. therein.
[7] (a) Tamao, K.; Kawachi, A.; Ito, Y. J Am Chem Soc 1992, 114, 3989; (b) Tamao, K.; Kawachi, A.; Nakagawa, Y.; Ito, Y. J Organomet Chem 1994, 473, 29; (c) Kawachi, A.; Tamao, K. Bull Chem Soc Jap 1997, 70, 945.
[8] Tamao, K.; Kawachi, A.; Ito, Y. Organometallics 1993, 12, 580.
[9] Unno, M.; Saito, M.; Matsumoto, H. J Organomet Chem 1995, 499, 221.
[10] Tamao, K.; Sun, G. R.; Kawachi, A.; Yamaguchi, S. Organometallics 1997, 16, 780.
[11] (a) Mantey, S.; Heinicke, J. In Organosilicon Chemistry: From Molecules to Materials III; Auner, N.; Weis, J., Eds.; VCH: Weinheim, 1997; p. 254; (b) Heinicke, J.; Mantey, S. Heteroatom Chem 1998, 9, 311.
[12] Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. Chem Commun 1995, 1931.
[13] Gilman, H.; Harrell, R. L. J Organomet Chem 1966, 5, 199.
[14] Hassler, K. Spectrochim Acta 1985, A 41, 729.
[15] Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. J Am Chem Soc 1991, 113, 1281.
[16] Matsumoto, H.; Yokoyama, N.; Sakamoto, A.; Aramaki, Y.; Endo, R.; Nagai, Y. Chem Lett 1986, 1643.
[17] (a) Ishikawa, M.; Kumada, M. Adv Organomet Chem 1981, 19, 51; (b) Michalczyk, M. J.; Fink, M. J.; DeYoung, D. J.; Carlson, C. W.; Welsh, K. W.; West, R.; Michl, J. Silicon, Germanium, Tin, Lead Compds 1986, 9, 75; (c) Bott, S. G.; Marshall, P.; Wagenseller, P. E.; Wang, Y.; Conlin, R. T. J Organomet Chem 1995, 499, 11.
[18] Heinicke, J.; Oprea, A.; Kindermann, M. K.; Kárpáti, T.; Nyulászi, L.; Veszprémi, T. Chem Eur J 1998, 4, 537.
[19] Lukevics, E.; Pudova, O.; Sturkovich, R. Molecular Structure of Organosilicon Compounds, Wiley & Sons: New York, 1989.
[20] Sheldrick, W. S. In The Chemistry of Organic Silicon Compounds; Patai, S.; Rappoport, Z. Eds.; Wiley & Sons: Chichester, 1989; Chapter 3, p 254.
[21] Wan, Y.; Verkade, J. G. Inorg Chem 1993, 32, 341.
[22] Tamao, K.; Kawachi, A.; Nakagawa, Y.; Ito, Y. J Organomet Chem 1994, 473, 29.
[23] Vilkov, L. V.; Tarasenko, N. A. Chem Commun 1969, 1176.
[24] Marsmann, C.; Raml, W.; Hengge, E. Z Naturforsch 1980, 35b, 1541–1547.
[25] Ernst, C. R.; Spilator, L.; Buell, G. R.; Wilhite, D. L. J Am Chem Soc 1974, 96, 5375.
[26] Williams, E. A.; Cargioli, J. D.; Sharp, K. G.; Sutov, P. A.; Farrar, T. C.; Ishibitsu, K. J Am Chem Soc 1976, 98, 1977.
[27] Williams, E. A. In The Chemistry of Organic Silicon Compounds; Patai, S. Rappoport, Z., Eds.; Wiley & Sons: Chichester, 1989; p. 511–553.
[28] Bent, H. Chem Rev 1961, 61, 275.
[29] Breederveld, H.; Waterman, H. I. Research 1952, 5, 537.
[30] Marsmann, H. C.; Raml, W.; Hengge, E. Z Naturforsch 1980, B35, 1541.