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Aminosubstituted Disilanes: Synthesis by Unsymmetrical and Symmetrical Reductive Coupling

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ABSTRACT: *The reductive coupling of chlorotris(diorganylamino)silanes* **1** *with chlorotrimethylsilane by the action of lithium in THF provides for steric reasons, an easy access to unsymmetrical aminosubstituted disilanes* $(R_2N)_3Si\text{-}SiMe_3$ **3.** *Similarly, cross-coupling to give pentakis(diethylamino)disilane* **4** *is observed between* **1a** *and bis(diethylamino)chlorohydridosilane* **2a** *on treatment with lithium. In reactions of the less bulky bis(diorganylamino)chlorohydridosilanes* **2** *with* $ClSiMe_3$ *and Li, however, the symmetrical coupling is preferred and affords SiH-functional substituted* $(R_2N)_{32}HSi\text{-}SiH(NR_2)_2$ **5.** *Aminosubstituted disilanes* **3–5** *are useful starting materials for modification of disilanes or syntheses of silicon heterocycles via generation and trapping of aminosilylenes, as exemplified by diethylaminosilacyclopent-3-ene* **6a.** © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:311–316, 1998

INTRODUCTION

The synthesis of aryl- or alkyl substituted disilanes by reductive coupling with lithium in THF or with sodium in toluene is a well-established procedure [1]. Functional substituted disilanes are commonly obtained by cleavage of aryl groups with $AlCl_3$/HCl [2–4], MeCOCl/$AlCl_3$ [3], or more easily with triflic acid [5]. With regard to the growing interest in aminosubstituted disilanes as precursors for new silicon-containing materials or for aminosilylenes and the easy substitution by halides, alkoxygroups, etc., an easier synthetic access to aminodisilanes is desirable. Tamao et al. [11] have recently described the synthesis of amino(phenyl)silyllithiums and their reactions with chlorosilanes to give aminosubstituted disilanes [6,7]. They reported also on the preparation of symmetrical coupling products of alkyl(amino)-chlorosilanes [8]. Unno et al. have shown by the same method the synthesis of aminosubstituted disilanes with bulky alkyl substituents [9]. Unsuccessful attempts to effect cross-coupling reactions of aminosubstituted chlorosilanes with different amino(chloro)silanes, with chlorotrimethylsilane, or with methyltrichlorosilane [8] prompted us to explore conditions or requirements to obtain unsymmetrical aminosubstituted disilanes and to find criteria for an estimation of the selectivity for symmetrical or unsymmetrical coupling. We report here our recent results, presented first at the 3. Münchner Silicontage 1996 [10]. In a just published article, Tamao et al. [11] also describe now several examples of the unsymmetrical coupling of chloro(diethylamino)methylsilanes and disilanes with lithium in THF to give aminodi- and oligosilanes.

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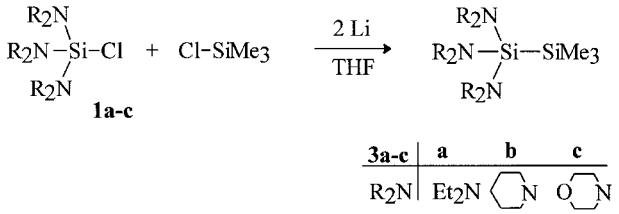
RESULTS AND DISCUSSION

Chlorotris(amino)silanes **1a–c** or SiH-functional bis(amino)chlorosilanes **2a–d** were used as precursors for the disilanes reported in this study. They were prepared in analogy to known methods from the reaction of $SiCl_4$ and the corresponding amines (six equivalents) in toluene [12] and from $HSiCl_3$ and amines (four equivalents) in ether [13], respectively. ^1H, ^{13}C, and ^{29}Si NMR data are given.

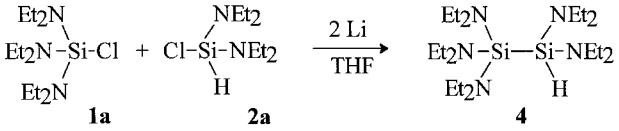
The cross-coupling of **1a–c** with trimethylchlorosilane by the action of lithium (equiv. 1) gives the corresponding 1,1,1-trimethyl-2,2,2-tris(diorganylamino)disilanes **3a–c** in reasonable yields for the diethylamino and piperidino compounds (**3a** and **3b**). The morpholino derivative **3c** could be obtained only in low yield in addition to a small amount of hexamethyldisilane and much insoluble material that might be a complex of the amino compounds with LiCl. Employment of a large excess of trimethylchlorosilane prevents formation of **3** (Scheme 1).

Cross-coupling was also achieved in the reaction of chlorotris(diethylamino)silane **1a** and bis(diethylamino)chlorosilane **2a** with Li in THF affording **4** (equiv. 2). The yield was low, however, and a small amount of $HSi(NEt_2)_3$ was formed as a side product. Compound **4** was first observed by Huppmann et al. [14], who investigated the formation of silylenes from diaminodichlorosilanes by the action of sodium/potassium alloy (Scheme 2).

Attempts to prepare cross-coupling products of hydridobis(amino)chlorosilanes **2a–d** and chlorotrimethylsilane failed; only the symmetrical coupling products **5a** and **5d** were obtained (equiv. 3). Surprisingly, in the absence of chlorotrimethylsilane, even the symmetrical coupling did not succeed.



SCHEME 1

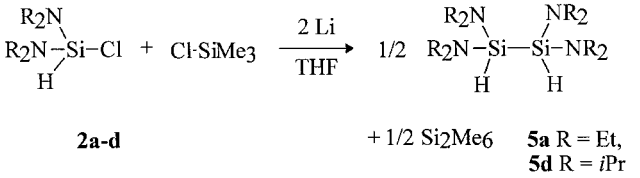


SCHEME 2

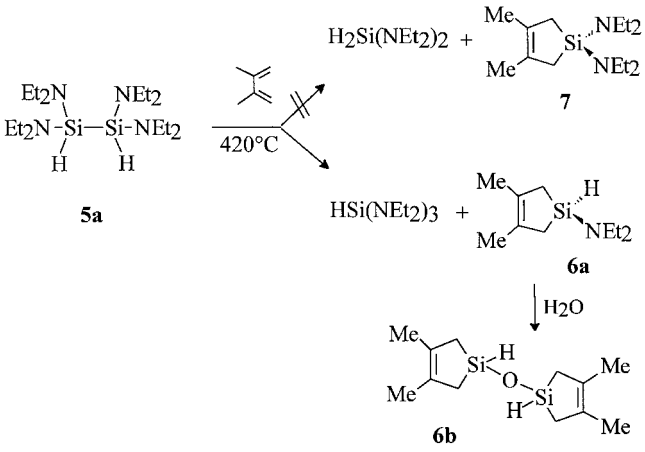
Thus, $HSi(pip)_3$ was formed from 2b in place of 5b when the reaction was carried out without the presence of $ClSiMe_3$ (Scheme 3).

The selectivity for unsymmetrical or symmetrical products in the cross-coupling experiments depends on electronic and steric factors. While $ClSiMe_3$ is well known to react with Li in THF to yield Si_2Me_6, no hexakis(diethylamino)disilane [15] can be detected if **1a** is treated in a similar manner, probably for steric reasons. On the assumption that the substitution reaction of intermediate Me_3Si^- with $ClSiMe_3$ is faster than that with the much bulkier $ClSi(NEt_2)_3$, the cross-coupling products should be formed from $(R_2N)_3Si^-$ anions and $ClSiMe_3$ rather than from Me_3Si^- and $ClSi(NEt_2)_3$. The primary electron transfer to silicon is probably less influenced by steric factors and controlled by a larger stabilization of the aminosubstituted silyl radical anion, caused by a weak electron-withdrawing effect of the amino groups [6,11,16]. Attempts to provide evidence of a lower reduction potential by examination of the cyclovoltamograms of $ClSi(NEt_2)_3$ in THF/nBu$_4$N$^+$ClO$_4^-$ failed; the reduction curve revealed broad and flat maxima that did not allow us to reach reliable conclusions. The lower energy of the LUMO of $(Me_2N)_3SiCl$ (-0.09 eV) compared to Me_3SiCl ($+0.12$ eV, see also Ref. [11]), estimated by semiempirical PM3 calculations [17], supports the supposed primary reduction of the aminochlorosilanes. The preference for symmetrical coupling of the aminochlorohydridosilanes **2** is certainly due to a lower steric hindrance in the substitution of intermediate aminosilyl (radical) anions by **2**. Further efforts will be made to find out if the use of amino substituents bulkier than isopropyl groups permits an access to unsymmetrical aminohydridodisilanes.

Aminodisilanes are useful starting materials to obtain synthetically valuable chloro- or alkoxydisilanes by convenient cleavage with HCl/ether or alcohols under mild conditions [8,11]. Another application is the controlled thermal decomposition of aminosubstituted disilanes in the presence of trapping reagents that may be used to synthesize silicon heterocycles by cycloaddition with intermediate aminosilylenes [18]. Thus, cothermolysis of **5a** with



SCHEME 3



SCHEME 4

2,3-dimethylbutadiene afforded $(Et_2N)_3SiH$ and 1-diethylamino-3,4-dimethyl-silacyclopent-3-ene **6a,** easily hydrolyzable to **6b** (Scheme 4). The thermolysis proceeded selectively by migration of an amino rather than a hydride group and subsequent Si–Si bond cleavage via (diethylamino)silylene. No trapping product **7** of the thermodynamically more stable bis(diethylamino)silylene could be detected. For comparison of spectral data, **7** was prepared independently by aminolysis of 1,1-dichloro-3,4-dimethyl-silacyclopent-3-ene [19].

The chemistry of aminosilylenes has attracted much attention owing to the electronic stabilization of these species [20], a factor which recently led to the isolation of stable diaminosilylenes [21]. Further studies of the reactivity of **3** and **5** are in progress.

EXPERIMENTAL

Materials and Spectroscopy

All reactions were carried out with use of freshly distilled, dried solvents and amines; chlorosilanes were recondensed in vacuo before use. NMR data 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). $CDCl_3$ was used as the solvent and as a reference for ^{1}H and ^{13}C NMR (δ 7.27 and 77.00, respectively). ^{29}Si NMR data are referred to external tetramethylsilane. CHN analyses of **3, 5,** and **7** are in accordance with calculated values.

Preparation of Aminochlorosilanes **1**

*Chlorotris(diethylamino)silane **1a** (modification of Ref. [10]).* Diethylamine (62.8 g, 0.86 mol) was dissolved in diethyl ether (250 mL). With vigorous stirring, a solution of 36.6 g (0.215 mol) of $SiCl_4$ in 150 mL of ether was added dropwise (temperature increasing from 25 to 35°C). Stirring was continued overnight to complete the reaction. The precipitate that had formed was removed and thoroughly washed with ether, and the solvent was distilled from the filtrate. Toluene (400 mL) and diethylamine (32.1 g, 0.44 mol) were added to the residual crude $Cl_2Si(NEt_2)_2$, and the mixture was heated under reflux for 8 hours. The precipitate that formed was filtered off and washed with toluene, the solvent removed, and the remainder distilled at 107°C/2 Torr, yielding 43.6 g (73%) of **1a.** ^{1}H NMR: δ 1.03 (t, J = 7.0 Hz, CH_3), 2.90 (q, J = 7.0 Hz, NCH_2). ^{13}C NMR: δ 14.2 (CH_3), 38.3 (NCH_2). ^{29}Si NMR: δ −30.2. MS (70 eV, EI): m/z = 279 (35%, M^+), 264 (30%, M^+-Me), 250 (21%, M^+-Et), 207 (42%, M^+-NEt_2), 194 (94%), 138 (13%), 136 (62%), 134 (100%, $SiClNEt_2^+$-H), 72 (81%, NEt_2^+) [assignment for ^{35}Cl].

Chlorotris(piperidino)silane **1b.** An 84.8 g (79%) amount of **1b,** bp 160°C/2 Torr, mp 75°C, was obtained from 57.5 g (0.338 mol) of $SiCl_4$ and 172.4 g (2.03 mol) of piperidine by reaction in toluene at reflux (compare Ref. [10]). ^{1}H NMR: δ 1.46 (m, 12H, β-CH_2), 1.59 (m, 6H, γ-CH_2), 2.89 (dd, J ca. 5.3, 5.2 Hz, 12H, NCH_2). ^{13}C NMR: δ 25.4 (γ-CH_3), 27.2 (β-CH_2), 45.8 (NCH_2). ^{29}Si NMR: δ −34.5. MS (70 eV, EI): m/z = 315 (27%, M^+), 231 (100%, M^+-pip), 147 (21%, M^+-2pip), 84 (51%, pip^+).

Chlorotris(morpholino)silane **1c.** A solution of 40 g (0.236 mol) $SiCl_4$ and 123 g (1.41 mol) of morpholine in toluene was refluxed to give, after the usual workup, 40.4 g (54%) of **1c,** bp 120°/0.3 Torr, mp 133°C. ^{1}H NMR: δ 2.97 (t, J = 4.7 Hz, 12H, NCH_2), 3.59 (t, m, J = 4.7 Hz, 12H, OCH_2). ^{13}C NMR: δ 45.5 (NCH_2), 67.6 (OCH_2). ^{29}Si NMR: δ −35.2. MS (70 eV, EI): m/z = 321 (22%, M^+), 270 (20%), 255 (22%), 201 (84%, M^+-Cl-C_4H_7O), 86 (100%, $morph^+$).

Preparation of Aminochlorohydridosilanes **2**

*Chlorobis(diethylamino)silane **2a** (Modification of Ref. [13]).* A solution of 92.1 g (1.26 mol) of diethylamine in ether (300 mL) was added within 1 hour to a solution of 42.7 g (0.315 mol) of $HSiCl_3$ in ether (300 mL) at room temperature. Stirring was continued overnight, the resulting precipitate removed and washed, and the filtrate distilled to give 35.1 g (53%) of **2a,** bp 90°C/20 Torr. ^{1}H NMR: δ 1.05 (t, J = 7.1 Hz, CH_3), 2.94 (q, J = 7.1 Hz, NCH_2), 4.94 (s, sb, $^1J_{SiH}$ = 274.7 Hz, SiH). ^{13}C NMR: δ 15.0 (CH_3), 38.7 (NCH_2). ^{29}Si NMR: δ −27.8. MS (70 eV, EI): $m/$

z = 208 (48%, M^+), 193 (59%, M^+-Me), 179 (13%, M^+-Et), 173 (17%, M^+-Cl), 138 (11%), 136 (58%), 134 (100%, M^+-NEt_2-2H), 138 (13%), 136 (62%), 134 (100%, $SiClNEt_2^+$-H), 72 (35%, NEt_2^+) [assignment for ^{35}Cl].

Chlorobis(piperidino)silane **2b.** Analogously to the preparation of ***2a,*** 40.0 g (0.3 mol) of $HSiCl_3$ and 100 g (1.2 mol) of piperidine were reacted in ether to give 38.6 g (56%) of **2b,** bp 90°C/0.3 Torr. ^1H NMR: δ 1.46 (m, 8H, β-CH_2), 1.60 (m, 4H, γ-CH_2), 2.95 (dd, J ca. 5.2, 5.4 Hz, 8H, NCH_2), 4.87 (s, sb, $^1J_{SiH}$ = 277.0 Hz, SiH). ^{13}C NMR: δ 25.3 (γ-CH_3), 27.2 (β-CH_2), 45.2 (NCH_2). ^{29}Si NMR: δ −30.2.

Chlorobis(morpholino)silane **2c.** As above, 40.0 g (0.3 mol) of $HSiCl_3$ was reacted with 103 g (1.18 mol) of morpholine in ether affording 35.8 g (51%) of **2c,** bp 100°C/0.3 Torr. ^1H NMR: δ 2.98 (m, 8H, NCH_2), 3.53 ("t," m, J = 4.7 Hz, 8H, OCH_2), 4.89 (s, sb, $^1J_{SiH}$ = 281.5 Hz, SiH). ^{13}C NMR: δ 44.0 (NCH_2), 67.4 (OCH_2). ^{29}Si NMR: δ −29.8.

Chlorobis(diisopropylamino)silane **2d.** Using the above procedure, 40.0 g (0.3 mol) of $HSiCl_3$ and 121.2 g (1.2 mol) of diisopropylamine in ether furnished 74 g (95%) of **2d,** bp 80°C/0.1 Torr. ^1H NMR: δ 1.18 (t, J = 6.8 Hz, CH_3), 3.43 (hept, J = 6.8 Hz, CH), 5.34 (s, sb, $^1J_{SiH}$ = 265.6 Hz, SiH). ^{13}C NMR: δ 23.8, 24.1 (CH_3), 44.7 (NCH). ^{29}Si NMR: δ −37.1. MS (70 eV, EI): m/z = 264 (7%, M^+), 249 (30%, M^+-Me), 221 (14%, M^+-Pr), 166 (2%), 164 (28%), 162 (63%, M^+-NPr_2-2H), 102 (10%, $NH_2Pr_2^+$), 86 (58%), 32 (100%).

General Procedure for the Reaction of Aminochlorosilanes with $ClSiMe_3$ and Lithium to Yield **3–5**

A solution of each of the aminochlorosilanes **1** or **2** (50–100 mmol) in 100–150 mL of THF was added to an excess (50%) of lithium dispersion under an argon atmosphere, followed by an equimolar amount of chlorotrimethylsilane. After the mixture had been stirred at room temperature for 3 days, a second equivalent of chlorotrimethylsilane was added, and the mixture was stirred for a further 3–4 days. THF and unreacted $ClSiMe_3$ was removed in vacuo, the residue extracted with dry *n*-hexane, the solvent evaporated, and the residue distilled to give the disilanes **3–5.**

1,1,1,-Trimethyl-2,2,2-tris(diethylamino)disilane **3a.** The reaction of 14.0 g (0.05 mol) of **1a,** 6.3 mL (0.05 mol) $ClSiMe_3$ and 1.0 g (0.14 mol) in THF gave 5.1 g (32%) **3a,** bp 120°C/0.1 Torr, mp 40°C. ^1H NMR: δ 0.14 (s, 9H, $SiCH_3$), 1.01 (t, J = 7.0 Hz, 18H, CH_3), 2.87 (q, J = 7.0 Hz, 12H, NCH_2). ^{13}C NMR: δ 0.5 ($SiCH_3$), 14.7 (CH_3), 38.2 (NCH_2). ^{29}Si NMR: δ −16.8, −25.9. MS (70 eV, EI): m/z = 317.5 (2%, M^+), 244 (100%, M^+-$SiMe_3$), 207 (12%), 173 (43%, M^+-2NEt_2), 172 [10%, $Si(NEt_2)_2^+$], 100 (47%), 73 (44%, $SiMe_3^+$), 32 (69%).

1,1,1,-Trimethyl-2,2,2-tris(piperidino)disilane **3b.** When 30.0 g (0.1 mol) of **1b,** 12.7 mL (0.1 mol) of $ClSiMe_3$, and 3.5 g (0.5 mol) of lithium were reacted in THF (3d), a mixture of **3b** and unreacted **1b** was obtained. A further portion of $ClSiMe_3$ (12 mL) and lithium (3.5 g) was added and (after 4 days) afforded 22.6 g (67%) of **3b.** ^1H NMR: δ 0.12 (s, 9H, $SiCH_3$), 1.39 (m, 12H, β-CH_2), 1.57 (m, 6H, γ-CH_2), 2.82 ("t," J ca. 5.2 Hz, 12H, NCH_2). ^{13}C NMR: δ 0.2 ($SiCH_3$), 26.0 (γ-CH_3), 28.0 (β-CH_2), 46.2 (NCH_2). ^{29}Si NMR: δ −20.7 (sb, J_{SiSi}, SiN_3), −24.5 (sb, $^1J_{SiC}$ = 42.9, $^1J_{SiSi}$ = 134.2 Hz, $SiMe_3$). GC-MS (70 eV, EI): m/z = 338 (3%, M^+-Me), 280 (100%, M^+-$SiMe_3$), 197 [65%, $Si(pip)_2H^+$].

1,1,1,-Trimethyl-2,2,2-tris(morpholino)disilane **3c.** Reaction of 10.0 g (31 mmol) of **1c,** 3.9 mL (31 mmol) of $ClSiMe_3$ and 0.9 g (130 mmol) of lithium in THF furnished a copious white precipitate, not yet further investigated, and 0.8 g (8%) of **3c,** bp 160°C/0.1 Torr. ^1H NMR: δ 0.15 (s, 9H, $SiCH_3$), 2.90 (t, J = 4.7 Hz, 12H, NCH_2), 3.56 (t, J = 4.7 Hz, 12H, OCH_2). ^{13}C NMR: δ −0.5 ($SiCH_3$), 44.9 (NCH_2), 68.1 (OCH_2). ^{29}Si NMR: δ −20.3, −24.9. MS (70 eV, EI): m/z = 359 (9%, M^+), 303 (14%), 288 (30%), 287 (100%), 286 (25%, M^+-$SiMe_3$), 285 (61%), 203 (44%), 201 (55%), 133 (41%), 86 (32%, $morph^+$), 75 (39%), 73 (72%, $SiMe_3^+$).

Pentakis(diethylamino)disilane **4.** A solution of **2a** (6.2 g, 29.7 mmol), **1a** (9.1 g, 32.8 mmol), and lithium (1.0 g, 144 mmol) in THF was caused to react and afforded 1.7 g (14%) of **4,** bp 90°C/0.03 Torr. ^1H NMR: δ 1.00 (t, J = 7.1 Hz, 12H, CH_3), 1.004 (t, J = 7.0 Hz, 18H, CH_3), 2.91 (q, J = 7.1 Hz, 8H, CH_2), 2.914 (q, J = 7.0 Hz, 12H, CH_2), 4.68 (s, sb, $^1J_{SiH}$ = 185, $^2J_{SiH}$ = 17.4 Hz, SiH). ^{13}C NMR: δ 14.1, 37.9 [$Si(NEt_2)_3$], 14.4, 40.6 [$Si(NEt_2)_2$]. ^{29}Si NMR: δ −20.0, −23.4. MS (70 eV, EI): m/z = 417.8 (9%, M^+), 251 (48%), 250 (90%), 249 (100%), 174 (80%), 100 (92%, $SiNEt_2^+$), 72 (42%, NEt_2^+).

1,1,2,2-Tetrakis(diethylamino)disilane ***5a.*** A reaction of 10.4 g (50 mmol) of **2a,** 6.3 mL (50 mmol) of $ClSiMe_3$ and 1.0 g (144 mmol) of lithium in THF yielded 4.0 g (46%) of **5a,** bp 120°C/0.3 Torr; no

$Me_3SiSiH(NEt_2)_2$ is observed. ^{1}H NMR: δ 1.02 (t, J = 7.0 Hz, 24H, CH_3), 2.92 (m, 16H, CH_2), 4.69 (s, sb, $^1J_{SiH}$ = 194.6, $^2J_{SiH}$ = 13.8 Hz, SiH). ^{13}C NMR: δ 15.3 (CH_3), 41.6 (NCH_2). ^{29}Si NMR: δ −23.0. MS (70 eV, EI): *m/z* = 346.5 (21%, M^+), 275 (22%), 274 (18%, M^+-NEt_2), 273 (25%), 247 (22%), 246 (52%), 245 (79%), 203 (23%), 202 (28%, M^+-$2NEt_2$), 177 (57%), 176 (100%), 175 (70%), 102 (77%), 100 (91%, $SiNEt_2^+$), 72 (98%, NEt_2^+).

1,1,2,2-Tetrakis(*diisopropylamino*)*disilane* **5d.** A reaction of **2d** (11.5 g, 43.5 mmol), $ClSiMe_3$ (5.5 mL, 43.5 mmol), and 1.5 g (216 mmol) of lithium in THF afforded 4.0 g (44%) **5d,** mp 100°C, that was purified by precipitation from concentrated hexane solution. ^{1}H NMR: δ 1.18 (2d, J = 6.7 Hz, 48H, CH_3), 3.39 (h, J = 6.7 Hz, 8H, CH_2), 5.01 (s, sb, $^1J_{SiH}$ = 190, $^2J_{SiH}$ = 17.3 Hz, SiH). ^{13}C NMR: δ 24.7, 25.4 (CH_3), 46.8 (NCH). ^{29}Si NMR: δ −38.3. MS (70 eV, EI): *m/z* = 458.6 (4%, M^+), 357.5 (2%, M^+-$NHPr_2$), 231 (25%), 230 [100%, $HSi(NPr_2)_2H^+$], 229 (66%), 185 (65%), 129 (72%), 128 (100%), 100 (40%, NPr_2^+), 88 (41%), 86 (48%), 44 (57%).

Co-thermolysis of **5a** *with 2,3-Dimethylbutadiene.* A solution of 2.1 g (6.1 mmol) of **5a** and 1.0 mL (mmol) of 2,3-dimethylbutadiene in benzene (10 mL) was dropped (1 drop per 5–7 s, corresponding $t_{res.}$ ca. 60 s) through a nearly vertically arranged pyrolysis tube (diameter 2.5 cm, length 40 cm) maintained at 420°C. The condensate was distilled at normal pressure to remove the benzene and then at 50 Torr/88–92°C to yield 1.0 g of colorless liquid, consisting of $HSi(NEt_2)_3$ (60 mol%) and 1-diethylamino-3,4-dimethyl-silacyclopent-3-ene **6a** (40 mol%). ^{1}H NMR (H,H-COSY): $HSi(NEt_2)_3$ δ 1.00 (t, J = 7.0 Hz, CH_3), 2.848 (q, J = 7.0 Hz, CH_2), 4.25 (s, sb, $^1J_{SiH}$ = 227 Hz, rel. int. 35, SiH); **6a** δ 1.01 (t, J = 7.0 Hz, CH_3), 1.39 (m, $4H_{rel}$, $SiCH_2$), 1.72 (br. t, J = 1.1 Hz, $6H_{rel}$, 3,4-Me), 2.85 (q, J = 7.0 Hz, CH_2), 4.60 (pent, sb, J = 2.7, $^1J_{SiH}$ = 200 Hz, rel. int. 20 = $1H_{rel}$, SiH). ^{13}C NMR: $HSi(NEt_2)_3$ δ 14.9, 38.4 (NEt); **6a** δ 15.6, 23.2 (NEt), 19.0 (3,4-Me), 130.3 (3,4-C_q). ^{29}Si NMR: $HSi(NEt_2)_3$ δ −28.2 ($^1J_{SiH}$ = 227 Hz); **6a** δ 0.7 ($^1J_{SiH}$ = 200 Hz).

6a is hydrolyzed in moist $CDCl_3$ to give **6b.** ^{1}H NMR: δ 1.01 (t, J = 7 Hz, CH_3), 1.39 (m, $SiCH_2$), 1.72 (brs, 3,4-Me), 1.44 (m, $SiCH_2$), 2.84 (q, J = 7 Hz, CH_2), 4.96 (pent, sb, J = 1.4, $^1J_{SiH}$ = 213.5 Hz, rel. int. 4, SiH). ^{13}C NMR: δ 15.4, 24.7 (NEt), 19.0 (3,4-Me), 129.8 (3,4-C_q). ^{29}Si NMR: δ 2.5 ($^1J_{SiH}$ = 214 Hz).

1,1-Bis(*diethylamino*)*-3,4-dimethyl-silacyclopent-3-ene* **7.** A 1.1 g (6.1 mmol) amount of 1,1-dichloro-3,4-dimethyl-silacyclopent-3-ene, bp 102°C/100 mbar, obtained by copyrolysis of Si_2Cl_6 with 2,3-dimethylbutadiene at 550°C [16], was dissolved in ether (30 mL) and transformed to **7** by reaction with a solution of diethylamine (2.6 mL, 24.5 mmol) in ether (20 mL). After filtration, 1.0 g (65%) of **7**, bp 120°C/1 Torr, was obtained from the filtrate. ^{1}H NMR: δ 0.98 (t, J = 7 Hz, 12H, CH_3), 1.27 (q, J = 1.1 Hz, 4H, CH_2), 1.70 (t, J = 1.1 Hz, 6H, CH_3), 2.81 (q, J = 7 Hz, 8H, NCH_2). ^{13}C NMR: δ 15.6 (CH_3), 19.4 (3,4-CH_3), 23.4 (CH_2), 40.1 (NCH_2), 130.2 (3,4-C_q). ^{29}Si NMR: δ 3.9.

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