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Synthesis and Structure of Silicon Compounds Intramolecularly Coordinated by Hydrazino Groups

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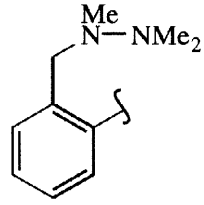
Abstract: Organosilicon compounds bearing the 2-(trimethylhydrazinomethyl)phenyl and 2-(trimethylhydrazino)phenyl substituent have been prepared by treatment of the corresponding aryllithium with Me_3SiCl and $SiCl_4$. Subsequent reactions of chlorosilanes **10**, **15**, **18**, and **22** afforded a variety of functionalized silanes. NMR spectroscopic data of most 2-(trimethylhydrazino)phenyl substituted silanes indicate a highly coordinated silicon center in solution. Diethoxy compound **20** is hexacoordinate in the solid state due to interaction with the hydrazino groups of both aromatic substituents, whereas in dichlorosilane **22** only the amino group of the 2-(trimethylhydrazino)phenyl substituent coordinates to the silicon center. The coordinating ability of the 2-(trimethylhydrazino)phenyl substituent has been used to stabilize silyl cations by formation of pentacoordinate siliconium ions **33** and **34**.

Introduction

Chelating substituents such as the 2-(dimethylaminomethyl)phenyl substituent (**Ar^1**), which makes use of the donor properties of the dimethylamino group, have been utilized extensively to synthesize a variety of stable penta[1]-, hexa[1]- and even heptacoordinate[2] saturated organosilicon compounds. In addition, this substituent has been shown to effectively stabilize low valent silicon centers in highly reactive compounds such as silylenes[3a,b] or silyl cations[3c] by intramolecular coordination.

Ar^1



Ar^2

Ar^3

Our continuing interest in highly coordinated organosilicon compounds initiated a search for chelating

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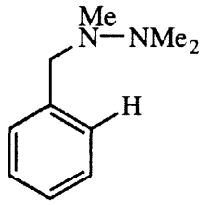
substituents, which have a structure similar to that of the Ar^1 substituent, but exhibit enhanced coordination properties. Having in mind that the nucleophilicity of hydrazines is more pronounced than that of amines (α-effect)[4] we started an investigation of the chelating properties of the 2-(trimethylhydrazinomethyl)phenyl (Ar^2) and 2-(trimethylhydrazino)phenyl (Ar^3) substituents towards silicon.

Results and Discussion

The 2-(Trimethylhydrazinomethyl)phenyl System. In view of the well investigated *ortho*-lithiation of benzylamine[5] the analogous metallation of hydrazine **1** and subsequent reaction of the resulting anion **2** with silicon halides appeared to be a straightforward way to attach the Ar^2 substituent to a silicon center.



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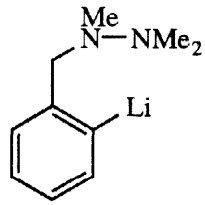
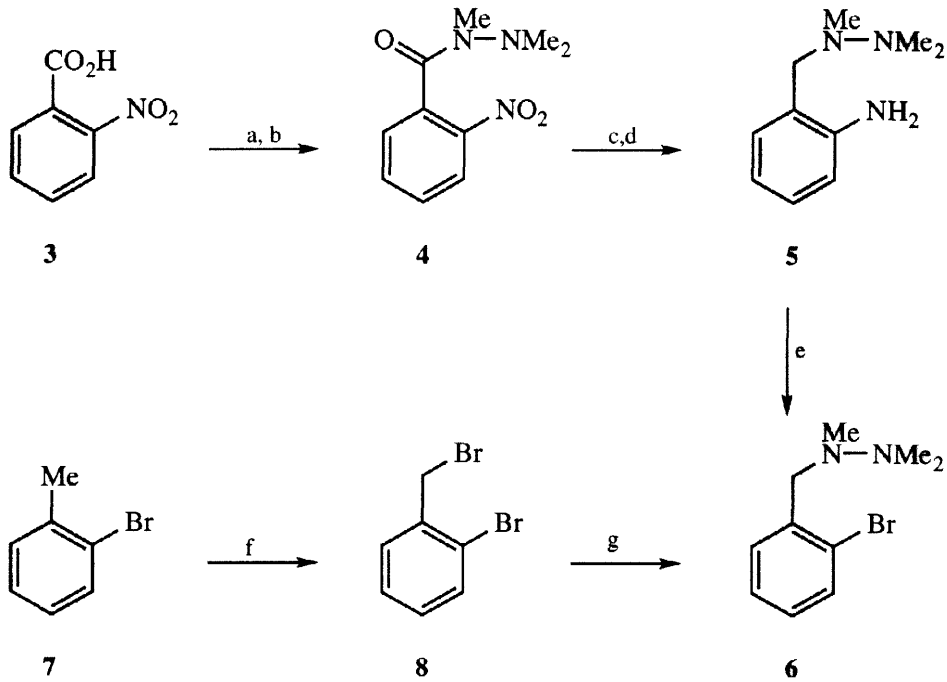


2

However, it turned out that **2** is not available using this approach: The reaction of bases such as *n*-butyllithium (*n*-BuLi) in hexane or diethyl ether, the *n*-BuLi/tetramethylethylenediamine (TMEDA) complex in hexane or lithium diisopropylamide (LDA) in THF and subsequent treatment of the reaction mixture with

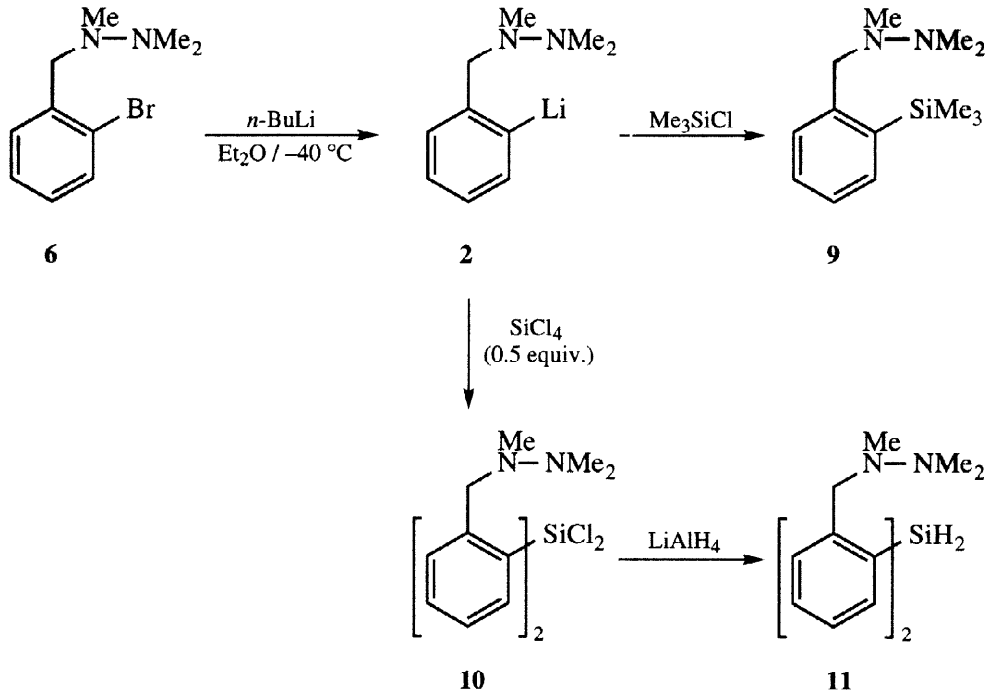


3 **4** **5** **7** **8** **6**

Scheme 1. Synthetic routes to **6** (yields in parentheses). a) $SOCl_2$; b) NEt_3, CH_2Cl_2, Me_2NNMeH (2 steps: 79%); c) Pd/C, MeOH, HCO_2NH_4 (86%); d) $LiAlH_4$, THF (70%); e) HBr/$NaNO_2$, $CO(NH_2)_2$, Cu (27%); f) Br_2, hv (90%); g) $Me_2NNMeLi$, Et_2O (45%).

Me_3SiCl led to complex product mixtures. The reaction of **1** with *n*-BuLi in diethyl ether was studied in more detail. No reaction occurred at temperatures up to −10 °C. Following the progress of the reaction at room temperature by withdrawing aliquots of the reaction mixture and examining the hydrolized samples by GC/MS revealed that compounds were formed, which arose from cleavage of the N–N bond as well as incorporation of the *n*-butyl group into the products.

The halogen-metal exchange reaction opens an alternative preparative pathway to organolithium compounds. To this end, aryl bromide **6** was synthesized starting from the benzoic acid derivative **3**, which was converted via its acyl cloride to hydrazide **4** by standard procedures (Scheme 1). Direct reduction of **4** to give hydrazine **5** by use of $LiAlH_4$ in THF or hydrazine/Raney-nickel was not successful. Thus, in a first step, the nitro substituent was transformed into the amino group by catalytic reduction using ammonium formate as hydrogen source. Subsequent reduction of the carbonyl group and Gattermann bromination of the resulting hydrazine **5** yielded the target compound in an overall yield of 13%. More conveniently, **6** was obtained from commercially available **7** via benzyl bromide **8**; the overall yield over two steps was 41%.



Scheme 2. Preparation and reactions of **2**

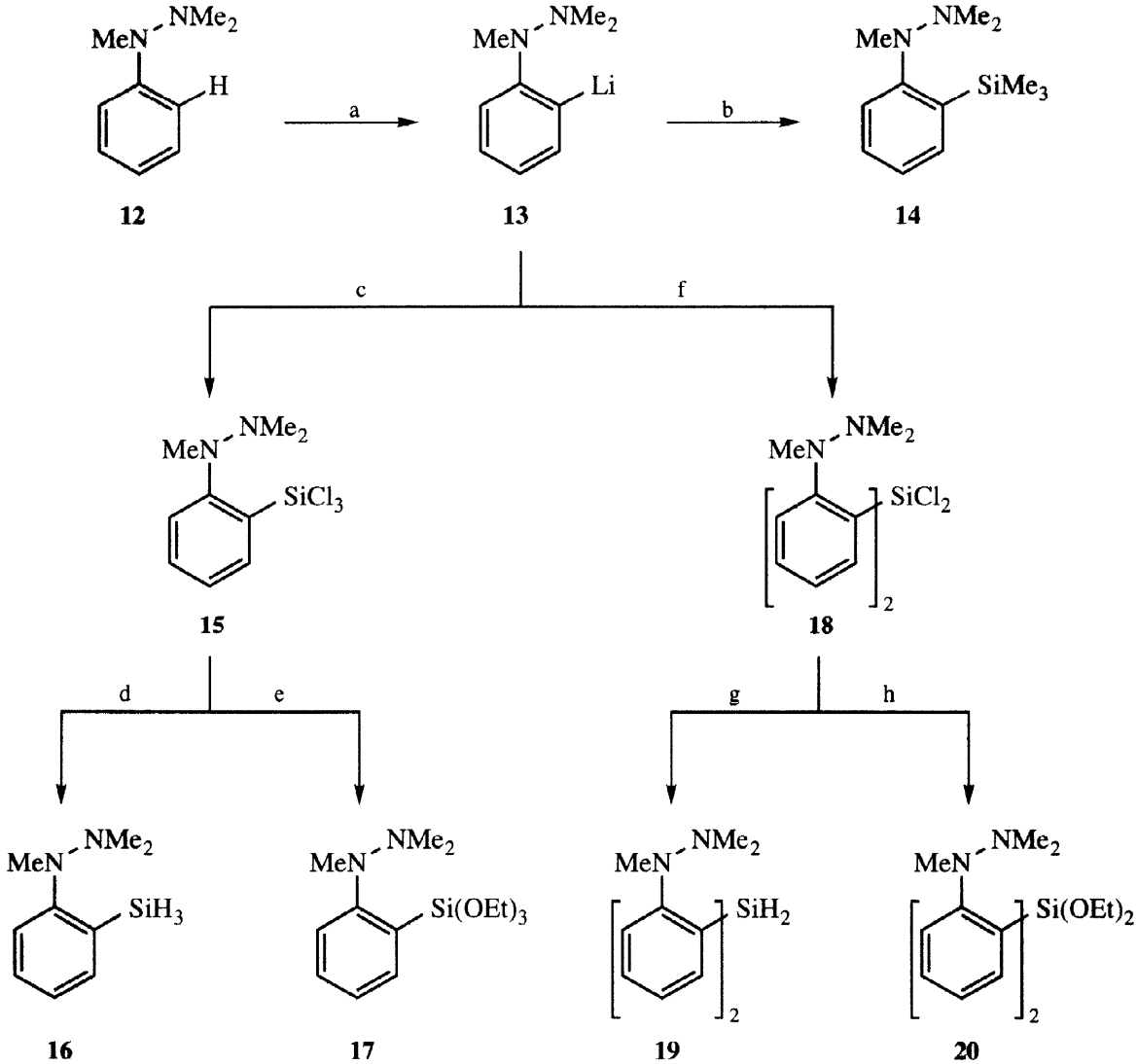
Halogen-metal exchange of **6** by means of *n*-BuLi and subsequent treatment of the resulting aryllithium **2** with Me_3SiCl proceeded under clean formation of silane **9** (Scheme 2), which was isolated in 56% yield. In contrast, the reaction of **9** with 0.5 equivalents $SiCl_4$, aiming at the preparation of dichlorosilane **10**, afforded a product mixture, from which no pure compound could be obtained by crystallization or distillation. By precipitation with hexane, a solid was obtained, which decomposed during a few days, even under exclusion of moisture and oxygen, to an intractable, green solid. Due to this instability, no unambiguous characterization of the precipitated solid by NMR spectroscopy or mass spectrometry was possible. However, on treatment of the solid with $LiAlH_4$, silane **11**, which might be formed by reduction of dichlorosilane **10**, was obtained in 19% yield (referring to **6**).

Table 1. ^{29}Si NMR Data of 2-(trimethylhydrazinomethyl)phenyl substituted and phenyl substituted silanes

compound	δ_{Ar2}[a,b]	$\Delta\delta$[c]	δ_{Ph}[b,d]
$RSiMe_3$ (9)	–4.5	+0.6	–5.1
R_2SiH_2 (11)	–40.9 (200)	–7.1	–33.8 (198)

[a] R = Ar^2 = 2-(trimethylhydrazinomethyl)phenyl. – [b] Data in parentheses refer to Si–H coupling constants. – [c] $\Delta\delta = \delta_{Ar2} - \delta_{Ph}$. – [d] Ref. 6, if not stated otherwise.

The ^{29}Si NMR signal of **11** is shifted upfield by 7.1 ppm in comparison with that of diphenylsilane[6] (Table 1). Shift differences of this order of magnitude have been shown to be indicative of the formation of a highly coordinated silicon center in silanes.[7] In addition, penta[8]- or hexacoordination[7] of a Si–H center should be accompanied by a significant increase of the Si-H coupling constant. However, the respective coupling

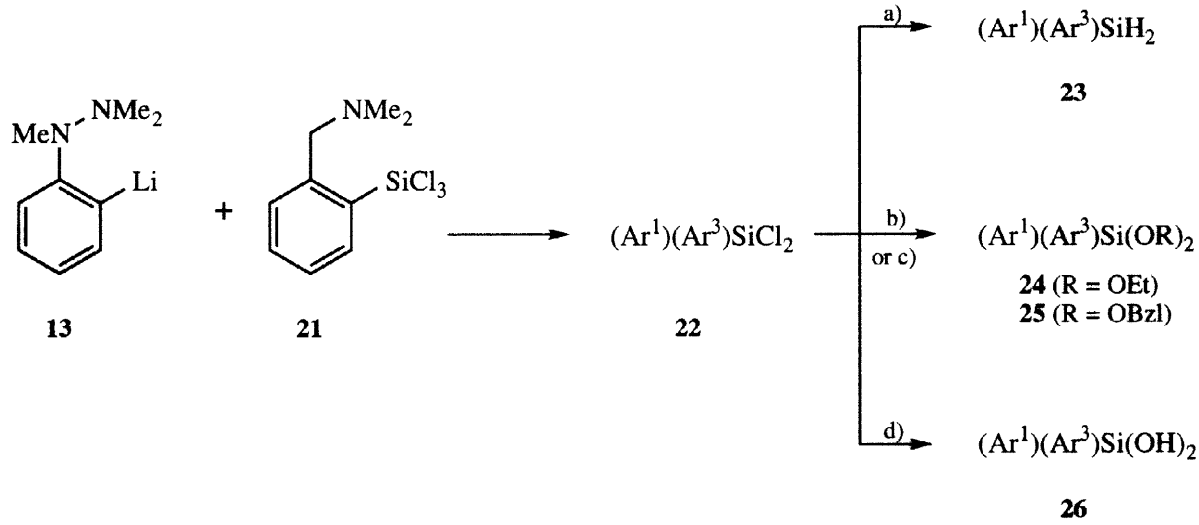


Scheme 3. Preparation and reactions of **13** (yields in parentheses). a) *n*-BuLi/TMEDA, hexane; b) Me_3SiCl (28%)c) 1 equiv. $SiCl_4$ (22%); d) $LiAlH_4$, Et_2O (30%); e) NaOEt, THF (25%); f) 0.5 equiv. $SiCl_4$ (68%); g) $LiAlH_4$, Et_2O (48%); h) NaOEt, THF/hexane (48%).

constants of **11** and diphenylsilane differ only marginally, and accordingly we assume that there is no or only a very weak coordinative N···Si interaction in **11**.

The 2-(Trimethylhydrazino)phenyl System. In contrast to **2**, intramolecularly coordinated aryllithium **13** was smoothly obtained from the corresponding hydrazine **12** by metalation with the *n*-BuLi/TMEDA complex in hexane (Scheme 3).[9] Treatment of **12** with chlorosilanes such as Me_3SiCl and $SiCl_4$ afforded silanes **14**, **15** and **18**. Chlorosilanes **15** and **18** were further transformed into silanes **16** and **19** as well as into silyl ethers **17** and **20** using standard procedures.

Treatment of trichlorosilane **21** with aryllithium **13** yielded the "mixed" dichlorosilane **22** (46%), which was converted subsequently into derivatives **23–25** using standard reactions (Scheme 4). In contrast to dichlorosilane **15**, which formed complex product mixtures under hydrolytic conditions, hydrolysis of **22** with aqueous NEt_3 proceeded under clean formation of the geminal diol **26**.



Scheme 4. Preparation and reactions of **22** (Ar^1 = 2-(Me_2NCH_2)C_6H_4, Ar^3 = 2-(Me_2NMeN)C_6H_4; yields in parentheses). a) $LiAlH_4$, Et_2O (72%); b) NaOEt, THF (22%); c) LiOBzl, THF (67%); d) H_2O/NEt_3, THF (48%).

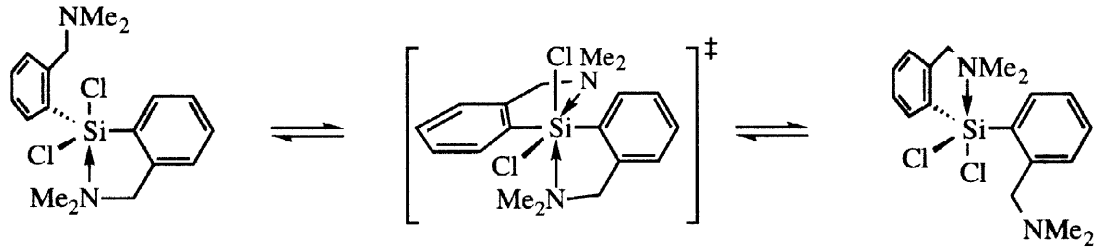
The ^{29}Si NMR signals of chlorosilanes bearing the 2-(trimethylhydrazino)phenyl substituent such as **15**, **18** and **22** are shifted to high field in comparison to the corresponding phenyl substituted silanes and thus indicate a highly coordinated silicon center in these compounds (Table 2). The coordination is fluxional at room temperature as it can be seen from the temperature dependent ^1H NMR spectra: The NMe_2 signal of **18** is a broad singlet at room temperature at 500 MHz. Upon cooling it splits into two singlets with equal intensity, whereas the signals of the NMe groups as well as of the aromatic protons, which are already sharp and well resolved at ambient temperature, remain essentially unchanged. Therefore we conclude that both aryl substituents are chemically equivalent at low temperature and that the splitting of the NMe_2 signal is due to the diastereotopicity of the two methyl groups attached to one terminal nitrogen center. From the coalescence temperature of 253 K the free energy of activation for the observed process was estimated to be $\Delta G^{\ddagger} = 48.2 \pm 0.2$ kJ mol^{-1}. Similarly, ethoxy compound **20** showed exclusive diastereotopicity of the terminal NMe groups at low temperature ($\Delta G^{\ddagger} = 41.0 \pm 0.4$ kJ mol^{-1}). These NMR spectroscopic results are in sharp contrast to that obtained for dichlorosilane **27**, the NMe_2 and benzylic protons of which form two singlets at room temperature.[10] Upon cooling the benzylic signal of **27** splits into an AB system, whereas

Table 2. ^{29}Si NMR Data of 2-(trimethylhydrazino)phenyl substituted and phenyl substituted silanes

compound[a]	δ_{Ar^3}[b]	$\Delta\delta$[c]	compound	δ_{Ph}[b,d]	compound[a,e]	$\delta_{Ar^1Ar^3}$[b]	$\Delta\delta$[f]
Ar^3SiMe_3 (**14**)	–9.2	–4.1	$PhSiMe_3$	–5.1			
Ar^3SiCl_3 (**15**)	–44.9	–44.1	$PhSiCl_3$	–0.8			
Ar^3SiH_3 (**16**)	–68.8	–8.7	$PhSiH_3$	–60.1			
	(196)			(200)			
$Ar^3Si(OEt)_3$ (**17**)	–62.9	–5.3	$PhSi(OEt)_3$	–57.6			
$(Ar^3)_2SiCl_2$ (**18**)	–28.7	–34.9	Ph_2SiCl_2	+6.2	$Ar^1Ar^3SiCl_2$ (**22**)	–31.0	–37.2
$(Ar^3)_2SiH_2$ (**19**)	–43.8	–10.0	Ph_2SiH_2	–33.8	$Ar^1Ar^3SiH_2$ (**23**)	–46.1	–12.3
	(213)			(198)		(212)	
$(Ar^3)_2Si(OEt)_2$ (**20**)	–47.6	–13.1	$Ph_2Si(OEt)_2$	–34.5	$Ar^1Ar^3Si(OEt)_2$ (**24**)	–42.1	–7.6
					$Ar^1Ar^3Si(OBz)_2$ (**25**)	–41.2	
			$Ph_2Si(OH)_2$	–34.2	$Ar^1Ar^3Si(OH)_2$ (**26**)	–30.2	+4.0

[a] Ar^3 = 2-(trimethylhydrazino)phenyl. – [b] Data in parentheses refer to Si-H coupling constants. – [c] $\Delta\delta = \delta_{Ar^3} - \delta_{Ph}$. – [d] Data from ref. 6. – [e] Ar^1 = 2-(dimethylaminomethyl)phenyl. – [f] $\Delta\delta = \delta_{Ar^1Ar^3} - \delta_{Ph}$.

the NMe_2 protons remain chemically equivalent. These observations were interpreted in terms of an intramolecular exchange reaction, during which both dimethylamino groups displace each other at the pentacoordinate silicon and which is supposed to proceed via a hexacoordinate, C_2 symmetrical transition state **27(TS)** (Scheme 5); the free energy of activation for this process was estimated to be $\Delta G^{\ddagger} = 46.5$ kJ mol^{-1}.[10]



27 **27 (TS)** **27**

Scheme 5. Dynamic pentacoordination of **27**

The singlets of the NMe_2 groups of **18** and **20** could be due to a similar coordination-dissociation process, which is rapid at room temperature. However, the chemical inequivalence of the terminal NMe groups of **18** and **20** at low temperature is not in agreement with a simple slowing down of this dynamic process as it was found for **27**, but can be explained with the formation of a stable hexacoordinated silicon center, in which the aryl substituents occupy equivalent positions. The assumption that the coordinating amino groups of **18** and **20** exchange via a hexacoordinate intermediate (as opposed to the suggested hexacoordinate transition state of **27**), is backed by the solid state structure of **20**, which reveals the hexacoordinate silicon center of the approximately C_2 symmetrical molecule (Figure 1). The terminal amino groups of the hydrazino "sidearms" are located *trans* to the oxygen centers forming N···Si–O bond angles of 169.7° and 169.5°. The resulting Si···N distances of 268.9 and 277.2 pm are in the range of dative Si···N distances of hexacoordinate silicon

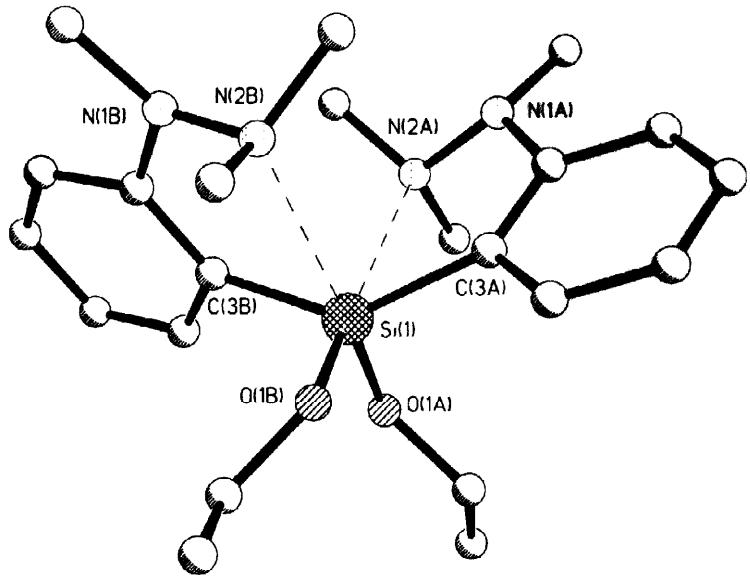


Fig. 1. X-ray structure of **20**; selected bond lengths [pm] and bond angles [°]: Si(1)···N(2a) 277.2(2), Si(1)···N(2b) 268.7(2), Si(1)–O(1a) 166.2(2), Si(1)–O(1b) 166.2(2), Si(1)–C(3a) 189.1(3), Si(1)–C(3b) 188.5(3); N(2a)···Si(1)–O(1a) 83.4(1), N(2a)···Si(1)–O(1b) 169.5(1), N(2a)···Si(1)–C(3a) 70.6(1), N(2a)···Si(1)–C(3b) 78.0(1), N(2a)···Si(1)···N(2b) 90.3(1), N(2b)···Si(1)–O(1a) 169.7(1), N(2b)···Si(1)–O(1b) 82.7(1), N(2b)···Si(1)–C(3a) 80.6(1), N(2b)···Si(1)–C(3b) 72.0(1), C(3a)–Si(1)–C(3b) 137.9(1), C(3a)–Si(1)–O(1a) 104.7(1), C(3a)–Si(1)–O(1b) 100.4(1), C(3b)–Si(1)–O(1a) 98.7(1), C(3b)–Si(1)–O(1b) 107.0(1), O(1a)–Si(1)–O(1b) 104.7(1).

compounds.[11] The coordination geometry around silicon is best described as that of a bicapped tetrahedron, the tetrahedron itself being distorted severely by the widening of the C(3b)–Si(1)–C(3a) angle to 137.8° in order to accommodate both amino groups in the coordination sphere of silicon. An alternative structural description of **20** as a distorted octahedron appears to be far less justified in view of the appreciable differences of the experimental bond lengths and angles to that of an ideal octahedron.

In contrast, the silicon center of dichlorosilane **22** is pentacoordinate in the solid state (Fig. 2). The lone pair of the terminal hydrazino amino group is directed towards the silicon center. The N(22)···Si(1) distance of 256.4 pm, though significantly longer than the average covalent N–Si single bond (170–176 pm),[12] is far below the sum of the van-der-Waals radii (365 ppm).[13] In contrast, the **Ar**^{1} substituent does not form a chelate as is evidenced by the "wrong" orientation of the dimethylamino group as well as the relatively long N(11)-Si(1) distance of 315.9 pm. The geometry around silicon is that of an distorted trigonal bipyramid with N(22) and Cl(1) occupying the axial positions (N(22)···Si(1)–Cl(1): 177.1°). Accordingly, the axial Si(1)–Cl(1) (211.8 pm) distance is significantly elongated as compared to the equatorial Si(1)–Cl(2) bond length (207.8 pm) . The sum of the equatorial bond angles is 349.4°, thus reflecting the transformation of a tetrahedral towards a trigonal bipyramidal coordination geometry around silicon due to the nucleophilic attack of N(22).

Contrasting the higher coordination of silyl ethers **20** and **24**, no N···Si interaction appears to be effective in silanediol **26** in solution according to its ^{29}Si NMR signal, which is shifted to low field in comparison to that of $Ph_2Si(OH)_2$ (Table 2). Auner et al. have shown that the hydroxy group of a silanol, which bears the **Ar**^{1} substituent, forms in the solid an intramolecular hydrogen bond to the amino group of that substituent.[14] Thus, it may be assumed that the amino groups of the **Ar**^{3} substituents of **26** are involved in a similar hydrogen bonding, even in solution; in consequence, the lone pair at nitrogen would no longer be available for coordination to the silicon center.

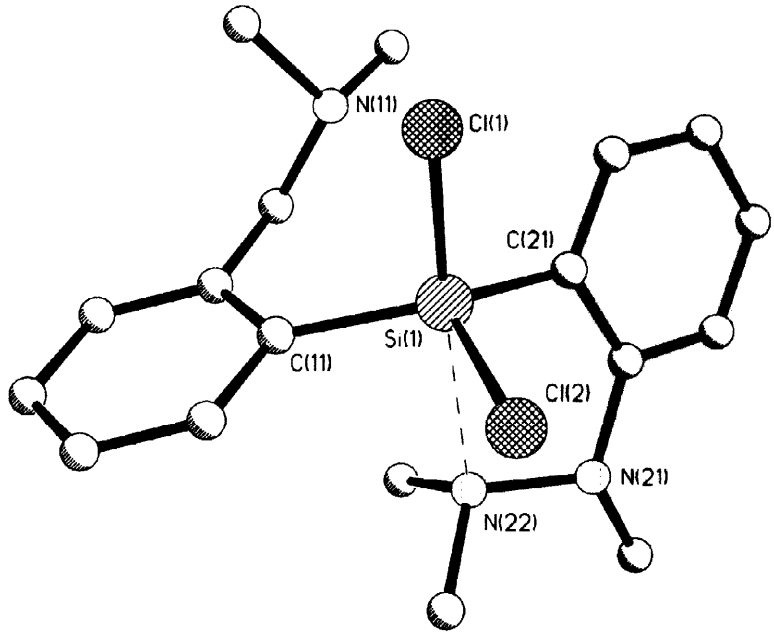


Fig. 2. X-ray structure of **22**; selected bond lengths [pm] and bond angles [°]: Si(1)···N(22) 256.4(2), Si(1)–Cl(1) 211.8(1), Si(1)–Cl(2) 207.8(1), Si(1)–C(11) 187.3(2), Si(1)–C(21) 186.1(2); N(22)···Si(1)–Cl(1) 177.1(1), N(22)···Si(1)–Cl(2) 82.8(1), N(22)···Si(1)–C(11) 81.5(1), N(22)···Si(1)–C(21) 74.2(1), Cl(1)–Si(1)–Cl(2) 95.6(1), Cl(1)–Si(1)–C(11) 101.4(1), Cl(1)–Si(1)–C(21) 104.2(1), Cl(2)–Si(1)–C(11) 110.1(1), Cl(2)–Si(1)–C(21) 109.5(1), C(11)–Si(1)–C(21) 129.8(1).

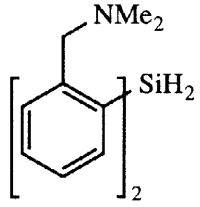
The ^{29}Si NMR signals of hydrogen bearing silanes **19** and **23** are slightly shifted to high field compared to the corresponding phenyl substituted reference compounds and thus indicate a weak N···Si coordination in solution. Further confirmation of a donor-acceptor interaction comes from the increased Si-H coupling constants[8] of these silanes compared to that of Ph_2SiH_2 (198 Hz) and the temperature dependency of their ^{29}Si NMR shifts (Table 3). It was shown by West, Corriu et al.[15] that an equilibrium between the open and the intramolecularly coordinated form of silanes, which are substituted by **Ar^1**, reveals itself by a small, but significant highfield shift of the ^{29}Si NMR signal upon cooling. This effect is assumed to reflect the shift of the equilibrium at low temperature towards the chelate structure, the silicon nucleus of which is magnetically more shielded than that of the tetracoordinate form. As shown in Table 3, small highfield shifts of the ^{29}Si NMR signals were observed when cooling a sample of these silanes from 296 K to 223 K. To further elucidate the significance of these quite small effects, we determined the temperature dependency of the ^{29}Si NMR shift of **28**, which is assumed to be dynamically pentacoordinate[2a], in the same temperature range. As can be seen from

Table 3. ^{29}Si NMR data of hydrogen bearing silanes at different temperatures (solvent $CDCl_3$)

silane[a]	δ [296 K][b]	δ [223 K][b]	Δδ[c]
$(Ar^3)_2SiH_2$ (**19**)	–45.4 (212)	–47.5 (214)	–2.1
$Ar^1Ar^3SiH_2$ (**23**)	–47.5 (212)	–49.9 (217)	–2.4
$(Ar^1)_2SiH_2$ (**28**)	–45.6 (209)	–48.6 (214)	–3.0
$(Ar^1)_2SiH_2 \cdot 2\ BH_3$ (**29**)	–37.5 (204)	–37.3 (204)	+0.2

[a] Ar^1 = 2-$(Me_2NCH_2)C_6H_4$, Ar^3 = 2-$(Me_2NMeN)C_6H_4$ – [b] Data in parentheses refer to Si-H coupling constants. – [c] Δδ = δ [223 K] – δ [296 K.]

Table 3, it is in the same order of magnitude as that of **19** and **23**. In contrast, the ^{29}Si NMR shift of tetracoordinate silane **29**, in which the lone pair is not available for coordination to the silicon center due to the complex formation of the amino substituent with BH_3, is essentially unchanged when lowering the temperature. In addition, a small lowfield shift of the ^{29}Si NMR resonance is observed upon complexation of **28** by BH_3 as expected for the breaking down of the dynamic intramolecular Si···N coordination. Taken together, these results indicate that the arylsubstituents of **19** and **23** are involved in a fast coordination-dissociation process.



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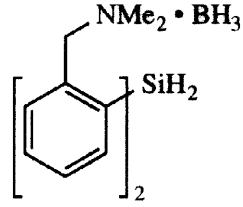

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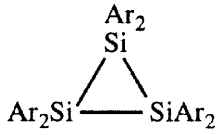
Having shown that the **Ar³** substituent coordinates to saturated silicon centers, it was of interest to us to examine if this substituent is able to stabilize low valent silicon compounds such as silylenes or silyl cations by intramolecular coordination, as it is known for the well investigated **Ar¹** substituent.[3]

To this end, dichlorosilane **18** was treated with magnesium in THF; under these conditions dichlorosilane **27** was converted cleanly into the silylene precursor **30** (Ar = 2-$(Me_2NCH_2)C_6H_4$).[16] However, a moisture sensitive mixture of compounds was obtained from **18**, which could not be separated by crystallization or distillation. Variation of the metal (Li, Na, K, Mg, Zn) and/or the solvent (hexane, toluene, Et_2O, THF) as well as of the reaction temperature resulted either in the re-isolation of **18** or in the formation of complex product mixtures. When using lithium in THF, silyl amide **31** was isolated in 22% yield. Obviously the N–N bond of the hydrazino group is not stable under the reaction conditions employed; initially formed lithium dimethylamide may subsequently substitute the silicon bound chlorines to afford eventually, after aqueous work-up, amide **31**. A control experiment starting with hydrazine **13** resulted in cleavage of the N–N bond as well and yielded aniline **32**. The attempt to trap the suspected by-product lithium dimethylamide by addition of *t*-$BuMe_2SiCl$, however, failed.



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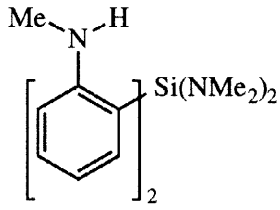

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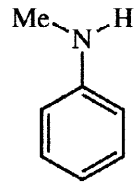

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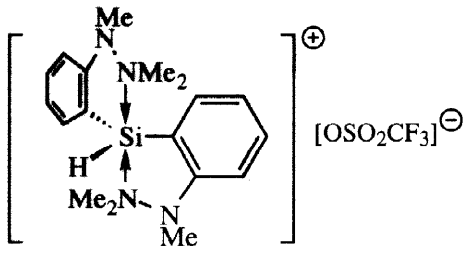
More successful were attempts to chelate a cationic silicon center by the **Ar³** substituent: When silanes **19** and **23** were treated with trimethylsilyl triflate, siliconium ions **33** and **34** were obtained in good yield, which, in contrast to the stable 2-(dimethylaminomethyl)phenyl substituted analogue[3c], decompose to mixtures of unidentified products in solution as well as in the solid during a few days. According to the ^1H NMR spectrum the silicon center of these compounds is pentacoordinate due to the dative N···Si bonds of the terminal amino groups of both substituents. Thus, the ^1H NMR spectrum of **34**, e.g., shows the signals of five chemically



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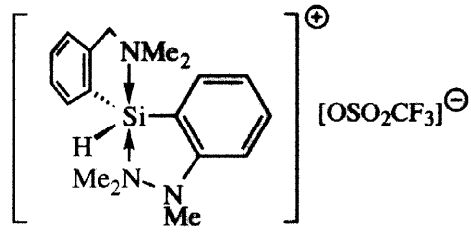

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inequivalent methyl groups as well as an AB pattern of the benzylic protons. This is in agreement with the structure of a siliconium ion, in which the chelating nitrogen centers occupy the axial positions of a trigonal bipyramid, as it was found for the solid state structure of other siliconium ions.[3c,18] The strength of the dative Si···N bond appears to be quite high as the ^{1}H NMR spectra of **34** do not show any differences when recorded at room temperature or at 60 °C. Further conformation of the proposed siliconium ion structure in solution comes from the upfield shift of the ^{29}Si NMR signal and the appreciable increase of the ^{29}Si-^{1}H coupling constant upon transformation of the silane into the siliconium ion, which is assumed to reflect the increased s-character of the Si–H bond in these ionic compounds (Table 4).[17]

Table 4. ^{29}Si NMR data of siliconium ions

compound[a]	δ	Δδ[b]	$^1J_{SiH}$ [Hz]	Δ^1J_{SiH}[c] [Hz]
$(Ar^3)_2SiH^+OTf^-$ (**33**)	–54.5	–10.7	283	70
$(Ar^1)(Ar^3)SiH^+OTf^-$(**34**)	–53.6	–7.5	291	79
$(Ar^1)_2SiH^+OTf^-$[3c]	–51.7	–6.6	272	63
$(Ar^4)_2SiH^+I_8^-$ [18]	–43.5	–3.7	290	74

[a] Ar^1 = 2-(dimethylaminomethyl)phenyl, Ar^3 = 2-(trimethylhydrazino)phenyl, Ar^4 = 8-(dimethylamino)naphthyl. – [b] $\Delta\delta = \delta(Ar_2SiHOTf) - \delta(Ar_2SiH_2)$. – [c] $\Delta^1J_{SiH} = {}^1J_{SiH}(Ar_2SiHOTf) - {}^1J_{SiH}(Ar_2SiH_2)$.

In conclusion, we have shown that the 2-(trimethylhydrazino)phenyl (**Ar^3**), but not the 2-(trimethylhydrazinomethyl)phenyl (**Ar^2**) substituent is able to coordinate intramolecularly to the silicon center of neutral and cationic organosilicon compounds. However, the use of the 2-(trimethylhydrazino)phenyl substituent for stabilization of low valent silicon centers by intramolecular coordination appears not to be superior to that of the 2-(dimethylaminomethyl)phenyl substituent (**Ar^1**) in view of the reduced stability of siliconium ions **33** and **34** as well as the unsuccessful attempts to generate a chelated silylene from dichlorosilane **18**, which failed due the instability of the N–N bond under reducing conditions.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 250 spectrometer (^{1}H NMR; 250 MHz; ^{13}C NMR; 62.9 MHz). CH, C_q, CH_2 and CH_3 were determined using the DEPT pulse sequence.

^{29}Si NMR spectra were recorded on a Bruker AMX 300 spectrometer (59.6 MHz) by use a refocused INEPT pulse sequence. Chemical shifts refer to $\delta_{TMS} = 0.0$. Mass spectra were recorded on a Varian MAT 311 A. High resolution mass spectra were obtained by preselective ion-peak-matching with R ~ 10000 in range of ± 2 ppm. Infrared spectra were recorded on Bruker IFS 66 spectrometer. Melting points are uncorrected. Elemental analyses were preformed at Mikroanalytisches Labor der Georg-August-Universität Göttingen.

All manipulations were carried out under an argon atmosphere using dried glassware. Etheral solvents and hexane used were dried by refluxing over sodium and benzophenone ketyl and distilled immediately before use; dichloromethane and chloroform were dried using molecular sieves (4 Å).

(2-Nitrobenzoyl)trimethylhydrazide (**4**). A solution of 16.71 g (0.1 mol) 2-nitrobenzoic acid (**3**) in 73 mL (1.0 mol) of $SOCl_2$ was heated at 70 °C for 18 h. Excess $SOCl_2$ was removed *in vacuo* and the crude 2-nitrobenzoyl chloride was dissolved in a mixture of 13.9 mL (0.12 mol) of triethylamine and 100 mL of dichloromethane. 7.41 g (0.1 mol) of trimethylhydrazine were added to the solution at 0 °C. After completion of the addition the solution was stirred for 30 min at 0 °C and then allowed to warm up to ambient temperature. After addition of 100 mL of a saturated, aqueous $NaHCO_3$ solution the organic layer was separated and the aqueous layer was extracted twice with 30 mL of dichloromethane. The combined organic layers were dried with Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (column 5 x 40 cm, Et_2O $R_f = 0.18$) and recrystallized from chloroform/petrol ether (2 : 1) to yield 17.71 g (79%) of **4** as a pale yellow solid (mp. 103 °C). ^1H NMR ($CDCl_3$): δ 2.36 (s, 6 H, $N(CH_3)_2$), 3.08 (s, 3 H, NCH_3), 7.37 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.49 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.66 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 8.11 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 22.5 (NCH_3), 42.8 ($N(CH_3)_2$), 123.9 (ar-CH), 127.5 (ar-CH), 128.8 (ar-CH), 133.7 (ar-CH), 134.8 (ar-C_q), 145.2 (ar-C_q), 169.1 (C=O). MS (EI), *m/z* (relative intensity): 223 (8) [M^+], 206 (20), 150 (2), 76 (8), 73 (100), 46 (7), 44 (14). Anal. Calcd. for $C_{10}H_{13}N_3O_3$ (223.22): C, 53.81; H, 5.87; N, 18.82. Found: C, 54.06; H, 5.97; N, 18.82.

(2-Aminobenzoyl)trimethylhydrazide.[19] To a suspension of 6.27 g (28.1 mmol) of **4** and 1.48 g of 10% Pd/C-catalyst in 50 mL of methanol were added 8.14 g (129 mmol) of ammonium formate. The solution started foaming after 20 min stirring at room temperature. After further 15 min the catalyst was filtered off, the solvent was removed *in vacuo* and the residue was dissolved in 40 mL of chloroform. After column filtration through 100 g silica gel the filtrate was dried over Na_2SO_4. The solvent was evaporated *in vacuo* and analytically pure (2-aminobenzoyl)trimethylhydrazide (4.71 g, 86%) was obtained from the residue by crystallization from petrol ether/chloroform (1 : 3) (mp. 86 °C). ^1H NMR ($CDCl_3$): δ 2.49 (s, 6 H, $N(CH_3)_2$), 3.02 (s, 3 H, NCH_3), 4.38 (s, 2 H, NH_2), 6.66 (ddd, ^3J = 7 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 6.68 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.12 (ddd, ^3J = 7 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.18 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 23.0 (NCH_3), 43.2 ($N(CH_3)_2$), 116.4 (ar-CH), 116.6 (ar-CH), 120.6 (ar-C_q), 128.4 (ar-CH), 130.0 (ar-CH), 145.7 (ar-C_q), 172.3 (C=O). MS (EI), *m/z* (relative intensity): 193 (41) [M^+], 150 (49), 120 (71), 92 (30), 73 (100). Anal. Calcd. for $C_{10}H_{15}N_3O$ (193.25): C, 62.15; H, 7.82; N, 21.74. Found: C, 62.10; H, 7.62; N, 21.74.

(2-Aminobenzyl)trimethylhydrazine (**5**).[20] A solution of 1.00 g (5.2 mmol) of (2-aminobenzoyl)trimethylhydrazide in 20 mL of THF was added to 0.48 g (12.1 mmol) of $LiAlH_4$ in 10 mL of THF. The resulting suspension was refluxed for 2 h. Excess of $LiAlH_4$ was destroyed by subsequent addition of 0.5 mL H_2O, 0.5 mL 15% NaOH and 1.5 mL H_2O. The resulting suspension was filtered and the filtrate was dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining yellowish oil remained was distilled to yield 0.65 g (70%) of **5** as a colorless liquid (bp. 230 °C/45 torr). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3 H, NCH_3), 2.41 (s, 6 H, $N(CH_3)_2$), 3.70 (s, 2 H, CH_2N), 4.42 (s, 2 H, NH_2), 6.62 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 6.65 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 6.96 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.07 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 33.3 (NCH_3), 39.0 ($N(CH_3)_2$), 57.4 (CH_2N), 115.4 (ar-CH), 117.5 (ar-CH), 122.6 (ar-C_q), 128.2 (ar-CH), 130.1 (ar-CH), 146.8 (ar-C_q). MS (EI), *m/z* (relative intensity): 179 (15) [M^+], 150 (2), 106 (14), 77 (7), 73 (100), 65 (2). Correct HRMS Calcd. for $C_{10}H_{17}N_3$ (179.1422).

2-(Bromobenzyl)trimethylhydrazine (**6**). a) Gattermann bromination: A solution of 0.51 g (7.4 mmol) of $NaNO_2$ in 2.8 mL H_2O was added to a solution of 1.25 g (7.0 mmol) of **5** in 9.8 mL of 48% HBr at –15 °C. The solution was stirred 15 min at room temperature and urea was added until the brown color nearly disappeared. After addition of 0.09 g (1.4 mmol) of Cu powder, the suspension was carefully heated until production of gas started. The heat was reduced, the reaction mixture was stirred further at room temperature and was finally heated until the gas formation ceased. The solution was made alkaline by addition of solid NaOH and extracted three times with 20 mL of Et_2O. The combined Et_2O layers were dried with Na_2SO_4. After removal of the solvent *in vacuo* the remaining oil was distilled at (bp. 75°C/0.1 torr) to yield 0.46 g (27%) of **6** as a colorless liquid.

b) Trimethylhydrazine (0.65 g, 8.8 mmol) was added to a solution of 2.4 mL (8.0 mmol) of *n*-BuLi (2.36 M in hexane) in 30 mL of Et_2O at –45 °C and the reaction mixture was stirred at ambient temperature for 1.5 h.[21] 2.0 g (8.0 mmol) of 2-bromobenzyl bromide (**8**)[22] in 15 mL of Et_2O were added at 0 °C and the slurry stirred at ambient temperature for 1 h. The reaction mixture was made alkaline by addition of 30 mL of 2 N NaOH. The organic layer was separated and the aqueous phase was extracted with two portions (20 mL) of Et_2O. The combined organic phases were washed with 15 mL of brine and dried over Na_2SO_4. 0.89 g (45%) of **6** was obtained by distillation (bp. 80.5 °C/0.25 torr) as a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3 H, NCH_3), 2.43 (s, 6 H, $N(CH_3)_2$), 3.74 (s, 2 H, CH_2N), 7.09 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.28 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.47–7.53 (m, 2 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 34.6 (NCH_3), 39.4 ($N(CH_3)_2$), 57.0 (CH_2N), 124.2 (ar-C_q), 127.2 (ar-CH), 128.2 (ar-CH), 130.6 (ar-CH), 132.5 (ar-CH), 138.3 (ar-C_q). MS (EI, 70 eV), *m/z* (relative intensity): 244/242 (43/50) [M^+], 198/196 (5/3), 171/169 (21/20), 118 (6), 91 (13), 89 (1), 73 (100), 77 (5), 65 (6). Anal. Calcd. for $C_{10}H_{15}BrN_2$: C, 49.40; H, 6.22; N, 11.52. Found: C, 49.60; H, 6.05; N, 11.39.

[2-(Trimethylhydrazinomethyl)phenyl]trimethylsilane (**9**). 1.2 mL (2.9 mmol) of *n*-BuLi (2.36 M in hexane) were added to a solution of 0.67 g (2.8 mmol) of **6** in 7.5 mL of Et_2O at –78 °C. The mixture was stirred for 45 min at –40 °C and 1 h at ambient temperature. 0.38 mL (3.0 mmol) Me_3SiCl were added at 0 °C and the resulting mixture was stirred at ambient temperature for 60 h. After addition of 10 mL of 2 N NaOH, the organic layer was separated and the aqueous phase was extracted twice with 10 mL of Et_2O. The

combined organic phases were washed with 10 mL of brine, dried with Na_2SO_4 and the solvent was removed *in vacuo*. The remaining oil was distilled to yield 3.63 g (56%) of **9** as a pale yellow oil (bp. 90 °C/10^{-3} torr). ^{1}H NMR ($CDCl_3$): δ 0.34 (s, 9 H, $SiCH_3$), 2.16 (s, 3 H, NCH_3), 2.43 (s, 6 H, $N(CH_3)_2$), 3.80 (s, 2 H, CH_2N), 7.21 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.33 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.50 (2 overlapping d, $^3J \approx 8$ Hz, 2 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 0.5 ($SiCH_3$), 33.0 (NCH_3), 39.2 ($N(CH_3)_2$), 58.6 (CH_2N), 126.1 (ar-CH), 128.5 (ar-CH), 129.1 (ar-CH), 134.5 (ar-CH), 138.4 (ar-C_q), 144.9 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –4.7 (s (quint, $^1J_{SiC}$ = 53 Hz)). MS (EI, 70 eV), *m/z* (relative intensity): 236 (39) [M^+], 221 (12), 206 (5), 176 (82), 162 (18), 133 (37), 91 (29), 73 (100). Anal. Calcd. for $C_{13}H_{24}N_2Si$: C, 66.04; H, 9.56; N, 11.85. Found: C, 66.36; H, 10.06; N, 11.81.

Bis[2-(trimethylhydrazinomethyl)phenyl]silane (**11**). 0.40 g (1.6 mmol) of **6** and 0.68 mL (1.6 mmol) of *n*-BuLi (2.36 M in hexane) were combined in 5 mL of Et_2O at –75 °C, stirred for 1 h at –40 °C, warmed to –15 °C during 1.5 h and finally stirred for 1 h at ambient temperature. The resulting solution was added carefully to a solution of 0.09 mL (0.8 mmol) of $SiCl_4$ in 2.5 mL of THF at 0 °C and stirred for 2 d at ambient temperature. After removal of the solvent *in vacuo* 10 mL of chloroform were added and the resulting suspension was filtered. The filtrate was reduced *in vacuo* to 5 mL and 10 mL of hexane were added. A pale brown solid precipitated, which was filtered off and dried *in vacuo*. The solid was dissolved in 10 mL of Et_2O, a suspension of 0.37 g (10.0 mmol) of $LiAlH_4$ in 10 mL of Et_2O was added and the suspension was heated to 40 °C for 1 h. After removal of the solvent *in vacuo*, 20 mL of hexane were added, insoluble material was filtered off and the solvent was removed from the filtrate *in vacuo*. 48 mg (19%) of **11** were isolated from the residue by distillation as a colorless liquid (bp. 180 °C/10^{-3} torr). ^{1}H NMR (C_6D_6): δ 1.97 (s, 6 H, NCH_3), 2.16 (s, 12 H, $N(CH_3)_2$), 3.83 (s, 4 H, CH_2N), 5.42 (s (d, $^1J_{SiH}$ = 209 Hz), 2 H, SiH_2), 7.07 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 2 H, ar-H), 7.22 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 2 H, ar-H), 7.35 (d, ^3J = 8 Hz, 2 H, ar-H), 7.61 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 2 H, ar-H). ^{13}C NMR (C_6D_6): δ 31.8 (NCH_3), 39.1 ($N(CH_3)_2$), 60.6 (CH_2N), 126.7 (ar-CH), 128.9 (ar-CH), 129.8 (ar-CH), 134.1 (ar-C_q), 138.0 (ar-CH), 146.3 (ar-C_q). ^{29}Si NMR (C_6D_6): δ –40.9 (t, $^1J_{SiH}$ = 209 Hz). IR (film): $\tilde{\nu}$ 2150 cm^{-1} (Si-H). - MS (EI, 70 eV), *m/z* (relative intensity): 356 (7) [M^+], 310 (18), 238 (25), 208 (13), 149 (27), 73 (100). Correct HRMS Calcd. for $C_{20}H_{32}N_4Si$ (356.2396).

[2-(Trimethylhydrazino)phenyl]trimethylsilane (**14**). A solution of 0.48 g (3.2 mmol) of **12**, 0.49 mL (3.3 mmol) of TMEDA and 1.4 mL (3.3 mmol) of *n*-BuLi (2.36 M in hexane) in 10 mL of hexane was stirred for 2 d at ambient temperature. 0.42 mL (3.3 mmol) of Me_3SiCl were added at 0 °C and the solution was stirred overnight at ambient temperature. After addition of 10 mL of 2 N NaOH the organic phase was separated and the aqueous layer was extracted twice with 10 mL of Et_2O. The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. 0.20 g (28%) of **14** was isolated from the residue by distillation as a colorless liquid (bp. 65 °C/10^{-2} torr). ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 9 H, $SiMe_3$), 2.33 (s, 6 H, NMe_2), 2.71 (s, 3 H, NMe), 6.69 (d, ^3J = 8 Hz, 1 H, ar-H), 6.88 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.24 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.57 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 0.9 ($SiMe_3$), 27.6 (NMe), 40.4 (NMe_2), 114.2 (ar-CH), 119.8 (ar-CH), 129.5 (ar-CH), 130.0 (ar-C_q), 136.8 (ar-CH), 155.6 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –9.2 (s (d, $^1J_{SiC}$ = 54.2 Hz). MS (EI, 70 eV): *m/z* (relative intensity): 222 (100) [M^+], 207 (46), 192 (19), 177 (15), 164 (67),

162 (49), 148 (20), 134 (14), 119 (9), 73 (44). Anal. Calcd. for $C_{12}H_{22}N_2Si$: C, 64.80; H, 9.97; N, 12.60. Found: C, 64.88; H, 9.85; N, 12.71.

[(2-Trimethylhydrazino)phenyl]trichlorosilane (**15**). A solution of 1.16 g (7.7 mmol) of **13**, 1.2 mL (7.9 mmol) of TMEDA and 3.4 mL (7.9 mmol) of *n*-BuLi (2.36 M in hexane) in 10 mL of hexane was stirred at ambient temperature for 2 d. After addition of 0.46 mL (4.0 mmol) of $SiCl_4$ at 0 °C, the slurry mixture was stirred for 12 h at ambient temperature. The pale brown precipitate was filtered off, the filtrate was concentrated and 2 mL of chloroform were added. Crystallization at –15 °C gave 0.47 g (22%) of **15** as pale brown needles (mp. 125 °C). ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 6 H, NMe_2), 2.88 (s, 3 H, NMe), 6.66 (d, ^3J = 8 Hz, 1 H, ar-H), 6.99 (dd, ^3J = 8, ^3J = 8 Hz, 1 H, ar-H), 7.45 (ddd, ^3J = 8, ^3J = 8, ^4J = 1 Hz, 1 H, ar-H), 8.24 (dd, ^3J = 8, ^4J = 1 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 28.7 (NMe), 41.1 (NMe_2), 111.8 (ar-CH), 118.8 (ar-C_q), 120.3 (ar-CH), 124.0 (ar-CH), 139.6 (ar-CH), 154.2 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –44.9 (s). MS (EI, 70 eV): *m/z* (relative intensity): 282/284/286/288 (64/65/21/2) [M^+], 267/269/271/272 (100/100/31/4), 247/249 (13/7), 209/211/213 (21/21/4), 175/177 (31/18), 150 (37), 133/135/137 (22/22/8). Correct HRMS Calcd. for $C_9H_{13}Cl_3N_2Si$ (281.9913). Anal. Calcd. for $C_9H_{13}Cl_3N_2Si$: C, 38.11; H, 4.62. Found: C, 38.16; H, 4.84.

2-(Trimethylhydrazino)phenyl]silane (**16**). A suspension of 0.84 g (22.1 mmol) of $LiAlH_4$ in 5 mL of Et_2O was added to a solution of 0.19 g (0.7 mmol) of **15** in 5 mL of Et_2O and heated under reflux for 2 h. Et_2O was removed *in vacuo*, 10 mL of hexane were added and solid material was filtered off. After removal of the solvent from the filtrate *in vacuo*, the remaining oil was distilled yielding 0.04 g (30%) of **16** as a colorless liquid (bp. 50 °C/10^{-2} torr). ^{1}H NMR (C_6D_6): δ 1.88 (s, 6 H, NMe_2), 2.20 (s, 3 H, NMe), 4.62 (s (d, $^1J_{SiH}$ = 197 Hz), 3 H, SiH_3), 6.26 (d, ^3J = 8 Hz, 1 H, ar-H), 6.84 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.23 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.95 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H). ^{13}C NMR (C_6D_6): δ 27.5 (NMe), 40.5 (NMe_2), 110.6 (ar-CH), 116.1 (ar-C_q), 119.5 (ar-CH), 131.9 (ar-CH), 139.9 (ar-CH), 155.5 (ar-C_q). ^{29}Si NMR (C_6D_6): δ –68.8 (q, $^1J_{SiH}$ = 196 Hz). IR (Film): ν̃ 2120, 2030 cm^{-1} (Si–H). MS (EI, 70 eV): *m/z* (relative intensity): 180 (100) [M^+], 165 (4), 150 (14), 136 (60), 135 (65), 134 (93), 122 (33), 107 (30), 105 (30), 77 (22), 73 (13). Correct HRMS Calcd. for $C_9H_{16}N_2Si$ (180.1082). Anal. Calcd. for $C_9H_{16}N_2Si$: C, 59.95; H, 8.94; N, 15.53. Found: C, 59.96; H, 8.99; N, 15.57.

[(2-Trimethylhydrazino)phenyl]triethoxysilane (**17**). A solution of 349 mg (5.13 mmol) of sodium ethoxide in 5 mL of THF was added to a solution of 485 mg (1.71 mmol) of **15** in 5 mL of THF at 0 °C and stirred for 3 d at ambient temperature. After addition of 5 mL of 2 N NaOH, the organic phase was separated and the aqueous layer was extracted twice with 5 mL of Et_2O. The combined organic phases were dried over Na_2SO_4 and the solvent was removed *in vacuo*. 90 mg (25%) of **17** were obtained by distillation as a colorless liquid (bp. 77 °C/10^{-4} torr). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, ^3J = 7 Hz, 9 H, Me), 2.37 (s, 6 H, NMe_2), 2.73 (s, 3 H, NMe), 3.83 (q, ^3J = 7 Hz, 6 H, CH_2O), 6.55 (d, ^3J = 8 Hz, 1 H, ar-H), 6.81 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 1 H, ar-H), 7.28 (dd, ^3J = 8 Hz, ^3J = 7 Hz, 1 H, ar-H), 7.93 (d, ^3J = 7 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 18.2 (Me), 27 2 (NMe), 41.0 (NMe_2), 58.1 (CH_2O), 111.6 (ar-CH), 118.0 (ar-C_q), 118.2 (ar-CH), 131.1 (ar-CH), 139.3 (ar-CH), 156.4 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –62.9. MS (EI, 70 eV): *m/z* (relative intensity): 312 (100) [M^+], 297 (2), 269 (40), 267 (13), 224 (36), 223 (41), 178 (13), 150 (10).

Bis[(2-trimethylhydrazino)phenyl]dichlorosilane (**18**). A solution of 2.12 g (14.1 mmol) **13**, 2.2 mL (14.1 mmol) of TMEDA and 6.0 mL (14.1 mmol) of *n*-BuLi (2.36 M in hexane) in 20 mL of hexane was stirred for 2 d at ambient temperature. The solvent was removed *in vacuo*, 20 mL of THF and 0.81 mL (7.1 mmol) of $SiCl_4$ were added at 0 °C and the reaction mixture was stirred at ambient temperature for 12 h. The solvent was removed *in vacuo*, 20 mL of chloroform were added and the precipitated solid was filtered off. The filtrate was reduced *in vacuo* to 2 mL and 15 mL of hexane were added. A pale brown solid precipitated, which was filtered off and dried *in vacuo* to yield 1.85 g (66%) of **18** (mp. 177 °C, dec.). ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 12 H, NMe_2), 2.71 (s, 6 H, NMe), 6.58 (d, ^3J = 8 Hz, 2 H, ar-H), 6.92 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 2 H, ar-H), 7.30 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H), 8.31 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 27.2 (NMe), 42.5 (NMe_2), 111.9 (ar-CH), 118.7 (ar-CH), 122.8 (ar-C_q), 130.9 (ar-CH), 136.1 (ar-CH), 152.6 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –28.7 (s). MS (EI, 70 eV): *m/z* (relative intensity): 400/398/396 (13/59/86) [M^+], 363/361 (2/5), 357/355/353 (1/5/9), 311/309/307 (5/21/27), 275/273 (14/40), 181 (31), 150 (14), 120 (100). Correct HRMS Calcd. for $C_{18}H_{26}Cl_2N_4Si$ (396.1303). Anal. Calcd. for $C_{18}H_{26}Cl_2N_4Si$: C, 54.40; H, 6.59; N, 14.10. Found: C, 54.57; H, 6.63; N, 14.06.

Bis(2-[trimethylhydrazino]phenyl)silane (**19**). 0.58 g (15 mmol) of $LiAlH_4$ in 5 mL of Et_2O were added to a solution of 0.16 g (0.4 mmol) of **18** in 5 mL of Et_2O. The reaction mixture was refluxed for 2 h, ether was removed *in vacuo*, 10 mL of hexane were added and solid material was filtered off. 0.07 g (48%) of **19** was obtained from the filtrate after removal of the solvent *in vacuo*. ^{1}H NMR (C_6D_6): δ 2.00 (s, 12 H, NMe_2), 2.35 (s, 6 H, NMe), 5.14 (s (d, $^1J_{SiH}$ = 212 Hz), 2 H, SiH_2), 6.44 (d, ^3J = 8 Hz, 2 H, ar-H), 6.86 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 2 H, ar-H), 7.24 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H), 7.75 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H). ^{13}C NMR (C_6D_6): δ 27.4 (NMe), 40.8 (NMe_2), 111.5 (ar-CH), 119.4 (ar-CH), 125.1 (ar-C_q), 130.0 (ar-CH), 139.2 (ar-CH), 155.4 (ar-C_q). ^{29}Si NMR (C_6D_6): δ –43.8 (t, J_{SiH} = 213 Hz). IR (Film): ν̃ 2080, 2190 cm^{-1} (Si–H). MS (EI, 70 eV): *m/z* (relative intensity): 328 (6) [M^+], 299 (4), 256 (9), 239 (15), 210 (23), 180 (22), 135 (62), 118 (100), 77 (47). Correct HRMS Calcd. for $C_{18}H_{28}N_4Si$ (328.2083).

Bis[(2-trimethylhydrazino)phenyl]diethoxysilane (**20**). A solution of 790 mg (2.4 mmol) of **18** in 15 mL of THF were added to a suspension of 0.33 g (4.8 mmol) of sodium ethoxide in 10 mL of hexane at –70 °C. The reaction mixture was warmed during 105 min to –30 °C and finally stirred at ambient temperature for 20 h. The solvent was removed *in vacuo*, 20 mL of Et_2O were added and the formed suspension was filtered. After evaporation of Et_2O *in vacuo* recrystallization of the residue from heptane yielded 479 mg (48%) of **20** as pale yellow plates (mp. 96 °C). ^{1}H NMR ($CDCl_3$): δ 1.14 (t, ^3J = 7 Hz, 6 H, Me), 1.89 (s, 12 H, NMe_2), 2.66 (s, 6 H, NMe), 3.52 (br. s; 4 H, CH_2O), 6.49 (d, ^3J = 8 Hz, 2 H, ar-H), 6.81 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 2 H, ar-H), 7.21 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H), 8.20 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 18.2 (Me), 27.4 (NMe), 41.6 (NMe_2), 57.2 (CH_2O), 111.0 (ar-CH), 117.3 (ar-CH), 122.6 (ar-C_q), 129.2 (ar-CH), 137.9 (ar-CH), 154.2 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –47.6 (s). MS (EI, 70 eV): *m/z* (relative intensity): 416 (100) [M^+], 371 (9), 326 (17), 312 (39), 283 (40), 239 (24), 223 (65), 150 (22). Correct HRMS Calcd. for $C_{22}H_{36}N_4O_2Si$ (416.2607). Anal. Calcd. for $C_{22}H_{36}N_4O_2Si$: C, 63.42; H, 8.71; N, 13.45. Found: C, 63.56; H, 8.72; N, 13.37.

2-(Dimethylaminomethyl)phenyl]trichlorosilane (**21**).[10] A solution of 11.6 mL (80 mmol) dimethylbenzylamine and 33.2 mL (88 mmol) of *n*-BuLi (2.36 M in hexane) in 100 mL of Et_2O was stirred for 2 d at room temperature. After evaporation of Et_2O *in vacuo* and addition of 100 mL of hexane to the residue, the resulting suspension was added to a solution of 13.8 mL (120 mmol) of $SiCl_4$ in 100 mL of hexane at –60 °C. The reaction mixture was allowed to warm to ambient temperature within 16 h. The solvent was removed *in vacuo*, 150 mL of Et_2O were added to the residue and insoluble material was filtered off. From the filtrate 14.7 g (68%) of **21** as colorless crystals (mp. 89 °C) were obtained at 5 °C. ^{1}H NMR ($CDCl_3$): δ 2.52 (s, 6 H, NMe_2), 3.88 (s, 2 H, CH_2N), 7.18 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.40–7.52 (m, 2 H, ar-H), 8.37 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 46.2 (NMe_2), 62.1 (CH_2N), 125.5 (ar-CH), 128.2 (ar-CH), 132.3 (ar-CH), 133.0 (ar-C_q), 139.5 (ar-CH), 142.2 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –61.7. MS (EI, 70 eV), *m/z* (relative intensity): 273/271/269/267 (2/21/65/66) [M^+], 236/234/232 (11/50/74), 227/225/223 (10/28/28), 207/205/203 (2/9/13), 91 (8), 58 (100). Anal. Calcd. for $C_9H_{12}Cl_3NSi$: C, 40.24; H, 4.50; N, 5.21. Found: C, 40.32; H, 4.89; N, 5.30.

[2-(Dimethylaminomethyl)phenyl][2'-(trimethylhydrazino)phenyl]dichlorosilane (**22**). A solution of 1.7 g (11.4 mmol) of **12**, 1.7 mL (11.4 mmol) TMEDA and 4.4 mL (11.4 mmol) of *n*-BuLi (2.36 M in hexane) in 30 mL of hexane was stirred at ambient temperature for 2 d. The solvent was evaporated *in vacuo* and subsequently 30 mL of Et_2O and a solution of 2.0 g (7.4 mmol) of **21** in 20 mL of Et_2O were added at 0 °C. The reaction mixture was stirred overnight at ambient temperature, the precipitate was filtered off, washed with Et_2O and the solvent was removed *in vacuo*. The remaining pale brown oil was distilled to yield 1.3 g (46%) of **22** as a ^{1}H NMR spectroscopically pure white solid (bp. 175 °C/10^{-4} torr, mp. 169 °C). **22** could be further purified by recrystallization from Et_2O (mp. 173 °C). ^{1}H NMR ($CDCl_3$): δ 1.87 (br. s, 6 H, NMe_2), 1.93 (br. s, 6 H, NMe_2), 2.65 (s, 3 H, NMe), 3.30, 3.68 (br. AB-System, ^2J not resolved.; 2 H, CH_2N), 6.59 (d, ^3J = 8 Hz, 1 H, ar-H), 6.99 (dd, ^3J = 8 Hz, ^3J = 8 Hz, 1 H, ar-H), 7.31–7.40 (m, 4 H, ar-H), 7.97 (br. s, 1 H, ar-H), 8.35 (d, ^3J = 8 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 28.0 (NMe), 41.8 (NMe_2), 45.2 (NMe_2), 63.9 (CH_2N), 112.3 (ar-CH), 120.0 (ar-CH), 120.8 (ar-C_q), 126.5 (ar-CH), 128.4 (ar-CH), 129.7 (ar-CH), 132.1 (ar-CH), 133.0 (ar-CH), 135.7 (ar-C_q), 138.6 (ar-CH), 143.4 (ar-C_q), 154.3 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –31.0. MS (EI, 70 eV), *m/z* (relative intensity): 385/383/381 (1/4/7) [M^+], 348/346 (2/6), 341/339/337 (1/5/10), 303/301 (21/52), 296/294/292 (5/21/31), 260/258 (6/18), 220/218/216 (6/28/41), 180 (23), 134 (100). Anal. Calcd. for $C_{18}H_{25}Cl_2N_3Si$: C, 56.54; H, 6.59; N, 10.99. Found: C, 56.61; H, 6.66; N, 10.77.

[2-(Dimethylaminomethyl)phenyl][2'-(trimethylhydrazino)phenyl]silane (**23**). A suspension of 310 mg (0.8 mmol) of **22** in 10 mL of Et_2O was added to a suspension of 400 mg (10.5 mmol) of $LiAlH_4$ in 10 mL of Et_2O at 0 °C and stirred at ambient temperature for 30 min. The reaction mixture was hydrolyzed at –65 °C by subsequent addition of 4 mL of H_2O, 0.4 mL of 15% NaOH and 1.2 mL of H_2O. The resulting suspension was filtered and the solvent was evaporated *in vacuo*. The remaining oil was redissolved in 10 mL of hexane and dried over $MgSO_4$. Evaporation of the solvent *in vacuo* and distillation of the residue yielded 181 mg (72%) of **23** (bp. 156 °C/10^{-4} torr) as a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 6 H, NMe_2), 2.05 (s, 6 H, NMe_2), 2.26 (s, 3 H, NMe), 3.53 (s, 2 H, CH_2N), 5.20 (s (t, $^1J_{SiH}$ = 212 Hz), 2 H, SiH_2),

6.34 (d, ^3J = 8 Hz, 1 H, ar-H), 6.76 (ddd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.16–7.29 (m, 3 H, ar-H), 7.44 (d, ^3J = 8 Hz, 1 H, ar-H), 7.58 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.81 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 27.5 (NMe), 40.6 (NMe_2), 44.9 (NMe_2), 64.6 (CH_2N), 111.2 (ar-CH), 119.3 (ar-CH), 120.4 (ar-C_q), 126.6 (ar-CH), 128.3 (ar-CH), 128.8 (ar-CH), 130.8 (ar-CH), 137.4 (ar-CH), 139.2 (ar-C_q), 139.5 (ar-CH), 145.9 (ar-C_q), 155.4 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –46.1 (t, $^1J_{SiH}$ = 212 Hz). MS (EI, 70 eV), *m/z* (relative intensity): 313 (23) [M^+], 268 (96), 253 (48), 224 (100), 194 (23), 164 (38), 149 (24), 134 (23). Anal. Calcd. for $C_{18}H_{27}N_3Si$: C, 68.96; H, 8.68; N, 13.40. Found: C, 68.90; H, 8.78; N, 13.45.

2-(Dimethylaminomethyl)phenyl][2'-(trimethylhydrazino)phenyl]diethoxysilane (**24**). A solution of 64 mg (0.94 mmol) of sodium ethoxide in 10 mL of THF was added to a solution of 179 mg (0.47 mmol) of **22** in 5 mL of THF at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for further 16 h . After removal of the solvent *in vacuo*, distillation of the residue yielded 42 mg (22 %) of **24** as a colorless liquid (bp. 100 °C/10^{-3} torr). ^{1}H NMR ($CDCl_3$): δ 1.16 (t, ^3J = 7 Hz, 6 H, Me), 1.79 (br. s, 6 H, NMe_2), 2.12 (s, 6 H, NMe_2), 2.64 (s, 3 H, NMe), 3.48 (s, 2 H, CH_2N), 3.63 (q, ^3J = 7 Hz, 4 H, OCH_2), 6.52 (d, ^3J = 8 Hz, 1 H, ar-H), 6.90 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.20 (ddd, ^3J = 7 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.26–7.34 (m, 2 H, ar-H), 7.46 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.82 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 8.29 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 18.2 (CH_3), 27.1 (NMe), 40.4 (NMe_2), 45.5 (NMe_2), 57.7 (CH_2O), 63.6 (CH_2N), 111.4 (ar-CH), 118.5 (ar-CH), 120.8 (ar-C_q), 125.1 (ar-CH), 127.3 (ar-CH), 128.4 (ar-CH), 130.9 (ar-CH), 134.2 (ar-CH), 135.9 (ar-C_q), 140.1 (ar-CH), 143.4 (ar-C_q), 155.8 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –42.1. MS (EI, 70 eV), *m/z* (relative intensity): 401 (6) [M^+], 357 (6), 311 (83), 268 (19), 252 (12), 236 (73), 224 (100), 134 (52). Correct HRMS Calcd. for $C_{22}H_{35}N_3O_2Si$ (401.24986).

[2-(Dimethylaminomethyl)phenyl][2'-(trimethylhydrazino)phenyl]dibenzoxysilane (**25**). Lithium benzoxide was prepared by addition of 0.67 mL (1.6 mmol) of *n*-BuLi (2.36 M in hexane) to a solution of 0.16 mL (1.6 mmol) of benzyl alcohol in 7 mL of Et_2O at –60 °C and stirring at ambient temperature for 30 min. After addition of 2 mL of THF, the solution of the benzoxide was added to a suspension of 295 mg (0.8 mmol) of **22** in 7 mL of Et_2O at 0 °C. The reaction mixture was stirred overnight at ambient temperature, the solvent was evaporated *in vacuo* and the residue was suspended in 10 mL of Et_2O. The resulting suspension was filtered, the solvent was evaporated *in vacuo* and the residue was distilled to afford 280 mg (67%) of **25** as a colorless liquid (bp. 220 °C/10^{-4} torr). ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 6 H, NMe_2), 2.03 (s, 6 H, NMe_2), 2.64 (s, 3 H, NMe), 3.48 (s, 2 H, CH_2N), 4.60, 4.66 (AB-System, ^2J = 14 Hz, 4 H, OCH_2), 6.57 (d, ^3J = 8 Hz, 1 H, ar-H), 6.96 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.15–7.47 (m, 14 H, ar-H), 8.00 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 8.46 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 27.1 (NMe), 40.5 (NMe_2), 45.5 (NMe_2), 63.7 (CH_2N), 64.0 (CH_2O), 111.4 (ar-CH), 118.7 (ar-CH), 119.9 (ar-C_q), 125.4 (ar-CH), 126.5 (ar-CH), 126.6 (2 ar-CH), 127.7 (ar-CH), 128.0 (2 ar-CH), 128.7 (ar-CH), 131.3 (ar-CH), 134.2 (ar-CH), 135.1 (ar-C_q), 140.3 (ar-CH), 141.6 (ar-C_q), 143.8 (ar-C_q), 155.5 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –41.2. MS (EI, 70 eV), *m/z* (relative intensity): 525 (4) [M^+], 481 (8), 436 (4), 373 (83), 360 (59), 330 (12), 134 (7), 91 (100). Correct HRMS Calcd. for $C_{32}H_{39}N_3O_2Si$ (525.28117).

2-(Dimethylaminomethyl)phenyl][2'-(trimethylhydrazino)phenyl]silanediol (**26**). 1 mL of H_2O was added to a solution of 481 mg (1.26 mmol) of **22** in 10 mL of THF and 5 mL of triethylamine at –60 °C and the reaction mixture was slowly warmed to ambient temperature. The solvent was evaporated *in vacuo*, the residue was redissolved in *tert.*-butylmethyl ether and the resulting suspension was filtered. 210 mg (48%) of **26** was obtained by crystallization from the filtrate as a colorless solid (mp. 128–129 °C). ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 6 H, NMe_2), 2.30 (s, 6 H, NMe_2), 2.74 (s, 3 H, NMe), 3.49 (s, 2 H, CH_2N), 6.82 (d, ^3J = 8 Hz, 1 H, ar-H), 6.93 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, ar-H), 7.11–7.14 (m, 1 H, ar-H), 7.22–7.37 (m, 3 H, ar-H), 7.70 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.75–7.79 (m, 1 H, ar-H), OH protons not detected. ^{13}C NMR ($CDCl_3$): δ 27.4 (NMe), 40.4 (NMe_2), 44.3 (NMe_2), 65.1 (CH_2N), 115.5 (ar-CH), 121.0 (ar-CH), 126.7 (ar-CH), 127.5 (ar-C_q), 128.6 (ar-CH), 130.6 (ar-CH), 130.6 (ar-CH), 135.9 (ar-CH), 138.0 (ar-CH), 139.6 (ar-C_q), 141.9 (ar-C_q), 155.1 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –30.2. – MS (EI, 70 eV), *m/z* (relative intensity): 345 (6) [M^+], 328 (2), 301 (7), 283 (100), 256 (18), 238 (17), 196 (31), 180 (57). Correct HRMS Calcd. for $C_{18}H_{27}N_3O_2Si$ (345.18726).

[2-(Dimethylaminomethyl)phenyl]silane • 2 BH_3 (**29**). 3.1 mL (3.1 mmol) of a solution of BH_3 in THF (1 M) was added to a solution of 307 mg (1.24 mmol) [2-(dimethylaminomethyl)phenyl]silane in 10 mL of Et_2O. After stirring for 3 d, the solution was concentrated *in vacuo* to a volume of 3 mL and filtered. The remaining solid was analytically pure **29** (279 mg, 69%). mp. 117–121 °C (dec.). IR (KBr): $\tilde{\nu}$ 2142, 2167 cm^{-1} (Si–H). ^{1}H-NMR (C_6D_6): δ 2.06 (s,12 H, NMe_2), 2.1–3.2 (br. s, 6 H, BH_3), 3.92 (s, 4 H, CH_2N), 5.20 (s (d, $^1J_{SiH}$ = 204 Hz), 2 H, SiH_2), 6.87–6.91 (m, 2 H, ar-H), 6.94–7.04 (m, 4 H, ar-H), 7.36–7.41 (m, 2 H, ar-H). ^{13}C-NMR (C_6D_6): δ 50.0 (NMe_2), 66.6 (CH_2N), 128.7 (ar-CH), 130.3 (ar-CH), 133.9 (ar-CH), 134.8 (ar-C_q), 138.2 (ar-CH), 138.5 (ar-C_q). ^{29}Si-NMR (C_6D_6): δ –37.5. ^{11}B-NMR (C_6D_6): δ = –7.08. MS (EI, 70 eV), *m/z* (relative intensity): 325 (<1) [M^+], 326 (2), 297 (21), 146 (99), 42. Anal. Calcd. for $C_{18}H_{32}B_2N_2Si$: C, 66.28; H, 9.89; B, 6.63. Found: C, 65.47; H, 9.77; B, 6.40.

Bis[(2-methylamino)phenyl]bis(dimethylamino)silane (**31**). A suspension of 360 mg (0.82 mmol) of **18** and 14 mg (2.0 mmol) of lithium in 15 mL of THF was stirred at ambient temperature for 6.5 h. The solvent was removed *in vacuo*, 15 mL of toluene were added and the suspension was filtered. The solvent was removed from the filtrate *in vacuo* and the residue was redissolved in 10 mL of Et_2O. After addition of 0.1 mL , the reaction mixture was filtrated and dried over $MgSO_4$. 59 mg (22%) of **31** (mp. 106 °C) were obtained by slow evaporation of the solvent at atmospheric pressure. ^{1}H NMR (C_6D_6): δ 2.53 (d, ^3J = 5 Hz, 6 H, NMe), 2.55 (s, 12 H, NMe_2), 5.29 (br. q, ^3J = 5 Hz, 2 H, NH), 6.57 (d, ^3J = 8 Hz, 2 H, ar-H), 6.80 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 2 H, ar-H), 7.33 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H), 7.85 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 2 H, ar-H). ^{13}C NMR (C_6D_6): δ 30.8 (NMe), 38.5 (NMe_2), 109.6 (ar-CH), 116.9 (ar-CH), 117.6 (ar-C_q), 132.0 (ar-CH), 137.3 (ar-CH), 155.6 (ar-C_q). ^{29}Si NMR (C_6D_6): δ –14.1. MS (EI, 70 eV); *m/z* (relative intensity): 328 (2) [M^+], 283 (93), 238 (100), 177 (11), 134 (12), 105 (6). Correct HRMS Calcd. for $C_{18}H_{28}N_4Si$ (328.2083).

Reaction of **12** *with lithium.* A solution of 224 mg (1.49 mmol) of **12** and 31 mg (1.49 mmol) of lithium in 5 mL of THF were stirred at room temperature for 6 d. The reaction mixture was filtered, 226 mg

(1.49 mmol) of *t*-BuMe$_2$SiCl were added to the filtrate and stirred for another 21 h at ambient temperature. THF was removed *in vacuo*, 5 mL of Et_2O were added, unsolved solids were filtered off and Et_2O was removed *in vacuo*. The liquid residue was dissolved in 10 mL of Et_2O and extracted with 10 mL of 2 N HCl solution. The aqueous phase was made alkaline by addition of solid NaOH and was extracted with Et_2O (3 × 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo*. 80 mg of a pail yellow liquid were obtained, which was identified by means of GC/MS as a **84** : 16 mixture of **31** and **12**. ^{1}H NMR ($CDCl_3$): δ 2.85 (s, 3 H, NMe), 3.70 (br. s, 1 H, NH), 6.64 (dd, ^3J = 9 Hz, ^4J = 1 Hz, 2 H, ar-H), 6.73 (t, ^3J = 7 Hz, 1 H, ar-H), 7.22 (dt, ^3J = 9 Hz, ^3J = 7 Hz, 2 H, ar-H). GC/MS (EI, 70 eV); *m/z* (relative intensity): 106 (100) [M$^+$ – H], 92 (3), 77 (29), 65 (11), 51 (19).

Bis[(2-trimethylhydrazino)phenyl]silyl triflate (**33**). To a solution of 63 mg (0.19 mmol) of **19** in 5 mL of Et_2O were added 35 µL (0.19 mmol) of trimethylsilyl triflate dropwise at –65 °C. The resulting suspension was warmed to ambient temperature and stirred for 1 h. Evaporation of the solvent left behind a white solid, which was washed twice with 5 mL of hexane to yield 88 mg (97%) of **33**. ^{1}H NMR ($CDCl_3$): δ 2.69 (s, 6 H, NMe), 2.90 (s, 6 H, NMe), 2.99 (s, 6 H, NMe), 4.45 (s (d, $^1J_{SiH}$ = 283 Hz), 1 H, SiH), 6.81 (d, ^3J = 8 Hz; 2 H, ar-H), 7.02 (dd, ^3J = 7 Hz, ^3J = 7 Hz; 2 H, ar-H), 7.43 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 1 Hz; 2 H, ar-H), 7.78 (dd, ^3J = 7 Hz, ^4J = 1 Hz; 2 H, ar-H). ^{13}C NMR ($CDCl_3$): δ 29.0 (NMe), 40.3 (NMe), 42.0 (NMe), 113.2 (ar-CH), 115.4 (ar-C_q), 122.3 (ar-CH), 133.1 (ar-CH), 135.5 (ar-CH), 155.8 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –54.5 (d, $^1J_{SiH}$ = 283 Hz).

[2-(Dimethylaminomethyl)phenyl][2'-(trimethylhydrazino)phenyl]silyl triflate (**34**). To a stirred solution of 938 mg (3.9 mmol) of **23** in 15 mL of Et_2O were added dropwise 0.7 mL (3.9 mmol) of trimethylsilyl triflate at 0 °C. The resulting suspension was stirred at room temperature for 1 h. Evaporation of the solvent left behind a white solid, which was washed three times with 10 mL of hexane to yield 1.385 g (91%) of **34** (mp. 142–144 °C). ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3 H, NMe), 2.55 (s, 3 H, NMe), 2.86 (s, 3 H, NMe), 3.06 (s, 3 H, NMe), 3.09 (s, 3 H, NMe), 3.81, 4.43 (AB-System, $^2J_{AB}$ = 14 Hz, 2 H, CH_2N), 4.55 (s (d, $^1J_{SiH}$ = 276 Hz), 1 H, SiH), 6.88 (d, ^3J = 7 Hz, 1 H, ar-H), 7.05 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 1 H, ar-H), 7.23–7.50 (m, 4 H, ar-H), 7.63 (d, ^3J = 7 Hz, 1 H, ar-H), 8.03 (d, ^3J = 7 Hz, 1 H, ar-H). ^{13}C NMR ($CDCl_3$): δ = 30.1 (NMe), 38.9 (NMe), 43.4 (NMe), 44.3 (NMe), 45.9 (NMe), 64.9 (CH_2N), 113.6 (ar-CH), 114.3 (ar-C_q), 122.0 (ar-CH), 126.2 (ar-CH), 127.8 (ar-CH), 129.7 (ar-C_q), 131.6 (ar-CH), 133.4 (ar-CH), 135.3 (ar-CH), 136.2 (ar-CH), 143.8 (ar-C_q), 156.4 (ar-C_q). ^{29}Si NMR ($CDCl_3$): δ –53.6 (d, $^1J_{SiH}$ = 281 Hz). Anal. Calcd. for $C_{19}H_{26}F_3N_3O_3SSi$: C, 49.44; H, 5.68; N, 9.10. Found: C, 49.19; H, 5.73; N, 9.02.

Single crystal X-ray diffraction analysis of **20** and **22**.

Data for **20**: Monoclinic, space group $P2_1/n$, a = 1016.0(2), b = 1559.2(3), c = 1473.3(3) pm, β = 97.28(3)°; V = 2.3151(8) nm^3, ρ_{calc} = 1.195 g cm^{-3}, 2Θ range from 7 to 45°, ($-10 \le h \le 10$, $0 \le k \le 16$, $-8 \le l \le 15$), $Mo_{K\alpha}$, λ = 71.073 pm, T = 293 K, crystal dimensions 1.0 × 0.8 × 0.3 mm, 3015 reflections, all 3008 independent (R_{int} = 0.044) reflections were used for the structure refinement; final R_1 value [$I > 2\sigma(I)$] = 0.050, wR_2 = 0.124 (all data), residual electron density: +609 and –415e nm^3. *Data for* **22**: Orthorhombic, space group $P2_12_12_1$, a = 1067.3(2), b = 1190.8(2), c = 1496.6(3) pm, V = 1.9021(6) nm^3, ρ_{calc} = 1.335

g cm^{-3}, 2Θ range from 8 to 45°, ($-4 \le h \le 11$, $-12 \le k \le 12$, $-16 \le l \le 16$), $Mo_{K\alpha}$, λ = 71.073 pm, T = 153 K, crystal dimensions 0.8 × 0.7 × 0.7 mm, 2149 reflections, all 1896 independent reflections (R_{int} = 0.021) were used for the structure refinement; absolute structure parameter:[23] 0.05(6), final R_1 value [$I > 2\sigma(I)$] = 0.023, wR_2 = 0.063 (all data), residual electron density: +223 and −259 e nm^3. Both structures were solved by direct methods[24] and refined vs F^2 (SHELXL-97).[25] The R-values were defined as $R1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$.[26]

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