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New cyclic and spirocyclic aminosilanes

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Abstract: New cyclic and spirocyclic aminosilanes were synthesised using ethylenediamine, 2-aminobenzylamine, 1,8-diaminonaphthalene, o-phenylenediamine, and *trans*-cyclohexane-1,2-diamine as starting material. These diamines were converted into aminosilanes using silicon tetrachloride and dimethyldichlorosilane directly and via the *N,N'*-bis(trimethylsilylated) amino derivatives. 15 new compounds of the type (diamino)$(SiMe_3)_2$, $(diamino)_2Si$, (diamino)$SiMe_2$, and (diamino)$SiCl_2$ have been prepared. The formation of two cyclotrisilazane derivatives was observed starting from (*N,N'*-2-aminobenzylamino)dichlorosilane by trimerisation. All synthesised compounds have been characterised with NMR-, Raman-, or IR-spectroscopy, mass-spectrometry, and boiling or melting point. Single-crystal X-ray structure analyses of several derivatives have been performed.

The degree of substitution with trimethylsilyl groups in the final compounds depends on the ring size of the spirocycles. It was shown with quantum chemical calculations on the M062X/6-31G(d) level that trimethylsilyl groups have a stabilising effect on 5-membered ring systems and a destabilising effect on 6-membered rings in these compounds.

Keywords: spiro compound, spirocyclic, aminosilane, silazane

1 Introduction

Aminosilanes, i.e., silicon organic compounds with at least one Si–NR_2 bond (R = H, hydrocarbyl), are the topic of research for several decades. They are often synthesised in non-polar aprotic solvents, such as pentane and hexane (Böhme et al., 2000, 2003a, 2003b; Herzog et al., 1998; Huber and Schmidbaur, 1999; Huber et al., 1997a, 1997b; Meinel et al., 2014, 2015; Schlosser et al., 1994; Tamao et al., 1994; Trommer et al., 1997). Up to four amino moieties can be bound to one silicon atom. Besides hydrolysis, alcoholysis and other substitution reactions, the Si–N bond can undergo insertion reactions with heteroallenes (Barluenga et al., 1989; Degl'Innocenti et al., 1992; Glidewell and Rankin, 1970; Herbig et al., 2018a; Kirilinet al., 2009; Kraushaar et al., 2017; Wolff et al., 1978). For example, CO_2 can insert into the Si–N bond to form a carbamoic moiety (Kraushaar et al., 2012, 2014).

Siloxanes as derivatives of silanediols are studied for decades (e.g., Jaçoviç, 1957). The corresponding diaminosilanes (and aminosilanes with three or four Si–NR_2 moieties) are less researched (Armitage, 1982). Interesting structural motifs for this class of aminosilanes are cyclic and oligocyclic structures. So far, many cyclic aminosilanes having two Si–N bonds per cycle are known (e.g., Herbig et al., 2018b). But only in a few compounds the silicon atom is part of one or two independent cyclic systems without sterically demanding substituents (Kaßner et al., 2016; Kummer and Rochow, 1963). Most of the known spirocyclic aminosilanes contain ethylene bridges like in Figure 1. The substituents R are either aliphatic (Me, Et – Yoder and Zimmermann (1964); ^{i}Pr – Schlosser et al. (1994)) or feature aryl groups (benzyl – Yoder and Zimmermann (1964); p-methylphenyl – Rong et al. (1998); benzenesulfonyl, tosyl – Schlosser et al. (1994). Wannagat and Eisle (1978) have synthesised compounds with either Me or TMS moieties on each ring. Cyclic aminosilanes with exocyclic silyl moieties starting from ethylenediamine are also known (Auner et al. 1992; Böhme et al., 2007; Daniéle et al., 2001; Diedrich et al., 2002).

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Prout et al. (1994) reported cyclic aminosilanes starting from *o*-phenylenediamine. Other compounds having a Si atom as spiro atom are derivatives of *o*-phenylenediamine and 2-aminobenzylamine (Kaßner et al., 2016; Kummer and Rochow, 1963) or spirosilazanes (Schlingmann and Wannagat, 1976a), a series of heavier congeners of the latter of which has also been studied (Schlingmann and Wannagat, 1976b).

In this work new cyclic and spirocyclic aminosilanes according to Figure 1 are described. We set out to prepare these compounds in order to obtain an overview about the preparative accessibility to this class of compounds and to use them later for further derivatisation reactions. The amines shown in Figure 2 were used for the investigations.

2 Results

The outcome of numerous reactions is summarised in Sections 2.1, 2.2, and 3.1 in order to provide a coherent overview for the reader. NMR spectroscopic data are condensed in Section 3.2. Molecular structures are discussed in detail in Section 3.3, in order to understand the diversity of the obtained structures. The results of quantum chemical calculations in Section 3.4 help to understand the formation of different products.

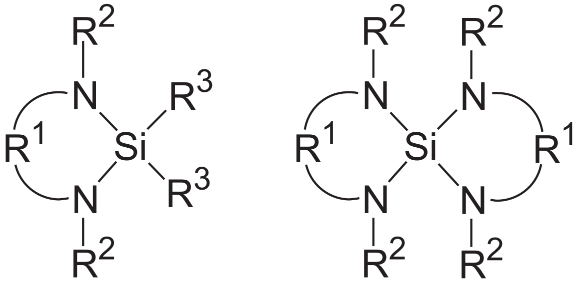


Figure 1: Generic structures of cyclic and spirocyclic aminosilanes in this work (with R^1 = ethylene, o-phenylene, 1,2-cyclohexanediyl, benzyl-2-yl, 1,8-naphthylene; R^2 = H, $SiMe_3$; R^3 = Me, Cl).

2.1 Syntheses of *N,N'*-bis(trimethylsilyl)ated aminosilanes

The *N,N'*-bis(trimethylsilyl)ated products (derivatives **1a-5a**) were obtained in high yields by reacting the amine with chlorotrimethylsilane in the presence of triethylamine (Scheme 1). Silylation reactions of that kind are often carried out in nonpolar solvents like *n*-pentane or *n*-hexane to support the separation (i.e., precipitation) of the amine hydrochloride formed as by-product. In the current case, however, THF was used because of the better solubility of some of the diamines in this solvent.

2.2 Syntheses of cyclic and spirocyclic derivatives

Two different routes are pursued for the synthesis of cyclic and spirocyclic aminosilanes: The reaction of the diamines **1-5** with the chlorosilane in the presence of triethylamine as base is denoted as **method A** (Scheme 2). The reaction of the *N,N'*-bis(trimethylsilyl)ated diamine derivatives **1a-5a** with the corresponding chlorosilane and triethylamine is denoted as **method B** (Scheme 2).

Synthesised spirocyclic compounds are labelled with the number of the parent diamine and the suffix **b**. Two types of cyclic aminosilanes were synthesised: Derivatives with the suffix **c** contain two methyl groups bound to the endocyclic silicon atom. Derivatives **d** contain two chlorine atoms at the endocyclic silicon atom. Additional trimethylsilyl groups at the nitrogen atoms are indicated by the suffix **-TMS** and the number of these moieties per molecule.

2.2.1 Syntheses with 1 and 1a

Compounds **1** and **1a** are colourless liquids. The reactions and experiments are shown in Scheme 3. All attempts to synthesise cyclic and spirocyclic silicon

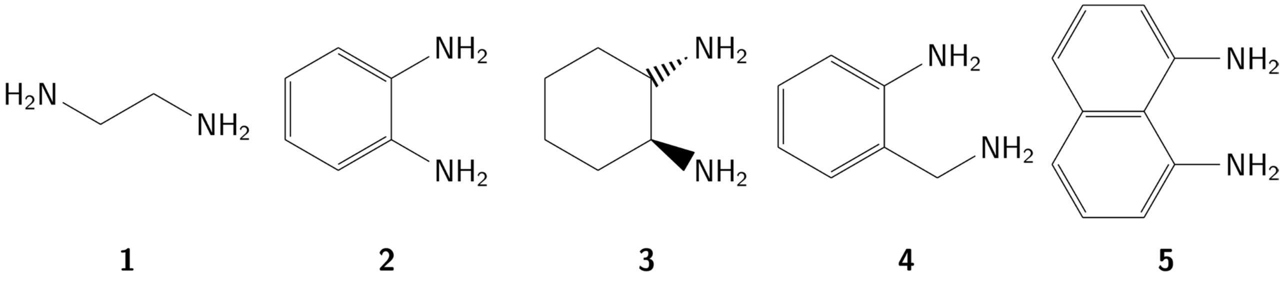
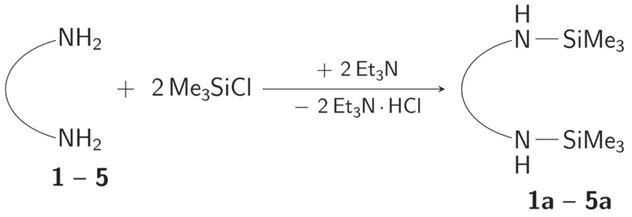


Figure 2: Amines used as starting materials.

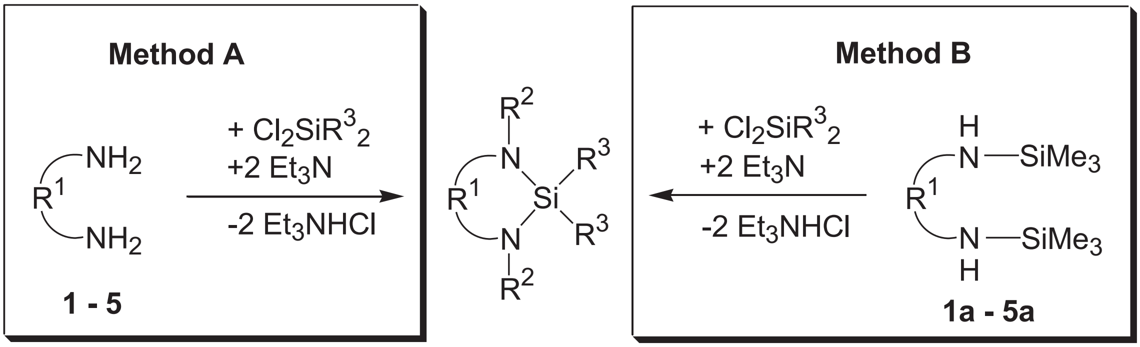
compounds starting with **1** lead to product mixtures from which no products could be isolated. Starting with the bis-trimethylsilylated derivative **1a** cyclic and spirocyclic compounds could be synthesised with all trimethylsilyl moieties retained. Compound **1d-TMS2** was synthesised by our group and published earlier (Böhme et al., 2007). The substance **1b-TMS4** is also a solid while **1c-TMS2** is a colourless liquid, the structure of which is confirmed by NMR spectroscopy and the molar mass by cryoscopy.



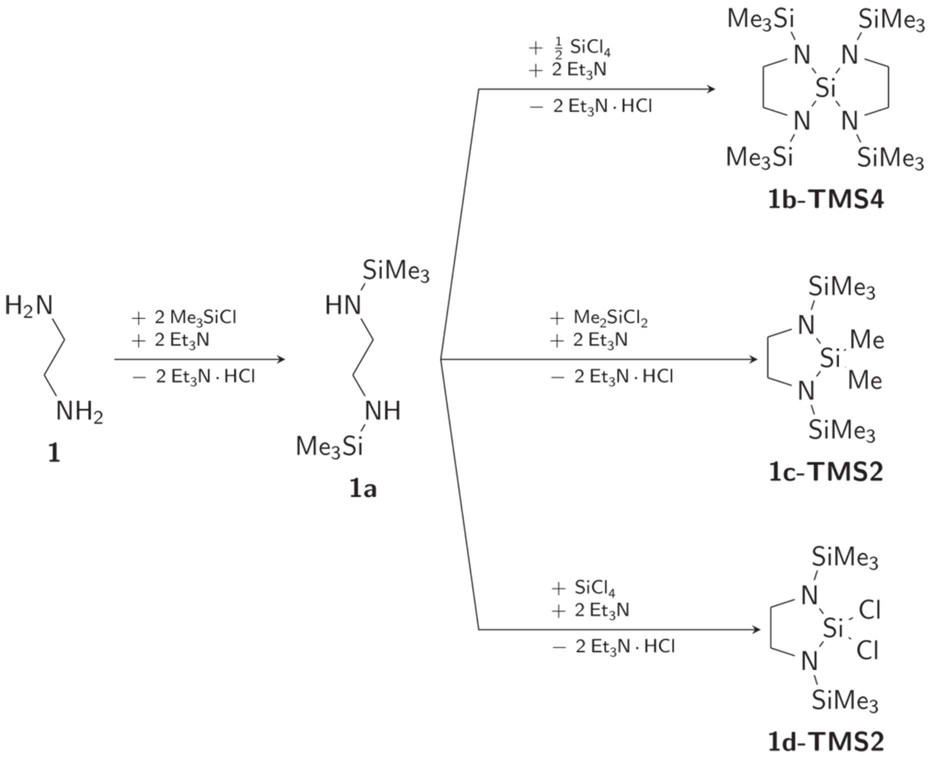
Scheme 1: Synthesis of derivatives **a** from amines and chlorotrimethylsilane in the presence of triethylamine.

2.2.2 Syntheses with 2 and 2a

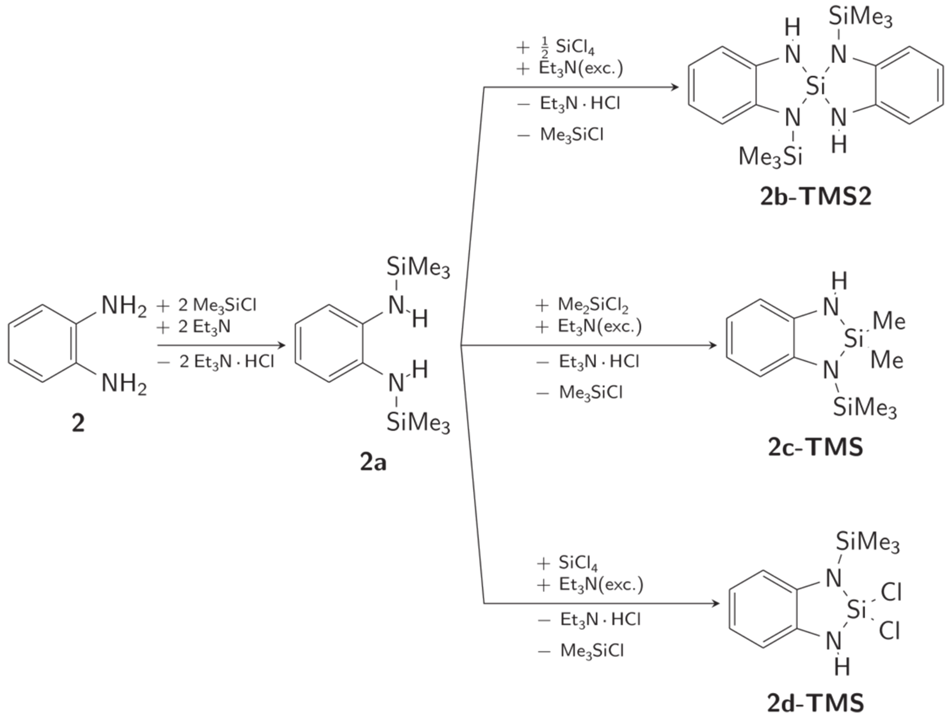
The attempts to synthesise aminosilanes with *o*-phenylenediamine **2** gave intractable product mixtures in reactions with silicon tetrachloride and dichlorodimethylsilane (see Scheme 4). In reactions with



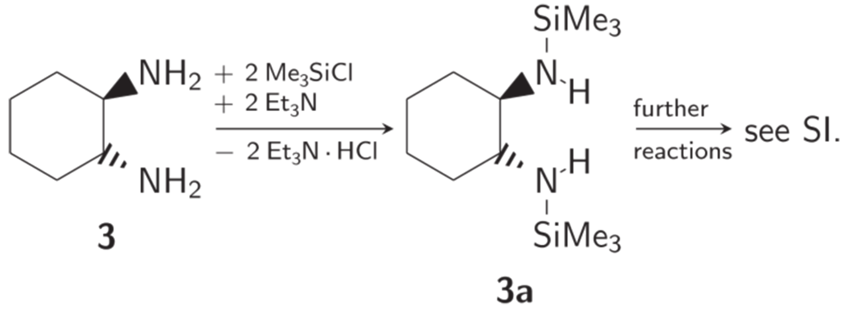
Scheme 2: Synthesis of cyclic aminosilanes with method A and B.



Scheme 3: Experiments with and reactions of ethylenediamine (**1**).



Scheme 4: Experiments with and reactions of *o*-phenylenediamine (**2**).



Scheme 5: Experiments with and reactions of 1,2-diaminocyclohexane (**3**).

2a half of the trimethylsilyl moieties are preserved in the cyclic and spirocyclic compounds. The compounds **2b-TMS2** and **2d-TMS** were crystallised and the molecular structures were determined. Earlier, **2d-TMS2** was reported as product of the reaction of **2a** with $SiCl_4$ and triethylamine in toluene (Wagler and Roewer, 2007). Obviously, changing the solvent alters the reactivity of **2a** significantly.

2.2.3 Syntheses with 3 and 3a

Compound **3** gave intractable product mixtures in reactions with silicon tetrachloride and dichlorodimethylsilane. Even though silylation of **3** afforded **3a** in good yield (Scheme 5), further reactions of **3a** with $SiCl_4$ and Me_2SiCl_2 afforded mixtures of products from which individual compounds could not be isolated or have been isolated in poor yield only. Thus, details related to the reactions of **3a** can be found in Supplementary material and have not been included in the discussion.

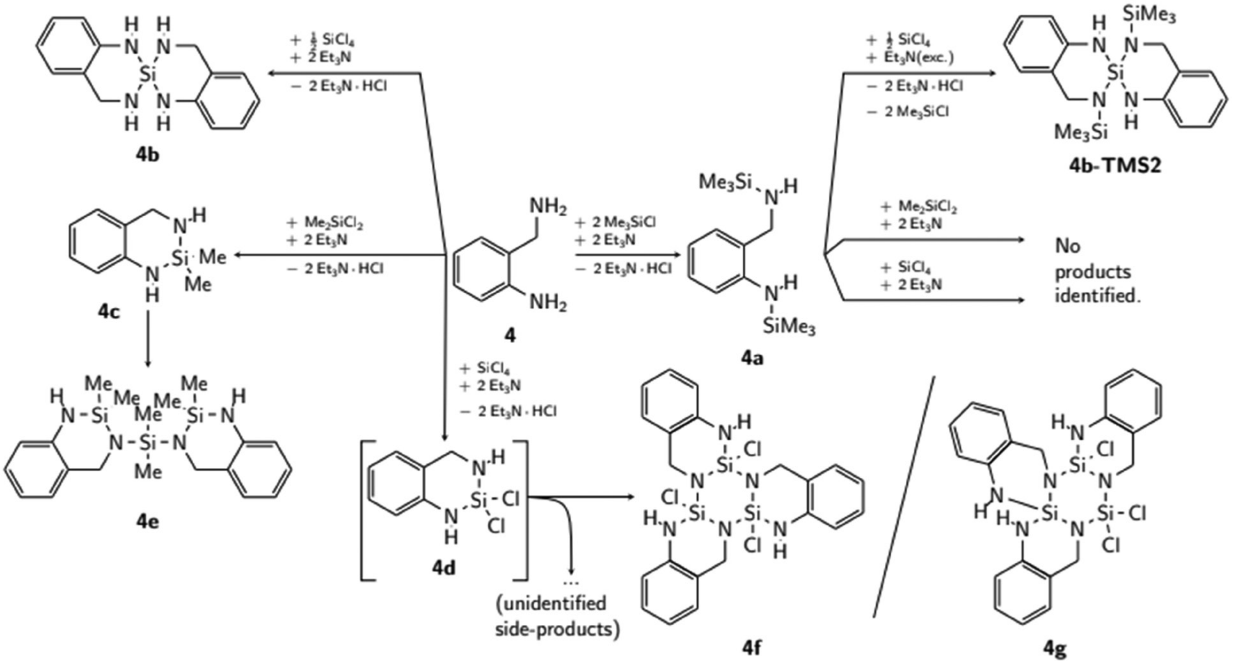
2.2.4 Syntheses with 4 and 4a

The outcome of the reactions of **4** are different from those of **1** to **3** because the cycle to be created is a 6-membered ring unlike the 5-membered one in the previous target products (see Scheme 6). The reactions with the amine **4** gave isolable products (**4b** and **4c**). Compound **4e** is formed together with **4c**. Therein, two molecules of **4c** are connected via a Me_2Si moiety at the aliphatic amine N atom. A changed reactivity pattern is also observed in the reaction which aimed at formation of the $SiCl_2$ containing derivative **4d**. The expected product was not obtained, but the cyclotrisilazane compounds **4f** and **4g** formed by subsequent substitution of Si–Cl bonds for Si–N with the aliphatic amine group. Both **4f** and **4g** contain 6-membered silazane rings in the centre supplemented by three 2-aminobenzylamine moieties fused to this ring. Both compounds, which are isomers, are obtained from the same reaction batch and vary only in the arrangement of the diamine moieties.

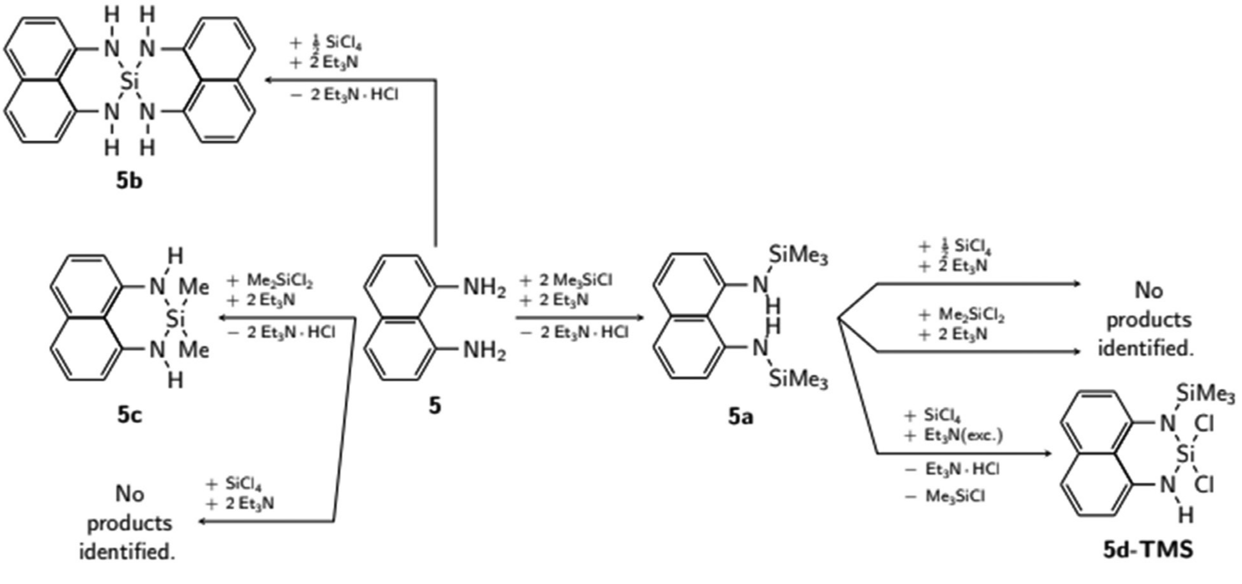
Starting with **4a** the synthesis of **4b-TMS2** is possible. The trimethylsilyl moieties on the aliphatic amine N atom are preserved. All cyclic and spirocyclic derivatives of **4** were crystallised and their molecular structures were determined (see Section 3.3).

2.2.5 Syntheses with 5 and 5a

The results of the reactions with **5** are similar to the reactions of **4**. Starting with **5**, the spirocyclic and cyclic products **5b** and **5c** are obtained (Scheme 7). The



Scheme 6: Experiments with and reactions of 2-aminobenzylamine (**4**).



Scheme 7: Experiments with and reactions of 1,8-diaminonaphthalene (**5**).

dichloro derivative **5d-TMS** was synthesised, preserving one of the two trimethylsilyl groups from **5a**. Further condensation reactions (as encountered with derivatives of **4**) were not observed. One reason is the lower reactivity due to the absence of any aliphatic amine moiety in **5**. The compounds **5b**, **5c**, and **5d-TMS** were crystallised and their molecular structures were determined (see Section 3.3).

3 Discussion

3.1 Discussion of the outcome of the syntheses

Our current observations indicate that for the syntheses of spiro-compounds with 6-membered rings the synthetic route starting with the amine (method A) is more favourable while compounds containing 5-membered rings should be synthesised starting from the trimethylsilyl derivatives **a** (method B). This fact can be explained with steric aspects. If method B is applied for the synthesis of **4b**, **4c**, **5b**, and **5c** side products are observed, as outlined in Schemes 6 and 7. In fact, within the same reaction time, no indication of spirocyclic compounds **b** or **c** can be found in the NMR spectra. Nevertheless, using method A for the synthesis of 5-membered silacycles, the formation of oligo- and polymers as main products is indicated in the NMR spectra by sets of very broad signals.

It must be pointed out that the synthesised spirocyclic aminosilanes show a tendency for polymerisation. So it happened regularly, that an already isolated substance formed a gelatinous compound shortly after being dissolved in solvents like $CDCl_3$. Most likely, ring opening reactions or further reactions with NH-functions took place. Polymerisations were not further investigated, since we were interested in the preparation of molecular compounds as precursors for insertion reactions. The results of insertion reactions will be reported in a forthcoming paper.

3.2 ^{29}Si NMR data of the synthesised compounds

All successfully synthesised and isolated compounds have been characterised in various ways such as NMR-, Raman-, and mass spectroscopy as well as melting points if possible. ^{29}Si NMR data of the new compounds are summarised in Table 1. In the literature, many other ethylenediamine derivatives are known. Table 2 shows a compilation of their ^{29}Si NMR shifts. The comparison of the ^{29}Si NMR data is in support of the assignment of the silicon containing moieties in the new products.

No data for comparison are known in literature for the aminosilanes **1a**, **2a**, **3a**, and **4a**. Only for **5a** the ^{29}Si NMR shift of 3.7 ppm (Gade et al., 2002) can be found, which is close to the shift we recorded. The ^{29}Si NMR shift for compound **4b** found in literature has the value -48.9 ppm (Lange A., Cox G., Wolf H., Csihony S., Spange S., Kaßner L. et al., 2014, Stickstoffhaltige Kompositmaterialien, deren Herstellung und Verwendung. World patent, 2015086461) and is also very close to the data obtained in our experiment. The ^{29}Si NMR shifts of derivatives **b**, **c**, and **d** (cyclic and spirocyclic compounds) reveal a clear difference between 6-membered and 5-membered rings. The silicon nuclei of derivatives of amines **1**, **2**, and **3** are less shielded while the ^{29}Si NMR signals of derivatives of the amines **4** and **5** are high field shifted. All TMS moieties exhibit a chemical shift similar to that of hexamethyldisilazane (2.4 ppm).

3.3 Molecular structures

Compound **2b-TMS2** crystallises in the monoclinic space group C2/c with a half molecule in the asymmetric unit. Compound **2d-TMS** crystallises in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. The molecular structures are shown in Figures 3 and 4, essential geometric parameters in Table 3. The 1,2-diaminobenzene units in both compounds carry one trimethylsilyl group each. This was already concluded from the NMR data. The bonds Si1–N1 are longer than the bonds

Table 1: ^{29}Si NMR data of the synthesised compounds

Amine	Derivative a	Derivative b	Derivative c	Derivative d
1	3.7	15.3 (TMS: 1.6)	12.1 (TMS: 1.4)	-18.6 (TMS: 6.2) (Böhme et al., 2007)
2	3.8	-24.6 (TMS: 4.2)	15.1 (TMS: 2.1)	-23.5 (TMS: 6.8)
3	1.6	exact assignment impossible	10.6 (TMS: -1.3)	-20.7 (TMS: 3.7)
4	1.6, 5.5	-49.0	-1.7	derivative not synthesised
5	3.6	-59.1	-5.6	-37.5

TMS: Trimethylsilyl moieties.

Table 2: ^{29}Si NMR data of compounds taken from literature

Amine	Substituents on endocyclic silicon atom	Substituents on N	Literature	Chemical shift of endocyclic silicon atom	Chemical shift of exocyclic silicon atom
2	Ph, Ph	H	Prout et al., 1994	11.8	--
2	Ph, Me	H	Prout et al., 1994	-0.7	--
2	Cl, Cl	TMS	Wagler and Roewer, 2007	-18.1	6.5
1	Me, CH(SiMe$_3$)CH(Me)$_2$	TMS	Auner et al., 1992	14.0	1.3 (NTMS), 3.0 (CTMS)
1	Vi, Ph	TMS	Auner et al., 1992	-9.4	2.8
1	Cl, Cl	TMS	Böhme et al., 2007	-18.6	6.2
1	Cl, Cl	SiMePh$_2$	Wagler and Roewer, 2007	-16.7	-8.4
1	Cl, Cl	SiMe$_2$Ph	Diedrich et al., 2002	-17.4	-1.4
1	Cl, Cl	SiMe$_2{}^t$Bu	Diedrich et al., 2002	-17.0	10.0
1	Cl, H	SiMe$_2{}^t$Bu	Diedrich et al., 2002	-15.2	9.1
1	Br, Br	SiMe$_2{}^t$Bu	Diedrich et al., 2002	-38.7	9.9
1	^{i}Pr, ^{i}Pr	TMS	Diedrich et al., 2002	17.7	0.8

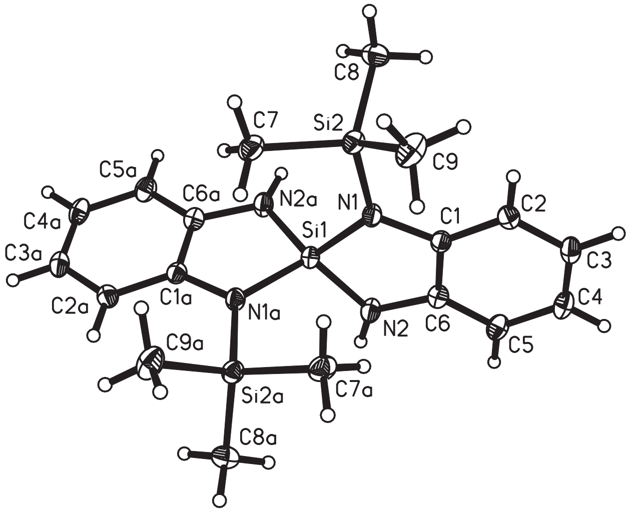


Figure 3: Molecular structure of **2b-TMS2** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

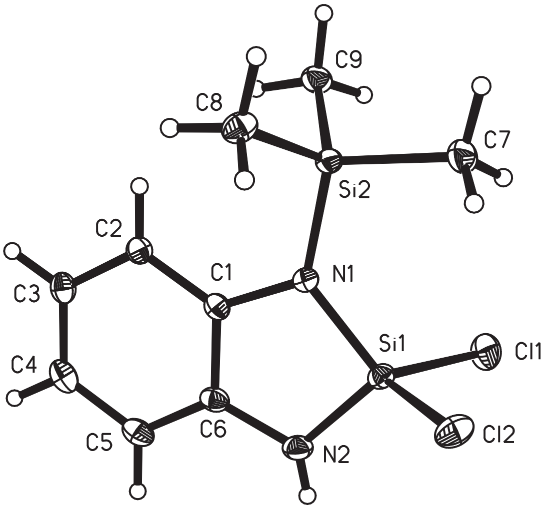


Figure 4: Molecular structure of **2d-TMS** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Si1–N2. This is attributed to the substitution of N1 with the trimethylsilyl group. As a result of the five-membered ring(s), the coordination sphere about silicon atom Si1 is rather distorted tetrahedral. The intra-chelate bond angle N1–Si1–N2 (93.06(8)° in **2b-TMS2** and 95.47(9)° in **2d-TMS**) is noticeably smaller than the other angles at Si1. All other bond angles are expanded to values between 115.52(8) to 121.31(12)° in **2b-TMS2** and 113.75(7)° to 115.48(6)° in **2d-TMS** (see Table 3). The (*N*,*N*'-o-phenylenediamino) silicon units (involving the atoms C1 to C6, N1, N2, and Si1) are essentially planar in both molecules. The two (*N*,*N*'-o-phenylenediamino)silicon units in **2b-TMS2** intersect at an angle of 83.32(4)°. This deviation from orthogonality can be explained with the steric bulk of the two trimethylsilyl groups within the molecule. However,

Table 3: Selected geometric parameters (Å, °) of **2b-TMS2** and **2d-TMS**

2b-TMS2		**2d-TMS**	
Si(1)–N(1)	1.7362(17)	Si(1)–N(1)	1.7259(16)
Si(1)–N(2)	1.7172(18)	Si(1)–N(2)	1.6983(19)
Si(2)–N(1)	1.7654(18)	Si(1)–Cl(1)	2.0480(7)
		Si(1)–Cl(2)	2.0435(7)
		Si(2)–N(1)	1.7756(17)
N(2)–Si(1)–N(1)	93.06(8)	N(2)–Si(1)–N(1)	95.47(9)
N(2)–Si(1)–N(1A)	115.52(8)	Cl(2)–Si(1)–Cl(1)	103.68(3)
N(1A)–Si(1)–N(1)	120.78(13)	N(1)–Si(1)–Cl(1)	114.43(6)
N(2A)–Si(1)–N(2)	115.52(8)		
N(2A)–Si(1)–N(1)			
N(1A)–Si(1)–N(1)	121.31(12)	N(1)–Si(1)–Cl(2)	115.48(6)
N(2A)–Si(1)–N(2)	120.78(13)		
N(1A)–Si(1)–N(1)	121.31(12)	N(2)–Si(1)–Cl(1)	113.75(7)
		N(2)–Si(1)–Cl(2)	114.54(7)

this value is very similar to the structural analogous thio compound Si[S_2(*o*-C_6H_4)]$_2$, where partial planarisation was already observed without additional substituents (Herzog et al., 2000). Partial planarisation of the silicon coordination sphere in spirocyclic tetrathiosilanes was explained with the high s-character of the Si–S-bonds (Wojnowski et al., 1985). The dihedral angle between the (*N*,*N*'-o-phenylenediamino)silicon unit in **2d-TMS** and the plane Cl1–Si1–Cl2 is 89.89(3)°. The Si1–Cl bonds in **2d-TMS** are 2.0480(7) and 2.0435(7) Å. These values are very similar to the Si–Cl bonds in analogous compounds (Böhme et al., 2007; Schlosser et al., 1994; Wagler and Roewer, 2007).

The single crystal structures of four derivatives of **1d** have been published previously, see Figure 5. In 2,2-dichloro-1,3-bis(trimethylsilyl)-1,3-diaza-2-silacyclopentane (Böhme et al., 2007), 1,3-dibenzyl-2,2-dichloro-1,3-diaza-2-silacyclopentane (Schlosser et al., 1994), and 2,2-dichloro-1,3-bis(methyldiphenylsilyl)-1,3-diaza-2-silacyclopentane (Wagler and Roewer, 2007) the ethylenediamine unit (N–C–C–N) adopts a torsion angle of 32° to 34°. In contrast, in 2,2-dichloro-1,3-diphenyl-1,3-diaza-2-silacyclopentane this torsion angle is 0° due to a crystallographically imposed C_s-symmetry (Schlosser et al., 1994).

Compound **3d-TMS2** has a similar topology like derivatives of **1d**. As the bond precision of this structure suffers from disorder effects and thus does not contribute to the discussion, this structure is presented in Supplementary material only.

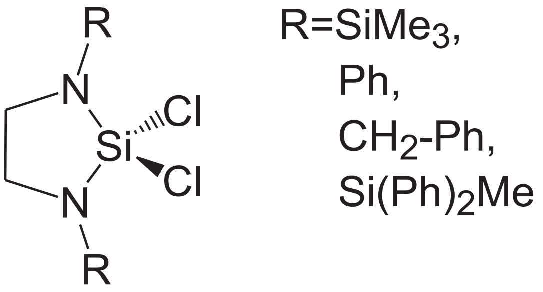


Figure 5: Previously published derivatives of **1d**.

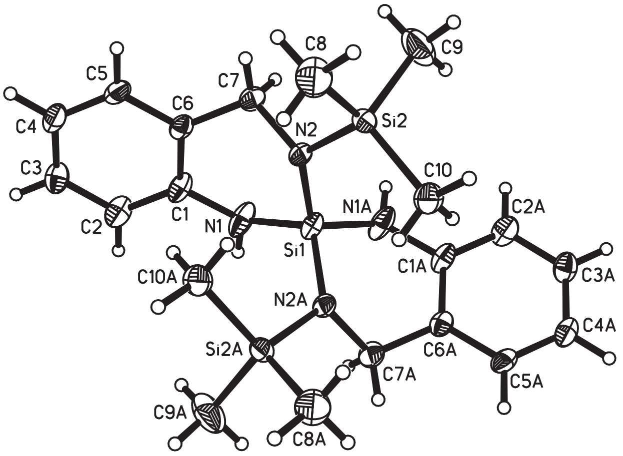


Figure 6: Molecular structure of **4b-TMS2** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Table 4: Selected geometric parameters (Å, °) of **4b-TMS2**

Si(1)–N(2)	1.7103(12)		
Si(1)–N(1)	1.7315(13)		
N(2)–Si(2)	1.7477(12)		
N(2A)–Si(1)–N(2)	113.64(8)	C(1)–N(1)–Si(1)	123.29(10)
N(2A)–Si(1)–N(1)	116.69(7)	C(1)–N(1)–H(1)	114.4(15)
N(2)–Si(1)–N(1)	102.00(6)	Si(1)–N(1)–H(1)	114.9(15)
N(1A)–Si(1)–N(1)	106.22(9)	C(7)–N(2)–Si(1)	115.48(10)
		C(7)–N(2)–Si(2)	113.87(9)
		Si(1)–N(2)–Si(2)	125.69(7)

Compound **4b-TMS2** crystallises in the monoclinic space group C2/c with a half molecule in the asymmetric unit. The molecular structure is shown in Figure 6, essential geometric parameters in Table 4. In accord with NMR data, there is a trimethylsilyl group bound at nitrogen atom N2. The coordination geometry at silicon atom Si1 is roughly tetrahedral and, with bond angles ranging from 102.00(6)° to 116.69(7)°, less distorted than in case of compound **2b-TMS2**. Unlike the latter, this molecule bears two different kinds of amine moieties: N1 bound to the aromatic ring whereas N2 is benzylic. This and the different additional substituents cause slightly different Si–N bond lengths for the central silicon atom Si1. The coordination spheres about the nitrogen atoms are noticeably planarised albeit not completely planar, as the sum of bond angles around nitrogen atoms N1 and N2 are 352.59° and 355.04°, respectively. This was rather unexpected for nitrogen atom N1, which is substituted with a phenyl group and a silicon atom, because with this substitution pattern it was expected to be planar (Meinel et al., 2014, 2015). Further steric requirements by the spirocycle and the additional trimethylsilyl groups might explain the deviation of both nitrogen atoms´ environments from planarity in order to fit into the conformation of the six-membered ring. As to the latter, ring puckering analysis reveals a boat conformation for the ring containing the atoms Si1–N1–C1–C6–C7–N2 with the parameters θ = 101.1(2)°, φ = 70.8(1)°, and a ring puckering amplitude Q = 0.549(2) Å. Ideal parameters for a boat conformation are θ = 90.0°; φ = k · 60° (Cremer and Pople, 1975), (Boeyens, 1978). The presence of the CH_2-group at C7 prevents the formation of a planar 6-membered ring as it was found in **5b** and **5c** (see below).

Compound **5b** co-crystallises with one unit of triethylammonium chloride and one molecule of chloroform per two molecules of **5b** in the triclinic space group P-1. Essential intermolecular interactions between these components are summarised in the Supplementary Information. Compound **5c** crystallises in the monoclinic space group $P2_1/c$. Two crystallographically independent aminosilane molecules are present in the crystal structures of both compounds. The molecular structures are shown in Figures 7 and 8, essential geometric parameters in Table 5. Since these have very similar geometric parameters, only one molecule will be discussed here as representative. No trimethylsilyl groups remained at the nitrogen atoms of both molecules (see Figures 7 and 8). The 1,8-diaminonaphthalene unit is bound to a silicon atom via both nitrogen atoms, thus forming six-membered diazasilacyclohexane rings. These heterocycles are planar in both molecules. The dihedral angle between both six-membered rings in **5b** is 88.58(5)°. The Si–N bond lengths in **5b** range from 1.696(2) (Si1A–N4A) to 1.712(2) Å (Si1A–N2A). This is rather short for Si–N-bonds and in accord with sp^2-hybridisation at the nitrogen atoms. Mean bond lengths have been determined from X-ray structural data with 1.713 Å for Si–N(sp^2)- and 1.739 Å for Si–N(sp^3)-bonds (Kaftory et al., 1998). This view is supported by the presence of planar nitrogen atoms in both molecules. The silicon atoms in both molecules are located in distorted tetrahedral coordination environments. The smallest bond angles at silicon are found inside the six-membered rings, i.e., 99.75(8)° for N1A–Si1A–N2A and 100.46(8)° for N3A–Si1A–N4A of compound **5b**; and 99.14(9)° for N1A–Si1A–N2A of compound **5c**. All other angles at the silicon atoms in **5b** and **5c** range between 110° and 115°.

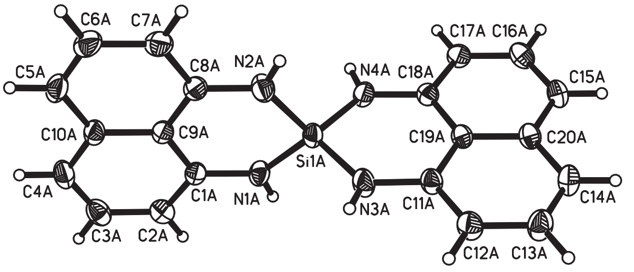


Figure 7: Molecular structure of **5b** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

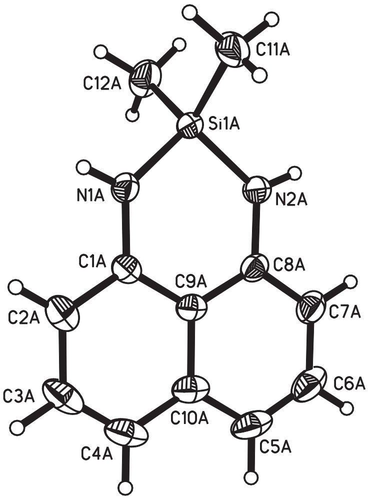


Figure 8: Molecular structure of **5c** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Table 5: Selected geometric parameters (Å, °) of **5b** and **5c**

5b		**5c**	
Si(1A)–N(1A)	1.7036(16)	Si(1A)–N(1A)	1.7217(18)
Si(1A)–N(2A)	1.7123(17)	Si(1A)–N(2A)	1.7220(19)
Si(1A)–N(3A)	1.7035(17)	Si(1A)–C(11A)	1.849(3)
Si(1A)–N(4A)	1.6965(16)	Si(1A)–C(12A)	1.848(2)
N(1A)–Si(1A)–N(2A)	99.75(8)	N(1A)–Si(1A)–N(2A)	99.14(9)
N(3A)–Si(1A)–N(1A)	115.48(9)	C(12A)–Si(1A)–C(11A)	109.31(14)
N(3A)–Si(1A)–N(2A)	113.65(9)	N(1A)–Si(1A)–C(11A)	112.38(11)
N(4A)–Si(1A)–N(1A)	115.46(8)	N(2A)–Si(1A)–C(11A)	110.75(11)
N(4A)–Si(1A)–N(2A)	112.74(8)	N(1A)–Si(1A)–C(12A)	110.63(10)
N(4A)–Si(1A)–N(3A)	100.46(8)	N(2A)–Si(1A)–C(12A)	114.38(12)

Compound **5d-TMS** crystallises in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The molecular structure is shown in Figure 9, essential geometric parameters in Table 6. The 1,8-diaminonaphthalene unit is bound via both nitrogen atoms at silicon atom Si1 forming a planar six-membered diazasilacyclohexane ring. One additional trimethylsilyl group is located at nitrogen atom N1. This was already concluded from the NMR data. The Si1–Cl bond lengths are 2.0462(5) and 2.0470(5) Å. These values are similar to the Si–Cl bonds in **2d-TMS**. The Si-N bond lengths in **5d-TMS** are 1.6977(12) (Si1–N1) and 1.6702(13) Å (Si1–N2). This is rather short for Si–N-bonds and hints again at sp^2-hybridisation at the nitrogen atoms (see discussion above). The bond Si2–N1 to the trimethylsilyl group is substantially longer with 1.7871(12) Å. The coordination geometry at silicon atom Si1 can be interpreted as distorted tetrahedral. The smallest bond angle is Cl1–Si–Cl2 with 103.21(2)°. This is a very similar value as in compound **2d-TMS**. The bond angle N1–Si1–N2 within the six-membered diazasilacyclohexane ring is 107.29(6)°. This is larger than the corresponding bond angles in **5b** and **5c** with values at 99°. The dihedral angle between the diazasilacyclohexane ring and the plane Cl1–Si1–Cl2 is 86.613(3)°.

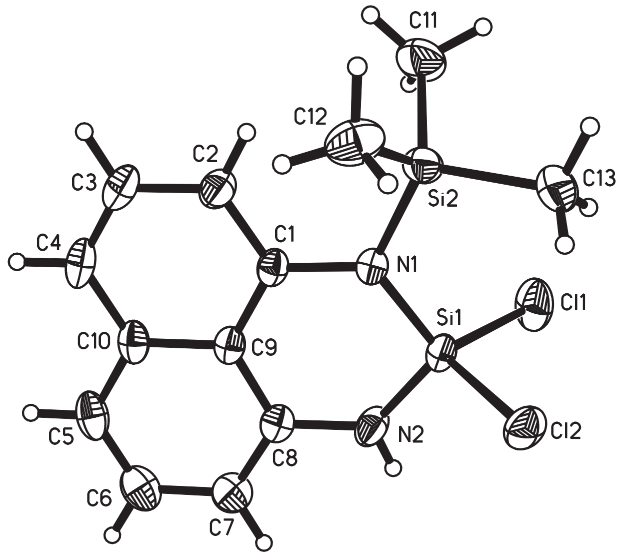


Figure 9: Molecular structure of **5d-TMS** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. The methyl groups at C11 and C12 are rotationally disordered. Their alternative positions C11A and C12A have been omitted for clarity.

Table 6: Selected geometric parameters (Å, °) of **5d-TMS**

Cl(1)–Si(1)	2.0462(5)
Cl(2)–Si(1)	2.0470(5)
Si(1)–N(1)	1.6977(12)
Si(1)–N(2)	1.6702(13)
Si(2)–N(1)	1.7871(12)
N(2)–Si(1)–N(1)	107.29(6)
Cl(1)–Si(1)–Cl(2)	103.21(2)
N(2)–Si(1)–Cl(1)	110.69(5)
N(1)–Si(1)–Cl(1)	113.37(4)
N(2)–Si(1)–Cl(2)	108.53(5)
N(1)–Si(1)–Cl(2)	113.70(4)

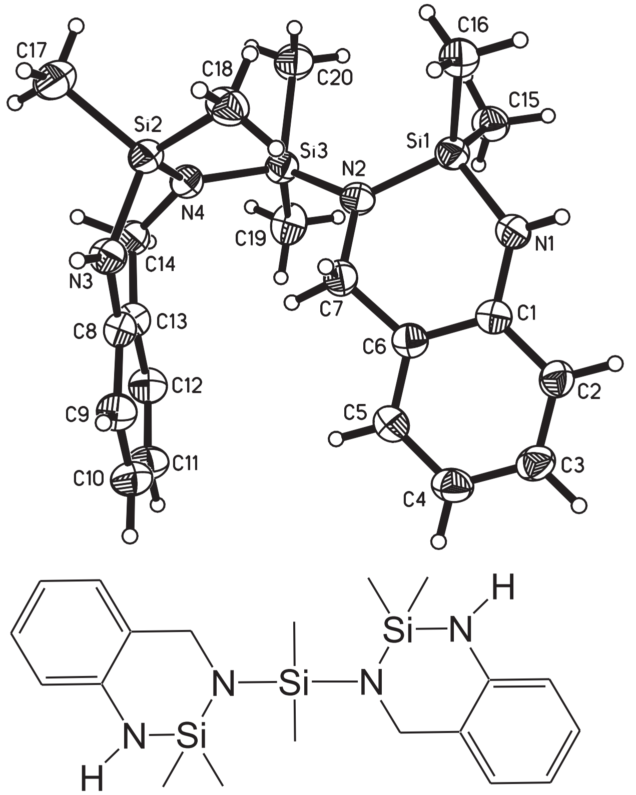


Figure 10: Molecular structure of **4e** including numbering scheme (top). The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. Schematic formula drawing of **4e** (bottom).

Table 7: Selected geometric parameters (Å, °) of **4e**

Si(1)–N(1)	1.737(2)	Si(2)–N(3)	1.745(2)
Si(1)–N(2)	1.724(2)	Si(2)–N(4)	1.729(2)
Si(1)–C(15)	1.867(2)	Si(2)–C(17)	1.858(2)
Si(1)–C(16)	1.866(2)	Si(2)–C(18)	1.863(2)
N(2)–Si(1)–N(1)	102.58(8)	N(4)–Si(2)–N(3)	101.52(8)
N(2)–Si(1)–C(15)	111.75(9)	N(4)–Si(2)–C(18)	113.51(9)
N(1)–Si(1)–C(15)	112.01(10)	N(3)–Si(2)–C(18)	112.83(9)
N(2)–Si(1)–C(16)	115.80(9)	N(4)–Si(2)–C(17)	113.39(10)
N(1)–Si(1)–C(16)	106.88(10)	N(3)–Si(2)–C(17)	109.10(10)
C(15)–Si(1)–C(16)	107.71(10)	C(18)–Si(2)–C(17)	106.54(11)
N(2)–Si(3)	1.737(2)	N(2)–Si(3)–N(4)	110.82(8)
N(4)–Si(3)	1.740(2)	N(2)–Si(3)–C(19)	108.57(9)
Si(3)–C(19)	1.860(2)	N(4)–Si(3)–C(19)	108.73(10)
Si(3)–C(20)	1.863(2)	N(2)–Si(3)–C(20)	110.02(10)
		N(4)–Si(3)–C(20)	108.61(9)
		C(19)–Si(3)–C(20)	110.09(12)

Compound **4e** crystallises in the monoclinic space group I2/c with one molecule in the asymmetric unit. The overall composition of this molecule is surprising: Six-membered diazasilacyclohexane rings have formed, but an additional dimethylsilyl group bridges two such units via the benzylamino nitrogen atoms N2 and N4 (see Figure 10). All three silicon atoms are situated in distorted tetrahedral coordination spheres. The smallest bond angles at silicon are found inside the diazasilacyclohexane rings with 102.6(1)° for N2–Si1–N1 and 101.5(1)° for N4–Si2–N3 (Table 7). The other bond angles at Si1 and Si2 adopt values between 106.5(2)° and 115.8(1)°. Interesting in this context is the comparison between coordination geometries of the silicon atoms Si1 and Si2, which are part of six-membered rings, and the silicon atom Si3, which is not part of a ring. The coordination sphere of silicon atom Si3 has a more "relaxed" geometry with bond angles between 108.6(1)° to 110.8(1)°, which is close to the angles of an ideal tetrahedron (109.5°). The Si–C bonds in this molecule have lengths close to 1.860 Å, which is the mean bond length for such bonds (Kaftory et al., 1998). There are two different types of nitrogen atoms in **4e**: The atoms N1 and N3 are bound each to an aromatic ring, to one hydrogen atom, and to one silicon atom. The atoms N2 and N4 are bound each to two different silicon atoms and a CH$_2$-group. This has implications for the bond lengths from these nitrogen atoms. The bonds Si1–N1, Si2–N3, Si3–N2, and Si3–N4 have lengths around 1.74 Å. This corresponds to Si-N(sp^3) bonds (Kaftory et al., 1998). The bonds Si1–N2 and Si2–N4 are slightly shorter with lengths of 1.724(2) and 1.729(2) Å, respectively.

The aromatic rings C1–C6 and C8–C13 are planar. The six-membered diazasilacyclohexane rings are fused to these. Conformational analysis has been performed. This reveals a boat conformation for the ring containing the atoms Si1–N1–C1–C6–C7–N2 with the parameters $\theta = 77.4(4)°$, $\varphi = 244.0(4)°$, and a ring puckering amplitude $Q = 0.430(3)$ Å. Ideal parameters for a boat conformation are $\theta = 90.0°$; $\varphi = k \cdot 60°$ (Boeyens, 1978; Cremer and Pople, 1975). The six-membered ring with the atoms Si2-N3-C8-C13-C14-N4 has the parameters $\theta = 65.7(3)°$, $\varphi = 269.3(3)°$, and a ring puckering amplitude $Q = 0.595(3)$ Å. This corresponds to a screw-boat conformation with ideal parameters $\theta = 67.5°$ and $\varphi = k \cdot 60° + 30°$.

On the attempt to synthesise compound **4d**, two unexpected compounds crystallised: **4f** and **4g**. Selected geometric parameters can be found in Table 8. Both compounds are structural isomers with a six-membered silazane ring in the centre. The nitrogen atoms of the 2-aminobenzylamino units (N2, N4, N6) are integrated into the silazane ring. Isomer **4f** crystallises in the monoclinic space group P2$_1$/c with one molecule in the asymmetric unit (see Figure 11). The compound co-crystallises with one molecule diethyl ether. The coordination geometries at the silicon atoms of **4f** are roughly tetrahedral with bond angles between 103.84(9)° and 117.97(9)°. The bond lengths of the Si–N (about 1.70 Å) bonds and the Si–Cl bonds (about 2.06 Å) are quite similar to the corresponding bonds of the other structures discussed in this paper. Ring-puckering analysis (see Table 9) shows that the silazane ring is in twist-boat conformation while the fused non-aromatic rings are in boat or screw-boat conformation. Compound **4g** crystallises in the monoclinic space group P2$_1$/n with

Table 8: Selected geometric parameters (Å, °) of **4f** and **4g**

4f		4g	
Cl(1)–Si(1)	2.0629(8)	Cl(1)–Si(2)	2.0644(15)
Cl(2)–Si(2)	2.0736(7)	Cl(2)–Si(3)	2.0435(16)
Cl(3)–Si(3)	2.0625(8)	Cl(3)–Si(3)	2.0410(15)
Si(1)–N(2)	1.6979(18)	Si(1)–N(5)	1.706(4)
Si(1)–N(1)	1.7047(18)	Si(1)–N(1)	1.706(4)
Si(1)–N(6)	1.7050(19)	Si(1)–N(2)	1.712(4)
Si(2)–N(3)	1.7000(19)	Si(1)–N(6)	1.729(4)
Si(2)–N(4)	1.7041(17)	Si(2)–N(3)	1.684(4)
Si(2)–N(2)	1.7050(17)	Si(2)–N(2)	1.710(4)
Si(3)–N(4)	1.6960(17)	Si(2)–N(4)	1.715(4)
Si(3)–N(6)	1.6994(19)	Si(3)–N(4)	1.679(4)
Si(3)–N(5)	1.7089(19)	Si(3)–N(6)	1.699(4)
N(2)–Si(1)–N(1)	104.57(9)	N(5)–Si(1)–N(1)	108.21(19)
N(2)–Si(1)–N(6)	109.02(9)	N(5)–Si(1)–N(2)	120.72(19)
N(1)–Si(1)–N(6)	117.97(9)	N(1)–Si(1)–N(2)	101.92(17)
N(2)–Si(1)–Cl(1)	112.74(7)	N(5)–Si(1)–N(6)	101.82(17)
N(1)–Si(1)–Cl(1)	106.58(7)	N(1)–Si(1)–N(6)	120.15(19)
N(6)–Si(1)–Cl(1)	106.12(7)	N(2)–Si(1)–N(6)	105.20(17)
N(3)–Si(2)–N(4)	104.72(9)	N(3)–Si(2)–N(2)	115.94(18)
N(3)–Si(2)–N(2)	115.51(9)	N(3)–Si(2)–N(4)	103.63(18)
N(4)–Si(2)–N(2)	109.43(8)	N(2)–Si(2)–N(4)	110.75(17)
N(3)–Si(2)–Cl(2)	106.45(7)	N(3)–Si(2)–Cl(1)	108.03(14)
N(4)–Si(2)–Cl(2)	112.93(6)	N(2)–Si(2)–Cl(1)	107.51(12)
N(2)–Si(2)–Cl(2)	107.89(7)	N(4)–Si(2)–Cl(1)	110.95(13)
N(4)–Si(3)–N(6)	111.35(9)	N(4)–Si(3)–N(6)	108.23(17)
N(4)–Si(3)–N(5)	117.43(9)	N(4)–Si(3)–Cl(3)	110.72(13)
N(6)–Si(3)–N(5)	103.84(9)	N(6)–Si(3)–Cl(3)	111.77(13)
N(4)–Si(3)–Cl(3)	106.05(7)	N(4)–Si(3)–Cl(2)	110.32(14)
N(6)–Si(3)–Cl(3)	113.30(7)	N(6)–Si(3)–Cl(2)	111.59(12)
N(5)–Si(3)–Cl(3)	104.94(8)	Cl(3)–Si(3)–Cl(2)	104.21(7)

Table 9: Ring puckering analysis of structures **4f** and **4g**

molecule	ring atoms	Θ [°]	φ [°]	Q [Å]	conformation
4f	Si(1)–N(2)–Si(2)–N(4)–Si(3)–N(6)	107.9(2)	260.1(2)	0.3312(13)	twist–boat
	Si(1)–N(2)–C(7)–C(6)–C(1)–N(1)	110.1(2)	79.3(2)	0.532(2)	twist–boat
	Si(2)–N(4)–C(14)–C(13)–C(8)–N(3)	103.64(19)	72.95(18)	0.586(2)	boat
	Si(3)–N(6)–C(21)–C(20)–C(15)–N(5)	70.4(2)	260.7(2)	0.557(2)	screw–boat
4g	Si(1)–N(2)–Si(2)–N(4)–Si(3)–N(6)	93.4(3)	108.6(2)	0.644(3)	boat
	Si(1)–N(2)–C(7)–C(6)–C(1)–N(1)	71.8(4)	258.5(4)	0.545(4)	screw–boat
	Si(1)–N(6)–C(21)–C(20)–C(15) –N(5)	79.0(4)	247.4(4)	0.578(4)	boat
	Si(2)–N(4)–C(14)–C(13)–C(8)–N(3)	82.1(4)	245.8(4)	0.554(4)	boat

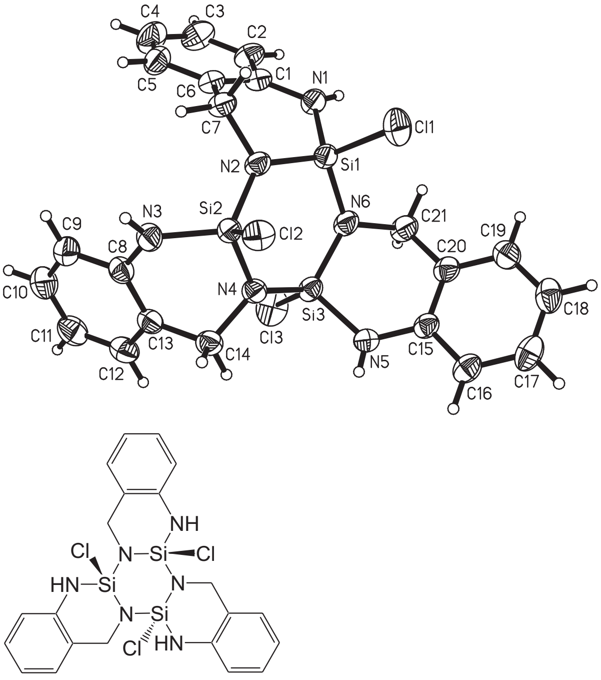


Figure 11: Molecular structure of **4f** including numbering scheme (top). The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. Schematic formula drawing of **4f** (bottom).

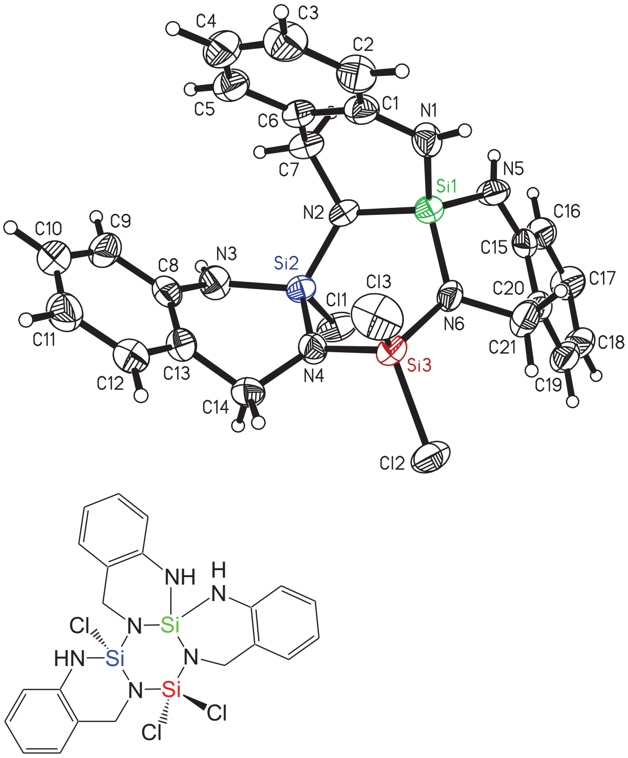
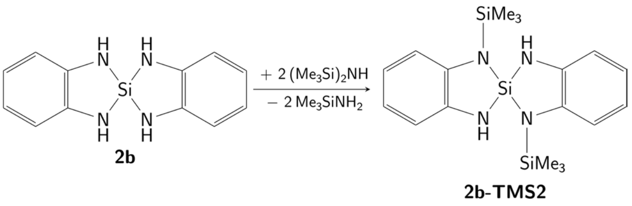


Figure 12: Molecular structure of **4g** including numbering scheme (top). The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. Schematic formula drawing of **4g** (bottom). The bonding situation of the silicon atoms is colour coded (see text for explanation).

two independent silazane molecules in the asymmetric unit (see Figure 12). Only one of the two silazane molecules in the asymmetric unit of **4g** is discussed in the further course. The constitution of **4f** is more symmetric than the constitution of **4g**. Both substances differ in the topology of one 2-aminobenzylamino moiety. One 2-aminobenzylamino moiety is inverted with respect to the topology of **4f**. This results in silicon atoms with three different coordination spheres in the structure of **4g**. Si1 is bound to four nitrogen atoms (marked green in Figure 12) and has the most distorted tetrahedral coordination geometry with bond angles from 101.82(17)° to 120.72(19)°. Si2 is bound to one chlorine atom and three nitrogen atoms (marked blue in Figure 12). This atom features a more "relaxed" tetrahedral geometry with bond angles between 103.63(18)° and 115.94(18)°. The atom Si3 is bound to two chlorine and two nitrogen atoms (marked red in Figure 12). The coordination geometry of this atom is even less distorted with bond angles between 104.21(7)° and 111.77(13)°. The Si-N bond length decreases with the increasing degree of chlorine substitution. Ring puckering analyses shows that the silazane ring is in twist-boat conformation while the fused non-aromatic rings have screw-boat or boat conformation (see Table 9).

3.4 Quantum chemical calculations

For a better understanding of the preferred number of TMS moieties remaining in the synthesised molecules (when starting from amines **1a-5a**), quantum chemical calculations were performed. As example, the trimethylsilylation of compounds **2b** (as a representative with 5-membered ring) and **4b** (as a representative with 6-membered ring) with hexamethydisilazane (HMDS) were compared (Scheme 8). The results are shown in Table 10. This hypothetical reaction has been chosen, since it is an isodesmic reaction in which the total number of each bond type is identical in the reactants and products



Scheme 8: The model reaction used for comparison of the relative stability of different silylation states of **2b** with quantum chemical calculations. The reaction of **2b** ⟶ **2b-TMS2** is shown here as an example.

Table 10: Calculated Gibbs free energies and enthalpies for the silylation reactions of **2b** and **4b** with HMDS, calculated at the M062X/6-31G(d) level in THF solution with the PCM model

Model reaction	Gibbs free energy (kJ/mol)	Enthalpy (kJ/mol)
Reactions of 2b		
2b → 2b-TMS2	-6.2	-15.8
2b-TMS2 → 2b-TMS4	-21.9	-27.1
2b→ 2b-TMS4	-28.1	-42.9
Reactions of 4b		
4b → 4b-TMS2 (aliph.)	15.6	-1.7
4b → 4b-TMS2 (arom.)	72.4	49.7
4b-TMS2 (aliph.) **→ 4b-TMS4**	58.3	33.8
4b-TMS2 (arom.) **→ 4b-TMS4**	1.5	-17.5
4b → 4b-TMS4	73.9	32.1

(Foresmann and Frisch, 2015). Isodesmic reactions are useful to predict ΔH and ΔG of chemical reactions.

It is obvious that the silylation of **2b** is exergonic in all reactions. Therefore, it must be assumed, that the sterical hindrance of the TMS moieties prevents the formation of **2b-TMS4**. Instead **2b-TMS2** is formed in our experiments. Additionally, all silylation reactions of **4b** are endergonic. The silylation of the aliphatic nitrogen atoms is less endergonic than the silylation of the aromatic nitrogen atoms. The silylation reaction of the aliphatic nitrogen atoms is only slightly endergonic (15.6 and 1.5 kJ/mol, respectively).

Further effects might play a role in the experiments which have been performed in the laboratory. These are for instance: reaction conditions like boiling under reflux, thus fostering the formation of the volatile Me_3SiCl, solvation effects, solubility of formed intermediates, or crystallisation enthalpies of products. All these effects are not taken into account in the model reaction used for the calculations. The calculated Gibbs enthalpy, which is slightly positive, could be turned to a negative value by such effects. This explains why **4b-TMS2** could be crystallised. In accord with the preferred retention of $SiMe_3$ groups at the aliphatic amine N atoms, the silicon atom of the bridging $SiMe_2$ moiety in **4e** is also bound to the benzylamine N atoms, and cyclosilazane formation via benzylamine N atoms in **4f** and **4g** indicates the same trend. The results of the quantum chemical calculations of both example systems show the stabilising effect of TMS moieties to five-membered ring systems and the destabilising effect on six-membered rings. These results are in agreement with the observed preparative accessibility of spirocyclic compounds.

Furthermore, we were interested to understand the occurrence of planar and nonplanar ring conformations in case of the derivatives of **1** and **2**, which feature 5-membered rings. Therefore, the energy necessary for the planarisation of **1b** has been calculated with quantum chemical methods. The planar form has D_{2d} symmetry and is 6.1 kJ/mol higher in Gibbs free energy than the same compound with bent ethylene diamine units (for details see Supplementary material). In contrast to that, the global minimum for compound **2b** is planar on both (*N,N'*-o-phenylenamino)silicon units. The annelation of the phenylene group makes the planar form more favourable. This was indeed observed in the solid state structures of **2b-TMS2** and **2d-TMS**.

Further on, the stabilities of the two isomers **4f** and **4g** were compared on the B3LYP/6-31G(d) level of theory. At 298 K (1 atm) the less symmetric derivative **4g** is 14.2 kJ/mol lower in energy. This small energy difference can be overcome by solvation effects and crystallisation energies. In effect both isomers crystallised side by side from one reaction batch.

4 Comparative reflections and conclusions

As a result of the accomplished experiments, the aminosilanes **1a-5a**, spirocyclic aminosilanes **1b-5b**, and several other cyclic aminosilanes were successfully synthesised, isolated, and characterised. Spirocyclic aminosilanes with six-membered rings were obtained only from direct reactions of the amines with tetrachlorosilane (method A). Spirocyclic aminosilanes with five-membered rings are obtained from reactions of tetrachlorosilane with trimethylsilyl substituted amines (method B).

Comparison of the angles N–Si–N in the crystal structures show smaller angles in the five-membered rings than in the six-membered rings, as one would expect. Derivatives **b**, the spirocyclic compounds, exhibit smaller bite angles than the derivatives **c** and **d**. The TMS moieties widen that angle. This could explain why derivatives of amines **1-3** only could be synthesised by method B. The wider angle N–Si–N lowers the ring-strain in the products. Additionally, the steric hindrance caused by the TMS moieties lowers the tendency of polymerisation. Furthermore, the TMS moieties lower the nucleophilicity of the lone pair of the nitrogen atom, thus suppressing side reactions, and the cyclic products can be obtained.

It was surprising, that the degree of substitution with trimethylsilyl groups differs noticeably between the final products. Quantum chemical calculations gave insight into the thermodynamic reasons for this phenomenon.

The degree of substitution with trimethylsilyl groups depends on the ring size of the spirocycles: Trimethylsilyl groups have a stabilising effect on five-membered ring systems and a destabilising effect on six-membered rings in this type of compounds.

The prepared compounds are useful as substrates for further investigations. These might be insertion reactions with carbon dioxide and with other heteroallenes into Si–N bonds, ring opening polymerisations, or the preparation of macrocyclic ligands in the coordination sphere of silicon.

Experimental

All reactions were carried out under argon using Schlenk technique (Böhme, 2020; Herzog and Dehnert, 1964). NMR spectra were recorded in $CDCl_3$ or C_6D_6 with TMS as internal standard either on a BRUKER DPX 400 spectrometer at 400.13, 100.61, and 79.49 MHz for ^{1}H, ^{13}C, and ^{29}Si, or on a BRUKER AVANCE III 500 MHz spectrometer at 500.13, 125.76, and 99.36 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively. Raman spectra were measured with a FT-Raman spectrometer RFS/100S from BRUKER using an air-cooled Nd:YAG-laser with a wavelength of 1064 nm and a nitrogen-cooled germanium detector. Melting points were measured using a Polytherm A hot stage microscope from Wagner and Munz with an attached 52II thermometer from Fluke. The measurement of boiling points was performed with an apparatus which has been published by Herbig and Kroke (2017). Mass spectra were recorded on a expression^L CMS from Advion using ESI (sample was dissolved in acetonitrile). The setup for cryoscopy is described in the Supplementary material (section S5).

Synthesis of trimethylsilylated amines

The synthesis of the trimethylsilylated derivatives **1a-5a** is shown for compound **2a** as example. The other four substances are synthesised in the same manner. Variation from this general method are pointed out in the paragraph of the related compound.

In a 2-necked round-bottomed flask, 5.01 g (46 mmol) of o-phenylenediamine and 9.42 g (93 mmol) triethylamine were dissolved in about 150 mL of dry THF. The solution was stirred while cooling in an ice-water bath, and 10.00 g (92 mmol) Me_3SiCl were added to the mixture dropwise. After complete addition, the suspension was heated under reflux for 2 h, followed by stirring at room temperature overnight. Thereafter, the suspension was filtered through a fritted glass filter (G4), and the solid was washed with THF (2 × 20 mL). From the combined filtrate and washings all volatile compounds were removed by distillation under reduced pressure. The residue (10.35 g, 89%) was an orange liquid which was identified as *N,N'*-bis(trimethylsilyl)-1,2-diaminobenzene (**2a**).

*N,N'-Bis(trimethylsilyl)-1,2-ethylenediamine (***1a***)*

NMR solvent: $CDCl_3$. ^{1}H NMR: δ [ppm] = -0.04 (s, 18 H, $SiMe_3$), 0.58 (s, 2 H, NH), 2.59 (s, 4 H, CH_2). ^{13}C NMR: δ [ppm] = -0.1 ($SiMe_3$), 45.7 (CH_2). ^{29}Si NMR: δ [ppm] = 3.7. bp: 35°C (0.35 mbar).

*N,N'-Bis(trimethylsilyl)-1,2-diaminobenzene (***2a***)*

NMR solvent: $CDCl_3$. ^{1}H NMR: δ [ppm] = 0.21 (s, 18 H, $SiMe_3$), 3.06 (s, 2 H, NH), 6.71 (m, 2 H, Ar), 6.80 (m, 2 H, Ar). ^{13}C NMR: δ [ppm] = 0.4 ($SiMe_3$), 119.7, 120.2, 137.6 (Ar). ^{29}Si NMR: δ [ppm] = 3.8. Raman: ν [cm^{-1}] = 3367 (vw), 3059 (w), 2958 (m), 2899 (vs), 1598 (w), 1499 (vw), 1410 (vw), 1300 (vw), 1250 (vw), 1189 (vw), 1156 (vw), 1044 (w), 920 (vw), 827 (vw), 780 (vw), 740 (vw), 689 (vw), 616 (m). MS: m/z = 253.2 g/mol [M+H]$^+$. bp: 236°C (975 mbar).

*N,N'-Bis(trimethylsilyl)-(±)-trans-1,2-diaminocyclohexane (***3a***)*

The substance was synthesised like **2a** using 9.51 g (83 mmol) **3**, 16.95 g (167 mmol) NEt_3 and, 18.10 g (167 mmol) Me_3SiCl. The reaction and workup afforded a colourless liquid (14.34 g, 67%).

NMR solvent: $CDCl_3$. ^{1}H NMR: δ [ppm] = 0.00 (s, 18 H, $SiMe_3$), 0.67 (s, 2 H, N–H), 1.03 (m, 2 H, ring), 1.19 (m, 2 H, ring), 1.57 (m, 2 H, ring), 1.81 (m, 2 H, ring), 2.15 (d, 2 H, $^3J_{H,H}$ = 7.0 Hz). ^{13}C NMR: δ [ppm] = 0.9 ($SiMe_3$), 25.5, 36.7, 58.8 (ring). ^{29}Si NMR: δ [ppm] = 1.6. Raman: ν [cm^{-1}] = 2954 (m), 2939 (m), 2897 (vs), 2856 (m), 1445 (vw), 1408 (vw), 1347 (vw), 1114 (vw), 1044 (vw), 849 (vw), 784 (vw), 742 (vw), 685 (vw), 617 (m). MS: m/z = 259.23 g/mol [M+H]$^+$. bp: 229°C (975 mbar).

*N,N'-Bis(trimethylsilyl)-2-aminobenzylamine (***4a***)*

The substance was synthesised like **2a** using 5.00 g (41 mmol) **4**, 8.40 g (83 mmol) NEt_3, and 9.00 g (83 mmol) Me_3SiCl. The reaction and workup afforded a yellow liquid (6.48 g, 59%).

NMR solvent: $CDCl_3$. ^{1}H NMR: δ [ppm] = 0.12 (s, 9 H, $SiMe_3$–N_{Ar}), 0.30 (s, 9 H, $SiMe_3$-N_{Aliph}), 0.51 (s, 1H, N_{Aliph}–H), 3.84 (d, 2 H, $^3J_{H,H}$ = 6.0 Hz, CH_2), 5.20 (s, 1 H, N_{Ar}–H), 6.65 (m, 1 H, Ar), 6.77 (m, 1 H, Ar), 7.02 (m, 1 H, Ar), 7.08 (m, 1 H, Ar). ^{13}C NMR: δ [ppm] = -0.4 ($SiMe_3$–N_{Ar}), 0.4 ($SiMe_3$-N_{Aliph}), 45.5 (CH_2), 115.9, 117.1, 128.1, 128.1, 129.5, 147.3 (Ar). ^{29}Si NMR: δ [ppm] = 1.6 ($SiMe_3$–N_{Aliph}), 5.5 ($SiMe_3$–N_{Ar}). Raman: ν [cm^{-1}] = 3056 (w), 2957 (m), 2898 (vs), 1606 (vw), 1583 (vw), 1496 (vw), 1458 (vw), 1410 (vw), 1296 (vw), 1248 (vw), 1187 (vw), 1158 (vw), 1045 (w), 915 (vw), 840 (vw), 776 (vw), 749 (vw), 708 (vw), 690 (vw), 626 (m), 603 (w), 553 (vw), 432 (vw). MS: m/z = 267.65 g/mol [M+H]$^+$. bp: >300°C (974 mbar).

*N,N'-Bis(trimethylsilyl)-1,8-diaminonaphthalene (**5a**)*

The substance was synthesised like **2a** using 7.30 g (46 mmol) **5**, 9.33 g (92 mmol) NEt_3, and 10.50 g (97 mmol) Me_3SiCl. The reaction and workup yielded a dark red solid (12.52 g, 90%).

NMR solvent: $CDCl_3$. ^{1}H NMR: δ [ppm] = 0.23 (s, 18 H, $SiMe_3$), 5.49 (s, 2 H, N–H), 6.65 (m, 2 H, Ar), 7.14 (m, 2 H, Ar), 7.21 (m, 2 H, Ar). ^{13}C NMR: δ [ppm] = 0.1 ($SiMe_3$), 115.4, 120.4, 121.3, 125.7, 137.4, 144.4 (Ar). ^{29}Si NMR: δ [ppm] = 3.6. MS: m/z = 302.40 g/mol [M]$^+$. mp: 42-44°C.

*Synthesis of cyclic and spirocyclic compounds (derivatives **b, c,** and **d**)*

For the synthesis of cyclic and spirocyclic compounds, two methods are used: method A starts from the amines **1-5** and method B starts from the bis-trimethylsilylated derivatives **1a-5a**. To synthesise the different derivatives, the composition of the reaction mixtures is varied. First, the preparation of **1b**, **1c**, and **1d** are given as examples. All following syntheses differ in the workup of the products. Therefore, the workup procedures are given in the subsequent sections for each compound individually.

*Synthesis of derivatives **b** – example **1b***

In dry *n*-heptane (80 mL), 2.43 g (12 mmol) **1a** and 2.38 g (24 mmol) triethylamine were dissolved. While cooling in an ice-water bath, a solution of 1.02 g (6 mmol) $SiCl_4$ in about 20 mL of *n*-heptane was added dropwise. Thereafter, the reaction mixture was heated under reflux for 7 h, followed by stirring at room temperature overnight. The resulting suspension was filtered through a fritted glass filter (G4), and the solid was washed with dry n-heptane (2 × 20 mL). From the combined filtrate and washings all volatile compounds were removed by distillation under reduced pressure. Further purification steps are pointed out below.

*Synthesis of derivatives **c** – example **1c***

In dry THF (70 mL), 3.25 g (16 mmol) **1a** and 3.7 g (36 mmol) triethylamine were dissolved. While cooling in an ice-water bath, 2.13 g (17 mmol) Me_2SiCl_2 was added dropwise. The reaction mixture was heated under reflux for 2 h, followed by stirring at room temperature overnight. The resulting suspension was filtered through a fritted glass filter (G4), and the solid was washed with dry THF (2 × 20 mL). From the combined filtrate and washings all volatile compounds were removed by distillation under reduced pressure. Further purification steps are pointed out below.

*Synthesis of derivatives **d** – example **1d***

In dry THF (100 mL), 3.27 g (16 mmol) **1a** and 3,63 g (36 mmol) triethylamine were dissolved. While cooling in an ice-water bath, 2.9 g (17 mmol) $SiCl_4$ was added dropwise. The reaction mixture was heated under reflux for 2 h, followed by stirring at room temperature overnight. The resulting suspension was filtered through a fritted glass filter (G4), and the solid was washed with dry THF (2 × 20 mL). From the combined filtrate and washings all volatile compounds were removed by distillation under reduced pressure. Further purification steps are pointed out below.

*spiro-Bis(N,N'-1,2-ethylene-bis-(trimethylsilylamino)) silane (**1b-TMS4**)*

This compound was synthesised by using method B: 60 mL dry *n*-heptane, 2.50 g (12 mmol) **1a**, 2.40 g (24 mmol) NEt_3, 1.00 g (6 mmol) $SiCl_4$ were used. The silicon tetrachloride was also dissolved in dry *n*-heptane (20 mL). The mixture was heated for 7 h. The compound received after removing volatiles in vacuo was recrystallised from *n*-pentane yielding a yellow substance (2.40 g, 40%). The obtained compound contains four trimethylsilyl moieties.

NMR solvent: $CDCl_3$. ^{1}H NMR: δ [ppm] = 0.07 (s, 36 H, $SiMe_3$), 3.02 (s, 8 H, CH_2). ^{13}C NMR: δ [ppm] = -0.2 ($SiMe_3$), 43.8 (CH_2). ^{29}Si NMR: δ [ppm] = 1.7 ($SiMe_3$), 15.3 (Si). Raman: ν [cm^{-1}] = 2956 (s), 2897 (vs), 2863 (w), 2682 (vw), 1471 (vw), 1411 (vw), 1254 (vw), 1230 (vw), 838 (vw), 750 (vw), 684 (vw), 634 (w), 460 (w). MS: m/z = 433.33 g/mol [M+H]$^+$. mp: 131°C.

*(N,N'-1,2-ethylene-bis-(trimethylsilylamino)) dimethylsilane (**1c-TMS2**)*

This compound was synthesised by using method B: 3.25 g (16 mmol) **1a**, 3.7 g (36 mmol) NEt_3, 2.13 g (17 mmol) Me_2SiCl_2, and 70 mL THF as solvent were used. The silicon tetrachloride was used neat. The mixture was heated for 4 h. The compound received after removing volatiles in vacuo was distilled at 0.2 mbar (bp = 35°C), yielding a colourless liquid (1.794 g, 43%). The obtained compound contains two trimethylsilyl moieties.

NMR solvent: $CDCl_3$. ^1H NMR: δ [ppm] = 0.08 (s, 18 H, $SiMe_3$), 0.13 (s, 6 H, $SiMe_2$), 3.00 (s, 4 H, CH_2). ^{13}C NMR: δ [ppm] = 0.4 ($SiMe_3$), 3.7 ($SiMe_2$), 46.9 (CH_2). ^{29}Si NMR: δ [ppm] = 1.4 (2 Si, $SiMe_3$), 12.8 (1 Si, $SiMe_2$). Raman: ν [cm^{-1}] = 2955.0 (m), 2899.0 (vs), 2836.0 (w), 2662.0 (vw), 1464.0 (vw), 1409.0 (vw), 1351.0 (vw), 1249.0 (vw), 1222.0 (vw), 1075.0 (vw), 749.0 (vw), 703.0 (vw), 626.0 (vw), 523.0 (m), 369.0 (vw), 346.0 (vw), 327.0 (vw), 288.0 (vw), 248.0 (vw), 180.0 (vw), 120.0 (vw). MS: 261 g/mol $[M+H]^+$. bp: 210°C (963 mbar). molecular mass: cryoscopy (see Supplementary material) calc. 206 g/mol, found 240 g/mol.

*Dichloro-(N,N'-bis(trimethylsilyl)-N,N'-1,2-ethylendiamino)silane (***1d-TMS2***)*

This compound was published earlier (Böhme et al., 2007).

*spiro-Bis(N,N'-o-phenyleneamino(trimethylsilylamino)) silane (***2b-TMS2***)*

This compound was synthesised by using method B: 5.02 g (20 mmol) **2a**, 4.05 g (40 mmol) NEt_3, 1.54 g (9.1 mmol) $SiCl_4$, and THF as solvent were used. The crude product was dissolved in diethyl ether, and after addition of *n*-pentane and storage for several days at 4°C a light brown solid (0.55 g, 16%) was yielded. The obtained compound contains two trimethylsilyl moieties.

NMR solvent: $CDCl_3$. ^1H NMR: δ [ppm] = 0.23 (s, 18 H, $SiMe_3$), 4.28 (s, 2 H, NH), 6.75 (m, 10 H, Ar). ^{13}C NMR: δ [ppm] = -0.06 ($SiMe_3$), 110.8, 113.7, 118.2, 119.4, 136.2, 137.2 (Ar). ^{29}Si NMR: δ [ppm] = -24.6 (Si), 4.2 ($SiMe_3$). (The integral of the multiplet indicates the existence of not converted starting material or products of hydrolysis.) Raman: ν [ppm] = 3460 (vw), 3400 (vw), 3080 (w), 3059 (m), 3013 (w), 2958 (m), 2900 (vs), 1598 (m), 1586 (w), 1489 (w), 1461 (vw), 1366 (m), 1309 (vw), 1266 (m), 1222 (vw), 1200 (vw), 1156 (w), 1112 (vw), 1032 (s), 948 (vw), 925 (vw), 845 (vw), 815 (vw), 752 (vw), 616 (m), 440 (vw), 403 (w). MS: m/z = 384.11 g/mol $[M]^+$. mp: 124°C. UV/VIS (0.00108 mol/L, d = 0.999 cm, in chloroform): [nm] 253.03 (ε = 2265.14 mol L^{-1} cm^{-1}), 288.11 (ε = 2279.78 mol L^{-1} cm^{-1}).

Crystals suitable for X-ray-diffraction were received from a solution in diethyl ether after addition of n-pentane and storing at 4°C for several days.

The received substance is unknown in literature, but a similar compound was synthesised by Kummer and Rochow (1963).

*N,N'-(N-trimethylsilyl-o-phenylenediamino) dimethylsilane (***2c-TMS***)*

This compound was synthesised by using method B: 4.99 g (20 mmol) **2a**, 4.05 g (40 mmol) NEt_3, 3.40 g (20 mmol) Me_2SiCl_2, and THF (80 mL) as solvent were used. A light brown compound mixture of the product and triethylammonium chloride was yielded. The obtained compound contains one trimethylsilyl moiety.

NMR solvent: $CDCl_3$. ^1H NMR: δ [ppm] = 0.32 (s, 9 H, $SiMe_3$), 0.36 (s, 6H, $SiMe_2$), 6.51-6.73 (m, 4H, Ar). ^{13}C NMR: δ [ppm] = 0.9 ($SiMe_3$), 4.6 ($SiMe_2$), 110.5, 113.4, 117.0, 118.6 (Ar), 140.0, 142.1(Ar^{ipso}). ^{29}Si NMR: δ [ppm] = 15.1 ($SiMe_2$), 2.1 ($SiMe_3$). Raman: ν [cm^{-1}] = 3252 (vw), 3233 (vw), 3057 (m), 2998 (m), 2980 (s), 2901 (m), 1594 (m), 1557 (w), 1505 (w), 1480 (w), 1464 (m), 1366 (w), 1337 (w), 1277 (m), 1160 (w), 1034 (s), 905 (w), 763 (m), 705 (w), 687 (w), 614 (w), 579 (w), 550 (w), 502 (w), 464 (w), 344 (w), 331 (w), 203 (m), 128 (m), 109 (m).

*Dichloro-N,N'-(N-trimethylsilyl-o-phenylenediamino) silane (***2d-TMS***)*

This compound was synthesised by using method B: 8.45 g (33 mmol) **2a**, 5.69 g (33 mmol) $SiCl_4$, 6.68 g (66 mmol) Et_3N, and THF as solvent were used. The crude product was dissolved in a mixture of $CHCl_3$/*n*-hexane (1:3 volume parts, 60 mL in total) and crystallises after serval days at 4°C as a light brown solid (3.43 g, 37.5%).

NMR solvent: $CDCl_3$. ^1H NMR: δ [ppm] = 0.47 (s, 9 H, $SiMe_3$), 4.65 (br, 1 H, NH), 6.69 – 6.90 (m, 4 H, Ar). ^{13}C NMR: δ [ppm] = 0.3 ($SiMe_3$), 111.5, 113.9, 118.9, 120.0 (Ar), 137.2, 136.5 (Ar^{ipso}). ^{29}Si NMR: δ [ppm] = 6.8 ($SiMe_3$), -23.5 ($SiCl_2$). IR: ν [cm^{-1}] = 3411, 3030, 2957, 2899, 2833, 2604, 1598, 1583, 1530, 1448, 1459, 1410, 1365, 1352, 132, 1254, 1229, 1202, 1184, 1111, 1047, 1033, 1018, 995, 901, 846, 814, 762, 742, 690, 677, 625, 576, 569, 559 527, 476, 447, 432. EA: C: 33.63% (calc. 38.98%), H: 5.92% (calc. 5.09%), N: 9.00% (calc. 10.10%). mp: 128-130°C (decomp.). UV/VIS (0.00099 mol/L, d = 0.999 cm, in $CHCl_3$): [nm] 212.68 (ε = 1640.93 mol L^{-1} cm^{-1}), 246.94 (ε = 2381.47 mol L^{-1} cm^{-1}), 290.16 (ε = 1780.97 mol L^{-1} cm^{-1}), 960.58 (ε = 477.65 mol L^{-1} cm^{-1}).

Crystals suitable for X-ray-diffraction were received from a solution of the crude product in chloroform/ n-hexane (1:3 volume parts) and storing at 4°C for several days.

*spiro-Bis(N,N'-2-aminobenzylamino)silane (***4b***)*

This compound was synthesised by using method A: 4.32 g (35 mmol) **4**, 7.20 g (71 mmol) NEt_3, and 2.99 g

(18 mmol) SiCl$_4$ and about 150 mL THF as solvent were used. The reaction mixture was not heated and stirred 21 h. A colourless substance (2.18 g, 46%) was received after filtration and removal of all volatiles.

NMR solvent: CDCl$_3$. ^{1}H NMR: δ [ppm] = 1.66 (s, 2 H, NH), 3.88 (s, 2 H, NH), 4.08 (qd, 4 H, $^3J_{H,H}$ = 14.8 Hz, $^3J_{H,H}$ = 5.5 Hz, CH$_2$), 6.61 (d, 4 H, $^3J_{H,H}$ = 7.8 Hz, Ar), 6.72 (m, 2 H, Ar), 6.93 (d, 2 H, $^3J_{H,H}$ = 7.3 Hz, Ar), 7,04 (m, 2 H, Ar). ^{13}C NMR: δ [ppm] = 44.5 (CH$_2$), 117.91, 118.9, 126.5, 127.6, 127.9, 144.9 (Ar). ^{29}Si NMR: δ [ppm] = -49.0 (-48.9; Kaßner et al., 2016). Raman: ν [cm^{-1}] = 3057 (vs), 3046 (vs), 3032 (m), 2938 (m), 2881 (vw), 1607 (s), 1585 (w), 1455 (vw), 1300 (vw), 1279 (vw), 1257 (w), 1221 (vw), 1194 (vw), 1158 (w), 1037 (m), 760 (s), 594 (vw). MS: m/z = 310.00 g/mol [M+AcN+H]$^+$. Decomposition: 155-160°C (Kaßner et al., 2016).

*spiro-Bis(N-trimethylsilyl-N,N'-2-aminobenzylamino)silane (***4b-TMS2***)*

This compound was synthesised by using method B: 1.34 g (11 mmol) **4**, 2.30 g (23 mmol) NEt$_3$, 1.02 g (6 mmol) SiCl$_4$, and about 100 mL dry THF as solvent were used. The reaction mixture was heated for 8 h under reflux. From the product mixture in THF a few crystals of **4b-TMS2** were obtained after several weeks.

*(N,N'-2-aminobenzylamino)dimethylsilanes (***4c*** and ***4e***)*

These compounds was synthesised by using method A: 4.64 g (38 mmol) **4**, 7.82 g (77 mmol) NEt$_3$, 6.464 g (38 mmol) Me$_2$SiCl$_2$, and about 150 mL of dry THF as solvent were used. A yellow substance was received after removing all volatiles in vacuo. After distillation under reduced pressure a residue and a distillate were obtained. The residue is **4e** (0.635 g) which crystallised from the melt with small amounts of CDCl$_3$, and the distillate is **4c** (0.748 g).

4e: NMR solvent: CDCl$_3$. ^{1}H NMR: δ [ppm] = 0.19 (s, 6 H, Si-exocyclic), 0.30 (s, 12 H, Si-endocyclic), 3.56 (s (br), 2 H; NH), 3.93 (s, 4 H, CH$_2$) 6.59-6.66 (m, 4 H, Ar), 6.8 (m, 2 H, Ar), 7.04-7.08 (m, 2 H, Ar). ^{13}C NMR: δ [ppm] = 1.5 (Si-exocyclic), 2.7 (Si-endocyclic), 45.2 (CH$_2$), 116.4, 117.6, 126.7, 127.7, 127.8, 145.9 (Ar). ^{29}Si NMR: δ [ppm] = -2.2 (Si-endocyclic), -3.6 (Si-exocyclic). Raman: *ν* [cm^{-1}] = 3358 (w), 3063 (w), 3048 (s), 2969 (s), 2903 (vs), 2834 (w), 1599 (w), 1586 (vw), 1455 (vw), 1368 (vw), 1339 (vw), 1306 (vw), 1277 (vw), 1200 (vw), 1156 (w), 1114 (vw), 1038 (w), 1009 (vw), 899 (vw), 732 (vw), 716 (w), 616 (w), 523 (w), 450 (vw), 350 (w), 311 (vw), 213 (w), 132 (m), 91 (w). After standing several days standing with small amount of CDCl$_3$, crystals, suitable for X-Ray diffraction, were obtained. mp = 97°C. EA: C: 57.86% (calc. 58.20%), H: 7.65% (calc. 7.81%), N: 14.60% (calc. 13.57%).

4c: NMR solvent: CDCl$_3$. ^{1}H NMR: δ [ppm] = 0.17 (s, 6 H, SiMe$_2$), 1.05 (s (br), 1 H; NH), 3.57 (s (br), 1 H, NH), 3.87 (s, 2 H, CH$_2$) 6.49 (m, 1 H, Ar), 6.62 (m, 1 H, Ar), 6.85 (m, 1 H, Ar), 6.99 (m, 1 H, Ar). ^{13}C NMR: δ [ppm] = 0.5 (SiMe$_2$), 44.2 (CH$_2$), 117.4, 117.5, 126.3, 127.4, 128.0, 145.5 (Ar). ^{29}Si NMR: δ [ppm] = -1.7. bp 270°C (963 mbar). mp = 52°C. MS: *m/z* = 178 g/mol [M+H]$^+$.

Silazanes ***4f*** *and* ***4g***

These compounds was synthesised by using method A: 0.98 g (8 mmol) **4**, 1.69 g (17 mmol) NEt$_3$, 1.53 g (9 mmol) SiCl$_4$, and 40 mL diethyl ether as solvent were used. During the addition of the silicon tetrachloride, the reaction mixture was cooled in a dry-ice/*iso*-propanol bath. Afterwards the mixture was allowed to attain room temperature and stirred overnight. A part of the solvent was removed in vacuo and from the resulting mixture **4f** and **4g** crystallised in the course of several weeks.

*spiro-Bis(N,N'-1,8-diaminonaphthalenyl)silane (***5b***)*

This compound was synthesised by using method A: 5.63 g (36 mmol) **5**, 7.26 g (72 mmol) NEt$_3$, 2.89 g (17 mmol) SiCl$_4$, and about 200 mL of dry THF as solvent were used. After removing volatiles in vacuo a dark red compound (9.97 g) was obtained, which contained residual THF (ca. 80 mol%) according to the NMR spectra.

NMR solvent: CDCl$_3$. ^{1}H-NMR: δ [ppm] = 4.44 (s, 4 H, N–H), 6.22 (d, 4 H, $^3J_{H,H}$ = 6.1 Hz, Ar), 7.00 (s, 8 H, Ar). ^{13}C NMR: 108.6, 115.3, 117.9, 127.0, 136.5, 143.4. ^{29}Si NMR: δ [ppm] = -59.1. MS: m/z = 341.06 g/mol [M+H]$^+$. Decomposition: 124°C. Raman: the Raman spectrum does not show sharp bands most likely due to luminescence effects of the compound.

Crystals suitable for X-ray-diffraction were received from the crude product with small amounts of CDCl$_3$ and storing at room temperature for several days.

*(N,N'-1,8-diaminonaphthalenyl)dimethylsilane (***5c***)*

This compound was synthesised by using method A: 12.18 g (77 mmol) **5**, 15.62 g (155 mmol) NEt$_3$, 13.08 g (77 mmol) Me$_2$SiCl$_2$, and 200 mL of dry benzene as solvent were used. The crude product was dissolved in 10 mL THF and stored at 4°C. After filtration and removal of volatiles in vacuo 14.39 g (87%) of this light pink product were obtained.

NMR solvent: CDCl$_3$. ^{1}H-NMR: δ [ppm] = 0.35 (s, 6 H, SiMe$_2$), 3.95 (s (br), 2 H, NH), 6.40 (d, 2 H, $^3J_{H,H}$ = 7.3 Hz, Ar), 7.08 (d, 2 H, $^3J_{H,H}$ = 8.3 Hz, Ar), 7.15 (t, 2 H, $^3J_{H,H}$ = 7.7 Hz, Ar). ^{13}C NMR: 2.6 (SiMe$_2$), 108.7 (Ar–H), 114.8 (Ar-quart), 117.6 (Ar–H), 126.9 (Ar-H), 136.7 (Ar-quart.), 142.9 (Ar-quart.). ^{29}Si NMR: δ [ppm] = -5.6. Raman: ν [cm^{-1}] = 3364 (vw), 3345 (vw), 3059 (m), 3023 (w), 2965 (vw), 2895 (w), 2157 (vw), 2145 (vw), 2060 (vw), 1580 (s), 1518 (vw), 1466 (m), 1445 (w), 1397 (vw), 1366 (vs), 1256 (m), 1169 (vw), 1125 (w), 1088 (w), 1067 (w), 845 (vw), 817 (w), 755 (vw), 682 (vw), 641 (w), 547 (s), 473 (w), 454 (w), 363 (w), 317 (w), 169(w), 113 (m). EA: C: 67.22% (calc. 67.24%), H: 6.68 (calc. 6.58%), N: 12.82 (calc. 13.07%). mp: 114°C.

Crystals suitable for X-ray-diffraction were obtained from the crude product with small amounts of CDCl$_3$ upon storing at room temperature for several days.

*Dichloro-(N-trimethylsilyl-N,N'-1,8-diaminonaphthalenyl) silane (**5d**)*

To a solution of 1,8-diaminonaphthalene (5.00 g, 31.6 mmol) and triethylamine (7.98 g, 79.0 mmol) in toluene (100 mL) at room temperature a solution of chlorotrimethylsilane (7.90 g, 72.7 mmol) in toluene (10 mL) was added dropwise with stirring, whereupon the mixture was heated and stirred under reflux for 2 h. Upon cooling to room temperature the triethylamine hydrochloride precipitate was filtered off and washed with toluene (36 mL). From the combined filtrate and washings the solvent and other volatiles were removed under reduced pressure. The remaining oily residue was dissolved in toluene (50 mL), stirred at room temperature, and triethylamine (7.34 g, 72.7 mmol) as well as a solution of SiCl$_4$ (5.64 g, 33.2 mmol) in toluene (6 mL) were added. This mixture was heated and stirred under reflux for 10 h. Upon cooling to room temperature the triethylamine hydrochloride precipitate was filtered off and washed with toluene (20 mL). From the combined filtrate and washings the solvent and other volatiles were removed under reduced pressure, and the solid residue was placed on a fritted glass filter and was extracted with *n*-hexane (70 mL). From the hexane extract the crude product crystallised in fine colourless needles, which, upon storage at 6°C overnight, were filtered off, washed with hexane (2 mL) and dried in vacuo. Yield: 7.46 g (22.8 mmol, 72%).

NMR solvent: CDCl$_3$. ^{1}H-NMR: *δ* [ppm] = 0.57 (s, 9 H, SiMe$_3$), 4.69 (s (br), 1H, NH), 6,46-7,32 (m, 6H, Ar). ^{13}C NMR: 2.7 (SiMe$_3$), 109.7, 115.0, 117.8, 119.9, 121.5, 125.9, 126.6, 136.4, 139.3, 141.2 (Ar). ^{29}Si NMR: *δ* [ppm] = 8.5 (SiMe$_3$); -35.5 (SiCl$_2$). EA: C: 47.73% (calc. 47.70%), N: 8.43% (calc. 8.56%), H: 5.04% (calc. 4.93%). mp = 122°C.

Crystal structure determination

Single crystal X-ray diffraction data of **2b-TMS2** and **2d-TMS** were collected on a BRUKER NONIUS X8 APEX2 CCD diffractometer using graphite monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å) using φ- and ω-scans. Data collections for the structures **3d-TMS2, 4b-TMS2, 4e, 4f, 4g, 5b**·[Et$_3$NH]Cl·HCCl$_3$, **5c**, and **5d-TMS** were performed on a STOE IPDS-2T image plate diffractometer equipped with a low-temperature device with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) using ω-scans. Software for data collection: X-AREA, cell refinement: X-AREA and data reduction: X-RED (Stoe & Cie, 2009, X-RED and X-AREA. Stoe & Cie, Darmstadt, Germany). Preliminary structure models were derived by direct methods (Sheldrick, 2008) and the structures were refined by full-matrix least-squares calculations based on F^2 for all reflections using SHELXL (Sheldrick, 2015). The positions of N-H-atoms have been refined without constraints. All other hydrogen atoms were included in the models in idealised positions and were refined as constrained to the pivot atoms. **2d-TMS** crystallises in the chiral space group P2$_1$2$_1$2$_1$. The molecule itself is not chiral. The absolute structure parameter was refined to a value of -0.01(2). There are rotational disorders at the methyl groups C11 and C12 in **5d-TMS**. These have been refined with split atom models. Further crystallographic data are listed in Table 11.

CCDC-2033885 (**2b-TMS2**), 2033886 (**2d-TMS**), 2043741 (**3d-TMS2**), 2033889 (**4b-TMS2**), 2033888 and 2043739 (**4e**), 2043742 (**4f** · Et$_2$O), 2043740 (**4g**), 2033887 (**5b** · Et$_3$NHCl · CHCl$_3$), 2033890 (**5c**), and 2043742 (**5d-TMS**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crytallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum chemical calculations

The quantum chemical calculations have been performed with GAUSSIAN 16 (Frisch et al., 2016). The molecules have been optimised with M062X/6-31G(d) (Francl et al., 1982; Hariharan and Pople, 1973; Zhao and Truhlar, 2008). The calculation of Hessian-matrices verified the presence of local minima on the potential energy surface with zero imaginary frequencies. The solvent THF was included into these calculations by placing the molecules in a cavity within the solvent reaction field. This method is described in the literature as Polarizable Continuum Model (PCM). See Tomasi et al. (2005) for a review about relevant literature. Enthalpy (H) and Gibbs free energy (G)

Table 11: Crystal data and structure refinement

	2b-TMS2	**2d-TMS**	**3d-TMS2**
Empirical formula	$C_{18}H_{28}N_4Si_3$	$C_9H_{14}Cl_2N_2Si_2$	$C_{12}H_{28}Cl_2N_2Si_3$
Formula weight	384.71	277.30	355.53
T (K)	93	93	200
Crystal system, space group	Monoclinic, C2/c	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/n$
a (Å)	15.0990(13)	7.8056(12)	9.6940(6)
b (Å)	14.1234(12)	9.0025(14)	12.1485(7)
c (Å)	10.5762(10)	18.713(2)	17.4157(9)
α (°)	90	90	90
β (°)	114.400(4)	90	105.242(4)
γ (°)	90	90	90
Volume (Å^3)	2053.9(3)	1315.0(3)	1978.9(2)
Z	4	4	4
ρ_{calc} (g/cm^3)	1.244	1.401	1.193
$\mu_{MoK\alpha}$ (mm^{-1})	0.240	0.647	0.501
F(000)	824	576	760
Crystal size (mm)	0.530 × 0.280 × 0.260	0.400 × 0.300 × 0.160	0.400 × 0.300 × 0.150
Reflections collected / unique	15493 / 2359 [R(int) = 0.0647]	17564 / 3174 [R(int) = 0.0295]	17820 / 4772 [R(int) = 0.0240]
Data / restraints / parameters	2359 / 0 / 120	3174 / 0 / 143	4772 / 15 / 197
Final R indices [I > 2sigma(I)]	R1 = 0.0491, wR2 = 0.1323	R1 = 0.0224, wR2 = 0.0574	R1 = 0.0375, wR2 = 0.0939
R indices (all data)	R1 = 0.0613, wR2 = 0.1494	R1 = 0.0236, wR2 = 0.0579	R1 = 0.0497, wR2 = 0.1049

	4b-TMS2	**4e**	**4f** · Et_2O	**4g**
Empirical formula	$C_{20}H_{32}N_4Si_3$	$C_{20}H_{32}N_4Si_3$	$C_{25}H_{31}Cl_3N_6OSi_3$	$C_{21}H_{21}Cl_3N_6Si_3$
Formula weight	412.76	412.76	622.18	548.06
T (K)	153	200	200	180
Crystal system, space group	Monoclinic, C2/c	Monoclinic, I2/c	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a (Å)	16.4390(11)	20.2108(13)	10.4899(4)	10.3542(7)
b (Å)	14.2531(12)	10.4857(4)	10.2209(6)	16.5306(8)
c (Å)	9.8574(6)	23.7581(14)	28.1420(13)	29.913(2)
α (°)	90	90	90	90
β (°)	94.821(5)	113.392(5)	91.244(4)	99.590(5)
γ (°)	90	90	90	90
Volume (Å^3)	2301.5(3)	4621.1(5)	3016.6(3)	5048.5(5)
Z	4	8	4	8
ρ_{calc} (g/cm^3)	1.191	1.187	1.370	1.442
$\mu_{MoK\alpha}$ (mm^{-1})	0.219	0.218	0.454	0.529
F(000)	888	1776	1296	2256
Crystal size (mm)	0.450 × 0.400 × 0.340	0.450 × 0.300 × 0.250	0.400 × 0.250 × 0.150	0.400 × 0.060 × 0.030
Reflections collected / unique	20017 / 2650 [R(int) = 0.0381]	35511 / 5313 [R(int) = 0.0277]	35175 / 6581 [R(int) = 0.0288]	39071/8882 [R(int) = 0.1097]
Data / restraints / parameters	2650 / 0 / 130	5313 / 0 / 258	6581 / 4 / 373	8882/0/614
Final R indices [I > 2sigma(I)]	R1 = 0.0332, wR2 = 0.0821	R1 = 0.0430, wR2 = 0.1082	R1 = 0.0377, wR2 = 0.0912	R1 = 0.0498, wR2 = 0.0947
R indices (all data)	R1 = 0.0404, wR2 = 0.0888	R1 = 0.0632, wR2 = 0.1205	R1 = 0.0555, wR2 = 0.1005	R1 = 0.1246, wR2 = 0.1154

(*continued*)

Table 11: (continued)

	5b·[Et$_3$NH]Cl·HCCl$_3$	**5c**	**5d-TMS**
Empirical formula	$C_{47}H_{49}Cl_4N_9Si_2$	$C_{12}H_{14}N_2Si$	$C_{13}H_{16}Cl_2N_2Si_2$
Formula weight	937.93	214.34	327.36
T (K)	153	153	180
Crystal system, space group	Triclinic, P-1	Monoclinic, P2$_1$/c	Monoclinic, P2$_1$/c
a (Å)	12.1354(6)	14.0807(5)	14.2310(4)
b (Å)	14.1506(7)	9.4389(2)	9.4966(2)
c (Å)	15.1245(8)	17.4383(6)	12.2393(4)
α (°)	102.395(4)	90	90
β (°)	98.013(4)	100.415(3)	108.065(2)
γ (°)	109.180(4)	90	90
Volume (Å^3)	2333.0(2)	2279.47(12)	1572.56(8)
Z	2	8	4
ρ_{calc} (g/cm^3)	1.335	1.249	1.383
$\mu_{MoK\alpha}$ (mm^{-1})	0.350	0.174	0.553
F(000)	980	912	680
Crystal size (mm)	0.450 × 0.380 × 0.300	0.380 × 0.280 × 0.210	0.300 × 0.200 × 0.150
Reflections collected / unique	50078 / 10055 [R(int) = 0.0427]	28952 / 5234 [R(int) = 0.0327]	27189 / 3791 [R(int) = 0.0318]
Data / restraints / parameters	10055 / 18 / 635	5234 / 0 / 291	3791 / 0 / 182
Final R indices [I > 2sigma(I)]	R1 = 0.0393, wR2 = 0.0902	R1 = 0.0496, wR2 = 0.1040	R1 = 0.0292, wR2 = 0.0740
R indices (all data)	R1 = 0.0555, wR2 = 0.1016	R1 = 0.0653, wR2 = 0.1170	R1 = 0.0336, wR2 = 0.0762

data derived from the calculations correspond to 298.15 K and 1 atmosphere of pressure.

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