Syntheses and structures of (*N′*,*N′*-dimethylhydrazido)silanes†

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The hydrazidosilanes $Ph_2Si(NHNMe_2)_2$ (**1**), $Me_2Si(NHNMe_2)_2$ (**2**), $PhSi(NHNMe_2)_3$ (**3**), $MeSi(NHNMe_2)_3$ (**4**), $PhClSi(NHNMe_2)_2$ (**5**), $MeClSi(NHNMe_2)_2$ (**6**), $Me_2ClSi(NHNMe_2)$ (**7**), $MeClHSi(NHNMe_2)$ (**8**), $MeHSi(NHNMe_2)_2$ (**9**), $Me_2HSi(NHNMe_2)$ (**10**), $Me_2NN[HSi(NHNMe_2)_2]_2$ (**11**) and $Si(NHNMe_2)_4$ (**12**) have been prepared by the reaction of the corresponding chlorosilanes with *N,N*-dimethylhydrazine. Some of the compounds containing Si–Cl and N–H functions simultaneously (**6**, **7**, **8**) are very reactive and tend to polymerise and could only be characterised by spectroscopic methods (^1H, ^{13}C, ^{29}Si NMR, IR, MS). All other compounds could additionally be characterised by elemental analyses. The structures of **1**, **2**, **5**, **9**, **11** and **12** in the solid state were determined by X-ray diffraction. These include the first structural determinations of compounds containing SiH–NH–N (**9**, **11**) and SiCl–NH–N (**5**) units.

Introduction

Hydrazidosilanes are potentially useful single source precursors for the chemical vapour deposition (CVD) of silicon nitride[1] and metal silicon nitride.[2] Silicon nitride is an important thin passivation layer and dielectric in the fabrication of semiconductor devices. The trend towards further down-scaling of these devices requires lower process temperatures. Hydrazides of silicon could have some potential in this context, due to the presence of weak N–N bonds, which can serve as predetermined breaking points. Therefore, hydrazidosilanes with high vapour pressure, zero chlorine content, low carbon but high nitrogen content are desirable synthetic targets.

Two main methods of preparation of hydrazidosilanes are known: the reaction of a hydrazine with a halosilane in the presence of an auxiliary base (triethylamine, hydrazine *etc.*) and the reaction of a halosilane with a lithiated hydrazine under elimination of lithium halide.[3] The resulting hydrazidosilanes are sensitive towards moisture, which transforms them into disiloxanes.

Here we distinguish between silylhydrazines (one or many silyl groups bonded to a hydrazine unit) and hydrazidosilanes (many hydrazine units bonded to a silicon atom). Whereas a large number of silylhydrazines have been prepared,[4] the chemistry of hydrazidosilanes[5] is much less developed. The syntheses of the first hydrazidosilanes were reported by Wannagat[6] and Tsitovich[7] in the early 1960s. Most of these compounds contain organic groups bound to the nitrogen and silicon atoms, which protect the sensitive hydrazine unit.

In order to reduce the carbon content, the introduction of hydrazide substituents with NH functions is desirable. From a thermodynamic view, SiH and NH functions near each other in one molecule are not stable,[8] but there are quite a few stable representatives of such compounds; 1,1,2,2-tetramethyldisilazane[9] for instance is commercially available.

Here we present a range of different hydrazidosilanes and show the limits of their stability with regard to the presence of mutually reacting groups and their intermolecular aggregation motifs.

Results and discussion

Diorganyl-dihydrazidosilanes

$Ph_2Si(NHNMe_2)_2$ (1) and $Me_2Si(NHNMe_2)_2$ (2). The compounds $Ph_2Si(NHNMe_2)_2$ (**1**), and $Me_2Si(NHNMe_2)_2$ (**2**) were synthesised previously,[7,10] but their crystal structures remained so far unknown. We obtained these compounds by the reaction of dichlorophenylsilane or dichlorodimethylsilane with a fourfold excess of unsymmetrical *N,N*-dimethylhydrazine (UDMH) in hexane after refluxing the reaction mixture for several hours to ensure complete substitution of all chlorine atoms.

$$R_2SiCl_2 + 4\ H_2NNMe_2 \rightarrow$$

$$R_2Si(NHNMe_2)_2 + 2\ [H_3NNMe_2]Cl$$

$$R = Ph\ (\mathbf{1}),\ Me\ (\mathbf{2})$$

After filtration of the precipitated salt and distillation, the bis(*N′*,*N′*-dimethylhydrazido)silanes crystallise from hexane solutions at −25 °C and were characterised by NMR (^1H, ^{13}C, ^{29}Si) and IR spectroscopy (see Table 1), by mass spectrometry and single crystal X-ray diffraction. Fig. 1 displays the solid-state structure of bis(*N′*,*N′*-dimethylhydrazido)diphenylsilane **1** and Fig. 2 the structure of bis(*N′*,*N′*-dimethylhydrazido)dimethylsilane **2**. Tables 2 and 3 contain selected structural parameter values.

Both compounds crystallise in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The Si–N, Si–C and

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Table 1 Selected spectroscopic parameter values of compounds **1–11**. NMR chemical shifts are given in ppm relative to TMS, IR frequencies are given in cm^{-1}

Compound	No.	$\delta(^{29}Si)$	$\delta(^{1}H)$ HN	$\delta(^{1}H)$ Me_2N	$\delta(^{1}H)$ HSi	$\delta(^{13}C)$ Me_2N	ν(NH)	ν(SiH)
$Ph_2Si(NHNMe_2)_2$	**1**	−38.6	2.34	2.40	—	52.4	3278	—
$Me_2Si(NHNMe_2)_2$	**2**	−12.7	2.04	2.25	—	52.4	3278	—
$PhSi(NHNMe_2)_3$	**3**	−22.2	2.00	2.43	—	51.6	3293	—
$MeSi(NHNMe_2)_3$	**4**	−28.9	2.08	2.29	—	52.7	3275	—
$PhClSi(NHNMe_2)_2$	**5**	1.7	2.37	2.23	—	52.6	3284	—
$MeClSi(NHNMe_2)_2$	**6**	−6.8	2.39	2.28	—	51.8	3268	—
$Me_2ClSi(NHNMe_2)$	**7**	8.5	2.36	2.45	—	51.8	3284	—
$MeClHSi(NHNMe_2)$	**8**	−19.5	2.42	2.69	5.17	48.1	3300	2218
$MeHSi(NHNMe_2)_2$	**9**	−28.4	2.22	2.36	4.78	51.8	3278	2131
$Me_2HSi(NHNMe_2)$	**10**	−14.7	1.81	2.22	4.67	51.7	3285	2135
$Me_2NN[SiH(NHNMe_2)]_2$	**11**	−45.8	2.18	2.33	4.79	52.4	3275	2146
$Si(NHNMe_2)_4$	**12**	−45.9	2.16	2.34	—	52.7	3200	—

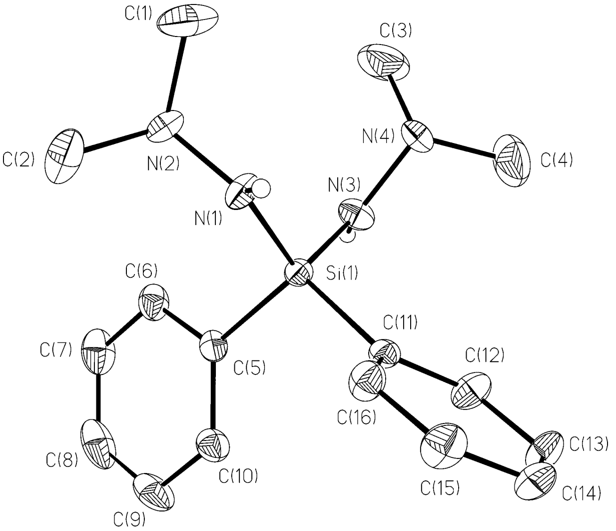

Fig. 1 Crystal structure of **1**. Ellipsoids are drawn at the 50% level, hydrogen atoms except those bound to N are omitted for clarity.

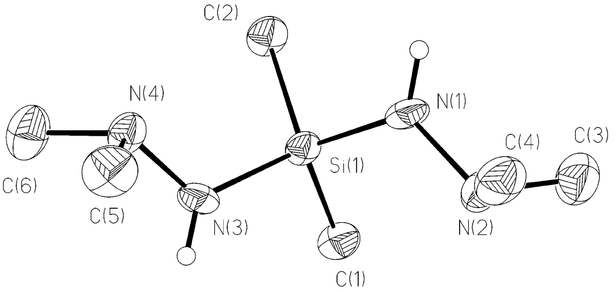

Fig. 2 Crystal structure of **2**. Ellipsoids are drawn at the 50% level, hydrogen atoms except those bound to N are omitted for clarity.

N–N bond lengths are all similar to those observed in other representative silylhydrazines.[2] While there is no intermolecular hydrogen bonding between the molecules with N···H contacts closer than 3 Å in **1**, compound **2** shows such N···H contacts of 2.64(4) Å and 2.67(3) Å lengths between neighbouring molecules as depicted in Fig. 3. According to the classification by Desiraju and Steiner,[11] these hydrogen bonds have to be specified as weak.

Although geminal intramolecular interactions between the silicon and nitrogen atoms in hydrazidosilanes, resulting in smaller Si–N–N angles, are known,[4o,p,5] in the case of compounds **1** and **2** the N–N–Si angles are close to 120°. This indicates the absence of β-donor Si···N interactions, which are frequently observed for isoelectronic hydoxylaminosilanes.[12]

The Si–N bonds in **1** and **2** are all of identical length within one standard deviation (average 1.704 Å). They are well within the established range for such lengths. The N–N bonds in **1** and **2** are relatively short as found for hydrazines, that bear only one silicon substituent (compare $H_3Si(Me)NNMe_2$: 1.432(2) and $(H_3Si)_2NNMe_2$: 1.461(3) Å).[4o]

Table 2 Selected structural parameters (Å, deg) of $Ph_2Si(NHNMe_2)_2$ (**1**)

Si–N(1)	1.703(2)	C(5)–Si–C(11)	111.4 (1)
Si–N(3)	1.704(3)	N(1)–Si–N(3)	112.5 (1)
N(1)–N(2)	1.426(3)	N(1)–Si–C(5)	113.9 (1)
N(3)–N(4)	1.418(3)	N(3)–Si–C(11)	113.3 (1)
Si–C(5)	1.866(3)	N(1)–Si–C(11)	104.0 (1)
Si–C(11)	1.874(3)	N(4)–N(3)–Si	123.0 (2)
		N(2)–N(1)–Si	120.6 (2)

Table 3 Selected structural parameters (Å, deg) of $Me_2Si(NHNMe_2)_2$ (**2**)

Si–N(1)	1.703(4)	C(1)–Si–C(2)	113.1(2)
Si–N(3)	1.704(4)	N(1)–Si–N(3)	117.2(2)
Si–C(1)	1.853(4)	N(1)–Si–C(1)	109.4(2)
Si–C(2)	1.841(4)	N(1)–Si–C(2)	104.1(2)
N(1)–N(2)	1.425(4)	N(2)–N(1)–Si	121.3(3)
N(3)–N(4)	1.420(4)	N(4)–N(3)–Si	120.3(3)

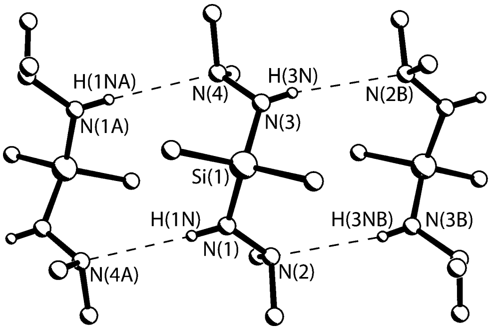

Fig. 3 Aggregation of **2** in the crystal showing the weak hydrogen bonding. Hydrogen atoms except those bound to N are omitted for clarity. Symmetry operations for generating neighbour molecules, A: $-x + 1, -y + 1, -z + 1$; B: $-x + 1, -y + 2, -z + 1$.

Organyl-trihydrazido-silanes $PhSi(NHNMe_2)_3$ (3) and $MeSi(NHNMe_2)_3$ (4)

Two compounds of this type were synthesised. Starting from trichloromethylsilane and trichlorophenylsilane the reactions with UDMH gave phenyltris(*N*′,*N*′-dimethylhydrazido)silane (**3**) and methyltris(*N*′,*N*′-dimethylhydrazido)silane (**4**)

$$RSiCl_3 + 6\ H_2NNMe_2 \rightarrow$$

$$RSi(NHNMe_2)_3 + 3\ [H_3NNMe_2]Cl$$

$$R = Ph\ (\mathbf{3}),\ Me\ (\mathbf{4})$$

Both compounds were characterised by NMR (^1H, ^{13}C, ^{29}Si) and IR spectroscopy, by mass spectrometry and elemental analyses. Despite various attempts, it was not possible to grow single crystals suitable for X-ray diffraction experiments.

The ^{29}Si NMR signals of the monoorganyl-trihydrazidosilanes **3** and **4** (−22.2 and −28.9 ppm) are low-field shifted with respect to the di-organyl-dihydrazidosilanes **1** and **2** (−38.6 and −12.7 ppm), whereas the other corresponding NMR parameters are quite similar (see Table 1).

Organyl-hydrazido-chlorosilanes

$Ph(Cl)Si(NHNMe_2)_2$ (5). We were able to isolate a partially hydrazido-substituted, while still retaining the Si–Cl function, compound bis(*N*′,*N*′-dimethylhydrazido)chlorophenylsilane, $Ph(Cl)Si(NHNMe_2)_2$ (**3**), from the reaction of trichlorophenylsilane and UDMH.

$$PhSiCl_3 + 4\ H_2NNMe_2 \rightarrow$$

$$Ph(Cl)Si(NHNMe_2)_2\ (\mathbf{5}) + 2\ [H_3NNMe_2]Cl$$

The identity of **5** was proven by NMR spectroscopy (^1H, ^{13}C, ^{29}Si), IR spectroscopy and mass spectrometry. The ^{29}Si NMR signal (1.7 ppm) shows a clear low-field shift compared to compounds **1** and **2** (−38.6 and −13.6 ppm) and also with respect to **3**, showing the different electronic influence of chloro and hydrazido substituents in an otherwise identical substitution pattern at the silicon atom. The other corresponding NMR parameters are quite similar and do not deserve more detailed comments (see Table 1).

Compounds containing SiCl–NH units are normally considered to easily undergo polymerisation reactions or condensation with HCl elimination often under formation of six-membered rings. For this reason only fluoro-substituted hydrazidosilanes with simultaneous presence of Si–F and Si–H functions were obtained so far, because the strength of the Si–F bond prevents the formation of HF kinetically.[13]

Compound **5** crystallises from pentane in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell and thus we were able to determine the first solid state structure of a simultaneously Si–Cl and N–H functional hydrazidosilane. Fig. 4 shows the structure of compound **5**, structural parameter values are listed in Table 4.

Table 4 Selected structural parameters (Å, deg) of $PhClSi(NHNMe_2)_2$ (**5**)

Si–N(1)	1.691(3)	C(5)–Si–C(11)	105.6(1)
Si–N(3)	1.697(3)	N(1)–Si–N(3)	106.1(1)
Si–Cl(1)	2.099(1)	N(1)–Si–C(5)	108.1(1)
Si–C(5)	1.851(3)	N(1)–Si–Cl(1)	113.4(1)
N1–N(2)	1.422(4)	N(2)–N(1)–Si	119.4(2)
N3–N(4)	1.434(3)	N(4)–N(3)–Si	120.6(2)

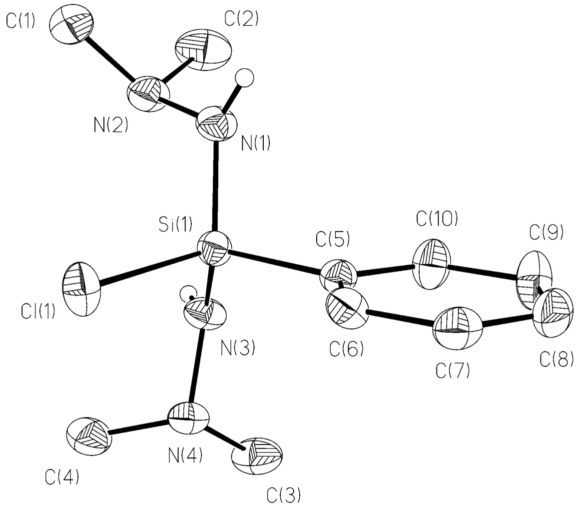

Fig. 4 Crystal structure of **5**. Ellipsoids are drawn at the 50% level, hydrogen atoms except those bound to N are omitted for clarity.

The Si–Cl bond length of **5** at 2.099(1) Å is quite long, *i.e.* longer than that in trichloro(dimethylamino)silane (Me_2NSiCl_3, 2.023(1) and 2.043(1) Å)[14] and longer than in standard Si/Cl compounds like $SiCl_4$ (2.019(3) Å) or Me_2SiCl_2 (2.055(2) Å).[15]

The bonds Si(1)–N(1) (1.692(3) Å) and Si–N(3) (1.697(3) Å) are at the short range end of Si–N bonds in such systems, due to the electronegative Cl substituent. This range can be defined by Cl_3SiNMe_2 (1.657(12) Å in the gas phase)[16] and $(Cl_3Si)_3N$ (1.763(3) Å, solid).[17] The Si–N bonds in **1** and **2** with no chlorine substituent at silicon are much longer.

A set of weak hydrogen bonds of the N–H···N and the N–H···Cl type can be identified as a motif for chain formation in the crystal structure of **5** (see Fig. 5).

Compound **5** contains relatively short N–N bonds with lengths of 1.422(4) and 1.434(3) Å, which are even shorter than those in **1** and **2**. This is obviously due to the electronegative chloro substituent. The silicon-bound atoms N(1) and N(3) show a planar coordination sphere. Wide N–N–Si angles at these atoms of about 120° indicate the absence of β-donor N···Si interactions.

$MeClSi(NHNMe_2)_2$ (6) and $Me_2ClSi(NHNMe_2)$ (7). The partially substituted hydrazidosilanes $MeClSi(NHNMe_2)_2$ (**6**) and $Me_2ClSi(NHNMe_2)$ (**7**) were obtained by carefully adding UDMH to cold solutions of Me_2SiCl_2 and $MeSiCl_3$, respectively.

$$MeSiCl_3 + 4\ H_2NNMe_2 \rightarrow$$

$$MeClSi(NHNMe_2)_2\ (\mathbf{6}) + 2\ [H_3NNMe_2]Cl$$

$$Me_2SiCl_2 + 2\ H_2NNMe_2 \rightarrow$$

$$Me_2ClSi(NHNMe_2)\ (\mathbf{7}) + [H_3NNMe_2]Cl$$

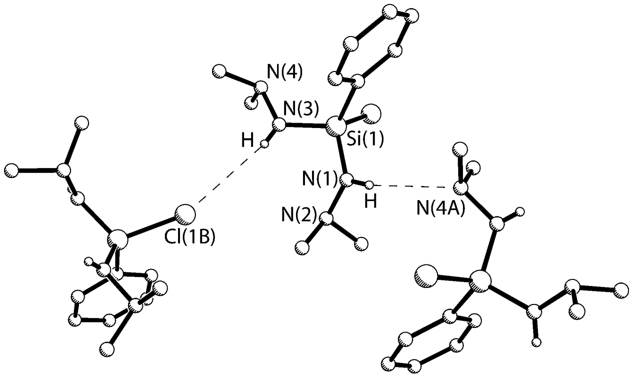

Fig. 5 Aggregation of **5** in the crystal showing the weak hydrogen bonding. Hydrogen atoms except those bound to N are omitted for clarity. Structural parameters are: N(1)–H 0.81(4) Å, N(4A)···H 2.68(4) Å, N(1)–H–N(4A) 160(2)°, N(1)–N(4A) 3.457(3) Å; N(3)–H 0.72(3) Å, Cl(1B)···H 3.11(3) Å, N(3)–H–Cl(1B) 166(3)°. Symmetry operations for generating neighbour molecules, A: $-x + 1, -y + 1, -z - 1$; B: $-x + 2, y, -z + 1$.

Unlike **5**, compounds **6** and **7** cannot be yielded as completely pure products, as attempts to distill the raw products leads to further condensation yielding polymeric materials and all attempts to crystallise them failed. Thus they were characterised by their NMR spectroscopic properties (see Table 1 and Experimental section).

Organyl-hydrazido-hydridosilanes

MeClHSi(NHNMe$_2$) (8). The reaction of dichloromethylsilane, MeSiHCl$_2$ with two equivalents UDMH resulted in the formation of MeClHSi(NHNMe$_2$) (**8**), but this compound is difficult to separate or purify due to its instability. This is due to possible redistribution and condensation reactions.

$$\mathrm{Me(H)SiCl_2 + 2\ H_2NNMe_2 \rightarrow}$$

$$\mathrm{MeClHSi(NHNMe_2)}\ (\mathbf{8}) + \mathrm{[H_3NNMe_2]Cl}$$

We could therefore only obtain a raw product and identify it as a major component (> 90%) by its spectroscopic data along with bis(N',N'-dimethylhydrazino)methylsilane (**9**), Me(H)Si(NHNMe$_2$)$_2$ and traces of other compounds. The instability of compound **8** finds its expression in the tendency to fully polymerise by elimination of hydrogen chloride and consequent hydrazinium salt formation over a few hours even at –25 °C. Thus we were not capable of obtaining single crystals of this compound.

Among all compounds in this paper it shows the most low-field shifted ^{1}H NMR resonance for its NH proton (2.42 ppm), along with the highest frequency for the N–H stretching mode (3300 cm^{-1}). Compound **8** also shows the most low-field shifted ^{1}H NMR resonance for its SiH proton (5.17 ppm) accompanied by the highest frequency for the Si–H stretching mode (2218 cm^{-1}) among the Si–H functional silanes described in this contribution (see following text).

Me(H)Si(NHNMe$_2$)$_2$ (9). Much more stable than **8** is compound **9**. This compound has already been described in the literature[1] and we have resynthesised it by reacting dichloromethylsilane with UDMH.

Table 5 Selected structural parameters (Å, deg) of Me(H)Si(NHNMe$_2$)$_2$ (**9**)

Si–N(1)	1.702(2)	N(2)–N(1)–Si	118.7(2)
Si–N(3)	1.699(2)	N(4)–N(3)–Si	120.6(2)
Si–C(1)	1.696(5)	C(1)–Si–N(1)	113.9(2)
Si–H	1.72(6)	C(1)–Si–N(3)	107.1(2)
N(1)–N(2)	1.418(3)	N(1)–Si–N(3)	118.4(1)
N(3)–N(4)	1.416(3)	N(1)–Si–H	107.4(2)
		N(3)–Si–H	99.8(2)

$$\mathrm{Me(H)SiCl_2 + 4\ H_2NNMe_2 \rightarrow}$$

$$\mathrm{Me(H)Si(NHNMe_2)_2}\ (\mathbf{9}) + 2\ \mathrm{[H_3NNMe_2]Cl}$$

Compound **9** has typical NMR spectroscopic properties (see Table 1) with deviations from the other compounds mentioned here too small to be worth discussing in detail. It could be crystallised from hexane and therefore its crystal structure could be determined. Fig. 6 presents the molecular structure of **9**. It crystallises in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and is the first structurally examined substance with an SiH–NH–N unit and quite stable despite simultaneously containing N–H and Si–H functions. As found for the molecules above, the N–N bonds are relatively short (average 1.417 Å, see Table 5).

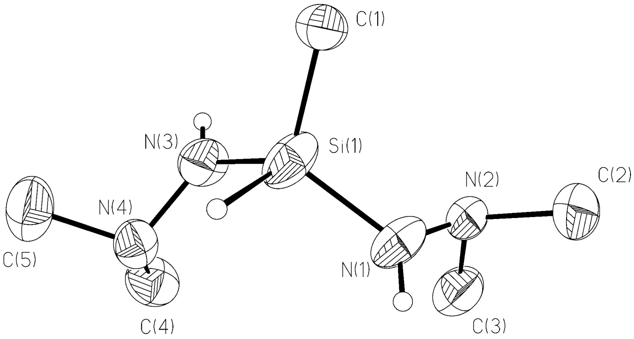

Fig. 6 Molecular structure of **9** in the crystal. The carbon atom C1 and the SiH hydrogen atom are disordered to either side of the silicon atom. Ellipsoids are drawn at the 50% level, hydrogen atoms except those bound to N and Si are omitted for clarity.

Hydrogen bridges between the N–H functions of one molecule and the NMe$_2$ groups of the other lead to the formation of ladder type endless aggregates as displayed in Fig. 7. There are two sorts of N–H···N bonding with shorter and longer N···H distances (N(1)–H(1 N)–N(4A): N···H 2.60(3) Å, N···N 3.376(4) Å, N–H–N 172(3)° and N(3)–H(3 N)–N(2B): N···H 2.51(3) Å, N···N 3.303(4) Å, N–H–N 169(3)°). This hydrogen bonding motif is very similar to that in **2** (with two methyl groups at silicon, see Figs. 2 and 3) and therefore probably the reason for the disorder of the single methyl group and hydrogen atom at silicon in **9** to both possible sides of the molecule.

Me$_2$HSi(NHNMe$_2$) (10). The reaction of UMDH with chlorodimethylsilane ClHSiMe$_2$ gave Me$_2$HSi(NHNMe$_2$) **10** as a colourless liquid, which is very sensitive to hydrolysis. Crystallisation for a structural analysis of **10** could not be achieved. It was characterised by NMR and IR spectroscopy (see Table 1), mass spectrometry and elemental analysis.

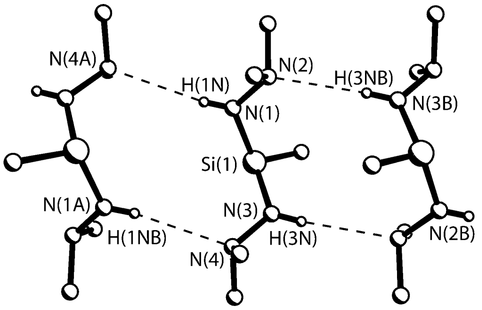

Fig. 7 Aggregation of **9** in the crystal showing the weak hydrogen bonding. Hydrogen atoms except those bound to N are omitted for clarity. Symmetry operations for generating neighbour molecules, A: $-x + 2, -y + 1, -z$; B: $-x + 2, -y, -z$.

$$Me_2HSiCl + 2\ H_2NNMe_2 \rightarrow$$

$$Me_2HSi(NHNMe_2)\ (\mathbf{10}) + [H_3NNMe_2]Cl$$

$Me_2NN[HSi(NHNMe_2)_2]_2$ (11) and $Si(NHNMe_2)_4$ (12). Unexpectedly, the reaction of trichlorosilane, $HSiCl_3$, with UMDH did not lead to the formation of tris(*N′*,*N′*-dimethylhydrazido)silane, $HSi(NHNMe_2)_3$. Instead two products were formed, *N′*,*N′*-bis[bis(2′,2′dimethylhydrazido)silyl]-2,2-dimethylhydrazine, $Me_2NN[HSi(NHNMe_2)_2]_2$ (**11**) by double deprotonation of one molecule of UDMH, and tetrakis(1,1-dimethylhydrazino)silane (**12**) by loss of one equivalent of hydrogen.

$$2\ HSiCl_3 + 11\ H_2NNMe_2 \rightarrow$$

$$Me_2NN[HSi(NHNMe_2)_2]_2\ (\mathbf{11}) + 6\ [H_3NNMe_2]Cl$$

$$HSiCl_3 + 7\ H_2NNMe_2 \rightarrow$$

$$Si(NHNMe_2)_4\ (\mathbf{12}) + 3\ [H_3NNMe_2]Cl + H_2$$

The composition of the product depends on the employed ratio between UDMH and $HSiCl_3$. Compound **11** is yielded preferentially by the reaction of two equivalents of $HSiCl_3$ with eleven equivalents of DMH. The formation of the **11** can be explained by the condensation of two molecules of the intermediate (*N′*,*N′*-dimethylhydrazido)chlorosilane, $HSiCl(NHNMe_2)_2$, with an UDMH molecule according to a similar mechanism to the one described by Voronkov and co-workers[1] for analogous cases.

$$HSiCl_3 + 4\ H_2NNMe_2 \rightarrow$$

$$HClSi(NHNMe_2)_2 + 2\ [H_3NNMe_2]Cl$$

$$2\ HClSi(NHNMe_2)_2 + 3\ H_2NNMe_2 \rightarrow$$

$$Me_2NN[Si(NHNMe_2)_2]_2\ (\mathbf{11}) + 2\ [H_3NNMe_2]Cl$$

However, this represents only one possibility and does not explain at which step of the substitution of the Si–Cl functions of one $HSiCl_3$ molecule the formation of the Si–N–Si bridge occurs.

The yields of the preparations of **11** and **12** are comparatively low and attempts of investigation of other products formed were difficult. The residues of distillations showed the occurrence of substantial amounts of substances of lower volatility and the large number of signals observed in NMR investigations showed these to consist probably of polymers containing Si–H, Si–Cl and Si–N–N functions. Further separation of these residues could not be achieved.

The constitution of **11** was proven by NMR spectroscopy (^1H, ^{13}C, ^{29}Si) and IR spectroscopy (Table 1). The ^1H NMR spectrum shows two singlet resonances of the NMe-groups with an integral ratio of 4:1. The proton resonance of the H–Si groups is a multiplet at 4.79 ppm. In the ^{29}Si NMR spectrum, both silicon nuclei give one doublet at –45.8 ppm with a $^1J_{SiH}$ coupling constant of 211 Hz. The infrared spectrum shows two sharp bands for the Si–H stretching mode at 2135 cm^{-1} and a broad band for the N–H stretching mode at 3300 cm^{-1}.

A crystal structure of **11** was obtained by X-ray diffraction with a single crystal in the form of colourless plates grown from hexane solution at –25 °C. Fig. 8 presents the molecular structure of **11**. The crystals contain two independent molecules in the asymmetric unit of a triclinic $P\bar{1}$ cell.

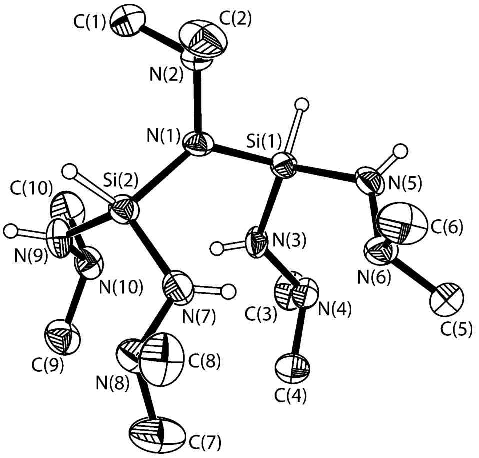

Fig. 8 Molecular structure of **11** in the crystal. Ellipsoids are drawn at the 50% level, hydrogen atoms except those bound to N and Si are omitted for clarity.

The doubly silicon-bonded atom N(1) has much longer bond lengths to the silicon atoms Si(1) (1.731(2) Å) and Si(2) (1.737(1) Å) and to the nitrogen atom N(2) (1.462(2) Å) than the other silicon bound nitrogen atoms, which show average Si–N distances of 1.692 Å and N–N distances of 1.423 Å.

Due to steric reasons the Si1–N1–Si2 angle is widened to nearly 130°. The planar coordination sphere of the nitrogen atom N(1) compensates for this by a compressed angle N2–N1–Si1 of 109.6(1)°, while the angle N2–N1–Si2 is 120.3(1)°. It might be speculated whether a weak β-Si···N attractive interaction between Si(1) and N(2) might also responsible for this deformation of the coordination sphere of N(1).

The environments of the silicon atoms are quite distorted tetrahedrons with some N–Si–N angles widened to over 117°, whereas others are compressed to 102° (Table 6). This effect was observed in some of the other structures in this paper and also other element amides and can be rationalised by Gillespie's ligand close packing model, with ligands, that are far from rotational symmetry like amide groups due to the presence of two substituents (here H and N) and one lone pair of electrons.[18]

Table 6 Selected structural parameters (Å, deg) of $Me_2NN[HSi(NHNMe_2)_2]_2$ (**11**)

Si(1)–N(1)	1.731(2)	N(2)–N(1)–Si(1)	109.6(1)
Si(2)–N(1)	1.737(2)	N(2)–N(1)–Si(2)	120.3(1)
Si(1)–N(3)	1.690(2)	Si(1)–N(1)–Si(2)	129.4(1)
Si(1)–N(5)	1.690(2)	N(4)–N(3)–Si(1)	125.5(2)
Si(2)–N(7)	1.687(2)	N(6)–N(5)–Si(1)	121.7(2)
Si(2)–N(9)	1.701(2)	N(8)–N(7)–Si(2)	120.3(2)
N(1)–N(2)	1.462(2)	N(10)–N(9)–Si(2)	120.5(2)
N(3)–N(4)	1.421(3)	N(5)–Si(1)–N(3)	112.0(1)
N(5)–N(6)	1.424(3)	N(5)–Si(1)–N(1)	117.3(1)
N(7)–N(8)	1.421(3)	N(3)–Si(1)–N(1)	101.9(1)
N(9)–N(10)	1.424(3)	N(5)–Si(1)–H(1)	102.1(8)
Si(1)–H(1)	1.33(2)	N(3)–Si(1)–H(1)	115.6(8)
Si(2)–H(2)	1.34(2)	N(1)–Si(1)–H(1)	108.6(8)
		N(7)–Si(2)–N(9)	114.9(1)
		N(7)–Si(2)–N(1)	103.7(1)
		N(9)–Si(2)–N(1)	115.2(1)
		N(7)–Si(2)–H(2)	112.5(8)
		N(9)–Si(2)–H(2)	99.7(8)
		N(1)–Si(2)–H(2)	111.2(9)

Table 7 Hydrogen bonding parameters (Å, deg) of the dimers of $Me_2NN[HSi(NHNMe_2)_2]_2$ (**11**)

N1	N2	N1···N2	N1-H	H···N2	N1–H–N2
N(3)	N(10)	3.004(3)	0.72(2)	2.29(2)	171(2)
N(5)	N(12)	3.256(3)	0.72(2)	2.55(2)	168(2)
N(7)	N(6)	3.332(3)	0.80(2)	2.57(2)	161(2)
N(13)	N(2)	3.290(3)	0.72(2)	2.58(2)	168(2)
N(15)	N(18)	3.133(3)	0.76(2)	2.39(2)	166(2)
N(19)	N(14)	3.334(3)	0.81(2)	2.56(2)	159(2)

The repulsion between these in different conformations leads to this highly distorted coordination geometry.

Weak hydrogen bonds of the N–H···N type link the two independent molecules of **11** to give unsymmetrical dimers (Fig. 9). In addition to this intermolecular hydrogen bonding there are also two intramolecular weak hydrogen bonds in each monomer leading to the formation of seven-membered HNSiNSiNN rings. The details of this hydrogen bonding pattern is listed in Table 7. The terminal N–H function at N(9) is not involved in such hydrogen bonding, as the shortest distances of this H atom to neighbouring N atoms of other molecules are far longer than 3 Å.

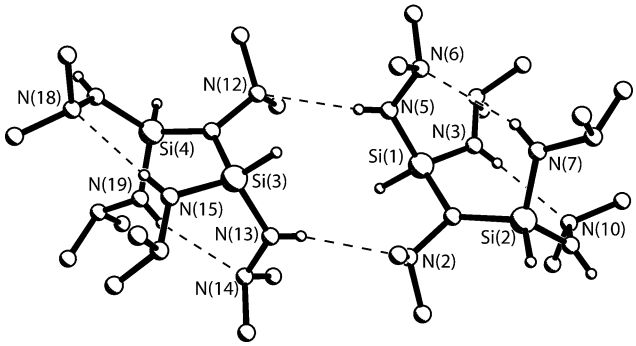

Fig. 9 Inter- and intramolecular aggregation of **11** showing hydrogen bonded dimers in the crystal. Only hydrogen atoms bound to N and Si are shown.

Table 8 Selected structural parameters (Å, deg) of $Si(NHNMe_2)_4$ (**12**). Symmetry transformations used to generate equivalent atoms: $-x + 1$, y, $-z + 3/2$

Si(1)–N(3)	1.700(2)	N(3A)–Si(1)–N(3)	100.1(2)
Si(1)–N(1)	1.705(2)	N(3A)–Si(1)–N(1)	114.3(1)
N(1)–N(2)	1.432(3)	N(3)–Si(1)—N(1)	114.8(1)
N(3)–N(4)	1.423(3)	N(1)–Si(1)—N(1A)	99.4(2)
		N(2)–N(1)–Si(1)	120.7(2)
		N(4)–N(3)–Si(1)	121.6(2)

Compound **12** can be obtained preferentially in yields up to 30% by reacting seven equivalents of UDMH with one of $HSiCl_3$. The loss of hydrogen in the reaction of trichlorosilane with compounds bearing acidic protons is well known. It has to be noted that compound **12** has already been described in the literature,[19] but then obtained from the reaction of $SiCl_4$ with H_2NNMe_2 and less completely characterised. After contact with air **12** forms an insoluble polymeric solid.

The constitution of compound **12** was proven by an ^1H NMR spectrum, which shows only one broad signal for the NH-groups at 2.16 ppm and one signal for the NMe_2-groups at 2.34 ppm with an integral ratio of 1:6.

Fig. 10 shows the molecular structure of **12** in the solid state. Structural parameter values are listed in Table 8. The compound crystallizes at −25 °C from hexane solutions in the monoclinic space group *P*2/*c*. It contains two crystallographically independent molecules in the unit cell, which are of very similar geometry. This allows the conclusion that structural features are not imposed by packing forces.

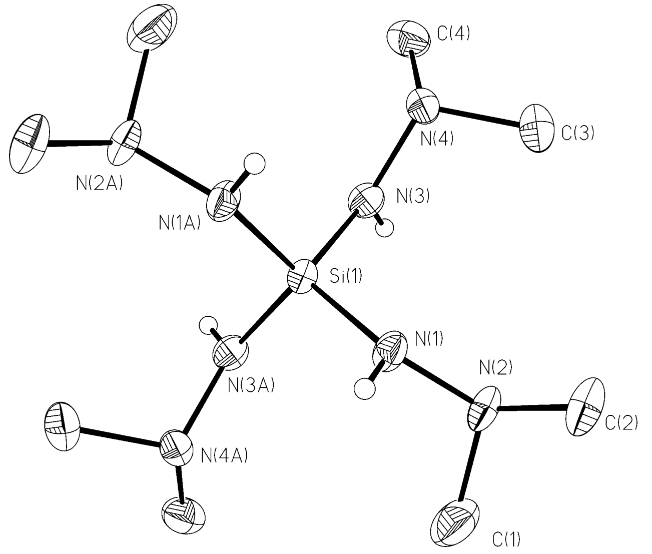

Fig. 10 Molecular structure of **12** in the crystal. Ellipsoids are drawn at the 50% level; hydrogen atoms except those bound to N are omitted for clarity. Only one of two independent molecules is shown. Symmetry transformations used to generate equivalent atoms: $-x + 1$, y, $-z + 3/2$.

The Si–N bond lengths are in the expected range. The N–N distances are again, as in the other hydrazidosilanes, comparatively short. Despite the presence of four identical substituents, the coordination geometry at the silicon atom is that of a substantially distorted tetrahedron. This can be rationalised by Gillespie's ligand close packing model under consideration of a local asymmetry of the binding atoms at silicon.[20]

Fig. 11 shows that **12** has a different aggregation motif by hydrogen bonds than the other compounds in this contribution. Here we find a total of eight interactions between the NH functions to two neighbour molecules, leading to the formation of endless aggregation polymers. In contrast to the other compounds the nitrogen atoms involved in hydrogen bonding here are the silicon-bonded ones (not the NMe_2 groups), which can be regarded as less basic due to their planar coordination geometry. As the NH functions serve at the same time as acceptors and donors, the resulting network contains strongly bent hydrogen bonds with N–H···N angles of 152 and 154°.

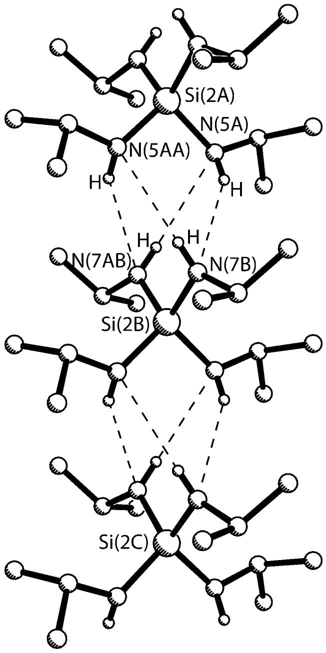

Fig. 11 Aggregation of **12** into endless strands by four hydrogen bridges between each pair of monomers. Only the hydrogen bound to N are shown. Structural parameters are: N(5A)–H 0.82(2) Å, N(7B)···H 2.61(3) Å, N(5A)–H–N(7B) 152(2)°, N(5A)···N(7B) 3.356(3) Å; N(7B)–H 0.80(3) Å, N(5AA)···H 2.62(3) Å, N(7B)–H–N(5AA) 154(3)°, N(7B)···N(5AA) 3.350(3) Å. Symmetry operations for generating neighbour molecules, A: *x*, *y* – 1, *z*.

Conclusions

We have reported the synthesis of some classes of hydrazidosilanes, namely those with organic substituents at silicon and different numbers of hydrazide units, hydrazidosilanes with Si–Cl and with Si–H functions. As all compounds contain the Me_2NNH- unit, the latter two classes of compounds simultaneously contain two reactive groups capable of undergoing condensation reactions with release of HCl or hydrogen. All Si–Cl group containing compounds were found to be unstable towards such reactions, which they undergo even at low temperatures. Only in one case, for $PhClSi(NHNMe_2)_2$ (**5**) it was possible to isolate such a compound with the SiCl-NH-N unit in completely pure form as single crystals and to obtain a crystal structure. The compounds containing SiH-NH-N units are much more stable. It is interesting to see, that only in one case the double N–H functional Me_2NNH_2 was doubly silylated at the nitrogen atom. But even for this compound, $Me_2NN[HSi(NHNMe_2)_2]$ (**11**), there are still four N–H functions left in the presence of two Si–H groups.

Only for the reaction of UDMH with $HSiCl_3$ we have observed the activation of an Si–H bond under the reaction conditions. This led finally to a fourfold substitution of $HSiCl_3$ and the formation of $Si(NHNMe_2)_4$ (**12**) under liberation of H_2.

The compounds, which have been structurally studied, have some common features. As expected all silylated nitrogen atoms are of planar coordination geometry and the N–N bond lengths in the compounds under investigation are generally short in comparison to silylhydrazines, which bear more than one silicon atom at the N–N unit. The presence of N–H functions makes hydrogen bonding a common motif for intermolecular aggregation. However, in all cases with such N–H···N bonds, these are relatively long and have to be categorised as weak. They are normally found between the N–H functions as hydrogen bond donors and the NMe_2 groups as hydrogen bond acceptors. Only for $Si(NHNMe_2)_4$ (**12**) the weak hydrogen bonds are found between the N–H groups of one and the silylated N atoms of a neighbouring molecule.

Experimental

General remarks

All reactions were carried out under dry nitrogen atmosphere in anhydrous and degassed solvents using Schlenk line techniques. *N,N*-Dimethylhydrazine (UMDH) was dried over calcium hydride and distilled. NMR spectra were detected on a Bruker Avance 400 instrument and were referenced relative to (residual) solvents resonance (^1H, ^{13}C) or relative to an external standard [^{29}Si; $SiMe_4$]. Infrared spectra were recorded on a Midac Prospect-IR or on a Shimadzu IR-Prestige-21 spectrometer. Mass spectra from solid compounds were obtained on a Varian Mat 212, mass spectra of volatile compounds with a Pfeiffer QMG 422, which was directly connected to a Stock high vacuum line. Elemental analyses were performed using an Elementar Vario EL III CHNS analyser.

General procedure for compounds 1, 2, 5, 9, 11 and 12. To a stirred solution of UMDH dissolved in a hydrocarbon solvent the halosilane (quantities given below) was added dropwise at 273 K (**1**, **2**) or 233 K (**5**, **9**, **11**, **12**). The reaction mixtures were slowly allowed to warm to ambient temperature (in the case of **1** and **2** they were stirred afterwards for 1 h and then refluxed for 3 h to ensure complete substitution) and the precipitated hydrazinium salts were filtered off. The solvents were distilled off and the liquid products were purified by fractional distillation. Crystals were grown from relatively concentrated solutions of the pure compounds in hexane at –25 °C.

$Ph_2Si(NHNMe_2)_2$ (1). UMDH (16.7 mL, 0.22 mol in 20 mL hexane), dichlorodiphenylsilane (2.4 mL 0.10 mol in 10 mL hexane). Colourless needles; yield 60%; m.p. 40 °C, b.p. 191 °C (13 mbar) (Found C, 63.38; H, 7.80; N, 18.61. $C_{16}H_{24}N_4Si$ [300.48] requires C 63.92, H 8.05, N 18.65); δ_H(400.13 MHz, C_6D_6, 21°C) 2.34 (2H, br s, NH), 2.40 (12H, s, NMe), 7.29 (2H, s, *o*-H), 7.34 (2H, s, *m*-H), 7.97 (1H, s, *p*-H); δ_C(100.62 MHz, C_6D_6, 21°C) 52.4 (2 C, NMe), 129.7 (*o*-C), 135.6 (*m*-C), 135.8 (*p*-C); δ_{Si}(79.49 MHz, C_6D_6, 21°C) –38.6; *ν*(Nujol) 3278 (*ν*(NH)) cm^{-1}; *m*/*z*(EI, 20 eV, 50 °C) 300 (M^+), 256 (M^+ – NMe$_2$), 241 (M^+ – NHNMe$_2$), 197 (M^+ – NH(NMe$_2$)$_2$), 59 (NHNMe$_2$).

Me$_2$Si(NHNMe$_2$)$_2$ (2). UMDH (24.4 mL, 0.32 mol in 40 mL hexane), dichlorodimethylsilane (2.4 mL 0.10 mol in 20 mL hexane). Colourless needles; yield 51%; b.p. 60 °C (28 mbar) (Found C, 40.99; H, 11.76; N, 32.02. $C_6H_{16}N_4Si$ [172.31] requires C, 40.87; H, 11.43; N, 31.77); δ_H(400.13 MHz, C_6D_6, 21 °C) −0.12 (6H, s, SiMe), 2.04 (2H, br s, NH), 2.25 (12H, s, NMe); δ_C(100.62 MHz, C_6D_6, 21 °C) −3.6 (2 C, SiMe), 52.4 (4 C, NMe); δ_{Si}(79.49 MHz, C_6D_6, 21 °C) −13.6; ν(Nujol) 3278 (NH) cm^{-1}; *m/z*(EI, 70 eV, 50 °C) 176 (M^+).

PhClSi(NHNMe$_2$)$_2$ (5). UMDH (9.1 mL, 0.12 mol in 20 mL toluene), trichlorophenylsilane (3.2 mL 0.02 mol in 20 mL toluene). Colourless blocks; yield 65% (Found C, 25.41; H, 10.11; N, 29.86. $C_6H_{16}N_4Si$ [186.76] requires C, 25.72; H, 10.25; N, 30.00); δ_H(400.13 MHz, C_6D_6, 21°C) 2.23 (12H, s, NMe), 2.37 (2H, s, NH), 7.23 (2H, s, *o*-H), 8.01 (2H, s, *m*-H), 8.18 (1H, s, *p*-H). δ_C(100.62 MHz, C_6D_6, 21°C) 52.6 (NMe), 130.6 (*o*-C), 134.1 (*m*-C), 135.2 (*p*-C). δ_{Si}(79.49 MHz, C_6D_6, 21 °C) 1.7; ν(Nujol) 3284 (ν(NH)), 516 (ν(SiCl)) cm^{-1}; *m/z*(EI, 70 eV, 50 °C) 258 (M^+), 223 (M^+ – Cl), 214 (M^+–NMe$_2$), 199 (M^+ – NHNMe$_2$), 92 (M^+ – (NMe$_2$)$_2$), 59 (M^+ – SiClNHNMe$_2$), 44 (NMe$_2$).

MeHSi(NHNMe$_2$)$_2$ (9). UMDH (9.1 mL, 0.12 mol in 20 mL hexane), dichloromethylsilane (3.8 mL 0.03 mol in 10 mL hexane). Colourless needles, yield 43%; b.p. 59 °C (22 mbar) (Found C, 36.87; H, 11.42; N, 34.74. $C_5H_{18}N_4Si$ [162.31] requires C, 37.00; H, 11.18; N, 34.52); δ_H(400.13 MHz, C_6D_6, 21 °C) 0.29 (3H, s, SiMe), 2.22 (2H, br s, NH), 2.36 (12H, s, NMe), 4.78 (1H, m, SiH); δ_C(100.62 MHz, C_6D_6, 21 °C) −5.1 (SiMe), 51.8 (NMe); δ_{Si}(79.49 MHz, C_6D_6, 21 °C) −28.4; ν(gas) 3278 (s, br, ν(NH)), 2131 (s, ν(SiH)) cm^{-1}.

Me$_2$NN[HSi(NHNMe$_2$)$_2$]$_2$ (11). UMDH (9.1 mL, 0.12 mol in 20 mL hexane), trichlorosilane (2.0 mL 0.02 mol in 10 mL hexane). Colourless plates; yield 27%; m.p. 80 °C (Found C, 34.98; H, 10.18; N, 38.89. $C_{10}H_{36}N_{10}Si_2$ [352.63] requires C, 34.06; H, 10.29; N, 39.72); δ_H(400.13 MHz, C_6D_6, 21°C) 2.18 (4H, br s, NH), 2.33 (24H, s, NHNMe), 2.37 (6H, s, NNMe), 4.79 (2H, m, SiH); δ_C(100.62 MHz, C_6D_6, 21 °C) 48.7 (NNMe), 52.4 (NHNMe); δ_{Si}(79.49 MHz, C_6D_6, 21 °C) −45.8 (d, $^1J_{SiH}$ = 211 Hz); ν(gas) 3275 (s, br, ν(NH)), 2146 (s, ν(SiH)) cm^{-1}.

Si(NHNMe$_2$)$_4$ (12). UMDH (15.2 mL, 0.20 mol in 20 mL hexane), trichlorosilane (2.0 mL 0.02 mol in 15 mL hexane). Colourless needles; yield 30%; m.p. 64 °C (Found C, 37.45; H, 10.86; N, 42.76. $C_8H_{28}N_8Si$ [264.45] requires C, 36.34; H, 10.67; N, 42.37); δ_H(400.13 MHz, C_6D_6, 21°C) 2.16 (4H, br s, NH), 2.34 (24H, s, NMe); δ_C(100.62 MHz, C_6D_6, 21 °C) 52.7 (NMe); δ_{Si}(79.49 MHz, C_6D_6, 21 °C) −45.9; ν(gas) 3300 (s, br, ν(NH)) cm^{-1}.

PhSi(NHNMe$_2$)$_3$(3). Trichlorophenylsilane (3.2 mL, 0.02 mol) was added dropwise to a solution of *N*,*N*-dimethylhydrazine (9.1 mL, 0.12 mol) at ambient temperature. After stirring the mixture for 24 h, it was heated to reflux for 6 h. The precipitated hydrazonium salts were removed by filtration. The solvents were evaporated under reduced pressure, leading to precipitation of the product, which is an air- and moisture-sensitive solid. Yield 2.1 g (37%), m.p. 75 °C (Found C, 52.12; H, 9.43; N, 28.98. $C_{12}H_{26}N_6Si$ [282.47] requires C, 51.03; H, 9.28; N, 29.75); δ_H(400.13 MHz, C_6D_6, 21°C) 2.00 (s, 3H, NH), 2.43 (s, 18H, NMe$_2$), 7.30 (s, 2H, o-H),7.74 (s, 2H, m-H), 7.75 (s, 1H, p-H); δ_C(100.62 MHz, C_6D_6, 21°C) 51.6 (s, NMe$_2$), 128.5 (s, *o*-C), 130.1 (s, *m*-C), 135.3 (s, *p*-C); δ_{Si}(79.49 MHz, C_6D_6, 21°C) −22.2; ν(film) 3293 (s, ν_s(NH)), 2980, 2891, 2850, 2827 (vs, ν(CH)), 1950, 1880, 1860, 1620 (s), 1460 (s, δ_{as}(CH3)), 1455, 1393 (vs, ν(SiN)), 1233 (s, ν(SiC)), 1149, 1116, 1075 (vs), 1001 (s), 882 (s), 732, 701 (s) cm^{-1}.

MeSi(NHNMe$_2$)$_3$ (4). A solution of trichloromethylsilane (2.3 mL, 0.02 mol) in hexane (10 mL) was added dropwise to a solution of *N*,*N*-dimethylhydrazine (16.0 mL, 0.20 mol) at ambient temperature. After stirring the mixture for 24 h, it was heated to reflux for 4 h. The precipitated hydrazonium salts were removed by filtration. The initially obtained product is an air- and moisture-sensitive liquid, which crystallises from concentrated hexane solution. Yield 2.7 g (60%); m.p. 55 °C (Found C, 38.16; H, 11.12; N, 38.45. $C_7H_{24}N_6Si$ [220.40] requires C, 38.15; H, 10.98; N, 38.13); δ_H(400.13 MHz, $CDCl_3$, 21 °C) 0.32 (s, 3H, SiMe), 2.08 (s, 3H, NH), 2.29 (s, 18H, NMe$_2$); δ_C(100.62 MHz, $CDCl_3$, 21 °C) −4.3 (SiMe), 52.7 (NMe$_2$). δ_{Si}(79.49 MHz, $CDCl_3$, 21 °C) −28.9; ν(film) 3275 (s, ν_s(NH)), 2969, 2890, 2800 (vs, ν(CH)), 1540, 1530 (vs), 1466 (s, δ_{as}(CH_3)), 1382 (vs, ν(SiN)), 1260, 1230 (w, ν(SiC)), 1097, 1085, 1070 (vs), 879 (w), 816 (s), 730 (s) cm^{-1}.

MeClSi(NHNMe$_2$)$_2$ (6). A solution of *N*,*N*-dimethylhydrazine (6.0 mL, 0.08 mol) in hexane (20 mL) was slowly added to a solution of trichloromethylsilane (2.3 mL, 0.02 mol) in hexane (20 mL) at −40 °C. The mixture was allowed to warm to ambient temperature and filtered. The solvent was removed by distillation under slightly reduced pressure. The product is a colourless liquid, which is very sensitive to hydrolysis. It polymerises within a few hours at ambient temperature. Yield 2.2 g (57%), δ_H(400.13 MHz, $CDCl_3$, 21 °C) 0.60 (s, 3H, SiMe), 2.28 (s, 12H, NMe$_2$), 2.39 (s, 2H, NH); δ_C(100.62 MHz, $CDCl_3$, 21 °C) 3.8 (s, SiMe), 51.8 (s, NMe$_2$); δ_{Si}(79.49 MHz, $CDCl_3$, 21 °C) −6.8; ν(film) 3268 (s, ν_s(NH)), 2970, 2910, 2870, 2780 (vs, ν CH), 1470 (s, δ_{as}(CH_3)), 1440, 1385 (vs, ν(SiN)), 1240 (s, ν(SiC)), 1150, 1141, 1073 (vs), 1009 (s), 892 (s), 732, 699 (s), 529 (s, ν_s(SiCl)), 108 cm^{-1}.

Me$_2$ClSi(NHNMe$_2$) (7). A solution of *N*,*N*-dimethylhydrazine (12.2 mL, 0.16 mol) in diethyl ether (15 mL) was dropped slowly into a solution of dichlorodimethylsilane (9.7 mL, 0.08 mol) in diethyl ether (55 mL) at −40 °C. The mixture was allowed to reach ambient temperature and the solution was separated from the precipitate by a cannula fitted with a filter. The solvent is evaporated under slightly reduced pressure. An oily product was obtained, which could not be further purified due to its instability. Yield 14.6 g (60%); δ_H(400 MHz, $CDCl_3$, 21 °C) 0.45 (s, 6H, SiMe2), 2.36 (s, 1H, NH), 2.45 (s, 6H, NMe$_2$); δ_C(100 MHz, $CDCl_3$, 21 °C) 0.9 (s, SiMe$_2$), 51.8 (s, NMe$_2$); δ_{Si}(79.49 MHz, $CDCl_3$, 21 °C) 8.5; ν(film) 3284 (s, ν_s(NH)), 2980, 2867 (vs, ν(CH)), 1454 (s, δ_{as}(CH_3)), 1390, 1381 (vs), 1366, 1350 (s, ν(SiN)), 1290, 1267 (w, ν(SiC)), 1132 (vs), 1074 (s), 852 (s), 742 (w), 568 (s, ν_s(SiCl)) cm^{-1}.

MeClHSi(NHNMe$_2$) (8). A solution of dichloromethylsilane (10.4 mL, 0.10 mol) in diethyl ether (50 mL) was slowly dropped to a solution of *N*,*N*-dimethylhydrazine (15.0 mL, 0.20 mol) in diethyl ether (20 mL) at −40 °C. The mixture was allowed to reach ambient temperature. The precipitated hydrazonium salt was filtered off and the diethyl ether solvent was removed by careful

Table 9 Data for the single crystal X-ray diffraction of compounds **1**, **2**, **5**, **9**, **11** and **12**

	1	**2**	**5**	**9**	**11**	**12**
Formula	$C_{16}H_{24}N_4Si$	$C_6H_{20}N_4Si$	$C_{10}H_{19}ClN_4Si$	$C_5H_{18}N_4Si$	$C_{10}H_{36}N_{10}Si_2$	$C_8H_{28}N_8Si$
M_r	300.48	176.35	258.83	162.32	352.67	264.47
Crystal system	triclinic	triclinic	orthorhombic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2/c$
a/Å	8.830(2)	8.239(8)	8.972(1)	8.326(5)	11.121(5)	17.998(5)
b/Å	9.907(2)	8.702(9)	12.116(1)	8.332(5)	11.644(6)	5.015(1)
c/Å	10.182(2)	8.730(9)	12.904(1)	9.182(5)	16.611(8)	18.163(5)
α/°	93.77(2)	117.44(2)	90	68.92(1)	80.46(1)	90
β/°	91.31(2)	97.65(2)	90	89.16(1)	89.01(1)	109.46(1)
λ/°	98.49(2)	92.13(2)	90	60.69(1)	84.81(1)	90
V/Å^3	878.5(3)	547.1(9)	1402.6(2)	507.9(5)	2112.5(18)	1545.8(7)
D_c/g cm^{-3}	1.136	1.071	1.226	1.061	1.109	1.136
Z	2	2	4	2	4	4
T/K	163(2)	153(2)	153(2)	153(2)	153(2)	153(2)
μ/mm^{-1}	0.134	0.172	3.084	0.180	0.181	0.149
$T_{\text{min/max}}$	—	0.921/0.983	0.934/0.349	0.919/0.986	0.931/0.993	0.994/0.939
Radiation	MoKα	MoKα	CuKα	MoKα	MoKα	MoKα
$2\theta_{\max}$/°	54.0	48.0	144.8	55.0	50.0	51.0
Refls. collected	13667	2368	8190	4763	16414	11890
Refls. unique	3509	1600	2651	2313	7431	2864
Refls. observed ($\lvert F_o \rvert > 4\sigma \lvert F_o \rvert$)	2633	1192	2338	1528	5367	1974
R_{int}	0.1390	0.0405	0.0358	0.0576	0.0367	0.0676
Parameters/restraints	194/0	114/0	157/0	117/0	465/0	179/0
$R_1[I > 2\sigma(I)]/wR_2$	0.0717/0.1820	0.0591/0.1416	0.0451/0.1093	0.0527/0.1207	0.0466/0.1141	0.0497/0.1137
R_1/wR_2 (all data)	0.0995/0.2056	0.0845/0.1551	0.0528/0.1154	0.0907/0.1340	0.0710/0.1241	0.0833/0.1293
ρ_{fin} (min/max)/e Å^3	–0.608/0.704	–0.384/0.566	–0.273/0.527	–0.429/0.321	–0.358/0.514	–0.327/0.472
Flack parameter	—	—	0.01(2)	—	—	—
CCDC no.	715611	715612	715613	715614	715615	715616

distillation. The product is a colourless air- and moisture-sensitive liquid, which decomposes upon keeping it at ambient temperature or upon attempts of further purification by distillation. Yield 4.1 g (30%); δ_H(400.13 MHz, CDCl$_3$, 21 °C) 0.61 (d, 3H, SiMe, $^3J_{HCSiH}$ = 2.5 Hz), 2.42 (s, 1H, NH), 2.69 (s, 6H, NMe$_2$), 5.17 (dq, 1H, SiH). δ_C(100.62 MHz, CDCl$_3$, 21°C) 1.8 (s, SiMe), 48.1 (s, NMe$_2$). δ_{Si}(79.49 MHz, CDCl$_3$, 21°C) −19.5 (d, $^1J_{SiH}$ = 195 Hz). ν(gas) 3300 (s, ν_s(NH)), 2988, 2870 (vs, ν(CH)), 2218 (s, ν_{as} (SiH)), 2189 (s, ν_s(SiH)), 1450 (s, δ_{as}(CH$_3$)), 1392, 1381 (vs), 1348 (s, ν(SiN)), 1294, 1265 (w, ν(SiC)), 1138 (vs), 1074 (s), 860 (s, δ_{as}(SiH)), 852 (s, δ_s(SiH)), 742 (w), 565 (s, ν_s(SiCl)) cm^{-1}.

$Me_2HSi(NHNMe_2)$ (10). A solution of chlorodimethylsilane (11.1 mL, 0.10 mol) in diethyl ether (10 mL) was slowly added to a solution of *N*,*N*-dimethylhydrazine (16.0 mL, 0.22 mol) at 0 °C. The mixture was allowed to warm to ambient temperataure and was stirred for 4 h. The mixture was filtered from the hydrazonium salts. The diethyl ether was carefully distilled off. Distillation of the residue gave the pure product at 74 °C under normal pressure. Yield 9.9 g (84%) (Found C, 39.98; H, 12.01; N, 23.48. $C_4H_{14}N_2Si$ [118.25] requires C, 40.63; H, 11.93; N, 23.69); δ_H(400.13 MHz, C$_6$D$_6$, 21 °C) 0.14 (d, 6H, SiMe, $^3J_{HCSiH}$ = 3.0 Hz), 1.81 (s, 1H, NH), 2.22 (s, 6H, NMe2), 4.67 (dsept, 1H, SiH, $^3J_{HSiNH}$ = 1.0 Hz, $^3J_{HSiCH}$ = 3.0 Hz); δ_C(100.62 MHz, C$_6$D$_6$, 21°C) −2.6 (SiMe), 51.7 (NMe); δ_{Si}(79.49 MHz, C$_6$D$_6$, 21 °C) −14.7 (d, $^1J_{SiH}$ = 193.5 Hz); ν(gas) 3285 (w, ν(NH)), 2992, 2963, 2856, 2818 (vs, ν(CH)), 2135 (s, ν_{as}(SiH)), 2112 (s, ν_s(SiH)), 1456 (w, δ_{as}(CH3)), 1377, 1324 (w, ν(SiN)), 1255 (s, ν(SiC)), 1068 (w), 918 (s, δ_{as}(SiH)), 898 (s, δ_s(SiH)), 837 (w), 735 (vs) cm^{-1}; *m*/*z* (EI, 70 eV) 118 (M$^+$), 103 (M$^+$–Me), 88 (M$^+$–2Me), 59 (M$^+$ − Me$_2$SiH), 44 (NMe$_2$), 15 (NH).

Single-crystal X-ray diffraction experiments. Single crystals of compounds were mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of the diffractometer. Crystallographic data sets were collected on an IPDS-1 (Fa. Stoe) (**1**), Bruker Smart CCD diffractometer (**2**, **5**, **11** and **12**) and a Bruker APEX CCD diffractometer (**9**) Crystal and refinement data are listed in Table 9. Structures were solved with the programs *SHELXS*[21] with direct methods and refined with *SHELXL*.[22] All non-hydrogen atoms were refined anisotropically. In the case of **1** protons at the silicon and nitrogen atoms were placed in calculated positions and included in the refinement, for **2**, **5**, **9**, **11** and **12** they were located in difference Fourier maps and refined isotropically. The molecular graphics were prepared with *ORTEP3*.[23]

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