The Structural Chemistry of Aziridino- and Azetidinosilanes☆

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In a continuation of structural investigations of poly(amino)-silanes, a series of silicon derivatives of aziridine and azetidine have been prepared. Analogies with the isoelectronic phosphorus ylide species and the high barrier to inversion at nitrogen in small N heterocycles were suggestive of steeply pyramidal and rather rigid configurations at the N atoms in the title compounds. Tetrakis(*N*-aziridino)silane (**1**) and tetrakis(*N*-azetidino)silane (**2**) have been synthesized from $SiCl_4$ and $LiN(CH_2)_x$ (x = 2, 3). Compound **1** is also formed when $LiN(CH_2)_2$ and $HSiCl_3$ are used as starting materials, but with free aziridine a non-volatile product (**1a**) is obtained. In neither case could any trace of $HSi[N(CH_2)_2]_3$ be detected. In contrast, $RSiCl_3$ (R = Me, Ph) could readily be converted into the corresponding tris(*N*-aziridino)silanes (**3**, **4**) by treatment with excess aziridine. Tris(*N*-azetidino)silane (**5**) was accessible from $HSiCl_3$ and excess azetidine, but the product was found to contain an unknown impurity. In order to determine the local symmetry and the dynamics of the aziridine rings, ^{1}H-NMR spectra were recorded at low temperature (−80°C). No splitting of the signals was observed, indicating that the inversion barriers are extremely low, even in the highly strained three-membered heterocycles. Nevertheless, single-crystal X-ray diffraction studies of the *N*-triphenylsilyl derivatives of aziridine (**6**) and azetidine (**7**) revealed an aziridinyl group with a steeply pyramidal configuration at nitrogen in **6** (sum of the angles at N 313.32°), and an azetidinyl group with a flat geometry in **7** (sum of the angles at N 350.96°). The Si−N bond is significantly shorter in **7** as compared to that in **6**.

Introduction

Aziridine derivatives of *phosphorus* have been extensively studied owing to their widely established application in pharmacology and agriculture.[1][2][3] The most important variants of this usage are based on cyclic phosphazene compounds in which all the phosphorus atoms are exclusively bound to nitrogen. In order to trace the physiological effects to structural parameters, the molecular structures of several representative examples have been investigated.[4][5][6][7][8] *Azetidine* derivatives of *phosphorus* are less well investigated. Only a limited selection of compounds of this family have been described in the literature, for which no comparable chemotherapeutic or agrochemical uses are discernible.[9]

The taxonomy of related *N-silylated aziridines* and *azetidines* is far less developed[10][11] and no systematic investigation has been made of their properties and structural characteristics.[12] This is particularly true for compounds based solely on silicon-nitrogen frameworks, with only one example appearing in the patent literature.[13] Fundamental representatives, such as tetrakis(*N*-aziridino)- or tetrakis(*N*-azetidino)silane (**1**, **2**), have not hitherto been described.

As part of an ongoing investigation of poly(amino)silanes[14][15] we have recently initiated a study of silicon derivatives of aziridine and azetidine, mainly oriented towards a full structural characterization of prototype compounds, and an account of our results is given in the present paper.

Our previous investigations had centered on tetrakis(*N*-pyrrolidino)- and tetrakis(*N*-morpholino)silanes, which are the higher members of the homologous series of *N*-silylated, saturated N-heterocycles, albeit with strain-free five- and six-membered rings, respectively. While these and other standard dialkylaminosilanes typically possess the much debated planar configuration at nitrogen,[14] the aziridine or azetidine substituents are the only analogs where a steeply pyramidal configuration can be expected. This is also suggested by findings for the isoelectronic phosphorus ylide species, which were shown to have pronounced pyramidality at the ylidic carbon atoms of the cyclopropylide and cyclobutylide groups, respectively.[16][17]

In view of the good leaving-group properties of silicon substituents, the silylated heterocycles reported herein are expected to be useful aziridinating/azetidinating agents, which might be employed as substitutes for the rather hazardous free heterocycles.[18][19][20][21]

Results

Preparative Results

Tetrakis(*N*-aziridino)silane (**1**) and tetrakis(*N*-azetidino)-silane (**2**) have been prepared by the reaction of silicon tetrachloride with slightly in excess of four equivalents of the appropriate lithiated heterocycles in diethyl ether at low temperature (−60°C). Compound **1** was obtained as a colorless, distillable liquid, solidifying at 8°C, while the homolog **2** was obtained as a crystalline solid at room temperature, melting at 45°C. All attempts to grow single crystals of **1** and **2** were unsuccessful owing to pertinacious twinning, regardless of the method employed (from the melt, from

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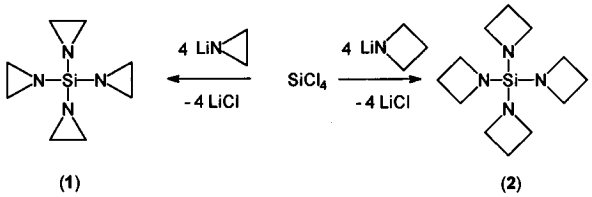
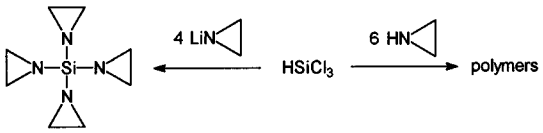
solution or by sublimation). Characterization of the compounds is therefore wholly based on the analytical and spectroscopic data (Experimental Section).



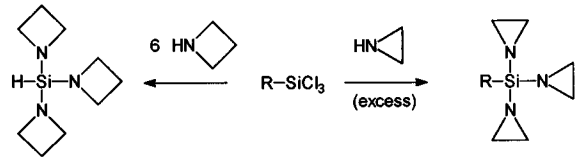
(1) (2)

Compound **1** was also generated in the reaction of *tri*-chlorosilane with lithium aziridinide, probably through an amide-catalyzed redistribution of the substituents [H/Cl/$N(CH_2)_2$] at silicon and/or hydride-induced aziridine ring opening. With $HSiCl_3$ and free aziridine in an organic solvent at −60°C, large amounts of a non-volatile, probably polymeric material were obtained. In neither reaction was any trace of the expected compound $HSi[N(CH_2)_2]_3$ detected.



(1) (1a)

Trichloro(*methyl-* and *-phenyl*)silane are readily converted to the corresponding tris(*N*-aziridino)silanes (**3**, **4**) upon treatment with excess aziridine.

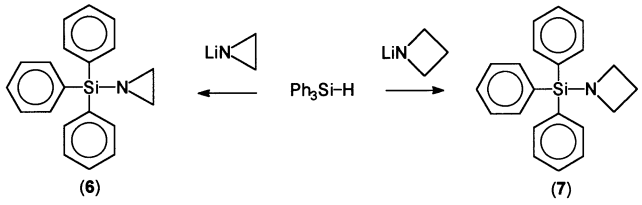


R = H (**5**) R = CH_3 (**3**)

Ph (**4**)

Tris(*N*-azetidino)silane (**5**) could be prepared from $HSiCl_3$ and excess azetidine, but purification of the product was not fully satisfactory. The analytical data seemingly indicate a rather pure product, but the values given in the Experimental Section nevertheless refer to a compound containing an unknown impurity. The MS and NMR data can be interpreted in terms of the presence of two isomers $\{HSi[N(CH_2)_3]_3\}_n$, but the nature of these isomers is not clear. Dimerization by azetidine ring-opening appears to be the most likely possible process.[22]

Because no poly(*N*-aziridino)- or poly(*N*-azetidino)silanes proved amenable to the growth of single crystals for structure determination, the *N-triphenylsilyl derivatives of aziridine* (**6**) and *azetidine* (**7**) were also prepared. Compound **6** has previously been synthesized from triphenylsilane, aziridine and alkali metals as catalysts in a dehydrocondensation reaction.[23] In the present study, **6** and **7** were obtained by the reaction of triphenylsilane with the appropriate lithiated heterocycles.



(6) (7)

Both compounds could be obtained in pure form, and single crystals of acceptable quality were readily grown from their solutions [m.p. 104°C (**6**), 86°C (**7**)].

NMR Spectroscopy

Assignment of the general patterns of the $^{29}Si\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectra of the new silanes was largely straightforward. Regarding the ^1H-NMR spectra, however, the aspects of local symmetry of the aziridine rings and their dynamics have to be considered: A flat configuration at nitrogen, or a rapid inversion at this atom, would render the hydrogen atoms above and below the ring equivalent [(virtual) local symmetry with two perpendicular mirror planes, point group C_{2v} (on the NMR time scale)], while a rigid pyramidal configuration or a very slow inversion requires non-equivalent hydrogen atoms at the CH_2 groups (point group C_S). This also applies to the azetidine homologs, where additionally a flexible puckering of the four-membered ring has to be taken into account.

All compounds investigated in the present study exhibit only singlet ^1H resonances for the aziridine rings or show only multiplets characteristic of C_{2v}-symmetrical azetidine rings in solution at room temperature. Because it is implausible to assume a fully planar ground state for the aziridine/azetidine nitrogen atom, this result indicates a low barrier to nitrogen inversion. It is even more surprising that the pseudo-symmetry of the aziridinyl and azetidinyl groups is retained at temperatures as low as −80°C in all cases. This is in contrast to the "rigidity" of other simple organic derivatives of these heterocycles, which were found to have much higher barriers to inversion.[24] It therefore appears that the presence of silicon as the N-substituent atom has a marked effect on the inversion energetics. As found for other pairs of alkyl- and silylamines, even for strained small-ring amines, there is clearly a very significant lowering of the energy of the transition state for inversion.

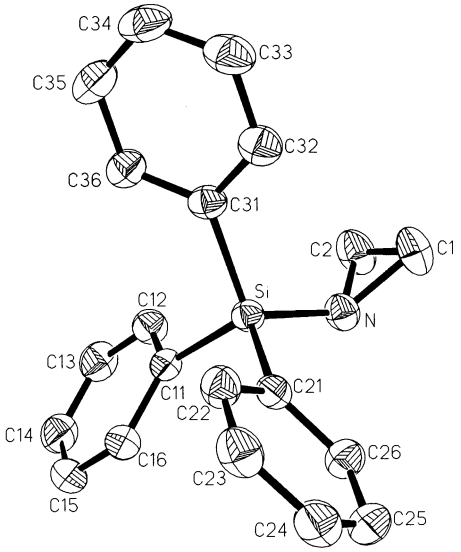
Unfortunately, the coalescence/splitting temperature of the signals of the hydrogen atoms above and below the ring planes could not be attained, and therefore the energy of activation can only be estimated. Assuming chemical shift differences $\Delta\delta$ of less than 1 ppm, the barrier must be lower than 8.5 (± 2.5) kcal/mol, and is thus less than half of that determined for *N*-alkyl- or *N*-arylaziridines.[24] When evaluating this result it should be kept in mind that for unstrained tri-, di- and monosilylamines, completely flat ground-state geometries were found experimentally, and that state-of-the-art theoretical calculations have confirmed this unusual geometry and predict extremely flat energy profiles for pyramidalization.[14][15] This general pattern is

still reflected in the most strained example of the silylaziridines.

Crystal Structures

Crystals of *N-triphenylsilylaziridine* (**6**) are triclinic, space group $P\bar{1}$ with $Z = 2$ formula units in the unit cell. The molecules have no crystallographically imposed symmetry owing to a propeller-type arrangement of the three phenyl groups at silicon (Figure 1).

Figure 1. Molecular structure of compound **6** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity)[a]

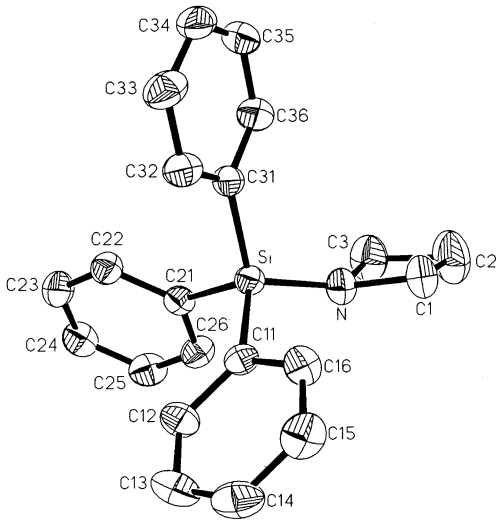


[a]Selected bond lengths [Å] and angles [°]: Si−N 1.7308(11), Si−C11 1.8658(13), Si−C21 1.8655(14), Si−C31 1.8744(13), N−C1 1.462(2), N−C2 1.456(2), C1−C2 1.470(2); N−Si−C11 105.94(6), N−Si−C21 105.81(6), N−Si−C31 114.28(6), C11−Si−C21 111.74(6), C11−Si−C31 109.59(6), C21−Si−C31 109.44(6), Si−N−C1 127.16(10), Si−N−C2 124.63(10), C2−N−C1 60.48(10), N−C1−C2 59.55(9), C1−C2−N 59.97(9).

The most important result of this structure determination is the geometry of the aziridinyl group, with its steeply pyramidal configuration at nitrogen. The plane of the three-membered ring forms an angle of 132.8° with the Si−N vector, and the sum of the angles at nitrogen amounts to only 312.3°. The conformation of the molecule with regard to the relative orientation of the $SiPh_3$ group and the $N(CH_2)_2$ unit, with its lone pair of electrons at the nitrogen atom, is staggered. The phenyl group *trans* to the lone pair at N has the largest N−Si−C angle [N−Si−C31 = 114.28(6)°]. The two remaining N−Si−C angles are almost equal, with individual values of N−Si−C11 = 105.94(6)° and N−Si−C21 = 105.81(6)°. The silicon atoms thus adopt a distorted tetrahedral geometry with bond lengths Si−N and Si−C in the range expected for standard single bonds (captions to Figure 1 and Table 1). The dimensions of the aziridine ring are also not unusual.

Crystals of *N-triphenylsilylazetidine* (**7**) are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The molecules have no crystallographically imposed symmetry because of an adverse orientation of the phenyl rings at silicon (Figure 2).

Figure 2. Molecular structure of compound **7** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity)[a]



[a]Selected bond lengths [Å] and angles [°]: Si−N 1.7059(14), Si−C11 1.871(2), Si−C21 1.869(2), Si−C31 1.873(2), N−C1 1.481(2), N−C3 1.477(2), C1−C2 1.523(3), C2−C3 1.522(3); N−Si−C11 107.79(7), N−Si−C21 107.03(7), N−Si−C31 113.54(7), C11−Si−C21 109.74(7), C11−Si−C31 107.48(7), C21−Si−C31 111.17(7), Si−N−C1 127.63(11), Si−N−C3 131.76(12), N−C1−C2 89.6(2), C1−C2−C3 88.3(2), C2−C3−N 89.7(2), C3−N−C1 91.60(14).

The nitrogen atom of the azetidinyl group has a rather flattened pyramidal configuration, which can be quantified by the angle between the plane through the atoms N, C1 and C3 and the Si−N vector (156.2°), and by the sum of the angles at nitrogen (351.0°). As expected, the geometry at the nitrogen in **7** is much closer to planar than at that in **6**, but is nevertheless still distinctly non-planar.

The azetidine is folded, with an angle of 170.3° between the planes N−C1−C3 and C1−C2−C3, representing a flat butterfly structure. As in compound **6**, the conformation of the molecule is staggered with a wide angle N−Si−C31 = 113.54(7)° and two very similar angles for N−Si−C11 [107.79(7)°] and N−Si−C21 [107.03(7)°]. The bond lengths at silicon and in the four-membered ring show no anomalies (captions to Figure 2 and Table 1). It should be noted, however, that the Si−N bond is significantly shorter in **7** as compared to that in **6**, while there are no differences in the Si−C bond lengths. This difference may reflect a strengthening of the Si−N bond as the geometry at nitrogen is flattened, in agreement with the traditional concept of (p−d)π bonding, which, although now widely abandoned, is also consistent with the presently accepted (p−σ*)π model.[25]

Discussion and Conclusions

The structural investigations of a silylaziridine and of a silylazetidine have provided valuable reference data for a comparison with the isoelectronic phosphonium ylides.[16][17] From Table 1, it appears that the lattices of neither of the two pairs of compounds are isomorphous, but that the individual molecules share the same structural motifs with regard to the configuration at the functional atom

(nitrogen and ylidic carbanion, respectively) and the conformation. In the staggered rotamers, the lone pair of electrons at N or C is clearly "stereochemically active" and co-determines the overall structure. However, the carbanions show more pronounced pyramidalization than the amine nitrogen atoms and give rise to large deviations of the phosphorus atoms from the plane of the heterocycle. This is strong evidence for the "ylide" model of bonding with a highly polar P−C function, which should definitely be favored over the "ylene" form with P=C multiple bonding. For $Ph_3PC(CH_2)_2$, the non-equivalence of the hydrogen atoms above and below the cyclopropane plane could be demonstrated by a splitting of the ^{1}H-NMR resonances in solution at −80°C. For $Ph_3SiN(CH_2)_2$, this low-temperature limit was not sufficient to observe the same phenomenon, which indicates that the silylamine is more flexible than the phosphonium ylide.

The comparatively flat geometries of the silylaziridine and the silylazetidine are probably a consequence of the much greater difference in electronegativity of silicon and nitrogen (relative to phosphorus and carbon), which makes an Si−N linkage a strongly polar bond. The energy profile of such inherently polar bonds has been correctly predicted to be rather insensitive e.g. to deformations of bond angles,[26] and this is borne out by the present family of silazanes with their enormous flexibility: Although the ground-state geometries are rather steep, the activation energies for inversion at nitrogen are still sufficiently low to make these molecules fluxional on the NMR time-scale (see above).

It has been noted previously in theoretical studies of phosphonium cyclopropylides, as well as of silylamines, that inversion at carbon or nitrogen, respectively, has to be accompanied by P−C/Si−N bond rotation in order to regenerate the ground-state geometry.[27] This should be a minor contribution as compared to inversion, however, because rotation about Si−N and P−C bonds is known to be associated with very low barriers indeed, generally not in excess of 1 kcal/mol.

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Experimental Section

All experiments were carried out under dry, pure nitrogen. Solvents and glassware were treated accordingly. Standard equipment was used throughout. Aziridine[28] and azetidine[29] were prepared according to literature procedures. Due to the method of preparation, the sample of azetidine contained benzene, which was quantified by ^{1}H-NMR spectroscopy. All other starting materials were commercially available. − NMR: Jeol GX 400 and Jeol GX 270, solutions in C_6D_6 at 23°C unless otherwise stated. − MS: GC/MS with mass-selective detector HP 5971 A (EI, 70 eV) and MAT 311 A (EI, 70 eV). − IR: Perkin-Elmer 1650 FT-IR.

Lithium Amides: In a typical reaction, *n*-butyllithium (1.7 M in hexane) was added dropwise to a solution of aziridine or azetidine in diethyl ether at −60°C. The reaction mixture was allowed to warm to room temperature and was stirred for 0.5 h. Then, the suspension was cooled to −60°C once more and used immediately in the subsequent reactions.

Tetrakis(N-aziridino)silane (**1**): A solution of silicon tetrachloride (0.86 ml, 7.5 mmol) or trichlorosilane (1.00 ml, 10 mmol) in 20 ml of diethyl ether was added dropwise to a suspension of lithium aziridinide [35 mmol, from 2.00 ml (39 mmol) of aziridine and 20.6 ml (35 mmol) of a 1.7 M solution of *n*-butyllithium in hexane] in 50 ml of diethyl ether at −60°C. After stirring the reaction mixture at room temperature for 15 h, the precipitate was separated, the solvent was removed from the filtrate in vacuo, and the remaining residue was extracted with pentane. **1** was separated from the extract by distillation (30°C, 0.05 mbar). Colorless liquid, 0.93 g (63%), m.p. 8°C. − ^{1}H NMR: δ = 1.77 (s, 24 H, CH_2). − ^{1}H NMR ([D$_8$]toluene, 23°C): δ = 1.73 (s, 24 H, CH_2). − ^{1}H NMR ([D$_8$]toluene, −80°C): δ = 1.77 (s, 24 H, CH_2). − ^{13}C{^{1}H} NMR: δ = 19.8 (CH_2). − ^{13}C NMR ([D$_8$]toluene, 23°C): δ = 19.6 (CH_2). − ^{29}Si{^{1}H} NMR: δ = −24.6. − ^{29}Si NMR: δ = −24.6 (m, $^3J_{Si,H}$ = 5 Hz). − ^{29}Si NMR ([D$_8$]toluene, 23°C): δ = −24.4 (m, $^3J_{Si,H}$ = 5 Hz). − ^{29}Si NMR ([D$_8$]toluene, −80°C): δ = −22.9 (m, br.). − ^{15}N NMR: δ = −390.2 (quint, $^2J_{N,H}$ = 2 Hz). − MS (EI, 70 eV) *m/z*: 196 [M$^+$], 154 [M$^+$ − $N(CH_2)_2$], 112 [154 − $N(CH_2)_2$], 70 [112 − $N(CH_2)_2$]. − IR (film): $\tilde{\nu}$ = 3041 m (ν NC_2H_4), 2983 m, 2900 m, 1276 s, 945 s, 683 s. − $C_{12}H_{24}N_4Si$ (196.32): calcd. C 48.9, H 8.2, N 28.5; found C 49.2, H 7.9, N 29.1.

Reaction of Trichlorosilane with Aziridine as Free Base (**1a**): 6 equiv. of aziridine (3.07 ml, 60 mmol) in 20 ml of diethyl ether was added dropwise to a solution of trichlorosilane (1.00 ml, 10 mmol) in 50 ml of diethyl ether at −60°C over a period of 15 min. After the reaction mixture had warmed to room temperature, stirring was continued for 1 h. The suspension was then filtered, the solvent was removed in vacuo, and a sample was prepared in C_6D_6 for NMR spectroscopy. − ^{1}H NMR: δ = 2.74 (m), 3.04 (m). − ^{13}C{^{1}H} NMR: δ = 42.7, 47.8. − ^{29}Si{^{1}H} NMR: δ = −34.6.

Tetrakis(N-azetidino)silane (**2**): A solution of silicon tetrachloride (0.22 ml, 2.0 mmol) in 10 ml of diethyl ether was added dropwise over a period of 5 min to a suspension of lithium azetidinide [10 mmol, from 2.00 ml (14.6 mmol) of a solution of azetidine, containing 42 mol-% of benzene and 5.9 ml (10 mmol) of a 1.7 M solution of *n*-butyllithium in hexane] in 50 ml of diethyl ether at −60°C. After stirring the reaction mixture at room temperature for 10 h, the precipitate was separated, the solvent was removed from the filtrate in vacuo, and the remaining residue was purified by distillation (40°C, 0.05 mbar). The crude product was crystallized from pentane at −60°C. Colorless crystals, 0.18 g (36%), m.p. 45°C. − ^{1}H NMR: δ = 2.24 (quint, 8 H, $^3J_{H,H}$ = 7 Hz, CCH_2), 3.94 (t, 16 H, $^3J_{H,H}$ = 7 Hz, NCH_2). − ^{13}C{^{1}H} NMR: δ = 21.8 (CCH_2), 49.4 (NCH_2). − ^{29}Si{^{1}H} NMR: not detected. − MS (EI, 70 eV) *m/z*: 252 [M$^+$], 196 [M$^+$ − $N(CH_2)_3$], 140 [196 − $N(CH_2)_3$].

Tris(N-aziridino)methylsilane (**3**): To a solution of trichloro(methyl)silane (1.17 ml, 10 mmol) in 50 ml of diethyl ether, 6 equiv. of aziridine (3.07 ml, 60 mmol) in 20 ml of diethyl ether was added dropwise over a period of 15 min at −60°C. After stirring for 20 h at room temperature, the reaction mixture was filtered and the solvent was removed in vacuo. The remaining oil was purified by distillation (50°C, 0.05 mbar). Colorless liquid, 1.12 g (66%). − ^{1}H NMR: δ = 0.11 (s, 3 H, CH_3), 1.70 (s, 12 H, CH_2). − ^{13}C{^{1}H} NMR: δ = −7.9 ($SiCH_3$), 19.7 (CH_2). − ^{29}Si NMR: δ = −4.5. − MS (EI, 70 eV) *m/z*: 169 [M$^+$], 127 [M$^+$ − $N(CH_2)_2$], 85 [127 − $N(CH_2)_2$]. − $C_7H_{15}N_3Si$ (169.30): calcd. C 49.7, H 8.9, N 24.8; found C 49.0, H 8.8, N 25.5.

Tris(N-aziridino)phenylsilane (**4**): Analogously to the preparation of **3**, **4** was prepared from 1.60 ml (10 mmol) of trichloro(phenyl)silane and 3.58 ml (70 mmol) of aziridine. After purification by distillation (100°C, 0.05 mbar), a colorless liquid was obtained. Yield 1.27 g (55%). − ^{1}H NMR: δ = 1.76 (s, 12 H, CH_2), 7.21 (m, 3 H, 3/4/5-H), 7.79 (m, 2 H, 2/6-H). − ^{13}C{^{1}H} NMR: δ = 20.1 (CH_2), 127.8 (C-2/6), 130.3 (C-4), 132.2 (C-3/5), 134.7 (C-1). − ^{29}Si{^{1}H} NMR: δ = −19.0. − MS (EI, 70 eV) *m/z*: 231 [M^+], 189 [$M^+ - N(CH_2)_2$]. − $C_{12}H_{17}N_3Si$ (231.37): calcd. C 62.3, H 7.4, N 18.2; found C 61.8, H 7.5, N 17.6.

Tris(N-azetidino)silane (**5**): To a solution of 7 equiv. of azetidine (2.00 ml of a solution of azetidine containing 42 mol-% of benzene, 14.6 mmol) in 50 ml of diethyl ether, trichlorosilane (0.20 ml, 2 mmol) in 10 ml of diethyl ether was added dropwise over a period of 15 min at −60°C. After the reaction mixture had warmed to room temperature, stirring was continued for 1 h. After filtration, the solvent was removed in vacuo and the remaining oil was distilled (100°C, 0.05 mbar) to give a colorless liquid. Yield 0.11 g (28%). − ^{1}H NMR: δ = 2.17 (quint, 6 H, $^3J_{H,H}$ = 7 Hz, CCH_2), 3.80 (t, 12 H, $^3J_{H,H}$ = 7 Hz, NCH_2), 4.36 (s, 1 H, SiH). − ^{13}C{^{1}H} NMR: δ = 21.9 (CCH_2), 48.7 (NCH_2). − ^{29}Si NMR: δ = −39.0 (d, $^2J_{Si,H}$ = 148 Hz). − MS (EI, 70 eV) *m/z*: 197 [M^+], 141 [$M^+ - N(CH_2)_3$], 85 [141 − $N(CH_2)_3$].

(N-Aziridino)triphenylsilane (**6**): A solution of triphenylsilane (1.04 g, 4 mmol) in 20 ml of diethyl ether was added dropwise to a suspension of lithium aziridinide [10 mmol, from 0.82 ml (16 mmol) of aziridine and 6.00 ml (10 mmol) of a 1.7 M solution of *n*-butyllithium in hexane] in 50 ml of diethyl ether at −60°C. After stirring the reaction mixture at room temperature for 15 h, the precipitate was separated, the solvent was removed from the filtrate in vacuo, and the remaining solid was extracted with pentane. **6** crystallized from this solution at 0°C. Colorless crystals, 1.48 g (61%), m.p. 104°C. − ^{1}H NMR: δ = 1.69 (s, 4 H, NCH_2), 7.20 (m, 9 H, 3/4/5-H), 7.77 (m, 6 H, 2/6-H). − ^{13}C{^{1}H} NMR: δ = 21.0 (NCH_2), 128.1 (C-2/6), 130.0 (C-4), 134.3 (C-3/5), 136.0 (C-1). − ^{29}Si{^{1}H} NMR: δ = −9.1. − MS (EI, 70 eV) *m/z*: 301 [M^+], 259 [$M^+ - N(CH_2)_2$], 182 [259 − C_6H_5], 105 [182 − C_6H_5]. − $C_{20}H_{19}NSi$ (301.46): calcd. C 79.7, H 6.4, N 4.7; found C 79.5, H 6.5, N 4.5.

(N-Azetidino)triphenylsilane (**7**): To a suspension of lithium azetidinide [5 mmol, from 1.00 ml (8 mmol) of a solution of azetidine containing 28 mol-% of benzene and 3.00 ml (5 mmol) of a 1.7 M solution of *n*-butyllithium in hexane] in 50 ml of diethyl ether, a solution of triphenylsilane (1.04 g, 4 mmol) in 20 ml of diethyl ether was added dropwise at −60°C. After stirring the reaction mixture at room temperature for 15 h, the precipitate was separated, and the filtrate was concentrated in vacuo. From this solution, compound **7** crystallized at −30°C. Colorless crystals, 0.61 g (48%), m.p. 86°C. − ^{1}H NMR: δ = 2.12 (quint, 2 H, $^3J_{H,H}$ = 7 Hz, CCH_2), 3.83 (t, 4 H, $^3J_{H,H}$ = 7 Hz, NCH_2), 7.21 (m, 9 H, 3/4/5-H), 7.71 (m, 6 H, 2/6-H). − ^{13}C{^{1}H} NMR: δ = 21.4 (CCH_2), 49.8 (NCH_2), 128.1 (C-2/6), 129.8 (C-4), 135.4 (C-3/5), 136.0 (C-1). − ^{29}Si{^{1}H} NMR: δ = −17.9. − MS (EI, 70 eV) *m/z*: 315 [M^+], 259 [$M^+ - N(CH_2)_3$], 182 [259 − C_6H_5], 105 [182 − C_6H_5]. − $C_{21}H_{21}NSi$ (315.49): calcd. C 80.0, H 6.7, N 4.4; found C 79.3, H 6.8, N 4.4.

Crystal Structure Determinations: Specimens of compounds **6** and **7** of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf-Nonius CAD4 diffractometer [Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å]. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. The structures were solved by direct methods (SHELXS-86)[30] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93)[31]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms of compounds **6** and **7** were found and refined with isotropic contributions. Further information on crystal data, data collection and structure refinement is summarized in Table 1. Selected interatomic distances and angles are given in the corresponding figure captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany. The data are available on request on quoting the depository numbers CSD-407949 (**6**) and CSD-407950 (**7**).

Table 1. Crystal data, data collection and structure refinement for compounds **6** and **7**

	6	**7**
crystal data		
formula	$C_{20}H_{19}NSi$	$C_{21}H_{21}NSi$
M_r	301.45	315.48
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [Å]	8.640(2)	10.923(1)
b [Å]	9.812(2)	8.468(1)
c [Å]	10.858(2)	19.255(3)
α [°]	65.55(3)	90
β [°]	89.01(3)	100.17(1)
γ [°]	83.13(3)	90
V [Å^{-3}]	831.4(3)	1753.0(4)
$D_{calcd.}$ [g cm^{-3}]	1.204	1.195
Z	2	4
F(000) [e]	320	672
μ (Mo-K_a) [cm^{-1}]	1.37	1.33
data collection		
T [°C]	−74	−80
scan mode	ω-θ	ω-θ
hkl ranges	0→+11	−13→+13
	−12→+12	0→+10
	−13→+13	0→+23
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.64	0.64
measured refl.	3612	3524
unique refl.	3612	3428 (R_{int} = 0.0235)
refl. used for refinement	3610	3425
absorption correction	none	none
structure refinement		
refined parameters	275	292
H atoms (found)	19	21
final *R* values [$I > 2\sigma(I)$]:		
*R*1[a]	0.0339	0.0351
*wR*2[b]	0.0907	0.0878
$(\text{shift/esd})_{max}$	< 0.001	< 0.001
$\Delta\rho_{fin}$(max/min) [eÅ^{-3}]	+0.382/−0.228	+0.353/−0.227

[a] $R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma|F_o|$. − [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0518 (**6**), 0.0466 (**7**); b = 0.2096 (**6**), 0.6142 (**7**).

☆ Dedicated to Professor *M. Weidenbruch* on the occasion of his 60th birthday.

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