Synthetic and Structural Studies of 1-Sila-2,5-diaryltetrazenes

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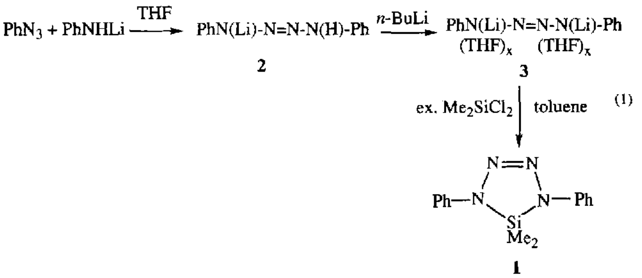
The reaction between aryl azides and lithiated aryl amines leads to tetrazenes **3** and **9** which contain a chain of four nitrogen atoms. Reaction with different halosilanes gives the cyclic silatetrazenes **10**, **12**, and **15** where substitutents on the silicon vary from alkyl to hydrogen and chlorine atoms. The structures of **10**, **12**, and **15** in the solid state are reported. Variation of the solvent and the Lewis acidity of the halosilane influence the ratio of silatetrazene to side products, bissilylated amines. These effects are studied for different halosilanes.

Introduction

1-Silatetrazenes are five-membered ring compounds containing a chain of four nitrogen atoms and one silicon. In 1989 Trogler et al. described the synthesis of the 1,1-dimethylsila-2,5-diphenyltetrazene **1**[1][2]. Its four-membered nitrogen chain is formed in a coupling reaction between phenyl azide and lithium anilide (eq. 1).

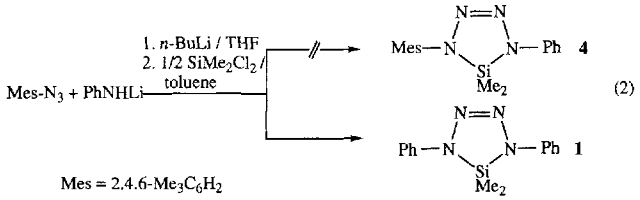


Our interest lay in the synthesis of further silatetrazenes. Variation of the aryl group bonded to the nitrogen and their effects on the coupling reaction and reactivity of the silicon atom was another aspect of our investigation. We herein report the synthesis and characterization of different silatetrazenes as well as their X-ray crystal structures, and the solid-state ^{29}Si-NMR spectrum of one of them.

Results

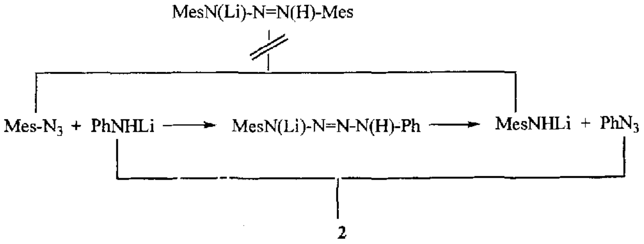
1. Reactions of Mesityl Azide

In an attempt to synthesize precursors for possible further reactions on the ring silicon atom, a bulky substituent like the mesityl group was chosen in the first step. However, no coupling product was found in the reaction between mesitylazide[3] and lithium mesitylamide. Addition of lithium anilide to the mesitylazide led to the formation of a yellow, very air-sensitive salt that appeared to be very similiar to compound **3**, described by Trogler et al.[1]. In fact, addition of dimethyldichlorosilane to the reaction mixture led to **1** instead of **4** (eq. 2).



Therefore the reaction proceeds with loss of the mesityl group. Examination of the mother liquor by NMR gave evidence for the presence of mesityl amine after addition of the azide to lithium anilide. The following reaction mechanism was postulated (Scheme 1).

Scheme 1. Mechanism for the formation of **3**



$SiCl_4$ does not react with **3** under the conditions described above to give the dichloro compound **6**, but to yield **7** (eq. 3). Bis(dimethylchlorosilyl)amine, analogous to **7**, was also identified as a side product by Trogler et al.[2]. It is formed in a decomposition reaction of the silyl substituted monolithiumtetrazene **5**, postulated as an intermediate,

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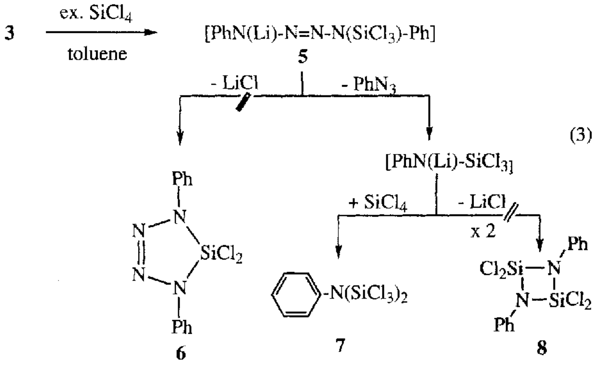
with loss of one molecule of azide (eq. 3). The second expected side product **8** was not observed.



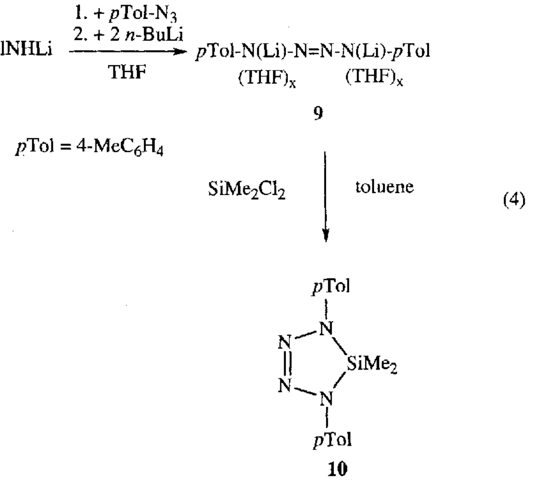
(3)

Due to the mechanism the total yield for reactions between mesityl azide and lithium anilide is limited to a maximum of 50%. Therefore variation of the aryl group was necessary.

2. Reactions of *para*-Tolylazide

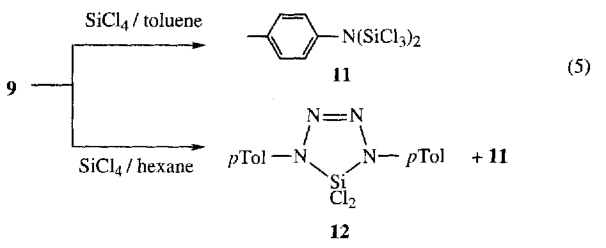
Since reactions of *ortho*-tolylazide[3] and lithium *ortho*-tolylamide did not lead to cyclic silatetrazenes but to bissilylated *ortho*-tolylamine, the steric hindrance around the nitrogen atoms of azide and amide was reduced further by using the *para*-tolyl substituent.

In the coupling reaction of *para*-tolylazide[3] and lithium *para*-tolylamide to **9** followed by addition of dimethyldichlorosilane in toluene the silatetrazene **10** was isolated (eq. 4).



(4)

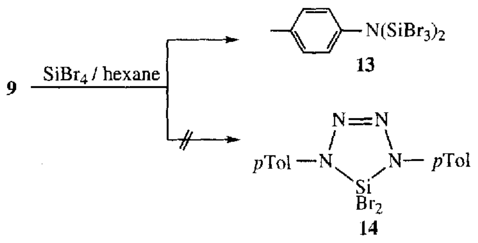
However, addition of $SiCl_4$ to **9** in toluene gave the bis(trichlorosilyl)amine **11** (eq. 5). The desired dichlorosilatetrazene **12** was identified by NMR in the crude product only in very low yield and could not be isolated.



(5)

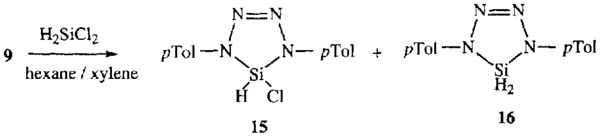
As described above, the formation of **11** is caused by cleavage of the monosilylated intermediate of a tetrazene. This reaction path is favored by polar solvents[2]. Therefore the reaction between $SiCl_4$ and **9** was repeated in hexane. The very small difference of polarity between the two solvents is of importance since the reaction proceeded in hexane led to formation of **12** which precipitates from the concentrated mother liquor and can be recrystallized from hexane (eq.5).

Besides the above described effect of the solvent on the formation of silatetrazenes the Lewis acidity of the halosilane is of further importance. Reaction of $SiCl_4$ with **9** mainly leads to **12**, but **11** forms as a side product (eq. 5). In contrast to this, use of $SiBr_4$ under the same reaction conditions leads exclusively to the formation of the bis(tribromosilyl)amine **13**. (eq. 6). We believe that the higher Lewis acidity of $SiBr_4$ results in a more polarized silylated intermediate than in the case of the chlorosilane, favoring decomposition to **13** and resulting in the complete absence of **14**.



(6)

Since the effects described above are diminished by alkyl- or hydrosilanes the reaction between **9** and H_2SiCl_2 was of interest. As shown in eq. 7 two different silatetrazenes **15** and **16** are formed.



(7)

15 precipitates from the concentrated mother liquor and can be recrystallized from hexane while **16** was characterized in solution.

3. Crystal Structures of Silatetrazenes 10, 12, and 15

Crystallographic and refinement data as well as selected bond lengths and angles for **10**, **12**, and **1** are given in Tables 1 and 2. The solid state structures are very similar; a thermal ellipsoid diagram of the molecular structure of **10** is shown in Figure 1 as a representative example. All three compounds crystallize in monoclinic space groups: *Pn* (**10**), $P2_1/c$ (**12**), and $P2_1/n$ (**15**). Bond lengths and angles vary somewhat depending on the substituents at the ring silicon atom. The aryl groups are twisted out of the plane of the planar central five-membered ring. The torsion angle between the rings varies depending on the substituent at the silicon atom: [N(3)−N(2)−C(3)−C(8): −37.0° (**10**), −31.7° (**12**), 4.2° (**15**)]. Due to less steric hindrance at the silicon atom the torsion angle for **15** is significantly smaller than

Table 1. Crystal data, data collection and structure refinement for compounds **10**, **12** and **15**

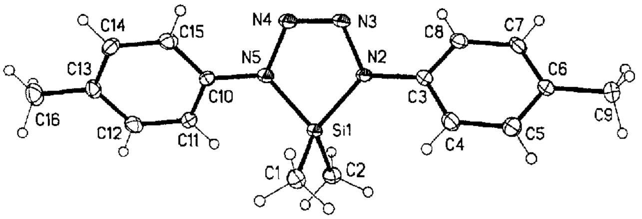
	10	**12**	**15**
Crystal data			
Empirical formula	$C_{16}H_{20}N_4Si$	$C_{14}H_{14}C_{l2}N_4Si$	$C_{14}H_{15}ClN_4Si$
M_r	296.45	337.28	302.84
Crystal System	monoclinic	monoclinic	monoclinic
Space group	*Pn*	$P2_1/c$	$P2_1/n$
Cryst. Dim. [mm]	0.46 × 0.44 × 0.24	0.56 × 0.32 × 0.24	0.58 × 0.46 × 0.32
a [Å]	10.6131(2)	5.7838(2)	9.8176(5)
b[Å]	5.9282(2)	10.5760(2)	8.5215(4)
c [Å]	12.5822(4)	25.5935(2)	17.2852(7)
α [°]	90	90	90
β [°]	97.208(2)	91.034(2)	92.488(2)
γ [°]	90	90	90
V [Å^3]	785.37(4)	1565.29(6)	1444.73(12)
ρ_{calc} [gcm^{-3}]	1.254	1.431	1.392
Z	2	4	4
Data collection			
Diffractometer	Siemens P4/CCD		
Radiation	Mo-K_α, 0.71073 Å, graphite monochromator		
θ range	2.37 to 28.05°	1.59 to 28.12°	2.34 to 28.34
hkl range	−6/13, ±7, −10/15	±7, −13/8, −26/33	−11/13, −7/10, −9/22
T [K]	133(2)	133(2)	133(2)
Collected refl.	3490	7567	5772
Independent refl.	1823	3354	3156
Used refl.	1823	3354	3156
Refinement			
Refined parameters	190	190	182
*R*1[a]	0.0373	0.0287	0.0602
*wR*2[a]	0.1022	0.0819	0.1797
ρ_{fin} (max/min) [eÅ^{-3}]	0.275 / −0.364	0.282 / −0.264	0.520 / −0.449

[a] $R1 = \Sigma (F_o - F_c)/\Sigma F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0644\ P)^2 + 0.0521\ P]$; $P = [F_o^2 + 2\ F_c^2]/3$.

Table 2. Selected bond lengths [Å] and angles [°] for compounds **10**, **12**, and **15**

	10	**12**	**15**
Si(1)−N(2)	1.758(2)	1.725(1)	1.726(3)
Si(1)−C(1)	1.849(3)	–	–
Si(1)−Cl(1)	–	2.0383(5)	2.0451(13)
N(2)−N(3)	1.394(3)	1.403(2)	1.392(4)
N(3)−N(4)	1.279(3)	1.275(2)	1.261(4)
N(2)−C(3)	1.420(3)	1.435(2)	1.415(4)
N(2)−Si(1)−N(5)	85.15(11)	88.19(6)	87.03(13)
Si(1)−N(2)−N(3)	114.0(2)	112.20(9)	112.7(2)
N(2)−N(3)−N(4)	113.6(2)	113.67(12)	113.8(3)
C(3)−N(2)−Si(1)	130.1(2)	132.34(10)	129.3(2)
N(3)−N(2)−C(3)	115.8(2)	115.36(12)	117.4(3)
N(2)−Si(1)−C(1)	118.12(12)	–	–
N(2)−Si(1)−Cl(1)	–	115.10(5)	113.79(11)
C(1)−Si(1)−C(2)	108.90(14)	–	–
Cl(1)−Si(1)−Cl)2)	–	104.90(2)	

Figure 1. Molecular structure of **10** with atomic numbering; displacement ellipsoids were drawn at the 50% probability level. The structures of **12** and **15** are very similar. Selected bond lengths and angles are given in Table 2.



for **10** and **12**. The silicon−nitrogen bond lengths are in the range typical for silicon−nitrogen single bonds. **10** shows a slightly longer silicon−nitrogen bond [Si(1)−N(2): 1.758 Å] than for **12** (1.725 Å) and **15** (1.726 Å). This might be due to the presence of chlorine atoms on the silicon in **12** and **15** which intensifies the p−σ* back bonding between nitrogen and silicon. In addition the bulkier methyl groups could cause stretching of the silicon−nitrogen bond. In accord with the longer bond the N(2)−Si(1)−N(5) angle decreases from 88.19° (**12**) and 87.03° (**15**) to 85.15° (**10**). The interatomic distances between the ring nitrogen atoms are consistent with single bonds for the N(2)−N(3) and N(4)−N(5) bond [N(2)−N(3): 1.394 (**10**), 1.403 (**12**), 1.392 Å (**15**)]. The N(3)−N(4)-bond [1.279 (**10**), 1.275 (**12**), 1.261 Å (**15**)] corresponds to a double bond and lies in the same range as described for the silatetrazene **1** by Trogler et al.[2]. The nitrogen atoms have a trigonal planar environment where the angle at N(2) and N(5) between the bonding carbon atom of the aryl group and the silicon atom is widened [Si(1)−N(2)−C(3): 130.1 (**10**), 132.34 (**12**), 129.3° (**15**)]. The ring silicon atom has a tetrahedral environment in all three compounds.

4. Silicon-29 Solid-State NMR of Silatetrazene 10

The chemical shift of a particular nucleus in the solid state depends on the orientation of the molecule in the external magnetic field. NMR spectra of stationary powder samples result in broad line shapes; however, magic angle spinning of the sample gives line narrowing and in the case of spinning frequencies lower than the total width of the powder pattern, spinning side bands flanking the isotropic peak[4], from which the principal values of the chemical shift tensor can be obtained[5]. The ^{29}Si-CPMAS NMR spectra of **10** was determined at 59.6 MHz and analyzed using the Herzfeld-Berger[5] method, yielding the principal values of the chemical shift tensor, δ_{11} = 67.6, δ_{22}= −0.4, and δ_{33}= −83.3. The isotropic chemical shift in the solid, −5.4 ppm, corresponds to that found in solution, 5.43 ppm. The span of the chemical shift tensor, Ω = 150.9 ppm, is large for tetrahedral silicon and therefore indicates considerable asymmetry in the charge distribution around the silicon atom.

Theoretical ab initio calculations[6] on the model silatetrazene with methyl substituents at silicon and nitrogen gave tensor values δ_{11} = 58.4, δ_{22}= −21.4, and δ_{33}= −76.9, in rather good agreement with the experimental values for **10**. The least shielded axis, δ_{11}, is the in-plane C_2 axis bisecting the N=N bond, and the most shielded axis is the one perpendicular to the ring. The rather large value of Ω may, in part, be due to ring strain and compression of the N−Si−N bond angle in **10**, but measurements and calculations on other compounds are needed before firm conclusions can be drawn[7].

Conclusion

The present studies show that silatetrazenes with different substituents, especially halosilatetrazenes, can be synthesized. However, variation of the aryl substituent on the nitrogen atoms is limited due to steric hindrance. Dihalosilatetrazenes should be good precursors for the reductive elimination of halide to give stable silylenes similar to the silylene of Denk et al.[8][9] since their N=N unit is isoelectronic with the CH=CH unit in the latter. Attempts to reduce the dichlorosilatetrazene **12** have been unsuccessful thus far but the silatetrazenes **15** and **16** should be precursors for bromosilatetrazenes which are also common starting materials for the synthesis of silylenes.

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Experimental Section

General: All operations were carried out under an atmosphere of dry nitrogen. Solvents were dried over sodium and stored under nitrogen; glassware was oven-dried or flame-dried and filled with nitrogen. Starting materials were commercially available or prepared and purified following published procedures. *n*-Butyllithium was used as a 1.6 M solution in *n*-hexane. All halosilanes (except H_2SiCl_2) were freshly distilled and degassed before use. – MS: Kratos MS-80RFA (45 eV), NMR: Bruker AC 300 (300.14 MHz and 75.40 MHz, for ^{1}H- and ^{13}C-NMR, int. TMS), Bruker AM 500 (99.36 MHz, ^{29}Si NMR, int. TMS); Varian UNITY 300 [59,6 MHz, ^{29}Si solid-state NMR, ext. Tetra(trimethylsilyl)silane]. All solution NMR spectra were recorded in C_6D_6.

1,1-Dimethyl-2,5-diphenylsilatetrazene (**1**): NMR data missing from the literature are added. ^{13}C NMR: $\delta = 0.47$ (s, CH_3), 116.42, 122.77, 129.89 (s, *ortho*-, *meta*-, and *para*-CH), 143.23 (s, N-C). – ^{29}Si NMR: $\delta = -4.82$ (s).

Bis(trichlorosilyl)aniline (**7**)

Synthesis of **1**: 1 equiv of *n*-butyllithium was syringed into a solution of 1.86 g (0.02 mol) of aniline in 20 ml of THF. After stirring for 1/2 h 3.22 g (0.02 mol) of mesityl azide[3] were added and a yellow precipitate was formed. After an additional hour at r.t. 2 equiv of *n*-butyllithium were dropped into the mixture. It was stirred 1 h at r.t. followed by separation of the yellow precipitate from the mother liquor by filtration and washing with 100 ml of pentane.

A suspension of **1** in 100 ml of toluene was cooled to −78°C and 8.49 g (0.05 mol) of $SiCl_4$ was added. The reaction mixture was slowly brought to r.t. and stirred overnight. After filtration the volatiles were evaporated. Distillation of the remaining residue under reduced pressure gave 4.35 g (61%) of **7**. – $C_6H_5Cl_6NSi_2$ (359.99). – MS (EI) *m/z* (%) = 359 (12) [M^+], 189 (100) [$M - SiCl_4$]$^+$. – ^{1}H NMR: $\delta = 6.86-7.01$ (m, Ph, 5 H); ^{13}C NMR: $\delta =$ 128.29, 130.09, 130.23 (s, *ortho*-, *meta*- and *para*-CH), 138.19 (s, N-C). – ^{29}Si NMR: $\delta = -25.18$ (s).

Silatetrazenes **10**, **12**, *and* **15**

Preparation of **9**: 1 equiv of *n*-butyllithium was syringed into a solution of 2.14 g (0.02 mol) of *p*-tolylamine in 20 ml of THF. After stirring for 1/2 h 2.66 g (0.02 mol) of *p*-tolyl azide[3] was added and a yellow precipitate was formed. After an additional hour at r.t. 2 equiv. of *n*-butyllithium were dropped into the mixture. It was stirred 1 h at r.t. followed by separation of the yellow precipitate from the mother liquor by filtration and washing with 100 ml of hexane.

1,1-Dimethylsila-2,5-di(p-tolyl)tetrazene (**10**): A suspension of **9** in 150 ml of toluene was cooled to −78°C and 3.23 g (0.05 mol) of Me_2SiCl_2 was added. The reaction mixture was slowly brought to r.t. and stirred overnight. After filtration the mother liquor was concentrated and **10** precipitated from the solution. Recrystallization from toluene gave 4.62 g (78%) of **10**. – $C_{16}H_{20}N_4Si$ (296.45): m.p. 165°C. – MS (EI): *m/z* (%) = 296 (23) [M^+], 163 (100) [$C_9H_{13}NSi$]$^+$. – ^{1}H NMR: $\delta = 0.15$ (s, Si-CH_3, 6 H), 2.10 (s, *para*-CH_3, 6 H), 6.98 (d, $^3J_{HH} = 8.46$ Hz, *meta*-CH, 4 H), 7.31 (d, $^3J_{HH} = 8.46$ Hz, *ortho*-CH, 4 H). – ^{13}C NMR: $\delta = 0.30$ (s, Si-CH_3), 20.68 (s, *para*-CH_3), 116.57, 130.42, 131.94 (s, *ortho*-, *meta*-, and *para*-C), 140.98 (s, N-C). – ^{29}Si NMR: $\delta = -5.43$ (s).

1,1-Dichlorosila-2,5-di(p-tolyl)tetrazene (**12**): A suspension of **9** in 100 ml of hexane was cooled to −78°C and 8.50 g (0.05 mol) of $SiCl_4$ was added. The reaction mixture was slowly brought to r.t. and stirred overnight. After filtration the mother liquor was concentrated and **12** precipitated from the solution. Recrystallization from hexane gave 2.00 g (30%) of **12**. – $C_{14}H_{14}Cl_2N_4Si$ (337.28): m.p. 115°C. – MS (EI): *m/z* (%) = 336 (5) [M^+], 106 (100) [C_7H_7N]$^+$. – ^{1}H NMR: $\delta = 2.02$ (s, *para*-CH_3, 6 H), 6.90 (d, $^3J_{HH} = 8.41$ Hz, *meta*-CH, 4 H), 7.46 (d, $^3J_{HH} = 8.41$ Hz, *ortho*-CH, 4 H). – ^{13}C NMR: $\delta = 20.68$ (s, *para*-CH_3), 118.38, 130.53, 135.00 (s, *ortho*-, *meta*-, and *para*-C), 137.47 (s, N-C). – ^{29}Si NMR: $\delta = -40.26$ (s).

1-Chloro-1-hydrosila-2,5-di(p-tolyl)tetrazene (**15**): A suspension of **9** in 150 ml of hexane was cooled to −78°C and 5.05 g (0.05 mol) of H_2SiCl_2 (25% in xylene) was added. The reaction mixture was slowly brought to r.t. and stirred overnight. After filtration the mother liquor was concentrated and **15** precipitated from the solution. Recrystallization from hexane gave 1.57 g (26%) of **15**. – $C_{14}H_{15}ClN_4Si$ (302.84): m.p. 128°C. – MS (EI): *m/z* (%) = 302 (24) [M^+], 274 (73) [$M-N_2$]$^+$. – ^{1}H NMR: $\delta = 2.05$ (s, *para*-CH_3, 6 H), 5.91 (s, SiH, 1 H), 6.92 (d, $^3J_{HH} = 8.41$ Hz, *meta*-CH, 4 H), 7.34 (d, $^3J_{HH} = 8.41$ Hz, *ortho*-CH, 4 H). – ^{13}C NMR: $\delta = 20.69$ (s, *para*-CH_3), 118.13, 130.46, 134.16 (s, *ortho*-, *meta*-, and *para*-C), 138.64 (s, N-C). – ^{29}Si-NMR: $\delta = -43.62$ (s).

1,1-Dihydrosila-2,5-di(para-tolyl)tetrazene (**16**): Compound **16** was characterized from the mother liquor. ^{29}Si NMR(C_6D_6/hexane/xylene): $\delta = -55.45$ (s).

Bis(trihalosilyl)-p-tolylamines **11** *and* **13**: Compound **9** was prepared as described above in a 0.02 mol scale. A suspension of **9** in 150 ml of hexane was cooled to −78°C and 3.40 g (0.02 mol) of $SiCl_4$ (**11**) or 17.41 (0.05 mol) of $SiBr_4$ (**13**) was added. The reaction mixture was slowly brought to r.t. and stirred overnight. After filtration the volatiles were removed under reduced pressure. Distillation of the residue gave 4.26 g (57%) of **11** and 5.88 g (48%) of **13**.

Bis(trichlorosilyl)-p-tolylamine (**11**): $C_7H_7Cl_6NSi_2$ (374.02): b.p. 76°C (0.01 Torr). – MS (EI): *m/z* (%) = 373 (20) [M^+], 203 (100) [$M - SiCl_4$]$^+$. – ^{1}H NMR: $\delta = 1.96$ (s, *para*-CH_3, 3 H), 6.79 (d, $^3J_{HH} = 8.41$ Hz, *meta*-CH, 2 H), 6.94 (d, $^3J_{HH} = 8.41$ Hz, *ortho*-CH, 2 H). – ^{13}C NMR: $\delta = 20.80$ (s, *para*-CH_3), 129.96, 130.73, 135.26, 138.27 (s, *ipso*-, *ortho*-, *meta*-, and *para*-C). – ^{29}Si NMR: $\delta = -25.32$ (s).

Bis(tribromosilyl)-p-tolylamine (**13**): $C_7H_7Br_6NSi_2$ (640.74): b.p. 155°C (0.01 Torr). – MS (EI): *m/z* (%) = 641 (28) [M^+], 293 (100) [$M - SiBr_4$]$^+$. – ^{1}H NMR: $\delta = 1.96$ (s, *para*-CH_3, 3 H), 6.82 (d, $^3J_{HH} = 8.11$ Hz, *meta*-CH, 2 H), 7.03 (d, $^3J_{HH} = 8.11$ Hz, *ortho*-

CH, 2 H). – ^{13}C NMR: $\delta = 21.09$ (s, *para*-CH_3), 130.56, 130.64, 137.23, 138.39 (s, *ipso*-, *ortho*-, *meta*-, and *para*-C). – ^{29}Si NMR: $\delta = -61.82$ (s).

Crystal Structure Determination: Suitable single crystals of compounds **10**, **12**, and **15** were examined with a Siemens P4/CCD-diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Structures were solved by direct methods[10] and refined by full-matrix least-square calculations against F^2[10]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were isotropically calculated in idealized positions and allowed to ride on their corresponding atoms. Further information on crystal data, data collection and structure refinement is summarized in Table 1. Important interatomic distances and angles are given in Table 2. Further information may be obtained from the Fachinformationszentrum Karlruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-100312, the names of the authors, and the full journal citation.

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